

Electronic and Optical Properties of Metal-Organic Frameworks: A Computational Study of Photoswitchable Charge Transfer and Two-Photon Absorption

Zur Erlangung des akademischen Grades einer

DOKTORIN DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

von der KIT-Fakultät für Chemie und Biowissenschaften

des Karlsruher Instituts für Technologie (KIT)

genehmigte

DISSERTATION

von

M.Sc. Helmy Pacheco Hernandez

aus Tlalixcoyan, Veracruz, Mexiko

1. Referentin: Dr. Mariana Kozłowska

2. Referent: Prof. Dr. Marcus Elstner

Tag der mündlichen Prüfung: 16.07.2026

The work was made possible with support of a scholarship from the German Academic Exchange Service (DAAD).

Acknowledgments

Primero quiero agradecer a Dios por ayudarme a comprender que los sueños no son imposibles, simplemente toma tiempo alcanzarlos. A mi yo de hace algunos años: por tus esfuerzos para alcanzar tus metas, hoy se ven reflejados. A mi familia, sobre todo a mis padres Sara y Hery, y a mi hermano Héctor, por su apoyo incondicional desde la distancia y por su comprensión al permitirme cumplir mis metas, aunque sea a 9,500 km. A mi abuelita Nacha, mi abuelita Lety, mi abuelito Silvio (por sus consejos), mi abuelito Hery, mi abuelita Licha y mi abuelita Lichita. A mis tías y tíos: Maye y Rochi (por su apoyo cuando me encontraba sola en Veracruz), Mina, Yara, Tania, Armando, Hilda y Nando (por su apoyo cuando estaba en Xalapa), Paco, Lili, Irasema y Alfredo (por su apoyo cuando estaba en CDMX).

Je remercie mon copain qui m'a accompagné pendant ce voyage, depuis le début quand je commençais à postuler aux différents doctorats jusqu'à la fin de ma thèse. Merci mon amour pour m'avoir toujours écouté, partagé des conseils, et compris quand je devais faire des heures supplémentaires. Merci également à ta famille qui a su m'inclure ; j'adore la culture française ! et vous m'avez ouvert les portes pour la vivre par moi-même.

Thanks to all the friends I have made during this journey. To the friends I left behind in Mexico, despite the distance our friendship holds. To the friends I met through my DAAD scholarship. To the AG Wenzel group for the opportunity to pursue my PhD here, to my supervisors and colleagues for your support. To our collaborators for bridging experiment and simulation to produce meaningful results.

Finally, to the friends I made outside the office, from different parts of the world, who shared not only the challenges of postgraduate life but also their cultures with me.

Thanks to all of you, I am a richer person than I could have ever imagined!

Abstract

Metal-organic frameworks (MOFs) are hybrid porous materials composed of organic linkers and inorganic metal nodes that can form networks with diverse topologies and dimensionalities. While MOFs have been extensively studied for applications such as CO₂ adsorption, gas storage, catalysis, and drug delivery, their electronic and optical properties received attention considerably later, partly due to the initial assumption that these materials were electrically insulating. More recently, different strategies have focused on enhancing charge transfer within MOFs to explore their potential applications in sensing, bio-imaging, and data storage. However, a systematic study of how molecular design and MOF topology govern these properties remains limited.

The aim of this thesis is to computationally investigate the electronic and optical properties of MOFs through two distinct design strategies: i) the incorporation of photoswitchable molecules within a paddle-wheel-type MOF to evaluate how photoswitching modulates the electronic coupling, and ii) the incorporation of two-photon absorption (2PA) active chromophores (H₄TBAPy and H₄TCPE) as organic linkers in MOFs to study how their conformations and relative arrangements influence the 2PA response. In the first part, the modulation of the electronic coupling upon spiropyran-to-merocyanine photoswitching is investigated by means of Density Functional Theory (DFT) and Molecular Dynamics (MD). The results reveal average on/off conductance ratios exceeding 530 and 4200 for p- and n-type conduction, respectively, with further modulation possible by functionalizing the photoswitches with electron-donating and electron-withdrawing groups. In the second part, the 2PA cross sections of two tetratopic linkers, H₄TCPE and H₄TBAPy, are studied through DFT and Time-Dependent DFT (TD-DFT) to understand the underlying charge transfer mechanisms and identify structure-property relationships. The 2PA response is found to be enhanced in topologies that provide large conjugation pathways, such as in NU-901, and in frameworks where the linkers are in closer proximity, as in BaTBAPy. Furthermore, the 2PA response was found to depend on the intrinsic nature of the linker, for instance, the flexible H₄TCPE linker exhibits aggregation-induced emission (AIE) as well as on the type of metal node. These results demonstrate that both strategies offer promising routes toward optically and electronically responsive MOFs, and that the computational approach presented here can be used to accelerate the rational design of such materials prior to synthesis.

Zusammenfassung

Metall-organische Gerüstverbindungen (MOFs) sind hybride poröse Materialien, die aus organischen Linkern und anorganischen Metallknoten bestehen und Netzwerke mit vielfältigen Topologien und Dimensionalitäten bilden können. Während MOFs intensiv für Anwendungen wie CO₂-Adsorption, Gasspeicherung, Katalyse und Drug Delivery untersucht wurden, rückten ihre elektronischen und optischen Eigenschaften erst deutlich später in den Fokus, teilweise aufgrund der anfänglichen Annahme, dass diese Materialien elektrisch isolierend seien. In jüngerer Zeit haben verschiedene Strategien darauf abgezielt, den Ladungstransfer innerhalb von MOFs zu verbessern, um deren potenzielle Anwendungen in der Sensorik, Bioimaging und Datenspeicherung zu erschließen. Eine systematische Untersuchung darüber, wie molekulares Design und MOF-Topologie diese Eigenschaften bestimmen, bleibt jedoch begrenzt.

Das Ziel dieser Arbeit ist die computergestützte Untersuchung der elektronischen und optischen Eigenschaften von MOFs durch zwei unterschiedliche Designstrategien: i) die Einbindung photoschaltbarer Moleküle in einen MOF vom Paddle-Wheel-Typ zur Bewertung der Ladungstransferraten, und ii) die Einbindung von Zwei-Photonen-Absorptions (2PA)-aktiven Chromophoren (H₄TBAPy und H₄TCPE) als organische Linker in MOFs, um zu untersuchen, wie deren Konformationen die 2PA-Antwort beeinflussen. In dem ersten Teil wird die Modulation der Leitfähigkeit beim Photoschaltvorgang von Spiropyran zu Merocyanin mithilfe der Dichtefunktionaltheorie (DFT) und der Molekulardynamik (MD) untersucht. Die Ergebnisse zeigen durchschnittliche Ein/Aus-Leitwert-Verhältnisse von mehr als 530 bzw. 4200 für p- und n-Typ-Leitung, wobei eine weitere Modulation durch Funktionalisierung der Photoschalter mit elektronendonierenden und elektronenziehenden Gruppen möglich ist. Im zweiten Teil werden die 2PA-Eigenschaften zweier tetratopischer Linker, H₄TCPE und H₄TBAPy, mittels DFT und zeitabhängiger DFT (TD-DFT) untersucht, um die zugrundeliegenden Ladungstransfermechanismen zu verstehen und Struktur-Eigenschafts-Beziehungen zu identifizieren. Es zeigt sich, dass die 2PA-Antwort in Topologien verstärkt wird, die große Konjugationspfade bieten, wie beispielsweise NU-901, sowie in Gerüsten, in denen die Linker näher beieinander liegen, wie in BaTBAPy. Darüber hinaus hängt die 2PA-Antwort von der intrinsischen Natur des Linkers ab, so zeigt beispielsweise der flexible H₄TCPE-Linker aggregationsinduzierte Emission (AIE), sowie von der Art des Metallknotens. Diese Ergebnisse zeigen, dass beide Strategien vielversprechende Wege zu optisch und elektronisch responsiven MOFs bieten und dass der hier vorgestellte computergestützte Ansatz das rationale Design solcher Materialien vor der Synthese beschleunigen kann.

Contents

Acknowledgments	i
Abstract	iii
Zusammenfassung	v
List of Abbreviations	ix
1 Introduction	1
1.1 Metal-Organic Frameworks	1
1.2 Electronic and Optical Properties of MOFs	2
1.2.1 Photoswitchable Molecules in MOFs	3
1.2.2 Two-Photon Absorption Properties of MOFs	6
1.3 Research Gap	8
1.4 General Objective	8
1.4.1 Specific Objectives for the Electronic Properties	9
1.4.2 Specific Objectives for the Optical Properties	9
2 Theoretical Background	11
2.1 Electronic Properties	11
2.1.1 Conductivity and Transport Mechanisms	11
2.1.2 Hopping Mechanism: Marcus Theory	13
2.2 Optical Properties	15
2.2.1 Two-Photon Absorption (2PA)	15
2.3 Theoretical Calculations	17
2.3.1 Density Functional Theory (DFT)	18
2.3.2 Time-Dependent Density Functional Theory (TD-DFT)	25
2.3.3 Molecular Dynamics	28
2.3.4 SimStack: A Workflow Framework for Multiscale Simulations	32
3 Electronic Properties: Photoswitching Conductivity in Spiropyran-Based MOFs	35
3.1 Methodology: Structure Generation, Optimization and Postprocessing with Sim-stack	36

3.2	Results and Discussion	40
3.3	Summary	45
4	Optical Properties: Two-Photon Absorption Structure-Property Relationship of H₄TCPE and H₄TBAPy MOF Organic Linkers	47
4.1	2PA Properties in H ₄ TCPE Linker	47
4.1.1	Methodology: Structure Generation and Conformational Screening	48
4.1.2	Results and Discussion	51
4.1.3	Summary	64
4.2	2PA Properties in H ₄ TBAPy-Based MOFs	65
4.2.1	Methodology: Structure Generation and Conformational Screening	65
4.2.2	Results and Discussion	67
4.3	Summary	76
5	Conclusions	77
5.1	Outlook	78
A	Appendix: Photoswitching Conductivity in Spiropyran-Based MOF	81
A.1	Functionalized Spiropyran and Merocyanine-Based MOFs	81
B	Appendix: Two-Photon Absorption Structure-Property Relationship of H₄TCPE and H₄TBAPy MOF Organic Linkers	83
B.1	2PA Properties in H ₄ TCPE: Monomer	83
B.2	2PA Properties in H ₄ TCPE: Dimer Systems	87
B.2.1	Orbitals Visualization	104
B.2.2	Multiwfn Analysis	108
B.3	2PA Properties in H ₄ TBAPy Linker	109
C	Permissions to Print	141
D	List of Publications	143
E	List of Conference Contributions	145
F	Statement of AI Utilization	147
G	Bibliography	149
H	List of Figures	171
I	List of Tables	179

List of Abbreviations

MOF	Metal-Organic Framework
ZIF	Zeolitic Imidazolate Framework
SURMOF	Surface-Anchored Metal-Organic Framework
HOF	Hydrogen-Bonded Organic Framework
SBU	Secondary Building Unit
DABCO	1,4-Diazabicyclo[2.2.2]octane
DMF	Dimethylformamide
SP	Spiropyran
MC	Merocyanine
DAE	Diarylethene
DASA	Donor-Acceptor Stenhouse Adduct
AB	Azobenzene
TCPE	Tetrakis[4-(4-Carboxyphenyl)phenyl]ethylene
TBAPy	1,3,6,8-Tetrakis(<i>p</i> -benzoic acid)pyrene
TPE	Tetraphenylethylene
CT	Charge Transfer
IntraCT	Intramolecular Charge Transfer
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
NLO	Nonlinear Optical
2PA	Two-Photon Absorption

IPA	One-Photon Absorption
MPA	Multiphoton Absorption
MPEF	Multiphoton-Excited Fluorescence
AIE	Aggregation-Induced Emission
ACQ	Aggregation-Caused Quenching
LE	Local Excitation
EDD	Electron Density Difference
IFCT	Inter-Fragment Charge Transfer
ICTP	Intrinsic Charge-Transfer Percentage
ACTP	Apparent Charge-Transfer Percentage
DFT	Density Functional Theory
TD-DFT	Time-Dependent Density Functional Theory
HF	Hartree-Fock
UHF	Unrestricted Hartree-Fock
SCF	Self-Consistent Field
KS	Kohn-Sham
LDA	Local Density Approximation
LSDA	Local Spin Density Approximation
GGA	Generalized Gradient Approximation
mGGA	Meta-Generalized Gradient Approximation
HMGGA	Hybrid Meta-Generalized Gradient Approximation
PAW	Projector Augmented Wave
PBE	Perdew-Burke-Ernzerhof
RI	Resolution of Identity
SOS	Sum-Over-States

COSMO	Conductor-like Screening Model
ECP	Effective Core Potential
LCAO	Linear Combination of Atomic Orbitals
MD	Molecular Dynamics
NVE	Microcanonical Ensemble (constant N, V, E)
NVT	Canonical Ensemble (constant N, V, T)
NpT	Isothermal-Isobaric Ensemble (constant N, p, T)
VASP	Vienna Ab initio Simulation Package
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
VMD	Visual Molecular Dynamics
ASE	Atomic Simulation Environment
HPC	High-Performance Computing
WaNo	Workflow Active Node

1. Introduction

1.1. Metal-Organic Frameworks

Framework materials are structural solids that are often crystalline, porous, and characterized by lattice-like architectures extending in one, two, or three dimensions.^[1] These hybrid materials are commonly classified according to their composition. First, framework materials consist of metal nodes connected by organic linkers; well-known examples include metal-organic frameworks (MOFs),^[2,3] zeolitic imidazolate frameworks (ZIFs),^[4] and surface-anchored MOFs (SURMOFs).^[5–7] In contrast, purely organic frameworks do not contain metal nodes and are constructed entirely from organic building blocks linked through covalent or non-covalent interactions. Representative examples include covalent organic frameworks (COFs),^[8–10] porous aromatic frameworks (PAFs),^[11] and hydrogen-bonded organic frameworks (HOFs).^[12–14]

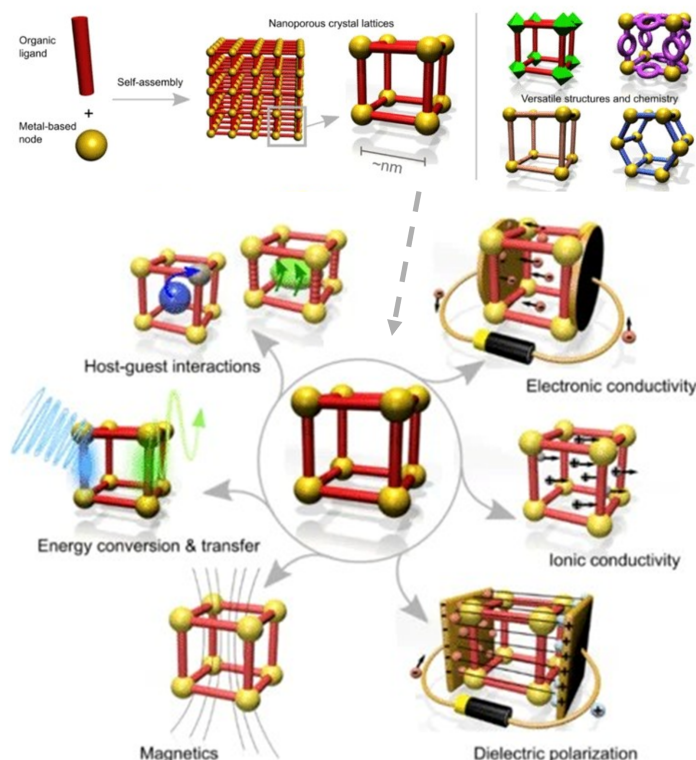


Figure 1.1. Schematic overview of the structural and chemical diversity of MOFs and their representative applications in functional devices. Adapted from Ivo Stassen *et al.*,^[15] with permission from the Royal Society of Chemistry, licensed under CC BY 3.0.

Among the previously mentioned framework materials, MOFs, also known as porous coordination polymers (PCPs), are among the most extensively studied since their early development in 1995.^[16] MOFs are assembled from metal ions or clusters and organic linkers (see Figure 1.1) through coordination bonds,^[3] typically involving terminal carboxylate groups, although nitrogen-based terminal groups have also been widely employed.^[17] The broad range of possible combinations between metal nodes and organic linkers provides exceptional synthetic versatility, enabling the rational design of materials with diverse topologies, that is, different patterns of connectivity between the building units, as well as large surface areas, tunable pore sizes, and high structural stability as visualized in Figure 1.1.^[18,19] In addition, active sites can be incorporated into the framework, which is particularly important for catalytic applications.^[20,21] Many MOFs also exhibit a “breathing” effect, that is, a reversible structural expansion or contraction, which is especially useful for gas adsorption.^[22] Furthermore, structural features such as framework dimensionality, degree of interpenetration, and rigidity strongly influence the optical properties of organic linkers, notably in systems showing aggregation-induced emission (AIE) behavior.^[23] Owing to these features, MOFs have been widely explored for applications including gas storage, separation,^[24] catalysis,^[20,21] and drug delivery.^[25] Beyond their structural and porous characteristics, MOFs have also attracted increasing interest as platforms for electronic and optical applications, including photoluminescence,^[26] sensing,^[27,28] magnetism,^[29] optoelectronics,^[3] bioimaging,^[30] conductivity,^[31] and energy storage.^[32] Although MOFs were originally considered insulating materials, recent research has increasingly focused on tailoring their electronic structure and incorporating charge-transfer-active components to improve their conductivity.^[31,33,34]

1.2. Electronic and Optical Properties of MOFs

From an electronic perspective, MOFs have been investigated for properties such as charge transport,^[30,35] redox activity,^[36] and magnetism, among others.^[29] In this context, electrical conductivity in MOFs can arise either intrinsically, through the electronic structure of the framework itself,^[37] or extrinsically,^[38] through the incorporation of guest species, dopants, or charge carriers that facilitate charge transport.^[35] Although ionic conductivity, including proton conduction, has been widely reported in MOFs,^[39–43] the present work focuses specifically on electron conductivity in MOFs (see section 2.1). Beyond the electronic properties, MOFs are also of great interest for optical applications. Particularly, because they can incorporate chromophores into well-defined, tunable framework environments.^[44] The interactions of the chromophores in MOFs with light have been the subject of interest because light offers a non-invasive external stimulus that can be precisely controlled in terms of intensity, duration, and spatial localization. Some studies have investigated how the chromophore integration into scaffolds can significantly alter its absorption and emission maxima,^[45] quantum yields,^[46–48] and fluorescence lifetimes^[49] compared with the behavior of the unrestricted chromophore (e.g., in solution). Moreover, MOFs allow the design of structures that accommodate a high density of chromophores per unit cell, which may further enhance

their optical response through cooperative intermolecular effects. For example, Collini^[50] reported that the organization of chromophores in supramolecular assemblies can enhance optical properties such as two-photon absorption (2PA). Since the optical properties of MOFs cover a broad range of phenomena, for the purposes of this work, the discussion is restricted to 2PA and will be described in the next chapter (see subsection 2.2.1).

It is important to emphasize that the electronic and optical properties of MOFs are closely interconnected, and this coupling is particularly evident in photoresponsive and optoelectronic MOFs, where light absorption can, for example, induce changes in the geometry of the chromophore, in electronic structure, and, consequently, in charge transport behavior. Several studies have reported conduction photoswitching in MOFs,^[1,31,35,38] and have proposed different strategies to enhance photoresponse. This will be discussed in subsection 1.2.1.

1.2.1. Photoswitchable Molecules in MOFs

Among photoresponsive molecules, photoswitchable molecules are of particular interest: they can reversibly undergo structural rearrangements upon light irradiation (e.g., photoisomerization), thereby altering their electronic structure. This is illustrated in Figure 1.2, where the insets show the molecular structure of the photoswitch in its OFF and ON states. The reversibility depends on the stability of the photogenerated state. When the photogenerated configuration is less stable than the initial state, the system can return to its original form upon removal of the stimulus.^[1] In this context, both i) thermally reversible (T-type) and ii) photochemically reversible (P-type) photoswitches are known.^[51] In this work, the discussion is focused on P-type photoswitches.

The photoisomerization mechanisms of photoswitches can generally be classified into two categories: i) (*E/Z*) isomerization and ii) ring-closing/ring-opening transformations. The (*E/Z*) isomerization involves the interconversion between the *E* (*entgegen*) and *Z* (*zusammen*) configurations around a double bond. This process does not involve bond breaking or bond formation, but rather a rearrangement of the atomic positions around the double bond, as observed, for example, in the *cis-trans* isomerization of azobenzene (AB) shown in Figure 1.3. In contrast, ring-opening/ring-closing transformations involve bond breaking and bond formation within a molecular ring system. This type of photoisomerization has been reported for spiropyrans (SP), diarylethenes (DAE),^[53] Donor-Acceptor Stenhouse Adducts (DASA),^[54] and related systems.^[55–57] Among these, spiropyran is particularly relevant for this work because its reversible transformation to the merocyanine (MC) form is accompanied by pronounced structural and electronic changes.

Photoswitchable molecules in solution can suffer from poor solubility or aggregation, especially in polar environments, which can negatively affect their absorption and emission properties and limit their photoisomerization efficiency.^[58] In the solid state, their motion is often restricted, which can hinder the structural rearrangements required for efficient switching.^[59,60] These limitations restrict the direct use of photoswitches in electronic devices, sensors, memristors, and related technologies.

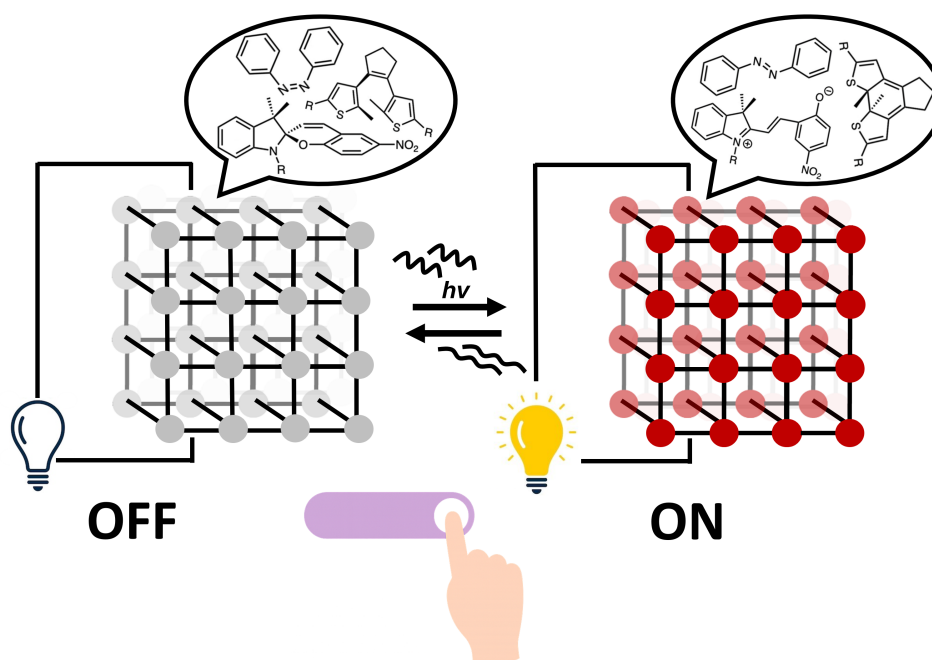


Figure 1.2. Schematic illustration of a photoswitchable framework showing reversible light-induced modulation of charge transport. Upon irradiation ($h\nu$), the molecular photoswitches in the material convert from an OFF state with low conductivity (left) to an ON state with enhanced charge transport (right). The reverse process restores the initial low-conductivity state. Reproduced from Pacheco Hernandez *et al.*,^[52] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

An attractive strategy to overcome these limitations is to incorporate photoswitchable molecules into metal-organic frameworks. The crystalline nanostructure of MOFs allows precise control over intermolecular distances and pore sizes, thereby reducing steric hindrance effects^[61,62] and facilitating the use of photoswitches in the solid state with improved photoconversion and without the need for solvents.^[63] In addition, MOFs can be prepared either as bulk crystals or as thin films, for example, as surface-mounted MOFs (SURMOFs),^[64] which offer different possibilities for harvesting photoswitchable responses. Several incorporation strategies have been reported, but they can be broadly grouped into three categories as shown in Figure 1.3: i) incorporation as guest molecules, ii) as backbone linkers, or iii) side groups attached to the main linker.

Photoswitchable MOFs have been investigated for applications such as controlled cargo release^[65–68] and gas adsorption.^[69,70] In the present work, however, the discussion is restricted to the modulation of the electron transfer rates in SP- and MC-based MOFs; the photoisomerization process is not studied; instead, the calculations are based on two systems, SP form and MC form, and later compared.

Several studies have examined the spectroscopic behavior of spiropyran in MOF environments. For example, Thaggard *et al.*^[71] showed that sterically demanding SP derivatives can increase the photoisomerization rate in rigid MOF matrices by up to three orders of magnitude compared with the same molecules in solution. At the same time, the conversion efficiency and switching behavior strongly depend on host-

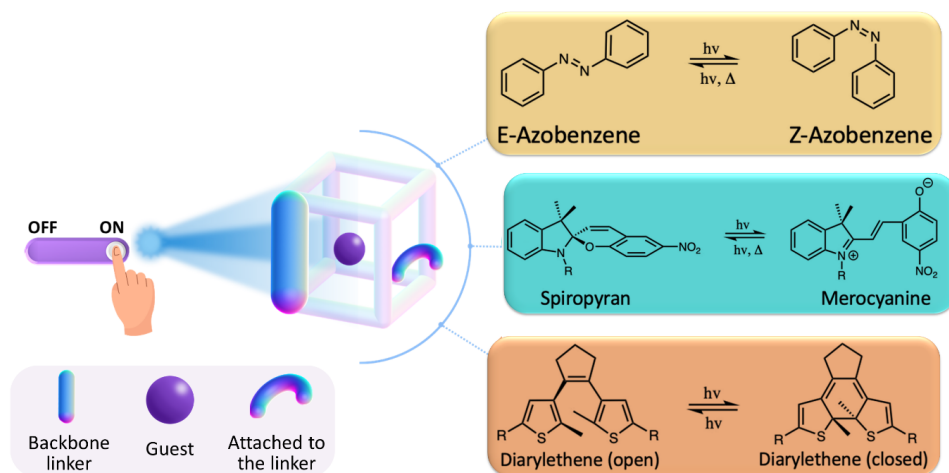


Figure 1.3. Photoswitchable molecules are commonly incorporated into framework materials in three different ways: (i) as backbone linkers, (ii) guest molecules, and (iii) attached to the linker. In this figure, azobenzene, spiropyran, and diarylethene are depicted as examples, but diverse photoswitches can be incorporated. Reproduced from Pacheco Hernandez *et al.*,^[52] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

guest interactions, metal-photoswitch interactions, steric constraints, and framework flexibility.^[72–74] For instance, SP functionalization in MOF-808 demonstrated that host polarity and structural changes influence both photoswitching efficiency and adsorption properties, with SP incorporation increasing CO₂ uptake but hindering reversibility because it stabilizes within the pores.^[75] Similarly, Schwartz *et al.*^[73] reported reversible photoswitching for SP encapsulated in MOF-5, MIL-68(In), and MIL-68(Ga). They concluded that the photoisomerization efficiency and kinetics depended strongly on the polarity of the host framework.

The mode of incorporation of the photoswitch into the MOF also plays an important role in determining the switching efficiency. Whether the photoswitch is incorporated as a guest molecule, attached to a linker, or integrated as a backbone linker affects the degree of steric confinement, pore accessibility, and structural flexibility.^[59] For backbone linkers, photoswitches that undergo only minor structural changes upon isomerization are generally preferred. Diarylethene-based linkers are a representative example, because their ring-opening/ring-closing process occurs largely within the molecular plane and therefore imposes only minimal structural distortions.^[64] By contrast, photoswitches with larger geometrical rearrangements, such as azobenzene, often exhibit hindered *cis-trans* isomerization when they are directly incorporated into the backbone linker.^[76] For this reason, photoswitches with larger structural changes perform better when added as pendant groups to a linker^[77] or incorporated as a guest molecule,^[64] although the latter strategy may still suffer from steric hindrance if the pores are too small to allow efficient photoisomerization.^[74]

Another important limitation in solid photoswitchable MOFs is the penetration depth of light, which may prevent efficient photoisomerization throughout the entire structure.^[78] In this respect, thin-film MOFs often exhibit faster and more efficient switching than bulk materials.^[79,80] In general, the penetration

depth of light depends strongly on the wavelength and on the absorption coefficient of the material. Strong absorption, particularly at the shorter wavelengths often used to trigger photoswitching,^[81] results in shallower penetration depths.^[82] Danowski *et al.* reviewed a range of photoresponsive porous materials and pointed out that photoisomerization in bulk samples is often confined to the surface because of scattering and limited light penetration, thereby restricting switching throughout the framework.^[83,84] One strategy proposed to address this limitation is the growth of MOFs as thin films with controllable thickness, which improves light accessibility and can reduce steric hindrance.^[85] In line with this, Zhang *et al.*^[86] demonstrated enhanced photochromic properties, reversibility, and stability in a nitrobenzospiropyran-embedded MOF thin film. For an azobenzene-based MOF film, Jiang *et al.*^[63] estimated the light penetration depth, defined as the depth at which the light intensity decreases to $1/e$ (approximately 37%) of its original value, to be on the order of hundreds of nanometers. Therefore, thick MOF films, pellets, and large crystals are often photoswitched only near their outer regions, while significant portions of the material remain in the dark state. As a result, not only the framework topology and the photoswitch incorporation strategy, but also the final physical form of the material, determine the light responsiveness of photoswitchable MOFs.

Among the different photoswitches explored in MOFs, spiropyran is particularly attractive for modulation of electron conductivity because the SP-to-MC transformation is accompanied by substantial changes in molecular geometry, conjugation, and charge distribution. The closed SP form is relatively compact and electronically less delocalized, whereas the open MC form is more extended and exhibits enhanced π -conjugation (see Figure 3.1). These differences can affect intermolecular distances, orbital overlap, and electronic coupling between neighboring photoswitches or linkers, which are key parameters for charge hopping. For this reason, SP/MC-based MOFs constitute a particularly relevant platform for understanding how light can reversibly modulate electron transport in framework materials.

1.2.2. Two-Photon Absorption Properties of MOFs

The interactions between light and matter in which the material response depends nonlinearly on the intensity of the incident light are described by nonlinear optical (NLO) processes.^[87] For these types of phenomena, usually intense laser irradiation is needed, enabling a wide range of effects, including multiphoton absorption (MPA),^[88] multiphoton-excited fluorescence (MPEF),^[89] and frequency upconversion processes such as second- and third-harmonic generation, among others.^[89]

When two or more photons of the same or different wavelengths are absorbed to populate an excited state of a material, the process is referred to as multiphoton absorption (MPA). After excitation, the system may subsequently relax either by emitting light^[90] or via nonradiative decay pathways.^[91] Although MPA can occur over a wide range of excitation wavelengths, it is most commonly studied using long-wavelength radiation, as this enables deeper light penetration into the material, reduces scattering effects, provides more precise control over the excitation volume, and minimizes photodamage.^[90,92]

For these reasons, materials exhibiting MPA properties are actively investigated for a variety of applications, particularly in biomedical imaging,^[90,93] as well as in three-dimensional optical data storage, long-range telecommunications, and advanced anticounterfeiting technologies, among others.^[94,95] Among MPA processes, 2PA corresponds to the transition of a material from the ground state to an excited state through the simultaneous absorption of two photons. This optical process is mediated by a virtual intermediate state. Its probability scales quadratically with the light intensity, allowing access to excited states that are weakly accessible or inaccessible under one-photon excitation.^[87] The strength of this process in a material is commonly expressed in Göppert-Mayer units (GM), where $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1}$,^[87] and is referred to as the 2PA cross section. Some studies also report the 2PA action cross-section, defined as the product of the absorption cross-section and the fluorescence quantum yield.

Larger 2PA cross sections are typically observed in molecules or materials that combine i) extended π -conjugation,^[96] ii) intramolecular charge transfer (IntraCT) character,^[88,97–99] and iii) high hyperpolarizabilities.^[97,100] Extended π -conjugation promotes delocalization and mobility of the electrons across the molecule or material, which favors the nonlinear optical response. In addition, IntraCT character can further enhance 2PA by increasing the change in polarizability upon excitation and by strengthening dipole coupling through low-lying charge-transfer intermediate states. As a result, aromatic molecules connected by conjugated bridges are commonly considered.^[95,101] Based on these observations, it has been possible over the years to design and synthesize organic molecules with increasingly large molecular 2PA cross sections, improving from typical values of about $1\text{--}10^2 \text{ GM}$ to values exceeding 10^3 GM .^[95] Some chromophores exhibit AIE, a phenomenon linked to enhanced 2PA cross sections. This behavior is especially relevant for structurally flexible chromophores that undergo significant nonradiative decay in solution. Upon aggregation, restricted intramolecular motions suppress these nonradiative pathways, enabling more efficient 2PA harvesting.^[102,103] Aggregation can further enhance 2PA by promoting extended conjugation between chromophores, increasing their collective polarizability, and facilitating intermolecular charge redistribution. These effects strengthen dipole coupling and can give rise to both intramolecular and intermolecular CT,^[104,105] both of which are known to amplify the 2PA response. In contrast, for rigid planar chromophores, specific conformations within aggregates can either enhance (J-aggregates) or quench (H-aggregates) the emission (see Figure 1.4), and have similarly been linked to modulation of the 2PA response. H-aggregates in particular, promote nonradiative decay leading to aggregation-caused quenching (ACQ).^[106] Consequently, developing strategies to increase the local concentration of 2PA-active moieties within well-defined, tunable structures while suppressing quenching pathways remains an active area of research.

In this context, immobilizing 2PA chromophores as photoactive linkers in ordered lattices, such as MOFs, enables high chromophore density and controlled alignment and spacing. This strategy has been shown to produce cross sections as high as 10^7 GM ,^[108] being particularly relevant for AIE-active linkers such as the H_4TCPE ^[91,109] linker studied here.

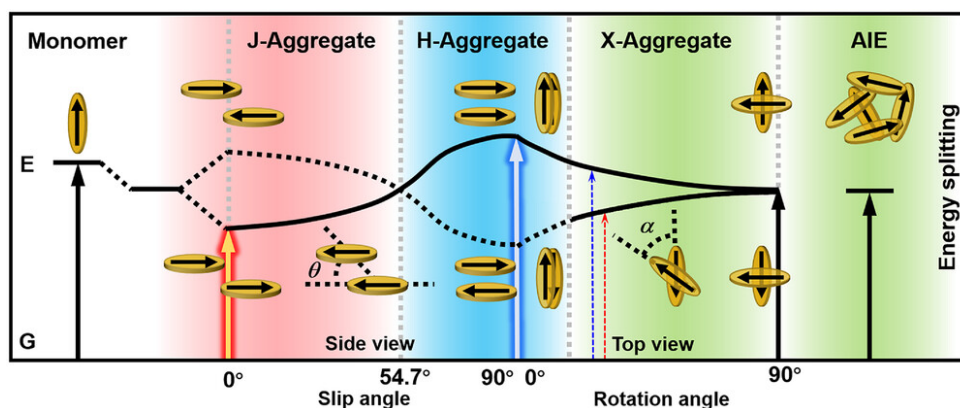


Figure 1.4. Schematic representation of excited state energy splitting for different molecular aggregate types (J-, H-, X-aggregates, and AIE). Reproduced from Ma *et al.*,^[107] with permission from John Wiley & Sons, 2021. Licensed under CC BY.

1.3. Research Gap

Despite the growing interest in multifunctional MOFs, important questions remain insufficiently explored.

First, incorporating a photoswitchable molecule, such as spiropyran, into a MOF could enable a switch from a non-conductive (off) to a conductive (on) MOF. If such a change is possible, it remains unclear whether the electronic coupling differs significantly between the SP and MC forms, and whether functionalization of the photoswitch with electron-donating or electron-withdrawing substituents can modulate the electronic coupling. To date, no study has systematically addressed these questions for paddle-wheel MOFs in which SP/MC units are attached to the MOF backbone linker.

A second important concern is how the structural constraint imposed by MOFs can modify the electronic environment and modulate the 2PA response of 2PA active chromophores. To the best of our knowledge, no systematic investigation has examined how linker conformation and relative arrangement, especially determined by the intrinsic nature of the linker, whether it is flexible as in H₄TCPE or rigid as in H₄TBAPy can affect the resulting 2PA cross-section and the associated changes in electronic density distribution. More specifically, for H₄TBAPy, no study has addressed how incorporation into different MOF topologies modulates its 2PA activity, while for H₄TCPE, despite being among the most studied NLO-active linkers, no work has combined controlled aggregation models with electronic-structure analysis to establish how aggregation type governs its 2PA response.

1.4. General Objective

The main objective of this thesis is to investigate two structure-property relationships in MOFs through computational modeling, specifically DFT, TD-DFT, and MD. First, we examine how the incorporation of SP/MC photoswitchable units into a MOF affects electronic coupling, and whether the photoswitch-

ing can drive a transition between distinct conductive states. Second, we study how the conformation and relative arrangements adopted by two different 2PA-active chromophores (H_4TCPE and H_4TBAPy) within a MOF environment governs their 2PA cross-section.

1.4.1. Specific Objectives for the Electronic Properties

With respect to the electronic properties of MOFs, this thesis focuses on understanding the electronic coupling in frameworks containing photoswitchable linkers. The specific objectives are:

1. To construct *in silico* MOF models attaching photoswitchable spiropyran to the linker backbone as well as its photoisomerized merocyanine form.
2. To investigate the structural dynamics of the MOF in the spiropyran and merocyanine state by means of MD simulations to identify relevant conformations.
3. To extract representative conformations from the MD trajectories for subsequent electronic-structure analysis.
4. To evaluate the electronic coupling between neighboring fragments (SP-SP and MC-MC).
5. To identify which structural arrangements and photoisomeric states provide the highest electronic coupling.

1.4.2. Specific Objectives for the Optical Properties

With respect to the optical properties, this thesis focuses on nonlinear optical behavior, particularly in the 2PA response, and on establishing structure-property relationships in MOF-based systems. The specific objectives are:

1. To evaluate the 1PA and 2PA properties of the isolated monomers (H_4TCPE and H_4TBAPy).
2. To investigate the 2PA response of dimer models in different relative conformations and packing arrangements.
3. To determine which intermolecular conformations and structural parameters are associated with enhanced 2PA response.
4. To analyze charge-transfer pathways in experimentally synthesized MOFs (H_4TBAPy -based) in order to rationalize their optical response.
5. To identify promising structural arrangements in hypothetical or not-yet-synthesized MOFs (H_4TCPE -based) that may exhibit improved nonlinear optical properties.
6. To establish structure-property relationships that can guide the future design of MOFs with enhanced 2PA performance.

2. Theoretical Background

2.1. Electronic Properties

Conductivity in photoswitchable MOFs is a topic where electronic and optical properties are well coupled. However, the project photoswitching conductivity in spiropyran-based MOFs is discussed in the context of electronic properties rather than optical ones. This is because, for this project, we calculate only the electronic coupling and electron-transfer rates for two separate systems (SP and MC), leaving the photoisomerization process outside the scope of this study and assuming complete conversion from SP to MC. In the following subsections, conductivity, transport mechanisms, and the methods to calculate the charge transfer rates in photoswitchable MOFs are described.

2.1.1. Conductivity and Transport Mechanisms

As mentioned in the previous section (see section 1.2), MOFs can be either intrinsically or extrinsically conductive. At the same time, MOFs can exhibit different charge transport pathways. The pathways can be broadly simplified into two main types: i) through-bond and ii) through-space transport.^[1] Although some reviews classify charge transport into several categories, such as guest-promoted transport, hopping, through-space, through-bond, and extended conjugation.^[29]

In i) through-bond transport, charge carriers move along continuous chains of chemical bonds connecting the building units of the framework. In ii) through-space transport, the transfer occurs between nearby units without a direct bonded pathway, mainly through orbital overlap, π - π stacking, or other weak intermolecular interactions. Depending on the type of charge carrier, transport can be classified as p-type (hole transport) or n-type (electron transport). In p-type conduction, the mobile carrier is a hole, corresponding to the absence of an electron. As electrons hop between neighboring occupied states, the hole effectively propagates through the material, which is commonly described as HOMO-HOMO hopping or hole transfer through HOMO-derived states. In contrast, n-type conduction involves the transport of electrons between neighboring unoccupied states and is commonly described as LUMO-LUMO hopping or electron transfer through LUMO-derived states.^[110]

More generally, the transport of charge in MOFs can be described in terms of two principal mechanisms: i) band-like conduction and ii) hopping conduction. In addition, an intermediate transient regime has also been proposed, lying at the boundary between localized hopping and fully delocalized transport. In this dynamically disordered and partially coherent regime, charge carriers are transiently localized by molecular fluctuations while still retaining some degree of delocalized character.^[111,112] In i) band-like

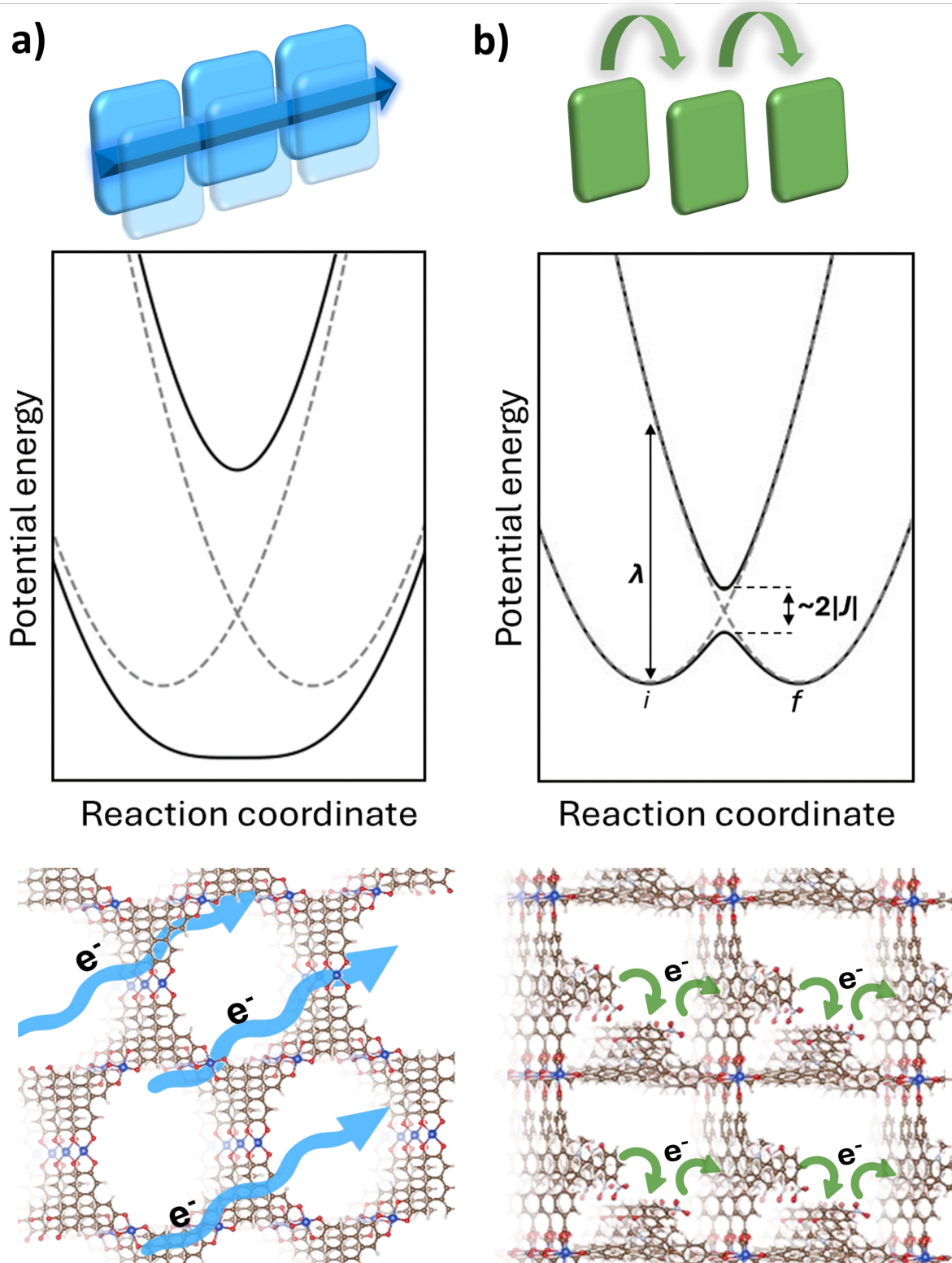


Figure 2.1. Schematic illustration of a) band-like and b) hopping transport mechanisms. Left: in the adiabatic regime with strong electronic coupling (solid curves), charge carriers are delocalized over multiple sites and move coherently through extended electronic states, as indicated by the blue arrows. Right: hopping between the diabatic potential energy surfaces (dashed curves) of the initial and final localized sites is shown. The microscopic parameters governing the charge-transfer rate in the weak-coupling regime are included for clarity and discussed in the text. The energy difference between hopping sites is neglected. Green arrows schematically indicate hopping within the MOF material. Reproduced from Pacheco Hernandez *et al.*,^[52] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

transport, the charge move through continuous energy bands and the charge carriers are delocalized over the material, allowing nearly barrierless motion, as illustrated in Figure 2.1 (left). This mechanism is generally associated with high electrical conductivity. However, it is relatively rare in MOFs and is typically observed only in frameworks with favorable topologies and chemical compositions, for example, certain 2D MOFs and COFs.^[33,113,114] In contrast, ii) hopping transport occurs between localized sites and requires overcoming an activation barrier for charge transfer from one site to another. This process depends on the energy difference between the localized states and on the reorganization energy, λ , required to reorganize the molecular or lattice environment, for example, through vibrational motions, see Figure 2.1 (right). The mechanism can be represented by parabolic potential energy surfaces (PESs) for the initial and final states, where the reorganization energy corresponds to the energetic cost of structural relaxation and the intersection region determines the probability of electron transfer. In this case, the strength of the interaction between neighboring sites, commonly described by the electronic coupling J , is a key parameter controlling the hopping rate. Stronger coupling generally increases the probability of charge transfer at the intersection of the two PESs. In the weak-coupling regime, where electron transfer is slower than nuclear motion, the charge remains localized and transfers by hopping after nuclear reorganization. Under these conditions, the charge-transfer rate depends quadratically on the electronic coupling. This framework is commonly described by Marcus theory, which is widely used to rationalize hopping transport in framework materials.^[110]

2.1.2. Hopping Mechanism: Marcus Theory

The hopping of charge carriers between localized states is widely accepted for most of the conductive MOFs, with only a few examples of band-like mechanism reported, especially for COFs or 2D MOFs.^[30,33] Some theories employed to quantify the hopping rates are Miller-Abrahams^[115] and Marcus,^[116] among others. Here, we focus on the Marcus theory to calculate the hopping rates between neighboring organic linkers within MOF as it explicitly accounts for nuclear reorganization upon charge transfer, which Miller-Abrahams theory neglects, since it was developed for rigid inorganic semiconductors where nuclear reorganization is minimal.

Rudolph A. Marcus developed a theory in the 50's to explain electron-transfer rates in reactions. Initially, the theory was developed for electron-transfer reactions in solution. The main idea is that for an electron to be transferred, it is necessary: i) molecules (or any reactant) must be sufficiently close so that their electronic orbitals overlap, and ii) the nuclear coordinates of the system must fluctuate to a configuration where energy is conserved during the transfer. These nuclear coordinates include the vibrational modes of the reactants and the orientational coordinates of the surrounding solvent molecules, both of which respond to changes in the charge distribution upon electron transfer. The potential energy of the entire system (molecules, reactants, and the surrounding medium) defines a multidimensional surface as a function of all nuclear coordinates. A one-dimensional profile is shown in Figure 2.2, where R and P are the reactant and product, respectively. Because electron transfer is much faster than nuclear motion

(as the electron mass is negligible compared to that of the nuclei), the Franck-Condon principle applies: transfer can only occur at nuclear configurations where the potential energy of the reactant surface equals that of the product surface, i.e., at their intersection (point B in Figure 2.2). The system reaches this intersection through thermal fluctuations away from the R minimum.

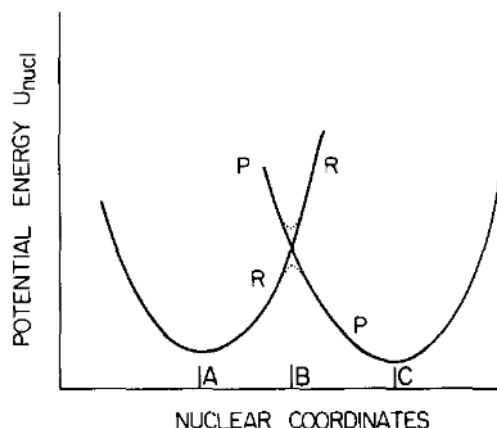


Figure 2.2. Profile of the many-dimensional potential energy surface of reactants plus surrounding medium (R) and products plus medium (P). Points A and C denote equilibrium nuclear configurations of reactants and products, respectively; B denotes the nuclear configuration at the intersection of the two surfaces. Dotted lines indicate the splitting due to electronic coupling between reactants. Reproduced from Marcus and Sutin,^[116] *Biochim. Biophys. Acta* **811**, 265-322 (1985), with permission from Elsevier.

The probability of going from the R to the P upon reaching the intersection B depends on the degree of electronic coupling (i.e., extent of orbital overlap), which in turn depends on the separation distance r of the reactants or, more precisely, on the dominant range of separation distances contributing to the reaction. In the classical adiabatic limit, where the coupling is strong, the transmission coefficient $\kappa \approx 1$ and every passage through the intersection results in a successful electron transfer. The rate constant is then governed entirely by the free energy of activation ΔG^* as shown in Equation 2.1:

$$k = \kappa A \sigma^2 \exp\left(-\frac{\Delta G^*}{RT}\right), \quad (2.1)$$

where $A\sigma^2$ is a pre-exponential factor with dimensions of collision frequency, σ is the average center-to-center distance in the reacting pair during the electron transfer, and ΔG^* is related to the reorganization energy (λ) and the standard free energy of reaction ΔG^0 as described by Equation 2.2:

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda}\right)^2. \quad (2.2)$$

In Equation 2.1, the nuclear motion was treated classically. For reactions with weak electronic coupling, where $\kappa \ll 1$, a quantum mechanical treatment to obtain the electron transfer rates at fixed separation distance r is given by:

$$k = \frac{2\pi}{\hbar} H_{AB}^2 \frac{1}{(4\pi\lambda RT)^{1/2}} \exp\left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda RT}\right], \quad (2.3)$$

where H_{AB} is the electronic coupling matrix element and $\lambda = \lambda_0 + \lambda_i$ is the total reorganization energy comprising outer-sphere (λ_0) and inner-sphere (λ_i) contributions. In chapter 3, this expression is employed in an equivalent form in which H_{AB} is denoted J_{if} and the thermal prefactor is expressed using the Boltzmann constant k_B rather than the molar gas constant R , related by $R = N_A k_B$.

2.2. Optical Properties

Nonlinear optical properties have been investigated in MOFs for applications including biomedical imaging,^[98] optical data storage,^[117] optical nanoprinting^[118] and long-range optical communications,^[119] among others. In this project, we focus especially on the two-photon absorption properties in metal-organic frameworks.

2.2.1. Two-Photon Absorption (2PA)

Photons are massless and chargeless particles of light that travel at the speed of light in vacuum, carry electromagnetic force, and exhibit wave-particle duality. The interaction between photons and molecules (or atoms) leads to an exchange between radiation and matter, which can be described as the absorption or emission of photons. Initially, only the one-photon absorption (1PA) or emission process was considered: a molecule (or atom) absorbs a photon from the incident light and simultaneously undergoes a transition to a higher energy level, or conversely, the molecule emits a photon when a transition from a higher to a lower energy level occurs. Maria Göppert-Mayer, in her doctoral dissertation in 1931,^[120] proposed for the first time the concept of two-photon absorption. She predicted theoretically that a simultaneous 2PA process should also lead to a transition from a lower to a higher energy level in atoms or molecules via a virtual intermediate state (see Figure 2.3). Thirty years later, in 1961, after the invention of the first laser device, her theory was experimentally confirmed by Kaiser and Garrett.^[121] Since then, research has continued, and it is now possible to observe three-photon absorption (3PA), four-photon absorption (4PA), and even higher-order multiphoton excitation processes.

In order to achieve higher-order multiphoton excitation, a high local intensity of the incident light (on the order of MW/cm²-GW/cm²) is required.^[95] The selection rules and pathways of the transitions upon multiphoton excitation can differ from those established for 1PA. In centrosymmetric molecules, for instance, states that are one-photon allowed are two-photon forbidden and vice versa, because 2PA requires the initial and final states to share the same parity. However, in non-centrosymmetric molecules, these parity-based selection rules no longer apply. The advantages of multiphoton absorption over 1PA include: i) the use of longer wavelengths (lower-energy photons), enabling access to excited states that may be inaccessible through 1PA due to different selection rules, ii) reduced photodamage and photo-

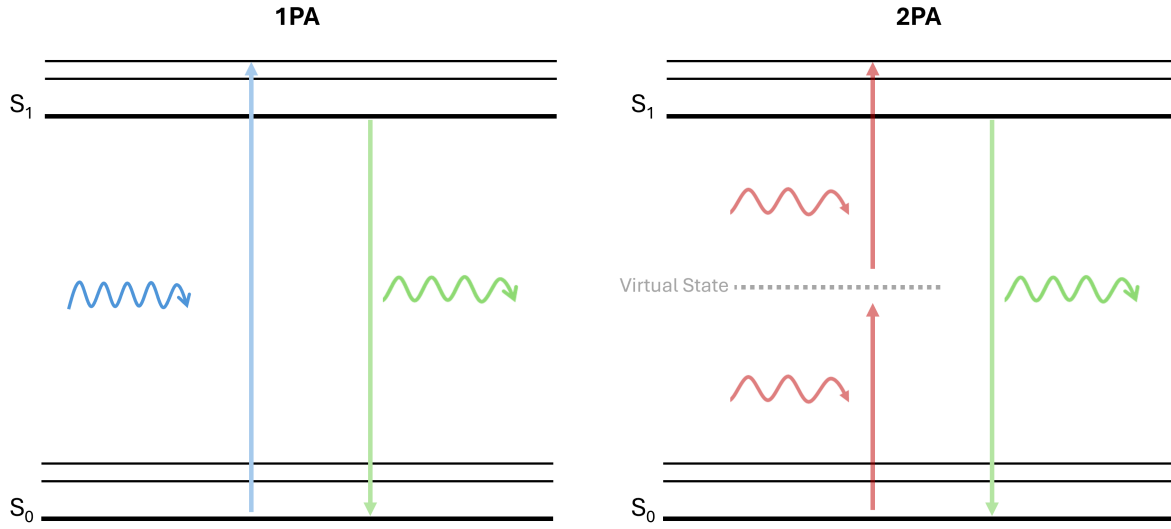


Figure 2.3. Simplified Jablonski diagram illustrating one-photon absorption (1PA, left) and two-photon absorption (2PA, right). In the 2PA process, two photons are absorbed simultaneously via a virtual intermediate state. The accessible excited states differ depending on the molecule's centrosymmetry.

bleaching outside the focal volume because lower-energy photons are less strongly absorbed, and (iii) deeper light penetration into materials and biological tissues due to the lower scattering and absorption of near-infrared light.

When an electromagnetic field interacts with a material, the induced polarization vector $\vec{\mathbf{P}}$ describes the collective response of the medium. In the case of applying a weak light field from an incoherent light source, $\vec{\mathbf{P}}$ is linearly proportional to the applied electric field $\vec{\mathbf{E}}$. If this field is a monochromatic wave with angular frequency ω , the linear case reads:

$$\vec{\mathbf{P}}(\omega) = \vec{\mathbf{P}}^{(1)}(\omega) = \varepsilon_0 \chi^{(1)}(\omega) \vec{\mathbf{E}}(\omega), \quad (2.4)$$

where $\chi^{(1)}(\omega)$ is the first-order (linear) susceptibility of a given medium and ε_0 is the permittivity. In general, $\chi^{(1)}(\omega)$ has the form of a second-rank tensor, where its real part determines the refractive index of the medium, while its imaginary part can be used to describe linear (one-photon) absorption.

In nonlinear optics, the optical response can be described as a generalization of Equation 2.4:

$$\begin{aligned} \vec{\mathbf{P}}(\omega) &= \vec{\mathbf{P}}^{(1)}(\omega) + \vec{\mathbf{P}}^{(3)}(\omega) + \vec{\mathbf{P}}^{(5)}(\omega) + \dots \\ &= \varepsilon_0 \left[\chi^{(1)}(\omega) \vec{\mathbf{E}}(\omega) + \chi^{(3)}(\omega, \omega, -\omega) \vec{\mathbf{E}}(\omega) \vec{\mathbf{E}}(\omega) \vec{\mathbf{E}}^*(\omega) \right. \\ &\quad \left. + \chi^{(5)}(\omega, \omega, -\omega, \omega, -\omega) \vec{\mathbf{E}}(\omega) \vec{\mathbf{E}}(\omega) \vec{\mathbf{E}}^*(\omega) \vec{\mathbf{E}}(\omega) \vec{\mathbf{E}}^*(\omega) + \dots \right], \end{aligned} \quad (2.5)$$

where $\vec{\mathbf{E}}^*(\omega)$ is the complex conjugate of the electric-field function $\vec{\mathbf{E}}(\omega)$ of the applied light wave. Note that only odd-order terms appear in Equation 2.5 because the even-order susceptibilities, such as $\chi^{(2)}$ (responsible for processes like second-harmonic generation), vanish in centrosymmetric and isotropic media by symmetry. The third-order nonlinear susceptibility $\chi^{(3)}(\omega, \omega, -\omega)$ is, in general, a complex fourth-rank tensor. Its real part describes the induced refractive-index change as a function of light intensity, while its imaginary part can be used to phenomenologically describe the 2PA process, which is central to this work. Similarly, the fifth-order term $\chi^{(5)}$ and higher-order susceptibilities correspond to higher-order multiphoton absorption processes such as 3PA and beyond. However, they are not discussed here. Third-order nonlinear optical interactions (described by $\chi^{(3)}$) can occur in both centrosymmetric and non-centrosymmetric media. The 2PA is a third-order nonlinear optical process, where the probability that a molecule simultaneously absorbs two photons to reach an excited state (mediated by a virtual state) scales quadratically with laser intensity.^[122] The imaginary part of the third-order susceptibility $\chi^{(3)}$ is related to the two-photon transition amplitude tensor $\mathbf{S}$, whose components S_{ab} can be evaluated via the quadratic response function of the electron density (see subsubsection 2.3.2).^[123] Although alternative approaches exist, such as the sum-over-states (SOS) formalism,^[124] the TD-DFT quadratic response method (see subsection 2.3.2), implemented in TURBOMOLE, offers a balance between computational efficiency and accuracy suitable for the molecular sizes considered in this work.

2.3. Theoretical Calculations

The structural complexity and chemical versatility of MOFs pose significant challenges for computational modeling. Their periodic crystalline framework, combined with large unit cells and the presence of open metal sites and flexible organic linkers, demands methods that can accurately describe both electronic structure and dynamical behavior at a reasonable computational cost. DFT has become the standard approach for ground-state electronic structure calculations in periodic systems, providing a balance between accuracy and tractability that higher-level methods, such as coupled-cluster theory, cannot offer for systems of this size. For the investigation of excited-state properties relevant to multiphoton absorption or emission, TD-DFT has proven to be a good approach. Complementarily, molecular dynamics (MD) simulations allow the study of thermodynamic and kinetic properties such as gas adsorption, diffusion, and structural flexibility, which are central to MOF applications (e.g., in gas storage and separation). However, in this work (see chapter 3), MD is used to study the dynamics of the linkers within the MOF. The following subsections describe each of the methods used to study the electronic and optical properties of MOFs, especially relevant in this work.

2.3.1. Density Functional Theory (DFT)

Many-Body Schrödinger Equation

Before starting the DFT section, it is important to explain (in short) the Schrödinger equation. More precisely, the time-independent, non-relativistic Schrödinger equation, which is written in its compact form as:

$$\hat{H}\Psi = E\Psi, \quad (2.6)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is the wavefunction, and E is the energy eigenvalue. For a molecule with n electrons and N atomic nuclei, the Hamiltonian operator consists of the kinetic energy of the nuclei ($\hat{T}_N$) and electrons ($\hat{T}_e$), as well as the nucleus-nucleus ($\hat{V}_{NN}$), nucleus-electron ($\hat{V}_{Ne}$), and electron-electron Coulomb interactions ($\hat{V}_{ee}$):

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (2.7)$$

It can be also described as follows:

$$\hat{H} = -\frac{1}{2} \sum_i^n \Delta_i - \frac{1}{2} \sum_I^N \frac{\Delta_I}{m_I} + \sum_I^N \sum_{J>I}^N \frac{Z_I Z_J}{r_{IJ}} - \sum_I^N \sum_i^n \frac{Z_I}{r_{Ii}} + \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} \quad (2.8)$$

where n and N are the number of electrons and nuclei, respectively; i and j denote electron indices, whereas I and J denote nuclear indices; m_I is the mass of nucleus I , Z_I is the atomic number (nuclear charge) of nucleus I , Δ_i and Δ_I are the Laplacian operators acting on the electronic and nuclear coordinates, respectively, r_{ij} is the distance between electrons i and j , r_{Ii} is the distance between nucleus I and electron i , and r_{IJ} is the distance between nuclei I and J .

The Hamiltonian operator can be simplified by decoupling the nuclear and electronic terms. This approach is known as the Born-Oppenheimer approximation. This approximation is physically motivated by the large mass difference between nuclei and electrons. For example, even the lightest nucleus (the proton) is approximately 1,800 times heavier than an electron, and for carbon this ratio exceeds 20,000 times.^[125] As a consequence, nuclei move more slowly than electrons. From the electrons' perspective, the nuclei appear to be stationary. This allows the total wavefunction to be separated into nuclear and electronic contributions, and the nuclear kinetic energy to be neglected ($\hat{T}_N$) in the electronic problem, while the nucleus-nucleus repulsion $\hat{V}_{NN}$ is considered as a constant.

Born-Oppenheimer Approximation

Considering this approach, the Equation 2.6 takes the form of the electronic Schrödinger equation:

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el} \quad (2.9)$$

reducing the Hamiltonian shown in Equation 2.7 and Equation 2.8 to:

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} \quad (2.10)$$

$$\hat{H}_{el} = -\frac{1}{2} \sum_i^n \Delta_i - \sum_I^N \sum_i^n \frac{Z_I}{r_{Ii}} + \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} \quad (2.11)$$

Within the Born-Oppenheimer approximation, the electronic Schrödinger equation can be solved exactly for single-electron systems (e.g., the hydrogen atom). Many-particle systems with multiple electrons, however, can only be described approximately due to electron-electron interactions. For this reason, the Hartree product approximates the full wave function as a product of individual one-electron wave functions, as shown in Equation 2.12:^[126]

$$\Psi \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \cdots \psi_n(\mathbf{r}_n), \quad (2.12)$$

However, the Hartree product approach is an approximation in which the electron-electron interaction is not accurately described. It assumes that electrons behave as independent particles, meaning that the motion of one electron is not explicitly influenced by the instantaneous positions of the others. Second, the Hartree product does not satisfy the antisymmetry requirement imposed by the Pauli exclusion principle, which states that the total wavefunction must change sign upon exchange of any two electrons. Both shortcomings are addressed by expressing the total wavefunction as a Slater determinant (Φ):

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix} \quad (2.13)$$

The $\frac{1}{\sqrt{N!}}$ prefactor ensures normalization. By construction, swapping two electrons (rows) or two orbitals (columns) changes the sign of the determinant, satisfying the antisymmetry requirement of the Pauli exclusion principle.^[127]

An approach to systematically improve the approximation to the true ground state is by applying the *variational principle*, which states that the expected energy $\langle E \rangle$ of any guessed (trial) wavefunction $\tilde{\Psi}$ is always greater than or equal to the true ground state energy E_0 of the system:^[125]

$$\langle E \rangle = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} \geq E_0, \quad (2.14)$$

where equality holds if and only if $\tilde{\Psi}$ is identical to the exact wavefunction Ψ_0 . This provides a practical optimization strategy by systematically varying the trial wavefunction to minimize $\langle E \rangle$, thereby approaching the true ground-state energy. In the Hartree-Fock method, which won't be fully described here, this minimization is carried out iteratively through a Self-Consistent Field (SCF) procedure, yield-

ing effective single-particle equations. However, HF neglects electron correlation entirely, motivating the development of DFT as a more complete and computationally tractable alternative.

DFT: Hohenberg-Kohn Theorems

The concept of a *functional* is central to DFT, while a function takes a number as input and returns a number (e.g., $f(x) = x^2 + 1$), a functional takes an entire function as input and returns a number. The total energy $E[\rho]$ is a functional of the electron density $\rho(\mathbf{r})$, which is where the name *density functional theory* comes from. DFT is built on two theorems proved by Hohenberg and Kohn in 1964.^[125]

The first Hohenberg-Kohn theorem (HK1) states that the external potential, and hence the total energy, is a unique functional of the ground-state electron density $\rho(\mathbf{r})$. Knowing $\rho(\mathbf{r})$ is therefore sufficient to determine all ground-state properties of the system.^[125,127] The second theorem (HK2) connects DFT to the variational principle (briefly mentioned in the previous subsection): the electron density that minimizes the total energy functional is the true ground-state density, providing a practical prescription to find the ground-state solution by minimizing $E[\rho]$.

The significance of working with $\rho(\mathbf{r})$ becomes clear when compared to the many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, which depends on $3N$ spatial coordinates in addition to the spin coordinate for each electron, and therefore grows unmanageably for systems with many electrons. The electron density, formally defined as:^[125]

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{s}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (2.15)$$

where $\mathbf{x}_i = (\mathbf{r}_i, \mathbf{s}_i)$ denotes the combined spin and spatial coordinates of electron i , always depends on only three spatial coordinates regardless of system size, with boundary conditions $\rho(\mathbf{r} \rightarrow \infty) = 0$ and $\int \rho(\mathbf{r}) d\mathbf{r} = N$.

Unfortunately, while HK1 rigorously proves that such an exact energy functional exists, the theorems say nothing about its actual form. In practice, this exact functional remains unknown, meaning that every DFT calculation carries an intrinsic approximation whose magnitude cannot be derived from first principles and must instead be assessed through comparison with experimental data or higher-level calculations.

The Kohn-Sham Formalism

The universal functional $F[\rho]$ contains two unknown contributions: the kinetic energy of the electrons and the non-classical electron-electron interactions. Early attempts to approximate the kinetic energy directly from the density, such as the Thomas-Fermi model, proved too inaccurate.^[125] Kohn and Sham resolved this by introducing the *non-interacting reference system*: a hypothetical system of electrons that do not repel each other, but are constrained to produce exactly the same electron density as the real, interacting system. Because this reference system has no electron-electron interactions, its kinetic energy

can be computed exactly using orbitals. In other words, this is analogous to the one-electron functions in Hartree-Fock theory. The small difference between this reference kinetic energy and the true kinetic energy, along with all remaining non-classical electron-electron effects, is collected into a single term: the exchange-correlation energy $E_{xc}[\rho]$.

Following Sholl and Steckel^[127] a useful way to write the functional described by the Hohenberg-Kohn theorem is in terms of the single-electron wave functions (see Equation 2.17), $\psi_i(r)$. Keeping in mind that is for practical purposes, since the electron density is constructed from them as:

$$\rho(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2, \quad (2.16)$$

where the factor of 2 accounts for the double occupancy of each spatial orbital by electrons of opposite spin. Therefore, $E[\{\psi_i\}]$ is equivalent to $E[\rho]$.

$$E[\{\psi_i\}] = E_{\text{known}}[\{\psi_i\}] + E_{xc}[\{\psi_i\}] \quad (2.17)$$

The E_{known} part, includes four contributions:

$$E_{\text{known}}[\{\psi_i\}] = -\frac{1}{2} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(\mathbf{r}) \rho(\mathbf{r}) d^3r + \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{\text{ion}} \quad (2.18)$$

first, the electron kinetic energies, then the Coulomb interactions between the electrons and the nuclei, the Coulomb interactions between pairs of electrons, and the Coulomb interactions between pairs of nuclei.

