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Review Article

Surface-anchored, oriented, monolithic Metal–Organic framework thin films: Surface and interface phenomena in crystalline MOF architectures

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ABSTRACT

Metal–organic frameworks (MOFs) are crystalline materials renowned for their high porosity, chemical tunability, and modular design. The development of surface-anchored and oriented MOF thin films—particularly those fabricated by layer-by-layer or epitaxial growth—has shifted MOF research from powder studies to investigations of well-defined, surface-confined architectures. This review examines MOF thin films from a surface-science perspective, emphasizing how controlled growth at well-defined interfaces enables quantitative studies of structure–property relationships, interfacial charge and energy transfer, polarization-dependent optical responses, and dynamic guest–host interactions. The long-range crystallographic order achievable in these oriented films gives rise to band-structure effects and anisotropic transport phenomena that cannot be observed in MOF thin films prepared from powder-derived particles. Their monolithic and defect-controlled nature allows detailed characterization by advanced surface-sensitive techniques such as IRRAS, XPS, NEXAFS, UPS, nanoindentation, ellipsometry, and AFM, providing direct links between microscopic structure and macroscopic functionality. Beyond serving as model systems, oriented MOF films represent versatile platforms for adsorption, catalysis, and electronic coupling at hybrid organic–inorganic interfaces. The review also highlights how computational modeling, machine learning, and AI-guided synthesis accelerate the rational design of interface-engineered MOF architectures with tailored properties.

1. Introduction

Metal organic frameworks (MOFs) comprise a huge class of materials known for their highly porous structures and the possibility to tailor their chemical, physical, and electronic functionalities in a rather straightforward fashion. With regard to the digitization of materials research in the context of the development of artificial intelligence (AI), and large language models, the virtually unlimited amounts of different structures and the possibility to predict properties of yet unknown MOFs by computer calculations is a particularly exciting topic. While so far, most MOFs have been synthesized in the form of powders with particle sizes typically between 100 nm and 10 μm, which are well-suited for applications ranging from gas storage to catalysis and separations, for more advanced applications it is crucial, as only then can structurally well-defined thin films be deposited on suitable substrates to fully harness their potential for optical, electrical, and electronic applications. In several cases, it has been demonstrated that MOF thin films have lower defect densities, and for example, in terms of utilizing their electrical conductivity, thin films have so far outperformed the small particles synthesized using solvothermal synthesis conditions. MOF thin films, which offer tailored advantages when it comes to the integration of MOFs into functional devices, can be fabricated using a number of different methods.

In this report, which aims to introduce the physical properties of MOF thin films to an audience that is not yet familiar with MOFs, we will focus on layer-by-layer methods, which yield films with properties typically superior to those obtained by other deposition methods. Such layer-by-layer films, which will henceforth be referred to as "Surface-anchored MOFs" (SURMOFs), can be precisely deposited on a variety of different substrates thus allowing for the integration of MOFs with semiconductor devices, optical fibers, and electronic circuits [1,2]. Compared with MOF thin films made from spin-coating or drop-casting MOF particle suspensions, SURMOFs are monolithic with smooth surfaces and enable precise control over film thickness, orientation, and uniformity [3,4]. For other types of MOF thin films the reader is referred to existing reviews [2,5]. The particular properties of SURMOFs ensure compatibility with electrically conducting, insulating, optically transparent, or reflecting substrates and are essential for developing innovative applications such as smart windows, photovoltaic cells, light-emitting diodes (LEDs), and sensors, both operated in the gas phase as well as in the liquid. Furthermore, the presence of oriented thin films with long-range crystalline order allows to study band-structure

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effects in MOFs, a topic which recently started to receive considerable attention [6,7]. Although synthesis of SURMOFs is not a topic of this article, we would like to note that due to the mild synthesis conditions variants of the lbl synthesis method can be used to fabricate SURMOFs where the corresponding analogue bulk MOF cannot be synthesized [8].

Furthermore, for such well-defined, monolithic thin films, many standard Surface-Science methods—IRRAS (infrared reflection-absorption spectroscopy), XPS (X-ray photoelectron spectroscopy), UPS (ultraviolet photoelectron spectroscopy), AFM (atomic force microscopy), and SE (spectroscopic ellipsometry)—can be used in a straightforward fashion. Here, we will not describe the experimental details of the different methods available for synthesizing SURMOFs or other MOF thin films fabricated using a variety of different methods. Instead, the reader is referred to existing literature [5,9–12]. Note, that a number of recent reviews have a main focus on SURMOFs [3,13,14].

2. Characterisation of MOF thin films

2.1. Studies of surface morphology by atomic force microscopy (AFM)

While the investigation of MOF powder particles and of thin films made by spin-coating or drop-casting particle suspensions with AFM requires substantial experimental effort, the application of the technique to high-quality, low-roughness and monolithic MOF thin films is relatively straightforward. In a paper by Munuera et al. [15], the growth of HKUST-1 SURMOFs on various nanopatterned substrates was investigated. Nanopatterning was achieved by employing micro-contact printing to yield squares of –COOH-terminated regions embedded in a matrix of CH_3-terminated areas. Whereas the SURMOF growth process proceeds readily on the –COOH-terminated regions, no deposition takes place on the CH_3-terminated areas of the substrate [16]. The number of immersion cycles used for the layer-by-layer growth of the SURMOFs was systematically varied prior to characterization using AFM. The thickness of the SURMOF layers was measured using height histograms and averaged profiles, ensuring accurate determination of film thickness. The selective deposition of MOFs on specific regions of the substrate is highlighted, demonstrating the effectiveness of the step-by-step preparation procedure. The resulting films exhibited fairly low roughness values, on the order of 4 nm—an important prerequisite for multi-heteroepitaxy.

For such homogeneous films, local probe techniques that combine AFM with spectroscopic methods have been successfully employed. For such homogeneous films, local probe techniques that combine AFM with spectroscopic methods have been successfully employed [17,18]. Furthermore, for these rather smooth MOF-based substrates, standard nanoindentation techniques can also be used to determine the mechanical properties of MOFs [19] (see section 4.5).

2.2. Characterisation using XPS, UPS, SE, IRRAS, and NEXAFS

A clear advantage of SURMOFs is the straightforward applicability of XPS, which is much more difficult to employ for MOF powders or powder-based MOF thin films due to charging problems. XPS is particularly useful for determining defect densities (e.g. identification of differently charged metal species [20], see below) and for probing the interactions of guest species loaded into the MOF pores. Moreover, NAP-XPS (near-ambient pressure XPS) can also be applied readily to these homogeneous MOF thin films. In recent studies on HKUST-1 SURMOFs, the binding of water, methanol, and pyridine was investigated with XPS at pressures of up to 4 mbar [21]. HKUST-1 SURMOFs have also been successfully used for near-ambient pressure NEXAFS (near edge x-ray absorption fine structure) studies [22]. In another application of this synchrotron-based method, SURMOFs made from bianthryl-linkers were studied [23]. Also for a thorough characterization of the MOF electronic structure via UPS SURMOFs are very beneficial, as demonstrated for porphyrin-based SURMOFs by Elzein et al. [24] and more recently by Scheiger et al. for hexahydroxytriphenylene (HHTP)-based SURMOFs [6]. Characterisation using SE is straightforward, for the monolithic SURMOFs with homogeneous thickness measurements using ellipsometry can be done in a routine fashion, see the work by Redel et al. [25] where the dielectric constant of HKUST-1 SURMOFs and Cu-BDC SURMOF-2 have been determined.

If MOF thin films are deposited on metal substrates, IRRAS (infrared reflection absorption spectroscopy) can be used – via employing the so-called surface selection rule – to infer the orientation of the molecular linkers of MOFs. Baumgartner et al. have used this approach to determine the orientation within terephthalate-based MOF thin films and SURMOFs [26].