The $E_{xc}[\{\psi_i\}]$ from Equation 2.17 (also written as $E_{xc}[\rho]$) is the exchange and correlation functional and includes all the quantum-mechanical effects that are not considered in the known part. Kohn-Sham demonstrated that the problem of finding the correct electron density can be formulated as solving a set of equations, each involving a single electron.^[127]

$$\left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.19)$$

where $V(\mathbf{r})$ is the electron-nuclear attraction, $V_H(\mathbf{r})$ is the Hartree potential describing the classical Coulomb repulsion between electrons, and $V_{xc}(\mathbf{r})$ is the exchange-correlation potential, which have the form:

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (2.20)$$

Since V_H and V_{xc} both depend on the electron density, which itself depends on the orbitals ψ_i , these equations must be solved *self-consistently*. This is done iteratively, following four steps:^[127]

1. Define an initial trial electron density $\rho(\mathbf{r})$.
2. Solve the Kohn-Sham equations to obtain the single-particle wave functions $\psi_i(\mathbf{r})$.
3. Compute a new electron density from the updated orbitals: $\rho(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2$.
4. Compare the new density with the previous one. If converged, compute the total energy; otherwise update $\rho(\mathbf{r})$ and return to step 2.

The only term that cannot be treated exactly is $E_{\text{xc}}[\rho]$, whose approximation is the central challenge of practical DFT and the subject of the following section.

Exchange-Correlation Functionals

The only term in the Kohn-Sham energy functional that cannot be treated exactly is the exchange-correlation energy $E_{\text{xc}}[\rho]$. The Hohenberg-Kohn theorem says it exists but the true form of the functional is not known (only for the ideal theoretical model "the uniform electron gas").^[127] This has motivated the development of approximations in the quantum chemistry community. A common graphical representation of increasing sophistication, is the *Jacob's ladder* of density functional approximations,^[128] climbing from the simplest local approximations toward the yet-unreached limit of chemical accuracy, (see Figure 2.4).

As visualized in Figure 2.4, the simplest approximation is the *Local Density Approximation* (LDA), which assumes that $E_{\text{xc}}[\rho]$ at each point in space depends only on the local electron density at that point, treating it locally. Its spin-polarized extension, the *Local Spin Density Approximation* (LSDA), is analogous to the Unrestricted Hartree-Fock (UHF) method for the treatment of the spin. LSDA assigns electrons to spin-up and spin-down states in different spatial KS orbitals (each with its own electron density function), which can handle systems with one or more unpaired electrons.^[128] While LDA and LSDA provide a practical starting point, their accuracy is limited for inhomogeneous systems with strongly varying electron densities.

A systematic improvement and one of the most employed $E_{\text{xc}}[\rho]$ approximations is the *Generalized Gradient Approximation* (GGA), which incorporates not only the local electron density but also its gradient $\nabla\rho(\mathbf{r})$, thereby accounting for spatial variations in the density. Widely used GGA functionals include PBE and BLYP.^[128] The next rung, *meta-GGA* (mGGA), further extends this by including the kinetic energy density, $\tau(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla\psi_i(\mathbf{r})|^2$, of the Kohn-Sham orbitals, providing a more flexible description of $E_{\text{xc}}[\rho]$ without a significant increase in computational cost.^[128]

Hybrid functionals mix a fraction of exact Hartree-Fock exchange with a GGA or meta-GGA functional, motivated by the adiabatic connection framework.^[128] A widely used example is B3LYP. Its range-separated extension, CAM-B3LYP,^[129] addresses a known limitation of global hybrids by applying a larger fraction of exact exchange at long range, which improves the description of charge-transfer exci-

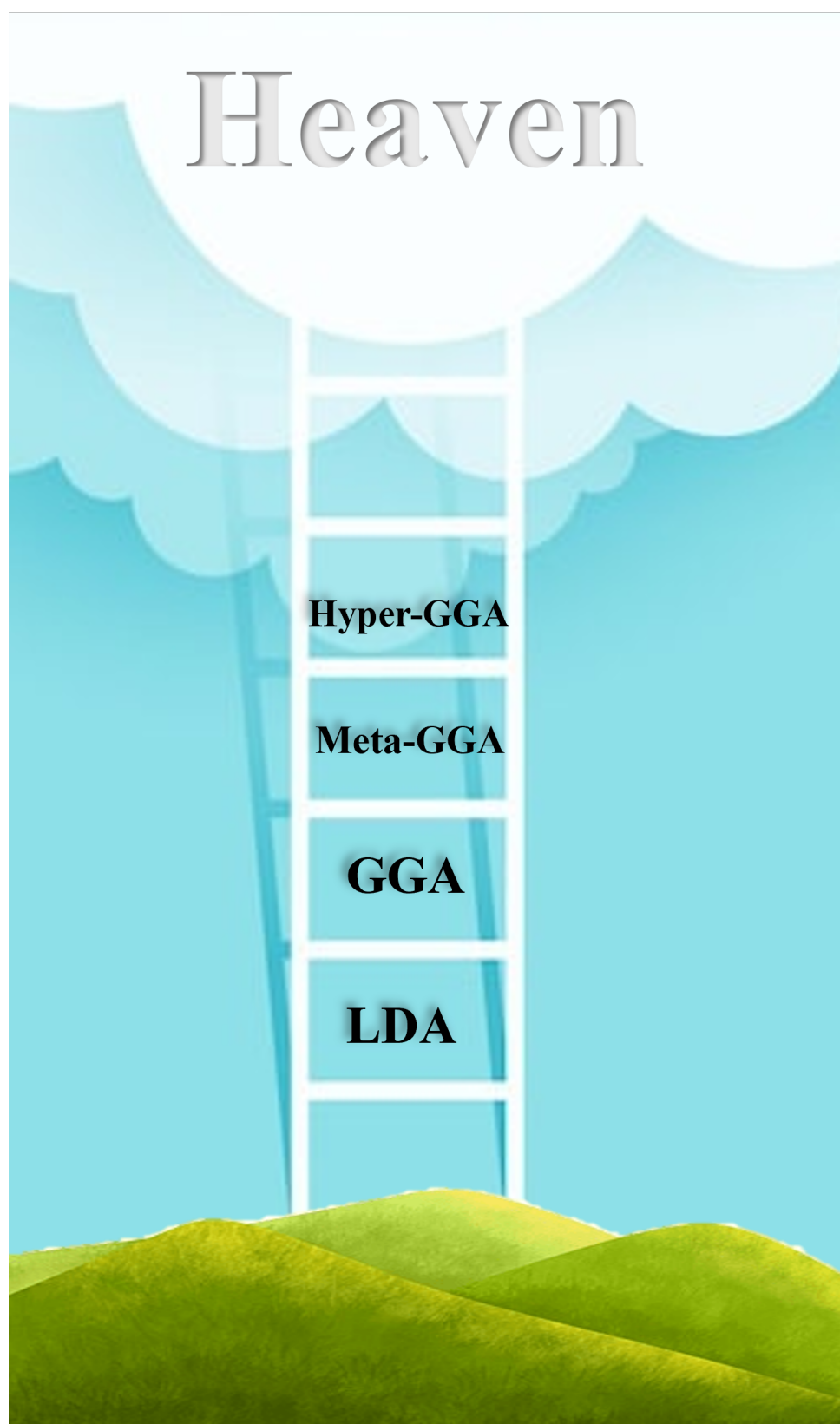


Figure 2.4. Perdew’s Jacob’s ladder of DFT exchange-correlation functionals, illustrating the hierarchy from the simplest LDA at the lowest rung to fully non-local (Earth), to “heaven” which represents the limit of chemical accuracy.

tations (particularly relevant for the systems studied in this work). Both B3LYP and CAM-B3LYP are employed in this thesis.

Higher rungs of Jacob’s ladder exist, such as *hybrid meta-GGA functionals* (e.g., M06-2X, TPSSh), which combine exact exchange with kinetic energy density, and *fully non-local functionals*. These represent the current practical limit of routine DFT calculations but are not employed in this work. It should be noted that increasing computational cost does not guarantee improved accuracy, and the choice of functional must always be validated against experimental data or higher-level calculations for the specific system under study.

Dispersion Corrections (D3, D3-BJ)

Dispersion interactions (also known as van der Waals interactions or London forces) are attractive interactions that arise as a result of electron correlation. A well-known limitation of standard GGA and hybrid functionals is their inability to accurately describe dispersion interactions.^[127]

These interactions arise from transient dipole moments induced by electron density fluctuations. Although they are weak at short range, they can induce a temporary dipole moment on other atoms or molecules by distorting their electron density. A practical way to introduce the dispersion interactions is the DFT-D approach,^[127] in which a classical dispersion-like contribution is added to the total DFT energy, as shown in Equation 2.21. Alternative approaches include Tkatchenko-Scheffler,^[130] nonlocal correlation functionals (DFT-NL)^[131] or the Minnesota functionals (e.g., M06-2X or M06-L) that include medium-range dispersion through their exchange-correlation form,^[132,133] among others, which are beyond the scope of this work.

$$E_{\text{DFT-D}} = E_{\text{DFT}} - S \sum_{i \neq j} \frac{C_{ij}}{r_{ij}^6} f_{\text{damp}}(r_{ij}), \quad (2.21)$$

Here, r_{ij} is the distance between atoms i and j , C_{ij} is a dispersion coefficient derived from tabulated atomic properties, $f_{\text{damp}}(r_{ij})$ is a damping function that avoids unphysical behavior at short distances, and S is a global scaling factor optimized for each functional. Among the most widely used dispersion correction variants (and also employed in this work) are Grimme’s D3 correction and its Becke-Johnson damped form (D3-BJ).^[134]

Basis Sets

To solve the Kohn-Sham equations numerically, the molecular orbitals $\psi_i(\mathbf{r})$ must be expressed in terms of a finite set of known mathematical functions, called basis functions. This approach, known as the Linear Combination of Atomic Orbitals (LCAO),^[126] expands each orbital as:

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \chi_{\mu}(\mathbf{r}), \quad (2.22)$$

where $\chi_\mu(\mathbf{r})$ are the basis functions, typically centered on atomic nuclei, and $c_{\mu i}$ are expansion coefficients determined variationally.^[126] The choice of basis set represents an independent source of error from the choice of functional: a larger basis set provides a more flexible representation of the orbitals and converges toward a better solution, but at increased computational cost. The basis set and the exchange-correlation functional must therefore be validated independently for the system under study.^[128] In this work, different basis sets such as def2-SVP and def2-TZVP were employed for the molecular systems (see chapter 3 and chapter 4).

For molecules and materials containing heavy atoms, representing all electrons explicitly becomes computationally prohibitive, since the core electrons of heavy atoms do not participate directly in chemical bonding. Effective Core Potentials (ECPs), also known as pseudopotentials, address this by replacing the core electrons with a parameterized potential, while retaining an explicit quantum mechanical treatment of the valence electrons that govern bonding and reactivity.^[127] This reduces the number of basis functions required and also implicitly incorporates scalar relativistic effects, which become significant for heavier elements. The ECPs are therefore widely used in calculations involving transition metals.

2.3.2. Time-Dependent Density Functional Theory (TD-DFT)

While standard DFT describes the ground-state properties of a system in terms of a static electron density $\rho(\mathbf{r})$, many experimentally relevant phenomena (e.g., light absorption or emission) involve *excited states*. Time-Dependent Density Functional Theory (TD-DFT) extends DFT, allowing the description of electronic systems under the influence of a time-dependent external perturbation, such as an oscillating electric field.^[135]

The formal foundation of TD-DFT rests on the *Runge-Gross theorems* (1984), which extend the Hohenberg-Kohn theorems for DFT to solve problems involving TD external potentials.^[135] The first Runge-Gross theorem establishes a one-to-one correspondence between the time-dependent external potential $V(\mathbf{r}, t)$ and the time-dependent electron density $\rho(\mathbf{r}, t)$, meaning that the density uniquely determines all properties of the system at any time t . The second theorem provides a variational principle for the time-dependent case through the Frenkel-Dirac action functional.

In practice, TD-DFT is implemented through the *time-dependent Kohn-Sham* (TDKS) equations:^[136]

$$i \frac{\partial \psi_i(\mathbf{r}, t)}{\partial t} = \hat{h}^{KS}[\rho](t) \psi_i(\mathbf{r}, t), \quad (2.23)$$

where $\hat{h}^{KS}[\rho](t)$ is the time-dependent Kohn-Sham Hamiltonian. Explicitly, this extends the ground-state KS equations (2.19) by allowing all quantities to depend on time:

$$i \frac{\partial \psi_i(\mathbf{r}, t)}{\partial t} = \left[-\frac{1}{2} \nabla^2 + V(\mathbf{r}, t) + V_H(\mathbf{r}, t) + V_{xc}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t), \quad (2.24)$$

which now includes:

- $V(\mathbf{r}, t)$: time-dependent external potential
- $V_H[\rho](\mathbf{r}, t)$: time-dependent Hartree potential
- $V_{xc}[\rho](\mathbf{r}, t)$: time-dependent exchange-correlation potential

The time-dependent electron density is reconstructed from the TDKS orbitals as:

$$\rho(\mathbf{r}, t) = \sum_i f_i |\psi_i(\mathbf{r}, t)|^2, \quad (2.25)$$

where f_i is the occupation number, reducing to $f_i = 2$ for closed-shell ground-state systems, consistent with Equation 2.16. A key practical challenge is that the exact $V_{xc}[\rho](\mathbf{r}, t)$ depends on the density from the initial time t_0 to the current time t , a property known as the *memory effect*. In practice, this is handled through the *adiabatic approximation* (A), which assumes that $V_{xc}[\rho](\mathbf{r}, t)$ depends only on the instantaneous density at time t , effectively using the ground-state exchange-correlation functional evaluated at the instantaneous density $\rho(\mathbf{r}, t)$, analogous to Eq. (2.20):

$$V_{xc}^A[\rho](\mathbf{r}, t) = \frac{\delta E_{xc}[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r})} \quad (2.26)$$

Linear Response TD-DFT

In the linear response regime, where the external perturbation is weak, the time-dependent density can be written as:

$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t), \quad (2.27)$$

where $\delta\rho$ is a small perturbation around the ground-state density ρ_0 . Within this approximation, excitation energies and transition moments are obtained by solving the Casida equation:^[137]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (2.28)$$

where Ω are the excitation energies, $\mathbf{X}$ and $\mathbf{Y}$ are the excitation and de-excitation response vectors, and the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ are defined as:

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia|jb) + (ia|f_{xc}|jb), \quad (2.29)$$

$$B_{ia,jb} = (ia|bj) + (ia|f_{xc}|bj), \quad (2.30)$$

where i, j and a, b denote occupied and virtual Kohn-Sham orbitals respectively, $\varepsilon_a - \varepsilon_i$ are orbital energy differences, $(ia|jb)$ are two-electron Coulomb integrals, and f_{xc} is the adiabatic exchange-correlation kernel. The oscillator strengths for one-photon absorption (1PA) are then obtained from the transition

dipole moments, which are constructed from the response vectors $\mathbf{X}$ and $\mathbf{Y}$. In Turbomole, this is implemented in the `escf` module using the adiabatic approximation.^[138]

While linear response TD-DFT yields 1PA properties, non-linear optical phenomena such as 2PA require going beyond the linear regime to the *quadratic response*, where the density response is expanded to second order in the perturbation:

$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho^{(1)}(\mathbf{r}, t) + \delta\rho^{(2)}(\mathbf{r}, t) + \dots, \quad (2.31)$$

where, $\rho_0(\mathbf{r})$ is the unperturbed ground-state electron density $\delta\rho^{(1)}(\mathbf{r}, t)$ is the first-order (linear) response, responsible for 1PA, and $\delta\rho^{(2)}(\mathbf{r}, t)$ is the second-order (quadratic) response, responsible 2PA.

Quadratic Response TD-DFT

The 2PA cross-sections were computed using the quadratic response formalism within TD-DFT, as implemented in TURBOMOLE.^[139,140] This approach naturally extends the linear response framework described in the previous section, where the time-dependent density is expanded to second order in the external perturbation (see Equation 2.31), with the second-order term $\delta\rho^{(2)}(\mathbf{r}, t)$ governing 2PA processes. The Cartesian components of the two-photon transition amplitude tensor $S_{ab} \equiv v_{0N}^{(ab)}$ are obtained from the *single residue* of the quadratic response function,^[123] which is evaluated by taking the limit as the response frequency ω' approaches the excitation energy Ω_N of state N :

$$\lim_{\omega' \rightarrow \Omega_N} (\omega' - \Omega_N) \langle \langle v^{(\gamma)}(-\omega'); v^{(\alpha)}(\omega), v^{(\beta)}(\omega' - \omega) \rangle \rangle = -v_{0N}^{(\alpha\beta)}(\omega) v_{0N}^{(\gamma)}, \quad (2.32)$$

where $v_{0N}^{(\gamma)}$ is the one-photon transition moment to state N , $v^{(\alpha)}$ and $v^{(\beta)}$ are the perturbation operators associated with the two photons, and ω is the single-photon frequency ($\omega = \Omega_N/2$ for degenerate 2PA). The TD-DFT working expression for the 2PA amplitude is then^[123]

$$v_{0N}^{(\alpha\beta)}(\omega) = \langle X^N, Y^N | P^{(\alpha\beta)}, Q^{(\alpha\beta)} \rangle, \quad (2.33)$$

where $|X^N, Y^N\rangle$ are the TD-DFT excitation vectors for state N , and $|P^{(\alpha\beta)}, Q^{(\alpha\beta)}\rangle$ are second-order perturbation vectors constructed from the first-order polarization response vectors at frequencies $\omega_\alpha = \omega$ and $\omega_\beta = \Omega_N - \omega$. A complete derivation of these quantities is given in Ref. 123. The resulting tensor components S_{ab} are used to construct the rotational invariants described below.

Degenerate 2PA ($\omega_1 = \omega_2 = \omega_f/2$) under linearly parallel polarized light was considered for this work (see excited-state calculations in chapter 4). The linearly perpendicular and circularly polarized condi-

tions are available in TURBOMOLE but not employed here. The rotational invariants of $\mathbf{S}$ are defined as:

$$\delta_F = \frac{1}{30} \sum_{a,b} S_{aa} S_{bb}, \quad (2.34)$$

$$\delta_G = \frac{1}{30} \sum_{a,b} S_{ab} S_{ab}, \quad (2.35)$$

$$\delta_H = \frac{1}{30} \sum_{a,b} S_{ab} S_{ba}. \quad (2.36)$$

For linearly parallel polarized light, the rotational invariants of the transition tensor S_{ab} are defined as:

$$\langle \delta \rangle^{\parallel} = 2\delta_F + 2\delta_G + 2\delta_H. \quad (2.37)$$

Discrete 2PA cross sections were obtained from $\langle \delta \rangle^{\parallel}$ as

$$\sigma_i^{\parallel} = \langle \delta \rangle_i^{\parallel} \cdot \omega_{1,i}^2 \cdot \frac{8\pi^2 \alpha a_0^5}{c \Gamma_0}, \quad (2.38)$$

where α is the fine-structure constant, a_0 the Bohr radius, c the speed of light, $\omega_{1,i} = \omega_{f,i}/2$ the single-photon frequency in atomic units, and $\Gamma_0 = 0.1$ eV is a reference energy denominator used for unit conversion to Göppert-Mayer units ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s}$). The discrete spectrum was subsequently broadened by convolution with an unnormalized Lorentzian line shape function (this broadening is applied for both 1PA and 2PA):

$$\sigma^{\parallel}(\lambda) = \sum_i \sigma_i^{\parallel} \cdot \frac{(\Gamma/2)^2}{(\Gamma/2)^2 + (\lambda - \lambda_i)^2}, \quad (2.39)$$

where λ_i is the two-photon excitation wavelength of the i -th transition and $\Gamma = 15$ nm is the full width at half maximum (FWHM) of the Lorentzian. The broadened spectrum was evaluated on a uniform grid of 3000 points over the range 100-1000 nm.

2.3.3. Molecular Dynamics

Molecular Dynamics (MD) is a simulation method that solves the equations of motion to obtain properties such as atomic trajectories, kinetic and potential energies, thermodynamic variables (temperature, pressure, density), and transport coefficients.^[141] In the classical formulation, the method is based on Newtonian mechanics: each atom is treated as a point mass, and its trajectory is determined by numerically integrating Newton's equations of motion. Although *ab initio* MD approaches exist, the present work focuses exclusively on classical MD. Classical MD provides an accurate approach that simultaneously accesses the statistical and dynamical properties of a broad range of material systems, including MOFs. Over time, force fields have been developed and refined for different systems, including

biomolecules, polymers, metals, and semiconductors,^[142–144] enabling MD to become one of the most widely used tools in computational materials science.

The origins of MD simulation date to 1957, when Alder and Wainwright^[145] reported the first MD calculation, investigating the phase behavior of a hard-sphere system in which particles move freely between instantaneous elastic collisions. Rahman^[146] performed the first simulation of liquid argon in 1964, using the Lennard-Jones potential, thereby establishing the methodological foundation upon which modern MD is built. The scope of MD was subsequently extended to molecular systems by Rahman and Stillinger,^[147] who modeled liquid water in 1971, and to biological macromolecules by McCammon *et al.*^[148], who reported the first MD simulation of a protein in 1977.

Fundamentals of MD

In classical MD simulation, the state of a system of N particles is fully described at any instant by the positions $R^N = \{r_1, r_2, \dots, r_N\}$ and momenta $P^N = \{p_1, p_2, \dots, p_N\}$ of all its particles. The total energy of the system, given by the Hamiltonian H , is the sum of the kinetic and potential energy contributions:

$$H(R^N, P^N) = \sum_i \sum_{\alpha} \frac{p_{i,\alpha}^2}{2m_i} + U(R^N), \quad (2.40)$$

where m_i is the mass of particle i , α runs over the three spatial directions x , y , and z , and $U(R^N)$ is the potential energy function, referred to as the *force field*, which contains all interatomic interactions in the system. It is typically expressed as a sum of bonded contributions (bond stretching, angle bending, and torsional terms) and non-bonded contributions (electrostatic and van der Waals interactions). Force fields are semiempirical expressions parametrized against experimental or *ab initio* data, and their accuracy determines the reliability of the resulting trajectories.

The force acting on each particle is obtained from the potential energy through:

$$F_i(R^N) = -\frac{\partial U(R^N)}{\partial r_i}, \quad (2.41)$$

which simply states that particles are pushed away from high-energy configurations and towards lower-energy ones. The time evolution of each particle then follows Newton's second law:

$$m_i \ddot{r}_i = F_i(R^N), \quad (2.42)$$

where $\ddot{r}_i$ is the acceleration of particle i . Given a set of initial positions and velocities, these equations of motion are integrated numerically at each time step, producing the trajectory of every particle over time. Even though the first MD simulation was reported in the late 1950s, it took several decades to become a well-accepted and widely adopted tool.^[141] Classical MD simulation generally follows the steps shown in Figure 2.5. First, the system conditions, such as initial atomic positions, velocities, boundary conditions, constraints, and the potential energy function, must be defined. Next, most calculations include a

structural optimization step to adjust the initial structure towards the equilibrium geometry. Importantly, this step is not always necessary: it can be omitted either i) when the simulation is continued from a previously equilibrated system, or ii) when the initial structure is already close to the equilibrium geometry corresponding to the chosen potential energy function. After that, the forces acting on each atom are computed from the potential energy function, followed by the numerical integration of the equations of motion (see Equation 2.42) for each particle over a time step Δt . Positions and velocities are updated iteratively until the target simulation time is reached. Finally, the physical quantities of interest are extracted from the recorded trajectory.

In MD simulations, rather than tracking every individual atom in detail, the goal is to obtain average properties that are meaningful at the macroscopic level. This is achieved through the concept of a statistical ensemble, in which a collection of many independent copies of the same system is simulated, all sharing the same macroscopic conditions (such as temperature, pressure, or volume), but differing at the atomic level. Averaging a property over all these copies yields a representative macroscopic value.

Four ensembles are commonly used in MD simulations, each defined by which thermodynamic variables are kept constant:

- **Microcanonical (NVE):** constant number of atoms N , volume V , and total energy E . The system is fully isolated.
- **Canonical (NVT):** constant N , V , and temperature T . A thermostat is used to maintain the temperature.
- **Isothermal-isobaric (NpT):** constant N , pressure p , and T . Both a thermostat and a barostat are applied.
- **Grand canonical (μ VT):** constant chemical potential μ , V , and T . The number of particles is allowed to fluctuate.

In practice, generating many independent copies of a system simultaneously is not necessary. According to the ergodic hypothesis, a system simulated for a sufficiently long time will naturally visit all accessible states. Therefore, the ensemble average can be replaced by a time average computed from a single long trajectory, which is precisely what an MD simulation produces.

Applications and Limitations of MD Simulations

Over the years, MD has established as a versatile tool across different disciplines. For example, in materials science, it is used to investigate thermodynamic properties, phase transitions, defects (such as vacancies, dislocations, and grain boundaries), and heat and mass transfer. MD is also well-suited for surface-related phenomena, including surface diffusion, reconstruction, and friction. Beyond materials science, MD has found broad applications in biophysics (protein folding, molecular structure prediction)

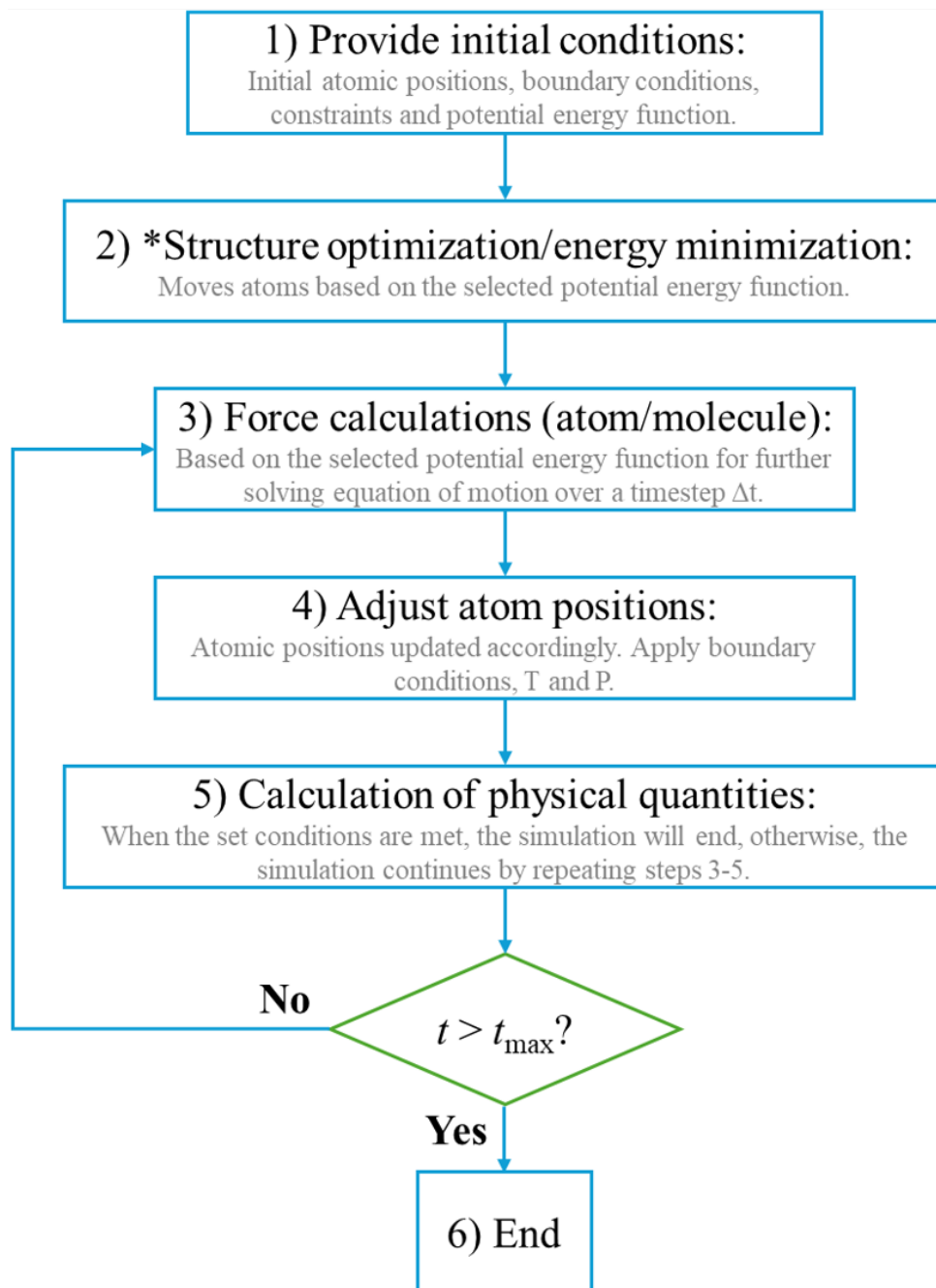


Figure 2.5. General flowchart of a classical MD simulation. *Step 2 is not always required. For instance, if a simulation is continued from a previously equilibrated system. In principle, a simulation started from scratch could also proceed if the initial structure happens to be close to the equilibrium geometry of the chosen force field, but this is rarely the case in practice, since initial structures are typically constructed from experimental data, *ab initio* calculations, or prior MD simulations performed under different conditions. Figure based on reference [141].

and chemistry (intermolecular interactions, free-energy calculations). Despite its versatility, MD simulation has important limitations: i) the most critical is its dependence on the accuracy of the potential energy function (force field). Since force fields are semiempirical expressions fitted to experimental or *ab initio* data, their transferability is limited: a force field developed for one phase or system may not perform reliably for another. While UFF4MOF,^[149] DREIDING,^[150] or MOF-FF^[151] are commonly used for MOF systems, their accuracy for newly discovered framework systems is often not validated. The lack of force-field validation often limits MD applicability. ii) MD is also constrained in its accessible time and length scales, typically handling systems on the order of nanometers to tens of nanometers and simulation times of hundreds of ns.^[141] While sufficient for many properties, some physical phenomena can exhibit relaxation times far exceeding this range.

As MD simulations are not the central methodology of this work, a deeper theoretical treatment is beyond the scope of this section. In chapter 3, MD simulations are employed to explore the dynamics of the SP and MC linkers within the MOF structure, and to generate a set of representative configurations of the dimers from which snapshots are extracted for the subsequent calculation of electronic couplings.

2.3.4. SimStack: A Workflow Framework for Multiscale Simulations

Overview and General Description

The calculations presented in chapter 3 were performed using the SimStack workflow framework, to connect different levels of theory, starting from the quantum-mechanical optimization of molecular building blocks using DFT, followed by the construction and optimization of periodic MOF structures, and finally the investigation of larger supercell model through MD simulations.

SimStack is an intuitive, open-source workflow management framework designed to facilitate the efficient implementation, adoption, and execution of complex multiscale simulation workflows in materials science, computational chemistry, and nanomaterials research.^[152] It was created to bridge the gap between the growing availability of powerful simulation codes and the practical difficulty of deploying, chaining, and managing them in a reproducible and scalable manner on high-performance computing (HPC) resources. At its core, SimStack provides a *drag-and-drop* graphical environment that allows researchers to rapidly assemble, modify, and execute complex simulation pipelines without requiring deep expertise in HPC administration, scripting, or inter-code data formats. Within a few hours, sophisticated modeling solutions can be rendered into easy-to-use, scalable software products, circumventing the time-consuming workflow setup and manual execution traditionally demanded by computational R&D.^[153] The SimStack framework is built on a lightweight client-server architecture that cleanly separates workflow construction from workflow execution.^[152,153] The two components operate as follows:

- **SimStack Client.** Installed on the researcher's local machine (Linux, Windows, or macOS), the client provides the graphical user interface (GUI) through which workflows are constructed, con-

figured, submitted, monitored, and analyzed. The client handles all file transfers automatically, requiring no manual intervention from the user once a workflow is submitted.

- **SimStack Server.** Deployed on remote HPC resources, the server component receives workflow instructions from the client, manages job submission and scheduling, and organizes the generated data in a hierarchical directory structure. Each workflow execution is stored in a dedicated directory labeled with a submission timestamp and the workflow name, ensuring traceability and reproducibility.

This architecture hides the complexity of HPC handling entirely from the end-user while preserving full flexibility for workflow developers.

Workflow Active Nodes (WaNos)

The fundamental building blocks of any SimStack workflow are called Workflow Active Nodes (WaNos).^[152,154] Each WaNo encapsulates a discrete computational task. For instance structure generation, geometry optimization, electronic-structure calculation, or post-processing (see Figure 3.3) and exposes its relevant parameters through an automatically generated GUI.

Technically, a WaNo is defined by an XML file that specifies:

1. The expected input files and configurable parameters,
2. The output files produced by the node,
3. The execution command to be run on the HPC resource.

WaNos are modular and portable because they do not depend on a specific HPC architecture, can be shared between research groups via public repositories (e.g., on GitHub under the KIT-Workflows organization), and can be combined in arbitrary sequences to form application-specific workflows. In general, SimStack helps perform multiscale simulation in a simple way by interfacing between consecutive WaNos, including file conversion and parameter passing, thereby eliminating a major source of manual effort and human error. This computational tool is particularly relevant and used in chapter 3 for the study of photoswitchable MOFs.

3. Electronic Properties: Photoswitching Conductivity in Spiropyran-Based MOFs

Materials whose electronic properties and conductance can be reversibly tuned by light across several orders of magnitude are highly desirable. MOF films functionalized with photoresponsive spiropyran molecules (see Figure 3.1) have already demonstrated that light can effectively switch their electrical conduction, achieving potentially large on-off ratios. However, fabricating such MOFs through trial-and-error approaches remains laborious and would greatly benefit from computational molecular design. Computationally designed photoswitchable MOFs that incorporate SP units at well-defined positions with controlled intermolecular distances and orientations were realized through multiscale modeling. Four MOF candidates are characterized to study their potential for light-induced conductivity switching. Ab initio calculations reveal that both lattice spacing and vibrational flexibility strongly influence the electronic coupling between SP- and MC-based frameworks upon photoisomerization. The resulting on-off ratios reach average values exceeding 530 and 4200 for p-type and n-type conduction, respectively.

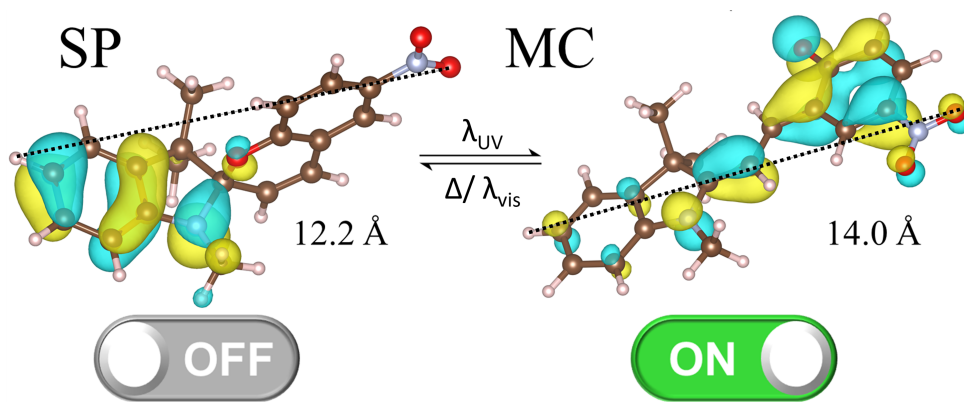


Figure 3.1. HOMO visualization of SP to MC photoisomerization: SP to MC under UV (λ_{UV}); MC to SP thermally or under visible light (λ_{vis}). Atom colors: C brown, O red, N light blue, H white. Reproduced from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

A Cu-paddlewheel MOF structure was employed to investigate the photoswitching between the SP and MC forms. This architecture was selected because it enables an ordered incorporation of the photo-switches while minimizing steric hindrance. Paddlewheel MOFs typically consist of layer and pillar linkers forming a 3D framework. In this study, SP and MC units were introduced as side groups on dicarboxylate layer linkers. Two different pillar linkers, i) 1,4-diazabicyclo[2.2.2]octane (DABCO) and ii) bipyridine (bipy), were examined to tune the interlayer distance. The four studied MOFs include: $\text{Cu}_2(\text{SP})_2(\text{dabco})$, $\text{Cu}_2(\text{SP})_2(\text{bipy})$, $\text{Cu}_2(\text{MC})_2(\text{dabco})$, and $\text{Cu}_2(\text{MC})_2(\text{bipy})$ (see Figure 3.2).

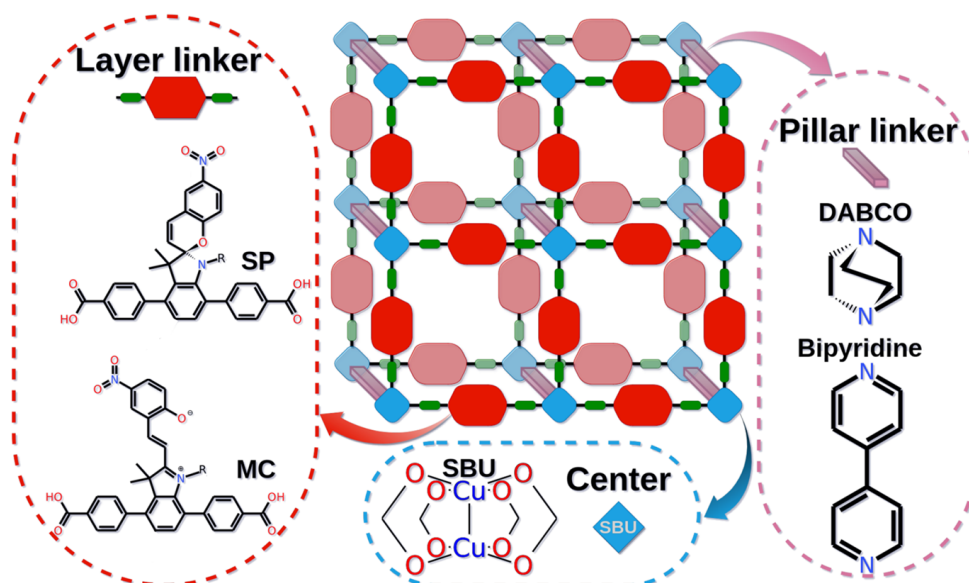


Figure 3.2. Graphic representation of the studied systems. Dabco and bipy act as pillar linkers, which regulate the interlayer distances of SP and MC layer linkers. This figure was adapted from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

The SP-to-MC photoisomerization is well established in the literature.^[155] However, the behavior of this photoswitch when incorporated into MOFs has only recently been explored. In one of the first photoswitchable MOF reports, Garg *et al.*^[156] demonstrated experimentally that SP and MC can reversibly switch under light irradiation when introduced as a guest molecule within the UiO-67 MOF pores, reaching a switching yield of 70% MC upon 365 nm UV light irradiation. Similarly, SP was introduced into a MOF structure. However, in this case study, the photoswitch was attached as a side group to the main MOF linker. The study was carried out *in silico*, assuming an idealization of 100% photoconversion between SP and MC. In this way, four separate MOF models were analyzed, each containing either SP or MC as layer linkers and dabco or bipy as pillar linkers. The ratio of their electronic couplings was used as a direct indicator of the expected change in electrical conduction.

3.1. Methodology: Structure Generation, Optimization and Postprocessing with Simstack

All MOF structures were generated and optimized implementing an automated multiscale workflow in SimStack, which was divided in three sections i) MOF structure generator, ii) MOF structure optimization and iii) MOF analyzer. The workflow includes several software packages that operate at different theoretical levels. Each software package is contained in a Workflow Active Node (WaNo) (see Figure 3.3).

MOF structure generator. In the *MOF-input* WaNo (see Figure 3.3), the geometry files of the layer and pillar linkers are provided in .xyz format. In this step, the metal node type and topology are

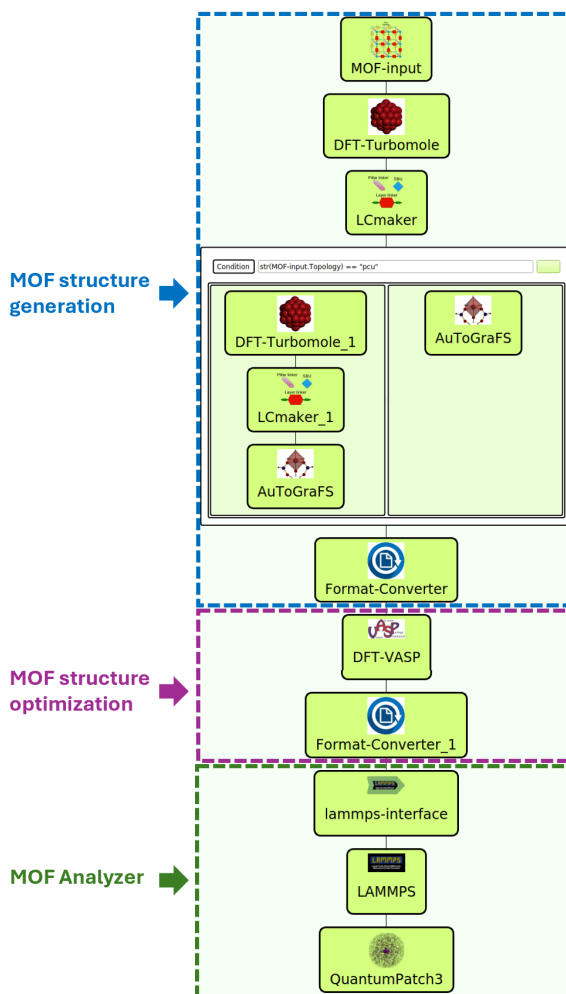


Figure 3.3. SimStack workflow to generate, optimize, and analyze MOF materials for automated structure–property prediction and design. The modules in the workflow are referred as WaNos and perform a specific type of calculation. Adapted from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

defined. In the *DFT-Turbomole* and *DFT-Turbomole_1* WaNos, each linker is optimized separately at the DFT level using TURBOMOLE version 7.4.1 with the B3LYP functional, the def2-TZVP basis set, and the Grimme D3 dispersion correction. The *LCmaker* WaNo is then used to specify the dummy atoms that later guide the connection of the linkers to the metal node. The pillar linkers, DABCO and bipy, are coordinated to the metal node through nitrogen atoms ($\text{Cu} \cdots \text{N}$), whereas the layer linkers, SP and MC, connect through the carboxylate group ($\text{Cu} \cdots \text{O}$). The *AuToGraFS* WaNo then constructs the periodic MOF structure by combining the predefined metal nodes and organic linkers according to the selected topology. In this study, the resulting MOFs have a *pcu* topology with a paddle-wheel Cu oxo node. As final step before optimization of the periodic structure, *Format-Converter* WaNo assures the compatibility of formats between *AuToGraFS* and *DFT-VASP*.

MOF structure optimization. The geometry optimization of the periodic framework was performed using VASP (version 5.4.4) within the *DFT-VASP* WaNo. The PBE functional was selected for the optimization process with a plane-wave energy cutoff of 500 eV and a $2 \times 2 \times 2$ k -point grid. The electron-ion interactions were described by the PAW (projector augmented wave) potentials. The convergence threshold of 10^{-4} eV and the ionic relaxation loop of 0.01 eV were set. The Tkatchenko–Scheffler method with iterative Hirshfeld partitioning was used to include dispersion corrections. The results from the *DFT-VASP* WaNo were directly used for MD simulations in LAMMPS. For this, the *Format-Converter_1* WaNo was employed to convert the output files as required by LAMMPS.

MOF analyzer. Molecular dynamics simulations of the MOFs at 298 K were performed to sample different linker positions within the MOFs. The UFF4MOF force field was implemented in LAMMPS. During the equilibration stage, the Langevin thermostat^[157] and a microcanonical ensemble (NVE) were applied for 30 ps, followed by a 10 ns production run in a canonical ensemble (NVT) employing the Nosé–Hoover thermostat.^[158,159] A supercell of $4 \times 4 \times 4$ was considered, with a time step of 1 fs. The MD trajectories were saved every 1,000 steps, resulting in 10,300 frames, of which 1,030 were analyzed using VMD.^[160] The first 30 frames, corresponding to the equilibration period, were excluded from further analysis. The identification of pairs of layer linkers within the MOF supercell was carried out based on the MD trajectories. Detailed analysis was necessary to identify pairs of layer linkers that represent dimers for subsequent electronic coupling calculations. A total of 250 snapshots (one every 20 ps) of the selected dimer (and trimer, in the case of $\text{Cu}_2(\text{MC})_2(\text{dabco})$) from the last 5 ns of the MD simulations were extracted. Subsequently, these structures were hydrogenated (COO^- groups previously linked to Cu nodes in the MOF) using the ATOMIC SIMULATION ENVIRONMENT (ASE)^[161] and OPENBABEL.^[162] For each snapshot, the electronic coupling between the molecules was calculated using Equation 3.2, employing QUANTUM PATCH.^[163] The B3LYP functional with the def2-SVP basis set and seven equilibration steps for the self-consistent charge-density equilibration of all molecules were used. The electronic coupling calculations were performed outside of the automated workflow depicted Figure 3.3.

In this study, we investigate how the electronic coupling between SP-SP and MC-MC linkers in the MOF changes when 100% photoisomerization is considered. The electronic coupling quantifies the strength of interaction between two molecules or species, reflecting the overlap of their electronic wavefunctions. A larger overlap indicates stronger coupling and enables faster electron transfer between the molecules. This parameter is central to CT theories, such as Marcus theory for hopping transport. It is important to note that the Marcus-type hopping mechanism describes charge transfer between localized states. Other transport regimes may also occur,^[112] such as band-like transport or intermediate mechanisms that bridge localized and delocalized behavior, commonly referred to as transient localization theory models.^[111,164,165] In the present work, however, a hopping mechanism is assumed. Within this framework, the CT rate constant k_{CT} can be calculated using Equation 3.1:

$$k_{\text{CT}} = \frac{2\pi}{\hbar} |J_{if}|^2 \sqrt{\frac{1}{4\pi\lambda k_{\text{B}}T}} \exp\left[-\frac{(\Delta E_{if} + \lambda)^2}{4\lambda k_{\text{B}}T}\right], \quad (3.1)$$

where J_{if} is the electronic coupling between the initial i and final f molecular states in charge transfer. The reorganization energy λ is the energy needed for the molecule to adjust its geometry when an electron moves from one molecule to another. The Boltzmann constant is represented by k_{B} , ΔE_{if} corresponds to the energy difference between the molecular orbitals participating in the CT, and T is the temperature. Mathematically, the transfer integral J is represented as follows:

$$J_{if} = \langle \varphi_i | \hat{H} | \varphi_f \rangle, \quad (3.2)$$

where φ_i and φ_f are the wavefunctions of the initial and final states, and $\hat{H}$ is the Hamiltonian operator representing the total energy of the system. Thus, the electronic coupling is a matrix element that quantifies the overlap between the initial and final state wavefunctions and the energy of the transition. The electronic coupling can be estimated using various computational techniques that differ in level of theory and complexity. Among the most common approaches are those based on Koopmans' theorem, molecular orbitals (MO), and perturbation theory.^[166] In this study, we used a MO approach to calculate the electronic coupling between SP-SP and MC-MC linkers. For this purpose, the MO obtained from calculations on the isolated linker was used as the basis set for the dimer system, consisting of two linkers extracted from the MOF structure. The electronic coupling was then computed using the Löwdin orthogonalization method,^[167,168] based on the Fock and overlap matrices of the dimer:

$$J_{if} = \frac{\left(H_{if} - \frac{1}{2}(H_{ii} + H_{ff})S_{if}\right)}{1 - S_{if}^2}, \quad (3.3)$$

with

$$H_{if} = \langle \varphi_i | \hat{H}_{\text{KS}} | \varphi_f \rangle, \quad (3.4)$$

and

$$S_{if} = \langle \varphi_i | \varphi_f \rangle. \quad (3.5)$$

φ_i and φ_f correspond to the HOMO and LUMO molecular orbitals of the respective isolated linkers, while H_{if} represents the charge-transfer integral. The operator $\hat{H}_{\text{KS}}$ denotes the Kohn-Sham Hamiltonian of the neutral dimer composed of two molecules, and H_{ii} and H_{ff} are the site energies of the individual monomers. The term S_{if} refers to the spatial overlap integral between the corresponding molecular orbitals. In the context of hopping transport, which is typically used to describe charge motion in MOFs

due to their relatively large intermolecular distances,^[169–171] the charge-carrier mobility can be expressed as:

$$\mu = \frac{eL^2}{k_B T} k_{CT}, \quad (3.6)$$

where L is the center-of-mass distance between the linker molecules, and k_{CT} is the CT rate defined in Equation 3.1. If the reorganization energy λ and the site-energy offset ΔE_{if} are approximately constant across the configurations considered, the exponential factor in Equation 3.1 becomes effectively constant, so that $k_{CT} \propto |J_{if}|^2$. In a hopping transport regime, the charge-carrier mobility scales with the hopping rate ($\mu \propto k_{CT}$), and the conductivity scales with the mobility ($\sigma \propto \mu$). Therefore, changes in the electronic coupling $|J_{if}|$ can be used as an indicator of corresponding changes in the MOF's conductivity. Dynamic disorder is an important factor in the study of CT in MOFs, as it accounts for the vibrational flexibility of the material, which can lead to variations in electronic coupling between molecules and, consequently, affect its semiconducting properties. In this study, the dynamic disorder of ordered MOFs refers to the local motions of the linkers within the framework (e.g., rotations, pedal motions). To account for this effect in the study, we calculated the electronic couplings between molecules, extracted from molecular dynamics simulations at 298 K. This approach directly reveals how the electronic coupling varies as a function of the vibrational flexibility of the system. The present study focuses on four MOFs: $\text{Cu}_2(\text{SP})_2(\text{dabco})$, $\text{Cu}_2(\text{SP})_2(\text{bipy})$, $\text{Cu}_2(\text{MC})_2(\text{dabco})$, and $\text{Cu}_2(\text{MC})_2(\text{bipy})$. In addition to these main systems, further calculations were carried out on functionalized SP and MC linkers with electron-withdrawing and electron-donating groups to assess how this modifications can modulate the electronic coupling; these results are provided in section A.1. All calculations were performed using the same computational setup, following the workflow depicted in Figure 3.3. Different dimers and trimers only in MC-MOF case, see Figure 3.4, were selected and extracted from the central part of the $4 \times 4 \times 4$ MOF supercell. For the calculation of the electronic coupling in our study, we employed DFT calculations using the QUANTUM PATCH code, as described in section 3.1. The MD trajectories of the extracted dimers (trimer in MC-MOF) were visualized. We selected some snapshots from the 10 ns MD simulations, as shown in Figure 3.6, to investigate how the electronic coupling between neighboring linkers evolves with time. Electronic coupling was calculated for 250 snapshots taken from the last 5 ns of the MD trajectory.

3.2. Results and Discussion

The absolute values of the coupling matrix elements obtained from the MD simulations at 298 K reached up to 100 meV for $\text{Cu}_2(\text{MC})_2(\text{dabco})$, see the left and center panel in Figure 3.7. The high results originates from the pronounced motions of the MC-based side chain of the layer linker, which promote attractive intermolecular interactions, see snapshots in the bottom panel of Figure 3.6. These dynamic configurations enhance the overlap between molecular orbitals, leading to a larger transfer integral. The orbitals depicted in Figure 3.1 show that the HOMO of MC is more delocalized on the entire molecule

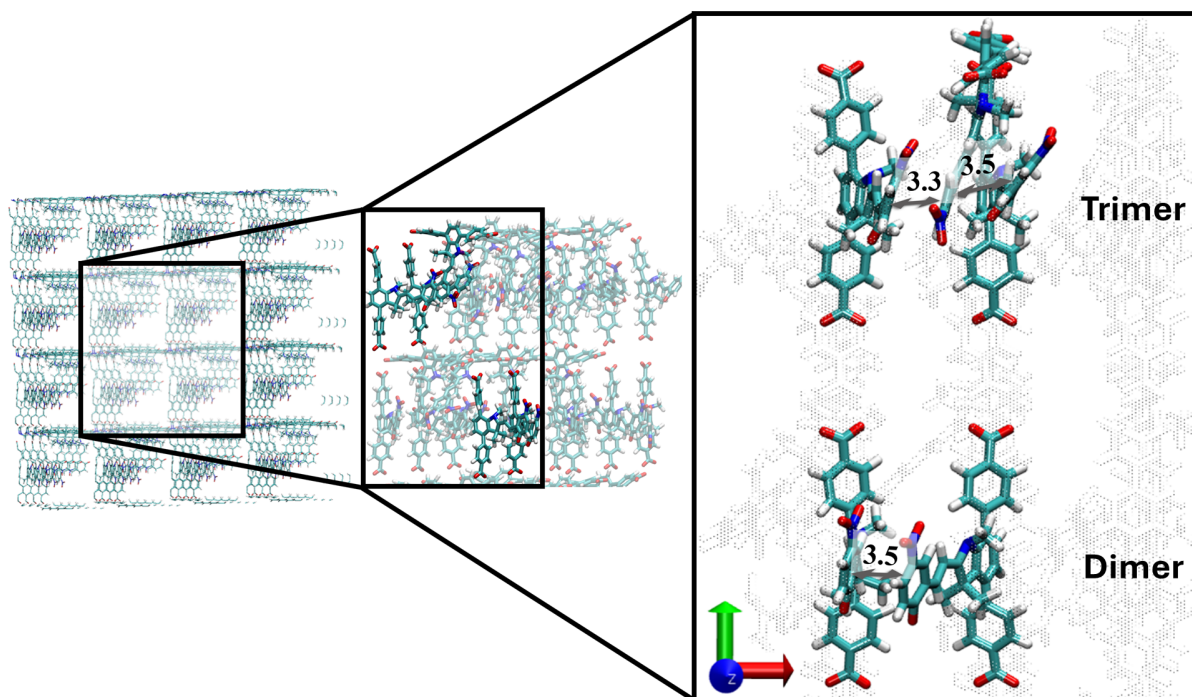


Figure 3.4. Graphic representation of the $4 \times 4 \times 4$ MC-MOF supercell (left). The analyzed systems were extracted from the central region of the supercell. Molecular dynamics analysis revealed that, in some cases, stacking occurred in dimer or trimer arrangements (right). Interaction distances given in Å.

with a high density on the $-\text{NO}_2$ substituted phenyl ring, while for SP, HOMO is mainly localized on the left phenyl ring (HOMO and LUMO orbitals of the functionalized SP and MC are depicted in Figure A.2 and Figure A.3, respectively). This pattern persists when the linkers are embedded in the MOF. MC linkers remain more charge-delocalized and, in combination with the molecule's flexibility, enable better orbital overlap with neighboring MC units, (see Figure 3.4) whereas in SP-MOFs the density stays localized near the linker backbone in addition to the molecule's rigidity, resulting in limited interaction with neighboring SP units Figure 3.5. Thus, for $\text{Cu}_2(\text{SP})_2(\text{dabco})$ case, the SP-SP electronic coupling gave results of around 1.15 meV, with some temporary increases up to 8 meV. The difference in vibrational flexibility and electronic structure between the isomers allows an average increase of the HOMO-HOMO electronic coupling by a factor of ~ 23 upon on-off $\text{SP} \rightleftharpoons \text{MC}$ photoswitching averaged over 5 ns. The arithmetic mean couplings for MC and SP are 26.79 ± 27.77 meV and 1.15 ± 2.03 meV, respectively. The geometric means are 15.27 meV (MC) and 0.55 meV (SP), with geometric standard deviations of 3.75 and 3.56, respectively. Because the electronic coupling fluctuates strongly over time at 298 K, it is not possible to directly calculate the effective CT rate using Equation 3.1 based on the average coupling value. Consequently, the estimated CT rate may increase by a factor of about ~ 530 or even more (see all the MC coupling values above 50 meV in Figure 3.7) when the inter-linker separation is around 9 Å (set by the dabco pillar).

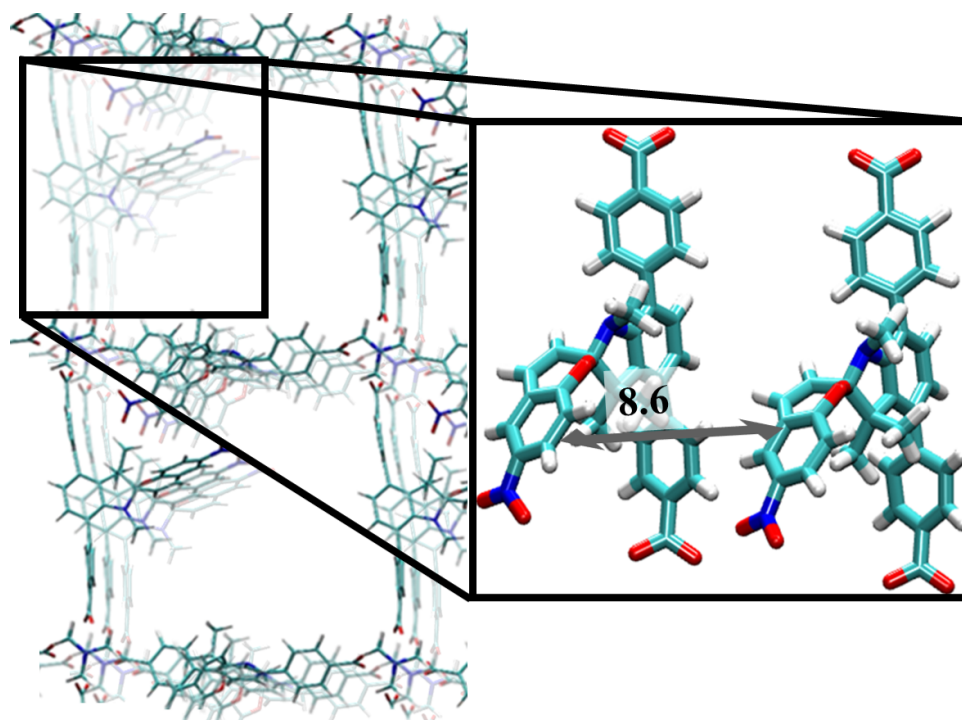


Figure 3.5. SP dimer extracted from the $4 \times 4 \times 4$ SP-MOF supercell. The analyzed systems were extracted from the central region of the supercell. Molecular dynamics analysis revealed that SP linkers remain rigid with long interaction distances of 8.6 Å, which prevent molecular orbital overlap. Adapted from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

In both HOMO and LUMO channels of $\text{Cu}_2(\text{MC})_2(\text{dabco})$, the direct electronic coupling varies strongly in time. In the left plot (LUMO panel) in Figure 3.7 the absolute LUMO–LUMO coupling of MC is slightly lower than the previously discussed HOMO–HOMO results. The electronic coupling peaks around 50 meV, with an average of 23.25 ± 20.26 meV. In the case of $\text{Cu}_2(\text{SP})_2(\text{dabco})$ the LUMO–LUMO coupling is remarkably lower (see inset in Figure 3.7) with an average of 0.36 ± 0.39 meV, compared with 1.15 ± 2.03 meV for the HOMO–HOMO case. Accordingly, the approximate on–off CT-rate ratio in *n*-type transport (averaged over 5 ns) may reach $\sim 6.5 \times 10^2$ and, in some instances, approach $\sim 4.2 \times 10^3$. Although the distance between linkers is determined by the pillar linker with lattice-plane spacing of 9.2 Å for dabco and 13.7 Å for bipy, the molecular flexibility of MC allows the formation of stable π -stacking channels throughout the MOF. In $\text{Cu}_2(\text{MC})_2(\text{dabco})$ intermolecular separations of ~ 3.3 – 3.5 Å between linkers (see Figure 3.4) were observed. In contrast, for $\text{Cu}_2(\text{SP})_2(\text{dabco})$ the SP-SP distances often exceed 8 Å, see Figure 3.5. In some cases, within $\text{Cu}_2(\text{MC})_2(\text{dabco})$ MOF, the MC isomer can also form $\pi \cdots \pi$ channels involving linkers oriented along different axes (see trimer in Figure 3.4). In such configurations, not only is the direct MC-MC coupling relevant, but also the coupling between two linkers mediated by a third one. This mechanism has previously been reported as superexchange.^[172] Here, we propose that certain arrangements observed within the $\text{Cu}_2(\text{MC})_2(\text{dabco})$ unit cell, the coupling follows a superexchange-like mechanism. To evaluate three pairwise couplings and obtain the total coupling, including the intermediate contribution, we used Equation 3.7:

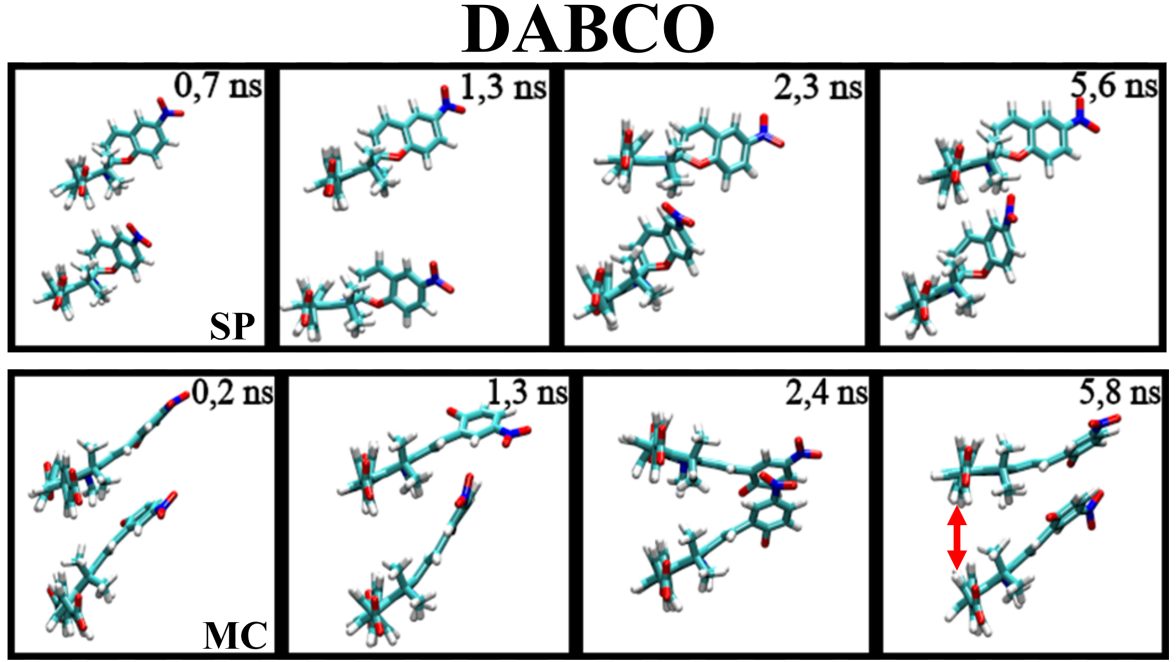


Figure 3.6. Representative snapshots of layer linker dimers from MD at 298 K. SP (top row) and MC (bottom row) of $\text{Cu}_2(\text{SP})_2(\text{dabco})$ and $\text{Cu}_2(\text{MC})_2(\text{dabco})$, respectively. Time stamps (ns) are shown at the upper right of each panel. Dabco pillar linkers are omitted for clarity (red arrow represents DABCO's position). Carbon, oxygen, nitrogen, and hydrogen are colored cyan, red, blue, and white, respectively. Reproduced from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

$$J_{gg'}^{\text{tot}} = J_{gg'}^{\text{dir}} + J_{gg'}^{\text{sx}} = J_{gg'}^{\text{dir}} + \sum_h \frac{J_{gh}^{\text{dir}} J_{hg'}^{\text{dir}}}{\Delta E_{\text{sx}} + \frac{1}{2} \lambda_h}, \quad (3.7)$$

again, λ is the reorganization energy, $J_{gg'}^{\text{dir}}$ represents the direct electronic coupling from site g to g' , $J_{gg'}^{\text{sx}}$ is the coupling matrix element arising from a superexchange-like process (where the charge hops from g to g' via h) and h denotes the virtually occupied (mediating) host state. The superexchange-like contribution $J_{gg'}^{\text{sx}}$ depends on the direct couplings between g and h , and between h and g' , as well as on the reorganization energy. The energy denominator ΔE_{sx} is defined as:

$$\Delta E_{\text{sx}} = E_h - \frac{1}{2} (E_g + E_{g'}), \quad (3.8)$$

is the difference in the site energies of the host state. This parameter is not considered because for this study, the mediator molecule is the same type of molecule as the ones involved in the direct coupling.

When comparing the electronic coupling obtained through direct and superexchange-like mechanisms in $\text{Cu}_2(\text{MC})_2(\text{dabco})$ (see Figure 3.7), one can observe that the superexchange-like mechanism yields values comparable to those found for the HOMO of MC linkers in the direct coupling. The average coupling is 14.5 meV, with temporal increases of 50–70 meV. However, for the LUMO orbitals of MC, the superexchange-like contribution is considerably lower than in the direct case. The frequently ob-

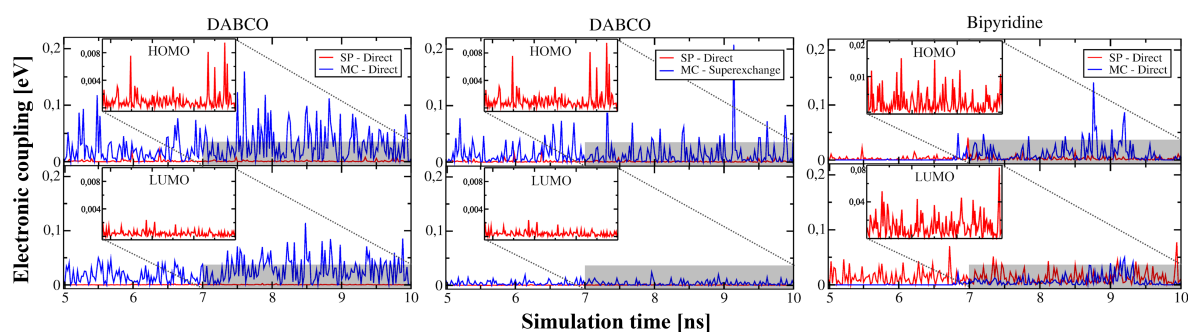


Figure 3.7. Time evolution of the electronic coupling during the last 5 ns of a 10 ns MD trajectory. The left panel shows the HOMO and LUMO results of the direct EC between dimers, with SP-SP in red and MC-MC in blue. The central panel presents the EC when superexchange is considered, where charge transfer occurs from the initial to the final state through an intermediate one. The right panel shows the electronic coupling calculated for a bipy-based MOF, which exhibits noticeably lower values due to the larger interlayer separation compared to the dabco-based MOF, where shorter interlayer distances are possible. Adapted from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

served high coupling values in the superexchange-like mechanism indicate that the mediating MC linker facilitates $\pi \cdots \pi$ pathways that lead to the observed high results.

It is well known that at large intermolecular separations, charge conduction becomes negligible. To examine how the electronic coupling evolves at larger linker distances, we performed MD simulations at 298 K using bipyridine as a pillar linker to control the interlayer separation (COM distance of 13.7 Å). Analysis of the MD trajectories shows that the flexible MC units attached to the backbone linker can rotate freely within the MOF. This behavior arises from the larger free volume around neighboring linkers, which prevents the formation of $\pi \cdots \pi$ channels. After approximately 7 ns of simulation (see Figure 3.8), the MC linkers begin to twist and form intermolecular contacts, leading to a temporary increase in EC. Despite this, the overall high flexibility of MC maintains a low average coupling. Interestingly, the SP systems display relatively higher average couplings of 2.7 meV and 13.3 meV for the HOMO and LUMO, respectively (see right plot in Figure 3.7). Therefore, it can be concluded that bipy-pillared MOFs are not efficient spiropyran-based photoswitchable conductors. The plots of the electronic coupling calculated for the -CHO and -OH groups are available in the appendix Figure A.1.

Finally, while on-off conduction depends strongly on the electronic coupling, we also observe a correlation with the frontier orbital energy offsets between SP and MC (see Figure A.2 and Figure A.3). Larger $\Delta E_{\text{orb}}^{\text{SP-MC}}$ generally improves switching. For the unmodified layer linkers (SP or MC), we find $\Delta E_{\text{HOMO}}^{\text{SP-MC}} = -0.35 \text{ eV}$ and $\Delta E_{\text{LUMO}}^{\text{SP-MC}} = +0.71 \text{ eV}$.

Based on our analyses, variations in the on-off conduction ratio upon spiropyran linker functionalization are jointly governed by the spatial distribution (localization vs. delocalization) of HOMO and LUMO electron density, the alignment and shifts of frontier-orbital energies upon $\text{SP} \rightarrow \text{MC}$ isomerization, the conformational/vibrational flexibility of the linkers at $T = 298 \text{ K}$ and the formation of transient $\pi \cdots \pi$ contacts (stacking pathways) between neighboring linkers.

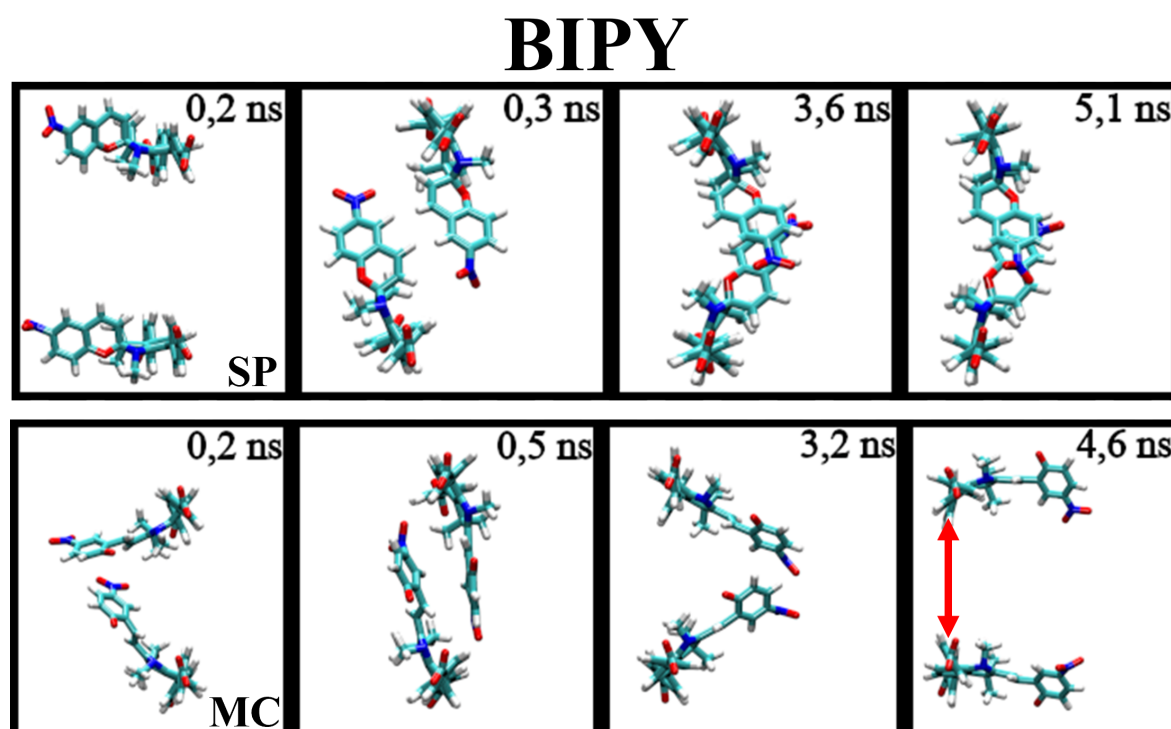


Figure 3.8. Representative snapshots of layer linker dimers from MD at 298 K. SP (top row) and MC (bottom row) of $\text{Cu}_2(\text{SP})_2(\text{bipy})$ and $\text{Cu}_2(\text{MC})_2(\text{bipy})$, respectively. Time stamps (ns) are shown at the upper right of each panel. Bipy pillar linkers are omitted for clarity (red arrow). Carbon, oxygen, nitrogen, and hydrogen are colored cyan, red, blue, and white, respectively. Reproduced from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

3.3. Summary

Photoisomerization from SP to MC significantly increases inter-linker electronic coupling, with average enhancements exceeding 23 $\times$ for HOMO-HOMO and 65 $\times$ for LUMO-LUMO interactions. Since charge-transfer rates scale as $k_{\text{CT}} \propto J^2$, these increases imply rate enhancements of at least $\gtrsim 530\times$ and $\gtrsim 4200\times$, respectively. Room-temperature dynamics further strengthen the switching response by enabling transient conformations with enhanced $\pi \cdots \pi$ interactions and intermolecular contacts. The efficiency of the switching process is strongly distance-dependent, with robust conductance switching observed only for pillar linkers within specific length ranges. The reported on-off ratios represent idealized upper limits, as the simulations assume complete photoconversion, defect-free frameworks, and initially aligned side chains; experimentally, partial conversion, defects, and orientational disorder will likely reduce these values. Nevertheless, the design principles established here, optimized inter-linker distances, transient $\pi \cdots \pi$ contacts, and highly coupled MC states, should also be applicable to other photochromes and framework materials.

4. Optical Properties: Two-Photon Absorption

Structure-Property Relationship of H₄TCPE and H₄TBAPy MOF Organic Linkers

Materials with NLO responses, such as 2PA, are attracting growing interest due to potential applications in biomedical imaging, optical data storage, and long-range communications.^[95,173] In organometallic hybrid materials, rational design is crucial because 2PA response depends not only on the intrinsic properties of the organic chromophore but also on its local environment. MOFs are an attractive platform to enhance the 2PA response thanks to i) the possibility of custom design, ii) their well-defined and ordered arrangements that allow iii) increasing the number of 2PA active chromophores within the framework. Moreover, the ordered incorporation (e.g., controlled orientations) can mitigate limitations often found in solution (e.g., AIE). For instance, typical molecular 2PA cross section values range 1-10³ GM,^[95] while incorporating the 2PA photoactive chromophores as linkers into MOFs, can result in cross sections of 10⁷ GM.^[108] In this work, we examine how the relative orientations of tetrakis[4-(4-carboxyphenyl)phenyl]ethylene (H₄TCPE) and 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H₄TBAPy) affect the 2PA response. This section is divided into two parts: i) in section 4.1 the flexible H₄TCPE linker is studied as a function of intra- and intermolecular conformations that were artificially set, and ii) in section 4.2 the linker is studied based on the orientations present in previously synthesized MOFs. In each case, we compute the 2PA response using finite (non-periodic) monomeric, dimeric, and, in selected cases, larger models. Finally, we compare the most favorable computed motifs with experimentally reported MOF structures and propose: for H₄TCPE, the conformations expected to maximize the 2PA response; and for H₄TBAPy, the reasons behind the increased 2PA response in the previously synthesized systems.

4.1. 2PA Properties in H₄TCPE Linker

Several studies have incorporated the H₄TCPE chromophore as linker in different MOF structures. For instance, Medishetty *et al.*^[174] investigated the incorporation of H₄TCPE into In- and Zn-based MOFs, reporting 2PA action cross sections ($\eta\sigma_2$) of 3072 GM for the In-MOF and 1053 GM for the Zn-MOF. Later, in the same group,^[175] the same chromophore in a series of rigid Zr- and Hf-based MOFs with cubic or Kagome topologies was studied. Across six MOFs, they noticed that H₄TCPE presents only $\eta\sigma_2 = 55$ GM per molecule. However, when it is incorporated into the framework, ($\eta\sigma_2$) results reached 3582 GM. In a similar way, other groups have observed enhanced 2PA responses using H₄TCPE as

a linker in MOFs. For example, Liu *et al.*^[108] synthesized Zn-based MOFs, reaching the highest reported $\eta\sigma_2$ of 1.2×10^6 – 7.4×10^7 GM. This exceptional performance was attributed to a densely packed framework constructed exclusively from Zn(NO₃)₂ nodes and H₄TCPE linkers. Notably, when the chromophore was combined with additional linkers in isostructural pillared-layer MOFs, the response dropped markedly (from ~ 0.3 up to 307 GM). These observations demonstrate that an ordered architecture with a closely spaced chromophore is crucial for maximizing the 2PA response. In another study, He *et al.*^[176] proposed that the 2PA response of H₄TCPE-based materials is strongly framework-dependent. It was observed that a more rigid and densely packed architecture yielded substantially larger absolute cross sections, reaching $\sigma_2 = 8801$ GM in Zr-based MOFs. Please note that $\eta\sigma_2 \neq \sigma_2$: $\eta\sigma_2$ is the product of the fluorescence quantum yield and the absolute σ_2 , and therefore 2PA values reported as $\eta\sigma_2$ and σ_2 are not directly comparable. Despite the reported data, it remains unclear how aggregation within MOFs (specifically, which intermolecular configurations) produces the highest 2PA response. In this section, we study through DFT and TD-DFT the 2PA response of H₄TCPE varying i) intra- and ii) intermolecular geometries of the linker. We first study how intramolecular flexibility (monomer-arm conformations) affects the absorption spectra and the 2PA cross sections (σ_2). After that, we quantify the 2PA response of different dimeric systems by changing stacking distances and relative orientations. Finally, we compare the most favorable motifs with experimentally reported H₄TCPE-based structures and propose design opportunities to further improve 2PA performance.

4.1.1. Methodology: Structure Generation and Conformational Screening

Monomer Systems

The H₄TCPE flexibility has been studied as a function of its 2PA response. Different monomeric structures were generated by varying the distances between selected carbon atoms, regulating the arm-arm distance d_{C-C} (see Figure 4.1) from 13 to 19 Å. After modification, all resulting structures were optimized at the DFT level as described in subsection 4.1.1 Ground-state calculations. During the optimization, to keep the arm-arm distances (d_{C-C}) unchanged, the ending carbon atoms were fixed, while all remaining atoms were relaxed.

Dimer Systems

Using the optimized monomer geometries with $d_{C-C} = 16$ – 18 Å as starting points, dimer configurations were generated by systematically sampling key intermolecular degrees of freedom, as detailed below. Notably, to keep the intra- and intermolecular orientations, only the terminal carbon atoms (highlighted in black in Figure 4.1) were constrained, while all other atomic coordinates were fully relaxed during geometry optimization.

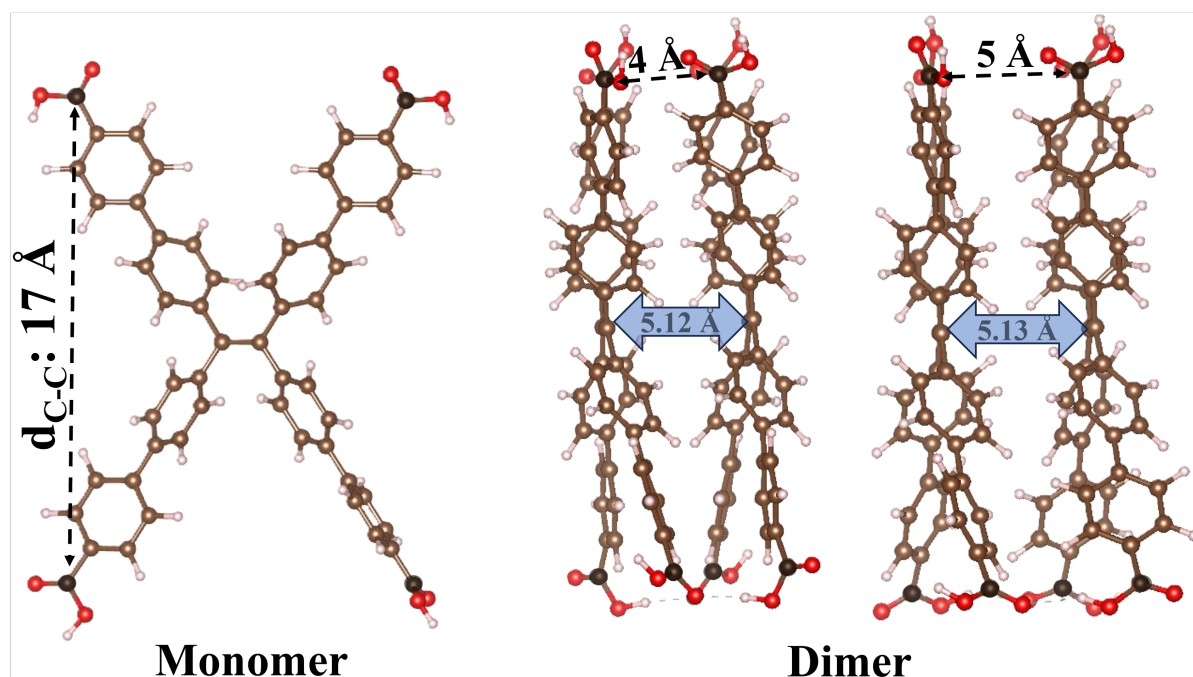


Figure 4.1. Schematic representation of the monomer (left) and dimer (right) systems for the H_4 TCPE molecule. Fixed carbon atoms, to preserve specific intra- and inter-molecular distances, are shown in black. For the monomer, intramolecular distances (d_{C-C}) were scanned from 13 to 19 Å. For the dimer, carbon atoms were fixed to preserve the initial intermolecular stacking distances of 4 and 5 Å. After geometry optimization, the converged stacking distances resulted in intermolecular separations of 5.12 and 5.13 Å, as indicated by the blue arrows. Reproduced from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

i) Book-opening angle: Starting from a parallel-stacked dimer at an intermolecular separation of 4 Å we varied the opening angle (θ) in two ways: i) by opening an angle between the molecular planes considering their long molecular axes (LA) and ii) short molecular axes (SA) as indicated in a) in Figure 4.2. In both cases, θ was scanned from 0° (parallel stacking at 4 Å) to 180° in steps of 45°.

ii) Stacking-plane displacement: Two initial stacking separations (Δ_z) of 4 and 5 Å were considered, see b) in Figure 4.2. For each Δ_z , lateral displacements were introduced by translating one monomer relative to the other within the stacking plane: along the x (left-right) direction with $\Delta x = \pm 5, \pm 10$ Å, and along the y (up-down) direction with $\Delta y = \pm 5, \pm 10$ Å.

iii) Plane-rotation angle: In the same way as in the plane displacements, here $L_z = 4$ and 5 Å were considered. One monomer was then rotated relative to the other from $\theta = 0^\circ$ to 90° in increments of $\theta = 30^\circ$ as shown in c) in Figure 4.2.

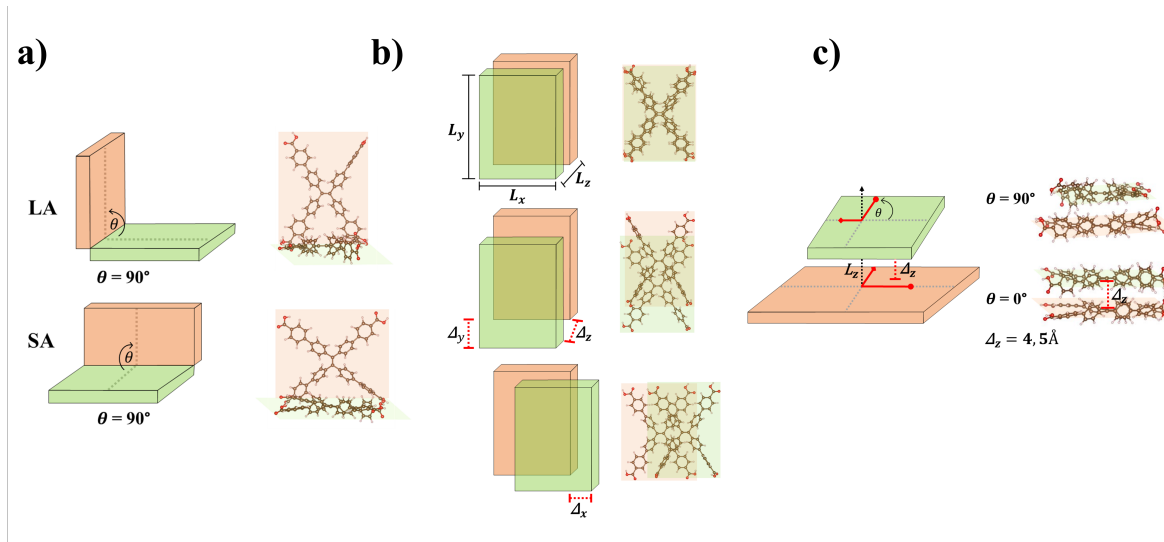


Figure 4.2. Representation of the three different dimer models. The different molecular planes are shown in green and orange. a) Book-like opening along the longer (LA) and shorter (SA) axes, the variation of the opening angle is marked as θ . b) Stacking-plane displacement along the x and y directions are defined as Δ_x and Δ_y respectively, and c) parallel-stacked dimers subjected to in-plane rotational scans, with the rotation angle θ . For b) and c) systems the variation in the sampled intermolecular distances are marked as Δ_z . Reproduced from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

Ground-State Calculations

All structures (monomers and dimers) were geometry-optimized in Gaussian16 (Rev. C.01)^[178] after applying the geometric modifications required to generate the targeted conformations. Gas-phase optimizations were carried out at the DFT level using the long-range corrected hybrid CAM-B3LYP functional^[129] and the def2-SVP (split-valence polarized) basis set.^[179] Dispersion interactions were included considering the D3 correction with Becke-Johnson damping (D3BJ).^[180] The total energy convergence threshold was set to 1×10^{-8} Hartree for both monomers and the generated dimers. Harmonic vibrational analyses confirmed that the optimized structures correspond to true minima (no imaginary frequencies).

Excited-State Calculations

Excited-state properties (1PA and 2PA) of the organic linker (monomer and dimer systems) were computed at the TD-DFT level using TURBOMOLE V7.7 with RI, employing the same computational setup as in the ground-state calculations (CAM-B3LYP/def2-SVP/D3BJ) and considering 10 singlet vertical excitations. The electronic energy convergence threshold was set to 1×10^{-7} Hartree. The 1PA and 2PA spectra were generated by Lorentzian broadening as described in subsection 2.2.1. The 2PA spectra were computed for a single, parallel linearly polarized laser beam. For the electronic-structure characterization, electron-density difference (EDD) maps and frontier and transition orbitals were analyzed.

Isosurfaces were visualized with VMD using isovalues of 0.02 a.u. (orbitals) and 0.0005 a.u. (EDD). Charge transfer was quantified using the post-processing program Multiwfn (v3.8).

4.1.2. Results and Discussion

Monomer Calculations

The first step was to explore the molecular flexibility by sampling different intramolecular distances, defined as d_{C-C} , and to assess how these geometrical changes affect the monomer optical properties. Geometry optimizations were performed for each distance (d_{C-C} =13-19 Å), where selected carbon atoms were fixed to ensure that the target d_{C-C} values were maintained. Among the seven sampled distances, $d_{C-C} = 17$ Å, corresponds to the lowest-energy minimum, as shown in Table 4.1. This most stable conformation falls within the range previously reported for H₄TCPE, in agreement with earlier studies.^[108,175,181–183]

Table 4.1. The energy values of the optimized structures as a function of d_{C-C} .

d_{C-C} (Å)	GEO_OPT_Energy (Hartree)	GEO_OPT_Energy (kcal/mol)	$\Delta E_i = E_i - E_{\min}$ (kcal/mol)
13	-2678.123	-1680522.61	14.14
14	-2678.132	-1680528.17	8.58
15	-2678.139	-1680532.33	4.42
16	-2678.144	-1680535.68	1.07
17	-2678.146	-1680536.75	0.00
18	-2678.144	-1680535.72	1.03
19	-2678.137	-1680530.97	5.78

Experimentally, solid-state H₄TCPE typically presents a UV-vis absorption maximum at around 390-400 nm,^[181,184] reported for intramolecular distances of $d_{C-C} \approx 16.5$ Å^[184] and 18 Å.^[181] Within the same distance range in our study ($d_{C-C} = 16-18$ Å), our TD-DFT calculations using the CAM-B3LYP functional predict a more blue-shifted first absorption band at 325-340 nm as visible in Figure 4.3. This may appear as a substantial difference between experiment and theory. However, this offset is well known for CAM-B3LYP, which tends to overestimate vertical excitation energies, leading to a systematic blue shift of roughly ~ 50 nm relative to coupled cluster benchmarks, which often show improved agreement with experiment.^[104,185] Similar blue shifts have also been reported for 2PA calculations.^[182,186] Although ten vertical excitations were computed, the discussion below focuses primarily on the lowest excited states, which are most relevant from an experimental perspective. Our excited-state calculation results show that, as d_{C-C} increases, both the 1PA and 2PA spectra undergo a progressive red shift. For the lowest excitation, the 1PA band red-shifts by ~ 10 nm, whereas the corresponding 2PA band red-shifts by ~ 20 nm (see Figure 4.4). To rationalize the geometric changes with the observed spectral shifts, we analyzed the dihedral angles of the flexible core phenyl rings, including the central C=C bond. The carbon atoms considered to calculate the torsion of the core phenyl rings are shown in red in Figure 4.5.

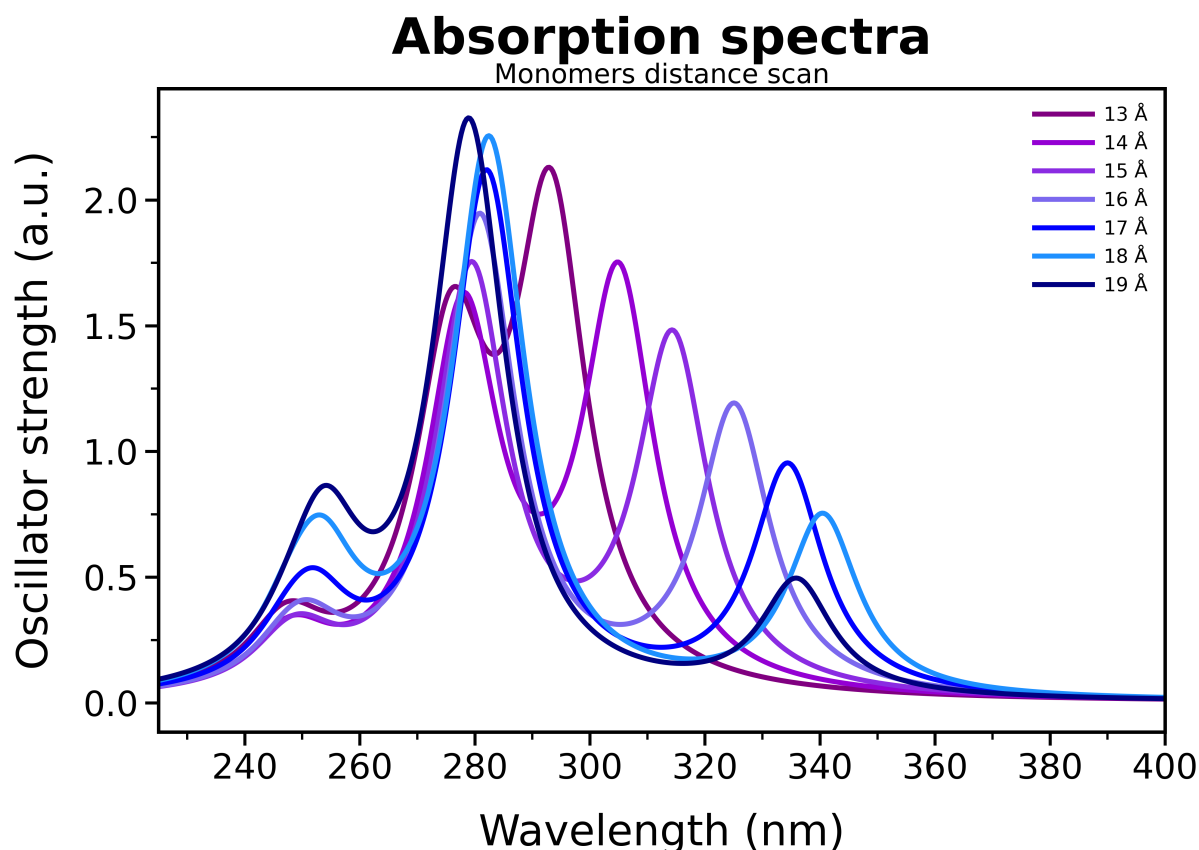


Figure 4.3. Calculated absorption spectra of the different sampled arm separation of the H_4TCPE monomer. Adapted from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

As shown in Table 4.2, the structure with $d_{C-C} = 17 \text{ \AA}$ exhibits the dihedral angle closest to 180° , indicating that it is the most planar conformation among the sampled monomers. Increased planarity in conjugated systems typically enhances π -orbital overlap and reduces charge localization, thereby stabilizing the frontier orbitals and narrowing the HOMO–LUMO gap. As a result, the vertical excitation energy is expected to decrease.^[187,188] Over the full set of sampled conformations ($d_{C-C} = 13\text{--}19 \text{ \AA}$), the lowest excited state ($S_0 \rightarrow S_1$) is mainly characterized by a HOMO→LUMO transition (see the full dataset in Figure B.1–Figure B.7 in the appendix). We observe that reduced planarity decreases the HOMO→LUMO weight. For instance, at $d_{C-C} = 13 \text{ \AA}$ the HOMO→LUMO contribution is 75.3%, whereas in the more planar structure at $d_{C-C} = 17 \text{ \AA}$ it increases to 85.8%. These results indicate that planarity not only modulates the spectral red shift but also the weight of the main orbital contribution.

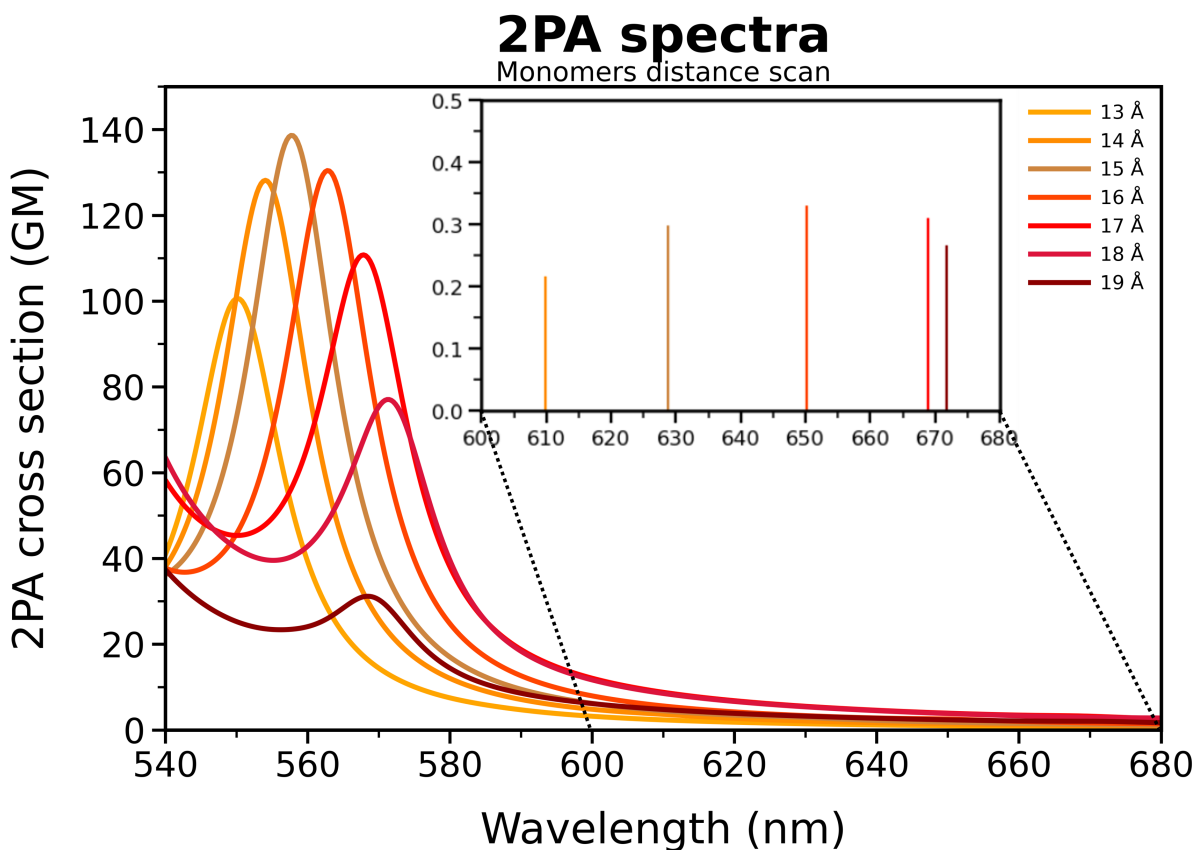


Figure 4.4. Calculated absorption spectra of the different sampled arm separation of the H₄TCPE monomer. Adapted from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

Table 4.2. CT parameters for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations of H₄TCPE at different d_{C-C} distances. The dihedral angle ω is reported in degrees ($^\circ$), where values closer to 180° indicate a more planar structure. S_r is dimensionless, whereas D , H_{CT} , H , and t are given in Å. The change in dipole moment relative to the ground state, $\Delta\mu$, is reported in atomic units (a.u.) and in Debye [D].

d_{C-C} (Å)	ω ($^\circ$)	Exc.	S_r	D (Å)	$\Delta\mu$ (a.u.) [D]	H_{CT} (Å)	H (Å)	t (Å)
13	125.86	$S_0 \rightarrow S_1$	0.77	0.59	1.06 [2.69]	3.18	5.06	-2.59
		$S_0 \rightarrow S_2$	0.67	1.03	1.71 [4.36]	3.42	5.81	-2.38
14	128.86	$S_0 \rightarrow S_1$	0.79	0.53	0.96 [2.45]	3.18	4.83	-2.65
		$S_0 \rightarrow S_2$	0.65	0.89	1.45 [3.69]	3.60	5.95	-2.71
15	130.56	$S_0 \rightarrow S_1$	0.75	0.54	0.95 [2.42]	3.14	4.56	-2.59
		$S_0 \rightarrow S_2$	0.64	1.35	2.20 [5.59]	3.33	5.82	-1.97
16	131.84	$S_0 \rightarrow S_1$	0.77	0.51	0.90 [2.30]	3.22	4.47	-2.71
		$S_0 \rightarrow S_2$	0.72	0.67	1.16 [2.94]	2.98	5.71	-2.30
17	132.37	$S_0 \rightarrow S_1$	0.77	0.50	0.89 [2.27]	3.30	4.38	-2.80
		$S_0 \rightarrow S_2$	0.74	0.60	1.04 [2.66]	2.57	5.56	-1.97
18	131.57	$S_0 \rightarrow S_1$	0.76	0.54	0.94 [2.39]	3.30	4.25	-2.76
		$S_0 \rightarrow S_2$	0.74	0.51	0.89 [2.28]	2.42	5.53	-1.91
19	125.83	$S_0 \rightarrow S_1$	0.75	0.67	1.17 [2.98]	3.44	4.20	-2.76
		$S_0 \rightarrow S_2$	0.72	0.50	0.84 [2.14]	2.13	5.60	-1.63

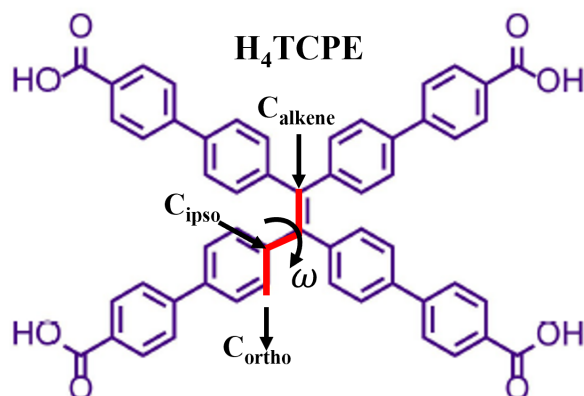


Figure 4.5. Schematic representation of the H_4TCPE linker and the four carbon atoms used to define the dihedral angle ω are highlighted in red. Reproduced from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

The evolution of the monomer electronic structure was analyzed using EDD plots. As the intramolecular geometry changes (via d_{C-C}), the electron-density redistribution upon excitation is modified, leading to changes in both the 1PA and 2PA responses. For the first singlet excitation ($S_0 \rightarrow S_1$), increasing d_{C-C} yields a gradual localization of the EDD on the inner phenyl rings (upper row in Figure 4.6), with a more core-centered redistribution at $d_{C-C} = 17 \text{ \AA}$ compared to $d_{C-C} = 13 \text{ \AA}$. Although the oscillator strength decreases from $f = 1.90$ at $13 \text{ \AA}$ to $f = 0.45$ at $19 \text{ \AA}$, the transition remains 1PA-bright. In contrast, the corresponding 2PA activity for $S_0 \rightarrow S_1$ remains weak, with cross sections in the range of 0.1-0.3 GM and a modest maximum of $\sigma_2 = 0.33 \text{ GM}$ at $d_{C-C} = 16 \text{ \AA}$. For the second singlet excitation ($S_0 \rightarrow S_2$), the EDD variations are more pronounced. At $d_{C-C} = 13 \text{ \AA}$, the density redistribution is more localized toward one side of the molecule, whereas at larger d_{C-C} values it becomes increasingly concentrated on the core phenyl rings. This evolution is accompanied by a strong reduction of 1PA intensity, with $f \approx 0.05$ - 0.06 for $d_{C-C} = 16$ - $19 \text{ \AA}$ (i.e., 1PA-dark or only weakly allowed), while the 2PA response is strongly enhanced, reaching a maximum of $\sigma_2 = 117.88 \text{ GM}$ at $d_{C-C} = 16 \text{ \AA}$. Overall, for the H_4TCPE monomer, 2PA predominantly populates the S_2 state. This behavior is consistent with the selection rules discussed by Amar *et al.*^[189] for quadrupolar chromophores, where 2PA preferentially accesses an excited state that is 1PA-forbidden (or only weakly allowed under slight symmetry distortions).

In addition to the qualitative EDD analysis, we quantified the hole-electron distribution^[190] using MULTIWFN^[191,192] and the indices proposed by Le Bahers *et al.*^[193] The resulting descriptors (S_r , D , H_{CT} , H , and t) are summarized in Table 4.2.

The S_r index is a dimensionless measure of the hole-electron overlap: values close to 1 correspond to strong overlap and predominantly locally excited (LE) character, whereas values approaching 0 indicate increased separation and stronger charge transfer (CT) character. Similarly, D reports the distance between the hole and electron centroids; larger values (e.g., $> 2 \text{ \AA}$) are generally associated with more pronounced CT character. The H index describes the average spatial extent of the hole and electron distributions (in the $x/y/z$ directions), while H_{CT} quantifies the corresponding extent projected along the CT

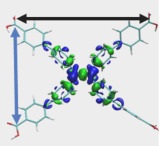
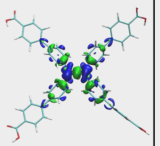
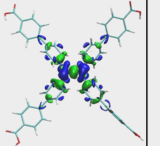
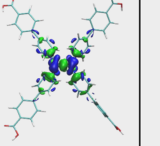
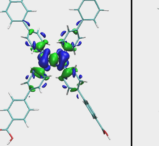
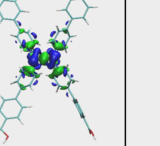
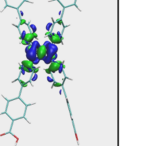
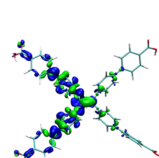
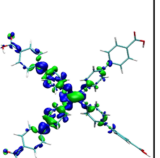
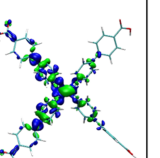
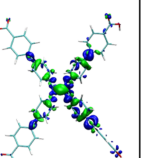
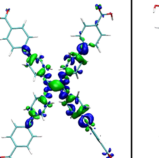
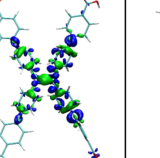
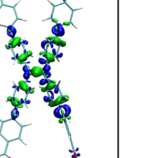
	13 x 16 [Å]	14 x 15 [Å]	15 x 14 [Å]	16 x 13 [Å]	17 x 12 [Å]	18 x 10 [Å]	19 x 8 [Å]
$S_0 \rightarrow S_1$	 1PA: 1.90 [293] 2PA: 0.11 [586]	 1PA: 1.64 [304] 2PA: 0.21 [610]	 1PA: 1.40 [314] 2PA: 0.29 [628]	 1PA: 1.13 [325] 2PA: 0.33 [650]	 1PA: 0.90 [334] 2PA: 0.31 [668]	 1PA: 0.71 [340] 2PA: 0.28 [681]	 1PA: 0.45 [335] 2PA: 0.26 [671]
$S_0 \rightarrow S_2$	 1PA: 1.13 [276] 2PA: 13.11 [552]	 1PA: 1.38 [278] 2PA: 9.26 [556]	 1PA: 1.54 [279] 2PA: 10.52 [559]	 1PA: 0.04 [281] 2PA: 117.88 [562]	 1PA: 0.05 [284] 2PA: 92.07 [568]	 1PA: 0.05 [285] 2PA: 59.67 [571]	 1PA: 0.06 [284] 2PA: 19.68 [569]

Figure 4.6. EDD visualization for the first and second excitations. The corresponding 1PA and 2PA results for each sampled monomer are shown at the top in blue. For each monomer, the 1PA oscillator strength (a.u.) is reported together with the excitation wavelength (nm) in brackets. The 2PA cross sections are given in GM, and the corresponding excitation wavelength (nm) is reported in brackets. Blue EDD isosurfaces denote electron-deficient regions upon excitation, whereas green sections indicate electron-rich regions. Reproduced from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

direction. Finally, t measures the hole-electron separation along the CT direction: $t < 0$ is typically associated with LE character, whereas positive values indicate CT character. Our results (Table 4.2) show that for $S_0 \rightarrow S_1$, the hole-electron overlap remains moderately high across the scan ($S_r \approx 0.75$ -0.79), consistent with predominantly LE character. The CT contribution is weak, as indicated by $D = 0.50$ -0.67 Å and consistently negative t values. Only modest changes in dipole moment are observed upon excitation ($\Delta\mu = 0.89$ -1.17 a.u.; 2.27-2.98 D). Moreover, H decreases with increasing d_{C-C} , consistent with the increasingly core-localized redistribution observed in the EDD plots. Overall, S_1 shows only minor variation in CT-related descriptors as d_{C-C} increases, remaining predominantly LE. In contrast, the $S_0 \rightarrow S_2$ excitation shows a markedly stronger dependence on molecular geometry and exhibits a partially mixed character. Two regimes can be distinguished: i) for shorter distances ($d_{C-C} = 13$ -15 Å), the hole-electron overlap is lower than for S_1 ($S_r = 0.64$ -0.67), accompanied by a larger dipole-moment change upon excitation, reaching $\Delta\mu = 2.20$ a.u. (5.59 D) at $d_{C-C} = 15$ Å. In addition, the spatial extent is larger ($H = 5.81$ -5.95 Å), consistent with the more distributed density redistribution observed in the EDD (bottom panel in Figure 4.6). ii) At larger distances ($d_{C-C} = 16$ -19 Å), the transition becomes more LE-like: the overlap increases ($S_r = 0.72$ -0.74), the centroid separation decreases ($D = 0.50$ -0.67 Å), and $\Delta\mu$ becomes less pronounced. The spatial extent is slightly reduced but remains larger than for S_1 (maximum $H = 5.71$ Å at $d_{C-C} = 16$ Å). Overall, these trends show that $S_0 \rightarrow S_2$ is more sensitive to structural changes than $S_0 \rightarrow S_1$: at shorter d_{C-C} the reduced overlap and larger $\Delta\mu$ indicate partial CT

mixing, whereas at larger distances the increased overlap is consistent with predominantly LE character. The systematic scan of d_{C-C} was performed to assess how the electronic and optical properties of the chromophore evolve with intramolecular geometric distortions. After geometry optimization, it became evident that the conformations corresponding to very small or very large d_{C-C} values are unlikely to be realized within a MOF environment. Therefore, in the construction of larger intermolecular packing models, we restrict our analysis to the energetically accessible range $d_{C-C} = 16\text{--}18$ Å, which is also consistent with the distances reported for previously synthesized MOFs.^[108,175,181–183]

Dimer Calculations

In this section, we analyze a set of H_4 TCPE dimer models constructed from the optimized monomer geometries with intramolecular distances $d_{C-C} = 16\text{--}18$ Å. The dimers were generated by duplicating the monomer and placing the two units in an initial parallel, non-offset arrangement. As for the monomer calculations, the terminal C atoms were kept fixed to preserve the intramolecular d_{C-C} values (16–18 Å). In addition, we defined an initial intermolecular stacking separation, Δ_z , of either 4 or 5 Å to control the initial interplanar distance. Because intermolecular separations can strongly affect the electronic and optical properties of organic chromophores,^[110,194] we explored both initial values, $\Delta_z = 4$ and 5 Å. The initial Δ_z was varied only for ii) the stacking-plane displacement and iii) the plane-rotation series. For the i) book-opening series, the starting separation was fixed to $\Delta_z = 4$ Å. After constructing these dimer conformations, all systems were geometry-optimized using the protocol described in subsubsection 4.1.1 for ground-state calculations. Notably, despite the fixed terminal C atoms, the dimers initialized at $\Delta_z = 4$ and 5 Å relaxed to a similar center-to-center distance of ~ 5 Å, as indicated by the blue arrow in Figure 4.1. Finally, although ten excited states were computed for each optimized dimer, the discussion below focuses on the two lowest-energy excitations (S_1 and S_2).

i) Book-opening angle. The H_4 TCPE chromophore is anisotropic, meaning that for this model, its geometry can be opened along two distinct molecular directions. We therefore define two book-opening scans: a short-axis (SA) opening angle and a long-axis (LA) opening angle, where the opening angle is θ as shown in Figure 4.2. The 2PA (σ_2) were plotted for all sampled opening angles in both SA and LA directions as shown in Figure 4.7. However, below we only discuss a representative dimer $d_{C-C} = 17$ Å from the full dataset ($d_{C-C} = 16\text{--}18$ Å). Overall, the LA series shows a stronger dependence of σ_2 on both d_{C-C} and θ than the SA series. This difference arises because the LA opening angle is oriented along the same direction that controls the arm separation d_{C-C} . In the next two subsections, we analyze the representative SA and LA dimers in more detail to rationalize the differences in their 2PA responses. Importantly, dimer formation modifies the electronic character relative to the monomer, leading to splitting of the lowest transition and increases of several orders of magnitude in the 2PA response in dimeric systems.

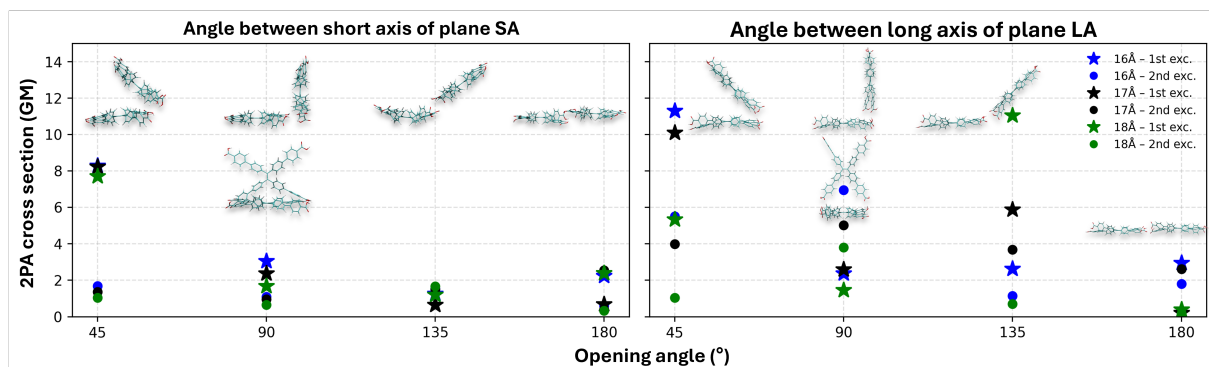


Figure 4.7. 2PA cross sections (σ_2 , GM) as a function of the book-opening angle θ . The short-axis (SA) opening scan is shown in the left panel and the long-axis (LA) opening scan in the right panel. Values corresponding to the first excitation are indicated by stars, and those for the second excitation by dots. Colors denote the intramolecular distance of the monomers within each dimer, $d_{C-C} = 16$ Å (blue), 17 Å (black), and 18 Å (green). Insets show representative geometries for selected configurations. Adapted from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

SA geometry. As shown in the left panel of Figure 4.7, the SA dimer reaches its maximum 2PA activity at $\theta = 45^\circ$. For the $S_0 \rightarrow S_1$ transition, this angle yields consistently large cross sections across the full intramolecular range $d_{C-C} = 16$ -18 Å: 8.29 GM at 653 nm (16 Å), 8.25 GM at 664 nm (17 Å), and 7.72 GM at 671 nm (18 Å). In contrast, the $S_0 \rightarrow S_2$ transition remains much weaker at the same angle, with a roughly sixfold reduction: 1.70 GM at 640 nm (16 Å), 1.36 GM at 651 nm (17 Å), and 1.04 GM at 658 nm (18 Å). This indicates that at $\theta = 45^\circ$ the lowest transition, $S_0 \rightarrow S_1$, is 2PA-allowed. Notably, this behavior differs from the monomer, where the $S_0 \rightarrow S_1$ transition is only weakly 2PA-active in the same d_{C-C} range, with $\sigma_2 \approx 0.28$ -0.33 GM. In contrast, dimer formation boosts the 2PA response (see Figure 4.8). For instance, the SA dimers present $\sigma_2 = 7.72$ -8.29 GM, corresponding to an enhancement of $\sim 26\times$ relative to the monomers, consistent with a cooperative effect upon aggregation^[50] (the LA dimers show the same qualitative trend but will be discussed in the next section). At the same time, the 1PA oscillator strength is reduced in the dimer models. While the monomers exhibit oscillator strengths of $f \approx 0.7$ -1.9 for $S_0 \rightarrow S_1$, the SA dimers decrease to $f \approx 0.5$ -0.7. The EDD analysis further shows the redistribution of the electron density. In the monomer, the density difference associated with $S_0 \rightarrow S_1$ is mainly localized on the inner part of the chromophore and is characterized by a large hole-electron overlap ($S_r \approx 0.76$ -0.77) and a small hole-electron separation ($D \approx 0.50$ -0.54 Å). Upon dimer formation (SA), the EDD becomes more spatially extended, the overlap decreases ($S_r \approx 0.68$ -0.70), and the hole-electron separation increases markedly ($D \approx 1.36$ -1.50 Å). In addition, the spatial extent index H increases from ~ 4.25 -4.47 Å in the monomer to ~ 5.0 -5.5 Å in the SA dimers (and up to ~ 6.6 -6.9 Å in the LA dimers). As evidenced by the reduced hole-electron overlap (S_r) and the increased charge-separation indices (D and H) in the dimer, we suggest that aggregation enhances the 2PA response and that this enhancement correlates with a more pronounced CT-like character in the $S_0 \rightarrow S_1$ state.

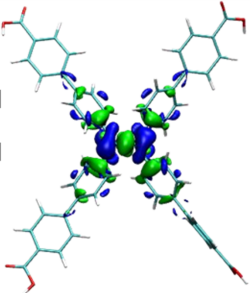
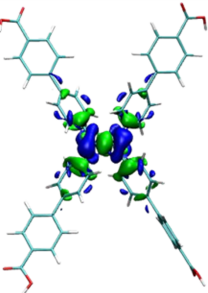
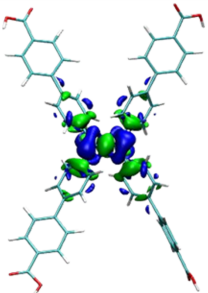
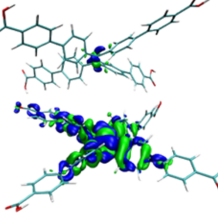
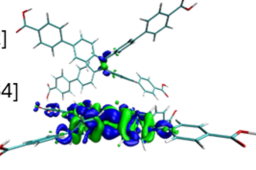
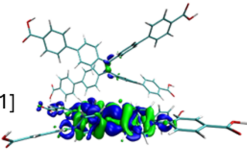
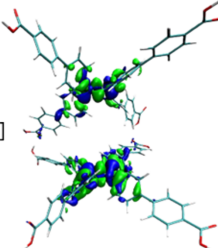
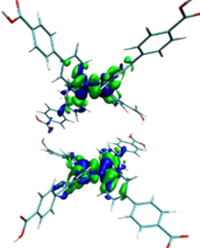
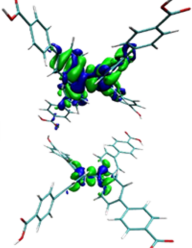
$S_0 \rightarrow S_1$			
d_{C-C}	16	17	18
Monomer	 1PA: 1.13 [325] 2PA: 0.33 [650] Sr: 0.77 D: 0.51 H: 4.47	 1PA: 1.90 [334] 2PA: 0.31 [668] Sr: 0.77 D: 0.50 H: 4.38	 1PA: 0.71 [340] 2PA: 0.28 [681] Sr: 0.76 D: 0.54 H: 4.25
Dimer (SA)	 1PA: 0.68 [326] 2PA: 8.288 [653] Sr: 0.68 D: 1.36 H: 5.50	 1PA: 0.58 [332] 2PA: 8.245 [664] Sr: 0.69 D: 1.40 H: 5.26	 1PA: 0.5 [335] 2PA: 7.720 [671] Sr: 0.7 D: 1.50 H: 5.01
Dimer (LA)	 1PA: 0.1 [327] 2PA: 11.29 [654] Sr: 0.63 D: 0.67 H: 6.61	 1PA: 0.034 [338] 2PA: 10.106 [677] Sr: 0.64 D: 0.50 H: 6.90	 1PA: 0.06 [341] 2PA: 5.339 [683] Sr: 0.71 D: 0.53 H: 6.69

Figure 4.8. Electron density difference (EDD) comparison for the $S_0 \rightarrow S_1$ transition in monomer and dimer systems across the $d_{C-C} = 16$ -18 Å range. For each structure, the excitation wavelength (nm), oscillator strength, and 2PA cross section σ_2 (GM) are reported. Multiwfn indices are also shown: S_r (dimensionless) and D and H (Å).

As observed in Figure 4.8, when the opening angle was increased, the 2PA response dropped drastically. At $\theta = 90^\circ$, σ_2 for S_1 drops to ~ 1.7 -3.0 GM, while S_2 remains small (~ 0.6 -1.0 GM) even for the $\theta = 45^\circ$ case. This decrease is consistent with a reduced π - π interaction in these systems that weakens the coupling. At $\theta = 135^\circ$, both excitations remain weak, with $S_1 \sim 0.6$ -1.6 GM. At $\theta = 180^\circ$, the σ_2 values recover only modestly, reaching ~ 0.6 -2.4 GM for S_1 and ~ 0.3 -2.5 GM for S_2 . The EDD analysis for $S_0 \rightarrow S_1$ at $\theta = 45^\circ$ shows that the excitation is largely localized on a single monomer, with only a minor contribution on the second unit. Consistently, the dominant orbital contribution (HOMO-1 $\rightarrow$ LUMO, 64.5%) corresponds to a pronounced IntraCT on the bottom monomer. In contrast, $S_0 \rightarrow S_2$ exhibits a weaker IntraCT character (see full dataset of the SA dimer systems in the appendix Table B.1-Table B.4 and Figure B.8): the main contribution (HOMO $\rightarrow$ LUMO+1, 70.1%) is more localized within one monomer and involves only limited charge redistribution.

LA geometry. As in the SA scan, the LA dimers show their highest 2PA activity at $\theta = 45^\circ$. For $S_0 \rightarrow S_1$, the corresponding cross sections are 11.30 GM at 654 nm (16 Å), 10.11 GM at 677 nm (17 Å), and 5.34 GM at 683 nm (18 Å). The $S_0 \rightarrow S_2$ transition is consistently weaker at this angle, but follows the same decreasing trend with $\sigma_2 = 5.52$ GM at 644 nm (16 Å), 3.98 GM at 667 nm (17 Å), and 1.04 GM at 675 nm (18 Å). The complete results for the first ten excitations are provided in appendix Table B.5-Table B.8. Increasing the opening angle reduces the 2PA response, following the same trend observed for the SA dimers. At $\theta = 90^\circ$, the response is already strongly suppressed, corresponding to a 4.5-fold decrease relative to the maximum ($\theta = 45^\circ$). At $\theta = 180^\circ$, both transitions remain weak, with values ranging $\sigma_2 \sim 0.2$ -2.9 GM for $S_0 \rightarrow S_1$ and ~ 0.1 -2.0 GM for $S_0 \rightarrow S_2$. A notable exception is the $\theta = 135^\circ$ LA geometry. For most angles, the three d_{C-C} conformations differ by only ~ 1 -2 GM; however, at $\theta = 135^\circ$ the 2PA response becomes strongly dependent on d_{C-C} . While $S_0 \rightarrow S_2$ remains comparatively small (~ 0.7 -3.6 GM), $S_0 \rightarrow S_1$ increases substantially from ~ 2.6 GM (16 Å) to ~ 5.8 GM (17 Å) and up to ~ 11 GM (18 Å). This indicates that, within the LA scan, the $d_{C-C} = 18$ Å conformation can become particularly favorable for enhancing σ_2 at $\theta = 135^\circ$. The EDD plots show a different behavior. While in SA the electron density was mostly localized in one of the monomers of the aggregate, here the, the density is present in both monomers as shown in Figure 4.8 (slightly reduced in the $d_{C-C} = 18$ Å, where density is more present in one of the chromophores than in the other). The dominant orbital contributions (see Figure B.8) involve transitions between orbitals largely localized on different monomers (HOMO $\rightarrow$ LUMO+1, 47.4%; HOMO-1 $\rightarrow$ LUMO, 29.2%). Since here the EDD reflects a coherently delocalized excitation spanning both monomers rather than a predominantly single-monomer redistribution (see Figure 4.8). We therefore assign this state to a Frenkel-type exciton, i.e., a locally excited state on each monomer that is coherently coupled in the dimer.^[195] This coupling increases the 2PA response by $\sim 10\%$ relative to the SA-based structures. With a similar trend observed for $S_0 \rightarrow S_2$ (see Figure B.8). Compared with SA at the same angle, the LA dimers exhibit a much smaller hole-electron centroid separation ($D = 0.50$ -0.67 Å), whereas SA showed substantially larger values ($D \approx 1.36$ -1.50 Å). At the same time, the spatial extent index is larger in LA ($H = 6.61$ -6.90 Å) than in SA ($H \approx 5.0$ -5.5 Å).

ii) Stacking-plane displacement. We explored lateral displacements between two initially stacked H₄TCPE monomers (see b in Figure 4.2) at two initial center-to-center separations, $\Delta z = 4$ and 5 Å (see Figure 4.1). Left-right shifts were defined as $\Delta x = \pm 5$ and ± 10 Å (negative = left; positive = right), and up-down shifts as $\Delta y = \pm 5$ and ± 10 Å (positive = up; negative = down). The Δx series yields consistently low 2PA cross sections (see Table B.13-Table B.16). In this direction, the displacement follows the short molecular axis, which reduces the effective interaction surface and thus the π - π contact. The weaker intermolecular coupling results in smaller σ_2 values. Therefore, the discussion below focuses on the Δy series (± 5 and ± 10 Å), summarized in Figure 4.9 for the first and second excitations.

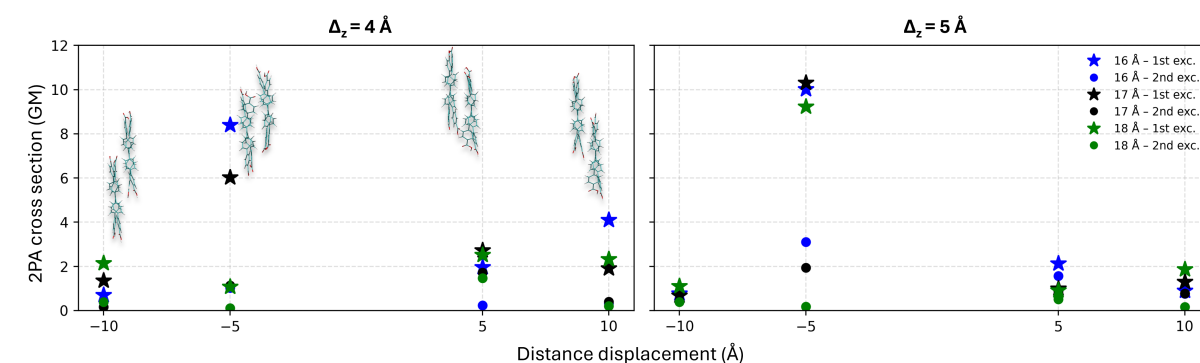


Figure 4.9. Stacking-plane displacement scan for H_4TCPE dimers. The 2PA cross section σ_2 is plotted against the in-plane displacement (± 5 and ± 10 Å) at two initial stacking distances, $\Delta z = 4$ Å (left) and 5 Å (right). Markers correspond to the transition considered (stars: first excited state; circles: second excited state). Line colors indicate the intramolecular distance d_{C-C} (16, 17, and 18 Å). Adapted from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

Among the sampled displacements, $\Delta y = -5$ Å systematically gives the largest σ_2 . Moreover, dimers initialized at $\Delta z = 5$ Å show higher and more stable σ_2 values (9.2-10.3 GM) than those started at $\Delta z = 4$ Å (1.0-8.3 GM). In contrast, the largest displacements ($\Delta y = \pm 10$ Å), which approach head-to-tail-like arrangements, lead to a pronounced decrease in σ_2 (below 4 GM, often below 2 GM). Based on these trends, the electronic-structure analysis is based on the $\Delta y = -5$ Å geometries. We examined EDD maps and the dominant orbital transitions (see Figure 4.10) for a representative geometry of $d_{C-C} = 17$ Å. The EDD plots are qualitatively similar for $\Delta z = 4$ and 5 Å, indicating comparable regions of electron depletion/accumulation upon excitation. However, the leading orbital contributions to $S_0 \rightarrow S_1$ change. For example, at $\Delta z = 4$ Å the dominant contributions depicted in Figure 4.10 (HOMO $\rightarrow$ LUMO with 64% and HOMO-1 $\rightarrow$ LUMO+1 with 14.7%) show a small inter- and IntraCT, where the electron density redistributes from the center (HOMO) to the bottom part of the same molecule as well as slightly in the other monomer (LUMO). At $\Delta z = 5$ Å the leading contribution depicted in Figure 4.10 (HOMO-1 $\rightarrow$ LUMO of 59.4%) shows mainly IntraCT. Consistent with this, the MULTIWFN indices show that increasing Δz from 4 to 5 Å decreases the hole-electron overlap ($S_r = 0.69 \rightarrow 0.61$) and increases the hole-electron centroid separation ($D = 1.33 \rightarrow 1.51$ Å), indicating a slightly more charge-separated excitation for $\Delta z = 5$ Å.

iii) Plane-rotation angle. As a final step, we investigated an in-plane rotation of initially parallel-stacked dimers. Starting from the fully aligned configuration ($\theta = 0^\circ$), we rotated one monomer within the stacking plane and sampled $\theta = 0^\circ, 30^\circ, 60^\circ$, and 90° . The resulting 2PA σ_2 for the first and second excitations are summarized in Figure 4.11. However, the complete dataset with the 10 excitations is available in Table B.17-Table B.20.

Overall, the rotated geometries ($\theta = 30^\circ, 60^\circ$, and 90°) display markedly reduced 2PA responses, with only a modest recovery at $\theta = 90^\circ$. In contrast, the highest 2PA values are obtained exclusively for the fully aligned arrangement ($\theta = 0^\circ$), discussed at the end of this section. At $\theta = 30^\circ$, the 2PA response is

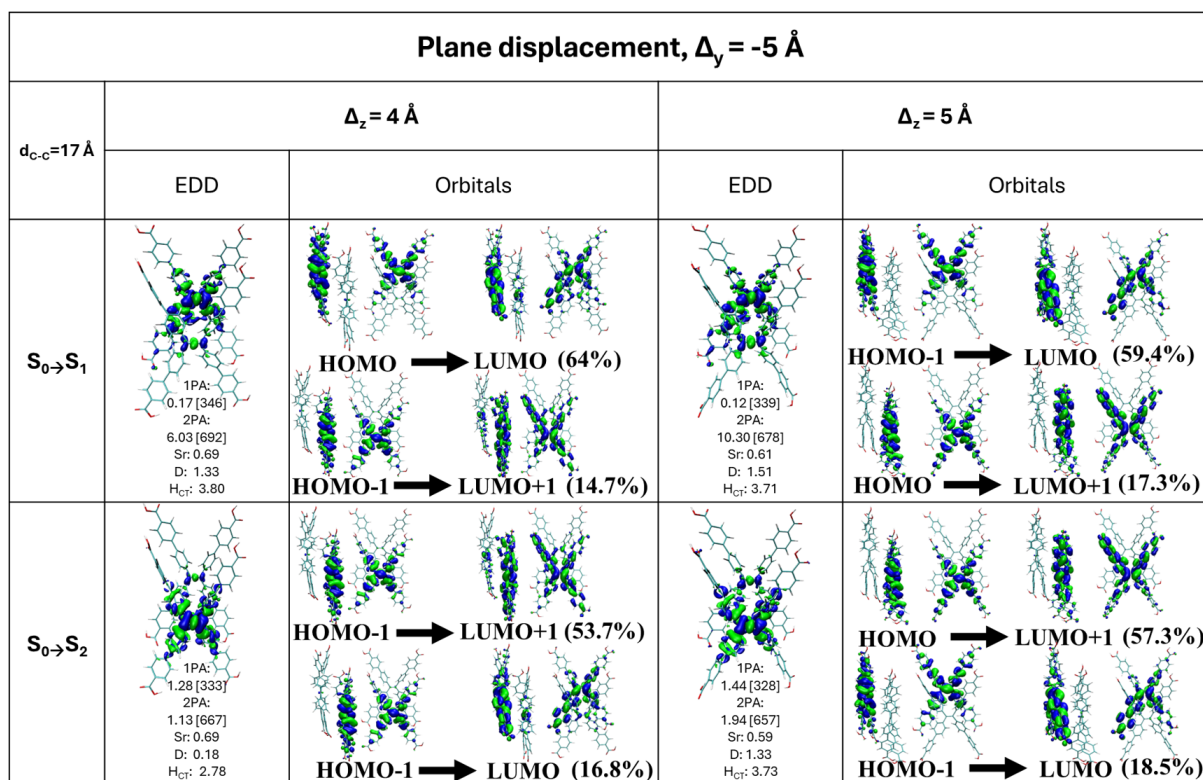


Figure 4.10. Representative geometry with $d_{C-C} = 17 \text{ \AA}$ at $\Delta_y = -5 \text{ \AA}$. EDD maps and the dominant orbital transitions are shown for the first and second excitations, together with the corresponding 1PA/2PA responses and CT indices. Results are compared for two initial stacking separations, $\Delta_z = 4 \text{ \AA}$ (left) and $5 \text{ \AA}$ (right). The analogous $d_{C-C} = 16$ and $18 \text{ \AA}$ conformations are provided in Figure B.9). In the EDD maps, blue regions indicate electron depletion (donor), while green regions indicate electron accumulation (acceptor) upon excitation. Adapted from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

essentially quenched for all sampled d_{C-C} values and for both initial separations, yielding $\sigma_2 < 0.5 \text{ GM}$ for both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$. Interestingly, despite being 2PA-dark, these geometries remain 1PA-active for $S_0 \rightarrow S_2$: the oscillator strengths are relatively large ($f \approx 1.1$ - 1.5) for $d_{C-C} = 16$ - $17 \text{ \AA}$, while $d_{C-C} = 18 \text{ \AA}$ shows smaller values ($f \approx 0.6$; see Table B.18 in appendix). At $\theta = 60^\circ$, a slight increase is observed, but only for $d_{C-C} = 17 \text{ \AA}$ at $\Delta_z = 5 \text{ \AA}$, where σ_2 reaches $\sim 4.05 \text{ GM}$ (see Table B.19 in appendix). This remains small compared with the configurations discussed above (book-opening and plane-displacement scans). At $\theta = 90^\circ$, σ_2 increases modestly relative to the 30° and 60° cases. The largest values occur for $d_{C-C} = 16 \text{ \AA}$ at $\Delta_z = 4 \text{ \AA}$, giving 1.7 GM ($S_0 \rightarrow S_1$) and 5.5 GM ($S_0 \rightarrow S_2$). At $\Delta_z = 5 \text{ \AA}$, the same distance yields 1.9 GM ($S_0 \rightarrow S_1$) and 0.6 GM ($S_0 \rightarrow S_2$) (see complete dataset in Table B.20 in appendix). Because these rotated conformations are generally 2PA-inactive and unlikely to represent experimentally relevant packing motifs, we do not analyze their electronic structure further. To the best of our knowledge, no experimental reports describe analogous MOFs in which the chromophore adopts such in-plane rotations ($\theta = 30^\circ$ - 90°); therefore, these geometries are primarily of theoretical interest. Finally, the aligned configuration ($\theta = 0^\circ$) exhibits the highest 2PA response, but predominantly for $S_0 \rightarrow S_1$. For $\Delta_z = 4 \text{ \AA}$, σ_2 ranges from 3.95 to 5.90 GM , increasing to 7.53 - 9.73 GM at $\Delta_z = 5 \text{ \AA}$

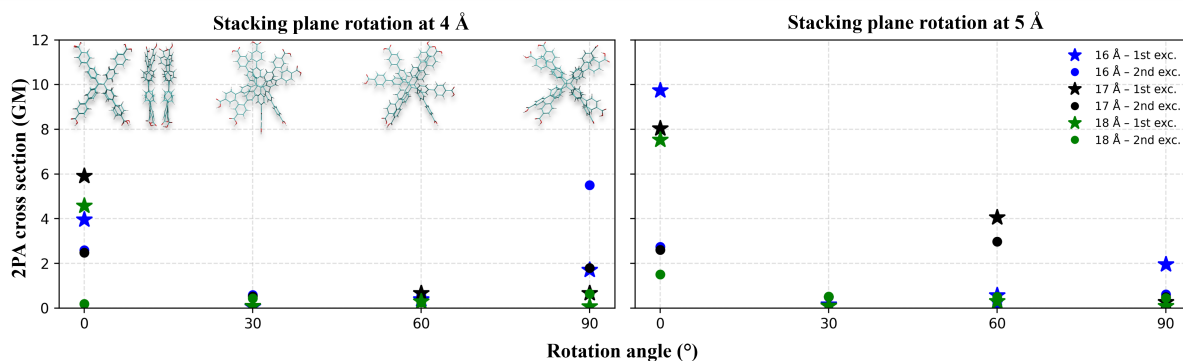


Figure 4.11. Effect of stacking-plane rotation on the 2PA response of H_4 TCPE dimers. The 2PA σ_2 is shown as a function of the stacking-plane rotation angle for initial separations of $\Delta z = 4$ Å (left) and 5 Å (right). Stars and circles denote the first and second excited-state transitions, respectively. Line colors indicate the intramolecular distance d_{C-C} (16 Å in blue, 17 Å in black, and 18 Å in green). Insets show representative geometries for selected configurations. Reproduced from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

(across $d_{C-C} = 16-18$ Å). In contrast, the $S_0 \rightarrow S_2$ transition remains comparatively weak, with $\sigma_2 = 0.2-2.5$ GM ($\Delta z = 4$ Å) and 1.5-2.7 GM ($\Delta z = 5$ Å). The complete dataset with the 10 excitations is provided in Table B.17.