2.3. Defect and domain boundary engineering

2.3.1. Reduced defect density

A major and highly important advantage of MOF thin films, and in particular SURMOFs, is the reduced defect density compared to bulk powders materials prepared using conventional solvothermal methods. Examples are HKUST-I [20] and UHM-3 [27] SURMOFs, where XPS and IRRAS of adsorbed CO (using the SLIR method [28]) applied to the metal ions present in the MOFs) was used to demonstrate defect densities were below 4 %, whereas the corresponding bulk powders exhibit defect densities in excess of 10 %. In the small particles comprising bulk MOFs, defects such as missing linkers or uncoordinated metal sites are more common and can affect the intrinsic performance of a MOF by introducing unwanted electronic states or disrupting the structural uniformity. Conversely, MOF thin films grown under controlled conditions, often exhibit a more ordered structure with a reduced number of defects, particularly with a reduced amount of domain boundaries (Fig. 1a) [29]. This reduction in defect density not only improves the optical and electronic properties of MOFs but also affects their performance as membranes and makes them more suitable for comparison with theoretical work, which typically assumes idealized structures. A particular interesting case in this context is the HKUST_1 MOF material. Whereas bulk powders exhibit a greenish or blueish color, SURMOFs made using optimized conditions are colorless and exhibit no pronounced absorption bands in UV–Vis spectroscopy, in agreement with predictions from accurate theoretical work (Fig. 1b) [30,31]. Although catalytic properties are not a topic of this review it is noted that such defects, i.e. Cu^+ species instead of Cu^{++} species, also strongly influence the chemical properties of HKUST-I MOFs [29].

The influence of defect density on the exciton diffusion length could be demonstrated for a palladium−porphyrin-based SURMOF by luminescence microscopy [32]. Transient absorption spectroscopy showed highly mobile triplets in the single-crystalline SURMOF domains, with transfer rates around 10^{10} s^{-1}, consistent with a Dexter-type mechanism enhanced by virtual charge-transfer intermediates. Despite predicted exciton diffusion lengths of several micrometers, interactions with domain boundaries limited diffusion to about 100 nm, still a very large value.

2.3.2. Eliminating domain boundaries in MOF thin films: enhancing diffusivity through epitaxial growth

A key challenge in studying and utilizing MOFs lies in their typically high defect density and polycrystalline morphology, which impede mass transport. In a recent novel approach (Fig. 2a), Thissen and coworkers have grown HKUST-1 single-crystals with cm-scale lateral dimensions on a single crystalline Si(111) substrate [33], demonstrating that domain boundaries—long known to hinder mass transport in porous materials like zeolites [34,35]—also dominate diffusion behavior in MOFs (Fig. 2b). By engineering monolithic HKUST-1 thin films epitaxially on nanopatterned Si(111) substrates, the authors eliminated rotational domain boundaries and achieved a dramatic, order-of-magnitude increase in molecular diffusion.

The growth strategy combined a nanopatterning approach

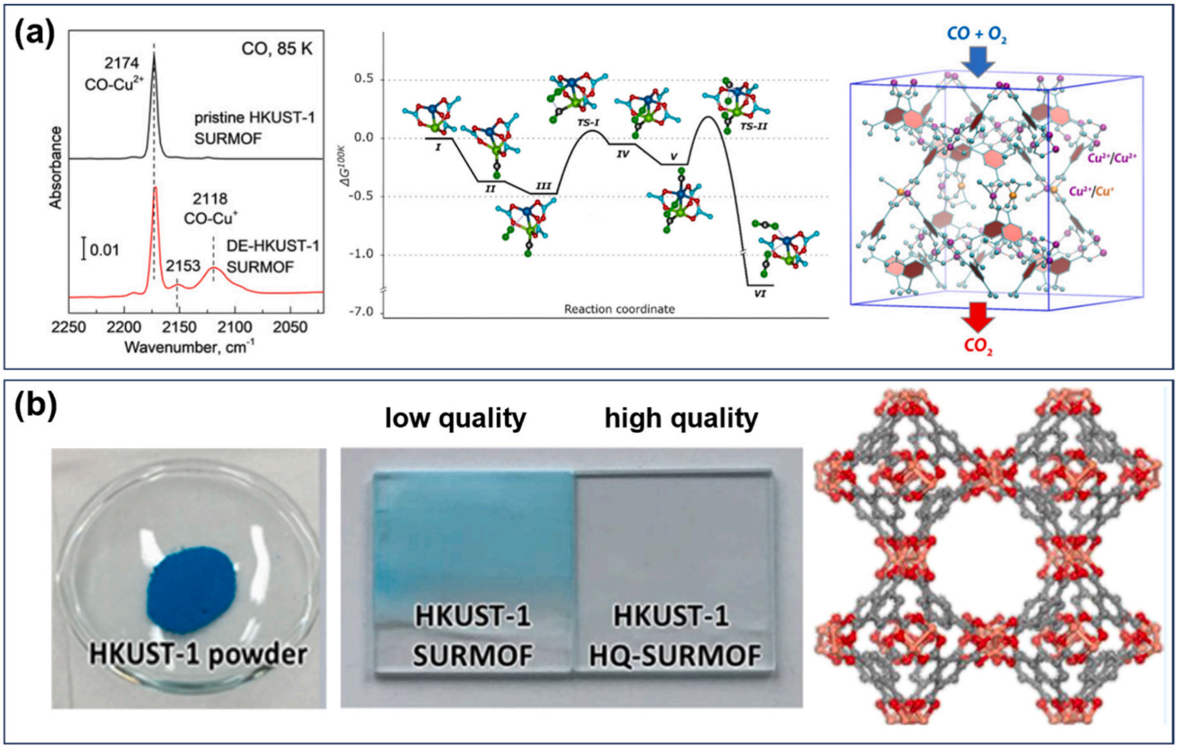

Fig. 1. (a) IRRAS analysis of CO adsorption on the defective HKUST-1 SURMOF, and its reaction mechanism of low-temperature CO oxidation with O_2 to CO_2. Picture taken from Ref. [29], with permission. (b) Photographs of HKUST-1 powder and HKUST-1 SURMOF at low and high quality, and the scheme of defect-free structure of HKUST-1. Picture taken from Ref. [31], with permission.

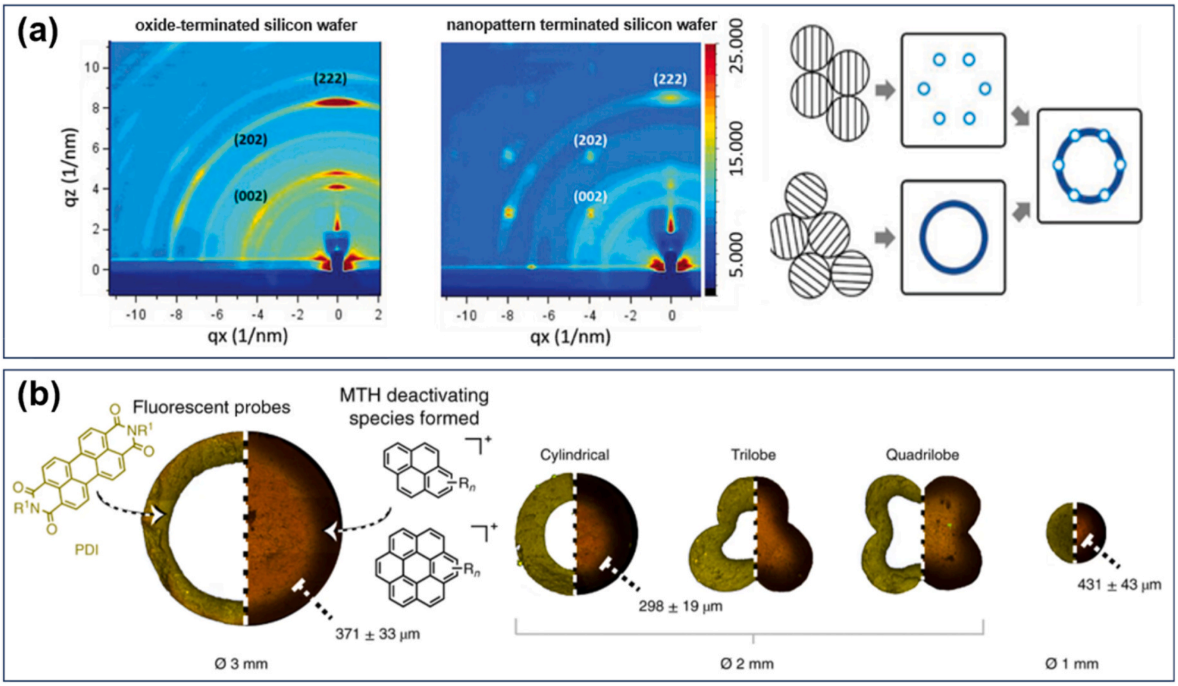

Fig. 2. (a) 2D GI-XRD images of HKUST-1, HKUST-1 grown on oxide-terminated silicon wafer and nanopattern terminated silicon wafer, and schematic diffraction rings of random distribution of HKUST-1 domains. Picture taken from Ref. [33], with permission. (b) The design of visualizing accessibility and deactivation in zeolite-based catalyst bodies. Picture taken from Ref. [35], with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(producing a R3 × R3 carboxylate-terminated surface on Si(111)) with automated liquid-phase epitaxy (LPE), yielding highly oriented SURMOFs. Grazing incidence X-ray diffraction (GI-XRD) revealed coherent epitaxial alignment of HKUST-1 crystals with the underlying substrate, in stark contrast to conventional MOF films, including SURMOFs, where domain misalignment is prevalent. AFM and Hough-transform analysis confirmed larger and uniformly aligned crystalline domains (≈380 nm) in the nanopatterned (NP-) SURMOFs compared to films on amorphous SiO_2 (≈150–200 nm).