The frontier-orbital analysis (Figure 4.12) reveals clear differences in the excitation pattern between $\Delta z = 4$ and 5 Å. For $\Delta z = 4$ Å (shown for $S_0 \rightarrow S_1$), the dominant contributions correspond to HOMO $\rightarrow$ LUMO (49.7%) and HOMO-1 $\rightarrow$ LUMO+1 (25.2%). In both channels, the hole density (HOMO/HOMO-1) is mainly delocalized over the dimer, while the electron density (LUMO/LUMO+1) shifts toward the terminal phenyl groups. But not uniformly distributed, instead, the electron density is more localized on one arm of each monomer, indicating an asymmetric redistribution within the dimer. Increasing the initial separation to $\Delta z = 5$ Å changes the degree of delocalization across the two monomers. Compared with the $\Delta z = 4$ Å case, the density becomes more unevenly distributed, localized on a single monomer (HOMO). For $S_0 \rightarrow S_1$ shown in Figure 4.11, the excitation is mainly described by HOMO $\rightarrow$ LUMO (47.3%) and HOMO $\rightarrow$ LUMO+1 (17.2%). The resulting redistribution transfers density from one of the monomers toward the arm termini, but with a more pronounced asymmetry between monomers. This change correlates with the higher 2PA response at $\Delta z = 5$ Å, where $\sigma_2(S_0 \rightarrow S_1)$ increases from $\sim 3.95-5.90$ GM to $\sim 7.53-9.73$ GM (see the EDD and main orbital contributions in Figure B.10 for $d_{C-C} = 16-18$ Å). A qualitatively similar redistribution is also observed for $S_0 \rightarrow S_2$. The EDD maps further support partial delocalization of the excitation over the dimer at $\Delta z = 4$ Å, with slightly higher density on one monomer. These excitations can be described as CT-mixed rather than purely Frenkel-like. This differs from the LA book-opening case ($\theta = 45^\circ$), where the excitation is largely localized on each monomer in a more symmetric manner (see Figure 4.8). Finally, MULTIWFN indices quantify the CT-mixed character for both separations. The hole-electron overlap remains low and nearly unchanged ($S_r = 0.61$ for $\Delta z = 4$ Å and $S_r = 0.62$ for $\Delta z = 5$ Å), consistent with reduced overlap compared with the book-opening geome-

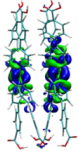
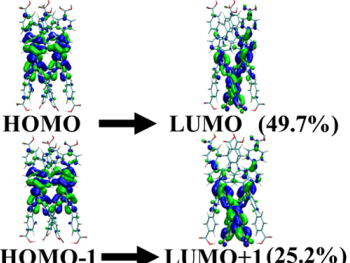
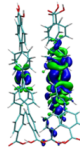
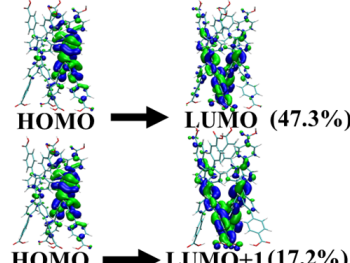
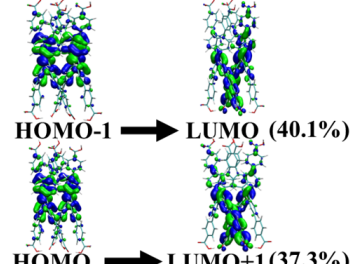
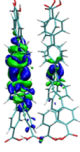
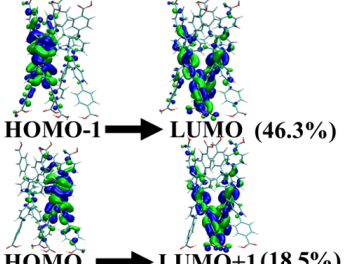
Plane rotation, $\theta = 0^\circ$				
$d_{C-C}=17\text{ \AA}$	$\Delta_z = 4\text{ \AA}$		$\Delta_z = 5\text{ \AA}$	
	EDD	Orbitals	EDD	Orbitals
$S_0 \rightarrow S_1$	 1PA: 0.10 [353] 2PA: 5.91 [706] Sr: 0.61 D: 1.55 H_{CT}: 3.85	 HOMO $\rightarrow$ LUMO (49.7%) HOMO-1 $\rightarrow$ LUMO+1 (25.2%)	 1PA: 0.21 [347] 2PA: 8.04 [694] Sr: 0.62 D: 1.137 H_{CT}: 3.58	 HOMO $\rightarrow$ LUMO (47.3%) HOMO $\rightarrow$ LUMO+1 (17.2%)
$S_0 \rightarrow S_2$	 1PA: 1.35 [340] 2PA: 2.47 [681] Sr: 0.61 D: 1.24 H_{CT}: 3.88	 HOMO-1 $\rightarrow$ LUMO (40.1%) HOMO $\rightarrow$ LUMO+1 (37.3%)	 1PA: 1.32 [335] 2PA: 2.59 [670] Sr: 0.66 D: 0.93 H_{CT}: 3.36	 HOMO-1 $\rightarrow$ LUMO (46.3%) HOMO $\rightarrow$ LUMO+1 (18.5%)

Figure 4.12. EDD and main orbital contribution for a representative geometry $d_{C-C} = 17\text{ \AA}$. Comparison of the initial separations $\Delta z = 4\text{ \AA}$ (left) and $5\text{ \AA}$ (right). Adapted from Pacheco Hernandez and Kozłowska,^[177] *Front. Chem.* (2026). Licensed under CC BY 4.0.

tries (SA and LA). Moreover, the hole-electron centroid separation is comparatively large ($D = 1.55\text{ \AA}$), exceeding the values found for SA ($D = 1.40\text{ \AA}$) and especially LA ($D = 0.50\text{ \AA}$) at $d_{C-C} = 17\text{ \AA}$. Together, the orbital, EDD, and index analyses (see Multiwfn analysis in Table B.23) indicate that the rotated/aligned configurations exhibit a more charge-separated (CT-mixed) excitation character than the book-opening dimers, consistent with their enhanced 2PA response under favorable packing. When comparing the most favorable plane-displacement geometry ($\Delta y = -5\text{ \AA}$) with the plane-rotation scan, the fully aligned case ($\theta = 0^\circ$) yields visibly lower σ_2 values than the corresponding displaced dimers. Nevertheless, these parallel-stacking configurations remain relevant as candidate packing motifs for further computational screening and, potentially, synthesis. Importantly, the aggregation of H_4 TCPE cannot be mapped unambiguously onto the classical J-/H-aggregate picture. In contrast to rigid chromophores with a well-defined transition dipole, H_4 TCPE comprises multiple aromatic subunits connected by rotatable bonds, leading to conformational flexibility and non-uniform local dipole orientations. As a result, applying the same geometric offset (e.g., displacement or parallel alignment) does not guarantee a single, well-defined coupling motif. Instead, the overall 2PA response is expected to reflect a superposition of contributions from differently coupled subunits within the dimer.

4.1.3. Summary

To summarize this section, we performed an *in silico* screening (DFT/TD-DFT) to map how the 2PA response of H₄TCPE varies with key structural degrees of freedom relevant to MOF-like packing. We observed the following:

Monomer flexibility (d_{C-C} scan): H₄TCPE behaves as a quadrupolar chromophore with complementary 1PA/2PA selection rules. For $d_{C-C} = 16-18$ Å: $S_0 \rightarrow S_1$ is 1PA-allowed but 2PA-forbidden, whereas $S_0 \rightarrow S_2$ is 1PA-forbidden and 2PA-allowed. The EDD/orbital and MULTIWFN analyses show that varying d_{C-C} mainly tunes electron-density redistribution: S_1 remains largely LE-like (increasingly core-centered at larger d_{C-C}), while S_2 is more geometry-sensitive and shows stronger redistribution within the experimentally relevant range ($\sim 16-19$ Å). Overall, monomer 2PA predominantly populates S_2 , consistent with quadrupolar behavior.

Packing models (built from $d_{C-C} = 16-18$ Å monomers): Three packing degrees of freedom were examined: i) Book-like opening along the short/long molecular axes (SA/LA) by varying the opening angle θ . ii) Stacking-plane translations along Δx and Δy . iii) In-plane rotations of parallel-stacked dimers by varying the rotation angle θ . The book-opening: SA(45°) enhances 2PA for $S_0 \rightarrow S_1$, consistent with stronger intramolecular redistribution (larger D for S_1 than S_2). LA(45°) yields $\sim 10\%$ higher σ_2 than SA due to stronger intermolecular coupling and a more delocalized Frenkel-type exciton. For the plane displacements, Δx gives negligible σ_2 (weak coupling). In contrast, Δy can yield large 2PA responses, especially for $\Delta y = -5$ Å conformation. In-plane rotations, the 2PA is generally quenched at 30° and most 60° geometries; 90° yields only modest σ_2 . For 0° , EDD/orbital analyses suggest mixed Frenkel/CT-like character and present the largest 2PA response among the sampled geometries. Finally, enforcing overly short separations (e.g., $\Delta z = 4$ Å) can impose geometric constraints and reduce the 2PA response. These results indicate that a higher 2PA response occurs at an optimal distance (e.g., $\Delta z = 5$ Å) rather than a minimal one.

Scope and limitations of this work: This approach is a qualitative, comparative screening based on finite (non-periodic) models; direct periodic multiphoton calculations for large MOF unit cells remain computationally prohibitive. Importantly, long-range interactions and explicit solvent/metal-node effects are not included; spectra rely on vertical electronic excitations and homogeneous (Lorentzian) broadening. Absolute σ_2 values should not be directly compared with experiment; conclusions focus on relative trends between packing motifs (often treated as approximately additive when linkers behave independently). Experimental studies report that denser chromophore packing (especially MOFs constructed exclusively from H₄TCPE) often yields higher 2PA responses. Therefore, we only studied H₄TCPE combinations. Fully parallel stacking is rarely observed in reported structures; screening suggests that

near-parallel, high-density packing remains a promising design space, though displaced stacking can be more favorable.

4.2. 2PA Properties in H₄TBAPy-Based MOFs

Only few studies have reported the 2PA properties of H₄TBAPy.^[194,196] This linker has been used primarily in the Zr-based MOFs NU-1000 and NU-901, which share the same stoichiometry but differ in topology. More recently, Deger *et al.*^[194] synthesized Sr- and Ba-based MOFs incorporating H₄TBAPy as organic linker and compared their 2PA performance. They have found that the order of the 2PA σ_2 was SrTBAPy (2.1×10^3 GM) < NU-1000 (1.2×10^4 GM) < NU-901 (1.8×10^4 GM) < BaTBAPy (8.2×10^4 GM). These results suggest that 2PA enhancement is governed not only by dense packing but also by linker orientation and the local coordination environment. Motivated by these trends, we computationally studied the 2PA properties of the four MOFs (NU-1000, NU-901, SrTBAPy, and BaTBAPy) to understand the origin of the pronounced differences in their reported σ_2 . We extracted monomers, dimers, trimers, and in some cases tetramers from the MOF crystal structures provided by Deger *et al.*^[194] Through TD-DFT calculations, we obtained the 2PA σ_2 , and further analyzed the electron-density difference to quantify the character of the relevant electronic transitions, focusing on LE and IntraCT.

4.2.1. Methodology: Structure Generation and Conformational Screening

Monomers and Larger Systems

The approach adopted here, for H₄TBAPy, differs from the one previously shown for H₄TCPE in section 4.1. In the previous section, we generated artificial packing orientations and applied constraints to prevent full structural relaxation, thereby probing conformations that are not necessarily realized experimentally. Here, in contrast, monomer, dimer, trimer, and (in selected cases) tetramer models were directly extracted from experimentally resolved crystal structures of NU-1000, NU-901, SrTBAPy, and BaTBAPy reported by Deger *et al.*^[194] Importantly, only the monomer was fully optimized in solvent to reproduce the chromophore behavior in solution, whereas the larger systems (dimers, trimers, and tetramers) were kept in their crystal-extracted geometries to preserve the intermolecular arrangements imposed by the periodic MOF environment.

Ground-State Calculations

Only the H₄TBAPy monomer was first geometry-optimized in the gas phase and later in solvent at the DFT level, employing TURBOMOLE V7.6 and the resolution-of-identity (RI) approximation to accelerate the computations. The long-range corrected hybrid CAM-B3LYP^[129] functional in combination with the def2-SVP (split-valence polarized) basis set^[179] were employed. The D3 dispersion correction with Becke–Johnson damping (D3BJ)^[180] was considered. For monomer optimizations, the total en-

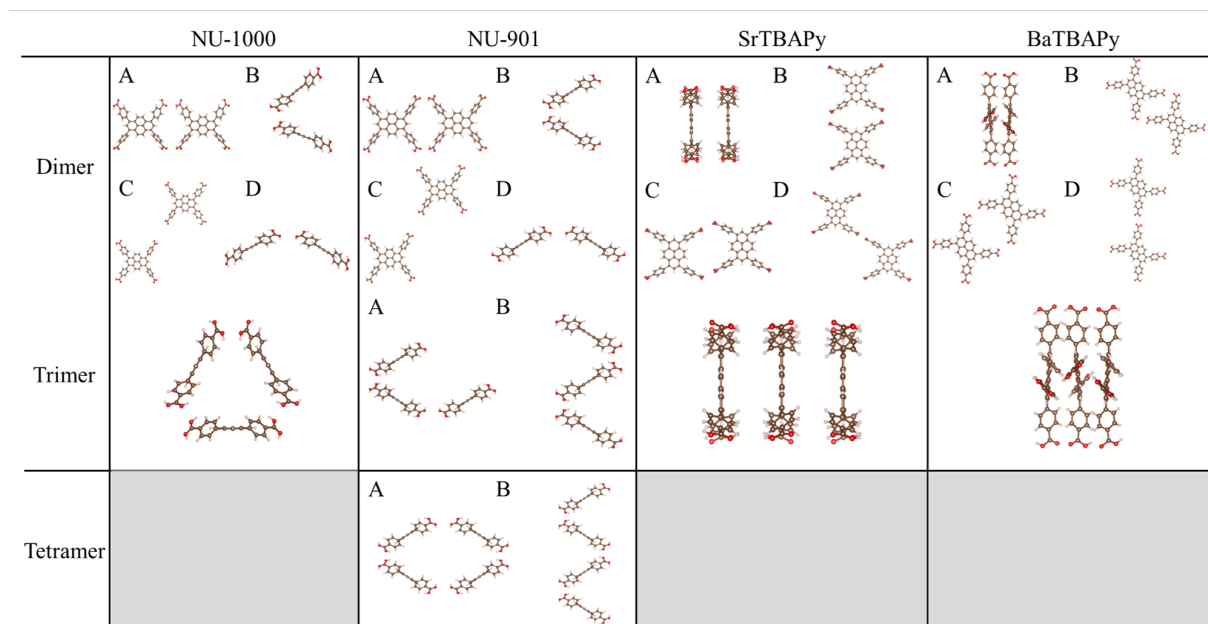


Figure 4.13. Representative assemblies extracted from the H_4TBAPy -based MOFs NU-901, NU-1000, SrTBAPy, and BaTBAPy. For each framework, contiguous dimers (DimerA-DimerD) were considered along the different closely packed directions; where applicable, the corresponding trimers were also analyzed, and for NU-901, a tetramer was additionally included. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

ergy convergence threshold was set to 1×10^{-8} Hartree. To mimic the linker in solution, we employed COSMO (Conductor-like Screening Model) solvation model^[197] using a dielectric constant of $\epsilon = 36.7$ and a refractive index of $n = 1.43$, corresponding to dimethylformamide (DMF). Harmonic vibrational analyses confirmed that the optimized structures correspond to true minima (no imaginary frequencies).

Excited-State Calculations

Excited-state properties were computed at the TD-DFT level using TURBOMOLE V7.6 with RI, employing the same computational setup as in the ground-state calculations (CAM-B3LYP/def2-SVP/D3BJ) and considering 10 singlet vertical excitations. Only for the previously optimized monomer, the 1PA and 2PA properties were calculated in DMF. For the larger systems, which were extracted from the crystal structure (see Figure 4.13), 1PA and 2PA were computed in gas-phase. For the corresponding single-point calculations, the electronic energy convergence threshold was set to 1×10^{-7} Hartree. NU-1000 and NU-901 share the same stoichiometry (H_4TBAPy linker and Zr-oxo SBU) but differ in linker orientations. To isolate packing and orientation effects, we focused only on the organic fragments and excluded the Zr-oxo SBU in these two polymorphs. In contrast, SrTBAPy and BaTBAPy incorporate different metal nodes that may affect the 2PA response; therefore, for these systems, we performed calculations both including and excluding the Sr/Ba SBU to assess the SBU contribution. For SBU-containing models, Sr and Ba were described using effective core potentials (def-ecp), while all other atoms were

treated with all-electron basis sets. To preserve the coordination environment in truncated SBU models, CCH_3 groups were added to the O atoms bound to the metal node (see Figure 4.14). Absorption spectra were generated by Lorentzian broadening as described in subsection 2.2.1. The 2PA spectra were computed for a single, parallel linearly polarized laser beam. For electronic-structure characterization, electron-density difference (EDD) maps and frontier and transition orbitals were analyzed. Isosurfaces were visualized with VMD using isovalues of 0.02 a.u. (orbitals) and 0.0005 a.u. (EDD). Charge transfer was quantified using the post-processing program Multiwfn (v3.8).

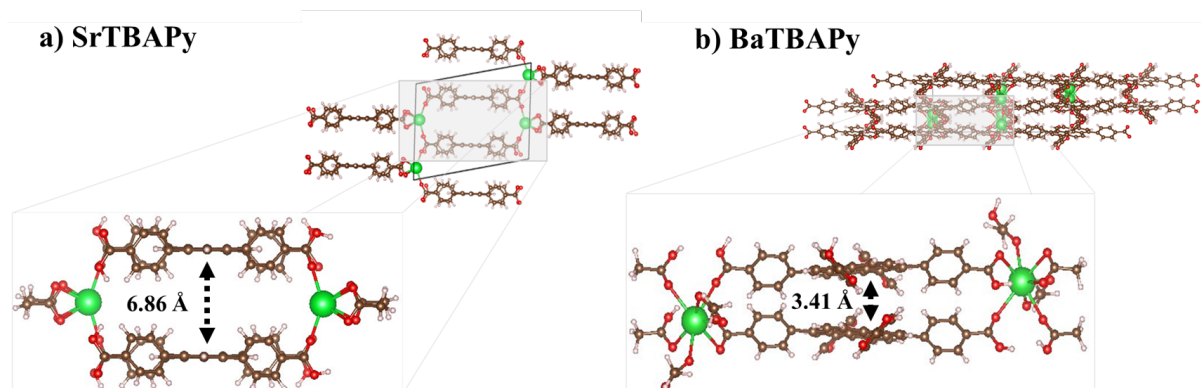


Figure 4.14. Representative SBU-containing fragments extracted from the SrTBAPy and BaTBAPy crystal structures. a) SrTBAPy-extracted dimer, illustrating the larger intermolecular separation (6.86 Å). b) BaTBAPy-extracted dimer, showing a much shorter stacking contact (3.41 Å). The gray highlighted region indicates the portion of the periodic structure used to define the extracted cluster. To preserve the coordination environment of the SBUs and avoid dangling bonds, terminal oxygen atoms were capped with methyl groups. In addition to the representative fragments shown here, monomer-1SBU, dimer-1SBU, and dimer-2SBU cluster models were considered for the analysis. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

4.2.2. Results and Discussion

Monomer Calculations

Single point calculations of extracted monomers: To compare the structural differences of the H_4TBAPy monomer across frameworks, we extracted one monomer from each crystal structure (NU-901, NU-1000, SrTBAPy, and BaTBAPy) and performed single-point calculations to obtain the 1PA spectra as described in subsubsection 4.2.1. The resulting spectra exhibit pronounced framework-dependent shifts, particularly for the lowest-energy (longest-wavelength) absorption band. The NU-901-extracted monomer is the most red-shifted, with a first maximum peak at 376 nm, whereas the SrTBAPy-extracted monomer is the most blue-shifted, with a corresponding first maximum peak at 336 nm. Comparison of the extracted geometries (see Figure 4.15) indicates that these spectral differences originate mainly from conformational variations in the flexible ending phenyl rings, while the central core overlaps almost perfectly among all monomers.

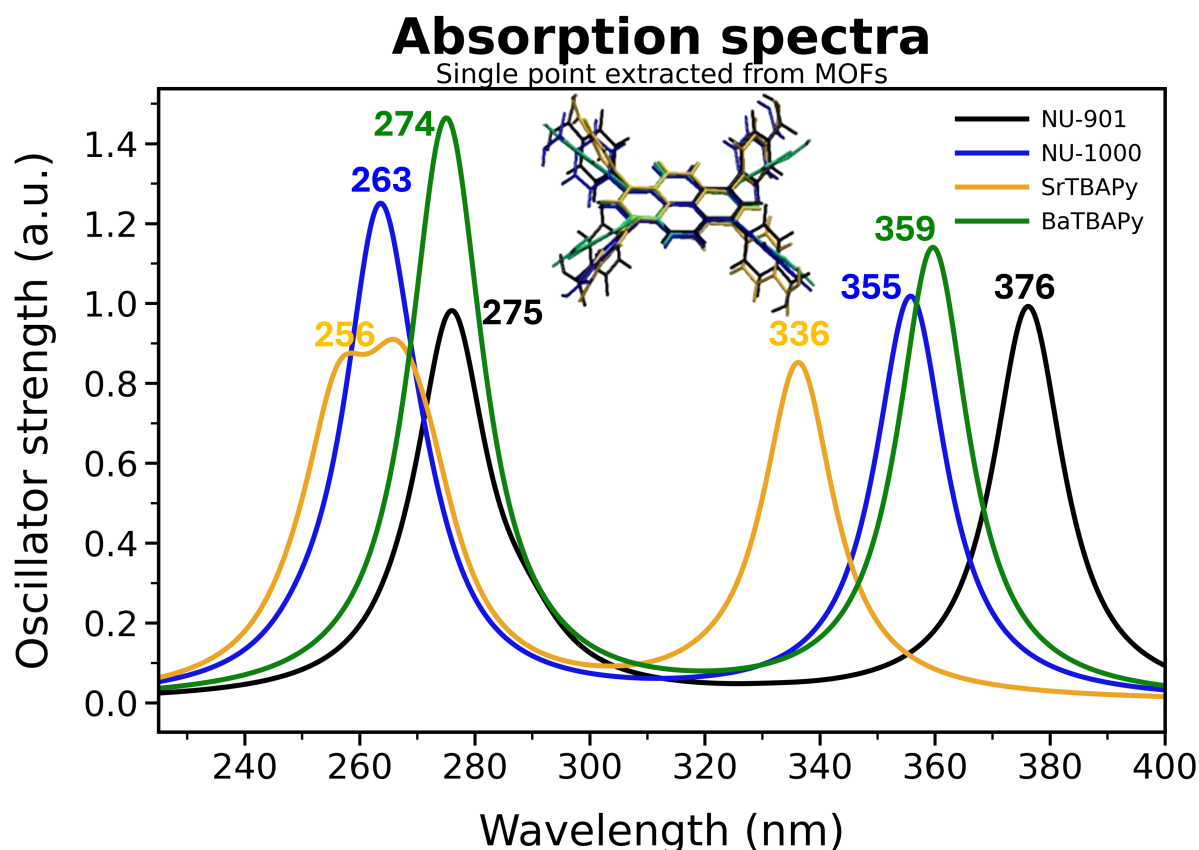


Figure 4.15. One-photon absorption (1PA) spectra of H_4TBAPy monomers extracted from the crystal structures of NU-901 (black), NU-1000 (blue), SrTBAPy (orange), and BaTBAPy (green), computed at the single-point level. The wavelengths of the main absorption maxima are shown in the corresponding colors. The inset shows an overlay of the extracted monomer geometries to highlight subtle framework-dependent distortions. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

Geometry optimization in DMF: The geometry of the monomers extracted from each MOF was optimized in implicit DMF, the 1PA and 2PA results reveal only minor spectral shifts among the optimized structures (< 10 nm). These differences are attributed to subtle geometric variations, as the MOF-extracted starting conformations converge to distinct local minima upon optimization. To quantify the relative stability of the optimized minima, the final electronic energies (kcal/mol) were compared: -1438015.64 (NU-901), -1438015.45 (NU-1000), -1438012.75 (BaTBAPy), and -1438012.56 (SrTBAPy). The corresponding ΔE values indicate negligible energy differences between the NU-derived monomers, whereas the Ba- and Sr-extracted monomers are higher in energy by 2.89 and 3.07 kcal/mol, respectively. Consequently, the NU-901-extracted monomer was selected as the representative H_4TBAPy structure (chromophore in solution) and will be compared with the larger systems (i.e., dimer, trimer, tetramer), as it corresponds to the lowest-energy minimum (1PA, 2PA results and main orbital transitions are available in Table B.24). Notably, the absorption shifts for the optimized monomers remain minimal (Figure 4.16), while the non-optimized, crystal-extracted monomers exhibit more pronounced spectral differences (~ 30 nm) as shown in Figure 4.15.

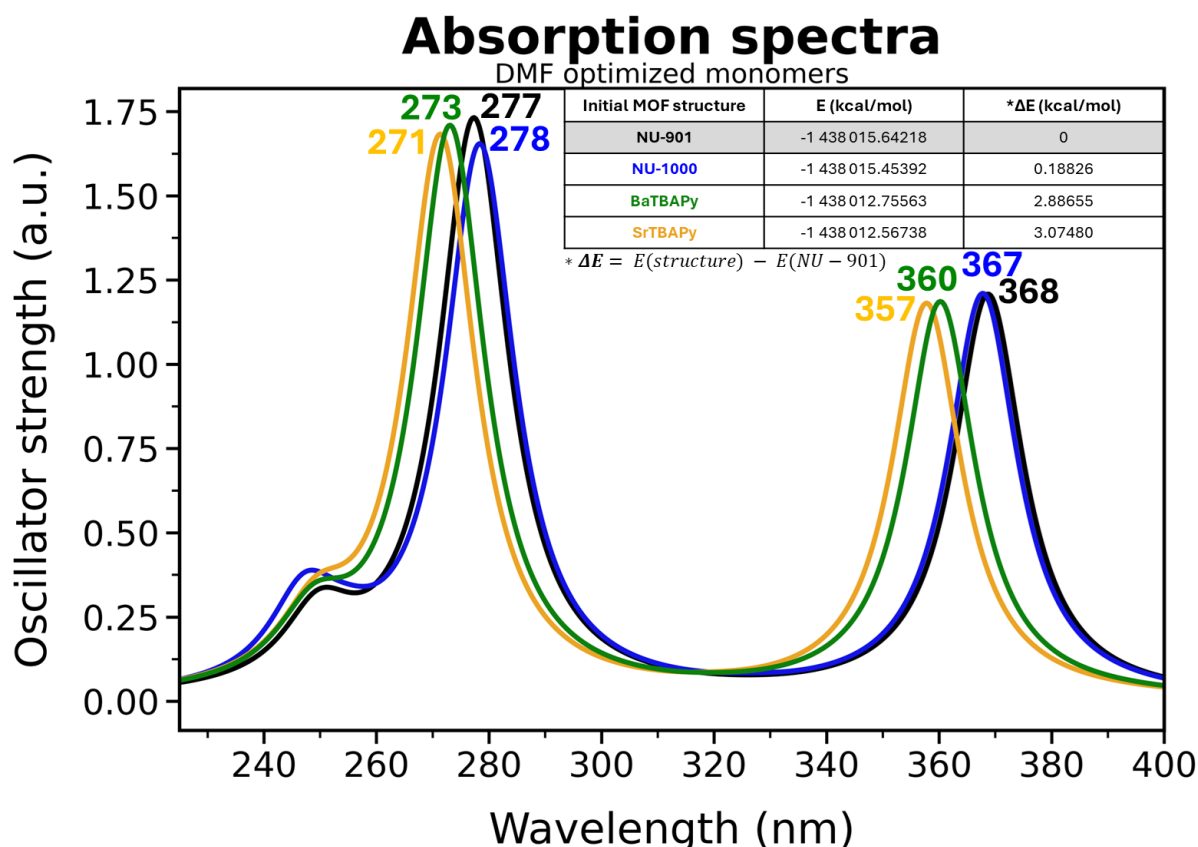


Figure 4.16. One-photon absorption (1PA) spectra of H_4TBAPy monomers extracted from the crystal structures of NU-901 (black), NU-1000 (blue), SrTBAPy (orange), and BaTBAPy (green), and further optimized in DMF. The wavelengths of the main absorption maxima are shown in the corresponding colors. The inset table shows the final energies after optimization and the . Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

Dimer, Trimer and Tetramer calculations

In this section, we first analyze each MOF individually by evaluating all relevant near-neighbor combinations. The dimer models are denoted DimerA-DimerD and sample all possible nearest-neighbor directions in each structure. In most cases, trimers were generated by adding a third monomer along the dimer arrangement that yielded the largest 2PA response. A tetramer was explored only for NU-901 to probe the additive effect of extending the assembly along selected directions. We then compare the best-performing configurations across all four MOFs. Finally, for the stacking frameworks (SrTBAPy and BaTBAPy), we examine i) the effect of the interlayer linker distance on the computed 2PA cross section by systematically varying the initial intermolecular separation, and ii) the role of the SBU in the resulting 2PA response.

NU-1000. This MOF has a *csq* topology. As shown in Figure 4.17, the framework contains two distinct pore types: i) large hexagonal channels with a diameter of ~ 31 Å and ii) smaller triangular pores

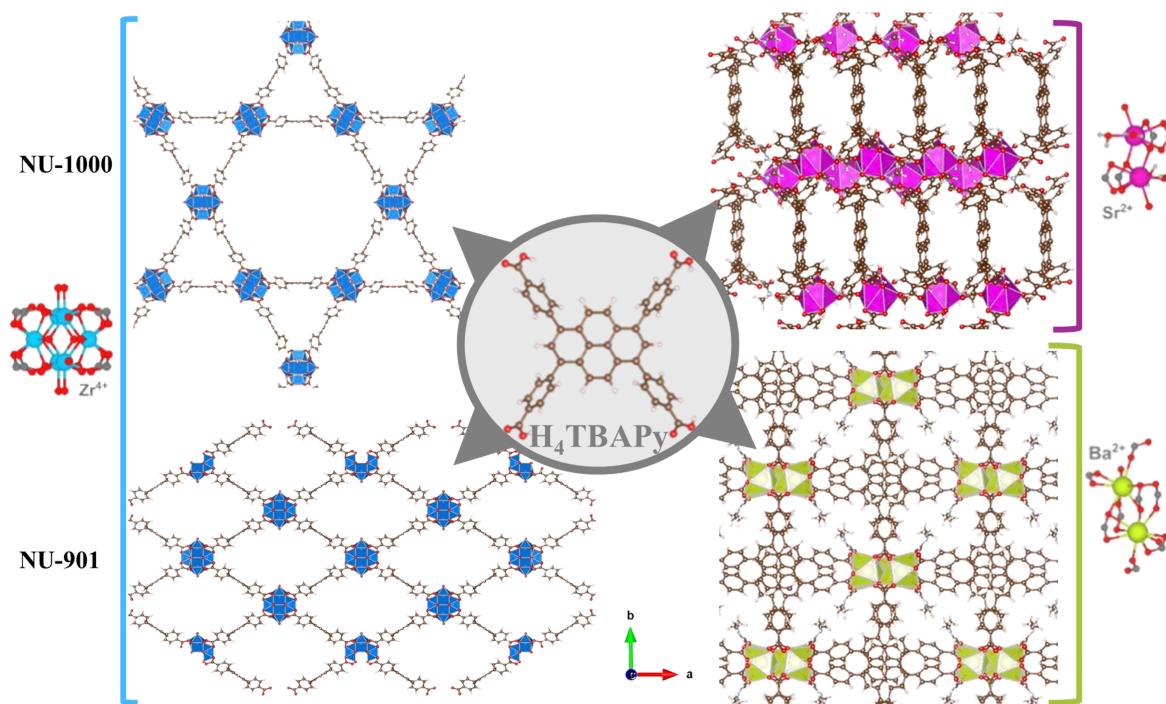


Figure 4.17. Overview of the four TBAPy-based MOFs investigated in this work (NU-1000, NU-901, SrTBAPy, and BaTBAPy). The same TBAPy linker is present in all frameworks, while the SBUs differ: Zr-oxo clusters in NU-1000/NU-901 (blue) and in SrTBAPy and BaTBAPy (yellow and pink). Structures are viewed along the crystallographic c -axis.

of ~ 11 Å. In the triangular ones, the shortest linker center-to-center separation is 10.94 Å. Owing to this geometry, several distinct proximity motifs can be defined (see Figure 4.13). Among the tested dimers, DimerB exhibits the largest 2PA response of $\sigma_2 = 2.9$ GM (see Table B.26 for the complete dataset of the 10 excitations), whereas DimerA, DimerC, and DimerD remain below 0.07 GM (see Table B.25-Table B.28). Using DimerB as a building reference, we constructed a trimer by adding a third monomer along the same direction, forming the arrangement associated with the triangular pore in NU-1000. This trimer shows an approximately threefold enhancement relative to DimerB, reaching $\sigma_2 = 8.1$ GM as shown in the left panel in Figure 4.18. To rationalize these differences at the electronic level, we performed EDD and frontier-orbital analyses. Overall, the low-energy excitations remain dominated by LE character with an additional contribution from IntraCT, consistent with a redistribution of electron density that remains largely confined within the chromophore units (see complete dataset, EDD and main orbital transition in Table B.29). The observed threefold increase from dimer to trimer is also consistent with exciton formation and confinement within the triangular micropores, an effect that has been reported previously and shown to enhance nonlinear optical responses relative to isolated chromophores.^[198,199] Despite the reported threefold increase, the *csq* topology does not allow the efficient transfer or propagation of excitonic effects through the whole network; instead, it restricts and confines the interactions within the triangular pores. This localized nature of the coupling may help explain the comparatively weak experimental 2PA response of NU-1000 relative to the other MOFs considered in this work.

NU-901. This MOF adopts a *scu* topology with rhomboid pores of ~ 11 Å in width (see Figure 4.17) and a shortest linker center-to-center separation of 9.52 Å. In contrast to the previously analyzed NU-1000, here we observe a more regular and periodically repeated arrangement of neighboring linkers across the network. This structural regularity defines a continuous interaction pathway that is better suited to support exciton propagation along the oriented zigzag direction. In particular, the DimerB, TrimerB, and TetramerB assemblies in Figure 4.13 illustrate the zigzag pathway that can promote cooperative enhancement as the aggregate size increases, an effect that has been studied in the context of 2PA in coupled chromophore systems.^[50] As presented in Figure 4.18, the corresponding dimer already yields a measurable response of $\sigma_2 = 1.60$ GM. Upon extending the assembly along the same zigzag direction, the 2PA cross section increases to $\sigma_2 = 3.50$ GM for TrimerB (see Table B.35) and reaches $\sigma_2 = 5.72$ GM for TetramerB (see Table B.37). The growth in σ_2 with the number of monomers strongly suggests a cooperative mechanism consistent with exciton hopping (or, more generally, delocalization/transfer of excitation) along the zigzag pathway, which is absent in NU-1000, where interactions are largely confined within isolated triangular motifs. Other dimer conformations such as DimerA, DimerC, DimerD (see Table B.30-Table B.33), and also larger systems such as TrimerA and TetramerA (see Table B.34 and Table B.36 respectively), produced negligible 2PA results. We therefore expect that further extension in the zigzag direction (e.g., pentamers and larger assemblies) could lead to 2PA responses surpassing those obtained for NU-1000. However, constructing and calculating pentameric (and larger) models was not feasible here due to rapidly increasing system size and computational cost.

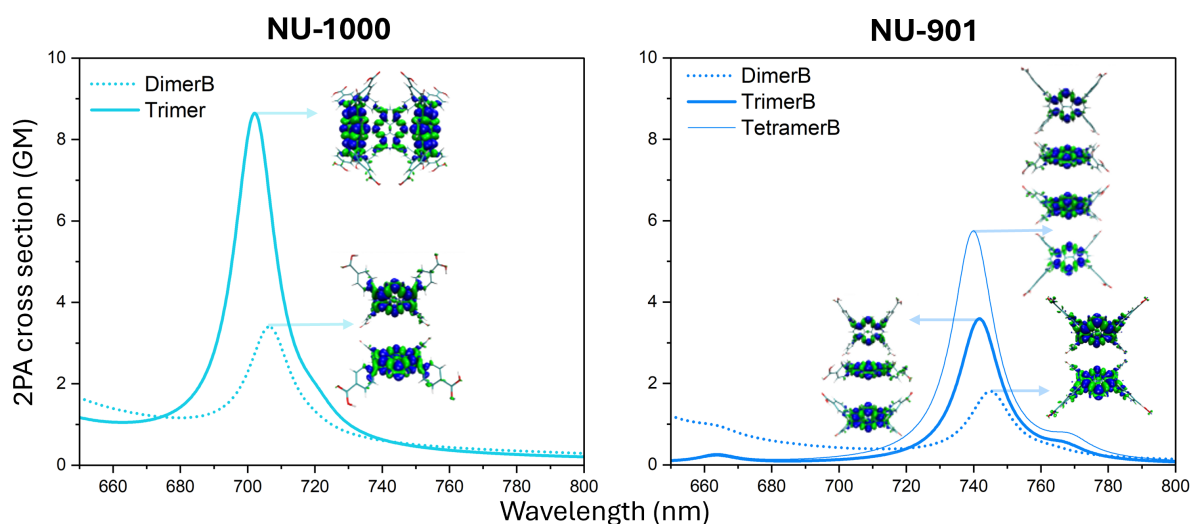


Figure 4.18. Effect of MOF packing on the 2PA response, shown as calculated 2PA spectra for assemblies extracted from the NU-1000 (left) and NU-901 (right) crystal structures. The H_4TBAPy monomer is omitted because its σ_2 is negligible over the plotted spectral range. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

SrTBAPy. It exhibits a markedly different linker arrangement compared with the previously discussed NU-series polymorphs, enabling a more parallel stacking motif with shorter center-to-center separations of ~ 6.86 Å. The framework adopts a *frz* topology (see Figure 4.17). Owing to these larger structural differences relative to NU-901/NU-1000, the near-neighbor analysis cannot be performed in an exactly analogous manner. Instead, because the Sr-based MOF shares more structural similarities with the Ba-based analog, we discuss SrTBAPy in close comparison with BaTBAPy, with emphasis on i) the nature of the metal node (SBU) and ii) the influence of intermolecular stacking distances on the computed 2PA response. In SrTBAPy, the SBU is formed by an infinite chain of alternating Sr and O atoms that connect the carboxylate groups, thereby enforcing a highly regular stacking of the pyrene cores. Notably, no lateral offset between the stacked pyrene units is observed. The evaluated closest-neighbor arrangements show negligible 2PA response, except for DimerA (see Figure 4.13) that yielded $\sigma_2 = 2.11$ GM. In contrast to NU-901, here, no cumulative enhancement is observed when increasing the assembly size. This behavior can be rationalized by the chromophore alignment, which is a nearly perfectly parallel, face-to-face arrangement that favors the formation of H-aggregates. This type of aggregate is typically associated with a hypsochromic (blue) shift of the absorption spectra relative to the monomer.^[200] Consistent with this picture, the first 2PA response of DimerA appears at 681.2 nm, whereas in the monomer at 715.6 nm (see Table B.38 and Table B.24). At the same time, the stacking distance of ~ 6.86 Å is still relatively large for strong π – π overlap, which likely limits efficient intermolecular electronic coupling and may explain why the enhancement remains modest (despite the closer geometry in comparison with NU-series). Upon decreasing the original MOF intermolecular separation by 2 Å, the 2PA σ_2 increases by approximately 1.5 GM as shown in the right panel of Figure 4.19. When a trimer system is considered, the 2PA response decreases to 0.72 GM at 683 nm, suggesting that aggregation does not enhance the response. As previously mentioned, other dimer conformations, such as DimerB, DimerC, and DimerD, produced negligible 2PA responses, and results can be found in Table B.39–Table B.41.

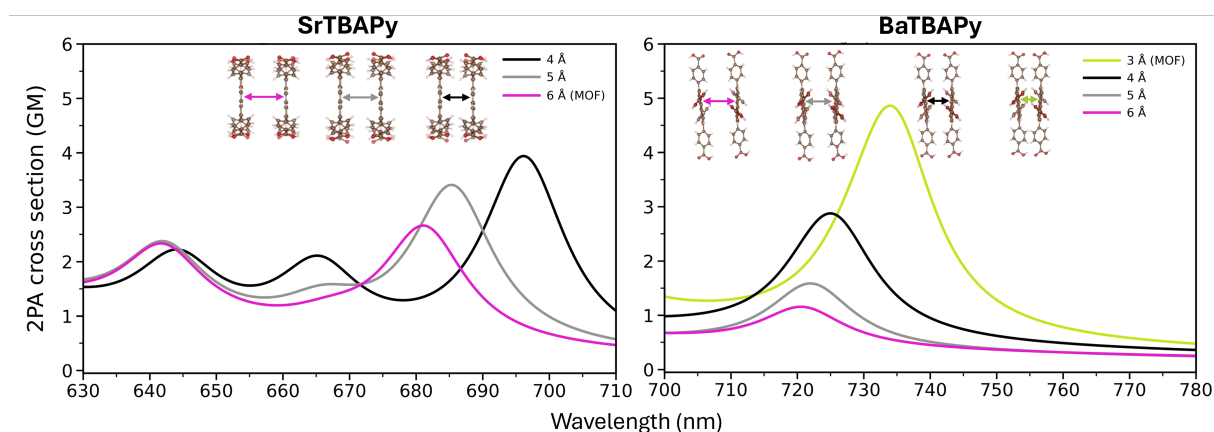


Figure 4.19. Distance screening in DimerA extracted from BaTBAPy (left) and SrTBAPy (right) MOFs. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

The effects of the SBU inclusion in the σ_2 in DimerA assembly were studied. We observed a substantial increase when one monomer is linked to one Sr-SBU, 2PA σ_2 reaches 10.8 GM. EDD analysis shows a change in the electron distribution, in the monomer-SBU, the electron density shifts towards the SBU as visualized in Figure 4.21. However, when increasing the number of elements in the assembly, the aggregation led to quenching of the 2PA responses, with the following values: dimer-SBU 2PA $\sigma_2 = 7.05$ GM and dimer-2SBUs 2PA $\sigma_2 = 5.14$ GM (see the complete dataset including 10 excitations from Table B.43 to Table B.45). Inter-fragment charge transfer (IFCT) analysis made in Multiwfn^[192] indicates that the Linker-metal CT decreases from 0.45% (monomer-SBU) to 0.21% (dimer-SBU) and finally reaches 0.14% (dimer-2SBUs) at the same time, the net CT between linkers in the dimer system is rather low (0.10%), consistent with inefficient intermolecular coupling. Notably, SBU inclusion also induces a systematic red shift of the spectra (see Figure 4.20). Overall, the low activity of SrTBAPy is attributed to weak chromophore-chromophore coupling and quenching of CT-related contributions upon coordination and aggregation with the SBUs.

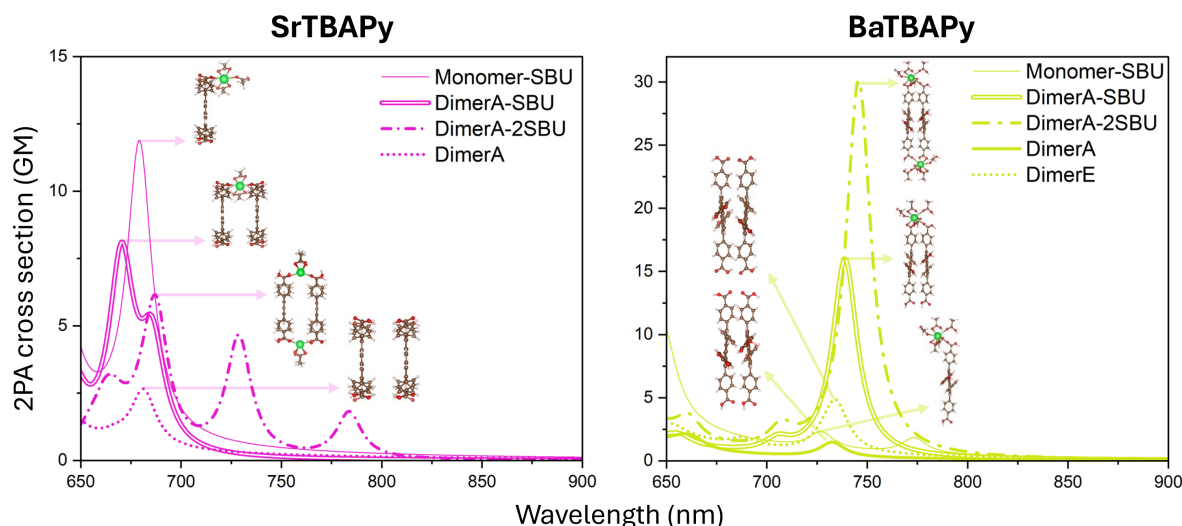


Figure 4.20. Effect of MOF packing on the 2PA response, shown as calculated 2PA spectra for assemblies extracted from the BaTBAPy (left) and SrTBAPy (right) crystal structures. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

BaTBAPy. This framework material presents the shortest center-to-center separations among the four studied systems with ~ 3.41 Å distance (see Figure 4.14). BaTBAPy forms a 3D porous network with channels accessible along the c -axis and adopts an unprecedented (4,5)-c net with transitivity [2 2] topology as reported by Krishnamoorthy *et al.*^[201] Structurally, BaTBAPy consists of infinite double strands of Ba nodes connected by O atoms growing along the c -axis. The TBAPy central part (π -cores) pack in a closely stacked arrangement, with a relative orientation of 10.17° , and a twisted configuration between them different from the completely parallel-stacked SrTBAPy structure (Figure 4.14). This particular conformation helps to enhance the 2PA properties of the material, also reporting a cumulative

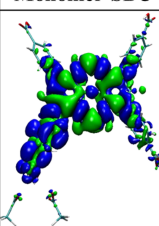
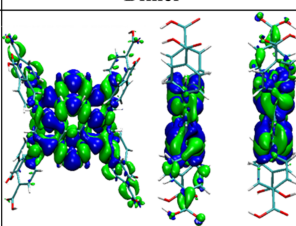
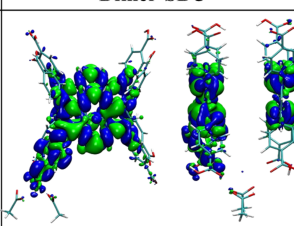
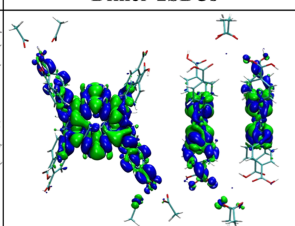
	Monomer-SBU	Dimer	Dimer-SBU	Dimer-2SBUs
EDD				
Excitation	1st	1st	2nd	4th
Cross section (Wavelength)	10.84 GM (679.2 nm)	2.109 GM (681 nm)	7.051 GM (670.3 nm)	5.145 GM (687.3 nm)
IFCT(%)	0.45	0.10	0.21	0.14

Figure 4.21. Comparison of SrTBAPy assemblies upon systematic modifications, showing the i) qualitative EDD, ii) 2PA response and iii) IFCT.

behavior similar to NU-901: the dimer yields $\sigma_2 = 3.96$ GM, increasing to 7.56 GM for the trimer (see Figure 4.20). The increase in the 2PA response upon aggregation correlates with an increase in the intermolecular CT (which is absent in the SrTBAPy case). The apparent CT reaches significantly higher values (up to 0.92% for DimerE) (see Table B.50). As observed in the distance screening analysis (see Figure 4.19) the 2PA σ_2 decreases as the intermolecular separation increases, and at 6 Å (comparable to SrTBAPy) the σ_2 is reduced by 78%. Proving in this way that the shorter distance in BaTBAPy and the twisted conformation strengthens intermolecular interactions and helps explain the observed increase in σ_2 relative to SrTBAPy. Here the increase upon aggregation is evident going from 13.8 GM for the dimer-SBU to 29.6 GM for the dimer-2SBUs (see Figure 4.20). Complete dataset is provided in the appendix in Table B.46-Table B.55. This behavior is consistent with changes in electron delocalization and enhanced CT both in dimers with and without SBUs considered. The IFCT analysis made in Multiwfn shows that in Dimer-2SBUs system the linker-metal CT is 0.18% (see Table B.56) (higher than the results observed for the same system in Sr case 0.14%). The shift in electron density upon 2PA excitation of the dimer, which is connected to two SBUs, is shown in Figure 4.22. The electron donating regions from where electron density moves upon the excitation is marked in blue, while the electron accepting region is in green. In the DimerA, the frontier orbitals involved in this transition exhibit a delocalized nature and the excitation demonstrates a mixed local exciton and CT character. In the presence of SBUs, orbital delocalization changes significantly with a higher hole localization on the linker part that is in close contact with the metal (regions in blue in Figure 4.22). We have observed that the orbital overlap between the molecules in the dimer linked to SBUs differs, demonstrating a strong impact of the SBU on communication within the dimer assembly. Importantly, we observed slight differences in the computed 2PA response depending on the crystallographic plane from which the dimer is extracted. For instance, DimerA corresponds to a parallel-stacked pair and matches the dimer systems used in the calculations, including the metal nodes (see the insets comparing dimers with and without SBU in Figure 4.20). In these configurations, the phenyl rings point in the same direction. By contrast, in DimerE the phenyl rings are oriented differently. A closer inspection shows that these two motifs originate from different

reference planes within the MOF. Both variants were therefore included in the present study, for more details see Figure B.11. To wrap everything up, we propose that the enhanced 2PA response in BaTBAPy arises from the combined contribution of i) improved stacking, which promotes intermolecular coupling between chromophores, and ii) linker-SBU coordination. Together, these factors alter the electronic structure of the assembly by increasing electron delocalization and yielding a more pronounced apparent CT character between the linker and the SBU. We therefore suggest that the observed enhancement reflects a cumulative effect in which topology-driven packing density and Ba-induced polarization jointly amplify the 2PA response in this framework.

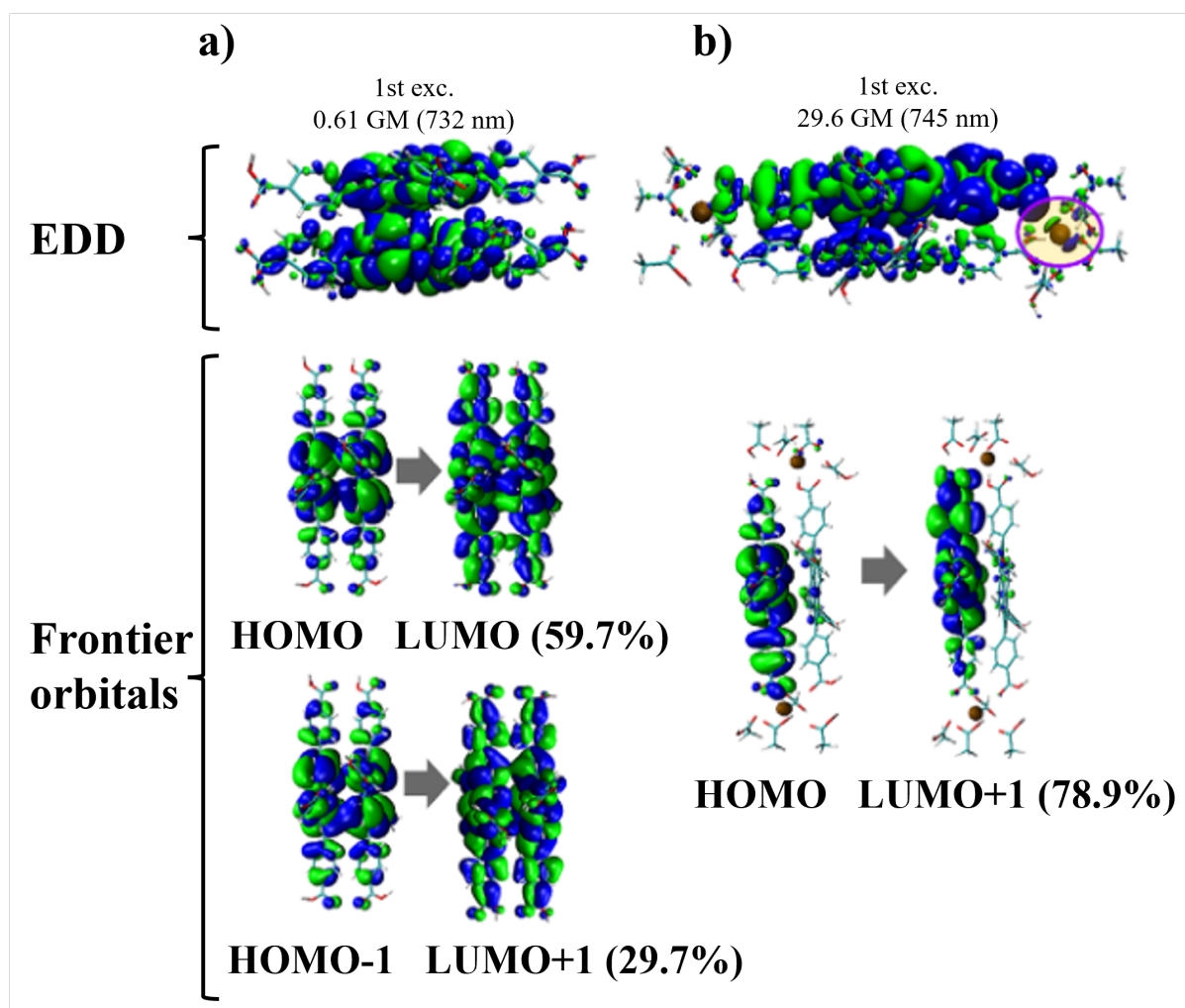


Figure 4.22. EDD between the first excitation and the ground state a) DimerA b) Dimer-2SBUs extracted from BaTBAPy. Electron-donating regions are indicated in blue, and electron-accepting regions are in green. Adapted from Deger *et al.*,^[194] *Adv. Funct. Mater.* (2025). Licensed under CC BY 4.0.

4.3. Summary

It was possible to investigate the 2PA response of a series of monomeric, dimeric, and trimeric assemblies extracted directly from experimentally obtained MOF crystal structures. To rationalize the differences in the 2PA results, we identified the dominant excitation character (e.g., LE or CT) using EDD analysis, complemented by IFCT analysis for the systems that included SBUs. Although absolute 2PA cross sections cannot be quantitatively reproduced using finite (non-periodic) fragments, the calculations capture the same topology-dependent activity trend reported experimentally^[194]: SrTBAPy < NU-1000 < NU-901 < BaTBAPy. Notably, SrTBAPy demonstrates that dense packing alone does not guarantee enhanced 2PA response: despite short intermolecular distances, the specific linker disposition leads to aggregation-induced quenching, resulting in the lowest activity among the studied frameworks. For the Zr-based polymorphs, the extended-network topology governs whether excitonic effects remain local or become cumulative across the framework. In NU-1000, exciton confinement within the triangular pores yields a local enhancement of σ_2 (notably in the trimer motif), but limits transfer through the network, restraining overall amplification. In contrast, NU-901 provides a continuous anisotropic pathway along the zigzag packing direction, enabling cooperative growth of σ_2 with assembly size and producing a higher response than NU-1000. Relative to SrTBAPy, NU-901 increases σ_2 by a factor of 8.4, highlighting the decisive role of chromophore arrangement beyond only closer intermolecular distances. BaTBAPy exhibits the highest activity because it combines short interchromophore separations (promoting stronger coupling and intermolecular CT) with a topology-dependent SBU contribution that further increases delocalization and polarization. In particular, coordination to Ba modifies the electronic structure, thereby substantially enhancing CT within the assembly. Overall, our strategy provides an effective route to probe trends in 2PA responses in periodic materials, such as MOFs, by analyzing non-periodic models derived from their crystal structures. These results reinforce the central importance of structure–property relationships as a design principle for engineering MOFs with targeted multiphoton absorption performance.

5. Conclusions

This thesis computationally explored the electronic and optical properties of various MOFs, with a particular focus on two key aspects. First, the incorporation of photoswitchable linkers (SP and MC) to investigate how the switching can modify the electronic coupling between neighboring molecules within the MOF. Second, the integration of 2PA-active chromophores (H_4TCPE and H_4TBAPy) to study how distinct aggregation orientations modify the 2PA response of different MOFs.

In the first study, SP-to-MC photoisomerization significantly enhanced electronic coupling between linkers. Structural analysis from molecular dynamics simulations reveals that the MC-based MOF with DABCO as pillar linker, adopts shorter MC-to-MC distances and more pronounced $\pi \cdots \pi$ interactions relative to the SP-based MOF. Given the strong distance dependence of electronic coupling, the MC-based MOF, where high orbital overlap is permitted, yields charge-transfer rates exceeding 530 $\times$ and 4200 $\times$ for p- and n-type conduction, respectively. In contrast, the geometry of the SP-based MOF impedes π -orbital overlap between the adjacent SPs. While for $Cu_2(MC)_2(dabco)$ and $Cu_2(SP)_2(dabco)$ MOFs, the electronic coupling difference is marked, in the case of $Cu_2(MC)_2(bipy)$ and $Cu_2(SP)_2(bipy)$ the on/off states show a small difference. Notably, for HOMO, the electronic coupling increased after 7 ns of simulation time. In this case, the orbital overlap occurs in a different orientation than for dabco pillar linker (see Figure 3.8 and Figure 3.6).

The SP and MC linker functionalized with -OH and -CHO and considering dabco as pillar linker, demonstrated comparable results with the unmodified SP and MC linkers. Still, unmodified version yielded the highest electronic coupling. It should be noted that the photoisomerization process itself was not explicitly modeled; rather, the SP- and MC-based MOFs were treated as independent systems and compared directly. Furthermore, these values represent an idealized scenario assuming complete SP-to-MC conversion; in practice, partial conversion, structural defects, and orientational disorder will likely reduce the predicted rates. Nevertheless, the design principles established here, optimized inter-linker distances, transient $\pi \cdots \pi$ contacts, and strongly coupled MC states, are expected to be transferable to other photochromic systems and framework materials.

In the second study, the 2PA response of two tetratopic linkers, H_4TCPE and H_4TBAPy , was investigated through systematic *in silico* screening. For H_4TCPE , one of the most extensively studied linkers for its 2PA properties, previous reports have demonstrated that high-density packing with short inter-chromophore separations yields the highest 2PA cross sections. Motivated by this, we investigated close-proximity dimer systems ($\Delta z \approx 4$ and 5 Å) across a range of conformations. Our results show

that near-parallel arrangements of H₄TCPE yield the highest 2PA cross sections, whereas unfavorable rotational or translational displacements significantly quench the response. Notably, conformations such as book-opening angles and plane displacements have been reported in the literature. However, parallel stacking arrangements have, to the best of our knowledge, not yet been described for H₄TCPE-based systems, representing a potential area for achieving enhanced 2PA responses in H₄TCPE-based MOFs. It should be noted that this is a qualitative study, intended to identify which conformations can enhance the 2PA response rather than to provide absolute cross-section values. Furthermore, as this study is based on a finite model system (monomers and dimers), direct comparison with experimentally synthesized MOFs (periodic system) is not straightforward; in extended frameworks, cooperative effects among chromophores may further enhance the response, leading to higher 2PA cross sections than those reported here. For H₄TBAPy, our computational results are in good agreement with experimental data. We find a topology-dependent 2PA activity following the trend: BaTBAPy > NU-901 > NU-1000 > SrTBAPy. The most densely packed structure with the shortest chromophore distances, BaTBAPy, presented the highest 2PA response. In the case of SrTBAPy, the parallel chromophore disposition quenched the 2PA response despite its highly packed topology. In both the Ba and Sr cases, not only the 2PA-active chromophore but also the metal node contributed to determining the response. For the Zr-based polymorphs, the response was mostly driven by the MOF topology. In the case of NU-901, the topology provides a continuous pathway along which σ_2 increases with the number of H₄TBAPy linkers considered in the zigzag direction. In contrast, the irregular topology of NU-1000, which combines large and small pores, confines exciton within the small triangular pores, thereby limiting the transfer of effects throughout the entire network.

Taking all results together, in this thesis we demonstrated that first, it is possible to modulate the charge transfer in MOFs through the incorporation of photoswitchable linkers (SP and MC), and secondly, we confirmed that by including 2PA-active chromophores in an ordered MOF, the 2PA response can be enhanced. This enhancement is determined not only by the nature of the organic linker (e.g., rigid or flexible), but also by the metal node and the conjugation pathway defined by the framework topology. The structure-property relationships studied computationally for both electronic and optical properties offer concrete design guidelines (prior to synthesis) for conductive and optically active MOFs.

5.1. Outlook

The central contribution of this thesis is the demonstration that the optical and electronic responses of MOFs can be rationalized and, to a useful degree, predicted before synthesis. This work identifies design principles that link molecular structure and framework arrangement to function. For example, in photo-switchable MOFs based on the SP–MC transformation, frameworks that restrict the rotational freedom of the MC form are expected to minimize fluctuations in the EC, leading to more stable and efficient

charge transfer rates. Furthermore, selecting photoswitches that undergo substantial structural rearrangement upon photoisomerization can maximize the difference between the two switching states, resulting in a higher on/off ratio, which is an important requirement for optoelectronic and electronic switching devices. For 2PA, the optimal MOF design depends strongly on the structural characteristics of the incorporated chromophore. For chromophores containing multiple rotatable units, rigid frameworks with dense packing or interpenetrated architectures can effectively suppress non-radiative structural relaxation, thereby enhancing the 2PA response. In contrast, for intrinsically rigid and planar 2PA-active linkers, framework architectures should be designed to minimize parallel π - π stacking, as this type of orientation may reduce the 2PA efficiency. The protocols here developed are modular: they can, in principle, be transferred to other photoswitches and other 2PA-active chromophores. In the short term, several concrete directions would extend this work.

The first is methodological. The approach developed here predicts the 2PA response only qualitatively, and only for molecular fragments (dimers and trimers) extracted from the periodic framework. A more quantitative description would require a method that considers hybrid periodic systems. Some codes already compute the 2PA response of periodic systems, but the many-body level of theory involved makes systems of MOF size and electron count computationally prohibitive at present. Developing, or adapting existing periodic methods toward an efficient treatment of 2PA in hybrid frameworks of this scale would move the field from qualitative to more quantitative predictions which can approximate better to experimental results. A related refinement is the inclusion of vibronic effects, which shape the intensities and band profiles of 2PA spectra and are neglected in the present work, accounting for them is a necessary step toward quantitative accuracy.

The second direction concerns the role of the metal. This work showed that the 2PA response depends not only on the linker and the relative positions of the 2PA-active units, but also on the linker-metal interaction, which can either enhance or suppress it. A systematic screening that keeps the linker type constant while varying the metal node would isolate this effect and reveal which combinations amplify the response. Such a screening should also control the conformation and packing of the linker, since these determine whether it shows AIQ or AIE behaviours that may in turn influence the 2PA response.

The third direction is to scale this exploration beyond case-by-case calculation. Machine learning models trained on combinations of metal node, organic linker, and framework topology could map this large design space and predict which combinations yield the highest 2PA cross sections and, more broadly, which pairings of photoswitchable and 2PA-active components give the most promising responsive materials. This would turn the design rules established here into a predictive screening tool.

Taken together, these directions point toward a broader goal: shifting the discovery of responsive functional materials from trial-and-error synthesis toward prediction first design. This shift carries a tangible benefit. Predicting properties before materials are made accelerates the identification of promising candidates and lowers the cost of discovery: less failed syntheses, less consumption of harmful solvents, and less waste of reagents. Such an approach contributes to a more sustainable practice of materials research.

5. Conclusions

Photoswitchable and 2PA-active MOFs are technologies that could be employed in photonics, optical limiting, sensing, bioimaging, and optoelectronics. The study of these materials is relevant to a more efficient use of energy and resources. Realizing this potential will depend on closing the methodological gap identified above, so that computational design can be trusted.

A. Appendix: Photoswitching Conductivity in Spiropyran-Based MOF

A.1. Functionalized Spiropyran and Merocyanine-Based MOFs

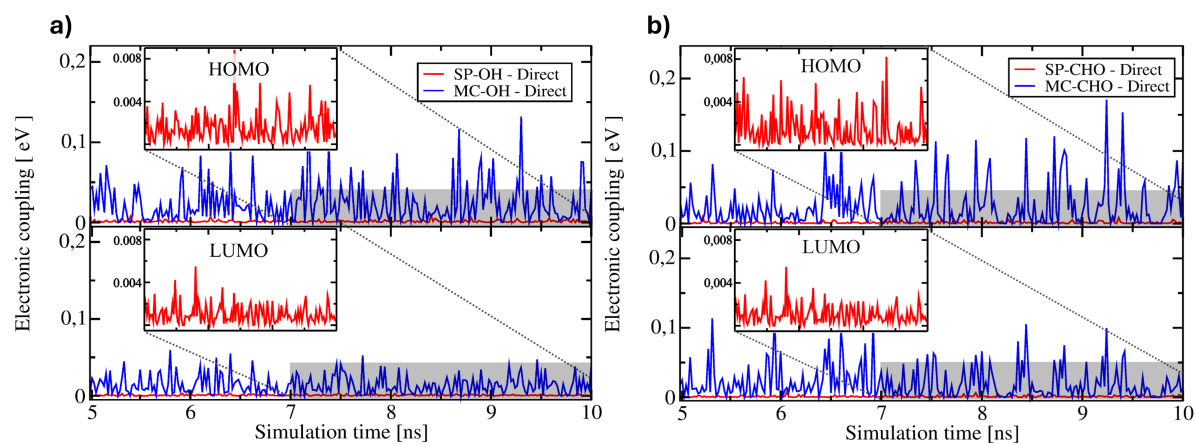


Figure A.1. Comparison of the electronic coupling between linkers in (a) $\text{Cu}_2(\text{SP-OH})_2(\text{dabco})$ and $\text{Cu}_2(\text{MC-OH})_2(\text{dabco})$ MOFs, and in (b) $\text{Cu}_2(\text{SP-CHO})_2(\text{dabco})$ and $\text{Cu}_2(\text{MC-CHO})_2(\text{dabco})$ MOFs. Reproduced from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

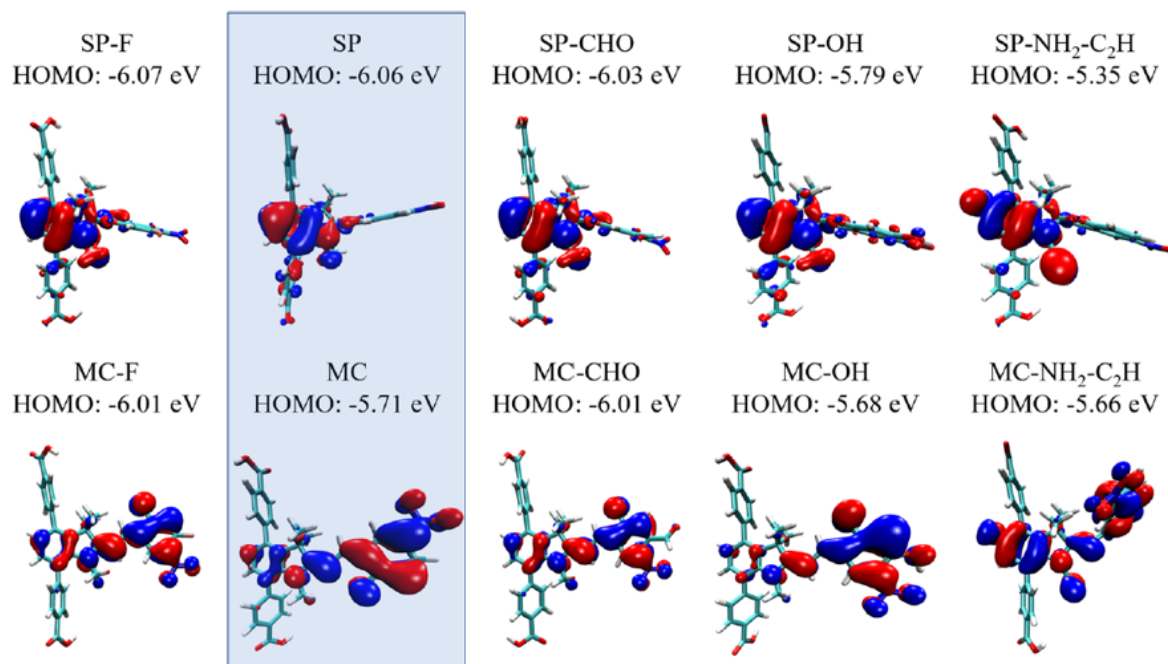


Figure A.2. Visualization of the HOMO orbitals of the investigated linkers. The corresponding orbital energies are given for each orbital. An isovalue of 0.02 a.u. was used for visualization. The unmodified SP and MC linkers are highlighted in light blue. MOFs containing SP, MC, SP-OH, MC-OH, SP-CHO, and MC-CHO as layer linkers were simulated. Reproduced from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

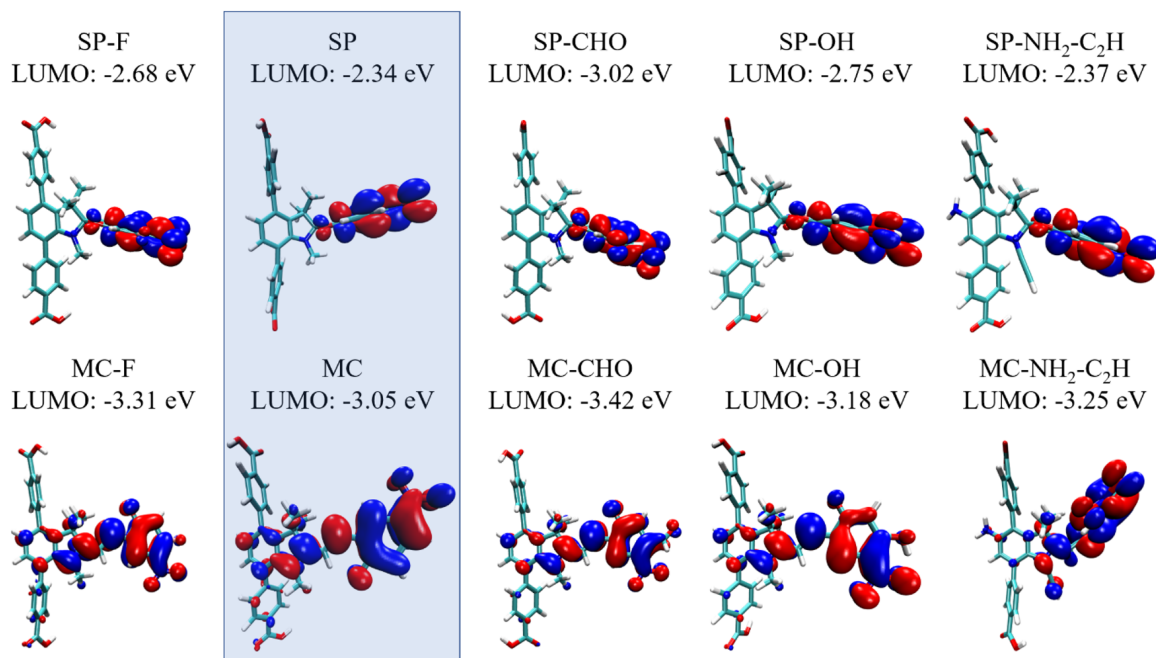


Figure A.3. Visualization of the LUMO orbitals of the investigated linkers. The corresponding orbital energies are given for each orbital. An isovalue of 0.02 a.u. was used for visualization. The unmodified SP and MC linkers are highlighted in light blue. MOFs containing SP, MC, SP-OH, MC-OH, SP-CHO, and MC-CHO as layer linkers were simulated. Reproduced from Mostaghimi *et al.*,^[110] *Commun. Chem.* **6**, 275 (2023). Licensed under CC BY 4.0.