To quantify the impact on transport, fluorescein dye uptake experiments were performed using inkjet-printed microdroplets deposited on top of the SURMOFs. The measured transport diffusion coefficient increased from $\sim 1.2 \times 10^{-16}$ m^2/s in standard HKUST-1 MOF thin films to $\sim 1.7 \times 10^{-15}$ m^2/s in NP-SURMOFs, a tenfold enhancement directly attributable to the suppression of inter-domain barriers. Importantly, spectroscopic ellipsometry and.

XPS confirmed that these structural improvements correlate with a lower refractive index and reduced Cu^+ defect concentrations.

This work establishes the first truly epitaxial MOF-on-semiconductor system and provides compelling evidence that domain boundary engineering is crucial for optimizing mass transport in MOF materials. Beyond diffusion, such monolithic thin films offer well-defined model systems for studying the influence of structural order on MOF optoelectronic and catalytic properties.

2.4. Surface engineering of MOF thin films

2.4.1. Grafting self-assembled monolayers on the outer surface of a SURMOF

In a recent demonstration [36] of the capabilities of the outer surfaces exposed by MOF thin films, a transformative strategy for achieving superhydrophobic surfaces was employed. Central to this advance was the unconventional realization of self-assembled monolayers (SAMs). On coinage metals or metal oxides, grafting of the SAM-forming monomers to the substrates typically yields tightly packed, low-entropy films with the individual hydrocarbon chains mostly in trans-conformation [37]. In contrast, anchoring the monomers on the surface exposed by the porous framework thin films enforces a low-density arrangement of hydrocarbon chains, containing a high density of gauche-conformations, enabling a brush-like configuration with significantly higher chain entropy.

Depending on the terminating group, the water contact angle (WCA) observed for such SAMs typically ranges between 80° and 120°. In stark contrast, the SAMs grafted to SURMOFs exhibited an extraordinary WCA in excess of 150°, the highest reported for any planar surface to date. This outcome is attributed to the unique scaffold provided by the crystalline MOF surface, on which the anchoring sites exhibit distances substantially larger than on coinage metal or oxidic substrates, thus preventing dense chain packing. The low grafting density enables a high-entropy, brush-like chain arrangement even for relatively short hydrocarbon chains (C18).

The experimental findings presented in this investigation were placed on a solid theoretical basis by carrying out molecular dynamics (MD) simulations [36], which confirmed that the increased entropy of the hydrocarbon chain configurations (i.e., the higher number of gauche-conformations in coiled carbon chains) directly contributes to the enhanced hydrophobicity. A key validation experiment involved replacing the hydrocarbon chains with perfluorinated analogs. Contrary to expectations—since fluorinated SAMs usually yield higher WCAs—this modification led to a reduced WCA, consistent with a loss of conformational entropy due to the rigidity of the fluorinated chains, which do not contain gauche defects.

Further extending the potential of this system, it was demonstrated that combining these low-density SAMs with surface nanostructuring can amplify the hydrophobicity beyond the already record-setting levels. Collectively, this work highlights the critical role of the underlying substrate in dictating SAM behavior and offers a powerful new route to engineering superhydrophobic surfaces through entropy-driven design principles.

2.4.2. Surfaces exposed by MOF thin films

MOFs have enormous internal pore surface areas, but the outer surface of a MOF nanoparticle or thin film - its external interface to the surrounding – holds unique importance distinct from the interior [38]. This outer surface is where the MOF contacts its surrounding environment or other materials, so tailoring it can impart new properties and functions not attainable through internal pore modifications alone. In this context, it is worth noting that MOF surfaces are intrinsically porous and feature binding sites that are spaced much farther apart than those on other substrates, such as metal or metal-oxide surfaces. For example, external surface functionalization can adjust a MOF's hydrophilicity or hydrophobicity, colloidal stability, and biocompatibility. While surface modifications can also be carried out on MOF powders—thereby influencing the properties of thin films fabricated from such particles—the application of traditional Surface-Science techniques is far more straightforward for monolithic, epitaxially grown SURMOFs. In the case of wetting, for example, MOF-based coatings fabricated from powders are intrinsically very rough, making it difficult to exclude Cassie–Baxter effects and to determine the intrinsic water contact angle [39].

As the MOF outer surface constitutes the contact interface with adjacent phases, it governs interfacial coupling and is therefore essential for the functional integration of MOFs into composite materials and device structures. The external surface also governs accessibility for guest species, serving as the entry point to the pores and sometimes causing "surface barrier" effects [40] that slow molecular diffusion into the porous MOF matrix if the surface chemistry or structure impedes transport. Conversely, it provides opportunities to engage species that cannot enter the pores: large biomolecules like proteins or enzymes can be immobilized on MOF outer surfaces, adding functionality (for sensing, catalysis, or targeting) without blocking the internal pore network [38].

Furthermore, the outer-surface chemistry can be tuned to enhance stability under operational conditions – for instance, rendering a MOF's exterior hydrophobic (e.g. by a polymer coating) protects it from moisture and improves performance in humid environments [41]. Both SAMs and polymer brushes can be assembled on the outer surface of MOFs to enhance their dispersity and stability in nonpolar solvents (Fig. 3a and b) [42,43]. By functionalizing the MOFs with stimuli-responsive polymers, on-demand release of the encapsulated guests can be facilitated by tuning external environments (e.g., response to pH, temperature) (Fig. 3c and d) [44–46].

The surface modification of MOFs thin films is an important strategy to achieve tunable optical properties and high stability. A robust superstructure with reflectivity tuned throughout the full optical range prepared by the self-assembly of monodisperse ZIF-8 nanocrystals capable of distinguishing chemicals with similar refractive indices (Fig. 3e) [47]. Robustness and solvent resistance of the MOF-based superstructures were achieved by deposition of hydrophobic nanoscale layer of poly(dimethylsiloxane) (PDMS). Homogeneous encapsulation of functional small guest molecules in MOF films contributes to specific physical–chemical properties that benefit device applications in optical communication and chemical sensing. In sum, although the external surface area is small relative to a MOF's vast internal surface, it plays an outsized role in interfacial interactions, the practical accessibility of the material's active sites, and the successful integration of MOFs into real-world applications.

3. Theoretical analysis and validation of theoretical models for MOFs and SURMOFs

Theoretical studies complement experimental characterization by deepening the understanding of reaction mechanisms, predicting spectroscopic signatures, and elucidating physical phenomena [48]. Their role in materials research has expanded rapidly, driven by advances in supercomputing and data-driven modeling approaches, which significantly shorten research cycles and reduce costs [49].

Because the unit cells of the crystalline MOF materials typically contain hundreds of atoms—many of them transition-metal

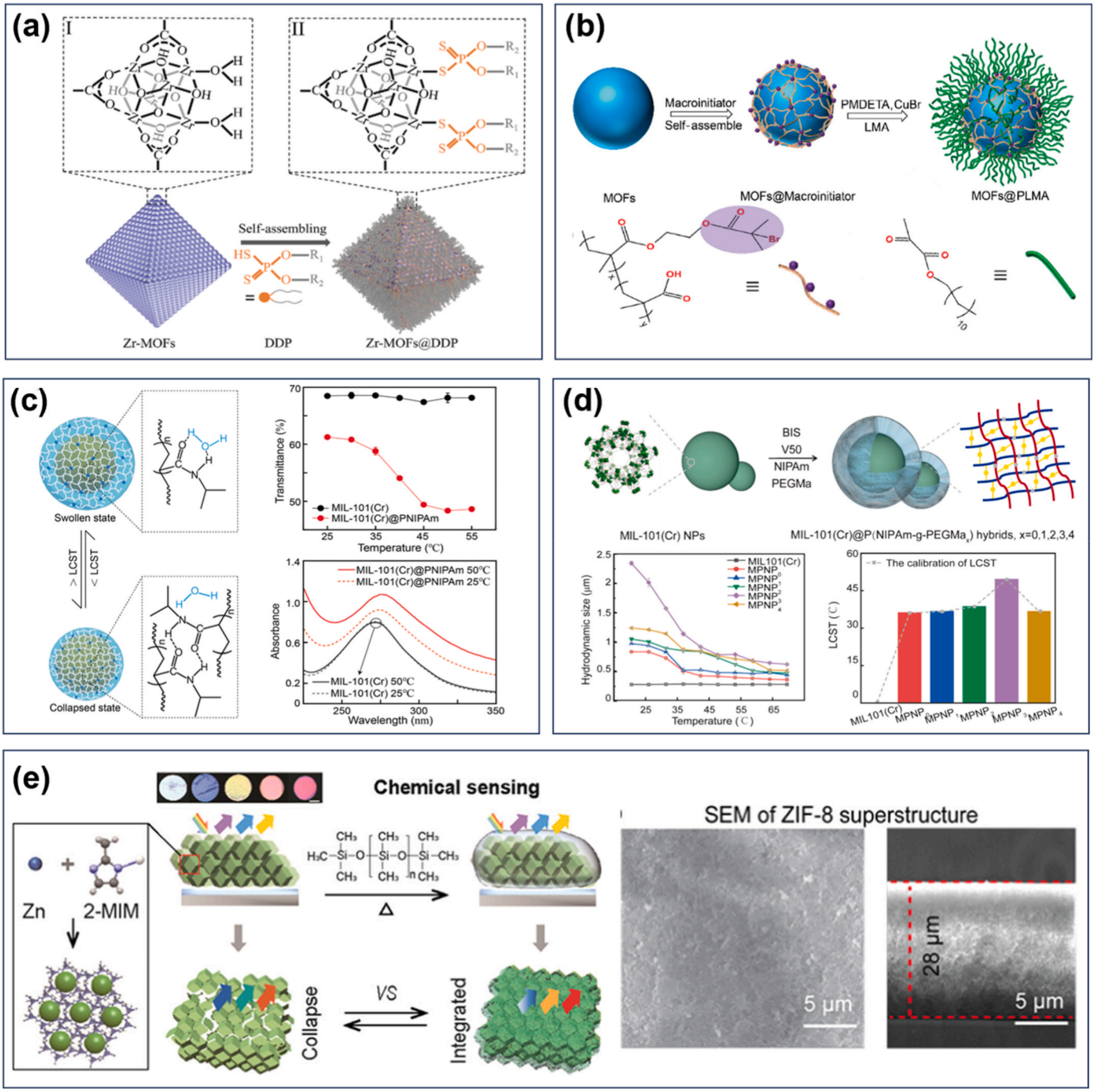

Fig. 3. Scheme of (a) surface functionalization of Zr-MOFs with DDP molecules. Picture taken from Ref. [42], with permission (b) MOFs nanoparticles functionalized with PLMA brushes. Picture taken from Ref. [43], with permission. (c) Reversible thermal-responsive swelling-collapsing behavior of MIL-101(Cr)@PNIPAm. Picture taken from Ref. [44], with permission. (d) Scheme of construction of MIL-101(Cr)@P(NIPAm-g-PEGMa$_x$), and their reversible swelling-collapsing behaviors. Picture taken from Ref. [45], with permission. All rights are reserved. (e) Scheme of construction of self-assembled MOFs-based Fabry-Pérot sensor, and the corresponding scanning electron microscope (SEM) images. Picture taken from Ref. [47], with permission.

centers—accurate quantum-chemical calculations remain computationally demanding [50]. Nevertheless, theoretical modeling has become indispensable for guiding the design of MOFs in applications ranging from gas storage to catalysis, supercapacitors, and energy conversion [51,52]. The emergence of high-throughput screening and predictive crystal engineering, especially for photophysical properties, has further strengthened the role of in silico approaches [53].

While theoretical studies are most straightforward for ideal, defect-free structures, MOF powders typically exhibit high defect densities and transport dominated by interparticle processes, making them poor benchmarks for theory—particularly in the presence of anisotropic properties. In contrast, oriented MOF thin films provide well-defined model systems whose structural order closely matches theoretical assumptions, enabling reliable validation of computational predictions and deeper insight into directional transport phenomena.

A key advantage of MOFs is their crystallinity, which allows for precise structural determination by X-ray diffraction (XRD) and thus provides nearly complete atomic coordinates for theoretical modeling. However, applying standard methods such as density functional theory (DFT) remains challenging. Selecting an appropriate exchange–correlation functional is critical, since MOFs combine organic linkers and inorganic metal nodes and therefore require a balanced description of covalent, electrostatic, and dispersion interactions [54]. Standard functionals often fail to capture weak van der Waals forces that are essential for structural stability and correct prediction of lattice constants and pore dimensions. The large and complex unit cells further demand extensive basis sets and computational resources, limiting system size and accuracy.

Electronic properties involving charge or exciton transport require more advanced electronic-structure methods. Standard DFT often underestimates HOMO–LUMO gaps, especially in systems containing transition metals, leading to errors in the description of optical and catalytic behavior. Moreover, real MOFs exhibit long-range disorder and high defect densities (see 2.2.1), which are difficult to capture in periodic DFT calculations and require large supercells or alternative approaches such as force-field or Monte Carlo simulations [55,56]. Accurate modeling of optical excitations in systems like HKUST-1 even necessitates wavefunction-based methods [31].

Given these challenges, oriented, monolithic MOF thin films with low defect densities and high structural regularity are essential as experimental benchmarks for validating theoretical models and refining computational methods.

In recent work, the predictable structure of SURMOFs has been used to carry out an in silico analysis of band alignment in In–oxo metal porphyrin SURMOF heterojunctions for photochemical and optoelectronic applications [57], and experimental validation of these predictions is expected to follow soon.

4. Physical properties of MOF thin films

4.1. Optical properties

4.1.1. Characterization of optical properties

One of the most obvious application fields where thin films outperform powders with particle sizes in the μm region is in applications connected with light. The optical properties of MOFs, such as luminescence, chromaticity, and light absorption can be significantly enhanced in the thin-film form. In MOF powders, the most common form of MOFs typically synthesized using solvothermal methods, the intrinsic optical properties of MOFs might be compromised due to scattering, non-uniform light penetration, and self-absorption. However, MOF thin films and in particular SURMOFs provide a uniform path for light propagation, and if the film thickness is 100 nm or below, self-absorption effects can also be reduced to a minimum. For instance, a patternable oriented MOF film fabricated by using a photomask under X-ray exposure can act simultaneously as a resist and functional porous material, used for the microfabrication of optical components for photonic devices (Fig. 4a) [58]. For homogeneous thin films, the scattering is reduced, thus allowing for more efficient light management. This uniformity is critical to applications such as organic light-emitting diodes (OLEDs) and optical sensors where consistent light handling is essential for device performance. Moreover, the layer-by-layer process allows engineers to create MOF thin films that exhibit specific optical responses, not only by adjusting their thickness but also by realizing more complicated structural hierarchies such as MOF-on-MOF epitaxies. The growth of such controlled architectures enables the production of photonic structures with tailored photonic band gaps, adjustable and non-isotropic exciton diffusion for reflecting and emitting specific wavelengths of light, again valuable for photonic devices and solar cells (Fig. 4b) [59]. A particular interesting case is the fabrication of Bragg stacks by combining thin layers of indium tin oxide (ITO) with a SURMOF [60]. In addition, the refractive index of MOF materials could be tailored by embedding nanoparticles, making them ideally suited as components for isostructural MOF-on-MOF photonic crystals (Fig. 4c) [61]. Importantly, the thin-film architecture also makes it possible to access nonlinear optical effects, such as second-harmonic generation (SHG) [62], opening new opportunities in frequency conversion, optical switching, and integrated photonics.