B. Appendix: Two-Photon Absorption Structure-Property Relationship of H₄TCPE and H₄TBAPy MOF Organic Linkers

B.1. 2PA Properties in H₄TCPE: Monomer

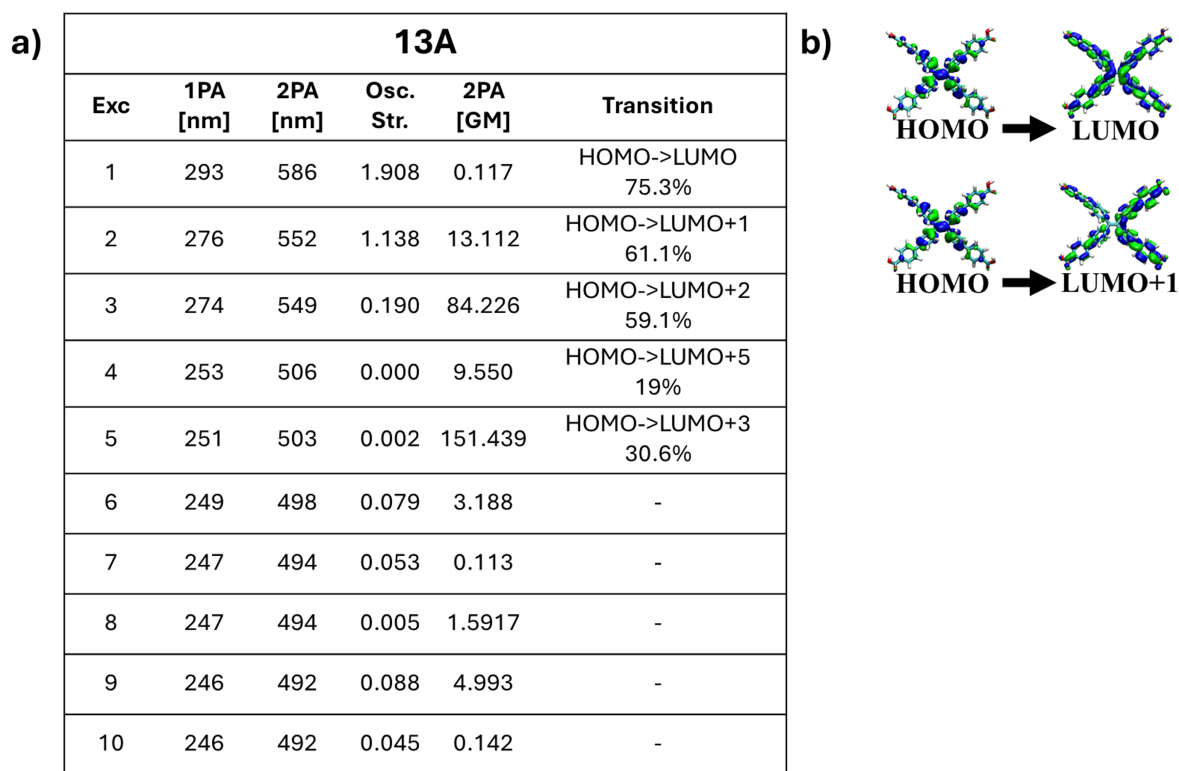


Figure B.1. TD-DFT results for $d_{C-C} = 13 \text{ \AA}$. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

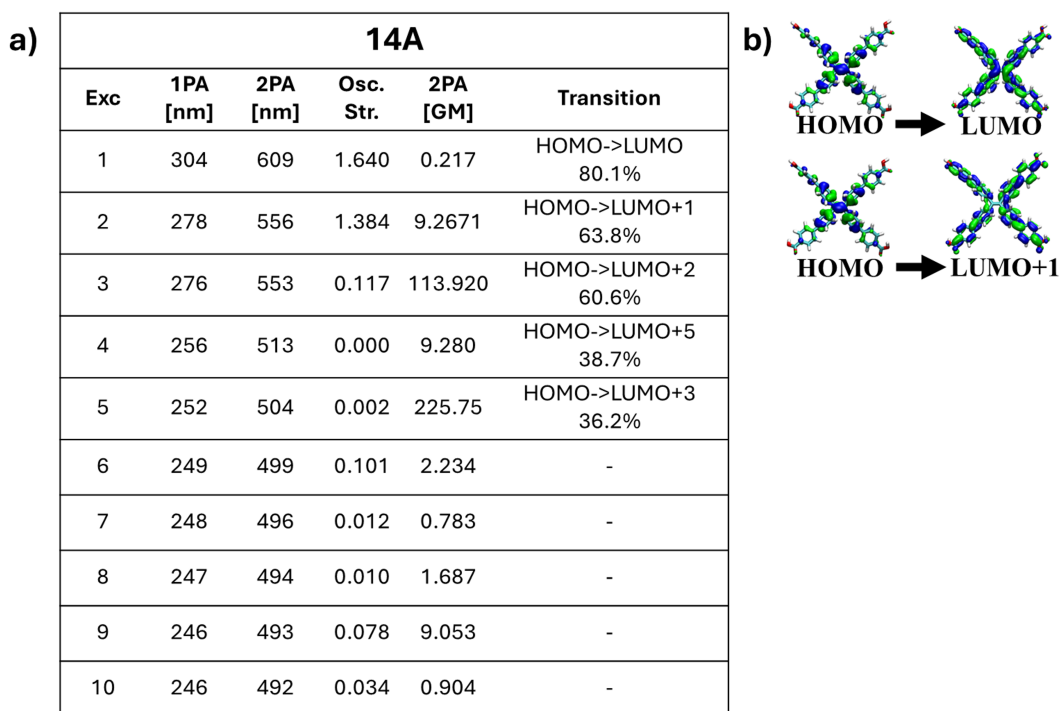


Figure B.2. TD-DFT results for $d_{C-C} = 14$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

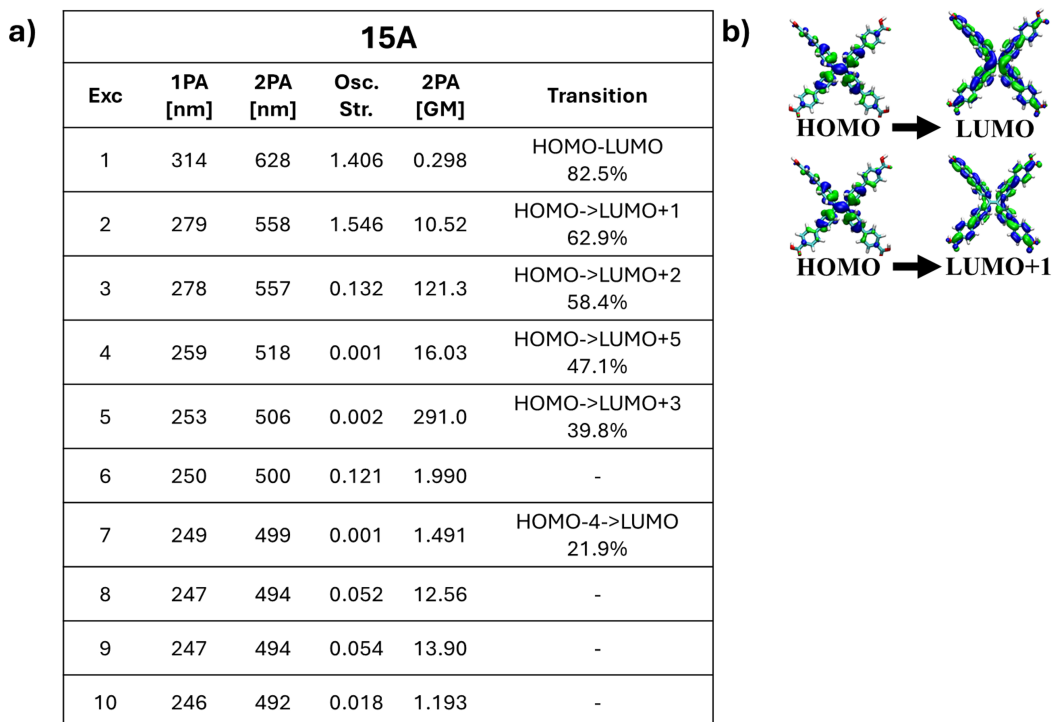


Figure B.3. TD-DFT results for $d_{C-C} = 15$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

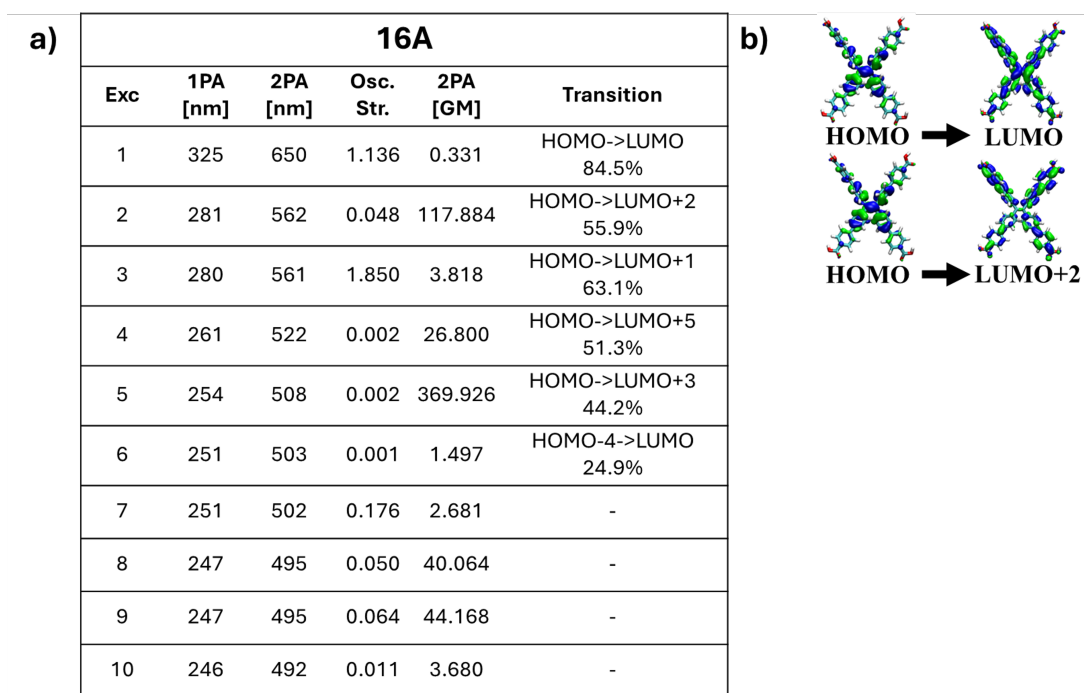


Figure B.4. TD-DFT results for $d_{C-C} = 16$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

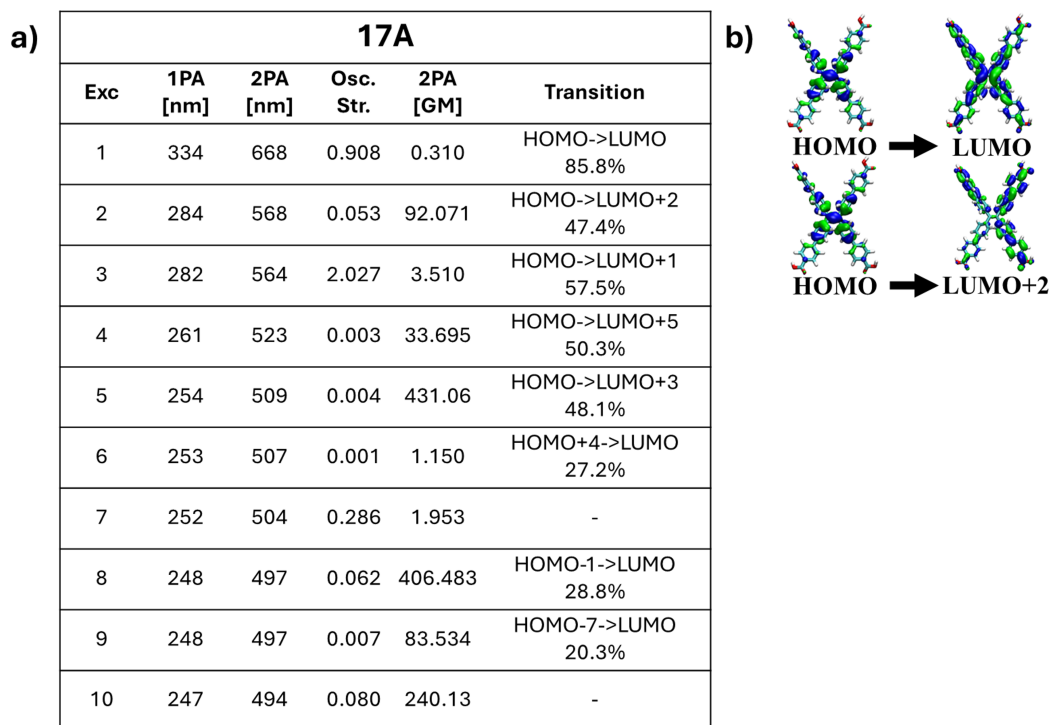


Figure B.5. TD-DFT results for $d_{C-C} = 17$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

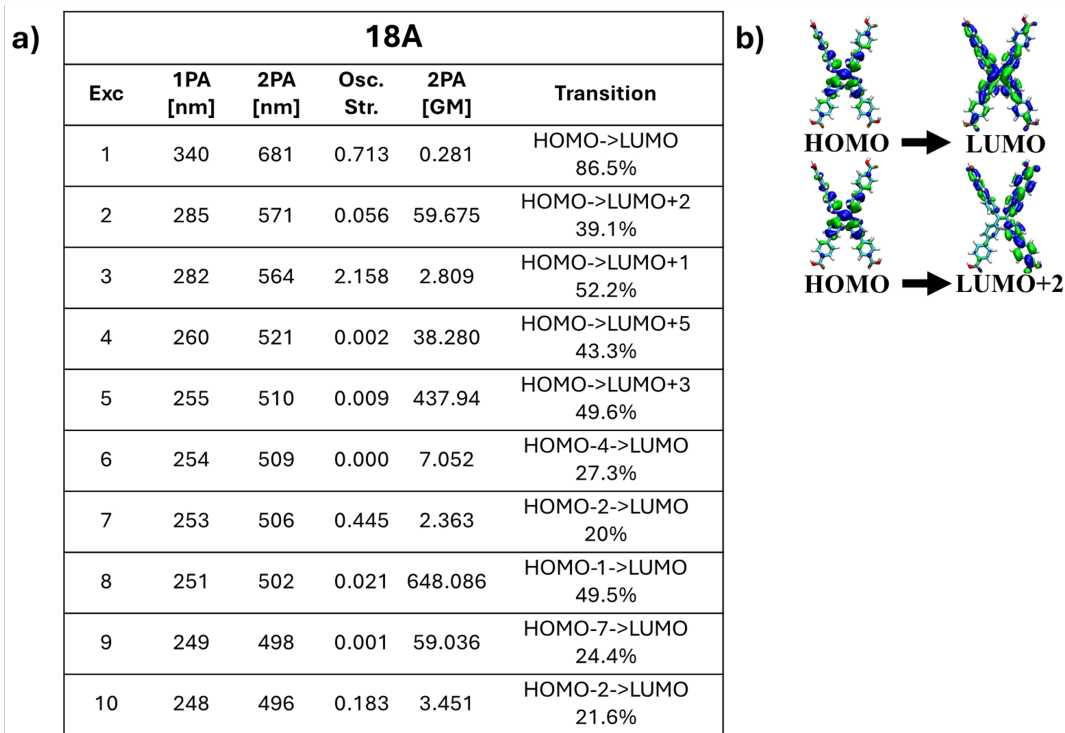


Figure B.6. TD-DFT results for $d_{C-C} = 18$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

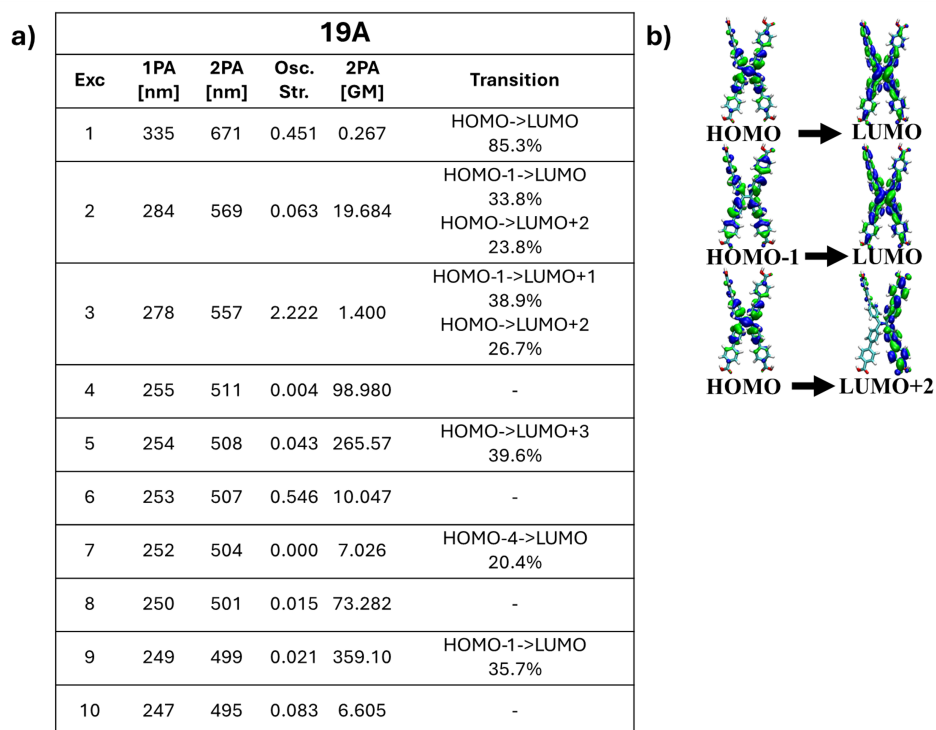


Figure B.7. TD-DFT results for $d_{C-C} = 19$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.

B.2. 2PA Properties in H₄TCPE: Dimer Systems

Table B.1. TD-DFT results for the H₄TCPE dimer in the SA(45°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

SA $\theta = 45^\circ$ (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 Å	326	653	0.683	8.288	HOMO-1->LUMO (62.5%) HOMO->LUMO+1 (11.3%)	17 Å	332	664	0.589	8.245	HOMO-1->LUMO (64.5%) HOMO->LUMO+1 (10.9%)	18 Å	335	671	0.507	7.720	HOMO-1->LUMO (66.5%) HOMO->LUMO+1 (9.2%)
2		320	640	1.508	1.685	HOMO->LUMO+1 (70.1%) HOMO-1->LUMO (10.5%)		325	651	1.181	1.360	HOMO->LUMO+1 (72.7%) HOMO-1->LUMO (10.1%)		329	658	0.880	1.038	HOMO->LUMO+1 (75.2%) HOMO-1->LUMO (8.4%)
3		283	566	0.087	57.988	HOMO->LUMO+3 (24.5%)		284	568	0.051	66.087	HOMO-1->LUMO+2 (28.7%)		284	569	0.046	61.774	HOMO-1->LUMO+2 (29.5%)
4		280	560	0.017	23.056	HOMO->LUMO+4 (16.3%)		280	561	0.048	28.901	HOMO->LUMO+3 (25.9%)		281	562	0.095	46.593	HOMO->LUMO+3 (23.5%)
5		279	558	0.943	107.983	HOMO-1->LUMO+4 (19.8%)		280	560	0.442	75.211	HOMO-1->LUMO+4 (28.9%)		280	561	0.144	21.696	HOMO-1->LUMO+4 (34.3%)
6		276	553	2.303	66.912	HOMO-1->LUMO+2 (30.6%)		277	554	3.051	35.138	HOMO->LUMO+3 (25.1%)		277	554	3.421	22.781	HOMO->LUMO+3 (26.8%)
7		260	521	0.007	35.405	HOMO->LUMO+11 (39%)		264	528	0.001	3.373	HOMO->LUMO (86.7%)		267	535	0.004	3.355	HOMO->LUMO (20.4%)
8		259	518	0.003	23.945	HOMO->LUMO+12 (45.8%)		260	520	0.016	39.522	HOMO-1->LUMO+11 (29%)		259	518	0.041	35.907	HOMO-1->LUMO+11 (29%)
9		257	514	0.000	5.614	HOMO->LUMO (84%)		259	518	0.005	27.234	HOMO->LUMO+12 (42.4%)		258	517	0.008	25.501	HOMO->LUMO+12 (31.8%)
10		255	510	0.020	59.255	HOMO->LUMO+6 (17.6%)		255	511	0.024	34.982	HOMO->LUMO+6 (14.5%)		256	512	0.027	24.844	HOMO->LUMO+6 (11.2%)

Table B.2. TD-DFT results for the H₄TCPE dimer in the SA(90°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

SA $\theta = 90^\circ$ (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	10 Å	330	660	1.222	3.056	HOMO->LUMO+1 (66.8%)	17 Å	339	679	0.979	2.376	HOMO->LUMO+1 (67%)	18 Å	345	691	0.775	1.688	HOMO->LUMO (81%)
2		320	640	1.156	1.094	HOMO-1->LUMO (69.9%)		327	654	0.926	0.951	HOMO-1->LUMO (68.4%)		329	659	0.725	0.649	HOMO-1->LUMO+1 (80.8%)
3		287	575	0.026	72.095	HOMO-1->LUMO+2 (28%)		289	579	0.023	61.259	HOMO->LUMO+3 (27.4%)		290	581	0.047	46.757	HOMO->LUMO+3 (34%)
4		282	564	0.408	90.798	HOMO-1->LUMO+2 (27.4%)		284	569	0.235	73.168	HOMO-1->LUMO+2 (27.7%)		285	570	0.027	39.625	HOMO-1->LUMO+2 (30%)
5		281	562	1.699	35.910	HOMO->LUMO+5 (42.1%)		282	565	1.635	28.773	HOMO->LUMO+5 (37.5%)		282	565	1.537	22.808	HOMO->LUMO+5 (28%)
6		278	557	1.355	41.540	HOMO-1->LUMO+4 (59.4%)		279	558	1.875	22.630	HOMO-1->LUMO+4 (54.5%)		279	558	2.339	10.088	HOMO-1->LUMO+4 (48.1%)
7		262	524	0.002	32.122	HOMO->LUMO+11 (36%)		262	525	0.005	36.027	HOMO->LUMO+11 (32.9%)		261	523	0.007	33.890	HOMO->LUMO+12 (27.9%)
8		259	519	0.012	21.406	HOMO-1->LUMO+10 (12.1%)		260	520	0.029	29.429	HOMO-1->LUMO+12 (10.8%)		258	517	0.047	37.466	HOMO-1->LUMO+13 (19.2%)
9		256	512	0.015	87.811	HOMO-1->LUMO+6 (19%)		256	513	0.034	110.28	HOMO->LUMO+7 (22.3%)		257	515	0.063	171.389	HOMO->LUMO+7 (28.2%)
10		254	509	0.014	491.95	HOMO-1->LUMO+6 (17.2%)		255	511	0.010	190.43	-		256	512	0.047	40.108	-

Table B.3. TD-DFT results for the H₄TCPE dimer in the SA(135°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

SA $\theta = 135^\circ$ (stacking 4 Å)																		
Exc	16 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		330	661	1.461	1.261	HOMO->LUMO+1 (79.6%)		339	678	1.266	0.657	HOMO->LUMO+1 (82.2%)		338	677	0.830	1.207	HOMO->LUMO (78.9%)
2		319	639	0.966	1.558	HOMO-1->LUMO (75.6%)		332	665	0.637	1.493	HOMO-1->LUMO (79.6%)		315	631	0.711	1.662	HOMO-1->LUMO+1 (75.1%)
3		286	572	0.080	110.05	HOMO->LUMO+3 (23%)		289	579	0.036	102.03	HOMO-1->LUMO+2 (39.2%)		291	583	0.302	61.758	HOMO->LUMO+2 (45.9%)
4		281	563	0.587	52.804	HOMO-1->LUMO+5 (55.4%)		284	569	0.017	27.624	HOMO->LUMO+5 (37.8%)		282	565	0.947	25.079	HOMO->LUMO+4 (52.3%)
5		279	558	0.181	85.767	HOMO-1->LUMO+2 (24.1%)		282	565	0.199	51.103	HOMO->LUMO+4 (32.3%)		277	554	0.457	39.045	HOMO-1->LUMO+5 (54.6%)
6		278	556	2.612	9.893	HOMO-1->LUMO+4 (30.1%)		281	562	3.478	2.426	HOMO-1->LUMO+3 (30.6%)		274	549	2.235	12.889	HOMO-1->LUMO+3 (47.3%)
7		263	526	0.003	23.531	HOMO->LUMO+11 (30.3%)		263	527	0.004	22.939	HOMO->LUMO+11 (31.3%)		261	523	0.006	20.125	HOMO->LUMO+11 (26.6%)
8		260	520	0.003	17.650	HOMO-1->LUMO+10 (51.9%)		261	522	0.003	27.477	HOMO-1->LUMO+10 (30.3%)		258	516	0.254	216.19	HOMO->LUMO+6 (29%)
9		255	511	0.030	205.877	HOMO->LUMO+7 (29.2%)		257	514	0.052	147.56	HOMO-1->LUMO+6 (36.1%)		256	513	0.003	38.641	HOMO-1->LUMO+12 (29.7%)
10	253	507	0.029	5.390	HOMO->LUMO+21 (15.2%)	255	511	0.016	292.11	HOMO->LUMO+7 (13%)	256	512	0.240	82.378	HOMO-7->LUMO (13.4%)			

Table B.4. TD-DFT results for the H₄TCPE dimer in the SA(180°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

SA $\theta = 180^\circ$ (stacking 4 Å)																		
Exc	16 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		323	647	1.906	2.253	HOMO-1->LUMO (76.2%)		337	675	1.891	0.695	HOMO-1->LUMO (45.4%)		340	681	1.359	2.403	HOMO-1->LUMO (69.4%)
2		319	638	0.634	0.610	HOMO->LUMO+1 (76.8%)		334	669	0.057	2.542	HOMO->LUMO+1 (52.8%)		337	675	0.205	0.324	HOMO->LUMO+1 (72.2%)
3		283	567	0.111	79.574	HOMO->LUMO+6 (28.9%)		289	578	0.015	116.37	HOMO->LUMO+2 (15.9%)		288	577	0.095	90.196	HOMO-1->LUMO+2 (40.8%)
4		279	559	0.589	67.043	HOMO-1->LUMO+3 (60.9%)		283	567	0.000	4.579	HOMO-1->LUMO+4 (15.2%)		284	568	0.010	11.860	HOMO->LUMO+5 (28.8%)
5		278	557	0.425	44.329	HOMO->LUMO+4 (48.7%)		282	564	0.026	60.061	HOMO->LUMO+5 (27.1%)		282	565	0.081	28.806	HOMO-1->LUMO+4 (34.9%)
6		276	553	2.337	24.229	HOMO-1->LUMO+2 (43.8%)		280	560	3.710	2.520	HOMO->LUMO+5 (15.7%)		280	561	3.833	11.54	HOMO->LUMO+3 (36.3%)
7		260	520	0.004	27.703	HOMO->LUMO+11 (19.2%)		262	524	0.010	56.907	HOMO->LUMO+12 (18.4%)		260	521	0.012	55.078	HOMO-1->LUMO+12 (18.1%)
8		260	520	0.005	19.935	HOMO-1->LUMO+9 (46.4%)		262	524	0.002	1.597	HOMO-1->LUMO+11 (24.5%)		260	520	0.004	26.342	HOMO->LUMO+12 (15.2%)
9		255	511	0.037	67.897	HOMO->LUMO+7 (24.2%)		256	513	0.007	11.004	-		256	512	0.010	175.20	HOMO-1->LUMO+6 (39.8%)
10	253	507	0.088	15.446	-	255	510	0.005	735.89	-	254	509	0.016	650.20	HOMO->LUMO+7 (39.8%)			

Table B.5. TD-DFT results for the H₄TCPE dimer in the LA(45°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

LA $\theta = 45^\circ$ (stacking $4 \text{ \AA}$)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 $\text{\AA}$	327	654	0.101	11.299	HOMO->LUMO+1 (50.3%) HOMO-1->LUMO (22.8%)	17 $\text{\AA}$	338	677	0.034	10.106	HOMO->LUMO+1 (47.4%) HOMO-1->LUMO (29.2%)	18 $\text{\AA}$	341	683	0.065	5.339	HOMO-1->LUMO (54.7%) HOMO->LUMO+1 (24.4%)
2		322	644	2.0025	5.521	HOMO-1->LUMO (37.4%) HOMO->LUMO+1 (30.7%)		333	667	1.676	3.981	HOMO-1->LUMO (38.3%) HOMO->LUMO+1 (36.2%)		337	675	1.273	1.040	HOMO->LUMO+1 (60.7%) HOMO-1->LUMO (22.1%)
3		289	578	0.511	109.68	HOMO-1->LUMO+2 (48.7%)		292	584	0.488	106.99	HOMO-1->LUMO+2 (47.1%)		290	581	0.354	65.568	HOMO-1->LUMO+2 (44.6%)
4		280	561	0.126	81.701	HOMO->LUMO+3 (44.1%)		287	575	0.443	21.844	HOMO->LUMO+3 (21.6%)		286	573	0.347	39.290	HOMO->LUMO+4 (32.6%)
5		278	557	1.538	13.937	HOMO->LUMO+4 (41.0%)		284	568	0.469	71.731	HOMO-1->LUMO+4 (17.4%)		284	569	0.315	26.770	HOMO-1->LUMO+3 (31%)
6		272	545	1.408	38.522	HOMO-1->LUMO+5 (47.6%)		281	562	2.572	10.631	HOMO->LUMO+5 (36.5%)		281	563	3.221	8.890	HOMO->LUMO+4 (24.9%)
7		263	527	0.002	6.451	HOMO->LUMO (73.8%)		273	546	0.000	3.441	HOMO->LUMO (80.7%)		262	525	0.002	3.058	HOMO->LUMO (81%)
8		260	521	0.004	26.964	HOMO->LUMO+12 (41.8%)		261	523	0.007	32.437	HOMO->LUMO+12 (22.8%)		261	522	0.014	57.436	HOMO-1->LUMO+10 (28.7%)
9		260	520	0.044	62.824	HOMO-1->LUMO+13 (31%)		261	523	0.007	90.552	HOMO-1->LUMO+11 (16.7%)		260	521	0.002	46.92	HOMO->LUMO+12 (25.5%)
10		255	510	0.015	59.646	-		259	518	0.060	115.71	HOMO-1->LUMO+6 (27.7%)		258	516	0.057	137.97	HOMO-1->LUMO+6 (22.1%)

Table B.6. TD-DFT results for the H₄TCPE dimer in the LA(90°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

LA $\theta = 90^\circ$ (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	18 Å	329	658	0.440	2.383	HOMO-1->LUMO (74.6%)	17 Å	341	682	0.462	2.598	HOMO->LUMO+2 (79.2%)	18 Å	346	693	0.505	1.470	HOMO->LUMO+2 (84.1%)
2		323	647	1.574	6.956	HOMO->LUMO+3 (72.6%)		334	668	1.189	5.021	HOMO-1->LUMO (73.9%)		334	668	0.838	3.811	HOMO-1->LUMO (77%)
3		285	570	1.063	53.896	HOMO->LUMO+5 (42.3%)		290	581	1.058	82.935	HOMO-1->LUMO+1 (33.4%)		288	577	0.495	62.818	HOMO-1->LUMO+3 (26.7%)
4		280	561	0.502	90.888	HOMO-1->LUMO+2 (31.5%)		287	575	0.790	61.395	HOMO->LUMO+5 (33.2%)		286	573	0.644	54.287	HOMO-1->LUMO+3 (24.8%)
5		277	555	1.420	37.572	HOMO-1->LUMO+1 (29%)		278	557	1.200	61.240	HOMO-1->LUMO+3 (34.7%)		285	570	1.948	39.908	HOMO-1->LUMO+1 (43.5%)
6		273	547	0.737	80.446	HOMO->LUMO+6 (30.2%)		276	552	0.976	84.064	HOMO->LUMO+6 (30%)		278	557	1.358	42.769	HOMO->LUMO+5 (33.3%)
7		261	523	0.015	27.602	HOMO-1->LUMO+11 (27.8%)		269	538	0.001	3.060	HOMO->LUMO (87.9%)		263	526	0.000	3.425	HOMO->LUMO (88.2%)
8		260	521	0.039	33.963	HOMO->LUMO+13 (42.6%)		263	527	0.025	30.576	HOMO->LUMO+13 (33.8%)		262	524	0.01	14.643	HOMO->LUMO+14 (39%)
9		257	515	0.000	0.5799	HOMO->LUMO (86.8%)		261	523	0.029	39.358	HOMO-1->LUMO+8 (22.8%)		259	519	0.001	41.948	HOMO-1->LUMO+11 (24.6%)
10		253	507	0.064	44.306	-		256	512	0.030	285.19	HOMO-1->LUMO+4 (29.6%)		257	514	0.012	299.1	HOMO-1->LUMO+4 (38.4%)

Table B.7. TD-DFT results for the H₄TCPE dimer in the LA(135°) geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{-}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

LA $\theta = 135^\circ$ (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	1e Å	326	653	0.360	2.639	HOMO->LUMO+1 (72.5%)	17 Å	335	671	0.417	5.893	HOMO->LUMO+1 (77%)	18 Å	341	682	0.021	11.051	HOMO->LUMO+1 (50.3%)
2		322	644	1.833	1.148	HOMO-1->LUMO (71.1%)		331	663	1.368	3.687	HOMO-1->LUMO (71.2%)		338	677	1.34	0.708	HOMO-1->LUMO (48.3%)
3		285	570	1.297	106.39	HOMO-1->LUMO+2 (56.6%)		287	575	0.184	177.02	HOMO-1->LUMO+2 (33.6%)		290	581	0.216	145.13	HOMO-1->LUMO+2 (37.5%)
4		284	568	1.389	76.973	HOMO->LUMO+3 (59%)		286	573	1.886	18.074	HOMO->LUMO+3 (42.8%)		289	578	1.626	15.374	HOMO->LUMO+3 (39.6%)
5		280	560	0.894	23.861	HOMO->LUMO+5 (47.2%)		283	567	1.989	14.826	HOMO-1->LUMO+4 (27.2%)		284	568	2.263	8.243	HOMO->LUMO+5 (34.3%)
6		278	557	0.688	26.228	HOMO-1->LUMO+4 (52.2%)		281	563	0.636	4.315	HOMO-1->LUMO+4 (25.2%)		280	561	1.002	8.752	HOMO-1->LUMO+4 (41.4%)
7		261	522	0.009	26.839	HOMO->LUMO+11 (44.2%)		261	523	0.007	47.835	HOMO->LUMO+12 (27%)		261	522	0.017	135.81	HOMO-1->LUMO+12 (24.5%)
8		260	521	0.006	21.664	HOMO-1->LUMO+8 (25.5%)		261	522	0.002	51.774	HOMO-1->LUMO+10 (34.2%)		260	521	0.012	27.671	HOMO->LUMO+13 (21.6%)
9		255	510	0.012	49.365	HOMO-1->LUMO+6 (22.1%)		257	514	0.004	96.491	HOMO-1->LUMO+6 (22.4%)		258	516	0.055	198.48	HOMO->LUMO+5 (19.5%)
10		254	508	0.012	581.34	HOMO->LUMO+7 (24.7%)		256	512	0.054	624.16	-		256	513	0.013	632.04	HOMO-1->LUMO+6 (17.1%)

Table B.8. TD-DFT results for the H₄TCPE dimer in the LA(180°) geometry ($\Delta z = 4$ Å, $d_{C-C} = 16-18$ Å), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

LA $\theta = 180^\circ$ (stacking 4 Å)																		
Exc	16 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		325	651	0.422	2.960	HOMO-1->LUMO (70%)		335	670	0.308	0.220	HOMO->LUMO+1 (72.7%)		339	679	0.009	0.401	HOMO-1->LUMO (44.6%)
2		320	641	1.750	1.811	HOMO->LUMO+1 (73.8%)		331	662	1.486	2.610	HOMO-1->LUMO (70.7%)		337	675	1.337	0.182	HOMO->LUMO+1 (43.3%)
3		284	568	1.032	183.38	HOMO-1->LUMO+2 (31.8%)		291	583	1.786	109.22	HOMO-1->LUMO+2 (50.1%)		285	571	0.084	108.51	HOMO-1->LUMO+4 (19.7%)
4		282	565	3.223	41.128	HOMO->LUMO+4 (33.4%)		286	573	0.109	42.304	HOMO->LUMO+3 (46%)		283	567	0.002	1.306	HOMO->LUMO+5 (18.2%)
5		280	561	0.155	5.643	HOMO->LUMO+5 (30.5%)		283	566	2.880	44.115	HOMO->LUMO+5 (40.2%)		283	566	4.931	3.725	HOMO-1->LUMO+2 (24.9%)
6		279	558	0.028	3.094	HOMO-1->LUMO+3 (34.8%)		280	560	0.123	6.713	HOMO-1->LUMO+4 (42.7%)		280	560	0.010	16.294	HOMO-1->LUMO+2 (23.9%)
7		261	522	0.001	43.476	HOMO-1->LUMO+9 (49%)		261	523	0.018	55.082	HOMO-1->LUMO+10 (22.6%)		260	521	0.004	59.732	HOMO-1->LUMO+10 (22.4%)
8		260	520	0.006	15.474	HOMO->LUMO+12 (37.3%)		261	523	0.008	24.253	HOMO->LUMO+11 (28.2%)		260	521	0.001	1.652	HOMO-1->LUMO+10 (21.7%)
9		256	512	0.005	24.944	HOMO->LUMO+7 (19.7%)		258	516	0.066	58.917	HOMO-1->LUMO+6 (19.8%)		255	510	0.077	0.492	-
10	255	510	0.011	517.29	HOMO-1->LUMO+6 (27.7%)	256	512	0.036	15.349	-	254	509	0.002	253.46	-			

Table B.9. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta y = +5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16$ -18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta y = +5$ Å (stacking 4 Å)															
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	340	680	0.369	1.965	HOMO->LUMO (71.9%)	350	700	0.116	2.726	HOMO-1->LUMO (51.2%)	358	717	0.117	2.526	HOMO-1->LUMO (48.1%)
2	323	646	1.513	0.233	HOMO-1->LUMO+1 (67.6%)	338	677	1.259	1.717	HOMO->LUMO+1 (45.6%)	347	694	0.966	1.474	HOMO->LUMO+1 (48.8%)
3	284	568	0.292	14.499	HOMO->LUMO+4 (25.9%)	288	576	0.282	23.256	HOMO->LUMO+2 (35.4%)	291	583	0.266	22.238	HOMO->LUMO+2 (40.2%)
4	279	558	0.819	86.663	HOMO-1->LUMO+2 (43.7%)	283	567	0.109	71.363	HOMO-1->LUMO+2 (17%)	288	576	0.067	43.904	HOMO-1->LUMO+3 (22%)
5	276	553	0.429	5.788	HOMO->LUMO+3 (48.6%)	279	559	0.920	1.938	HOMO-1->LUMO+3 (29%)	282	564	0.405	3.245	HOMO-1->LUMO+3 (18.4%)
6	272	544	1.664	37.995	HOMO-1->LUMO+5 (32.2%)	276	553	0.087	4.029	HOMO->LUMO (49.7%)	280	560	0.122	3.229	HOMO->LUMO (38.5%)
7	269	538	0.049	3.506	HOMO-1->LUMO (70.8%)	274	549	1.365	10.051	HOMO->LUMO+5 (24.2%)	278	557	0.481	3.341	HOMO-1->LUMO+1 (45.6%)
8	266	532	0.005	17.907	HOMO->LUMO+10 (35%)	273	546	0.821	6.925	HOMO-1->LUMO+1 (45.9%)	277	555	2.466	7.981	HOMO->LUMO+5 (22.2%)
9	262	524	0.061	15.162	HOMO-1->LUMO+11 (21.5%)	267	534	0.015	41.074	-	267	535	0.013	27.465	-
10	261	523	0.003	5.430	HOMO->LUMO+1 (59.8%)	265	531	0.027	1.091	-	266	533	0.024	5.331	-
$\Delta y = +5$ Å (stacking 5 Å)															
1	332	664	0.360	2.136	HOMO-1->LUMO (68.3%)	347	694	0.500	0.994	HOMO->LUMO (81.5%)	355	710	0.423	0.919	HOMO->LUMO (84%)
2	319	638	1.588	1.573	HOMO->LUMO+1 (59.4%)	322	645	1.068	0.872	HOMO-1->LUMO+1 (72.8%)	326	652	0.798	0.520	HOMO-1->LUMO+1 (75%)
3	282	565	0.127	12.206	HOMO->LUMO+2 (31.6%)	291	582	0.511	25.875	HOMO->LUMO+4 (37%)	291	583	0.373	21.447	HOMO-2->LUMO (27%)
4	279	559	0.850	89.390	HOMO->LUMO+2 (20.8%)	282	564	0.420	25.054	HOMO->LUMO+3 (37.7%)	283	566	0.538	8.307	HOMO->LUMO+3 (35.8%)
5	276	553	0.458	3.128	HOMO-1->LUMO+3 (25.8%)	279	558	1.174	42.758	HOMO-1->LUMO+2 (35.9%)	278	557	0.262	46.638	HOMO-1->LUMO+2 (22.1%)
6	273	547	2.045	53.489	HOMO->LUMO+5 (36.5%)	275	550	1.551	34.385	HOMO-1->LUMO+5 (42.5%)	276	553	2.672	8.630	HOMO->LUMO+5 (26.1%)
7	267	535	0.007	2.821	HOMO->LUMO (67.1%)	268	537	0.004	4.814	HOMO-1->LUMO (69.6%)	270	540	0.002	1.256	HOMO-1->LUMO (84.5%)
8	264	529	0.011	20.821	HOMO-1->LUMO+10 (18.6%)	266	533	0.008	13.339	HOMO->LUMO+8 (19.7%)	266	532	0.008	6.027	HOMO->LUMO+11 (22.9%)
9	260	520	0.008	16.926	HOMO->LUMO+12 (36.7%)	262	524	0.027	40.002	HOMO->LUMO+1 (75%)	263	527	0.057	95.314	HOMO->LUMO+1 (67.5%)
10	258	516	0.002	3.548	HOMO-1->LUMO+1 (74%)	259	519	0.005	48.174	HOMO-1->LUMO+12 (35.7%)	260	520	0.018	166.97	-

Table B.10. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta y = -5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16$ -18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta y = -5 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 $\text{\AA}$	335	671	0.232	8.395	HOMO-1->LUMO (64.5%) HOMO->LUMO+1 (13.7%)	17 $\text{\AA}$	346	692	0.176	6.033	HOMO->LUMO (64%) HOMO-1->LUMO+1 (14.7%)	18 $\text{\AA}$	362	725	0.138	1.087	HOMO->LUMO (58%) HOMO->LUMO+1 (15%)
2		323	646	1.644	1.023	HOMO->LUMO+1 (58.6%) HOMO-1->LUMO (15.3%)		333	667	1.228	1.131	HOMO-1->LUMO+1 (53.7%) HOMO-1->LUMO (16.8%)		350	701	0.955	0.115	HOMO-1->LUMO+1 (55.6%) HOMO-1->LUMO (17.7%)
3		281	563	0.140	18.899	-		286	573	0.336	40.136	HOMO->LUMO+2 (41%)		294	588	0.263	24.829	HOMO->LUMO+2 (41.3%)
4		277	555	0.626	97.070	HOMO-1->LUMO+4 (20.7%)		281	563	0.065	35.709	HOMO-1->LUMO+3 (46.2%)		287	575	0.190	35.372	HOMO-1->LUMO+3 (28.4%)
5		276	552	0.102	4.815	HOMO->LUMO+5 (21.9%)		277	555	0.018	19.952	HOMO->LUMO+5 (20.5%)		283	566	0.304	1.544	HOMO-1->LUMO+4 (28.5%)
6		275	550	0.012	2.679	HOMO->LUMO (75.2%)		277	554	0.271	6.914	HOMO-1->LUMO (65.5%)		278	557	2.379	2.788	HOMO->LUMO+5 (26.3%)
7		272	545	2.440	29.342	HOMO->LUMO+5 (31.7%)		274	549	2.965	3.560	HOMO->LUMO+5 (17.6%)		277	554	0.506	3.339	HOMO-1->LUMO (59.7%)
8		265	531	0.011	22.006	-		268	536	0.024	16.652	HOMO->LUMO+11 (23.4%)		273	546	0.140	5.402	HOMO->LUMO+1 (67.8%)
9		262	524	0.037	11.438	HOMO->LUMO+12 (34.9%)		263	527	0.003	3.325	HOMO->LUMO+1 (71.1%)		266	533	0.025	6.270	HOMO->LUMO+11 (22.4%)
10		257	515	0.009	8.573	HOMO-1->LUMO+1 (81.2%)		262	525	0.023	19.030	HOMO-1->LUMO+12 (21.2%)		265	530	0.011	14.162	HOMO-1->LUMO+12 (18.3%)
$\Delta y = -5 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
1	16 $\text{\AA}$	334	668	0.079	10.019	HOMO-1->LUMO (54%) HOMO->LUMO+1 (22.8%)	17 $\text{\AA}$	339	678	0.127	10.308	HOMO-1->LUMO (59.4%) HOMO->LUMO+1 (17.3%)	18 $\text{\AA}$	339	679	0.215	9.238	HOMO-1->LUMO (67.1%) HOMO->LUMO+1 (9.8%)
2		324	649	1.874	3.109	HOMO->LUMO+1 (51.7%) HOMO-1->LUMO (24.4%)		328	657	1.444	1.946	HOMO->LUMO+1 (57.3%) HOMO-1->LUMO (18.5%)		328	656	1.064	0.185	HOMO->LUMO+1 (67.7%) HOMO-1->LUMO (9.8%)
3		286	573	0.251	18.104	HOMO->LUMO+4 (26%)		286	572	0.096	24.935	HOMO-1->LUMO+2 (25.4%)		287	575	0.411	38.782	HOMO-1->LUMO+3 (26.9%)
4		281	563	1.047	84.958	HOMO-1->LUMO+2 (25.9%)		283	567	0.137	6.789	HOMO->LUMO (75.3%)		285	570	0.602	22.151	HOMO-1->LUMO+2 (31.5%)
5		280	561	0.051	6.048	HOMO->LUMO (79.4%)		281	563	0.952	65.323	-		278	557	0.144	36.414	HOMO->LUMO+5 (31.3%)
6		277	555	0.109	11.301	HOMO->LUMO+5 (18.6%)		278	557	0.019	17.384	HOMO->LUMO+5 (21.8%)		277	554	0.975	5.600	HOMO->LUMO (53.4%)
7		274	548	2.003	52.660	HOMO->LUMO+5 (23.7%)		275	550	2.548	22.358	-		275	550	1.803	1.485	HOMO->LUMO (28.4%)
8		265	531	0.025	19.959	HOMO-1->LUMO+10 (19.7%)		266	532	0.040	21.712	HOMO-1->LUMO+10 (19.7%)		264	528	0.016	31.923	-
9		263	526	0.009	10.414	HOMO->LUMO+13 (35.6%)		262	525	0.010	13.576	HOMO->LUMO+13 (36.8%)		260	520	0.044	14.164	HOMO->LUMO+12 (28.8%)
10		257	515	0.047	35.961	HOMO-1->LUMO+6 (18.1%)		258	516	0.079	79.726	HOMO-1->LUMO+6 (18.2%)		259	518	0.084	119.54	HOMO-1->LUMO+6 (21.9%)

Table B.11. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta y = +10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16$ -18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta y = +10 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc	16 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		336	672	0.264	4.097	HOMO->LUMO (53.3%)		342	684	0.069	1.918	HOMO-1->LUMO+1 (36.3%)		348	696	0.062	2.330	HOMO->LUMO+1 (40.8%)
2		326	653	1.830	0.316	HOMO-1->LUMO+1 (45.9%)		334	668	1.508	0.406	HOMO-1->LUMO (37.1%)		340	680	1.15745	0.205	HOMO-1->LUMO (42.6%)
3		287	574	0.758	56.149	HOMO->LUMO+3 (42.4%)		287	574	0.182	88.297	HOMO->LUMO+3 (25.3%)		289	578	0.16257	62.277	HOMO->LUMO+4 (32.4%)
4		282	565	0.906	107.91	HOMO-1->LUMO+4 (17.7%)		284	569	0.052	61.809	HOMO-1->LUMO+2 (17.3%)		285	570	0.05513	45.173	HOMO-1->LUMO+3 (24.1%)
5		282	564	0.325	16.193	HOMO->LUMO+4 (28.1%)		284	568	1.836	12.809	-		284	569	1.5606	17.664	-
6		280	561	1.654	23.914	HOMO-1->LUMO+5 (37.4%)		281	562	1.853	14.409	HOMO-1->LUMO+3 (26.8%)		281	562	2.30681	6.6877	HOMO-1->LUMO+2 (27.9%)
7		266	532	0.008	13.195	HOMO->LUMO+8 (31.7%)		265	530	0.016	17.318	-		269	539	0.04058	5.438	HOMO->LUMO (54.6%)
8		263	526	0.011	21.215	HOMO-1->LUMO+11 (36%)		264	528	0.002	15.361	HOMO->LUMO+12 (29.1%)		265	531	0.011	30.988	HOMO-1->LUMO+10 (21%)
9		260	521	0.014	7.458	HOMO-1->LUMO (54.6%)		263	527	0.002	23.795	HOMO->LUMO (30.6%)		264	528	0.00143	46.639	HOMO->LUMO+13 (25.7%)
10	257	515	0.031	233.85	HOMO->LUMO+1 (26.4%)	258	517	0.000	111.96	HOMO-1->LUMO+1 (30.2%)	260	520	0.00178	70.226	HOMO-1->LUMO+1 (46.2%)			
$\Delta y = +10 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
	16 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		327	655	0.024	0.901	HOMO->LUMO+1 (39.6%)		336	672	0.048	1.309	HOMO-1->LUMO (48.6%)		346	692	0.410	1.872	HOMO->LUMO (81.8%)
2		321	643	2.026	0.767	HOMO-1->LUMO (38.9%)		329	659	1.603	0.770	HOMO->LUMO+1 (48.9%)		329	658	0.886	0.174	HOMO-1->LUMO+1 (80.3%)
3		283	566	0.785	57.430	HOMO->LUMO+3 (30.8%)		285	571	0.118	38.630	HOMO-1->LUMO+2 (39.7%)		288	576	0.147	55.022	HOMO->LUMO+3 (34%)
4		281	563	0.422	97.638	HOMO-1->LUMO+2 (52.1%)		285	570	0.889	105.92	HOMO->LUMO+3 (33.7%)		284	568	1.729	19.636	HOMO->LUMO+2 (43.7%)
5		280	561	1.746	37.024	HOMO->LUMO+5 (32.2%)		281	563	2.351	28.494	HOMO-1->LUMO+4 (19.8%)		280	561	0.242	49.110	HOMO-1->LUMO+5 (45.2%)
6		278	557	0.787	25.173	HOMO-1->LUMO+4 (20.4%)		281	562	0.684	17.261	HOMO-1->LUMO+5 (36.2%)		279	558	2.147	7.660	HOMO-1->LUMO+4 (55.5%)
7		261	522	0.003	16.829	HOMO-1->LUMO+9 (34.9%)		262	525	0.004	27.969	HOMO-1->LUMO+10 (28.2%)		264	528	0.004	26.32	HOMO->LUMO+10 (40.7%)
8		261	522	0.003	26.688	HOMO->LUMO+11 (37.6%)		261	523	0.004	28.044	HOMO->LUMO+11 (30.6%)		259	518	0.001	31.865	HOMO-1->LUMO+11 (32.9%)
9		254	509	0.024	396.91	HOMO->LUMO+7 (34.2%)		256	512	0.004	703.13	-		257	515	0.013	3.863	HOMO-1->LUMO (64.8%)
10	253	507	0.051	232.59	HOMO-1->LUMO+6 (29.5%)	255	511	0.105	2.959	-	257	514	0.051	284.77	-			

Table B.12. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta y = -10 \text{ \AA}$, comparing stacking distances of 4 and 5 $\text{\AA}$ for $d_{C-C} = 16\text{-}18 \text{ \AA}$: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta y = -10 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 $\text{\AA}$	332	664	0.083	0.705	HOMO-1->LUMO (44.4%)	17 $\text{\AA}$	342	684	0.060	1.365	HOMO->LUMO+1 (36.6%)	18 $\text{\AA}$	342	684	0.108	2.146	HOMO->LUMO+1 (59.7%)
2		324	648	1.946	0.384	HOMO->LUMO+1 (32.2%)		334	668	1.498	0.169	HOMO-1->LUMO (37.9%)		334	669	1.103	0.390	HOMO-1->LUMO+2 (27.2%)
3		283	567	0.466	184.24 2	HOMO->LUMO+5 (22.8%)		287	574	0.157	94.082	HOMO->LUMO+4 (18.3%)		287	575	0.243	86.584	HOMO->LUMO+3 (30.8%)
4		282	565	0.074	7.091	HOMO-1->LUMO+2 (20.8%)		284	569	0.012	64.913	HOMO-1->LUMO+3 (20.6%)		285	570	0.341	41.691	HOMO->LUMO+3 (23.9%)
5		282	564	2.184	14.460	HOMO->LUMO+3 (46.7%)		283	567	1.709	9.230	HOMO->LUMO+2 (19.4%)		282	565	1.597	13.190	HOMO-1->LUMO+2 (25.3%)
6		280	560	0.939	20.730	HOMO-1->LUMO+4 (48.5%)		281	563	2.063	6.353	HOMO-1->LUMO+2 (25.2%)		280	561	1.943	5.841	HOMO->LUMO+5 (30.1%)
7		263	526	0.005	33.665	-		264	529	0.017	23.921	HOMO-1->LUMO+10 (21.5%)		266	533	0.069	4.747	HOMO->LUMO (59.1%)
8		262	525	0.006	8.565	-		264	528	0.003	11.851	HOMO->LUMO+6 (24.9%)		262	525	0.014	65.565	HOMO-1->LUMO+12 (28.7%)
9		257	514	0.094	37.160	-		263	526	0.001	23.866	HOMO->LUMO (38%)		261	522	0.007	33.796	HOMO->LUMO+13 (37.1%)
10		256	512	0.005	635.18	-		258	516	0.001	135.17	HOMO-1->LUMO+1 (28%)		258	516	0.075	369.37	HOMO-1->LUMO+6 (24.2%)
$\Delta y = -10 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
1	16 $\text{\AA}$	324	649	0.011	0.777	HOMO-1->LUMO (38.2%)	17 $\text{\AA}$	332	664	0.179	0.678	HOMO-1->LUMO (60.6%)	18 $\text{\AA}$	339	678	0.229	1.111	HOMO-1->LUMO (69.3%)
2		318	637	2.055	0.519	HOMO->LUMO+1 (38.7%)		324	649	1.462	0.751	HOMO->LUMO+1 (61.2%)		330	660	1.057	0.383	HOMO->LUMO+1 (70.1%)
3		282	564	1.047	111.01	HOMO->LUMO+4 (31.3%)		283	567	0.182	88.315	HOMO-1->LUMO+3 (40.5%)		286	572	0.017	75.498	HOMO-1->LUMO+3 (50.7%)
4		282	564	0.277	38.327	HOMO-1->LUMO+2 (25.4%)		282	565	0.470	71.916	HOMO->LUMO+4 (39.5%)		283	567	0.009	51.036	HOMO->LUMO+4 (36.4%)
5		279	559	2.313	76.065	HOMO-1->LUMO+3 (24.9%)		281	562	2.432	12.477	HOMO-1->LUMO+2 (42.7%)		283	566	1.936	15.272	HOMO-1->LUMO+2 (44.8%)
6		278	557	0.093	1.665	HOMO->LUMO+5 (36.5%)		278	557	0.941	20.925	HOMO->LUMO+5 (46%)		281	563	2.265	9.303	HOMO->LUMO+5 (32.7%)
7		260	521	0.001	22.162	HOMO-1->LUMO+6 (36.4%)		261	523	0.001	31.316	HOMO-1->LUMO+11 (27.2%)		262	525	0.024	4.351	HOMO->LUMO (54%)
8		260	520	0.013	22.219	HOMO->LUMO+7 (28.7%)		260	520	0.014	27.301	HOMO->LUMO+13 (36.6%)		261	523	0.003	54.353	HOMO-1->LUMO+12 (24.3%)
9		254	509	0.051	304.01	HOMO-1->LUMO+6 (36.3%)		256	513	0.011	138.52	HOMO->LUMO (45.7%)		260	520	0.000	33.698	HOMO->LUMO+13 (35%)
10		254	509	0.018	381.92	HOMO->LUMO+7 (34.4%)		255	511	0.070	455.56	HOMO-1->LUMO+6 (35.9%)		257	515	0.078	538.66	HOMO-1->LUMO+6 (33.5%)

Table B.13. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta x = +5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta x = +5 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc	16 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		341	683	0.459	0.885	HOMO->LUMO (65.1%)		344	689	0.015	1.057	HOMO-1->LUMO (49%)		351	702	0.041	0.102	HOMO-1->LUMO (52.4%)
2		332	665	1.439	1.115	HOMO-3->LUMO+1 (67.8%)		341	683	1.507	0.592	HOMO->LUMO+1 (28.1%)		349	698	1.148	0.770	HOMO->LUMO (28.9%)
3		288	577	0.089	32.053	HOMO-1->LUMO+3 (39.3%)		290	580	0.007	42.731	HOMO->LUMO+2 (24.8%)		290	581	0.087	0.349	HOMO-1->LUMO+3 (20.6%)
4		286	573	0.025	14.582	HOMO->LUMO+2 (28.3%)		289	578	0.000	0.404	-		289	579	0.024	38.187	HOMO->LUMO+2 (27.7%)
5		283	566	0.175	118.93	HOMO->LUMO+5 (35.1%)		286	572	0.030	77.644	HOMO->LUMO+5 (25.7%)		288	576	0.019	33.957	HOMO->LUMO+5 (21.4%)
6		280	561	2.842	14.488	HOMO-1->LUMO+4 (28.7%)		282	564	3.430	9.497	HOMO->LUMO+3 (19.1%)		282	564	3.460	11.476	HOMO-1->LUMO+2 (23.4%)
7		268	537	0.011	1.100	HOMO-1->LUMO (43.7%)		270	541	0.017	2.057	HOMO->LUMO (64.5%)		272	545	0.023	2.493	HOMO->LUMO (58.5%)
8		268	536	0.013	1.120	HOMO->LUMO+1 (47%)		268	536	0.007	1.927	HOMO-1->LUMO+1 (62.1%)		270	541	0.021	3.664	HOMO-1->LUMO+1 (53.7%)
9		266	533	0.005	24.010	HOMO->LUMO+8 (27.3%)		265	531	0.005	32.773	HOMO-1->LUMO+8 (18.1%)		265	530	0.003	33.278	-
10		264	529	0.003	12.620	HOMO-1->LUMO+8 (18.3%)		265	530	0.003	10.447	-		264	529	0.002	13.479	-
$\Delta x = +5 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
Exc	16 $\text{\AA}$	335	671	0.022	0.422	HOMO->LUMO+1 (38.5%)	17 $\text{\AA}$	345	691	0.033	0.205	HOMO->LUMO+1 (45.2%)	18 $\text{\AA}$	351	703	0.054	0.084	HOMO->LUMO+1 (48.7%)
2		331	663	1.896	1.210	HOMO-1->LUMO+1 (31.9%)		343	686	1.517	1.200	HOMO-1->LUMO+1 (30.7%)		350	700	1.181	1.156	HOMO-1->LUMO+1 (31.8%)
3		286	573	0.009	38.444	HOMO-1->LUMO+2 (21.6%)		290	580	0.016	47.883	HOMO-1->LUMO+2 (20.4%)		291	582	0.019	38.177	HOMO->LUMO+2 (19%)
4		285	570	0.175	0.881	HOMO->LUMO+5 (23.5%)		288	576	0.105	0.946	HOMO->LUMO+5 (25.4%)		289	579	0.009	3.837	HOMO->LUMO+5 (27.2%)
5		281	563	0.166	137.52	HOMO-1->LUMO+4 (19.7%)		284	569	0.042	91.948	HOMO->LUMO+4 (18.2%)		286	572	0.019	48.609	HOMO->LUMO+4 (27.1%)
6		280	560	2.876	16.434	HOMO->LUMO+3 (32%)		281	563	3.345	13.673	HOMO->LUMO+3 (26.7%)		282	565	3.628	12.841	HOMO->LUMO+3 (23.9%)
7		265	531	0.008	7.177	HOMO->LUMO (17.5%)		270	541	0.018	3.273	HOMO->LUMO (46.1%)		272	545	0.023	3.886	HOMO->LUMO (49.2%)
8		264	529	0.005	27.878	-		268	537	0.009	2.119	HOMO-1->LUMO+1 (52.2%)		271	542	0.013	3.586	HOMO-1->LUMO+1 (48%)
9		263	526	0.002	6.148	HOMO->LUMO (31%)		265	531	0.011	41.634	HOMO-1->LUMO+8 (23.5%)		265	531	0.007	41.721	HOMO->LUMO+9 (21.1%)
10		262	525	0.011	7.475	HOMO-1->LUMO (30.6%)		265	530	0.001	9.878	HOMO-1->LUMO+8 (19.1%)		264	529	0.000	12.962	HOMO-1->LUMO+9 (24.2%)

Table B.14. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta x = -5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta x = -5 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc	16 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		343	686	0.508	1.419	HOMO-1->LUMO (76.1%)		352	704	0.474	0.699	HOMO-1->LUMO (46.8%)		357	715	0.432	0.129	HOMO-1->LUMO (52.6%)
2		333	667	1.346	1.476	HOMO->LUMO+1 (72.4%)		343	687	1.035	1.546	HOMO->LUMO+1 (40.2%)		350	700	0.754	0.639	HOMO->LUMO+1 (47.9%)
3		288	577	0.061	36.964	HOMO-1->LUMO+2 (45.4%)		291	583	0.021	66.894	HOMO->LUMO+2 (35.1%)		292	584	0.043	30.722	HOMO-3->LUMO (25.6%)
4		286	572	0.007	13.470	HOMO->LUMO+3 (34.5%)		290	581	0.039	9.950	HOMO-1->LUMO+2 (19.6%)		291	582	0.049	17.601	HOMO->LUMO+2 (23.9%)
5		283	566	0.255	100.79	HOMO->LUMO+5 (37.8%)		285	571	0.388	53.924	HOMO-1->LUMO+4 (18.7%)		288	576	0.113	27.655	HOMO->LUMO+5 (18.8%)
6		280	560	2.798	20.212	HOMO-1->LUMO+4 (24.7%)		281	563	3.009	7.418	HOMO->LUMO+5 (19.8%)		282	564	3.425	4.532	-
7		271	542	0.015	0.562	HOMO->LUMO (79.1%)		274	549	0.007	1.423	HOMO->LUMO (47.5%)		276	552	0.021	2.773	HOMO->LUMO (53.6%)
8		268	536	0.005	15.404	HOMO-1->LUMO+8 (35.8%)		271	542	0.016	4.091	HOMO-1->LUMO+1 (48.5%)		272	544	0.011	5.422	HOMO-1->LUMO+1 (54.6%)
9		265	530	0.004	11.322	HOMO-1->LUMO+1 (36.9%)		268	536	0.006	31.055	-		267	535	0.004	26.248	-
10	264	529	0.017	9.874	HOMO-1->LUMO+1 (44.3%)	266	532	0.005	18.406	-	265	530	0.005	18.266	HOMO->LUMO+12 (17.8%)			
$\Delta x = -5 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
	16 $\text{\AA}$	336	672	0.158	3.150	HOMO->LUMO+1 (51.5%)	17 $\text{\AA}$	346	692	0.065	1.366	HOMO-1->LUMO (43.2%)	18 $\text{\AA}$	351	702	0.013	0.642	HOMO-1->LUMO (43.5%)
1		331	663	1.827	0.619	HOMO-1->LUMO (37.8%)		343	686	1.517	0.538	HOMO->LUMO (44.2%)		349	698	1.232	0.225	HOMO->LUMO (45.9%)
2		289	578	0.043	68.976	HOMO-1->LUMO+2 (22.5%)		291	583	0.039	61.244	HOMO->LUMO+2 (35.9%)		292	584	0.036	37.452	HOMO->LUMO+2 (33.7%)
3		287	574	0.439	3.770	HOMO-1->LUMO+2 (23.9%)		289	579	0.187	2.360	HOMO-1->LUMO+2 (19.6%)		289	579	0.004	1.789	-
4		282	564	1.441	65.150	HOMO-1->LUMO+4 (46.6%)		284	569	0.514	67.215	HOMO->LUMO+4 (26.1%)		286	572	0.061	44.605	HOMO->LUMO+4 (26.6%)
5		276	553	1.229	42.396	HOMO->LUMO+5 (50.5%)		281	563	2.792	15.840	HOMO->LUMO+5 (19.3%)		282	565	3.622	5.210	HOMO->LUMO+3 (24.6%)
6		267	534	0.020	1.733	HOMO->LUMO (58.4%)		271	542	0.019	2.749	HOMO-1->LUMO (27.1%)		272	544	0.010	4.140	HOMO-1->LUMO+1 (27.3%)
7		265	531	0.001	3.735	HOMO-1->LUMO+1 (22.8%)		269	539	0.004	2.281	HOMO->LUMO (28.8%)		271	542	0.005	5.678	HOMO->LUMO+1 (29%)
8		264	529	0.010	35.223	HOMO->LUMO+8 (22.2%)		266	532	0.005	38.667	-		265	531	0.001	34.295	-
9		262	525	0.001	6.928	HOMO-1->LUMO+1 (42.2%)		265	531	0.002	16.966	-		264	529	0.006	16.203	HOMO->LUMO+12 (17.4%)