4.1.2. MOF thin films as a platform for advanced photonic functions

The integration of photoactive organic molecules into MOFs provides a structured and chemically versatile environment for designing advanced light-responsive materials. Incorporating chromophores—organic molecules capable of responding to light—into solid-state materials without compromising their intrinsic photophysical properties remains a fundamental challenge in photonics and materials science. Photo-responsive molecules employed in conjunction with optically active MOF materials can generally be categorized into two main classes. The first includes molecules whose structures remain largely unchanged following light-induced electronic excitation. The second class comprises molecular species that undergo structural or conformational changes upon photon absorption—commonly referred to as molecular switches.

Conventional strategies for incorporating photoactive molecules into solid materials—typically by embedding chromophores in polymers or amorphous matrices—frequently suffer from fluorescence quenching, uncontrolled intermolecular coupling, and diminished switching efficiency arising from structural disorder [63]. MOFs, with their crystalline lattices and precisely tunable architectures, offer a promising solution to these limitations [64,65]. However, MOF powders are typically unsuitable for a thorough determination of photophysical properties due to strong scattering and self-absorption effects—thus, homogeneous MOF thin films are required [66].

There are three primary strategies for incorporating photoactive species into MOFs [66]. In the first, photochromic molecules are used as linkers to construct the MOF framework itself. The second involves attaching photoactive moieties to pre-existing linkers, either during synthesis or via post-synthetic modification. The third method is based on guest loading, wherein chromophores are simply inserted into the MOF's pores. Each approach offers distinct advantages and can be tailored to specific applications and desired photophysical behaviors.

As noted above, powder-based materials are poorly suited for optical applications. Optical characterization of powders is hindered by light scattering due to the heterogeneous morphology of the particles, and absorption effects in the case of larger particle sizes. In contrast, thin films—particularly SURMOFs—exhibit high and uniform optical transparency, low defect densities, and homogeneous thicknesses [67]. Additionally, these films can be deposited on a variety of substrates—transparent, reflective, electrically conductive, or insulating. These features make SURMOFs ideal candidates for integration into optoelectronic devices, where consistent light–matter interaction and full accessibility of the material volume are critical. Moreover, the precise control over thickness and morphology in SURMOFs facilitates in-depth photophysical studies and enhances compatibility with techniques such as transient absorption spectroscopy and impedance measurements.

In several previous studies, optically active SURMOFs have been used to investigate the complex behavior of photoexcited states within chromophoric MOFs [72]. These investigations enabled differentiation between short-lived excited states—such as singlet states that lead to fluorescence—and long-lived states, including triplet states responsible for phosphorescence and delayed fluorescence. Furthermore, anisotropic transport could be demonstrated [71]. By confining chromophores within the rigid MOF framework, non-radiative relaxation pathways, such as those induced by molecular vibrations or aggregation, are effectively suppressed. This structural constraint enhances quantum yields and lifetimes, as demonstrated in MOFs based on pyrene [68] (Fig. 5a) and tetraphenylethylene (TPE) (Fig. 5b) [69]. The aggregation-induced emission observed in these systems results directly from the restricted intramolecular rotations imposed by the MOF lattice.

The potential of MOF thin films clearly extends beyond luminescence. SURMOFs also enable the mediation and control of energy and

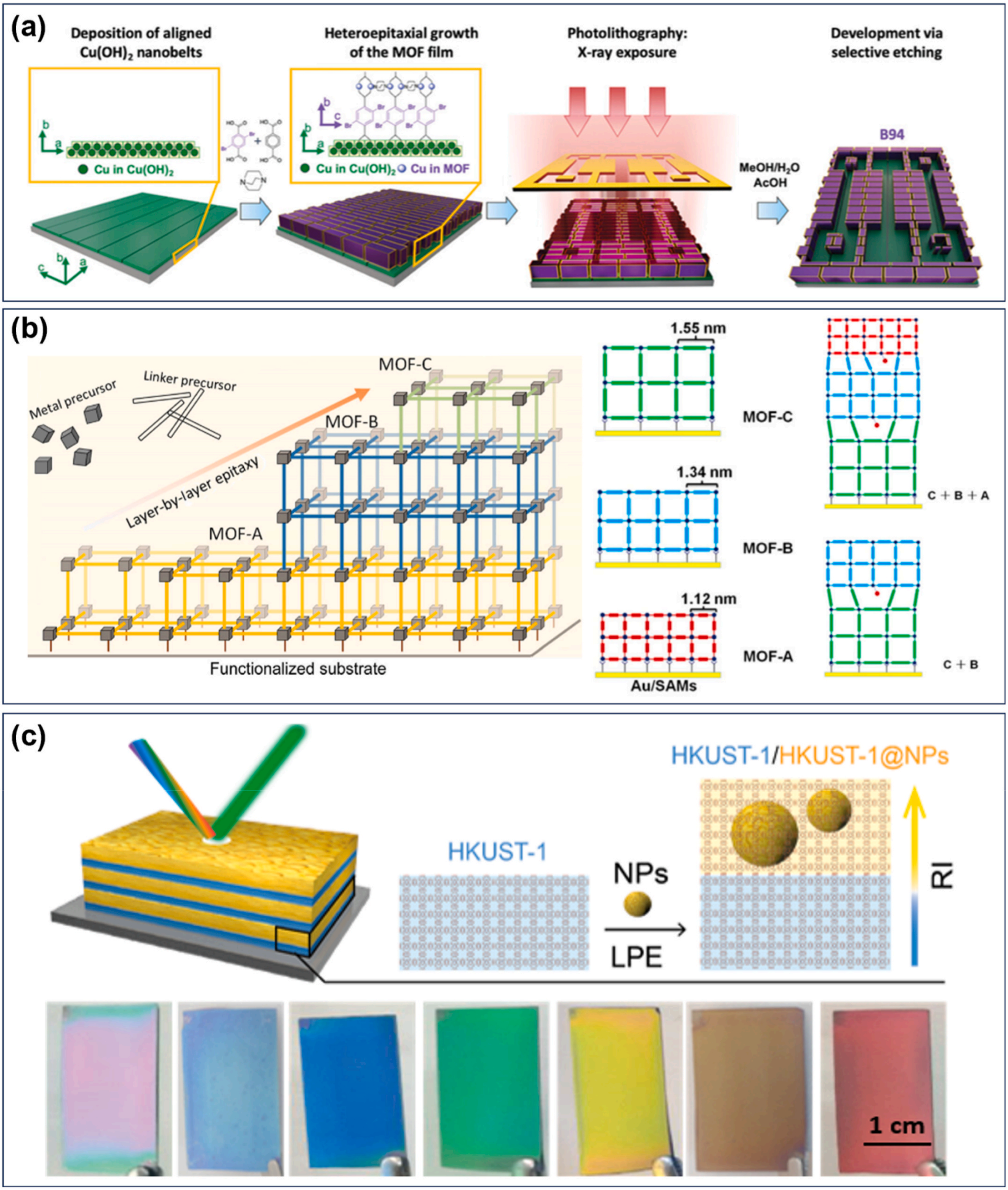

Fig. 4. Scheme of (a) 3D oriented MOF films and the different fabrication steps. Picture taken from Ref. [58], with permission. (b) Layer-by-layer liquid-phase epitaxy approach to constructing a MOF-on-MOF structures. Picture taken from Ref. [59], with permission. (c) Photonic crystals constructed by isostructural MOFs films, and the reflected color of corresponding spectrum. Picture taken from Ref. [61] with permission. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

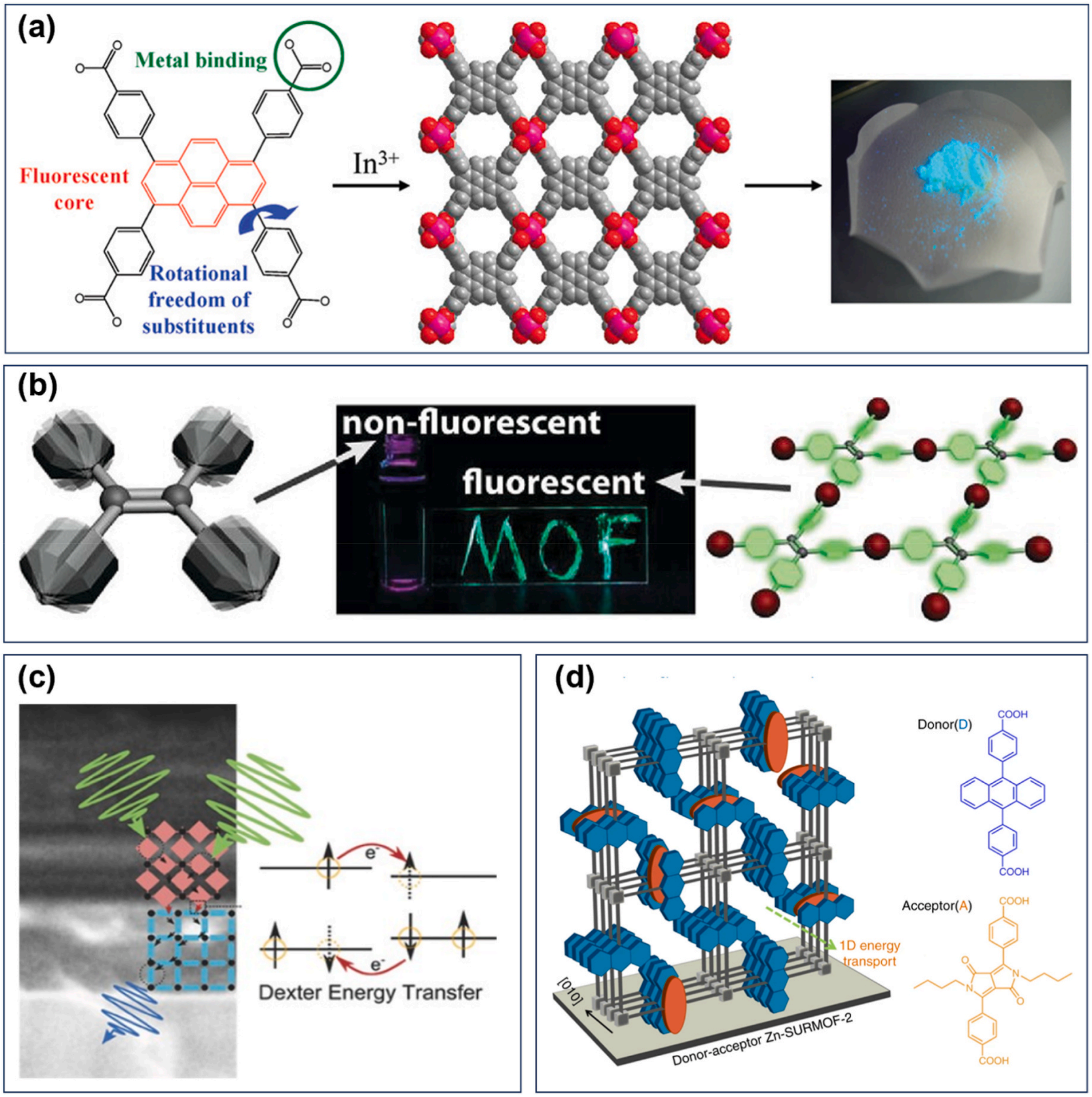

Fig. 5. Scheme of (a) reaction of In^{3+} and H_4TBAPy Ligand in acidic solution for forming the fluorescent framework. Picture taken from Ref. [68], with permission. (b) Functionalized tetraphenylethylene coordination with rigid MOF matrix turning on fluorescence. Picture taken from Ref. [69], with permission. (c) Triplet transfer across a surface-anchored MOF heterojunction. Picture taken from Ref. [70], with permission. (d) Anisotropic architecture of donor-acceptor Zn-SURMOF-2. Picture taken from Ref. [71], with permission.

anisotropic charge transfer. In particular, the ordered crystalline environment of MOFs allows precise positioning of donor and acceptor chromophores at defined distances and orientations, supporting detailed studies of Förster Resonance Energy Transfer (FRET) and Dexter transfer mechanisms (Fig. 5c) [70]. These insights are essential for developing materials for artificial photosynthesis, light harvesting, and photon upconversion. For example, specifically tailored multilayer SURMOFs have enabled studies of directional exciton migration and anisotropic diffusion of excimers in anisotropically packed anthracene-based linkers (Fig. 5d) [71]. Note, that for applications requiring energy transfer between two (or more) types of MOFs the heteroepitaxial growth that can be achieved with the layer-by-layer (LbL) method is very beneficial, as described in a recent review [59].

A particularly interesting topic in the area of optically active framework materials is the development of photo-switchable MOFs using chromophores such as azobenzene, spiropyran, and diarylethene. These photochromic molecules undergo reversible structural changes upon light absorption, which—when embedded in MOFs—can lead to macroscopic changes in material properties [73]. In this context, one distinguishes between different modes of incorporation: loading the photo-switch as a guest, tethering it as a side group, or integrating it into the framework backbone. For instance, azobenzene-loaded MOFs have demonstrated light-induced control over guest adsorption and release, color change, and even magnetization when combined with magnetic guest molecules. However, switching efficiency depends strongly on the steric freedom within the MOF, as overly rigid or densely packed environments can suppress isomerization altogether [74]. If the switchable chromophores are embedded in the backbone of the MOF, the corresponding SURMOFs can be used as photoactuators, i.e. for transforming light into macroscopic displacements [73].

Another area of significant interest is understanding how light-induced structural changes in photochromic MOFs translate into functional outcomes. For gas storage and separation, light can modulate the uptake of molecules such as CO_2 or CH_4 by switching the dipole moment or sterically blocking adsorption sites, thereby reversibly altering the MOF's affinity for specific gases. Similarly, membrane permeability and selectivity can be dynamically controlled. In one compelling example, a thin MOF membrane containing azobenzene moieties reversibly switched its selectivity for H_2 over CO_2—an effect relevant to industrial gas separation processes [75]. Photoswitching can also influence the diffusivity of guest molecules within the MOF, enabling remote control of molecular transport. This feature is especially useful in the design of controlled-release systems and responsive chemical containers [76].

Looking forward, light-responsive MOFs hold great promise for catalytic applications. By integrating chromophores capable of regulating energy transfer to catalytic sites, it becomes possible to modulate the generation of reactive species—such as singlet oxygen—with light. This approach has been employed to develop MOF-based materials and coatings for photodynamic therapy, where light triggers the generation of cytotoxic agents for cancer treatment [77]. The ability to optically toggle catalytic activity presents an exciting frontier for MOF research, particularly in biomedical and environmental contexts.

To fully realize this potential, it will be necessary to expand the library of photochromic molecules beyond azobenzene. For example, spiropyran offers larger dipole changes and could enable more pronounced switching effects [78]. When exploring new compounds, rigorous characterization of photo-responsive MOFs is essential—particularly regarding quantification of the photo-stationary state (PSS) and assessing the influence of the molecular environment on switching efficiency. Thin film platforms, due to their homogeneity and compatibility with in situ monitoring techniques, are well positioned to play a central role in advancing this goal.

Liu and coworker described a materials platform to achieve hybridized modes of excitons and lattice plasmons in MOF integrated with plasmonic nanostructures [79]. Thin films of porphyrin-based MOFs were deposited through a layer-by-layer method on arrays of silver nanoparticles that sustains surface lattice resonances (SLR). Coupling of excitons with the lattice plasmons led to a SLR-like mixed mode in both transmission and transient absorption spectra, and strong enhancement of the emission. Further, they presented a surface-interface engineered plasmonic superlattice with confined polyelectrolyte-functionalized MOFs hybrid layers, which enabled tunable plasmon resonance for ultrafast chemical sensing [80]. Plasmonic nanostructures coupled with MOFs established a new type of materials system for both energy exchange and sensing application.

In a recent study, Heine, Hecht, Heinke, and co-workers realized a SURMOF incorporating ortho-fluorinated azobenzene molecules that undergo light-induced trans→cis isomerization and electrocatalytic back-conversion. The coupled photoisomerization and charge-transfer processes enable a self-erasing, domino-like information-transfer mechanism, providing a new molecular concept for data processing and encryption [81].