Table B.15. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta x = +10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16$ -18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta x = +10 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc	16 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 $\text{\AA}$	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		328	656	1.798	0.364	HOMO->LUMO (57.2%)		335	670	1.359	0.486	HOMO->LUMO (80.9%)		341	682	1.520	0.714	HOMO->LUMO (32%)
2		323	646	0.531	0.0719	HOMO-1->LUMO+1 (48.9%)		329	659	0.530	1.083	HOMO-1->LUMO+1 (80.2%)		338	676	0.000	0.167	HOMO-1->LUMO (41.5%)
3		285	571	0.074	63.192	HOMO-1->LUMO+2 (33%)		287	575	0.143	59.151	HOMO->LUMO+2 (46.3%)		290	581	0.039	52.194	HOMO->LUMO+2 (35%)
4		281	563	0.438	82.170	HOMO->LUMO+3 (55.4%)		282	565	0.625	51.088	HOMO-1->LUMO+3 (46.1%)		285	570	0.408	13.247	HOMO-1->LUMO+3 (35.5%)
5		280	560	0.005	48.490	HOMO-1->LUMO+4 (23.3%)		282	564	0.281	48.810	HOMO->LUMO+4 (51.9%)		283	567	0.087	36.243	HOMO->LUMO+4 (33.5%)
6		278	556	2.733	20.642	-		277	555	2.642	19.109	HOMO-1->LUMO+5 (32.4%)		278	557	3.261	9.161	HOMO-1->LUMO+2 (24%)
7		262	525	0.004	13.354	HOMO->LUMO+10 (36.3%)		263	526	0.004	23.264	HOMO->LUMO+11 (27.4%)		262	525	0.022	7.856	-
8		261	523	0.000	9.881	HOMO->LUMO+6 -		261	522	0.003	23.897	HOMO-1->LUMO+10 (40.9%)		260	521	0.001	1.595	-
9		260	520	0.015	34.152	HOMO-1->LUMO+11 (24%)		256	513	0.044	141.07	HOMO->LUMO+6 (34.7%)		260	521	0.015	56.002	-
10	258	517	0.003	293.75	-	255	510	0.007	15.363	-	254	509	0.008	83.410	-			
$\Delta x = +10 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
	16 $\text{\AA}$						17 $\text{\AA}$						18 $\text{\AA}$					
1		327	655	2.23	1.238	HOMO->LUMO+1 (59.1%)		332	664	1.208	1.929	HOMO-1->LUMO (74.6%)		348	696	0.971	0.748	HOMO->LUMO (85.2%)
2		325	650	0.134	1.0595	HOMO-1->LUMO (50.2%)		325	651	0.713	2.455	HOMO->LUMO+1 (75.7%)		338	677	0.554	0.844	HOMO-1->LUMO+1 (82.5%)
3		287	574	0.012	87.627	HOMO->LUMO+3 (29.5%)		285	570	0.124	69.888	HOMO-1->LUMO+2 (46.2%)		294	588	0.245	55.002	HOMO->LUMO+2 (45.2%)
4		282	564	0.335	7.772	HOMO-1->LUMO+2 (23.7%)		281	562	0.553	28.861	HOMO-1->LUMO+4 (51.3%)		286	572	0.006	10.832	HOMO-1->LUMO+3 (23%)
5		280	560	0.149	110.36	HOMO-1->LUMO+4 (37.3%)		279	559	1.165	53.406	HOMO->LUMO+5 (31.7%)		284	568	0.396	50.865	HOMO->LUMO+5 (36.7%)
6		279	558	2.874	10.294	HOMO->LUMO+5 (30.1%)		276	552	1.764	54.976	HOMO->LUMO+3 (29.2%)		281	563	3.287	12.263	HOMO-1->LUMO+4 (28.3%)
7		261	523	0.007	26.680	HOMO->LUMO+11 (39.3%)		261	522	0.007	32.614	HOMO-1->LUMO+12 (25.1%)		264	529	0.003	19.057	HOMO->LUMO+11 (26%)
8		261	522	0.006	22.983	HOMO-1->LUMO+12 (35.8%)		260	520	0.008	25.148	HOMO->LUMO+11 (34.8%)		260	521	0.009	42.396	HOMO-1->LUMO+12 (29.5%)
9		255	511	0.013	9.3049	-		254	509	0.023	224.43	HOMO-1->LUMO+6 (38.6%)		259	519	0.122	119.77	HOMO->LUMO+6 (25.5%)
10	254	509	0.064	492.56	HOMO-1->LUMO+7 (19.3%)	253	506	0.005	1.254	-	257	515	0.002	7.599	-			

Table B.16. TD-DFT excitation summary for the H₄TCPE dimer at $\Delta x = -10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16$ -18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\Delta x = -10 \text{ \AA}$ (stacking 4 $\text{\AA}$)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 $\text{\AA}$	327	655	1.678	0.186	HOMO-1->LUMO (76.8%)	17 $\text{\AA}$	335	670	1.593	0.929	HOMO-1->LUMO (52.4%)	18 $\text{\AA}$	384	768	0.031	1.821	HOMO->LUMO (42.7%)
2		321	643	0.658	0.687	HOMO->LUMO+1 (75.3%)		330	661	0.277	1.380	HOMO->LUMO+1 (61.2%)		340	681	0.978	7.560	HOMO-1->LUMO (36.8%)
3		284	659	0.068	58.554	HOMO->LUMO+2 (33.6%)		284	569	0.052	64.893	HOMO->LUMO+2 (27.6%)		339	678	0.433	1.808	HOMO->LUMO+1 (51.3%)
4		280	560	0.498	67.982	HOMO-1->LUMO+3 (53.3%)		281	563	0.555	38.095	HOMO-1->LUMO+3 (50.4%)		333	666	0.180	2.337	HOMO-2->LUMO+1 (27.3%)
5		279	558	0.105	53.614	HOMO->LUMO+5 (50.9%)		280	560	0.305	30.320	HOMO->LUMO+5 (47.3%)		297	594	0.263	97.998	HOMO-1->LUMO+2 (26.1%)
6		277	554	2.678	9.792	-		275	551	2.677	5.118	HOMO-1->LUMO+2 (23%)		286	573	0.001	8.957	HOMO-38->LUMO (42.5%)
7		262	524	0.005	21.750	HOMO-1->LUMO+10 (45.8%)		262	525	0.007	22.274	HOMO-1->LUMO+11 (20.6%)		284	569	0.208	9.372	HOMO->LUMO+5 (20.7%)
8		260	520	0.011	18.960	HOMO->LUMO+12 (35.2%)		261	523	0.012	16.618	HOMO-1->LUMO+12 (30.6%)		282	565	0.312	37.269	HOMO-1->LUMO+4 (41.4%)
9		256	512	0.002	159.13	-		258	516	0.018	12.046	-		278	557	2.847	17.048	-
10		254	509	0.004	136.62	-		254	508	0.007	84.073	-		270	540	0.043	14.474	HOMO->LUMO (30.8%)
$\Delta x = -10 \text{ \AA}$ (stacking 5 $\text{\AA}$)																		
1	16 $\text{\AA}$	326	652	1.872	0.136	HOMO->LUMO (70.5%)	17 $\text{\AA}$	337	675	1.586	1.991	HOMO->LUMO+1 (71%)	18 $\text{\AA}$	342	684	1.553	0.889	HOMO-1->LUMO (43%)
2		321	643	0.499	0.367	HOMO-1->LUMO+1 (64.9%)		333	666	0.308	2.629	HOMO-1->LUMO (62.6%)		338	677	0.003	0.115	HOMO->LUMO+1 (47.2%)
3		285	570	0.034	59.036	HOMO-1->LUMO+2 (25.3%)		289	578	0.154	73.670	HOMO-1->LUMO+2 (43.8%)		290	581	0.025	57.073	HOMO-1->LUMO+2 (21.3%)
4		280	560	0.163	2.770	HOMO-1->LUMO+3 (28.6%)		284	569	0.510	60.596	HOMO->LUMO+3 (51.6%)		285	570	0.158	0.681	HOMO->LUMO+4 (22%)
5		279	559	0.051	126.02	HOMO->LUMO+5 (28.2%)		281	563	0.065	27.752	HOMO-1->LUMO+4 (42.1%)		284	568	0.051	47.821	HOMO-1->LUMO+3 (33.8%)
6		278	556	3.135	6.249	HOMO->LUMO+4 (26.9%)		279	558	2.873	6.669	HOMO->LUMO+5 (27.3%)		280	560	3.675	7.349	HOMO->LUMO+5 (22.9%)
7		261	523	0.007	22.592	HOMO->LUMO+11 (35.9%)		268	536	0.035	9.316	HOMO->LUMO (27%)		262	525	0.013	27.677	HOMO->LUMO (32.9%)
8		260	520	0.007	20.663	HOMO-1->LUMO+12 (32.6%)		262	525	0.006	19.205	HOMO->LUMO+10 (43.5%)		261	522	0.009	67.010	HOMO-1->LUMO+10 (26.9%)
9		255	510	0.003	137.95	HOMO-1->LUMO+6 (20.2%)		261	523	0.020	37.986	HOMO-1->LUMO+11 (43.3%)		260	521	0.005	12.631	HOMO->LUMO+11 (25.8%)
10		254	508	0.002	221.99	-		259	518	0.008	8.229	-		256	513	0.027	380.04	HOMO-1->LUMO+6 (31.8%)

Table B.17. TD-DFT excitation summary for the H₄TCPE dimer at plane rotation = 0°:., comparing stacking distances of 4 and 5 Å for d_{C-C} = 16-18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

θ = 0° (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 Å	350	700	0.163	3.958	HOMO->LUMO (38.1%) HOMO->LUMO+1 (20.4%)		353	706	0.102	5.916	HOMO->LUMO (49.7%) HOMO-1->LUMO+1 (25.2%)		364	728	0.353	4.583	HOMO->LUMO (49.5%) HOMO-1->LUMO (29.4%)
2		336	673	1.680	2.590	HOMO-1->LUMO (48.1%) HOMO->LUMO+1 (32.2%)		340	681	1.351	2.475	HOMO-1->LUMO (40.1%) HOMO->LUMO+1 (37.3%)		338	676	0.817	0.191	HOMO->LUMO+1 (40%) HOMO-1->LUMO+1 (35.7%)
3		295	591	0.222	34.272	HOMO->LUMO+3 (39.2%)		297	594	0.234	54.322	HOMO->LUMO+2 (31.2%)		302	605	0.198	54.256	HOMO->LUMO+2 (29.2%)
4		291	582	0.054	86.758	HOMO-1->LUMO+2 (26.7%)		292	585	0.049	80.082	HOMO->LUMO+3 (29.9%)		298	596	0.692	2.744	HOMO->LUMO+3 (29.4%)
5		285	570	0.009	97.689	-		285	570	0.012	59.695	-		292	585	0.015	4.999	HOMO-1->LUMO (50.4%)
6		283	567	0.131	17.078	HOMO->LUMO (28.7%)		284	568	0.060	1.605	HOMO-1->LUMO (27.1%)		285	570	0.068	39.228	-
7		280	560	2.622	12.013	-		280	561	0.566	1.138	HOMO-1->LUMO+1 (40.3%)		281	562	2.520	6.718	-
8		277	554	0.010	0.152	HOMO-1->LUMO+1 (64.7%)		279	558	2.377	10.487	-		272	545	0.024	32.024	-
9		271	542	0.012	22.455	HOMO->LUMO+8 (38%)		270	541	0.011	38.818	HOMO->LUMO+8 (30.1%)		272	544	0.002	0.868	HOMO-1->LUMO+1 (44.5%)
10		268	537	0.014	5.527	HOMO-1->LUMO+8 (33.7%)		268	537	0.036	8.241	HOMO-1->LUMO+8 (32.2%)		268	537	0.103	111.99	-
θ = 0° (stacking 5 Å)																		
1	16 Å	341	683	0.249	9.737	HOMO->LUMO (49.5%) HOMO->LUMO+1 (14.0%)		347	694	0.211	8.045	HOMO->LUMO (47.3%) HOMO->LUMO+1 (17.2%)		342	685	0.075	7.533	HOMO->LUMO (37.2%) HOMO->LUMO+1 (18.2%)
2		328	657	1.621	2.743	HOMO-1->LUMO (42.9%) HOMO->LUMO+1 (17.8%)		335	670	1.324	2.598	HOMO-1->LUMO (46.3%) HOMO->LUMO+1 (18.5%)		333	667	1.136	1.503	HOMO-1->LUMO (46.3%) HOMO-1->LUMO+1 (24.1%)
3		292	584	0.307	43.712	HOMO->LUMO+3 (44.7%)		292	585	0.247	39.737	HOMO->LUMO+3 (38.7%)		291	583	0.308	37.472	HOMO-1->LUMO+2 (43%)
4		288	576	0.037	67.53	HOMO-1->LUMO+2 (34.9%)		290	580	0.051	65.660	HOMO-1->LUMO+2 (35.8%)		289	579	0.127	31.797	HOMO->LUMO+3 (42.8%)
5		282	564	0.089	87.026	-		283	567	0.067	58.602	-		281	562	0.568	25.635	-
6		279	558	2.665	8.702	HOMO->LUMO+5 (21.5%)		280	561	1.762	3.2295	HOMO->LUMO+1 (21.6%)		277	555	2.688	3.661	HOMO->LUMO+5 (29.7%)
7		276	553	0.156	1.598	HOMO->LUMO+1 (42%)		279	558	1.366	3.140	HOMO->LUMO+1 (21.4%)		275	551	0.095	0.777	HOMO->LUMO (47.1%)
8		271	542	0.052	2.008	HOMO-1->LUMO+1 (42.2%)		273	547	0.089	1.281	HOMO-1->LUMO+1 (45.5%)		268	537	0.019	2.302	HOMO-1->LUMO+1 (56%)
9		267	535	0.009	31.908	HOMO->LUMO+8 (25.3%)		267	535	0.006	40.250	-		264	529	0.004	47.605	-
10		265	530	0.029	8.291	HOMO-1->LUMO+8 (22.1%)		265	531	0.034	15.814	-		263	527	0.032	16.560	-

Table B.18. TD-DFT excitation summary for the H₄TCPE dimer at plane rotation = 30°: comparing stacking distances of 4 and 5 Å for d_{C-C} = 16-18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\theta = 30^\circ$ (stacking 4 Å)																		
Exc	16 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	17 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	18 Å	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1		337	675	0.181	0.058	HOMO->LUMO (46.7%)		346	692	0.219	0.094	HOMO-1->LUMO (30.9%)		351	703	0.355	0.091	HOMO-1->LUMO (58.6%)
2		331	662	1.550	0.579	HOMO-1->LUMO (43%)		342	685	1.110	0.519	HOMO-1->LUMO+1 (32.6%)		349	699	0.662	0.429	HOMO->LUMO+1 (42.5%)
3		283	566	0.218	23.447	HOMO->LUMO+2 (29.5%)		285	571	0.032	36.514	HOMO->LUMO+2 (19.2%)		287	575	0.009	19.235	HOMO-1->LUMO+4 (19.5%)
4		281	563	0.133	20.407	HOMO->LUMO+3 (30.7%)		284	568	0.367	1.714	-		287	574	0.110	30.845	HOMO->LUMO+4 (22.7%)
5		279	559	0.032	106.50	HOMO->LUMO+5 (29.3%)		283	566	0.035	70.246	HOMO->LUMO+4 (21.9%)		285	571	0.314	7.513	-
6		277	554	2.719	1.910	HOMO->LUMO+4 (31.4%)		278	557	3.018	3.318	HOMO-1->LUMO+2 (21.4%)		280	560	2.561	5.672	HOMO-1->LUMO+2 (26.2%)
7		270	540	0.022	0.476	HOMO-1->LUMO (45.4%)		275	550	0.010	0.714	HOMO->LUMO+1 (48.1%)		278	556	0.610	0.609	HOMO->LUMO (47.8%)
8		269	539	0.003	0.079	HOMO->LUMO (41.5%)		275	550	0.065	0.111	HOMO-1->LUMO (47.5%)		276	552	0.146	1.5597	HOMO-1->LUMO+1 (56.6%)
9		265	530	0.010	17.797	HOMO->LUMO+8 (28.3%)		266	532	0.008	18.932	HOMO->LUMO+8 (24.3%)		266	532	0.008	10.295	HOMO->LUMO+8 (24.7%)
10	264	529	0.004	16.114	HOMO-1->LUMO+8 (28.3%)	265	531	0.003	13.949	HOMO-1->LUMO+8 (24.5%)	265	531	0.010	9.860	HOMO-1->LUMO+8 (28.1%)			
$\theta = 30^\circ$ (stacking 5 Å)																		
1	16 Å	334	668	0.188	0.152	HOMO->LUMO (34.1%)	17 Å	341	682	0.212	0.109	HOMO-1->LUMO (35.8%)	18 Å	347	694	0.382	0.103	HOMO-1->LUMO (74.9%)
2		328	657	1.570	0.505	HOMO-1->LUMO (45.6%)		337	675	1.179	0.505	HOMO->LUMO+1 (48.5%)		344	688	0.698	0.514	HOMO->LUMO+1 (73.6%)
3		282	565	0.321	5.600	HOMO-1->LUMO+2 (20.3%)		284	569	0.054	33.479	HOMO-1->LUMO+2 (20.1%)		287	574	0.010	27.95	HOMO-3->LUMO (23.6%)
4		282	565	0.029	38.055	HOMO->LUMO+3 (17.4%)		284	568	0.289	11.188	HOMO->LUMO+3 (27.2%)		286	572	0.107	33.315	HOMO->LUMO+5 (30.2%)
5		280	561	0.065	115.77	HOMO->LUMO+5 (28.4%)		283	566	0.102	72.568	HOMO->LUMO+5 (30.5%)		285	570	0.346	6.837	HOMO-1->LUMO+2 (19.8%)
6		278	556	2.888	3.474	HOMO->LUMO+4 (25.7%)		279	558	3.189	3.801	HOMO-1->LUMO+2 (19.1%)		280	560	3.337	4.995	HOMO-1->LUMO+2 (21.6%)
7		267	534	0.001	0.273	HOMO->LUMO (52.1%)		272	544	0.002	0.046	HOMO->LUMO (79.5%)		274	549	0.044	0.321	HOMO->LUMO (85.3%)
8		265	531	0.010	0.376	HOMO-1->LUMO+1 (56.5%)		269	538	0.001	0.572	HOMO-1->LUMO+1 (80.9%)		270	541	0.006	1.683	HOMO-1->LUMO+1 (87.3%)
9		263	527	0.011	25.377	HOMO->LUMO+8 (32.4%)		264	529	0.007	22.178	HOMO-1->LUMO+8 (26%)		264	529	0.004	15.179	HOMO-1->LUMO+8 (20%)
10		263	527	0.001	10.402	HOMO-1->LUMO+8 (34.6%)		264	528	0.002	16.752	HOMO->LUMO+11 (24%)		264	528	0.006	14.178	HOMO->LUMO+11 (21.8%)

Table B.19. TD-DFT excitation summary for the H₄TCPE dimer at plane rotation = 60°; comparing stacking distances of 4 and 5 Å for d_{C-C} = 16-18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\theta = 60^\circ$ (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 Å	338	677	0.961	0.386	HOMO->LUMO (38.9%)	17 Å	342	684	0.747	0.671	HOMO-1->LUMO (37.4%)	18 Å	359	718	0.497	0.290	HOMO->LUMO (54%)
2		336	673	0.509	0.573	HOMO-1->LUMO (45.6%)		338	677	0.417	0.443	HOMO->LUMO+1 (56.5%)		352	704	0.381	0.256	HOMO->LUMO+1 (42.8%)
3		286	573	0.030	25.639	HOMO->LUMO+3 (24.4%)		286	572	0.572	18.088	HOMO->LUMO+2 (22.7%)		299	599	0.292	6.026	HOMO->LUMO+2 (35.7%)
4		285	571	1.048	2.840	HOMO->LUMO+2 (20.9%)		282	564	0.154	79.180	HOMO->LUMO+3 (30.9%)		294	588	0.616	4.651	HOMO->LUMO+3 (31.1%)
5		283	566	0.061	126.30	HOMO->LUMO+4 (22.1%)		279	559	0.969	18.200	-		288	577	0.282	57.845	HOMO-1->LUMO+2 (26%)
6		281	563	2.171	11.030	HOMO->LUMO+5 (22.6%)		276	553	1.121	32.780	-		286	573	0.811	13.374	HOMO-1->LUMO (28.7%)
7		271	543	0.154	0.655	HOMO->LUMO (41.7%)		272	545	0.601	2.933	HOMO->LUMO (40.6%)		278	557	1.625	1.169	HOMO->LUMO+6 (24.3%)
8		269	538	0.101	0.274	HOMO-1->LUMO+1 (45.5%)		269	538	0.057	0.734	HOMO-1->LUMO+1 (55.3%)		278	557	0.150	0.080	HOMO-1->LUMO+1 (35.8%)
9		267	534	0.008	3.225	HOMO->LUMO+8 (35.3%)		266	532	0.074	4.965	HOMO->LUMO+8 (25.6%)		274	549	0.016	7.108	-
10		266	532	0.000	28.160	HOMO-1->LUMO+8 (34.4%)		264	529	0.046	40.545	HOMO-1->LUMO+8 (24.4%)		267	534	0.009	22.131	HOMO-1->LUMO+9 (30.1%)
$\theta = 60^\circ$ (stacking 5 Å)																		
1	16 Å	338	676	0.881	0.572	HOMO->LUMO (64.9%)	17 Å	350	701	0.642	4.058	HOMO->LUMO+1 (66.6%)	18 Å	348	697	0.567	0.306	HOMO->LUMO (64.4%)
2		333	666	0.691	0.148	HOMO-1->LUMO+1 (48.4%)		342	685	0.556	2.973	HOMO-1->LUMO (70.1%)		341	682	0.398	0.509	HOMO-1->LUMO+1 (45.5%)
3		288	577	0.164	40.031	HOMO->LUMO+3 (27%)		291	583	0.621	35.599	HOMO->LUMO+3 (54.9%)		289	578	0.455	14.465	HOMO->LUMO+2 (35.8%)
4		286	573	1.124	10.197	HOMO->LUMO+2 (33%)		289	578	0.596	44.595	HOMO-1->LUMO+2 (42.5%)		283	567	0.439	37.020	-
5		284	568	1.142	65.600	HOMO-1->LUMO+3 (28.3%)		284	569	0.233	27.580	HOMO->LUMO (52.6%)		283	566	0.843	14.578	HOMO->LUMO+3 (19.5%)
6		280	560	1.031	39.212	HOMO-1->LUMO+5 (38.2%)		280	560	0.587	42.736	HOMO-1->LUMO+4 (27.8%)		278	557	1.617	25.350	-
7		269	538	0.091	0.232	HOMO-1->LUMO (61.1%)		278	556	1.385	12.665	HOMO->LUMO+5 (28.1%)		273	546	0.403	2.713	HOMO-1->LUMO (52.4%)
8		267	535	0.055	0.817	HOMO->LUMO+1 (61.9%)		270	541	0.075	2.244	HOMO-1->LUMO+1 (79.5%)		271	543	0.052	1.480	HOMO->LUMO+1 (53.6%)
9		267	534	0.009	8.586	HOMO->LUMO+8 (32.5%)		268	536	0.080	4.098	HOMO->LUMO+8 (22.8%)		267	534	0.031	3.668	HOMO->LUMO+8 (28%)
10		265	530	0.014	20.803	HOMO-1->LUMO+8 (31.7%)		266	533	0.056	28.273	HOMO-1->LUMO+8 (24%)		264	528	0.014	25.791	HOMO-1->LUMO+8 (23.2%)

Table B.20. TD-DFT excitation summary for the H₄TCPE dimer at plane rotation = 90°: comparing stacking distances of 4 and 5 Å for d_{C-C} = 16-18 Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.

$\theta = 90^\circ$ (stacking 4 Å)																		
Exc		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition		1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition
1	16 Å	341	682	0.729	1.709	HOMO->LUMO+1 (55.8%)	17 Å	351	703	0.600	0.663	HOMO->LUMO+1 (69.8%)	18 Å	365	731	0.421	0.074	HOMO->LUMO+1 (57.9%)
2		333	667	0.783	5.503	HOMO->LUMO (31.5%)		341	682	0.651	1.788	HOMO-1->LUMO (57.8%)		359	719	0.540	0.635	HOMO->LUMO (47.5%)
3		298	596	0.511	1.901	HOMO->LUMO+2 (34.9%)		295	590	0.249	4.473	-		298	597	0.243	0.459	HOMO->LUMO+2 (26.6%)
4		290	581	0.863	48.149	-		291	583	1.189	2.263	-		295	591	0.549	0.188	HOMO-1->LUMO (30.4%)
5		289	578	1.485	20.458	-		289	579	1.150	50.416	HOMO-1->LUMO+2 (27.6%)		294	588	0.505	7.804	HOMO-1->LUMO+1 (47.9%)
6		284	568	0.435	85.368	HOMO->LUMO+5 (23.9%)		287	574	0.391	72.713	HOMO->LUMO+5 (24.8%)		292	585	0.002	74.167	-
7		277	554	0.072	16.143	HOMO->LUMO (33.3%)		283	567	0.717	4.693	HOMO->LUMO (33.5%)		287	574	1.601	1.607	HOMO->LUMO+4 (23.9%)
8		273	546	0.183	2.386	HOMO-1->LUMO+1 (34.3%)		275	551	0.128	0.881	HOMO-1->LUMO+1 (62.7%)		286	573	1.044	2.079	-
9		271	542	0.027	1.831	-		270	541	0.009	4.518	HOMO->LUMO+8 (38.7%)		271	542	0.009	0.147	HOMO->LUMO+8 (40.4%)
10		268	536	0.046	2.436	HOMO->LUMO+8 (24.2%)		266	533	0.003	30.998	HOMO-1->LUMO+8 (30%)		268	536	0.001	25.386	HOMO-1->LUMO+8 (32.4%)
$\theta = 90^\circ$ (stacking 5 Å)																		
1	16 Å	335	670	0.678	1.957	HOMO-1->LUMO (39.7%)	17 Å	345	691	0.585	0.266	HOMO->LUMO+1 (63.8%)	18 Å	361	722	0.397	0.087	HOMO->LUMO (34.1%)
2		331	663	0.833	0.606	HOMO->LUMO+1 (38.7%)		339	678	0.698	0.486	HOMO-1->LUMO (44.2%)		355	711	0.590	0.443	HOMO->LUMO+1 (29.6%)
3		293	586	0.494	17.090	HOMO-1->LUMO+2 (29.9%)		292	584	0.395	20.046	HOMO-1->LUMO+2 (27.9%)		294	589	0.175	1.963	HOMO->LUMO+2 (30.5%)
4		289	578	1.249	20.105	HOMO->LUMO+4 (33.8%)		288	577	1.331	3.163	HOMO->LUMO+3 (23.8%)		292	584	0.859	0.971	HOMO-1->LUMO+1 (21.4%)
5		285	570	1.293	2.054	-		285	571	0.864	60.597	HOMO->LUMO+4 (26.9%)		290	581	0.428	4.752	HOMO-1->LUMO (32.7%)
6		283	567	0.217	137.64	HOMO-1->LUMO+3 (22.4%)		284	569	0.730	51.081	HOMO->LUMO+5 (28.1%)		289	579	0.081	75.022	HOMO-1->LUMO+2 (22.2%)
7		278	556	0.443	12.572	HOMO->LUMO (48.3%)		278	557	0.434	1.487	HOMO->LUMO (40.6%)		284	569	1.322	3.131	HOMO->LUMO+4 (25%)
8		267	534	0.018	0.704	HOMO-1->LUMO+8 (26.8%)		274	548	0.130	0.555	HOMO-1->LUMO+1 (54.2%)		283	566	1.108	2.892	HOMO-1->LUMO+4 (20.5%)
9		265	531	0.057	21.183	-		268	536	0.015	2.643	HOMO->LUMO+8 (39.7%)		269	538	0.015	0.414	HOMO->LUMO+8 (41.1%)
10		265	530	0.024	32.502	-		265	531	0.004	37.740	HOMO-1->LUMO+8 (32.8%)		266	533	0.000	33.000	HOMO-1->LUMO+8 (32.5%)

B.2.1. Orbitals Visualization

The electron density difference upon excitation was calculated using Turbomole and visualized with Visual Molecular Dynamics (VMD). An isovalue of 0.02 a.u. was applied for the visualization of individual molecular orbitals, while an isovalue of 0.0002 a.u. was used for the electron density difference plots. The regions where electron density is depleted upon excitation are shown in blue, whereas the regions where electron density accumulates are shown in green. The extent of charge transfer upon excitation was quantified using Multiwfn (version 3.8).

$d_{C-C}=16 \text{ \AA}$	SA		LA	
	EDD	Orbitals	EDD	Orbitals
$S_0 \rightarrow S_1$		 HOMO-1 $\rightarrow$ LUMO (62.5%) HOMO $\rightarrow$ LUMO+1 (11.3%)		 HOMO $\rightarrow$ LUMO+1 (50.3%) HOMO-1 $\rightarrow$ LUMO (22.8%)
$S_0 \rightarrow S_2$		 HOMO $\rightarrow$ LUMO+1 (70.1%) HOMO-1 $\rightarrow$ LUMO (10.5%)		 HOMO-1 $\rightarrow$ LUMO (37.4%) HOMO $\rightarrow$ LUMO+1 (30.7%)
$d_{C-C}=17 \text{ \AA}$	SA		LA	
	EDD	Orbitals	EDD	Orbitals
$S_0 \rightarrow S_1$		 HOMO-1 $\rightarrow$ LUMO (64.5%) HOMO $\rightarrow$ LUMO+1 (10.9%)		 HOMO $\rightarrow$ LUMO+1 (47.4%) HOMO-1 $\rightarrow$ LUMO (29.2%)
$S_0 \rightarrow S_2$		 HOMO $\rightarrow$ LUMO+1 (72.7%) HOMO-1 $\rightarrow$ LUMO (10.1%)		 HOMO-1 $\rightarrow$ LUMO (38.3%) HOMO $\rightarrow$ LUMO+1 (36.2%)
$d_{C-C}=18 \text{ \AA}$	SA		LA	
	EDD	Orbitals	EDD	Orbitals
$S_0 \rightarrow S_1$		 HOMO-1 $\rightarrow$ LUMO (66.5%) HOMO $\rightarrow$ LUMO+1 (9.2%)		 HOMO-1 $\rightarrow$ LUMO (54.7%) HOMO $\rightarrow$ LUMO+1 (24.4%)
$S_0 \rightarrow S_2$		 HOMO $\rightarrow$ LUMO+1 (75.2%) HOMO-1 $\rightarrow$ LUMO (8.4%)		 HOMO $\rightarrow$ LUMO+1 (60.7%) HOMO-1 $\rightarrow$ LUMO (22.1%)

Figure B.8. Book-opening angle 45° : comparison of short- and long-axis configurations for $d_{C-C} = 16\text{-}18 \text{ \AA}$. Electron density difference (EDD) plots and dominant orbital transitions for the first and second excitations.

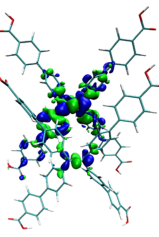
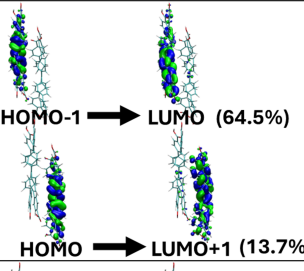
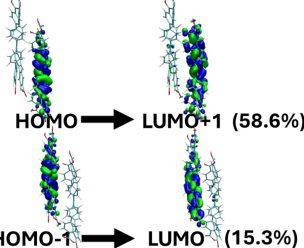
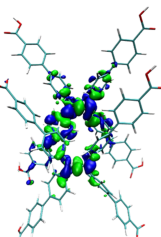
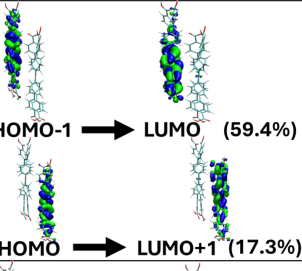
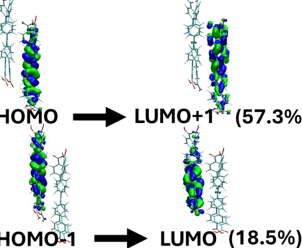
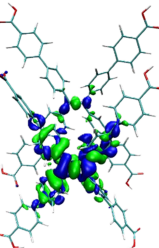
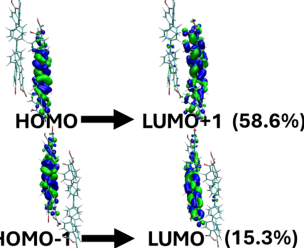
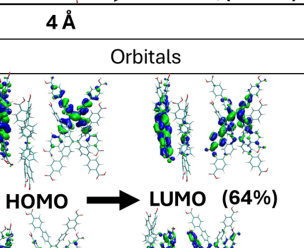
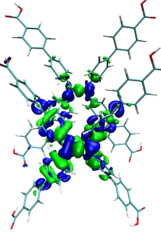
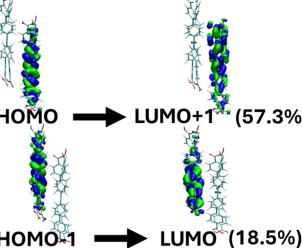
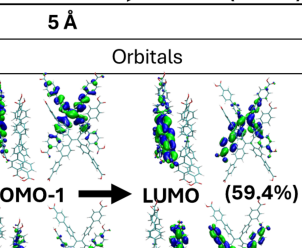
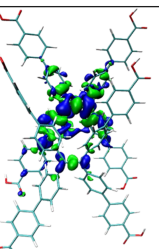
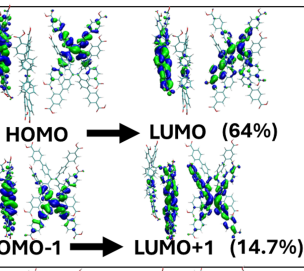
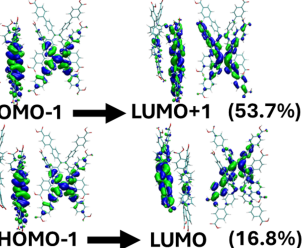
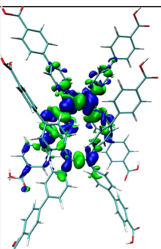
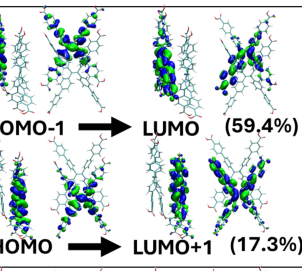
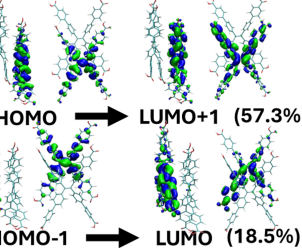
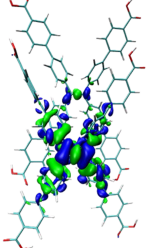
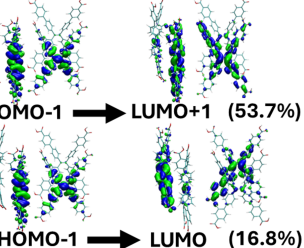
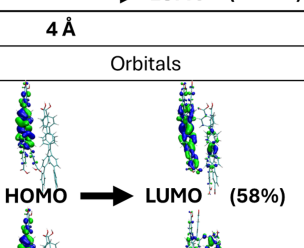
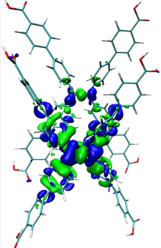
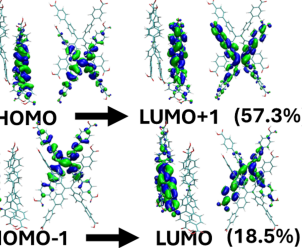
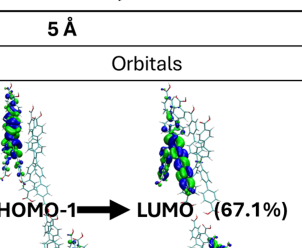
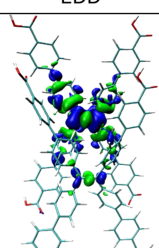
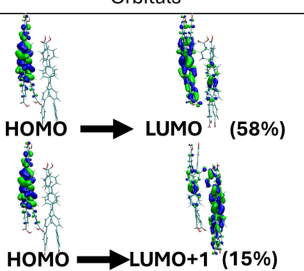
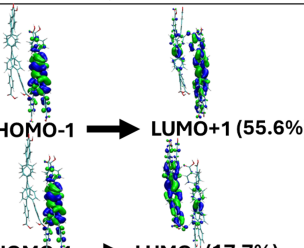
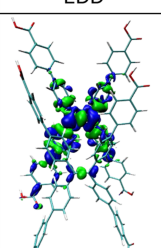
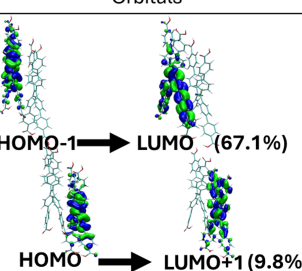
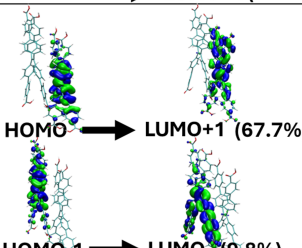
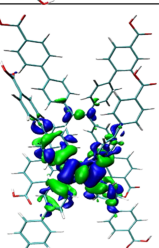
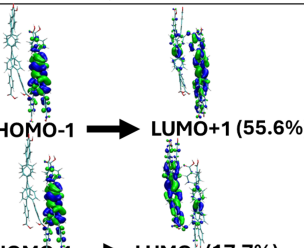
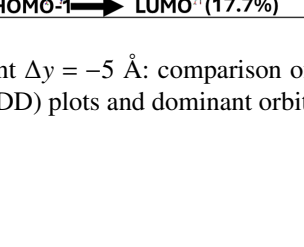
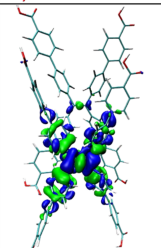
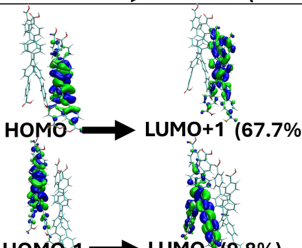
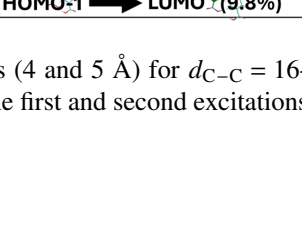
$d_{C-C}=16 \text{ \AA}$	4 $\text{\AA}$		5 $\text{\AA}$	
	EDD	Orbitals	EDD	Orbitals
S0-S1		 HOMO-1 $\rightarrow$ LUMO (64.5%)  HOMO $\rightarrow$ LUMO+1 (13.7%)		 HOMO-1 $\rightarrow$ LUMO (59.4%)  HOMO $\rightarrow$ LUMO+1 (17.3%)
S0-S2		 HOMO $\rightarrow$ LUMO+1 (58.6%)  HOMO-1 $\rightarrow$ LUMO (15.3%)		 HOMO $\rightarrow$ LUMO+1 (57.3%)  HOMO-1 $\rightarrow$ LUMO (18.5%)
$d_{C-C}=17 \text{ \AA}$	4 $\text{\AA}$		5 $\text{\AA}$	
	EDD	Orbitals	EDD	Orbitals
S0-S1		 HOMO $\rightarrow$ LUMO (64%)  HOMO-1 $\rightarrow$ LUMO+1 (14.7%)		 HOMO-1 $\rightarrow$ LUMO (59.4%)  HOMO $\rightarrow$ LUMO+1 (17.3%)
S0-S2		 HOMO-1 $\rightarrow$ LUMO+1 (53.7%)  HOMO-1 $\rightarrow$ LUMO (16.8%)		 HOMO $\rightarrow$ LUMO+1 (57.3%)  HOMO-1 $\rightarrow$ LUMO (18.5%)
$d_{C-C}=18 \text{ \AA}$	4 $\text{\AA}$		5 $\text{\AA}$	
	EDD	Orbitals	EDD	Orbitals
S0-S1		 HOMO $\rightarrow$ LUMO (58%)  HOMO $\rightarrow$ LUMO+1 (15%)		 HOMO-1 $\rightarrow$ LUMO (67.1%)  HOMO $\rightarrow$ LUMO+1 (9.8%)
S0-S2		 HOMO-1 $\rightarrow$ LUMO+1 (55.6%)  HOMO-1 $\rightarrow$ LUMO (17.7%)		 HOMO $\rightarrow$ LUMO+1 (67.7%)  HOMO-1 $\rightarrow$ LUMO (9.8%)

Figure B.9. Plane displacement $\Delta y = -5 \text{ \AA}$: comparison of stacking distances (4 and 5 $\text{\AA}$) for $d_{C-C} = 16-18 \text{ \AA}$. Electron density difference (EDD) plots and dominant orbital transitions for the first and second excitations.

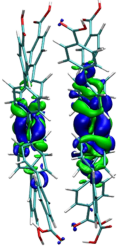
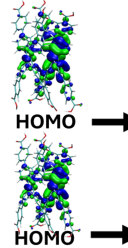
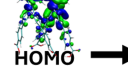
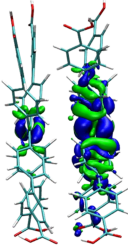
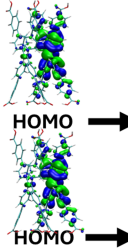
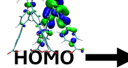
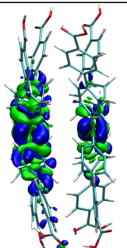
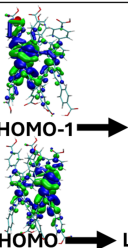
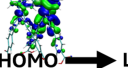
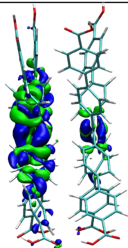
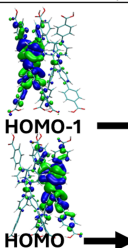
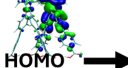
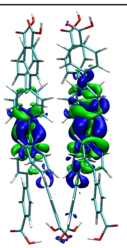
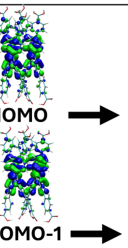
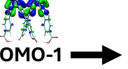
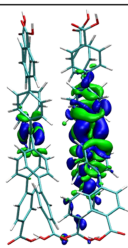
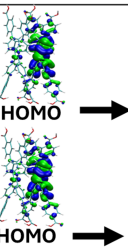
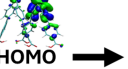
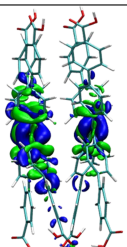
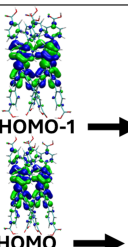
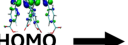
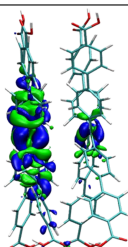
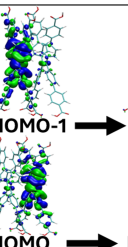
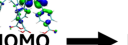
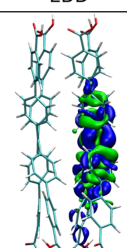
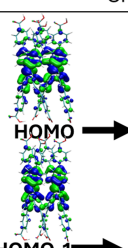
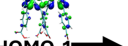
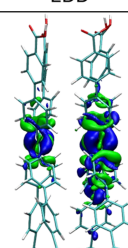
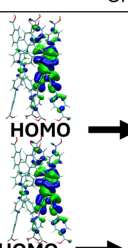
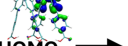
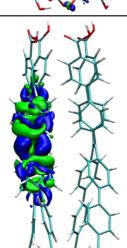
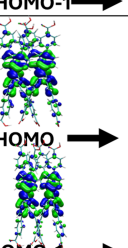
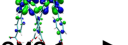
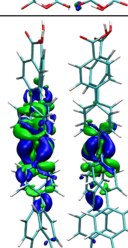
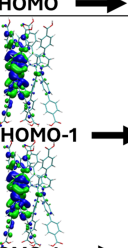
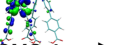
$d_{C-C}=16 \text{ \AA}$	4 $\text{\AA}$		5 $\text{\AA}$	
	EDD	Orbitals	EDD	Orbitals
S0-S1		 HOMO $\rightarrow$ LUMO (38.1%)  HOMO $\rightarrow$ LUMO+1 (20.4%)		 HOMO $\rightarrow$ LUMO (49.5%)  HOMO $\rightarrow$ LUMO+1 (14%)
S0-S2		 HOMO-1 $\rightarrow$ LUMO (48.1%)  HOMO $\rightarrow$ LUMO+1 (32.2%)		 HOMO-1 $\rightarrow$ LUMO (42.9%)  HOMO $\rightarrow$ LUMO+1 (17.8%)
$d_{C-C}=17 \text{ \AA}$	4 $\text{\AA}$		5 $\text{\AA}$	
	EDD	Orbitals	EDD	Orbitals
S0-S1		 HOMO $\rightarrow$ LUMO (49.7%)  HOMO-1 $\rightarrow$ LUMO+1 (25.2%)		 HOMO $\rightarrow$ LUMO (47.3%)  HOMO $\rightarrow$ LUMO+1 (17.2%)
S0-S2		 HOMO-1 $\rightarrow$ LUMO (40.1%)  HOMO $\rightarrow$ LUMO+1 (37.3%)		 HOMO-1 $\rightarrow$ LUMO (46.3%)  HOMO $\rightarrow$ LUMO+1 (18.5%)
$d_{C-C}=18 \text{ \AA}$	4 $\text{\AA}$		5 $\text{\AA}$	
	EDD	Orbitals	EDD	Orbitals
S0-S1		 HOMO $\rightarrow$ LUMO (49.5%)  HOMO-1 $\rightarrow$ LUMO (29.4%)		 HOMO $\rightarrow$ LUMO (37.2%)  HOMO $\rightarrow$ LUMO+1 (18.2%)
S0-S2		 HOMO $\rightarrow$ LUMO+1 (40%)  HOMO-1 $\rightarrow$ LUMO+1 (35.7%)		 HOMO-1 $\rightarrow$ LUMO (46.3%)  HOMO-1 $\rightarrow$ LUMO+1 (24.1%)

Figure B.10. Plane rotation 0° : comparison of stacking distances (4 and 5 $\text{\AA}$) for $d_{C-C} = 16\text{--}18 \text{ \AA}$. Electron density difference (EDD) plots and dominant orbital transitions for the first and second excitations.

B.2.2. Multiwfn Analysis

Table B.21. Book-opening angle 45° : Multiwfn analysis of the first and second excited states across the SA and LA configurations for $d_{C-C} = 16-18$ Å.

Structure	d_{C-C} (Å)	State	Sr (au)	D (Å)	Variation of dipole moment with respect to ground state:	H_{CT} (Å)	H (Å)	t (Å)
SA	16	S0-S1	0.6815	1.36	2.232012	3.31	5.504	-1.95
		S0-S2	0.65572	0.736	1.175076	3.21	5.516	-2.475
	17	S0-S1	0.69416	1.408	2.336031	3.354	5.268	-1.946
		S0-S2	0.6857	0.328	0.536	3.158	5.248	-2.83
	18	S0-S1	0.70012	1.504	2.50932	3.399	5.014	-1.895
		S0-S2	0.69975	0.206	0.34069	3.161	5.000	-2.955
LA	16	S0-S1	0.63359	0.673	1.053828	3.462	6.616	-2.789
		S0-S2	0.66099	0.626	1.006645	3.407	6.595	-2.781
	17	S0-S1	0.64206	0.507	0.799367	4.008	6.900	-3.501
		S0-S2	0.6507	0.599	0.953785	3.812	6.913	-3.213
	18	S0-S1	0.71215	0.534	0.893537	3.637	6.690	-3.103
		S0-S2	0.7093	0.318	0.532361	3.766	6.739	-3.448

Table B.22. Plane displacement $\Delta y = -5$ Å: Multiwfn analysis of the first and second excited states comparison of $\Delta z = 4$ and 5 Å for $d_{C-C} = 16-18$ Å.

Structure	d_{C-C} (Å)	State	Sr (au)	D (Å)	Variation of dipole moment with respect to ground state:	H_{CT} (Å)	H (Å)	t (Å)
4 Å	16	S0-S1	0.64468	1.663	2.661847	3.193	4.994	-1.53
		S0-S2	0.64506	0.797	0.797	3.344	5.244	-2.547
	17	S0-S1	0.69254	1.338	2.213774	3.809	5.194	-2.471
		S0-S2	0.69379	0.184	0.306299	2.788	5.137	-2.603
	18	S0-S1	0.7229	1.092	1.853855	3.723	5.02	-2.631
		S0-S2	0.72103	0.258	0.436178	3.156	5.159	-2.898
5 Å	16	S0-S1	0.60018	1.649	2.534674	3.405	5.507	-1.756
		S0-S2	0.63441	0.82	1.296532	3.162	5.478	-2.342
	17	S0-S1	0.61627	1.513	2.328625	3.712	5.352	-2.2
		S0-S2	0.59496	1.335	2.03456	3.736	5.607	-2.401
	18	S0-S1	0.65474	1.579	2.506749	3.282	5.091	-1.703
		S0-S2	0.6663	1.09	1.763403	3.736	4.996	-2.646

Table B.23. Plane rotation 0°: Multiwfn analysis of the first and second excited states comparison of $\Delta z = 4$ and 5 Å for $d_{C-C} = 16-18$ Å.

Structure	d_{C-C} (Å)	State	Sr (au)	D (Å)	Variation of dipole moment with respect to ground state:	H_{CT} (Å)	H (Å)	t (Å)
4 Å	16	S0-S1	0.65873	0.573	0.916858	3.724	5.544	-3.15
		S0-S2	0.68283	0.626	1.020028	3.341	5.342	-2.715
	17	S0-S1	0.61019	1.553	2.383342	3.851	5.538	-2.298
		S0-S2	0.61735	1.244	1.911875	3.88	5.58	-2.636
	18	S0-S1	0.65804	1.712	2.740125	3.809	5.091	-2.097
		S0-S2	0.67245	0.267	0.430328	2.41	5.044	-2.143
5 Å	16	S0-S1	0.60426	1.437	2.171809	3.501	5.401	-2.064
		S0-S2	0.65683	0.883	1.406369	3.212	5.139	-2.329
	17	S0-S1	0.6235	1.137	1.743746	3.584	5.31	5.31
		S0-S2	0.66976	0.939	1.514424	3.364	5.139	-2.425
	18	S0-S1	0.65841	0.583	0.929486	3.593	5.582	-3.009
		S0-S2	0.63771	0.844	1.324619	4.072	5.619	-3.229

B.3. 2PA Properties in H₄TBAPy Linker

Table B.24. Summary of the electronic transitions involved in 1PA and 2PA for the H₄TBAPy monomer in implicit DMF.

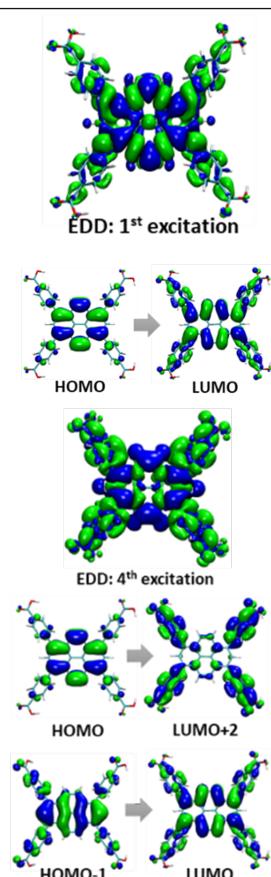
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	368	737	1.1962	0.006646	HOMO->LUMO	94.4%	IntraCT	 EDD: 1st excitation HOMO → LUMO EDD: 4th excitation HOMO → LUMO+2 HOMO-1 → LUMO
2	326	652	0.0009	0.000853	HOMO-1->LUMO HOMO->LUMO+4 HOMO->LUMO+2	37.5% 26.8% 26.8%		
3	280	561	0.0003	125.1374	HOMO->LUMO+3 HOMO->LUMO+6	63.7% 15.4%		
4	277	554	1.7058	1.429650	HOMO->LUMO+2 HOMO-1->LUMO	49.2% 40.2%	IntraCT LE	
5	276	553	0.0033	744.0011	HOMO->LUMO+1	87.2%		
6	258	517	0.0000	39.75893	HOMO-4->LUMO HOMO-3->LUMO	28.3% 23.2%		
7	256	513	0.0007	78.05637	HOMO->LUMO+6 HOMO-3->LUMO	30.8% 20.2%		
8	252	505	0.0219	0.085925	HOMO->LUMO+4	65.5%		
9	249	499	0.1910	0.881616	HOMO->LUMO+5	66.4%		
10	246	492	0.0002	41.34335	-	-		

Table B.25. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF NU-1000.

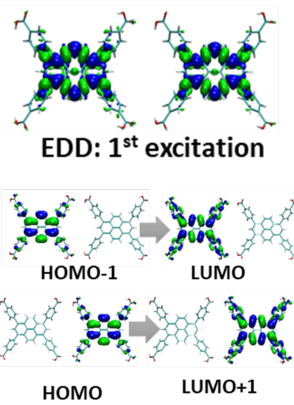
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	357	715	2.2137	0.0715	HOMO-1->LUMO HOMO->LUMO+1	51.9% 42.5%	LE+Int raCT	 EDD: 1st excitation HOMO-1 LUMO HOMO LUMO+1
2	353	707	0.0053	0.0163	HOMO->LUMO+1 HOMO-1->LUMO	51.8% 42.4%		
3	319	638	0.0009	0.0261	HOMO-4->LUMO HOMO-1->LUMO+2	38.6% 21.5%		
4	319	638	0.0009	0.0208	HOMO-2->LUMO+1 HOMO->LUMO+10	38.1% 26.0%		
5	271	543	0.0135	38.9812	-	-		
6	271	542	0.0003	13.5656	-	-		
7	270	541	0.0000	0.6477	HOMO->LUMO	91.1%		
8	270	541	0.0173	91.4504	HOMO-1->LUMO+4	47.9%		
9	269	538	0.0017	78.9781	-	-		
10	268	537	0.0976	112.712	-	-		

Table B.26. Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF NU-1000.

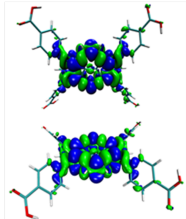
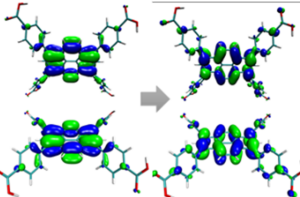
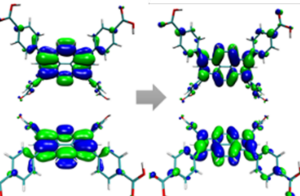
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	359	718	0.0000	0.1238	HOMO->LUMO HOMO-1->LUMO+1	47.5% 46.8%		 EDD: 2 nd excitation
2	353	706	1.8294	2.6929	HOMO-1->LUMO HOMO->LUMO+1	47.1% 46.9%	LE+IntraCT	
3	319	638	0.0006	0.0305	HOMO-3->LUMO+1	19.0%		
4	319	638	0.0016	0.1684	HOMO-3->LUMO	19.0%		
5	273	547	0.1331	37.4975	HOMO->LUMO+2 HOMO-1->LUMO+3	23.6% 20.9%		 HOMO-1 LUMO
6	272	545	0.1578	94.1417	-	-		
7	270	541	0.0212	15.0051	-	-		 HOMO LUMO+1
8	270	541	0.0789	54.4503	-	-		
9	268	537	0.0017	9.8734	-	-		
10	268	537	0.0026	114.436	-	-		

Table B.27. Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF NU-1000.

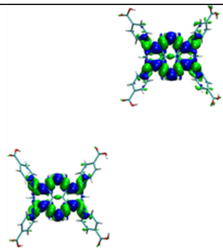
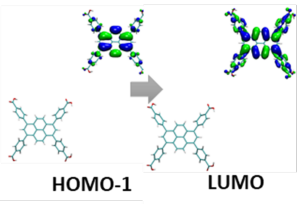
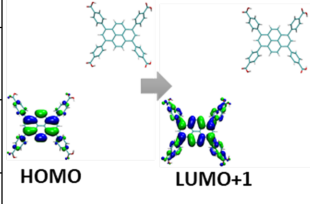
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	355	711	2.0259	0.6129	HOMO-1->LUMO HOMO->LUMO+1	52.1% 42.2%	LE+IntraCT	 EDD: 1st excitation
2	355	711	0.0056	0.0110	HOMO->LUMO+1 HOMO-1->LUMO	52.1% 42.2%		
3	319	638	0.0010	0.0249	HOMO-3->LUMO HOMO-1->LUMO+8	38.7% 28.2%		
4	319	638	0.0010	0.0288	HOMO-2->LUMO+1 HOMO->LUMO+9	38.7% 28.5%		
5	271	542	0.1090	80.6817	HOMO-1->LUMO+2 HOMO-1->LUMO+6	36.7% 20.4%		 HOMO-1 LUMO
6	271	542	0.1432	94.2598	HOMO->LUMO+3 HOMO->LUMO+7	25.4% 21.8%		
7	269	538	0.0030	61.1885	-	-		 HOMO LUMO+1
8	268	537	0.0011	93.2961	HOMO-14->LUMO+2	21.2%		
9	267	535	0.0084	52.4627	HOMO-15->LUMO+3	18.5%		
10	267	535	0.0094	32.2651	-	-		

Table B.28. Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF NU-1000.

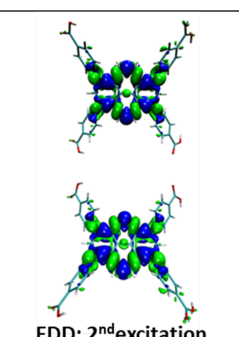
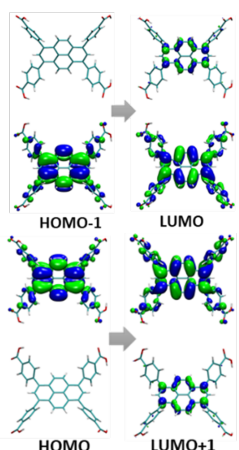
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	357	714	0.0000	0.0189	HOMO->LUMO+1 HOMO-1->LUMO	35.2% 35.0%		 EDD: 2nd excitation
2	354	708	1.9427	0.0932	HOMO-1->LUMO HOMO->LUMO+1	42.6% 42.4%	LE+ InterCT	
3	318	637	0.0013	0.0218	-	-		
4	318	637	0.0005	0.0610	HOMO-3->LUMO	22.3%		
5	273	547	0.0287	3.8393	-	-		 HOMO-1 LUMO HOMO LUMO+1
6	273	547	0.0106	1.7809	-	-		
7	270	540	0.0838	132.5116	-	-		
8	269	539	0.0146	146.2211	-	-		
9	267	535	0.0494	47.6994	-	-		
10	267	535	0.0045	16.1086	-	-		

Table B.29. Summary of the electronic transitions involved in 1PA and 2PA for the Trimer extracted from MOF NU-1000.

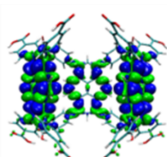
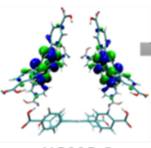
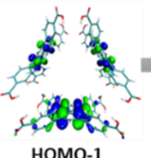
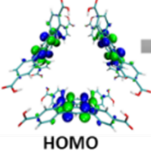
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	360	720	0.0000	0.23438	HOMO->LUMO+1 HOMO-1->LUMO+2	33.6% 31.6%		 EDD: 3rd excitation
2	360	720	0.0000	0.23472	HOMO-2->LUMO+2 HOMO->LUMO	30.4% 29.8%		
3	351	702	2.4859	8.16298	HOMO-2->LUMO HOMO-1->LUMO+1 HOMO->LUMO+2	31.4% 31.3% 31.1%	LE +IntraC T	
4	319	638	0.0000	0.00257	-	-		 HOMO-2 → LUMO
5	319	638	0.0016	0.11503	HOMO-5->LUMO	12.8%		
6	319	638	0.0016	0.11482	HOMO-3->LUMO+2	12.4%		 HOMO-1 → LUMO+1
7	275	551	0.0000	0.06171	HOMO->LUMO+3	20.0%		
8	273	547	0.2901	86.5636	HOMO-2->LUMO+3	16.5%		
9	273	547	0.2902	86.6264	HOMO-1->LUMO+3	16.2%		 HOMO → LUMO+2
10	271	543	0.0001	0.76958	-	-		

Table B.30. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF NU-901.

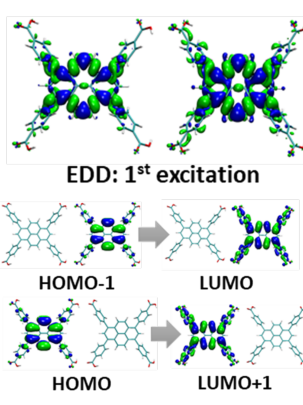
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	378	757	2.2077	0.4995	HOMO-1->LUMO HOMO->LUMO+1	54.0% 40.6%	IntraCT	 EDD: 1st excitation HOMO-1 LUMO HOMO LUMO+1
2	373	747	0.0107	0.0795	HOMO->LUMO+1 HOMO-1->LUMO	53.9% 40.5%		
3	331	663	0.0022	0.0099	HOMO-1->LUMO+8 HOMO-3->LUMO	39.3% 25.3%		
4	331	663	0.0030	0.0249	HOMO-2->LUMO+1 HOMO->LUMO+11	28.6% 17.7%		
5	292	585	0.0109	3.8006	HOMO-5->LUMO+9	15.3%		
6	292	584	0.0010	13.5820	-	-		
7	291	582	0.0000	8.1285	HOMO->LUMO	90.7%		
8	290	581	0.0072	33.552	HOMO-1->LUMO+4	29.1%		
9	289	579	0.0420	27.5037	HOMO->LUMO+16 HOMO->LUMO+7	21.8% 18.6%		
10	289	578	0.0001	75.622	HOMO-23->LUMO+4	19.5%		

Table B.31. Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF NU-901.

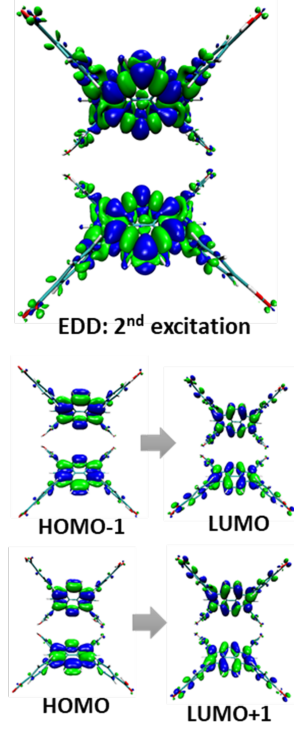
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	381	763	0.0001	0.1041	HOMO->LUMO HOMO-1->LUMO+1	48.5% 45.9%		 EDD: 2nd excitation HOMO-1 LUMO HOMO LUMO+1
2	372	744	1.7610	1.5968	HOMO-1->LUMO HOMO->LUMO+1	47.6% 46.7%	LE+ IntraCT	
3	331	663	0.0019	0.0014	HOMO->LUMO+10	19.2%		
4	331	663	0.0035	0.1594	HOMO-1->LUMO+10	19.1%		
5	310	621	0.0187	0.1283	-	-		
6	298	596	0.0092	0.4274	-	-		
7	293	587	0.0294	6.6952	-	-		
8	293	586	0.0481	43.919	-	-		
9	290	581	0.0057	9.0456	-	-		
10	290	580	0.0145	29.049	-	-		

Table B.32. Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF NU-901.

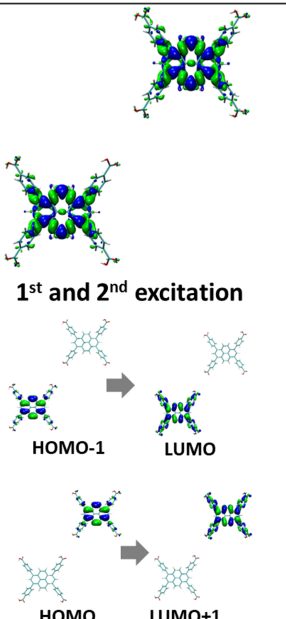
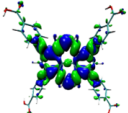
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	376	752	1.9859	0.190	HOMO-1->LUMO HOMO->LUMO+1	50.7% 43.9%	LE	 1st and 2nd excitation HOMO-1 LUMO HOMO LUMO+1
2	375	751	0.0026	0.021	HOMO->LUMO+1 HOMO-1->LUMO	50.7% 43.9%	LE	
3	331	663	0.0028	0.006	HOMO-1->LUMO+10 HOMO-3->LUMO	40.0% 29.9%		
4	331	663	0.0024	0.007	HOMO->LUMO+11 HOMO-2->LUMO+1	40.1% 30.0%		
5	291	582	0.0269	16.609	HOMO->LUMO+7 HOMO->LUMO+13	14.6% 13.0%		
6	290	581	0.0214	35.959	HOMO-1->LUMO+12 HOMO-1->LUMO+4	18.8% 18.3%		
7	290	580	0.0328	18.366	-	-		
8	289	579	0.0018	48.216	HOMO->LUMO+4	10.6%		
9	288	577	0.0282	52.877	HOMO-20->LUMO+4 HOMO-1->LUMO+2	11.6% 10.9%		
10	288	577	0.0501	26.096	-	-		

Table B.33. Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF NU-901.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	377	755	0.000	0.023	HOMO->LUMO HOMO-1->LUMO+1	38.9% 38.9%		
2	374	748	1.887	0.017	HOMO-1->LUMO HOMO->LUMO+1	45.6% 45.6%	LE+Low IntraCT	
3	331	663	0.004	0.004	HOMO->LUMO+10 HOMO-1->LUMO+11	16.8% 16.7%		
4	331	663	0.001	0.082	HOMO-1->LUMO+10 HOMO-1->LUMO+11	17.7% 17.6%		
5	295	590	0.029	1.367	-	-		
6	295	590	0.007	2.014	-	-		
7	291	582	0.003	24.174	-	-		
8	290	581	0.000	37.635	-	-		
9	289	579	0.047	23.782	-	-		
10	289	579	0.008	17.590	-	-		

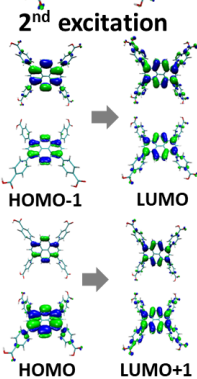


Table B.34. Summary of the electronic transitions involved in 1PA and 2PA for the TrimerA extracted from MOF NU-901.

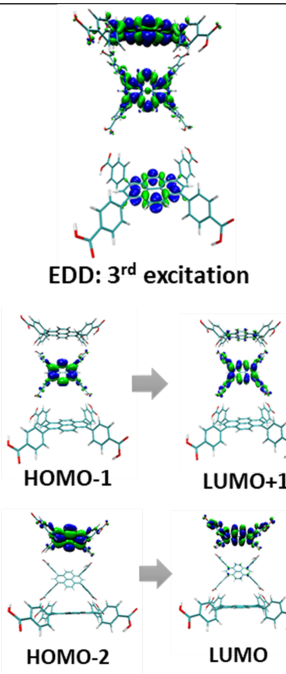
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	381	763	0.0138	0.1111	HOMO-1->LUMO+1 HOMO-2->LUMO	42.1% 39.7%		 EDD: 3rd excitation HOMO-1 → LUMO+1 HOMO-2 → LUMO
2	376	753	0.1707	0.1430	HOMO->LUMO+2	80.5%		
3	371	743	2.4460	1.0257	HOMO-1->LUMO+1 HOMO-2->LUMO	43.0% 37.6%	LE+IntraCT	
4	331	663	0.0020	0.0470	HOMO-2->LUMO+13	27.1%		
5	331	663	0.0037	0.0433	HOMO-1->LUMO+9	27.7%		
6	331	663	0.0025	0.0436	HOMO->LUMO+16 HOMO-4->LUMO+2	38.0% 29.8%		
7	310	621	0.0180	0.1385	-	-		
8	298	596	0.0100	0.4058	-	-		
9	295	591	0.0279	1.4636	-	-		
10	294	589	0.0142	1.7364	-	-		

Table B.35. Summary of the electronic transitions involved in 1PA and 2PA for the TrimerB extracted from MOF NU-901.