4.1.3. *Non-centrosymmetric structure in MOF thin films*

SHG plays a pivotal role in the development of advanced optical materials. MOFs, owing to their structural tunability and ability to arrange chromophores in periodic, well-ordered architectures, are promising candidates for SHG-active systems. However, a fundamental requirement for SHG is the absence of inversion symmetry. Most MOFs crystallize in centrosymmetric space groups, which inherently suppress SHG activity. This limitation is particularly pronounced in MOFs incorporating dipolar linkers, as these tend to adopt energetically favorable anti-parallel orientations that cancel out macroscopic polarization. The resulting suppression of SHG due to the self-assembly of dipolar building blocks is commonly referred to as the “center-symmetry trap.” [82].

In a pioneering study [62], Nefedov and coworkers introduced a novel strategy to circumvent this symmetry limitation by constructing non-centrosymmetric (NC), porous, and crystalline MOF thin films using a LbL liquid-phase epitaxy technique. This approach, applied to SURMOFs, enables the deterministic alignment of dipolar building blocks, thereby avoiding the thermodynamically preferred anti-parallel arrangements typical in bulk systems.

A central achievement of this work lies in demonstrating the necessity and effectiveness of the LbL method in enforcing non-centrosymmetric ordering of dipolar linkers. In contrast to bulk MOFs, where even asymmetric linkers tend to orient randomly due to thermodynamic degeneracy, the LbL growth on functionalized substrates offers directional control and promotes alignment along a specific crystallographic axis. The authors employed an asymmetric linker, 2,6-dimethyl-4,4′-bipyridine (Me_2-BPY), in a pillared-layer framework of Cu (BPDC) (Me_2-BPY). The preferential binding of the methylated versus non-methylated pyridyl groups induced directional growth along the [001] axis, perpendicular to the substrate, yielding thin films with built-in electric fields.

The presence of such internal fields was confirmed by XPS using bromine-functionalized top layers (forming the outer surface of the SURMOF) as markers. A thorough analysis of the experimental XPS data revealed an electrostatic potential shift of up to 0.9 eV. These results provide clear evidence of macroscopic dipole alignment across the SURMOF thin film. Importantly, such effects were absent in bulk MOFs or disordered films, where local dipoles cancel due to random orientation.

The non-centrosymmetric character of the films was further validated by SHG spectroscopy (Fig. 6a) [62]. Strong SHG signals were observed in the asymmetric Cu(BPDC) (Me_2-BPY) films, while control samples using symmetric BPY linkers showed negligible response. The SHG intensity correlated with theoretical predictions based on molecular hyperpolarizabilities, underscoring that even slight deviations from perfect alignment significantly diminish the nonlinear optical (NLO) response. This highlights the critical importance of precise structural control in achieving efficient SHG in MOF films.

Beyond confirming NC order and SHG activity, the broader implications of this work are far-reaching. Embedding intrinsic electric fields within porous, crystalline materials opens new avenues for band structure engineering, charge transport modulation, and field-assisted guest–host interactions. Functional guests such as electron donors or acceptors (e.g., C_{60}) introduced into the pores could have their properties finely tuned by the internal electrostatic field, enabling novel device functionalities in organic electronics, nonlinear optics, and responsive materials. It should be noted, however, that the observed electrostatic shifts (up to 0.9 eV) fall short of values expected were observed, in excellent agreement with DFT calculations for a perfectly aligned film composed exclusively of uniformly oriented dipolar linkers. A detailed analysis revealed that the actual orientation distribution was approximately 52 % “up” and 48 % “down.” In a subsequent study [83], the authors identified this deviation as arising from steric, entropic, and topological effects during the LbL growth process. Nevertheless, the same work outlined strategies to overcome these limitations, suggesting that near-perfect polar alignment—and thus even greater electrostatic and optical responses—should be attainable with further optimization.

Furthermore, a full-color, highly saturated humidity sensor was fabricated by constructing a MIM resonator, which consisted of a humidity-responsive polymer grafted on the surface of MOF thin film. This structure enables programmable tuning of the reflected color by controlling the polymer thickness (Fig. 6b) [84]. The MOF–polymer resonator achieved an ultrafast response (≈0.75 s) for detecting trace amounts of H_2O in an H_2O/methanol mixture, outperforming the response time of a pure polymer-based MIM resonator. Notably, such performance is unattainable with bulk MOFs, highlighting the distinct advantage of MOF thin-film architectures.

4.2. *Electrical and electronic transport properties*

4.2.1. *Superior electrical and electronic properties*

In the field of electronics, the ordered structure and low-defect density of MOF thin films facilitate more efficient electron and exciton transport compared to their bulk counterparts. Particularly important is

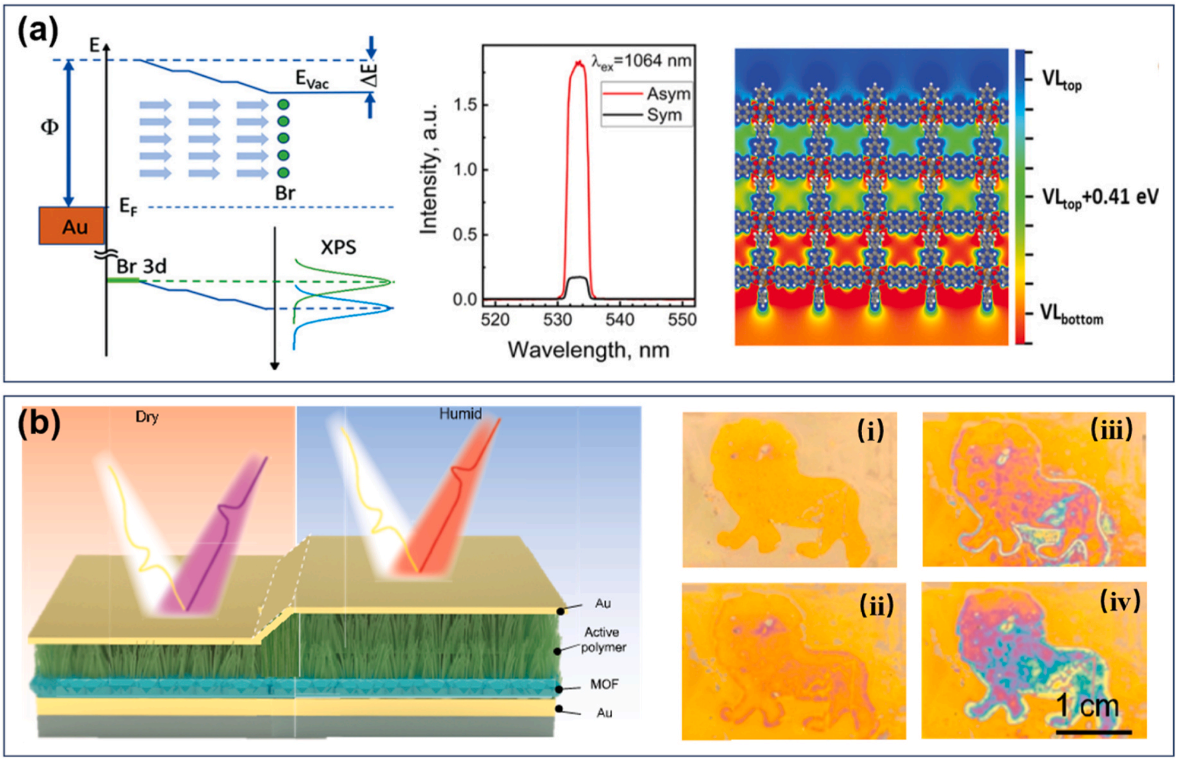

Fig. 6. (a) Illustration of electrostatic field design using asymmetric subunits in SURMOF, including the electrostatic energy shift and its SHG spectrum. Picture taken from Ref. [62], with permission. (b) Scheme of construction of colorimetric Fabry-Pérot sensor for humidity monitoring, and corresponding real-time optical images. Picture taken from Ref. [84], with permission.

the possibility to control the transport and to realize a system where the diffusion of charges and exciton becomes highly anisotropic. The regular arrangement of metal nodes and organic linkers in thin films can be used to create pathways for directing charged carriers, enhancing the electrical conductivity of MOFs, especially 2D MOFs [85]. This feature is particularly beneficial for the development of electronic devices like thin film transistors (TFTs) and integrated circuits where precise electronic control is required. Because their tailorable structures can open channels for chemo-, shape-, size-, and stereo-selective interactions [86], several approaches have been reported which make MOF thin films compatible with advanced lithographic techniques, another major requirement for the realization of devices.