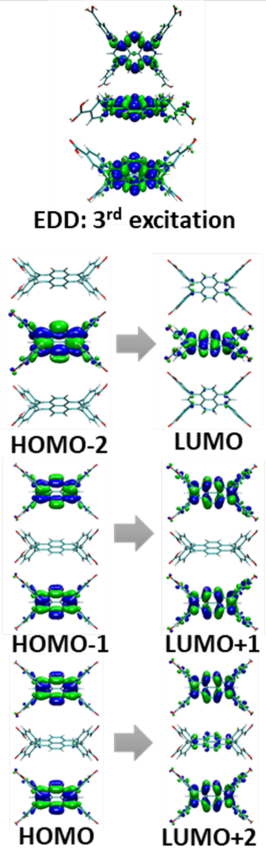
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	383	766	0.0451	0.2602	HOMO-2->LUMO HOMO-1->LUMO+1	42.3% 20.9%		 EDD: 3rd excitation HOMO-2 LUMO HOMO-1 LUMO+1 HOMO LUMO+2
2	377	755	0.0002	0.0451	HOMO->LUMO+1 HOMO-1->LUMO+2	46.0% 41.4%		
3	370	741	2.4638	3.5556	HOMO-2->LUMO HOMO-1->LUMO+1 HOMO->LUMO+2	39.6% 26.2% 26.0%	LE IntraCT InterCT	
4	331	663	0.0024	0.0110	HOMO-2->LUMO+13	25.9%		
5	331	663	0.0002	0.1351	HOMO->LUMO+15 HOMO-1->LUMO+14	17.7% 17.5%		
6	331	663	0.0054	0.0392	HOMO-1->LUMO+15	17.6%		
7	310	621	0.0428	0.2426	-	-		
8	310	620	0.0000	0.0545	-	-		
9	298	596	0.0144	0.0493	-	-		
10	298	596	0.0014	0.8785	-	-		

Table B.36. Summary of the electronic transitions involved in 1PA and 2PA for the TetramerA extracted from MOF NU-901.

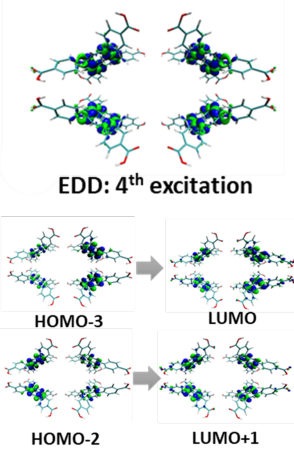
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	382	764	0.0000	0.1019	HOMO->LUMO HOMO-1->LUMO+1	20.9% 20.9%		 EDD: 4th excitation HOMO-3 → LUMO HOMO-2 → LUMO+1
2	380	760	0.0002	0.0000	HOMO-1->LUMO HOMO->LUMO+1	23.6% 23.6%		
3	374	749	0.0000	0.0459	HOMO-2->LUMO HOMO-3->LUMO+1	20.5% 20.5%		
4	370	740	3.3034	1.4843	HOMO-3->LUMO HOMO-2->LUMO+1	23.1% 23.1%	LE	
5	331	663	0.0000	0.0028	-	-		
6	331	663	0.0033	0.0000	-	-		
7	331	663	0.0069	0.0350	-	-		
8	331	663	0.0013	0.0258	-	-		
9	310	621	0.0002	0.0962	-	-		
10	310	621	0.0338	0.1929	-	-		

Table B.37. Summary of the electronic transitions involved in 1PA and 2PA for the TetramerB extracted from MOF NU-901.

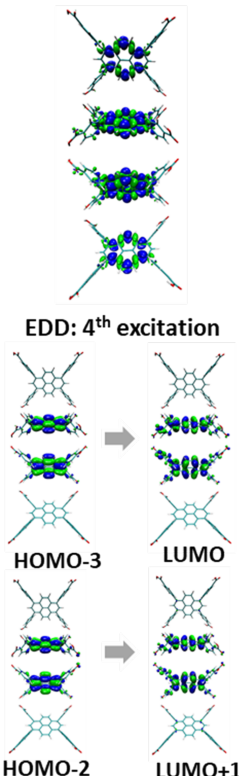
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	384	768	0.0000	0.39767	HOMO-2->LUMO HOMO-3->LUMO+1	35.4% 32.2%		 EDD: 4th excitation HOMO-3 LUMO HOMO-2 LUMO+1
2	380	761	0.1108	0.02585	HOMO-1->LUMO+2 HOMO->LUMO+3	26.5% 24.9%		
3	375	750	0.0002	0.00502	HOMO->LUMO+2 HOMO-1->LUMO+3	31.6% 30.5%		
4	369	739	3.1382	5.71641	HOMO-3->LUMO HOMO-2->LUMO+1	30.7% 29.4%	LE + low intraCT	
5	332	664	0.0029	0.00134	HOMO-2->LUMO+18	16.0%		
6	331	663	0.0020	0.03162	HOMO-3->LUMO+18	15.8%		
7	331	663	0.0015	0.00181	HOMO->LUMO+19	15.9%		
8	331	663	0.0043	0.17362	HOMO-1->LUMO+19	16.3%		
9	311	622	0.0668	0.39717	-	-		
10	310	621	0.0000	0.00868	-	-		

Table B.38. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF SrTBAPy.

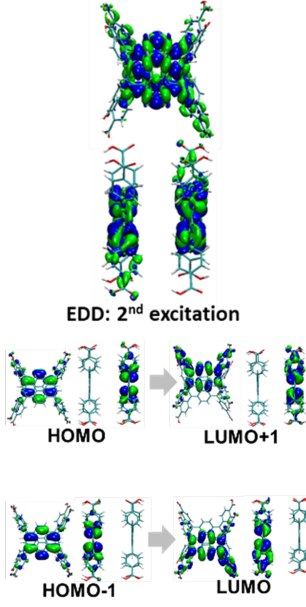
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	340	681	0.0037	2.1097	HOMO-1->LUMO HOMO->LUMO+1	50.9% 41.7%	LE+IntraCT	 EDD: 2nd excitation HOMO → LUMO+1 HOMO-1 → LUMO
2	333	666	1.4422	0.2320	HOMO->LUMO+1 HOMO-1->LUMO	50.2% 40.8%	LE+IntraCT	
3	321	642	0.0023	0.9348	HOMO->LUMO+2 HOMO-2->LUMO+1	33.4% 31.4%		
4	320	641	0.0096	0.3933	HOMO-3->LUMO HOMO-1->LUMO+2	31.4% 24.6%		
5	276	553	0.0000	0.0071	HOMO->LUMO	99.3%		
6	275	551	0.0014	0.0625	HOMO-4->LUMO+9	32.8%		
7	275	550	0.1672	98.6116	HOMO-1->LUMO+2	48.8%		
8	271	543	0.2487	30.3391	HOMO->LUMO+7	29.3%		
9	266	533	0.0013	14.1566	-	-		
10	266	533	0.0484	2.6717	-	-		

Table B.39. Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF SrTBAPy.

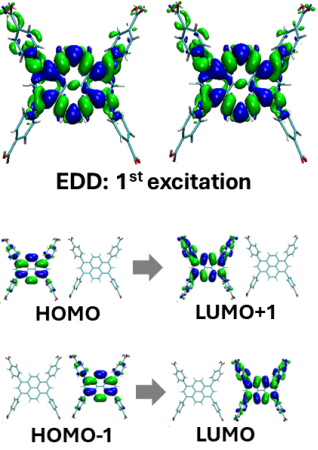
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	338	676	1.893	1.0141	HOMO->LUMO+1 HOMO-1->LUMO	42.7% 42.6%	Low intraCT + LE	 EDD: 1st excitation HOMO → LUMO+1 HOMO-1 → LUMO
2	334	669	0.000	0.0568	HOMO-1->LUMO HOMO->LUMO+1	45.8% 45.7%		
3	321	642	0.000	0.0379	HOMO-1->LUMO+2 HOMO-3->LUMO HOMO->LUMO+3	22.1% 17.1% 13.9%		
4	321	642	0.010	2.2419	HOMO->LUMO+3 HOMO-2->LUMO+1 HOMO-3->LUMO HOMO-1->LUMO+2	19.9% 19.9% 12.9% 12.3%		
5	279	559	0.027	0.0443	-	-		
6	275	551	0.073	2.7044	-	-		
7	274	549	0.001	0.0362	HOMO-5->LUMO+11 HOMO-5->LUMO+7	21.3% 15.9%		
8	271	543	0.003	0.1421	HOMO-7->LUMO+6 HOMO-7->LUMO+10	16.1% 13.3%		
9	271	542	0.058	25.0487	HOMO->LUMO+3 HOMO->LUMO+7	20.5% 20.1%		
10	270	541	0.211	121.974	HOMO-1->LUMO+6 HOMO->LUMO+7 HOMO-1->LUMO+2	27.4% 13.2% 11.2%		

Table B.40. Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF SrTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	337	675	0.007	1.6697	HOMO-1→LUMO HOMO→LUMO+1	52.1% 39.9%		EDD: 2nd excitation HOMO → LUMO HOMO-1 → LUMO+1
2	335	671	1.591	0.0820	HOMO→LUMO+1 HOMO-1→LUMO	52.0% 39.8%	Low intraCT + LE	
3	321	642	0.007	0.7899	HOMO-3→LUMO HOMO-1→LUMO+2	33.0% 32.1%		
4	320	641	0.004	1.1958	HOMO-2→LUMO+1 HOMO→LUMO+3	33.2% 29.0%		
5	281	563	0.011	0.0186	HOMO-11→LUMO+5	14.4%		
6	277	555	0.005	0.1390	HOMO-4→LUMO+11 HOMO-4→LUMO+7	32.5% 18.9%		
7	275	551	0.119	2.1869	HOMO-10→LUMO+2	11.1%		
8	271	543	0.503	53.711	HOMO→LUMO+6 HOMO→LUMO+3	26.9% 24.3%		
9	271	542	0.186	97.9861	HOMO-1→LUMO+7 HOMO-1→LUMO+2	27.9% 21.3%		
10	269	538	0.006	1.3731	HOMO-8→LUMO+9	22.6%		

Table B.41. Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF SrTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	337	674	1.7089	1.5457	HOMO→LUMO+1 HOMO-1→LUMO	50.1% 40.7%	Low intraCT + LE	EDD: 1st excitation HOMO → LUMO+1 HOMO-1 → LUMO
2	336	673	0.0042	0.0015	HOMO-1→LUMO HOMO→LUMO+1	50.2% 40.7%		
3	321	642	0.0059	1.1801	HOMO-2→LUMO+1 HOMO→LUMO+2 HOMO→LUMO+5	33.4% 30.7% 11.1%		
4	320	641	0.0052	0.7918	HOMO-3→LUMO HOMO-1→LUMO+3	33.3% 31.8%		
5	275	550	0.1052	4.7629	-	-		
6	272	545	0.3590	52.874	HOMO→LUMO+2 HOMO→LUMO+6	18.3% 14.5%		
7	271	543	0.0063	0.2030	HOMO-7→LUMO+11 HOMO-7→LUMO+6	20.6% 18.5%		
8	271	542	0.1889	87.5601	HOMO-1→LUMO+7 HOMO-1→LUMO+3	32.2% 18.8%		
9	270	540	0.0367	51.969	HOMO→LUMO+6	20.0%		
10	267	535	0.0779	10.924	HOMO-9→LUMO+10 HOMO-9→LUMO+7	13.9% 13.8%		

Table B.42. Summary of the electronic transitions involved in 1PA and 2PA for the TrimerA extracted from MOF SrTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	341	683	0.0455	0.72033	HOMO-2->LUMO+1	18.6%		
2	337	675	0.0038	1.17607	HOMO-1->LUMO+2 HOMO->LUMO	30.9% 27.4%		
3	331	663	1.9703	0.5298	HOMO-1->LUMO+2	21.8%	InterCT	
4	320	641	0.0036	0.92602	HOMO-2->LUMO+5	25.2%		
5	320	641	0.0077	0.19765	HOMO->LUMO+3	21.6%		
6	320	641	0.0058	0.38450	HOMO-1->LUMO+4	26.6%		
7	276	552	0.0017	0.0506	HOMO-6->LUMO+17	27.9%		
8	275	550	0.1785	81.6169	HOMO->LUMO+3	49.4%		
9	270	541	0.0351	7.0119	-	-		
10	270	540	0.0023	0.4212	HOMO-1->LUMO+1 HOMO-1->LUMO	36.2% 33.3%		

Table B.43. Summary of the electronic transitions involved in 1PA and 2PA for the Monomer+SBU(Sr) extracted from MOF SrTBAPy.

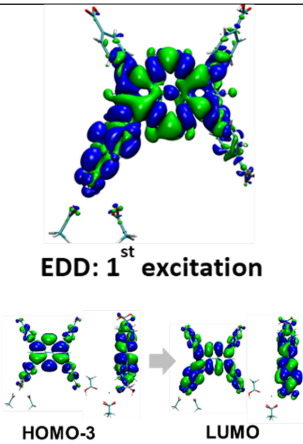
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	339	679	0.8255	10.8425	HOMO-3->LUMO	90.1%	IntraCT + 0.45% LMCT	 EDD: 1st excitation HOMO-3 LUMO
2	321	642	0.0050	3.0070	HOMO->LUMO	32.7%		
3	321	642	0.0120	0.85237	HOMO->LUMO	29.1%		
4	301	603	0.0000	0.0437	HOMO-1->LUMO HOMO-1->LUMO+1	57.5% 28.5%		
5	296	592	0.0011	0.51509	HOMO-2->LUMO HOMO-2->LUMO+1	55.9% 28.7%		
6	285	570	0.0190	1.7546	HOMO-8->LUMO+3	22.9%		
7	283	566	0.3209	199.116	HOMO-3->LUMO+1	64.5%		
8	271	543	0.0001	0.0520	HOMO-4->LUMO	36.3%		
9	270	541	0.0002	1.04045	HOMO-5->LUMO	54.9%		
10	269	539	0.0005	0.2744	HOMO->LUMO+6 HOMO->LUMO+8	54.9% 21.3%		

Table B.44. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+SBU(Sr) extracted from MOF SrTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	342	685	0.0379	3.8424	HOMO-3->LUMO HOMO-4->LUMO+1	58.5% 31.2%		
2	335	670	1.4064	7.0511	HOMO-4->LUMO+1 HOMO-3->LUMO	56.0% 27.8%	LE+Inte rCT+ 0.21% LMCT	
3	323	647	0.0007	1.4406	HOMO->LUMO HOMO->LUMO+2	60.4% 31.7%		
4	321	642	0.0165	1.2868	HOMO-9->LUMO	28.0%		
5	321	642	0.0050	0.34987	HOMO-8->LUMO+1	30.4%		
6	305	610	0.0022	3.44603	HOMO->LUMO+3 HOMO->LUMO+1	49.4% 36.3%		
7	304	608	0.0001	0.06519	HOMO-1->LUMO HOMO-1->LUMO+2	54.8% 28.1%		
8	299	598	0.0006	0.3631	HOMO-2->LUMO HOMO-2->LUMO+2	53.4% 27.7%		
9	289	579	0.0071	0.16712	HOMO-10->LUMO+7	20.4%		
10	285	570	0.0004 0	1.5973	HOMO-1->LUMO+3 HOMO-1->LUMO+1	48.0% 39.8%		

Table B.45. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+2SBU(Sr) extracted from MOF SrTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	391	783	0.0008	1.69588	HOMO->LUMO HOMO->LUMO+2	60.5% 29.7%		EDD: 4th and 6th excitation HOMO-10 → LUMO+1 HOMO-12 → LUMO
2	364	728	0.0027	4.40234	HOMO->LUMO+1 HOMO->LUMO+4	40.6% 30.7%		
3	358	716	0.0000	0.04727	HOMO-1->LUMO HOMO-1->LUMO+2	61.0% 29.3%		
4	343	687	0.0036	5.14536	HOMO-12->LUMO HOMO-10->LUMO+1	46.2% 34.5%	+ Low interCT +0.34% LMCT	
5	340	681	0.0035	0.80947	HOMO-3->LUMO HOMO-3->LUMO+2	57.4% 28.1%		
6	336	672	1.4369	0.23626	HOMO-10->LUMO+1 HOMO-12->LUMO	43.3% 39.3%	Low interCT + intraCT +0.33% LMCT	
7	333	666	0.0024	0.99488	HOMO-1->LUMO+1 HOMO-1->LUMO+4	43.2% 29.5%		
8	331	662	0.0032	1.42893	HOMO-2->LUMO+1 HOMO-2->LUMO+3	51.2% 27.1%		
9	327	654	0.0004	0.55646	HOMO->LUMO+1 HOMO->LUMO+4	47.1% 23.1%		
10	322	644	0.0003	0.07089	HOMO->LUMO+2 HOMO->LUMO	31.5% 25.6%		

Table B.46. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF BaTBAPy.

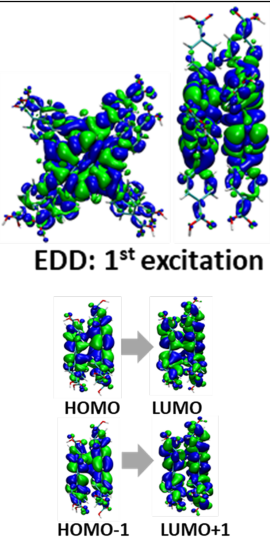
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	366	732	0.7331	0.61299	HOMO->LUMO HOMO-1->LUMO+1	59.7% 29.7%	LE+IntraCT	 EDD: 1st excitation
2	366	732	0.6972	0.5540	HOMO-1->LUMO HOMO->LUMO+1	49.0% 42.2%		
3	332	664	0.0042	0.4169	HOMO->LUMO+1 HOMO-1->LUMO	35.9% 32.2%		
4	329	659	0.0176	0.7200	HOMO-1->LUMO+1 HOMO->LUMO	54.0% 26.5%		
5	326	653	0.0052	0.1490	HOMO-3->LUMO HOMO-2->LUMO+1	18.1% 11.4 %		
6	325	650	0.0026	0.1767	HOMO->LUMO+1 HOMO-2->LUMO	13.0% 12.1%		
7	314	629	0.0022	0.0148	HOMO-9->LUMO+2	12.3%		
8	303	607	0.0044	0.04231	HOMO-6->LUMO+6	13.0%		
9	285	571	0.0828	54.580	HOMO->LUMO+3	28.6%		
10	282	565	0.0240	91.895	HOMO->LUMO+6 HOMO->LUMO+4	23.1% 14.6%		

Table B.47. Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF BaTBAPy.

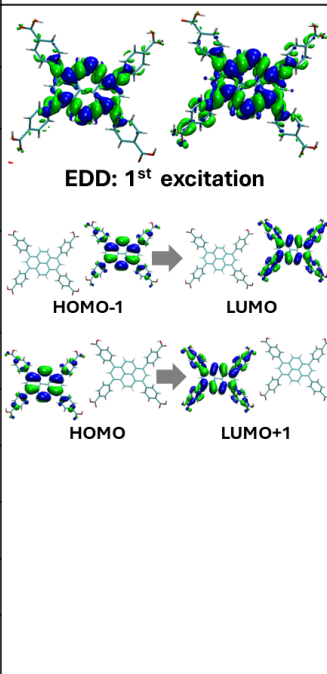
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	362.4	724	2.47739	0.754	HOMO-1 → LUMO HOMO → LUMO	55.1% 38.4%	Low intraCT + LE	 EDD: 1st excitation HOMO-1 → LUMO HOMO → LUMO+1
2	357.7	715	0.01978	0.494	HOMO → LUMO+1 HOMO-1 → LUMO	55.0% 38.3%		
3	325.4	650	0.00114	0.006	HOMO-3 → LUMO HOMO-1 → LUMO+8 HOMO-1 → LUMO+3 HOMO-1 → LUMO+2	36.6% 18.4% 15.5% 14.7%		
4	325.4	650	0.00019	0.201	HOMO-2 → LUMO+1 HOMO → LUMO+4 HOMO → LUMO+9 HOMO → LUMO+6	36.0% 18.1% 17.0% 15.9%		
5	296.0	592	0.00518	0.089	HOMO-7 → LUMO+3	22.8%		
6	292.6	585	0.00815	0.041	HOMO-9 → LUMO+4 HOMO-9 → LUMO+1	42.8% 12.1%		
7	280.4	560	0.02112	165.45	HOMO-1 → LUMO+5 HOMO-1 → LUMO+2	34.2% 19.4%		
8	279.6	559	0.13346	135.29	HOMO → LUMO+7 HOMO → LUMO+4	33.5% 28.7%		
9	278.8	557	0.01232	7.0309	HOMO-10 → LUMO+7	18.7%		
10	276.7	553	0.12911	118.87	HOMO-1 → LUMO+5 HOMO-3 → LUMO HOMO-1 → LUMO+2	18.9% 18.9% 13.9%		

Table B.48. Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF BaTBAPy.

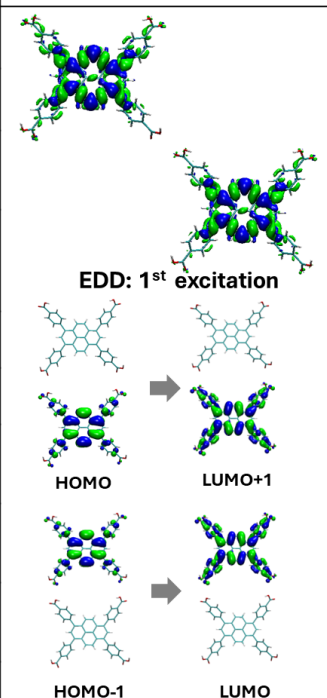
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	361	722	0.00417	0.0097	HOMO-1 → LUMO HOMO → LUMO+1	50.8% 42.6%	Low intraCT + LE	 EDD: 1st excitation HOMO-1 → LUMO+1 HOMO-1 → LUMO
2	357	715	2.13846	0.1075	HOMO → LUMO+1 HOMO-1 → LUMO	50.8% 42.6%		
3	325	650	0.00000	0.0928	HOMO-3 → LUMO HOMO-1 → LUMO+3 HOMO-1 → LUMO+8	36.5% 26.1% 19.7%		
4	325	650	0.00002	0.0424	HOMO-2 → LUMO+1 HOMO → LUMO+5 HOMO → LUMO+10 HOMO → LUMO+6	35.6% 20.2% 18.2% 14.5%		
5	296	592	0.00741	0.0476	HOMO-4 → LUMO+6 HOMO-6 → LUMO+6	21.5% 20.2%		
6	293	587	0.00952	0.0096	HOMO-11 → LUMO+3	33.2%		
7	280	560	0.02112	228.57	HOMO-1 → LUMO+4 HOMO-1 → LUMO+2 HOMO-1 → LUMO+12	28.9% 23.9% 12.8%		
8	279	558	0.01237	43.115	HOMO → LUMO+7 HOMO → LUMO+6 HOMO → LUMO+16	28.6% 15.2% 13.5%		
9	278	557	0.09647	7.7216	HOMO-7 → LUMO+7 HOMO-7 → LUMO+11 HOMO-7 → LUMO+1	23.6% 16.3% 11.3%		
10	276	553	1.67326	1.0273	HOMO-3 → LUMO HOMO-1 → LUMO+3	17.9% 16.5%		

Table B.49. Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF BaTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	360	720	2.33452	0.1500	HOMO-1 → LUMO HOMO → LUMO+1	48.0% 45.4%	Low intraCT + LE	EDD: 1st excitation HOMO-1 LUMO HOMO LUMO+1
2	359	718	0.00049	0.5496	HOMO → LUMO+1 HOMO-1 → LUMO	48.0% 45.4%		
3	325	650	0.00029	0.0090	HOMO-3 → LUMO HOMO-1 → LUMO+8 HOMO-1 → LUMO+2 HOMO-1 → LUMO+5	36.4% 17.2% 17.1% 14.9%		
4	325	650	0.00022	0.1122	HOMO-2 → LUMO+1 HOMO → LUMO+3 HOMO → LUMO+9	35.4% 31.3% 18.6%		
5	305	611	0.00659	0.3793	HOMO-4 → LUMO+4 HOMO-4 → LUMO+7	26.5% 11.7%		
6	292	585	0.00930	0.0292	HOMO-9 → LUMO+2 HOMO-9 → LUMO	40.9% 11.6%		
7	279	559	0.09993	109.74	HOMO-1 → LUMO+6 HOMO-1 → LUMO+2	39.2% 23.2%		
8	279	558	0.00084	170.409	HOMO → LUMO+7 HOMO → LUMO+13	45.7% 15.7%		
9	277	555	0.00671	0.1557	HOMO-10 → LUMO+5 HOMO-10 → LUMO+6	14.5% 13.3%		
10	276	552	1.65880	55.356	HOMO-3 → LUMO HOMO-2 → LUMO+1	11.4% 11.0%		

Table B.50. Summary of the electronic transitions involved in 1PA and 2PA for the DimerE extracted from MOF BaTBAPy.

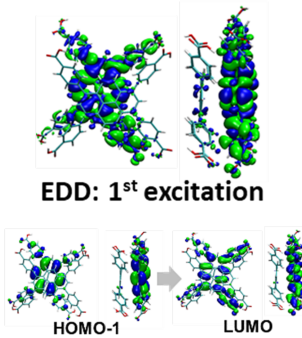
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	367	734	0.7035	3.96317	HOMO-1->LUMO	80.1%	LE+IntraCT+low InterCT	 EDD: 1st excitation HOMO-1 LUMO
2	364	728	0.6900	0.4457	HOMO->LUMO+1	82.8%		
3	344	688	0.0286	0.62132	HOMO->LUMO	81.0%		
4	327	654	0.0019	0.3401	HOMO-3->LUMO HOMO-1->LUMO+4	32.8% 19.5%		
5	326	653	0.0002	0.10241	HOMO-2->LUMO+1 HOMO->LUMO+10	31.0% 19.9%		
6	316	633	0.0061	1.2700	HOMO-1->LUMO+1	90.9%		
7	294	589	0.0122	0.6212	-	-		
8	285	571	0.4634	254.355	HOMO-1->LUMO+2	59.1%		
9	283	567	0.0199	0.62268	-	-		
10	282	565	0.0281	19.6371	HOMO-1->LUMO+3	38.7%		

Table B.51. Summary of the electronic transitions involved in 1PA and 2PA for the Trimer extracted from MOF BaTBAPy.

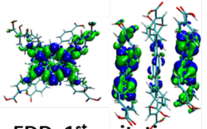
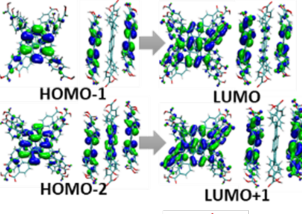
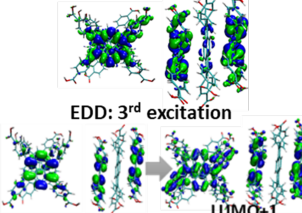
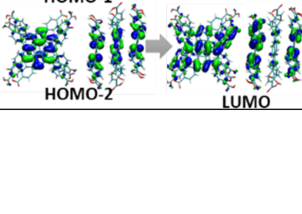
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	370	740	0.0003	7.5574	HOMO-1->LUMO HOMO-2->LUMO+1	44.4% 35.3%	InterCT	 EDD: 1st excitation
2	368	736	0.4699	0.0035	HOMO->LUMO+2	65.8%		
3	364	729	1.2812	0.0005	HOMO-1->LUMO+1 HOMO-2->LUMO	42.7% 36.0%	Intra+InterCT	 HOMO-1 LUMO HOMO-2 LUMO+1
4	339	679	0.0004	1.5748	HOMO->LUMO+1	75.6%		
5	338	677	0.0262	0.02296	HOMO->LUMO	59.7%		 HOMO-1 LUMO+1 HOMO-2 LUMO
6	328	657	0.0012	0.0000	HOMO-3->LUMO+2	24.0%		
7	327	654	0.0006	0.61442	-	-		 HOMO-1 LUMO+1 HOMO-2 LUMO
8	327	654	0.0036	0.09715	-	-		
9	322	644	0.0000	2.31530	HOMO-1->LUMO+2	88.1%		 HOMO-1 LUMO+1 HOMO-2 LUMO
10	320	641	0.0136	0.00067	HOMO-2->LUMO+2	72.2%		

Table B.52. Summary of the electronic transitions involved in 1PA and 2PA for the Monomer+SBU(Ba) extracted from MOF BaTBAPy.

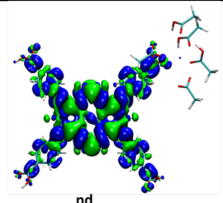
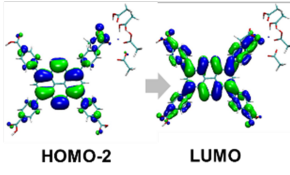
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	386	773	0.0013	1.24477	HOMO->LUMO+1 HOMO->LUMO	49.3% 42.6%		 EDD: 2nd excitation  HOMO-2 LUMO
2	363	726	1.2022	1.29766	HOMO-2->LUMO	86.2%	LE+Intr aCT+ 0.04% LMCT	
3	326	652	0.0002	0.82748	HOMO-7->LUMO HOMO-2->LUMO+5	36.2% 23.7%		
4	323	647	0.0146	6.8613	HOMO-1->LUMO+1 HOMO-1->LUMO	48.7% 39.7%		
5	314	628	0.0004	0.15616	HOMO->LUMO HOMO-3->LUMO+1	40.9% 19.0%		
6	307	614	0.0002	0.07101	HOMO-3->LUMO HOMO->LUMO+1	29.1% 23.5%		
7	306	612	0.0007	0.25014	HOMO->LUMO+7 HOMO->LUMO+8	49.9% 24.1%		
8	287	574	0.2983	369.505	HOMO-2->LUMO+1	57.3%		
9	286	572	0.0007	0.35001	HOMO->LUMO+4 HOMO->LUMO+7	71.4% 20.2%		
10	281	562	0.0115	8.05966	HOMO-4->LUMO HOMO-4->LUMO+1	50.9% 41.1%		

Table B.53. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+SBU(Ba) extracted from MOF BaTBAPy.

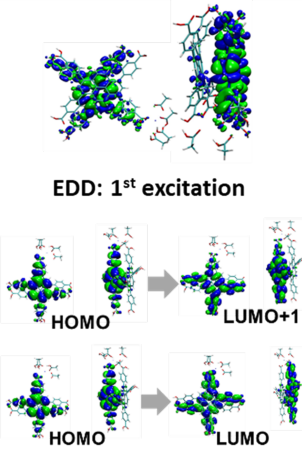
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	369	739	0.6524	13.788	HOMO->LUMO+1	82.5%	IntraCT +low InterCT +0.01% MLCT	 EDD: 1st excitation
2	368	737	0.7521	1.9488	HOMO-2->LUMO HOMO-1->LUMO	68.3% 16.3%		
3	352	705	0.0571	0.9220	HOMO->LUMO	81.4%		
4	328	657	0.0006	0.1742	HOMO->LUMO+9	20.1%		
5	328	657	0.0003	0.1097	HOMO-1->LUMO+2 HOMO-1->LUMO	35.7% 30.6%		
6	327	655	0.0025	0.4983	HOMO-9->LUMO HOMO-2->LUMO+8	32.1% 17.7%		
7	313	627	0.0140	0.7419	HOMO-2->LUMO+1 HOMO-1->LUMO+1	74.8% 16.8%		
8	302	605	0.0076	2.6786	HOMO-1->LUMO+1 HOMO-1->LUMO+19	23.9% 13.4%		
9	297	594	0.0669	5.4284	HOMO->LUMO+2 HOMO-3->LUMO	25.3% 22.6%		
10	291	583	0.3056	106.00	HOMO-2->LUMO+2 HOMO->LUMO+2	31.4% 14.5%		

Table B.54. Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+2SBU(Ba) extracted from MOF BaTBAPy.

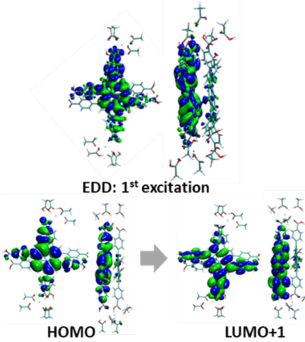
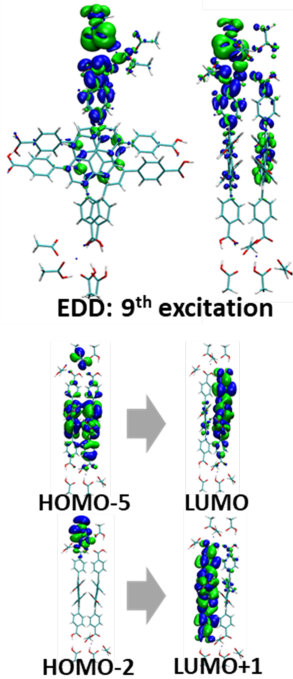
Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	372	745	0.6579	29.5991	HOMO->LUMO+1	78.9%	LE + Low intraC T+0.18 % LMCT	
2	369	738	0.8007	0.31699	HOMO-3->LUMO	83.2%		
3	353	707	0.0600	1.60884	HOMO->LUMO	80.8%		
4	330	661	0.0001	0.55071	HOMO-2->LUMO HOMO-2->LUMO+2	36.0% 29.9%		
5	330	660	0.0018	1.26410	HOMO->LUMO+9	16.7%		
6	327	655	0.0022	0.06622	HOMO-15->LUMO HOMO-3->LUMO+8	28.2% 18.5%		
7	315	631	0.0194	1.94932	HOMO-3->LUMO+1	87.3%		
8	307	615	0.0000	0.05558	HOMO-1->LUMO HOMO-1->LUMO+4	46.6% 25.42%		
9	305	610	0.0093	3.91181	HOMO-2->LUMO+1 HOMO-2->LUMO+22	30.0% 14.1%		
10	300	600	0.3286	95.5379	HOMO->LUMO+3	47.0%		

Table B.55. Summary of the electronic transitions involved in 1PA and 2PA for the DimerE+2SBU(Ba) extracted from MOF BaTBAPy.

Exc	1PA [nm]	2PA [nm]	Osc. Str.	2PA [GM]	Transition	Contrib	Type	Orbitals main transition
1	511	1022	0.0000	0.0329	HOMO->LUMO HOMO->LUMO+2	63.5% 26.2%		 EDD: 9th excitation HOMO-5 → LUMO HOMO-2 → LUMO+1
2	484	968	0.0000	0.0457	HOMO->LUMO+1 HOMO->LUMO+3	46.4% 20.6%		
3	409	818	0.0014	2.6352	HOMO-1->LUMO HOMO-1->LUMO+2	64.2% 26.4%		
4	396	792	0.0000	0.0505	HOMO->LUMO+2 HOMO->LUMO	64.7% 25.9%		
5	391	782	0.0005	0.8025	HOMO-1->LUMO+1 HOMO-1->LUMO+3	46.9% 20.5%		
6	387	774	0.0000	0.0225	HOMO->LUMO+1 HOMO->LUMO+5	39.4% 17.7%		
7	386	772	0.0003	0.2137	HOMO-2->LUMO HOMO-2->LUMO+2	52.3% 20.1%		
8	376	753	0.3962	17.7228	HOMO-5->LUMO HOMO-2->LUMO+1	30.5% 16.6%		
9	376	753	0.2875	24.9148	HOMO-5->LUMO HOMO-2->LUMO+1	24.1% 19.6%	Low intraCT + InterCT + 4% MLCT	
10	368	736	0.7990	2.1700	HOMO-7->LUMO+1 HOMO-5->LUMO+1	52.9% 29.0%		

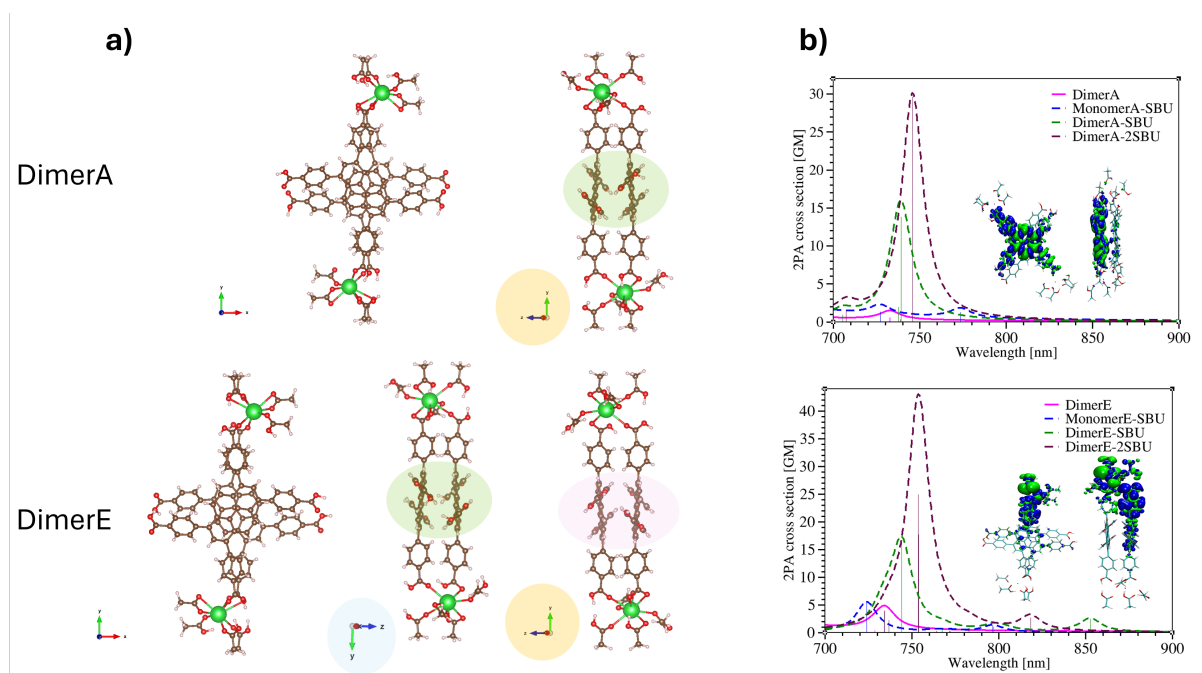


Figure B.11. Comparison of two stacking motifs extracted from the BaTBAPy MOF. In panel a), DimerA is shown in the upper row and DimerE in the lower row. The highlighted circles indicate different viewing orientations: in one view (yellow/pink), DimerE appears different from DimerA, whereas after rotating the view (blue), the relative arrangement in DimerE becomes analogous to that of DimerA. Panel b) shows the corresponding 2PA absorption spectra for the extracted systems; the insets display the electron density difference (EDD) plots of the first excitation.

Table B.56. Summary of the inter-fragment charge transfer (IFCT) analysis performed for the characteristic excitations contributing to the 2PA response of the BaTBAPy and SrTBAPy MOFs, as discussed in the main text and identified in the tables above, in Table B.38-Table B.55. All values are given in % and were calculated using molecular fragments (mol1 and mol2) defined as the complete H₄TBAPy linkers. H and E denote the contribution of each fragment to the hole and electron, respectively, in the charge-transfer matrix, while 1→2 and 2→1 indicate the % of electron transfer between the fragments. The intrinsic charge-transfer percentage (ICTP) and apparent charge-transfer percentage (ACTP) corresponding to the CT contribution are also reported. The local excitation (LE) contribution can be estimated as 100% – CT. For clarity, the ACTP between the dimer and the SBU (i.e., CT_{dimer-SBU}, mainly indicating LMCT) is also provided. CT contributions arising from dimer-dimer interactions were calculated for the extracted dimers and under the influence of the SBU (indicated with an asterisk, *). Although SBU fragments were not explicitly included in the IFCT analysis, they were present in the EDD analysis. The corresponding 2PA cross-section values are also listed. The corresponding excitation in the isolated monomer exhibits a purely LE character.

	H _{mol1}	H _{mol2}	E _{mol1}	E _{mol2}	1→2	2→1	ICTP CT	ACTP CT	CT _{dimer-SBU} ^a	2PA
Ba-based MOF										
dimerA	37.37	62.63	37.21	62.79	23.46	23.31	46.77	0.15	-	0.61
dimerE	3.25	96.75	2.33	97.67	3.17	2.25	5.42	0.92	-	3.96
dimerA-2SBU*	98.30	1.53	95.97	3.76	3.69	1.46	5.16	2.23	0.18 and 0.01 ^b	29.60
Sr-based MOF										
dimerA	45.04	54.96	45.06	54.94	24.75	24.76	49.51	0.02	-	2.11
dimerA-2SBU*	44.55	55.10	44.45	52.20	24.59	24.49	49.08	0.10	0.20 and 0.14 ^c	5.14

^a - calculated considering SBU explicitly using a dimer as a single fragment

^b - 0.04 % in the monomer-1SBU case (2PA of 1.30 GM) and 0.01 % for the dimer-1SBU (2PA of 13.80 GM)

^c - 0.45 % in the monomer-1SBU case (2PA of 10.84 GM) and 0.21 % for the dimer-1SBU (2PA of 7.05 GM)

C. Permissions to Print

This work contains material adapted from previously published scientific journal articles. Permissions for reuse or reprint of the relevant content have been obtained from the respective copyright owners.

1. chapter 2: Parts of the theoretical background regarding photoswitchable framework materials were adapted from:

H. Pacheco Hernandez, S. Hecht, W. Wenzel, L. Heinke, M. Kozłowska. “Photoswitching Conduction in Framework Materials.” *Advanced Functional Materials*, 2025, **36**, e202512262. DOI: 10.1002/adfm.202512262

Licensed under CC BY 4.0.

2. chapter 3: Content was adapted from:

M. Mostaghimi, **H. Pacheco Hernandez***, Y. Jiang, W. Wenzel, L. Heinke, M. Kozłowska. “On-off conduction photoswitching in modelled spiropyran-based metal-organic frameworks.” *Communications Chemistry*, 2023, **6**, 275. DOI: 10.1038/s42004-023-01072-4

Licensed under CC BY 4.0. *Shared first authorship.

3. chapter 4: Content was adapted from the following publications:

(a) S. N. Deger, **H. Pacheco Hernandez**, Y. Cui, H. Hao, V. Ramm, D. C. Mayer, K. N. Truong, R. A. Fischer, J. Hauer, M. Kozłowska, A. Pöthig. “Modulating Two-Photon Absorption in a Pyrene-Based MOF Series: An In-Depth Investigation of Structure–Property Relationships.” *Advanced Functional Materials*, 2025. DOI: 10.1002/adfm.202506660

Licensed under CC BY 4.0. *Computational work performed by H. Pacheco Hernandez.*

(b) **H. Pacheco Hernandez**, M. Kozłowska. “Intermolecular Packing Effects on the Two-Photon Absorption of the H₄TCPE Linker.” *Frontiers in Chemistry*, 2026, **14**, 1805869. DOI: 10.3389/fchem.2026.1805869

Licensed under CC BY.

D. List of Publications

Peer-Reviewed Articles

1. M. Mostaghimi, **H. Pacheco Hernandez**^{*}, Y. Jiang, W. Wenzel, L. Heinke, M. Kozłowska. “On-off conduction photoswitching in modelled spiropyran-based metal-organic frameworks.” *Communications Chemistry*, 2023, **6**, 275. DOI: 10.1038/s42004-023-01072-4
**Shared first authorship*
2. S. N. Deger, **H. Pacheco Hernandez**, Y. Cui, H. Hao, V. Ramm, D. C. Mayer, K. N. Truong, R. A. Fischer, J. Hauer, M. Kozłowska, A. Pöthig. “Modulating Two-Photon Absorption in a Pyrene-Based MOF Series: An In-Depth Investigation of Structure-Property Relationships.” *Advanced Functional Materials*, 2025. DOI: 10.1002/adfm.202506660
Computational work performed by H. Pacheco Hernandez
3. **H. Pacheco Hernandez**, S. Hecht, W. Wenzel, L. Heinke, M. Kozłowska. “Photoswitching Conduction in Framework Materials.” *Advanced Functional Materials*, 2025, **36**, e202512262. DOI: 10.1002/adfm.202512262
4. **H. Pacheco Hernandez**, M. Kozłowska. “Intermolecular Packing Effects on the Two-Photon Absorption of the H₄TCPE linker.” *Frontiers in Chemistry*, 2026, **14**, 1805869. DOI: 10.3389/fchem.2026.1805869
5. E. López-López, A. Delgado Monzón, A. C. Forero-Girón, N. M. Aguilar, S. T. R. Velásquez, E. G. Sánchez-Rueda, M. F. del Cid Hernández, R. Mojica, H. Salamanca-Ortiz, N. Rehnitz, K. M. Aguilar-Pérez, M. I. Quant Amézquita, G. López-Molina, **H. Pacheco Hernández**, E. Cienfuegos-Pecina, P. Madrazo de Otaduy, M. Escobar-Rosales. “Huella latinoamericana en Lindau Nobel Laureate Meeting 2025 (#LINO2025).” *Latin American Journal of Clinical Sciences and Medical Technology*, 2025, **7**, 67-72. DOI: 10.34141/LJCS9882940

E. List of Conference Contributions

1. **H. Pacheco Hernandez.** The 3DMM2O Conference, Germany, 2026. (Poster)
2. **H. Pacheco Hernandez.** EWMB 2025, Mexico, 2025. (Poster)
3. **H. Pacheco Hernandez.** 74th Lindau Nobel Laureate Meeting in Chemistry, Lindau, Germany, 2025.
Breaking Barriers in Science Workshop participant; contributed to the Lindau Annual Report on the Formal and Hidden Career Curriculum.
4. **H. Pacheco Hernandez.** CRYSTAL23, Italy, 2025. (Poster)
Best Poster Award
5. **H. Pacheco Hernandez.** MOF International 2024, Singapore, 2024. (Poster)
6. **H. Pacheco Hernandez.** ETSF 2024, France, 2024. (Poster)
7. **H. Pacheco Hernandez.** SIMPLAIX 2024, Karlsruhe, Germany, 2024. (Poster)
8. **H. Pacheco Hernandez.** PISACMS 2023, France, 2023. (Poster)
Best Poster Award
9. **H. Pacheco Hernandez.** eChem 2023, Poland, 2023. (Poster)

F. Statement of AI Utilization

I hereby declare the use of the following generative AI tools in the preparation of this assignment:

1. **Grammarly:** Used for language proofreading, suggesting sentence structure improvements, and text formatting.
2. **Claude (Anthropic):** Used for proofreading, translation of the English abstract to German which was further reviewed and edited by a German native speaker for accuracy and terminology. Finally, for typesetting purposes into LaTeX syntax. The underlying content is my own work; the tool was used only to assist with formatting.

I take full responsibility for the content, accuracy, and originality of this thesis.

G. Bibliography

- [1] Helmy Pacheco Hernandez, Stefan Hecht, Wolfgang Wenzel, Lars Heinke, and Mariana Kozłowska. Photoswitching conduction in framework materials. *Advanced Functional Materials*, n/a(n/a):e12262. doi: <https://doi.org/10.1002/adfm.202512262>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adfm.202512262>.
- [2] Vadia Foziya Yusuf, Naved I. Malek, and Suresh Kumar Kailasa. Review on metal–organic framework classification, synthetic approaches, and influencing factors: Applications in energy, drug delivery, and wastewater treatment. *ACS Omega*, 7(49):44507–44531, 2022. doi: [10.1021/acsomega.2c05310](https://doi.org/10.1021/acsomega.2c05310). URL <https://doi.org/10.1021/acsomega.2c05310>.
- [3] Dongxiao Li, Anurag Yadav, Hong Zhou, Kaustav Roy, Pounraj Thanasekaran, and Chengkuo Lee. Advances and applications of metal-organic frameworks (mofs) in emerging technologies: A comprehensive review. *Global Challenges*, 8(2):2300244, 2024. doi: <https://doi.org/10.1002/gch2.202300244>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/gch2.202300244>.
- [4] Zhiling Zheng, Zichao Rong, Ha L. Nguyen, and Omar M. Yaghi. Structural chemistry of zeolitic imidazolate frameworks. *Inorganic Chemistry*, 62(51):20861–20873, 2023. doi: [10.1021/acs.inorgchem.3c02322](https://doi.org/10.1021/acs.inorgchem.3c02322). URL <https://doi.org/10.1021/acs.inorgchem.3c02322>. PMID: 38063312.
- [5] Antoine Mazel, Lucas Rocco, Nicolas Penin, and Aline Rougier. Oriented surface-anchored metal–organic frameworks (surmofs) as electrochromic thin films. *Advanced Optical Materials*, 11(9):2202939, 2023. doi: <https://doi.org/10.1002/adom.202202939>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adom.202202939>.
- [6] Yi-Hong Xiao, Yi-Bo Tian, Zhi-Gang Gu, and Jian Zhang. Surface-coordinated metal-organic framework thin films (surmofs): From fabrication to energy applications. *EnergyChem*, 3(6): 100065, 2021. ISSN 2589-7780. doi: <https://doi.org/10.1016/j.enchem.2021.100065>. URL <https://www.sciencedirect.com/science/article/pii/S2589778021000154>.
- [7] Jinxuan Liu, Binit Lukose, Osama Shekhah, Hasan Kemal Arslan, Peter Weidler, Hartmut Gliemann, Stefan Bräse, Sylvain Grosjean, Adelheid Godt, Xinliang Feng, Klaus Müllen, Ioan-Bogdan Magdau, Thomas Heine, and Christof Wöll. A novel series of isorecticular metal organic

- frameworks: realizing metastable structures by liquid phase epitaxy. *Scientific Reports*, 2(1):921, 2012. doi: 10.1038/srep00921. URL <https://doi.org/10.1038/srep00921>.
- [8] Keyu Geng, Ting He, Ruoyang Liu, Sasanka Dalapati, Ke Tian Tan, Zhongping Li, Shanshan Tao, Yifan Gong, QiuHong Jiang, and Donglin Jiang. Covalent organic frameworks: Design, synthesis, and functions. *Chemical Reviews*, 120(16):8814–8933, 2020. doi: 10.1021/acs.chemrev.9b00550. URL <https://doi.org/10.1021/acs.chemrev.9b00550>. PMID: 31967791.
- [9] Shengbo Ge, Kexin Wei, Wanxi Peng, Runzhou Huang, Esther Akinlabi, Hongyan Xia, Muhammad Wakil Shahzad, Xuehua Zhang, Ben Bin Xu, and Jianchun Jiang. A comprehensive review of covalent organic frameworks (cofs) and their derivatives in environmental pollution control. *Chemical Society Reviews*, 53:11259–11302, 2024. doi: 10.1039/D4CS00521J. URL <http://dx.doi.org/10.1039/D4CS00521J>.
- [10] Taewoong Kim, Jaewon Kim, Nayeon Kim, and Hyunseob Lim. Recent advances in single crystal cofs from synthesis to applications. *Chemical Communications*, 61:17516–17529, 2025. doi: 10.1039/D5CC04701C. URL <http://dx.doi.org/10.1039/D5CC04701C>.
- [11] Yuyang Tian and Guangshan Zhu. Porous aromatic frameworks (pafs). *Chemical Reviews*, 120(16):8934–8986, 2020. doi: 10.1021/acs.chemrev.9b00687. URL <https://doi.org/10.1021/acs.chemrev.9b00687>. PMID: 32101403.
- [12] Jiantang Li and Banglin Chen. Flexible hydrogen-bonded organic frameworks (hofs): opportunities and challenges. *Chemical Science*, 15:9874–9892, 2024. doi: 10.1039/D4SC02628D. URL <http://dx.doi.org/10.1039/D4SC02628D>.
- [13] Penghao Li, Matthew R. Ryder, and J. Fraser Stoddart. Hydrogen-bonded organic frameworks: A rising class of porous molecular materials. *Accounts of Materials Research*, 1(1):77–87, 2020. doi: 10.1021/accountsmr.0c00019. URL <https://doi.org/10.1021/accountsmr.0c00019>.
- [14] Rui-Biao Lin, Yabing He, Peng Li, Hailong Wang, Wei Zhou, and Banglin Chen. Multifunctional porous hydrogen-bonded organic framework materials. *Chemical Society Reviews*, 48:1362–1389, 2019. doi: 10.1039/C8CS00155C. URL <http://dx.doi.org/10.1039/C8CS00155C>.
- [15] Ivo Stassen, Nicholas C. Burtch, A. A. Talin, Paolo Falcaro, Mark D. Allendorf, and Rob Ameloot. An updated roadmap for the integration of metal–organic frameworks with electronic devices and chemical sensors. *Chemical Society Reviews*, 46:3853–3914, 2017. doi: 10.1039/C7CS90048A.
- [16] O. M. Yaghi, Guangming Li, and Hailian Li. Selective binding and removal of guests in a microporous metal–organic framework. *Nature*, 378(6558):703–706, 1995. doi: 10.1038/378703a0. URL <https://doi.org/10.1038/378703a0>.

- [17] Ralph Freund, Stefano Canossa, Seth M. Cohen, Wei Yan, Hexiang Deng, Vincent Guillermin, Mohamed Eddaoudi, David G. Madden, David Fairen-Jimenez, Hao Lyu, Lauren K. Macreadie, Zhe Ji, Yuanyuan Zhang, Bo Wang, Frederik Haase, Christof Wöll, Orysia Zaremba, Jacopo Andreato, Stefan Wuttke, and Christian S. Diercks. 25 years of reticular chemistry. *Angewandte Chemie International Edition*, 60(45):23946–23974, 2021. doi: <https://doi.org/10.1002/anie.202101644>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.202101644>.
- [18] Omar M. Yaghi, Michael O’Keeffe, Nathan W. Ockwig, Hee K. Chae, Mohamed Eddaoudi, and Jaheon Kim. Reticular synthesis and the design of new materials. *Nature*, 423(6941):705–714, 2003. doi: 10.1038/nature01650. URL <https://doi.org/10.1038/nature01650>.
- [19] Introduction to metal–organic frameworks. *Chemical Reviews*, 112(2):673–674, 2012. doi: 10.1021/cr300014x. URL <https://doi.org/10.1021/cr300014x>. PMID: 22280456.
- [20] Riki Nakatani, Saikat Das, and Yuichi Negishi. Metal–organic frameworks as promising electrocatalysts for the nitrogen reduction reaction: mapping the research landscape and identifying future trends. *Journal of Materials Chemistry A*, 12:26350–26366, 2024. doi: 10.1039/D4TA04817B. URL <http://dx.doi.org/10.1039/D4TA04817B>.
- [21] Nur-Sultan Mussa, Kainaibek Toshtay, and Franck Dumeignil. Recent developments in the field of mof-based catalytic systems: A review. *Applied Catalysis A: General*, 708:120555, 2025. ISSN 0926-860X. doi: <https://doi.org/10.1016/j.apcata.2025.120555>. URL <https://www.sciencedirect.com/science/article/pii/S0926860X25004569>.
- [22] Mays Alhamami, Huu Doan, and Chil-Hung Cheng. A review on breathing behaviors of metal-organic-frameworks (mofs) for gas adsorption. *Materials*, 7(4):3198–3250, 2014. ISSN 1996-1944. doi: 10.3390/ma7043198. URL <https://www.mdpi.com/1996-1944/7/4/3198>.
- [23] Longyi Zhu, Bin Zhu, Jun Luo, and Bin Liu. Design and property modulation of metal–organic frameworks with aggregation-induced emission. *ACS Materials Letters*, 3(1):77–89, 2021. doi: 10.1021/acsmaterialslett.0c00477. URL <https://doi.org/10.1021/acsmaterialslett.0c00477>.
- [24] Bin Li, Hui-Min Wen, Hailong Wang, Hui Wu, Madhusudan Tyagi, Taner Yildirim, Wei Zhou, and Banglin Chen. A porous metal–organic framework with dynamic pyrimidine groups exhibiting record high methane storage working capacity. *Journal of the American Chemical Society*, 136(17):6207–6210, 2014. doi: 10.1021/ja501810r. URL <https://doi.org/10.1021/ja501810r>. PMID: 24730649.
- [25] Harrison D. Lawson, S. Patrick Walton, and Christina Chan. Metal–organic frameworks for drug delivery: A design perspective. *ACS Applied Materials & Interfaces*, 13(6):7004–7020, 2021.

doi: 10.1021/acsami.1c01089. URL <https://doi.org/10.1021/acsami.1c01089>. PMID: 33554591.

- [26] Yuanjing Cui, Yanfeng Yue, Guodong Qian, and Banglin Chen. Luminescent functional metal–organic frameworks. *Chemical Reviews*, 112(2):1126–1162, 2012. doi: 10.1021/cr200101d. URL <https://doi.org/10.1021/cr200101d>. PMID: 21688849.
- [27] Yifang Zhao, Heng Zeng, Xiao-Wei Zhu, Weigang Lu, and Dan Li. Metal–organic frameworks as photoluminescent biosensing platforms: mechanisms and applications. *Chemical Society Reviews*, 50:4484–4513, 2021. doi: 10.1039/D0CS00955E. URL <http://dx.doi.org/10.1039/D0CS00955E>.
- [28] Jing Dong, Dan Zhao, Yi Lu, and Wei-Yin Sun. Photoluminescent metal–organic frameworks and their application for sensing biomolecules. *Journal of Materials Chemistry A*, 7:22744–22767, 2019. doi: 10.1039/C9TA07022B. URL <http://dx.doi.org/10.1039/C9TA07022B>.
- [29] Agnes E. Thorarinsdottir and T. David Harris. Metal–organic framework magnets. *Chemical Reviews*, 120(16):8716–8789, 2020. doi: 10.1021/acs.chemrev.9b00666. URL <https://doi.org/10.1021/acs.chemrev.9b00666>. PMID: 32045215.
- [30] Yanfei Liu, Ting Jiang, and Zhenbao Liu. Metal-organic frameworks for bioimaging: Strategies and challenges. *Nanotheranostics*, 6(2):143–160, 2022. doi: 10.7150/ntno.63458. URL <https://doi.org/10.7150/ntno.63458>.
- [31] Lilia S. Xie, Grigorii Skorupskii, and Mircea Dincă. Electrically conductive metal–organic frameworks. *Chemical Reviews*, 120(16):8536–8580, 2020. doi: 10.1021/acs.chemrev.9b00766. URL <https://doi.org/10.1021/acs.chemrev.9b00766>. PMID: 32275412.
- [32] Zeshan Ali Sandhu, Muhammad Asam Raza, Nasser S. Awwad, Hala A. Ibrahim, Umme Farwa, Sawera Ashraf, Arooj Dildar, Eman Fatima, Sufyan Ashraf, and Furqan Ali. Metal–organic frameworks for next-generation energy storage devices; a systematic review. *Materials Advances*, 5: 30–50, 2024. doi: 10.1039/D3MA00822C. URL <http://dx.doi.org/10.1039/D3MA00822C>.
- [33] Renhao Dong, Peng Han, Himani Arora, Marco Ballabio, Melike Karakus, Zhe Zhang, Chandra Shekhar, Peter Adler, Petko St. Petkov, Artur Erbe, Stefan C. B. Mannsfeld, Claudia Felser, Thomas Heine, Mischa Bonn, Xinliang Feng, and Enrique Cánovas. High-mobility band-like charge transport in a semiconducting two-dimensional metal–organic framework. *Nature Materials*, 17(11):1027–1032, 2018. doi: 10.1038/s41563-018-0189-z. URL <https://doi.org/10.1038/s41563-018-0189-z>.
- [34] Jonas F. Pöhls and R. Thomas Weitz. Mofs and cofs in electronics: Bridging the gap between intrinsic properties and measured performance. *Advanced Functional Materials*, n/a(n/a):e13932.

- doi: <https://doi.org/10.1002/adfm.202513932>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adfm.202513932>.
- [35] Ruby A. Kharod, Justin L. Andrews, and Mircea Dincă. Teaching metal-organic frameworks to conduct: Ion and electron transport in metal-organic frameworks. *Annual Review of Materials Research*, 52:103–128, 2022. doi: 10.1146/annurev-matsci-080619-012811. URL <https://www.annualreviews.org/content/journals/10.1146/annurev-matsci-080619-012811>.
- [36] Sayed Ali Akbar Razavi, Wenmiao Chen, Hong-Cai Zhou, and Ali Morsali. Tuning redox activity in metal–organic frameworks: From structure to application. *Coordination Chemistry Reviews*, 517:216004, 2024. ISSN 0010-8545. doi: <https://doi.org/10.1016/j.ccr.2024.216004>. URL <https://www.sciencedirect.com/science/article/pii/S0010854524003503>.
- [37] Molly McVea, Christian B. Nielsen, Oliver Fenwick, and Petra Ágota Szilágyi. The design of intrinsically conductive metal-organic frameworks for thermoelectric materials. *Small Science*, 5(3): 2400469, 2025. doi: <https://doi.org/10.1002/smssc.202400469>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/smssc.202400469>.
- [38] Rajat Saha and Carlos J. Gómez García. Extrinsicly conducting mofs: guest-promoted enhancement of electrical conductivity, thin film fabrication and applications. *Chemical Society Reviews*, 53:9490–9559, 2024. doi: 10.1039/D4CS00141A. URL <http://dx.doi.org/10.1039/D4CS00141A>.
- [39] Dae-Woon Lim and Hiroshi Kitagawa. Proton transport in metal–organic frameworks. *Chemical Reviews*, 120(16):8416–8467, 2020. doi: 10.1021/acs.chemrev.9b00842. URL <https://doi.org/10.1021/acs.chemrev.9b00842>. PMID: 32407101.
- [40] Minyoung Yoon, Kyungwon Suh, Srinivasan Natarajan, and Kimoon Kim. Proton conduction in metal–organic frameworks and related modularly built porous solids. *Angewandte Chemie International Edition*, 52(10):2688–2700, 2013. doi: <https://doi.org/10.1002/anie.201206410>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.201206410>.
- [41] Kainan Xue, Shabab Hussain, Shuaikang Fan, and Xinsheng Peng. Proton conducting metal–organic frameworks with light response for multistate logic gates. *RSC Advances*, 13:12646–12653, 2023. doi: 10.1039/D3RA01252B. URL <http://dx.doi.org/10.1039/D3RA01252B>.
- [42] Fahui Xiang, Shimin Chen, Zhen Yuan, Lu Li, Zhiwen Fan, Zizhu Yao, Chulong Liu, Shengchang Xiang, and Zhangjing Zhang. Switched proton conduction in metal–organic frameworks. *JACS Au*, 2(5):1043–1053, 2022. doi: 10.1021/jacsau.2c00069. URL <https://doi.org/10.1021/jacsau.2c00069>.

- [43] Liyu Zhu, Hongbin Yang, Ting Xu, Feng Shen, and Chuanling Si. Precision-engineered construction of proton-conducting metal–organic frameworks. *Nano-Micro Letters*, 17(1):87, 2024. doi: 10.1007/s40820-024-01558-3. URL <https://doi.org/10.1007/s40820-024-01558-3>.
- [44] Gabrielle A. Leith, Corey R. Martin, Jacob M. Mayers, Preecha Kittikhunnatham, Randy W. Larsen, and Natalia B. Shustova. Confinement-guided photophysics in mofs, cofs, and cages. *Chemical Society Reviews*, 50:4382–4410, 2021. doi: 10.1039/D0CS01519A. URL <http://dx.doi.org/10.1039/D0CS01519A>.
- [45] Hang Xu and Peng Cheng. Metal–organic frameworks with aggregation-induced emission. *Aggregate*, 5(3):e518, 2024. doi: <https://doi.org/10.1002/agt2.518>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/agt2.518>.
- [46] Enrico Angioni, Ross J. Marshall, Neil J. Findlay, Jochen Bruckbauer, Benjamin Breig, David J. Wallis, Robert W. Martin, Ross S. Forgan, and Peter J. Skabara. Implementing fluorescent mofs as down-converting layers in hybrid light-emitting diodes. *Journal of Materials Chemistry C*, 7:2394–2400, 2019. doi: 10.1039/C9TC00067D. URL <http://dx.doi.org/10.1039/C9TC00067D>.
- [47] Wesley J. Newsome, Suliman Ayad, Jesus Cordova, Eric W. Reinheimer, Andres D. Campiglia, James K. Harper, Kenneth Hanson, and Fernando J. Uribe-Romo. Solid state multicolor emission in substitutional solid solutions of metal–organic frameworks. *Journal of the American Chemical Society*, 141(28):11298–11303, 2019. doi: 10.1021/jacs.9b05191. URL <https://doi.org/10.1021/jacs.9b05191>. PMID: 31265284.
- [48] Yuhan Lin, Liang Yu, Hao Wang, and Jing Li. Enhanced fluorescence by increasing dimensionality: a novel three-dimensional luminescent metal–organic framework with rigidified ligands. *CrystEngComm*, 22:5946–5948, 2020. doi: 10.1039/D0CE01092H. URL <http://dx.doi.org/10.1039/D0CE01092H>.
- [49] Jialuo Li, Shuai Yuan, Jun-Sheng Qin, Lan Huang, Riya Bose, Jiandong Pang, Peng Zhang, Zhifeng Xiao, Kui Tan, Anton V. Malko, Tahir Cagin, and Hong-Cai Zhou. Fluorescence enhancement in the solid state by isolating perylene fluorophores in metal–organic frameworks. *ACS Applied Materials & Interfaces*, 12(23):26727–26732, 2020. doi: 10.1021/acsami.0c05512. URL <https://doi.org/10.1021/acsami.0c05512>. PMID: 32406228.
- [50] E. Collini. Cooperative effects to enhance two-photon absorption efficiency: intra- versus intermolecular approach. *Physical Chemistry Chemical Physics*, 14:3725–3736, 2012. doi: 10.1039/C2CP24030K. URL <http://dx.doi.org/10.1039/C2CP24030K>.
- [51] Zbigniew L. Pianowski, editor. *Molecular Photoswitches: Chemistry, Properties, and Applications*. John Wiley & Sons, 2022. ISBN 978-3-527-82762-6. doi: 10.1002/9783527827626.

- [52] Helmy Pacheco Hernandez, Stefan Hecht, Wolfgang Wenzel, et al. Photoswitching conduction in framework materials. *Advanced Functional Materials*, 2025. doi: 10.1002/adfm.202512262.
- [53] Masahiro Irie, Tuyoshi Fukaminato, Kenji Matsuda, and Seiya Kobatake. Photochromism of diarylethene molecules and crystals: Memories, switches, and actuators. *Chemical Reviews*, 114(24):12174–12277, 2014. doi: 10.1021/cr500249p. URL <https://doi.org/10.1021/cr500249p>. PMID: 25514509.
- [54] Romain Berraud-Pache, Eduardo Santamaría-Aranda, Bernardo de Souza, Giovanni Bistoni, Frank Neese, Diego Sampredo, and Róbert Izsák. Redesigning donor-acceptor stenhouse adduct photoswitches through a joint experimental and computational study. *Chemical Science*, 12(8): 2916–2924, 2021. doi: 10.1039/d0sc06575g.
- [55] R. T. F. Jukes, J. Kühni, N. Salluce, P. Belser, L. De Cola, and F. Hartl. Photochemical, photo-physical and redox properties of novel fulgimide derivatives with attached 2,2'-bipyridine (bpy) and $[m(bpy)_3]^{2+}$ ($m = ru$ and os) moieties. *Dalton Transactions*, pages 3993–4002, 2009. doi: 10.1039/B821637C.
- [56] Sariful Molla and Subhajit Bandyopadhyay. Visible light mediated efficient photoswitching of dimethyldihydropyrenes in thin films for all-photonic logic gate applications and dynamic encryption/decryption capabilities. *Journal of Materials Chemistry C*, 12:17511–17518, 2024. doi: 10.1039/D4TC03321C.
- [57] Søren Lindbæk Broman and Mogens Brøndsted Nielsen. Dihydroazulene: from controlling photochromism to molecular electronics devices. *Physical Chemistry Chemical Physics*, 16:21172–21182, 2014. doi: 10.1039/C4CP02442G.
- [58] Jana Volarić, Wiktor Szymanski, Nadja A. Simeth, and Ben L. Feringa. Molecular photoswitches in aqueous environments. *Chemical Society Reviews*, 50:12377–12449, 2021. doi: 10.1039/D0CS00547A. URL <http://dx.doi.org/10.1039/D0CS00547A>.
- [59] S. Castellanos, F. Kapteijn, and J. Gascon. Photoswitchable metal organic frameworks: turn on the lights and close the windows. *CrystEngComm*, 18:4006–4012, 2016. doi: 10.1039/C5CE02543E. URL <http://dx.doi.org/10.1039/C5CE02543E>.
- [60] Maria-Melanie Russew and Stefan Hecht. Photoswitches: From molecules to materials. *Advanced Materials*, 22(31):3348–3360, 2010. doi: <https://doi.org/10.1002/adma.200904102>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adma.200904102>.
- [61] Allison M. Rice, Corey R. Martin, Vladimir A. Galitskiy, Anastasia A. Berseneva, Gabrielle A. Leith, and Natalia B. Shustova. Photophysics modulation in photoswitchable metal-organic frameworks. *Chemical Reviews*, 120(16):8790–8813, 2020. doi: 10.1021/acs.chemrev.9b00350.

- [62] Zhengbang Wang, Lars Heinke, Jelena Jelic, Murat Cakici, Marcel Dommaschk, Reinhard J. Maurer, Harald Oberhofer, Sylvain Grosjean, Rainer Herges, Stefan Bräse, Karsten Reuter, and Christof Wöll. Photoswitching in nanoporous, crystalline solids: an experimental and theoretical study for azobenzene linkers incorporated in mofs. *Physical Chemistry Chemical Physics*, 17: 14582–14587, 2015. doi: 10.1039/C5CP01372K.
- [63] Yunzhe Jiang and Lars Heinke. Photoswitchable metal–organic framework thin films: From spectroscopy to remote-controllable membrane separation and switchable conduction. *Langmuir*, 37(1):2–15, 2021. doi: 10.1021/acs.langmuir.0c02859. URL <https://doi.org/10.1021/acs.langmuir.0c02859>. PMID: 33347762.
- [64] Allison M. Rice, Corey R. Martin, Vladimir A. Galitskiy, Anna A. Berseneva, Gabrielle A. Leith, and Natalia B. Shustova. Photophysics modulation in photoswitchable metal–organic frameworks. *Chemical Reviews*, 120(16):8790–8813, 2020. doi: 10.1021/acs.chemrev.9b00350. URL <https://doi.org/10.1021/acs.chemrev.9b00350>. PMID: 31638383.
- [65] X. Yu, Z. Wang, M. Buchholz, N. Füllgrabe, S. Grosjean, F. Bebensee, S. Bräse, C. Wöll, and L. Heinke. Cis-to-trans isomerization of azobenzene investigated by using thin films of metal-organic frameworks. *Physical Chemistry Chemical Physics*, 17:22721–22725, 2015. doi: 10.1039/C5CP03091A.
- [66] J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart, and O. M. Yaghi. Photophysical pore control in an azobenzene-containing metal-organic framework. *Chemical Science*, 4:2858–2864, 2013. doi: 10.1039/C3SC21659D.
- [67] Lars Heinke, Murat Cakici, Marcel Dommaschk, Sylvain Grosjean, Rainer Herges, Stefan Bräse, and Christof Wöll. Photoswitching in two-component surface-mounted metal-organic frameworks: optically triggered release from a molecular container. *ACS Nano*, 8(2):1463–1467, 2014. doi: 10.1021/nn405469g.
- [68] Xiangshi Meng, Bo Gui, Daqiang Yuan, Matthias Zeller, and Cheng Wang. Mechanized azobenzene-functionalized zirconium metal-organic framework for on-command cargo release. *Science Advances*, 2(8):e1600480, 2016. doi: 10.1126/sciadv.1600480.
- [69] Sonia Castellanos, Alexis Goulet-Hanssens, Fangli Zhao, Alla Dikhtiarenko, Alexey Pustovarenko, Stefan Hecht, Jorge Gascon, Freek Kapteijn, and David Bléger. Structural effects in visible-light-responsive metal-organic frameworks incorporating ortho-fluoroazobenzenes. *Chemistry – A European Journal*, 22:746–752, 2016. doi: 10.1002/chem.201503503.

- [70] Jihye Park, Dawei Feng, Shuai Yuan, and Hong-Cai Zhou. Photochromic metal-organic frameworks: Reversible control of singlet oxygen generation. *Angewandte Chemie International Edition*, 54(2):430–435, 2015. doi: 10.1002/anie.201408862.
- [71] Grace C. Thaggard, Kyoung Chul Park, Jaewoong Lim, B. K. P. Maldeni Kankanamalage, Johannes Haimerl, Grace R. Wilson, Matthew K. McBride, Katelyn L. Forrester, Emily R. Adelson, Victoria S. Arnold, S. T. Wetthasinghe, Vitaly A. Rassolov, Mark D. Smith, Dmitry Sosnin, Ivan Aprahamian, Manisha Karmakar, Suman K. Bag, Arunabha Thakur, Mingming Zhang, Ben Zhong Tang, Jose A. Castaño, Manisha N. Chaur, Michael M. Lerch, Roland A. Fischer, Joanna Aizenberg, Rainer Herges, Jean-Marie Lehn, and Natalia B. Shustova. Breaking the photoswitch speed limit. *Nature Communications*, 14:7556, 2023. doi: 10.1038/s41467-023-43405-w.
- [72] Grace C. Thaggard, Johanna Haimerl, Kyoung Chul Park, Jaewoong Lim, Roland A. Fischer, B. K. P. Maldeni Kankanamalage, Brandon J. Yarbrough, Gina R. Wilson, and Natalia B. Shustova. Metal-photoswitch friendship: From photochromic complexes to functional materials. *Journal of the American Chemical Society*, 144(51):23249–23263, 2022. doi: 10.1021/jacs.2c09879.
- [73] Heidi A. Schwartz, Selina Olthof, Dominik Schaniel, Klaus Meerholz, and Uwe Ruschewitz. Solution-like behavior of photoswitchable spiropyrans embedded in metal-organic frameworks. *Inorganic Chemistry*, 56(21):13100–13110, 2017. doi: 10.1021/acs.inorgchem.7b01908.
- [74] Nobuhiro Yanai, Takashi Uemura, Masafumi Inoue, Ryotaro Matsuda, Tetsuya Fukushima, Masaki Tsujimoto, Shuji Isoda, and Susumu Kitagawa. Guest-to-host transmission of structural changes for stimuli-responsive adsorption property. *Journal of the American Chemical Society*, 134(10):4501–4504, 2012. doi: 10.1021/ja2115713.
- [75] Katherine Healey, Weibin Liang, Peter D. Southon, Tamara L. Church, and Deanna M. D’Alessandro. Photoresponsive spiropyran-functionalised mof-808: postsynthetic incorporation and light dependent gas adsorption properties. *Journal of Materials Chemistry A*, 4:10816–10819, 2016. doi: 10.1039/C6TA04160D. URL <http://dx.doi.org/10.1039/C6TA04160D>.
- [76] Antje Modrow, Dordaneh Zargarani, Rainer Herges, and Norbert Stock. The first porous mof with photoswitchable linker molecules. *Dalton Transactions*, 40:4217–4222, 2011. doi: 10.1039/C0DT01629B. URL <http://dx.doi.org/10.1039/C0DT01629B>.
- [77] Bo Gui, Yi Meng, Yang Xie, Ke Du, Andrew C.-H. Sue, and Cheng Wang. Immobilizing organic-based molecular switches into metal-organic frameworks: A promising strategy for switching in solid state. *Macromolecular Rapid Communications*, 39(1):1700388, 2018. doi: <https://doi.org/10.1002/marc.201700388>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/marc.201700388>.

- [78] Ritesh Haldar, Lars Heinke, and Christof Wöll. Advanced photoresponsive materials using the metal–organic framework approach. *Advanced Materials*, 32(20):1905227, 2020. doi: <https://doi.org/10.1002/adma.201905227>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adma.201905227>.
- [79] Mohammad Mehdi Sabzehmeidani, Shadi Gafari, Sara Jamali, and Mahmood Kazemzad. Concepts, fabrication and applications of mof thin films in optoelectronics: A review. *Applied Materials Today*, 38:102153, 2024. doi: 10.1016/j.apmt.2024.102153.
- [80] Alejandra Gonzalez, Magdalena Odaybat, My Le, Jake L. Greenfield, Andrew J. P. White, Xiang Li, Matthew J. Fuchter, and Grace G. D. Han. Photocontrolled energy storage in azobispyrazoles with exceptionally large light penetration depths. *Journal of the American Chemical Society*, 144(42):19430–19436, 2022. doi: 10.1021/jacs.2c07537.
- [81] A. Ahamed, C. Bartolo-Perez, A. S. Mayet, S. Ghandiparsi, G. Ariño-Estrada, X. Zhou, J. Bec, S.-Y. Wang, L. Marcu, and S. Islam. Optimizing the light penetration depth in apds and spads for high gain-bandwidth and ultra-wide spectral response. In M. Razeghi, G. A. Khodaparast, and M. S. Vitiello, editors, *Quantum Sensing and Nano Electronics and Photonics XVIII*, volume 12009, page 1200905. SPIE, 2022. doi: 10.1117/12.2610526.
- [82] I. K. Januariyasa, F. Borbone, M. Salvatore, and S. L. Oscurato. Wavelength-dependent shaping of azopolymer micropillars for three-dimensional structure control. *ACS Applied Materials & Interfaces*, 15:43183–43192, 2023. doi: 10.1021/acsami.3c09264.
- [83] Wojciech Danowski, Thomas van Leeuwen, Wesley R. Browne, and Ben L. Feringa. Photoreponsive porous materials. *Nanoscale Advances*, 3:24–40, 2021. doi: 10.1039/D0NA00647E. URL <http://dx.doi.org/10.1039/D0NA00647E>.
- [84] J.-S. M. Lee and H. Sato. Photoswitching to the core. *Nature Chemistry*, 12(7):584–585, 2020. doi: 10.1038/s41557-020-0499-z.
- [85] A. B. Kanj, K. Müller, and L. Heinke. Stimuli-responsive metal-organic frameworks with photo-switchable azobenzene side groups. *Macromolecular Rapid Communications*, 39:1700239, 2018. doi: 10.1002/marc.201700239.
- [86] Feng Zhang, Xiaoqin Zou, Wei Feng, Xiaojun Zhao, Xiaofei Jing, Fuxing Sun, Hao Ren, and Guangshan Zhu. Microwave-assisted crystallization inclusion of spiropyran molecules in indium trimesate films with antidromic reversible photochromism. *Journal of Materials Chemistry*, 22:25019–25026, 2012. doi: 10.1039/C2JM34618D. URL <http://dx.doi.org/10.1039/C2JM34618D>.

- [87] Robert W. Boyd. *Nonlinear Optics*. Elsevier, San Diego, 4 edition, 2020. ISBN 978-0-12-811002-7.
- [88] S. J. Weishäupl, D. C. Mayer, Y. Cui, P. Kumar, H. Oberhofer, R. A. Fischer, J. Hauer, and A. Pöthig. Recent advances of multiphoton absorption in metal–organic frameworks. *Journal of Materials Chemistry C*, 10(18):6912–6934, 2022. doi: 10.1039/D2TC00191H.
- [89] Q. Huo, T. Meng, X. Lu, and D. Li. Multiphoton excited fluorescence imaging over metal-organic frameworks. *ChemBioChem*, 26:e202400782, 2025. doi: 10.1002/cbic.202400782.
- [90] R. K. P. Benninger and D. W. Piston. Two-photon excitation microscopy for the study of living cells and tissues. *Current Protocols in Cell Biology*, 59:4.11.1, 2013. doi: 10.1002/0471143030.cb0411s59.
- [91] N. B. Shustova, T.-C. Ong, A. F. Cozzolino, V. K. Michaelis, R. G. Griffin, and M. Dincă. Phenyl ring dynamics in a tetraphenylethylene-bridged metal–organic framework: Implications for the mechanism of aggregation-induced emission. *Journal of the American Chemical Society*, 134:15061, 2012. doi: 10.1021/ja306042w.
- [92] J. K. Zaręba, M. Nyk, and M. Samoć. Nonlinear optical properties of emerging nano- and microcrystalline materials. *Advanced Optical Materials*, 9:2100216, 2021. doi: 10.1002/adom.202100216.
- [93] W. R. Zipfel, R. M. Williams, and W. W. Webb. Nonlinear magic: multiphoton microscopy in the biosciences. *Nature Biotechnology*, 21:1369, 2003. doi: 10.1038/nbt899.
- [94] M. Pawlicki, H. A. Collins, R. G. Denning, and H. L. Anderson. Two-photon absorption and the design of two-photon dyes. *Angewandte Chemie International Edition*, 48:3244, 2009. doi: 10.1002/anie.200805257.
- [95] G. S. He, L.-S. Tan, Q. Zheng, and P. N. Prasad. Multiphoton absorbing materials: Molecular designs, characterizations, and applications. *Chemical Reviews*, 108:1245, 2008. doi: 10.1021/cr050054x.
- [96] S. Lee, K. R. J. Thomas, S. Thayumanavan, and C. J. Bardeen. Dependence of the two-photon absorption cross section on the conjugation of the phenylacetylene linker in dipolar donor–bridge–acceptor chromophores. *The Journal of Physical Chemistry A*, 109:9767, 2005. doi: 10.1021/jp053864l.
- [97] R. Medishetty, J. K. Zaręba, D. Mayer, M. Samoć, and R. A. Fischer. Nonlinear optical properties, upconversion and lasing in metal–organic frameworks. *Chemical Society Reviews*, 46:4976, 2017. doi: 10.1039/C7CS00162B.

- [98] Qiong Zhang, Xiaohe Tian, Hongping Zhou, Jieying Wu, and Yupeng Tian. Lighting the way to see inside two-photon absorption materials: Structure–property relationship and biological imaging. *Materials*, 10(3), 2017. ISSN 1996-1944. doi: 10.3390/ma10030223. URL <https://www.mdpi.com/1996-1944/10/3/223>.
- [99] A. Cesaretti, P. Foggi, C. G. Fortuna, F. Elisei, A. Spalletti, and B. Carlotti. Uncovering structure–property relationships in push–pull chromophores: A promising route to large hyperpolarizability and two-photon absorption. *The Journal of Physical Chemistry C*, 124:15739, 2020. doi: 10.1021/acs.jpcc.0c03536.
- [100] F. Terenziani, C. Katan, E. Badaeva, S. Tretiak, and M. Blanchard-Desce. Enhanced two-photon absorption of organic chromophores: Theoretical and experimental assessments. *Advanced Materials*, 20:4641, 2008. doi: 10.1002/adma.200800402.
- [101] M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, and C. Xu. Design of organic molecules with large two-photon absorption cross sections. *Science*, 281:1653, 1998. doi: 10.1126/science.281.5383.1653.
- [102] R. Haldar, M. Jakoby, M. Kozłowska, M. R. Khan, H. Chen, Y. Pramudya, B. S. Richards, L. Heinke, W. Wenzel, F. Odobel, S. Diring, I. A. Howard, U. Lemmer, and C. Wöll. Tuning optical properties by controlled aggregation: Electroluminescence assisted by thermally-activated delayed fluorescence from thin films of crystalline chromophores. *Chemistry – A European Journal*, 26:17016, 2020. doi: 10.1002/chem.202003712.
- [103] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, and B. Z. Tang. Aggregation-induced emission: Together we shine, united we soar! *Chemical Reviews*, 115:11718, 2015. doi: 10.1021/acs.chemrev.5b00263.
- [104] M. T. P. Beerepoot, D. H. Frieze, and K. Ruud. Intermolecular charge transfer enhances two-photon absorption in yellow fluorescent protein. *Physical Chemistry Chemical Physics*, 16:5958, 2014. doi: 10.1039/c3cp55205e.
- [105] S. R. Valandro, P. Jagadesan, F. Feng, and K. Schanze. Aggregation-enhanced two-photon absorption of anionic conjugated polyelectrolytes. *The Journal of Physical Chemistry Letters*, 11:8292, 2020. doi: 10.1021/acs.jpclett.0c02152.
- [106] C. J. Zeman, G. Kang, and K. L. Kohlstedt. Controlling aggregation-induced two-photon absorption enhancement via intermolecular interactions. *ACS Applied Materials & Interfaces*, 14:45644, 2022. doi: 10.1021/acsami.2c12436.

- [107] Suqian Ma, Sijia Du, Guocui Pan, Shuting Dai, Bin Xu, and Wenjing Tian. Organic molecular aggregates: From aggregation structure to emission property. *Aggregate*, 2:e96, 2021. doi: 10.1002/agt2.96.
- [108] N. Liu, Z. Chen, W. Fan, J. Su, T. Lin, S. Xiao, J. Meng, J. He, J. J. Vittal, and J. Jiang. Highly efficient multiphoton absorption of zinc-AIEgen metal–organic frameworks. *Angewandte Chemie International Edition*, 61:e202115205, 2022. doi: 10.1002/anie.202115205.
- [109] Y. Hong, J. W. Y. Lam, and B. Z. Tang. Aggregation-induced emission. *Chemical Society Reviews*, 40:5361, 2011. doi: 10.1039/C1CS15113D.
- [110] Mersad Mostaghimi, Helmy Pacheco Hernandez, Yunzhe Jiang, Wolfgang Wenzel, Lars Heinke, and Mariana Kozłowska. On–off conduction photoswitching in modelled spiropyran-based metal-organic frameworks. *Communications Chemistry*, 6(1):275, 2023. doi: 10.1038/s42004-023-01072-4. URL <https://doi.org/10.1038/s42004-023-01072-4>.
- [111] Simone Fratini, Didier Mayou, and Sergio Ciuchi. The transient localization scenario for charge transport in crystalline organic materials. *Advanced Functional Materials*, 26(14):2292–2315, 2016. doi: <https://doi.org/10.1002/adfm.201502386>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adfm.201502386>.
- [112] Samuele Giannini and Jochen Blumberger. Charge transport in organic semiconductors: The perspective from nonadiabatic molecular dynamics. *Accounts of Chemical Research*, 55(6):819–830, 2022. doi: 10.1021/acs.accounts.1c00675. URL <https://doi.org/10.1021/acs.accounts.1c00675>. PMID: 35196456.
- [113] Shuai Fu, Enquan Jin, Hiroki Hanayama, Wenhao Zheng, Heng Zhang, Lucia Di Virgilio, Matthew A. Addicoat, Markus Mezger, Akimitsu Narita, Mischa Bonn, Klaus Müllen, and Hai I. Wang. Outstanding charge mobility by band transport in two-dimensional semiconducting covalent organic frameworks. *Journal of the American Chemical Society*, 144(16):7489–7496, 2022. doi: 10.1021/jacs.2c02408. URL <https://doi.org/10.1021/jacs.2c02408>. PMID: 35420808.
- [114] Samrat Ghosh, Yusuke Tsutsui, Takahiro Kawaguchi, Wakana Matsuda, Shusaku Nagano, Katsuaki Suzuki, Hironori Kaji, and Shu Seki. Band-like transport of charge carriers in oriented two-dimensional conjugated covalent organic frameworks. *Chemistry of Materials*, 34(2):736–745, 2022. doi: 10.1021/acs.chemmater.1c03533. URL <https://doi.org/10.1021/acs.chemmater.1c03533>.
- [115] Allen Miller and Elihu Abrahams. Impurity conduction at low concentrations. *Physical Review*, 120:745–755, Nov 1960. doi: 10.1103/PhysRev.120.745. URL <https://link.aps.org/doi/10.1103/PhysRev.120.745>.

- [116] R.A. Marcus and Norman Sutin. Electron transfers in chemistry and biology. *Biochimica et Biophysica Acta (BBA) - Reviews on Bioenergetics*, 811(3):265–322, 1985. ISSN 0304-4173. doi: [https://doi.org/10.1016/0304-4173\(85\)90014-X](https://doi.org/10.1016/0304-4173(85)90014-X). URL <https://www.sciencedirect.com/science/article/pii/030441738590014X>.
- [117] Joseph Lott, Christopher Ryan, Brent Valle, Jack R. Johnson III, David A. Schiraldi, Jie Shan, Kenneth D. Singer, and Christoph Weder. Two-photon 3d optical data storage via aggregate switching of excimer-forming dyes. *Advanced Materials*, 23(21):2425–2429, 2011. doi: <https://doi.org/10.1002/adma.201100458>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adma.201100458>.
- [118] Zi-Xin Liang, Yuan-Yuan Zhao, Jing-Tao Chen, Xian-Zi Dong, Feng Jin, Mei-Ling Zheng, and Xuan-Ming Duan. Two-photon absorption under few-photon irradiation for optical nanoprinting. *Nature Communications*, 16(1):2086, 2025. doi: 10.1038/s41467-025-57390-9. URL <https://doi.org/10.1038/s41467-025-57390-9>.
- [119] Kazuya Niizeki, Daisuke Yoshida, Ko Ito, Ippei Nakamura, Nobuyuki Takei, Kotaro Okamura, Ming-Yang Zheng, Xiu-Ping Xie, and Tomoyuki Horikiri. Two-photon comb with wavelength conversion and 20-km distribution for quantum communication. *Communications Physics*, 3(1):138, 2020. doi: 10.1038/s42005-020-00406-1. URL <https://doi.org/10.1038/s42005-020-00406-1>.
- [120] Maria Göppert-Mayer. Über Elementarakte mit zwei Quantensprüngen. *Annalen der Physik*, 401(3):273–294, 1931. doi: 10.1002/andp.19314010303.
- [121] W. Kaiser and C. G. B. Garrett. Two-photon excitation in $\text{CaF}_2\text{:Eu}^{2+}$. *Physical Review Letters*, 7(6):229–231, 1961. doi: 10.1103/PhysRevLett.7.229.
- [122] Robert W. Boyd. *Nonlinear Optics*. Academic Press, Amsterdam, 4 edition, 2020. ISBN 978-0-12-811002-7. doi: 10.1016/C2015-0-05510-1.
- [123] Shane M. Parker, Dmitrij Rappoport, and Filipp Furche. Quadratic response properties from TDDFT: Trials and tribulations. *Journal of Chemical Theory and Computation*, 14:807–819, 2018.
- [124] B. J. Orr and J. F. Ward. Perturbation theory of the non-linear optical polarization of an isolated system. *Molecular Physics*, 20:513–526, 1971. doi: 10.1080/00268977100100481.
- [125] Wolfram Koch and Max C. Holthausen. *A Chemist’s Guide to Density Functional Theory*. Wiley-VCH Verlag GmbH, Weinheim, Germany, 2 edition, 2001. ISBN 3-527-30372-3.
- [126] Christopher J. Cramer. *Essentials of Computational Chemistry: Theories and Models*. John Wiley & Sons, Chichester, West Sussex, England, 2 edition, 2004. ISBN 978-0-470-09182-1.

- [127] David S. Sholl and Janice A. Steckel. *Density Functional Theory: A Practical Introduction*. John Wiley & Sons, Hoboken, New Jersey, 2009. ISBN 978-0-470-37317-0.
- [128] Errol G. Lewars. *Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics*. Springer, Dordrecht, Netherlands, 2 edition, 2011. ISBN 978-90-481-3860-9. doi: 10.1007/978-90-481-3862-3.
- [129] Takeshi Yanai, David P. Tew, and Nicholas C. Handy. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chemical Physics Letters*, 393: 51–57, 2004. doi: 10.1016/j.cplett.2004.06.011.
- [130] Alexandre Tkatchenko and Matthias Scheffler. Accurate molecular van der waals interactions from ground-state electron density and free-atom reference data. *Physical Review Letters*, 102: 073005, 2009. doi: 10.1103/PhysRevLett.102.073005.
- [131] Oleg A. Vydrov and Troy Van Voorhis. Nonlocal van der waals density functional: The simpler the better. *Journal of Chemical Physics*, 133:244103, 2010. doi: 10.1063/1.3521275.
- [132] Lars Goerigk. Treating london-dispersion effects with the latest minnesota density functionals: Problems and possible solutions. *Journal of Physical Chemistry Letters*, 6:3891–3896, 2015. doi: 10.1021/acs.jpcclett.5b01591.
- [133] Yan Zhao and Donald G. Truhlar. The m06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements. *Theoretical Chemistry Accounts*, 120:215–241, 2008. doi: 10.1007/s00214-007-0310-x.
- [134] Cameron J. Nickerson, Kyle R. Bryenton, Alastair J. A. Price, and Erin R. Johnson. Comparison of density-functional theory dispersion corrections for the des15k database. *The Journal of Physical Chemistry A*, 127(41):8712–8722, 2023. doi: 10.1021/acs.jpca.3c04332. URL <https://doi.org/10.1021/acs.jpca.3c04332>. PMID: 37793049.
- [135] Miquel Huix-Rotllant, Nicolas Ferré, and Mario Barbatti. Time-dependent density functional theory. In Leticia González and Roland Lindh, editors, *Quantum Chemistry and Dynamics of Excited States: Methods and Applications*, chapter 2. Wiley, Hoboken, NJ, 2020. doi: 10.1002/9781119417774.
- [136] Carsten A. Ullrich. *Time-Dependent Density-Functional Theory: Concepts and Applications*. OUP Oxford, 2012. ISBN 9780199563029. URL https://books.google.de/books?id=j_4nodMFCa4C.
- [137] Mark E. Casida. Time-dependent density functional response theory for molecules. In D. P. Chong, editor, *Recent Advances in Density Functional Methods*, pages 155–192. World Scientific, Singapore, 1995.

- [138] R. Bauernschmitt and R. Ahlrichs. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chemical Physics Letters*, 256:454–464, 1996.
- [139] TURBOMOLE V7.6 2021, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <https://www.turbomole.org>.
- [140] Sree Ganesh Balasubramani, Guo P. Chen, Sonia Coriani, Michael Diedenhofen, Marius S. Frank, Yannick J. Franzke, Filipp Furche, Robin Grotjahn, Michael E. Harding, Christof Hättig, Arnim Hellweg, Benjamin Helmich-Paris, Christof Holzer, Uwe Huniar, Martin Kaupp, Alireza Marefat Khah, Sarah Karbalaee Khani, Thomas Müller, Fabian Mack, Brian D. Nguyen, Shane M. Parker, Eva Perlt, Dmitriy Rappoport, Kevin Reiter, Saswata Roy, Matthias Rückert, Gunnar Schmitz, Marek Sierka, Enrico Tapavicza, David P. Tew, Christoph van Wüllen, Vamsee K. Voora, Florian Weigend, Artur Wodyński, and Jason M. Yu. TURBOMOLE: Modular program suite for *ab initio* quantum-chemical and condensed-matter simulations. *Journal of Chemical Physics*, 152: 184107, 2020. doi: 10.1063/5.0004635.
- [141] Kun Zhou and Bo Liu. *Molecular Dynamics Simulation: Fundamentals and Applications*. Elsevier, Amsterdam, Netherlands, 1 edition, 2022. ISBN 978-0-12-816419-8.
- [142] Scott A. Hollingsworth and Ron O. Dror. Molecular dynamics simulation for all. *Neuron*, 99 (6):1129–1143, 2018. ISSN 0896-6273. doi: <https://doi.org/10.1016/j.neuron.2018.08.011>. URL <https://www.sciencedirect.com/science/article/pii/S0896627318306846>.
- [143] Hesam Makki, Colm Burke, and Alessandro Troisi. 9 - molecular dynamics simulation of semiconducting polymers. In Paola Carbone and Nigel Clarke, editors, *Computational Methods for the Multiscale Modeling of Soft Matter*, pages 291–318. Elsevier, 2026. ISBN 978-0-443-27314-8. doi: <https://doi.org/10.1016/B978-0-44-327314-8.00019-1>. URL <https://www.sciencedirect.com/science/article/pii/B9780443273148000191>.
- [144] Weichen Yang, Zhe Gao, Shaoxiong Li, Linxing Deng, Biao Liang, Xiangfeng Kong, Xiumin Chen, Dachun Liu, and Bin Yang. Review of molecular dynamics simulation in extraction metallurgy. *Computational Materials Science*, 258:114111, 2025. ISSN 0927-0256. doi: <https://doi.org/10.1016/j.commatsci.2025.114111>. URL <https://www.sciencedirect.com/science/article/pii/S0927025625004549>.
- [145] B. J. Alder and T. E. Wainwright. Phase transition for a hard sphere system. *The Journal of Chemical Physics*, 27(5):1208–1209, 1957. doi: 10.1063/1.1743957.
- [146] Aneesur Rahman. Correlations in the motion of atoms in liquid argon. *Physical Review*, 136(2A): A405–A411, 1964. doi: 10.1103/PhysRev.136.A405.

- [147] Aneesur Rahman and Frank H. Stillinger. Molecular dynamics study of liquid water. *The Journal of Chemical Physics*, 55(7):3336–3359, 1971. doi: 10.1063/1.1676585.
- [148] J. Andrew McCammon, Bruce R. Gelin, and Martin Karplus. Dynamics of folded proteins. *Nature*, 267:585–590, 1977. doi: 10.1038/267585a0.
- [149] Damien E. Coupry, Matthew A. Addicoat, and Thomas Heine. Extension of the universal force field for metal-organic frameworks. *Journal of Chemical Theory and Computation*, 12(10):5215–5225, 2016. doi: 10.1021/acs.jctc.6b00664.
- [150] Stephen L. Mayo, Barry D. Olafson, and William A. Goddard. DREIDING: A generic force field for molecular simulations. *The Journal of Physical Chemistry*, 94(26):8897–8909, 1990. doi: 10.1021/j100389a010.
- [151] Sareeya Bureekaew, Saeed Amirjalayer, Maxim Tafipolsky, Christian Spickermann, Tapta Kanchan Roy, and Rochus Schmid. MOF-FF – a flexible first-principles derived force field for metal-organic frameworks. *Physica Status Solidi (b)*, 250(6):1128–1141, 2013. doi: 10.1002/pssb.201248460.
- [152] Teerachot Pakornchote et al. SimStack: An intuitive workflow framework. *Frontiers in Materials*, 9, 2022. doi: 10.3389/fmats.2022.877597.
- [153] Nanomatch GmbH and KIT. The SimStack concept. https://www.simstack.de/?page_id=120, 2024. Accessed: 2025.
- [154] Nanomatch GmbH and KIT. SimStack documentation. <https://simstack.readthedocs.io/en/latest/>, 2024. Accessed: 2025.
- [155] Jaber Keyvan Rad, Zahra Balzade, and Ali Reza Mahdavian. Spiropyran-based advanced photoswitchable materials: A fascinating pathway to the future stimuli-responsive devices. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 51:100487, 2022. ISSN 1389-5567. doi: <https://doi.org/10.1016/j.jphotochemrev.2022.100487>. URL <https://www.sciencedirect.com/science/article/pii/S1389556722000065>.
- [156] Shubham Garg, Heidi Schwartz, Mariana Kozłowska, Anemar Bruno Kanj, Kai Müller, Wolfgang Wenzel, Uwe Ruschewitz, and Lars Heinke. Conductance photoswitching of metal–organic frameworks with embedded spiropyran. *Angewandte Chemie International Edition*, 58(4):1193–1197, 2019. doi: <https://doi.org/10.1002/anie.201811458>. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.201811458>.
- [157] Paul Langevin. Sur la théorie du mouvement brownien. *Comptes Rendus de l’Académie des Sciences*, 146:530–533, 1908.

- [158] Shuichi Nosé. A unified formulation of the constant temperature molecular dynamics methods. *The Journal of Chemical Physics*, 81(1):511–519, 1984. doi: 10.1063/1.447334.
- [159] William G. Hoover. Canonical dynamics: Equilibrium phase-space distributions. *Physical Review A*, 31(3):1695–1697, 1985. doi: 10.1103/PhysRevA.31.1695.
- [160] William Humphrey, Andrew Dalke, and Klaus Schulten. VMD: Visual molecular dynamics. *Journal of Molecular Graphics*, 14(1):33–38, 1996. doi: 10.1016/0263-7855(96)00018-5.
- [161] Ask Hjorth Larsen, Jens Jørgen Mortensen, Jakob Blomqvist, Ivano E. Castelli, Rune Christensen, Marcin Dułak, Jesper Friis, Michael N. Groves, Bjørk Hammer, Cory Hargus, Eric D. Hermes, Paul C. Jennings, Peter Bjerre Jensen, James Kermode, John R. Kitchin, Esben Leonhard Kolsbjerg, Joseph Kubal, Kristen Kaasbjerg, Steen Lysgaard, Jón Bergmann Maronsson, Tristan Maxson, Thomas Olsen, Lars Pastewka, Andrew Peterson, Carsten Rostgaard, Jakob Schiøtz, Ole Schütt, Mikkel Strange, Kristian S. Thygesen, Tejs Vegge, Lasse Vilhelmsen, Michael Walter, Zhenhua Zeng, and Karsten W. Jacobsen. The atomic simulation environment—A Python library for working with atoms. *Journal of Physics: Condensed Matter*, 29(27):273002, 2017. doi: 10.1088/1361-648X/aa680e.
- [162] Noel M. O’Boyle, Michael Banck, Craig A. James, Chris Morley, Tim Vandermeersch, and Geoffrey R. Hutchison. Open Babel: An open chemical toolbox. *Journal of Cheminformatics*, 3:33, 2011. doi: 10.1186/1758-2946-3-33.
- [163] Pascal Friederich, Franz Symalla, Velimir Meded, Tobias Neumann, and Wolfgang Wenzel. Ab initio treatment of disorder effects in amorphous organic materials: Toward parameter free materials simulation. *Journal of Chemical Theory and Computation*, 10(9):3720–3725, 2014. doi: 10.1021/ct500418f. URL <https://doi.org/10.1021/ct500418f>. PMID: 26588517.
- [164] Simone Fratini, Sergio Ciuchi, Didier Mayou, Guy Trambly de Laissardière, and Alessandro Troisi. A map of high-mobility molecular semiconductors. *Nature Materials*, 16:998–1002, 2017. doi: 10.1038/nmat4970.
- [165] Tahereh Nematiram, Sergio Ciuchi, Xin Xie, Simone Fratini, and Alessandro Troisi. Practical computation of the charge mobility in molecular semiconductors using transient localization theory. *The Journal of Physical Chemistry C*, 123(11):6989–6997, 2019. doi: 10.1021/acs.jpcc.9b01395.
- [166] Hong Li, Jean-Luc Brédas, and Christian Lennartz. First-principles theoretical investigation of the electronic couplings in single crystals of phenanthroline-based organic semiconductors. *The Journal of Chemical Physics*, 126(16):164704, 2007. doi: 10.1063/1.2727480.

- [167] Per-Olov Löwdin. On the nonorthogonality problem. In Per-Olov Löwdin, editor, *Advances in Quantum Chemistry*, volume 5, pages 185–199. Academic Press, 1970. doi: 10.1016/S0065-3276(08)60339-1.
- [168] V. Stehr, J. Pfister, R. F. Fink, B. Engels, and C. Deibel. First-principles calculations of anisotropic charge-carrier mobilities in organic semiconductor crystals. *Physical Review B*, 83(15):155208, 2011. doi: 10.1103/PhysRevB.83.155208.
- [169] Sameer Patwardhan and George C. Schatz. Theoretical investigation of charge transfer in metal organic frameworks for electrochemical device applications. *The Journal of Physical Chemistry C*, 119(43):24238–24247, 2015. doi: 10.1021/acs.jpcc.5b06065.
- [170] Subhadip Goswami, Idan Hod, Jiaxin Dawn Duan, Chung-Wei Kung, Martino Rimoldi, Christos D. Malliakas, Rebecca H. Palmer, Omar K. Farha, and Joseph T. Hupp. Anisotropic redox conductivity within a metal–organic framework material. *Journal of the American Chemical Society*, 141(44):17696–17702, 2019. doi: 10.1021/jacs.9b07658.
- [171] Chung-Wei Kung, Subhadip Goswami, Idan Hod, Timothy C. Wang, Jiaxin Duan, Omar K. Farha, and Joseph T. Hupp. Charge transport in zirconium-based metal–organic frameworks. *Accounts of Chemical Research*, 53(6):1187–1195, 2020. doi: 10.1021/acs.accounts.0c00106.
- [172] Tobias Neumann, Jianxi Liu, Tobias Wächter, Pascal Friederich, Franz Symalla, Alexander Welle, Veronica Mugnaini, Velimir Meded, Michael Zharnikov, Christof Wöll, and Wolfgang Wenzel. Superexchange charge transport in loaded metal organic frameworks. *ACS Nano*, 10(7):7085–7093, 2016. doi: 10.1021/acsnano.6b03226.
- [173] Miłosz Pawlicki, Hazel A. Collins, Robert G. Denning, and Harry L. Anderson. Two-photon absorption and the design of two-photon dyes. *Angewandte Chemie International Edition*, 48(18):3244–3266, 2009. doi: 10.1002/anie.200805257.
- [174] Raghavender Medishetty, Venkatram Nalla, Lydia Nemec, Sebastian Henke, David Mayer, Handong Sun, Karsten Reuter, and Roland A. Fischer. A new class of lasing materials: Intrinsic stimulated emission from nonlinear optically active metal–organic frameworks. *Advanced Materials*, 29(17):1605637, 2017. doi: 10.1002/adma.201605637.
- [175] R. Medishetty, L. Nemec, V. Nalla, S. Henke, M. Samoć, K. Reuter, and R. A. Fischer. Multi-photon absorption in metal–organic frameworks. *Angewandte Chemie International Edition*, 56:14743, 2017. doi: 10.1002/anie.201706492.
- [176] Huihui He, Ji Li, Jiayi Zhuang, Jinyi Huang, Yuxuan Meng, Xi Lin, Zhang-Wen Wei, Liangliang Zhang, Yu Fang, and Mei Pan. Boosting one- and two-photon excited fluorescence of interpen-

etrated tetraphenylethene-based metal–organic frameworks (TPE-MOFs) by linker installation. *Angewandte Chemie International Edition*, 64:e202420912, 2025. doi: 10.1002/anie.202420912.

- [177] Helmy Pacheco Hernandez and Mariana Kozłowska. Intermolecular packing effects on the two-photon absorption of the h4tpe linker. *Frontiers in Chemistry*, 2026. doi: 10.3389/fchem.2026.1805869. in press.
- [178] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian 16, Revision C.01, 2016. Gaussian, Inc., Wallingford CT.
- [179] Florian Weigend and Reinhart Ahlrichs. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics*, 7:3297–3305, 2005. doi: 10.1039/B508541A.
- [180] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *Journal of Chemical Physics*, 132:154104, 2010. doi: 10.1063/1.3382344.
- [181] Weijie Yuan and Wei Ji. Tunable nonlinear optical properties based on metal–organic framework single crystals. *Advanced Optical Materials*, 12:2302405, 2024. doi: 10.1002/adom.202302405.
- [182] Sebastian Henke, Andreas Schneemann, Robert Zalesny, Marek Samoć, and Roland A. Fischer. Postsynthetic framework contraction enhances the two-photon absorption properties of pillar-layered metal–organic frameworks. *Chemistry of Materials*, 32(17):7463–7474, 2020. doi: 10.1021/acs.chemmater.0c01417.
- [183] Qingli Guan, Chao Han, Yuhui Xing, Jing Liu, Fengyun Bai, Zhan Shi, and Lixin Sun. Extremely stable thorium-MOF assembly of tetraphenylethylene derivative with tunable AIE property and highly selective detection of nitro aromatic compounds. *Advanced Materials Interfaces*, 9:2201547, 2022. doi: 10.1002/admi.202201547.

- [184] Shanshan Mao, Yuhao Lin, Xingyu Li, and Hao Wang. Highly luminescent metal–organic frameworks based on binary chromophoric ligands derived from tetraphenylethylene. *Crystal Growth Design*, 22(10):5791–5795, 2022. doi: 10.1021/acs.cgd.2c00441.
- [185] Nanna Holmgaard List, Jógvan Magnus Haugaard Olsen, Tomas Rocha-Rinza, Ove Christiansen, and Jacob Kongsted. Performance of popular XC-functionals for the description of excitation energies in GFP-like chromophore models. *International Journal of Quantum Chemistry*, 112: 789–800, 2012. doi: 10.1002/qua.23059.
- [186] Cheng-Xia Chen, Shu-Ya Yin, Zhi-Wei Wei, Qian-Feng Qiu, Nan-Xia Zhu, Ya-Nan Fan, Mei Pan, and Cheng-Yong Su. Pressure-induced multiphoton excited fluorochromic metal–organic frameworks for improving MPEF properties. *Angewandte Chemie International Edition*, 58:14379–14385, 2019. doi: 10.1002/anie.201908793.
- [187] Mohamed A. Salem, Iain Twelves, and Alex Brown. Prediction of two-photon absorption enhancement in red fluorescent protein chromophores made from non-canonical amino acids. *Physical Chemistry Chemical Physics*, 18:24408–24416, 2016. doi: 10.1039/C6CP03865D.
- [188] Ibtisam Juma Al-Busaidi, Ashanul Haque, John Husband, Nawal K. Al-Rasbi, Osama K. Abou-Zied, Rayya A. Al-Balushi, Muhammad S. Khan, and Paul R. Raithby. Electronic and steric effects of platinum(II) di-yne and poly-yne substituents on the photo-switching behaviour of stilbene: Experimental and theoretical insights. *Dalton Transactions*, 50:2555–2569, 2021. doi: 10.1039/D0DT03502E.
- [189] Abdou Amar, Azzedine Elkechai, Jean-François Halet, Frédéric Paul, and Abdou Boucekkine. Two-photon absorption of dipolar and quadrupolar oligothiophene-cored chromophore derivatives containing terminal dimesitylboryl moieties: A theoretical (DFT) structure–property investigation. *New Journal of Chemistry*, 45:15074–15086, 2021. doi: 10.1039/D1NJ01467F.
- [190] Zhibo Liu, Tian Lu, and Qianjin Chen. An sp-hybridized all-carboatomic ring, cyclo[18]carbon: Electronic structure, electronic spectrum, and optical nonlinearity. *Carbon*, 165:461–467, 2020. doi: 10.1016/j.carbon.2020.05.023.
- [191] Tian Lu. A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn. *Journal of Chemical Physics*, 161:082503, 2024. doi: 10.1063/5.0216272.
- [192] Tian Lu and Feiwu Chen. Multiwfn: A multifunctional wavefunction analyzer. *Journal of Computational Chemistry*, 33:580–592, 2012. doi: 10.1002/jcc.22885.
- [193] Tanguy Le Bahers, Carlo Adamo, and Ilaria Ciofini. A qualitative index of spatial extent in charge-transfer excitations. *Journal of Chemical Theory and Computation*, 7:2498–2506, 2011. doi: 10.1021/ct200308m.

- [194] Simon N. Deger, Helmy Pacheco Hernandez, Yang Cui, Hongxing Hao, Vanessa Ramm, David C. Mayer, Khai-Nghi Truong, Roland A. Fischer, Jürgen Hauer, Mariana Kozłowska, and Alexander Pöthig. Modulating two-photon absorption in a pyrene-based mof series: An in-depth investigation of structure–property relationships. *Advanced Functional Materials*, n/a(n/a):e06660. doi: <https://doi.org/10.1002/adfm.202506660>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adfm.202506660>.
- [195] Merle Schröter, Sergei D. Ivanov, Jan Schulze, Sergey P. Polyutov, Yijing Yan, Tõnu Pullerits, and Oliver Kühn. Exciton–vibrational coupling in the dynamics and spectroscopy of Frenkel excitons in molecular aggregates. *Physics Reports*, 567:1–78, 2015. doi: 10.1016/j.physrep.2014.12.001.
- [196] Yangdan Pan, Soheila Sanati, Marzieh Nadafan, Reza Abazari, Junkuo Gao, and Alexander M. Kirillov. Postsynthetic modification of NU-1000 for designing a polyoxometalate-containing nanocomposite with enhanced third-order nonlinear optical performance. *Inorganic Chemistry*, 61(47):18873–18882, 2022. doi: 10.1021/acs.inorgchem.2c02709.
- [197] Andreas Klamt and Georg Schüürmann. COSMO: A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *Journal of the Chemical Society, Perkin Transactions 2*, pages 799–805, 1993. doi: 10.1039/P29930000799.
- [198] Dong-Gwang Ha, Ruomeng Wan, Changhae Andrew Kim, Ting-An Lin, Luming Yang, Troy Van Voorhis, Marc A. Baldo, and Mircea Dincă. Exchange controlled triplet fusion in metal–organic frameworks. *Nature Materials*, 21:1275–1281, 2022. doi: 10.1038/s41563-022-01368-1.
- [199] Sreehari Surendran Rajasree, Jierui Yu, Saied Md Pratik, Xinlin Li, Rui Wang, Amar S. Kumbhar, Subhadip Goswami, Christopher J. Cramer, and Pravas Deria. Superradiance and directional exciton migration in metal–organic frameworks. *Journal of the American Chemical Society*, 144(3):1396–1406, 2022. doi: 10.1021/jacs.1c11979.
- [200] Mounia Más-Montoya and René A. J. Janssen. The effect of H- and J-aggregation on the photophysical and photovoltaic properties of small thiophene–pyridine–DPP molecules for bulk-heterojunction solar cells. *Advanced Functional Materials*, 27:1605779, 2017. doi: 10.1002/adfm.201605779.
- [201] Krishnamoorthy Muralirajan, Il Son Khan, Luis Garzon-Tovar, Rajesh Kancherla, Nikita Kolobov, Alla Dikhtiarenko, Maram Almalki, Aleksander Shkurenko, Alejandra Rendón-Patiño, Vincent Guillermin, Khoa N. Le, Genrikh Shterk, Huabin Zhang, Christopher H. Hendon, Mohamed Eddaoudi, Jorge Gascon, and Magnus Rueping. Ba/ti mof: A versatile heterogeneous photoredox catalyst for visible-light metallaphotocatalysis. *Advanced Materials*, 37(4):2405646, 2025. doi: <https://doi.org/10.1002/adma.202405646>. URL <https://advanced.onlinelibrary.wiley.com/doi/abs/10.1002/adma.202405646>.

H. List of Figures

1.1	Schematic overview of the structural and chemical diversity of MOFs and their representative applications in functional devices. Adapted from Ivo Stassen <i>et al.</i> , ^[15] with permission from the Royal Society of Chemistry, licensed under CC BY 3.0.	1
1.2	Schematic illustration of a photoswitchable framework showing reversible light-induced modulation of charge transport. Upon irradiation ($h\nu$), the molecular photoswitches in the material convert from an OFF state with low conductivity (left) to an ON state with enhanced charge transport (right). The reverse process restores the initial low-conductivity state. Reproduced from Pacheco Hernandez <i>et al.</i> , ^[52] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	4
1.3	Photoswitchable molecules are commonly incorporated into framework materials in three different ways: (i) as backbone linkers, (ii) guest molecules, and (iii) attached to the linker. In this figure, azobenzene, spiropyran, and diarylethene are depicted as examples, but diverse photoswitches can be incorporated. Reproduced from Pacheco Hernandez <i>et al.</i> , ^[52] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	5
1.4	Schematic representation of excited state energy splitting for different molecular aggregate types (J-, H-, X-aggregates, and AIE). Reproduced from Ma <i>et al.</i> , ^[107] with permission from John Wiley & Sons, 2021. Licensed under CC BY.	8
2.1	Schematic illustration of a) band-like and b) hopping transport mechanisms. Left: in the adiabatic regime with strong electronic coupling (solid curves), charge carriers are delocalized over multiple sites and move coherently through extended electronic states, as indicated by the blue arrows. Right: hopping between the diabatic potential energy surfaces (dashed curves) of the initial and final localized sites is shown. The microscopic parameters governing the charge-transfer rate in the weak-coupling regime are included for clarity and discussed in the text. The energy difference between hopping sites is neglected. Green arrows schematically indicate hopping within the MOF material. Reproduced from Pacheco Hernandez <i>et al.</i> , ^[52] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	12

2.2	Profile of the many-dimensional potential energy surface of reactants plus surrounding medium (R) and products plus medium (P). Points A and C denote equilibrium nuclear configurations of reactants and products, respectively; B denotes the nuclear configuration at the intersection of the two surfaces. Dotted lines indicate the splitting due to electronic coupling between reactants. Reproduced from Marcus and Sutin, ^[116] <i>Biochim. Biophys. Acta</i> 811 , 265-322 (1985), with permission from Elsevier.	14
2.3	Simplified Jablonski diagram illustrating one-photon absorption (1PA, left) and two-photon absorption (2PA, right). In the 2PA process, two photons are absorbed simultaneously via a virtual intermediate state. The accessible excited states differ depending on the molecule's centrosymmetry.	16
2.4	Perdew's Jacob's ladder of DFT exchange-correlation functionals, illustrating the hierarchy from the simplest LDA at the lowest rung to fully non-local (Earth), to "heaven" which represents the limit of chemical accuracy.	23
2.5	General flowchart of a classical MD simulation. *Step 2 is not always required. For instance, if a simulation is continued from a previously equilibrated system. In principle, a simulation started from scratch could also proceed if the initial structure happens to be close to the equilibrium geometry of the chosen force field, but this is rarely the case in practice, since initial structures are typically constructed from experimental data, <i>ab initio</i> calculations, or prior MD simulations performed under different conditions. Figure based on reference [141].	31
3.1	HOMO visualization of SP to MC photoisomerization: SP to MC under UV (λ_{UV}); MC to SP thermally or under visible light (λ_{vis}). Atom colors: C brown, O red, N light blue, H white. Reproduced from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	35
3.2	Graphic representation of the studied systems. Dabco and bipy act as pillar linkers, which regulate the interlayer distances of SP and MC layer linkers. This figure was adapted from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	36
3.3	SimStack workflow to generate, optimize, and analyze MOF materials for automated structure-property prediction and design. The modules in the workflow are referred as WaNos and perform a specific type of calculation. Adapted from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	37
3.4	Graphic representation of the $4 \times 4 \times 4$ MC-MOF supercell (left). The analyzed systems were extracted from the central region of the supercell. Molecular dynamics analysis revealed that, in some cases, stacking occurred in dimer or trimer arrangements (right). Interaction distances given in Å.	41

3.5	SP dimer extracted from the $4 \times 4 \times 4$ SP-MOF supercell. The analyzed systems were extracted from the central region of the supercell. Molecular dynamics analysis revealed that SP linkers remain rigid with long interaction distances of 8.6 Å, which prevent molecular orbital overlap. Adapted from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	42
3.6	Representative snapshots of layer linker dimers from MD at 298 K. SP (top row) and MC (bottom row) of $\text{Cu}_2(\text{SP})_2(\text{dabco})$ and $\text{Cu}_2(\text{MC})_2(\text{dabco})$, respectively. Time stamps (ns) are shown at the upper right of each panel. Dabco pillar linkers are omitted for clarity (red arrow represents DABCO's position). Carbon, oxygen, nitrogen, and hydrogen are colored cyan, red, blue, and white, respectively. Reproduced from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	43
3.7	Time evolution of the electronic coupling during the last 5 ns of a 10 ns MD trajectory. The left panel shows the HOMO and LUMO results of the direct EC between dimers, with SP-SP in red and MC-MC in blue. The central panel presents the EC when superexchange is considered, where charge transfer occurs from the initial to the final state through an intermediate one. The right panel shows the electronic coupling calculated for a bipy-based MOF, which exhibits noticeably lower values due to the larger interlayer separation compared to the dabco-based MOF, where shorter interlayer distances are possible. Adapted from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	44
3.8	Representative snapshots of layer linker dimers from MD at 298 K. SP (top row) and MC (bottom row) of $\text{Cu}_2(\text{SP})_2(\text{bipy})$ and $\text{Cu}_2(\text{MC})_2(\text{bipy})$, respectively. Time stamps (ns) are shown at the upper right of each panel. Bipy pillar linkers are omitted for clarity (red arrow). Carbon, oxygen, nitrogen, and hydrogen are colored cyan, red, blue, and white, respectively. Reproduced from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	45
4.1	Schematic representation of the monomer (left) and dimer (right) systems for the H_4TCPE molecule. Fixed carbon atoms, to preserve specific intra- and inter-molecular distances, are shown in black. For the monomer, intramolecular distances ($d_{\text{C-C}}$) were scanned from 13 to 19 Å. For the dimer, carbon atoms were fixed to preserve the initial inter-molecular stacking distances of 4 and 5 Å. After geometry optimization, the converged stacking distances resulted in intermolecular separations of 5.12 and 5.13 Å, as indicated by the blue arrows. Reproduced from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	49

4.2	Representation of the three different dimer models. The different molecular planes are shown in green and orange. a) Book-like opening along the longer (LA) and shorter (SA) axes, the variation of the opening angle is marked as θ . b) Stacking-plane displacement along the x and y directions are defined as Δ_x and Δ_y respectively, and c) parallel-stacked dimers subjected to in-plane rotational scans, with the rotation angle θ . For b) and c) systems the variation in the sampled intermolecular distances are marked as Δ_z . Reproduced from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	50
4.3	Calculated absorption spectra of the different sampled arm separation of the H ₄ TCPE monomer. Adapted from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	52
4.4	Calculated absorption spectra of the different sampled arm separation of the H ₄ TCPE monomer. Adapted from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	53
4.5	Schematic representation of the H ₄ TCPE linker and the four carbon atoms used to define the dihedral angle ω are highlighted in red. Reproduced from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	54
4.6	EDD visualization for the first and second excitations. The corresponding 1PA and 2PA results for each sampled monomer are shown at the top in blue. For each monomer, the 1PA oscillator strength (a.u.) is reported together with the excitation wavelength (nm) in brackets. The 2PA cross sections are given in GM, and the corresponding excitation wavelength (nm) is reported in brackets. Blue EDD isosurfaces denote electron-deficient regions upon excitation, whereas green sections indicate electron-rich regions. Reproduced from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	55
4.7	2PA cross sections (σ_2 , GM) as a function of the book-opening angle θ . The short-axis (SA) opening scan is shown in the left panel and the long-axis (LA) opening scan in the right panel. Values corresponding to the first excitation are indicated by stars, and those for the second excitation by dots. Colors denote the intramolecular distance of the monomers within each dimer, $d_{C-C} = 16$ Å (blue), 17 Å (black), and 18 Å (green). Insets show representative geometries for selected configurations. Adapted from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	57
4.8	Electron density difference (EDD) comparison for the $S_0 \rightarrow S_1$ transition in monomer and dimer systems across the $d_{C-C} = 16$ -18 Å range. For each structure, the excitation wavelength (nm), oscillator strength, and 2PA cross section σ_2 (GM) are reported. Multiwfn indices are also shown: S_r (dimensionless) and D and H (Å).	58

4.9	Stacking-plane displacement scan for H ₄ TCPE dimers. The 2PA cross section σ_2 is plotted against the in-plane displacement (± 5 and ± 10 Å) at two initial stacking distances, $\Delta z = 4$ Å (left) and 5 Å (right). Markers correspond to the transition considered (stars: first excited state; circles: second excited state). Line colors indicate the intramolecular distance d_{C-C} (16, 17, and 18 Å). Adapted from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	60
4.10	Representative geometry with $d_{C-C} = 17$ Å at $\Delta y = -5$ Å. EDD maps and the dominant orbital transitions are shown for the first and second excitations, together with the corresponding 1PA/2PA responses and CT indices. Results are compared for two initial stacking separations, $\Delta z = 4$ Å (left) and 5 Å (right). The analogous $d_{C-C} = 16$ and 18 Å conformations are provided in Figure B.9). In the EDD maps, blue regions indicate electron depletion (donor), while green regions indicate electron accumulation (acceptor) upon excitation. Adapted from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	61
4.11	Effect of stacking-plane rotation on the 2PA response of H ₄ TCPE dimers. The 2PA σ_2 is shown as a function of the stacking-plane rotation angle for initial separations of $\Delta z = 4$ Å (left) and 5 Å (right). Stars and circles denote the first and second excited-state transitions, respectively. Line colors indicate the intramolecular distance d_{C-C} (16 Å in blue, 17 Å in black, and 18 Å in green). Insets show representative geometries for selected configurations. Reproduced from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	62
4.12	EDD and main orbital contribution for a representative geometry $d_{C-C} = 17$ Å. Comparison of the initial separations $\Delta z = 4$ Å (left) and 5 Å (right). Adapted from Pacheco Hernandez and Kozłowska, ^[177] <i>Front. Chem.</i> (2026). Licensed under CC BY 4.0.	63
4.13	Representative assemblies extracted from the H ₄ TBAPy-based MOFs NU-901, NU-1000, SrTBAPy, and BaTBAPy. For each framework, contiguous dimers (DimerA-DimerD) were considered along the different closely packed directions; where applicable, the corresponding trimers were also analyzed, and for NU-901, a tetramer was additionally included. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	66

4.14	Representative SBU-containing fragments extracted from the SrTBAPy and BaTBAPy crystal structures. a) SrTBAPy-extracted dimer, illustrating the larger intermolecular separation (6.86 Å). b) BaTBAPy-extracted dimer, showing a much shorter stacking contact (3.41 Å). The gray highlighted region indicates the portion of the periodic structure used to define the extracted cluster. To preserve the coordination environment of the SBUs and avoid dangling bonds, terminal oxygen atoms were capped with methyl groups. In addition to the representative fragments shown here, monomer-1SBU, dimer-1SBU, and dimer-2SBU cluster models were considered for the analysis. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	67
4.15	One-photon absorption (1PA) spectra of H ₄ TBAPy monomers extracted from the crystal structures of NU-901 (black), NU-1000 (blue), SrTBAPy (orange), and BaTBAPy (green), computed at the single-point level. The wavelengths of the main absorption maxima are shown in the corresponding colors. The inset shows an overlay of the extracted monomer geometries to highlight subtle framework-dependent distortions. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	68
4.16	One-photon absorption (1PA) spectra of H ₄ TBAPy monomers extracted from the crystal structures of NU-901 (black), NU-1000 (blue), SrTBAPy (orange), and BaTBAPy (green), and further optimized in DMF. The wavelengths of the main absorption maxima are shown in the corresponding colors. The inset table shows the final energies after optimization	the
	.Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	69
4.17	Overview of the four TBAPy-based MOFs investigated in this work (NU-1000, NU-901, SrTBAPy, and BaTBAPy). The same TBAPy linker is present in all frameworks, while the SBUs differ: Zr-oxo clusters in NU-1000/NU-901 (blue) and in SrTBAPy and BaTBAPy (yellow and pink). Structures are viewed along the crystallographic <i>c</i> -axis. . .	70
4.18	Effect of MOF packing on the 2PA response, shown as calculated 2PA spectra for assemblies extracted from the NU-1000 (left) and NU-901 (right) crystal structures. The H ₄ TBAPy monomer is omitted because its σ_2 is negligible over the plotted spectral range. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	71
4.19	Distance screening in DimerA extracted from BaTBAPy (left) and SrTBAPy (right) MOFs. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	72

4.20	Effect of MOF packing on the 2PA response, shown as calculated 2PA spectra for assemblies extracted from the BaTBAPy (left) and SrTBAPy (right) crystal structures. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	73
4.21	Comparison of SrTBAPy assemblies upon systematic modifications, showing the i) qualitative EDD, ii) 2PA response and iii) IFCT.	74
4.22	EDD between the first excitation and the ground state a) DimerA b) Dimer-2SBUs extracted from BaTBAPy. Electron-donating regions are indicated in blue, and electron-accepting regions are in green. Adapted from Deger <i>et al.</i> , ^[194] <i>Adv. Funct. Mater.</i> (2025). Licensed under CC BY 4.0.	75
A.1	Comparison of the electronic coupling between linkers in (a) Cu ₂ (SP-OH) ₂ (dabco) and Cu ₂ (MC-OH) ₂ (dabco) MOFs, and in (b) Cu ₂ (SP-CHO) ₂ (dabco) and Cu ₂ (MC-CHO) ₂ (dabco) MOFs. Reproduced from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	81
A.2	Visualization of the HOMO orbitals of the investigated linkers. The corresponding orbital energies are given for each orbital. An isovalue of 0.02 a.u. was used for visualization. The unmodified SP and MC linkers are highlighted in light blue. MOFs containing SP, MC, SP-OH, MC-OH, SP-CHO, and MC-CHO as layer linkers were simulated. Reproduced from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	82
A.3	Visualization of the LUMO orbitals of the investigated linkers. The corresponding orbital energies are given for each orbital. An isovalue of 0.02 a.u. was used for visualization. The unmodified SP and MC linkers are highlighted in light blue. MOFs containing SP, MC, SP-OH, MC-OH, SP-CHO, and MC-CHO as layer linkers were simulated. Reproduced from Mostaghimi <i>et al.</i> , ^[110] <i>Commun. Chem.</i> 6 , 275 (2023). Licensed under CC BY 4.0.	82
B.1	TD-DFT results for $d_{C-C} = 13$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	83
B.2	TD-DFT results for $d_{C-C} = 14$ Å. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	84

B.3	TD-DFT results for $d_{C-C} = 15 \text{ \AA}$. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	84
B.4	TD-DFT results for $d_{C-C} = 16 \text{ \AA}$. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	85
B.5	TD-DFT results for $d_{C-C} = 17 \text{ \AA}$. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	85
B.6	TD-DFT results for $d_{C-C} = 18 \text{ \AA}$. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	86
B.7	TD-DFT results for $d_{C-C} = 19 \text{ \AA}$. (a) Calculated 1PA and 2PA excitation wavelengths, along with their oscillator strengths, and 2PA cross sections (σ_2 , GM) for the ten lowest singlet excited states. (b) Frontier molecular orbitals involved in the dominant transitions of the first and second excited states.	86
B.8	Book-opening angle 45° : comparison of short- and long-axis configurations for $d_{C-C} = 16\text{-}18 \text{ \AA}$. Electron density difference (EDD) plots and dominant orbital transitions for the first and second excitations.	105
B.9	Plane displacement $\Delta y = -5 \text{ \AA}$: comparison of stacking distances (4 and 5 $\text{\AA}$) for $d_{C-C} = 16\text{-}18 \text{ \AA}$. Electron density difference (EDD) plots and dominant orbital transitions for the first and second excitations.	106
B.10	Plane rotation 0° : comparison of stacking distances (4 and 5 $\text{\AA}$) for $d_{C-C} = 16\text{-}18 \text{ \AA}$. Electron density difference (EDD) plots and dominant orbital transitions for the first and second excitations.	107
B.11	Comparison of two stacking motifs extracted from the BaTBAPy MOF. In panel a), DimerA is shown in the upper row and DimerE in the lower row. The highlighted circles indicate different viewing orientations: in one view (yellow/pink), DimerE appears different from DimerA, whereas after rotating the view (blue), the relative arrangement in DimerE becomes analogous to that of DimerA. Panel b) shows the corresponding 2PA absorption spectra for the extracted systems; the insets display the electron density difference (EDD) plots of the first excitation.	138

I. List of Tables

4.1	The energy values of the optimized structures as a function of d_{C-C}	51
4.2	CT parameters for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations of H_4TCPE at different d_{C-C} distances. The dihedral angle ω is reported in degrees ($^\circ$), where values closer to 180° indicate a more planar structure. S_r is dimensionless, whereas D , H_{CT} , H , and t are given in $\text{\AA}$. The change in dipole moment relative to the ground state, $\Delta\mu$, is reported in atomic units (a.u.) and in Debye [D].	53
B.1	TD-DFT results for the H_4TCPE dimer in the $SA(45^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	87
B.2	TD-DFT results for the H_4TCPE dimer in the $SA(90^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	88
B.3	TD-DFT results for the H_4TCPE dimer in the $SA(135^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	88
B.4	TD-DFT results for the H_4TCPE dimer in the $SA(180^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	89
B.5	TD-DFT results for the H_4TCPE dimer in the $LA(45^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	89
B.6	TD-DFT results for the H_4TCPE dimer in the $LA(90^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	90
B.7	TD-DFT results for the H_4TCPE dimer in the $LA(135^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	90
B.8	TD-DFT results for the H_4TCPE dimer in the $LA(180^\circ)$ geometry ($\Delta z = 4 \text{ \AA}$, $d_{C-C} = 16\text{--}18 \text{ \AA}$), including 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	91

B.9	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta y = +5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	92
B.10	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta y = -5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	93
B.11	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta y = +10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	94
B.12	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta y = -10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	95
B.13	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta x = +5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	96
B.14	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta x = -5$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	97
B.15	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta x = +10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	98
B.16	TD-DFT excitation summary for the H ₄ TCPE dimer at $\Delta x = -10$ Å, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	99
B.17	TD-DFT excitation summary for the H ₄ TCPE dimer at plane rotation = 0°:, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	100
B.18	TD-DFT excitation summary for the H ₄ TCPE dimer at plane rotation = 30°:, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	101
B.19	TD-DFT excitation summary for the H ₄ TCPE dimer at plane rotation = 60°:, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	102
B.20	TD-DFT excitation summary for the H ₄ TCPE dimer at plane rotation = 90°:, comparing stacking distances of 4 and 5 Å for $d_{C-C} = 16-18$ Å: 1PA/2PA wavelengths, oscillator strengths, σ_2 , and dominant orbital transitions.	103

B.21	Book-opening angle 45° : Multiwfn analysis of the first and second excited states across the SA and LA configurations for $d_{C-C} = 16-18 \text{ \AA}$	108
B.22	Plane displacement $\Delta y = -5 \text{ \AA}$: Multiwfn analysis of the first and second excited states comparison of $\Delta z = 4$ and $5 \text{ \AA}$ for $d_{C-C} = 16-18 \text{ \AA}$	108
B.23	Plane rotation 0° : Multiwfn analysis of the first and second excited states comparison of $\Delta z = 4$ and $5 \text{ \AA}$ for $d_{C-C} = 16-18 \text{ \AA}$	109
B.24	Summary of the electronic transitions involved in 1PA and 2PA for the H_4TBAPy monomer in implicit DMF.	110
B.25	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF NU-1000.	111
B.26	Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF NU-1000.	112
B.27	Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF NU-1000.	113
B.28	Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF NU-1000.	114
B.29	Summary of the electronic transitions involved in 1PA and 2PA for the Trimer extracted from MOF NU-1000.	115
B.30	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF NU-901.	116
B.31	Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF NU-901.	117
B.32	Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF NU-901.	117
B.33	Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF NU-901.	118
B.34	Summary of the electronic transitions involved in 1PA and 2PA for the TrimerA extracted from MOF NU-901.	119
B.35	Summary of the electronic transitions involved in 1PA and 2PA for the TrimerB extracted from MOF NU-901.	120
B.36	Summary of the electronic transitions involved in 1PA and 2PA for the TetramerA extracted from MOF NU-901.	121
B.37	Summary of the electronic transitions involved in 1PA and 2PA for the TetramerB extracted from MOF NU-901.	122
B.38	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF SrTBAPy.	123

B.39	Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF SrTBAPy.	123
B.40	Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF SrTBAPy.	124
B.41	Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF SrTBAPy.	124
B.42	Summary of the electronic transitions involved in 1PA and 2PA for the TrimerA extracted from MOF SrTBAPy.	125
B.43	Summary of the electronic transitions involved in 1PA and 2PA for the Monomer+SBU(Sr) extracted from MOF SrTBAPy.	126
B.44	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+SBU(Sr) extracted from MOF SrTBAPy.	127
B.45	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+2SBU(Sr) extracted from MOF SrTBAPy.	128
B.46	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA extracted from MOF BaTBAPy.	129
B.47	Summary of the electronic transitions involved in 1PA and 2PA for the DimerB extracted from MOF BaTBAPy.	130
B.48	Summary of the electronic transitions involved in 1PA and 2PA for the DimerC extracted from MOF BaTBAPy.	130
B.49	Summary of the electronic transitions involved in 1PA and 2PA for the DimerD extracted from MOF BaTBAPy.	131
B.50	Summary of the electronic transitions involved in 1PA and 2PA for the DimerE extracted from MOF BaTBAPy.	132
B.51	Summary of the electronic transitions involved in 1PA and 2PA for the Trimer extracted from MOF BaTBAPy.	133
B.52	Summary of the electronic transitions involved in 1PA and 2PA for the Monomer+SBU(Ba) extracted from MOF BaTBAPy.	134
B.53	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+SBU(Ba) extracted from MOF BaTBAPy.	135
B.54	Summary of the electronic transitions involved in 1PA and 2PA for the DimerA+2SBU(Ba) extracted from MOF BaTBAPy.	136
B.55	Summary of the electronic transitions involved in 1PA and 2PA for the DimerE+2SBU(Ba) extracted from MOF BaTBAPy.	137

B.56 Summary of the inter-fragment charge transfer (IFCT) analysis performed for the characteristic excitations contributing to the 2PA response of the BaTBAPy and SrTBAPy MOFs, as discussed in the main text and identified in the tables above, in Table B.38-Table B.55. All values are given in % and were calculated using molecular fragments (mol1 and mol2) defined as the complete H₄TBAPy linkers. H and E denote the contribution of each fragment to the hole and electron, respectively, in the charge-transfer matrix, while 1→2 and 2→1 indicate the % of electron transfer between the fragments. The intrinsic charge-transfer percentage (ICTP) and apparent charge-transfer percentage (ACTP) corresponding to the CT contribution are also reported. The local excitation (LE) contribution can be estimated as 100% – CT. For clarity, the ACTP between the dimer and the SBU (i.e., CT_{dimer-SBU}, mainly indicating LMCT) is also provided. CT contributions arising from dimer-dimer interactions were calculated for the extracted dimers and under the influence of the SBU (indicated with an asterisk, *). Although SBU fragments were not explicitly included in the IFCT analysis, they were present in the EDD analysis. The corresponding 2PA cross-section values are also listed. The corresponding excitation in the isolated monomer exhibits a purely LE character. 139