4.2.2. *Electrically conducting MOFs: from powder materials to thin films*

MOFs have arguably been among the most intensely studied material classes of the past decade. With over 120,000 compounds synthesized and millions more predicted computationally, MOFs have been tailored for diverse applications ranging from gas separation and catalysis to sensing and energy storage. Despite this extensive exploration, one key physical property has so far remained essentially unexplored: high electrical conductivity—particularly metallic conductivity. The first remarkable realization of an electrically conductive MOF was achieved by Allendorf and coworkers in 2014, who reported an increase of the electrical conductivity of HKUST-1 SURMOFs by 6 orders of magnitude when embedding a redoxactive molecule, TCNQ (7,7,8,8-tetracyanoquinododimethane), into the pores of the MOF framework [87].

While later theoretical studies have predicted metallic behavior in certain MOFs [88], experimental realization of non-activated electrical transport in MOF thin films has remained elusive. This is especially true for thin films deposited on solid substrates, which are essential for integration into electronic devices and for more fundamental studies on the electronic behavior of quasi-2D MOF materials, including superconductivity [89], the formation of spin liquids [90], and Klein tunneling [91]. While a few MOFs with metallic conductivity have been developed, they exist only as microcrystalline powders or small single crystals, typically no larger than a few hundred micrometers. This limits their integration into electronic and optoelectronic devices, which require thin, oriented, and homogeneous films on patterned substrates. Despite growing interest in using MOFs for field-effect transistors, memory devices, supercapacitors, and quantum materials, their poor electrical conductivity—most being insulators or wide bandgap semiconductors with low carrier mobility and hopping transport—remains a major obstacle to practical application in electrocatalysis, charge storage, and chemiresistive sensing, among others. In recent years, broad strategies of imbuing MOFs with mobile charge carriers and pathways for charge transport achieve to gain the electrically conductive MOFs [92].

A small class of conductive MOFs (cMOFs) has emerged as an exception [12,93], exhibiting enhanced charge transport through extended π-d conjugation networks. Yet, truly metallic cMOFs-those that show a decrease in resistance with decreasing temperature-remain rare and, until recently, have only been observed in bulk powders or isolated single crystals, such as the Ln-based systems reported by Dinca and coworker in 2022s [94]. (Note that earlier reports (2017) on metallicity in cobalt-based Co-THT MOFs [95], have been withdrawn [96].)The fabrication of conductive MOF thin films with comparable performance has proved extremely difficult, limiting their applicability in practical device architectures. Until 2025, no MOF thin film with true metallic behavior and/or a conductivity above 100 S/m has been reported.

Among the most extensively studied cMOFs is Cu$_3$(HHTP)$_2$, one of the family of triphenylene-based cMOFs [97,98]. This two-dimensional honeycomb framework is composed of copper(II) centers coordinated by hexahydroxytriphenylene (HHTP) ligands. Its stacked 2D layers belong to the class of honeycomb lattices and provide a promising pathway for in-plane charge delocalization. In single-crystal form, Cu$_3$(HHTP)$_2$ exhibits conductivities up to ∼150 S/m at room temperature [99] - placing it among the top-performing MOFs to date, with resistivities comparable to those of lightly doped semiconductors, like silicon, and conductive polymers such as poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS).

Yet, this promising performance of a MOF has not translated to thin-film architectures. Conventional layer-by-layer synthesis methods and solution-based film deposition techniques have only achieved conductivities below 10 S/m in thin films of this material [78]. Moreover, metallic behavior—i.e., increased conductivity at lower temperatures—has not previously been observed, neither for the $Cu_3(HHTP)_2$ bulk powder materials nor for these film-based samples.

The recent study by Scheiger et al. [6] represents a pivotal advance in this field (Fig. 7). Using a machine learning (ML)-guided robotic synthesis platform, the authors developed a strategy to fabricate high-quality $Cu_3(HHTP)_2$ thin films—SURMOFs—on technologically relevant SiO_2 substrates. Crucially, the process involved systematic optimization of multiple synthesis parameters via an AI-driven algorithm, guided by surrogate properties such as UV–Vis absorption features and in-plane XRD peak widths. This surrogate approach allowed rapid, reproducible identification of growth conditions that yield films with excellent crystallinity and large domain sizes, without relying on direct electrical measurements during optimization.

The true test of this approach came from precision conductivity measurements using a four-point probe method [6]. By reducing the contact spacing between electrodes to below the average domain size (~100 nm), the researchers were able to bypass grain boundary effects and probe the intrinsic transport behavior. Strikingly, the optimized thin films exhibited conductivities up to 240 S/m at room temperature, exceeding previously reported values (150 S/m [99]) even for single crystals. Even more importantly, the conductivity increased to nearly 300 S/m upon cooling to 100 K—a clear, unambiguous signature of metallic conduction. This marks the first demonstration of metallic behavior in a MOF thin film, representing a paradigm shift in the field. In addition, Chen and coworkers [100] have characterized the electrical properties of pristine HKUST-1 and TCNQ loaded compact HKUST-1 SURMOF films with high morphological quality and low surface roughness by employing the controlled process of quasi LPE on functionalized Si/Au substrates. They also demonstrated that the electrical conductivity is anisotropic and depends on the crystal orientation.

Complementary theoretical insights provided additional confirmation [6]. DFT calculations revealed that the hexagonal symmetry (D_6h) of $Cu_3(HHTP)_2$ monolayers leads to the formation of a Dirac cone at the K-point of the Brillouin zone [101]—an electronic structure feature also found in graphene. For the electrons in such 2D sheets, this results in low effective mass, yielding highly mobile Dirac fermions capable of supporting metallic transport. The more recent calculations reported in the paper by Scheiger et al. [6] revealed that in the stacked bulk form of the MOF, the Dirac cone is preserved with only minor distortions, resulting in a finite density of states at the Fermi level. These findings were further supported by UPS data, which showed no detectable bandgap in the optimized thin films.

This confluence of experimental and theoretical results provides the most compelling evidence yet that MOFs can, under the right synthetic conditions, exhibit intrinsic metallic conductivity in thin-film form. The study highlights the critical importance of domain size, crystallographic order, and nanoscale electrode patterning in revealing the true electronic nature of these materials. It also demonstrates the power of ML-guided robotic labs in exploring high-dimensional synthesis parameter spaces more efficiently than traditional trial-and-error approaches.

The realization of metallic conductivity in $Cu_3(HHTP)_2$ thin films is a landmark achievement that redefines the potential of conductive MOFs. It opens a new frontier for their use in practical electronic and quantum devices, from sensors and transistors to spintronic platforms. Importantly, this advance is not restricted to a single material such as $Cu_3(HHTP)_2$. In principle, it applies broadly to other layered MOFs—particularly those based on other metal centers like nickel or lanthanides, as well as alternative conjugated organic linkers such as extended triphenylene derivatives. It also provides a roadmap for designing and synthesizing 2D MOFs with Dirac-like electronic structures, suggesting that symmetry-engineered MOFs could become a new class of tunable, high-performance materials for next-generation electronics.

4.3. *Magnetic properties*

MOFs have recently emerged as promising candidates for exploring low-dimensional magnetism (Fig. 8a) [102]. Unlike traditional one-dimensional (1D) or two-dimensional (2D) magnetic materials, which are often difficult to synthesize and offer limited tunability, MOFs combine structural versatility with the potential to host both magnetic metal centers and guest species, enabling the design of hybrid magnetic systems. In this context, SURMOFs, in particular the SURMOF-2 series [103], provide a model platform for studying low-dimensional magnetic order in a highly controlled and modular architecture (Fig. 8b).

The SURMOF-2 family [103] consists of iso-reticular MOFs grown as oriented thin films via liquid-phase epitaxy. It should be pointed that although the SURMOF-2 family resembles some of the structural features of the MOF-2 compound—a powder material synthesized using solvothermal methods—it is distinct in composition and formation. However, no detailed structural characterization of these bulk MOFs

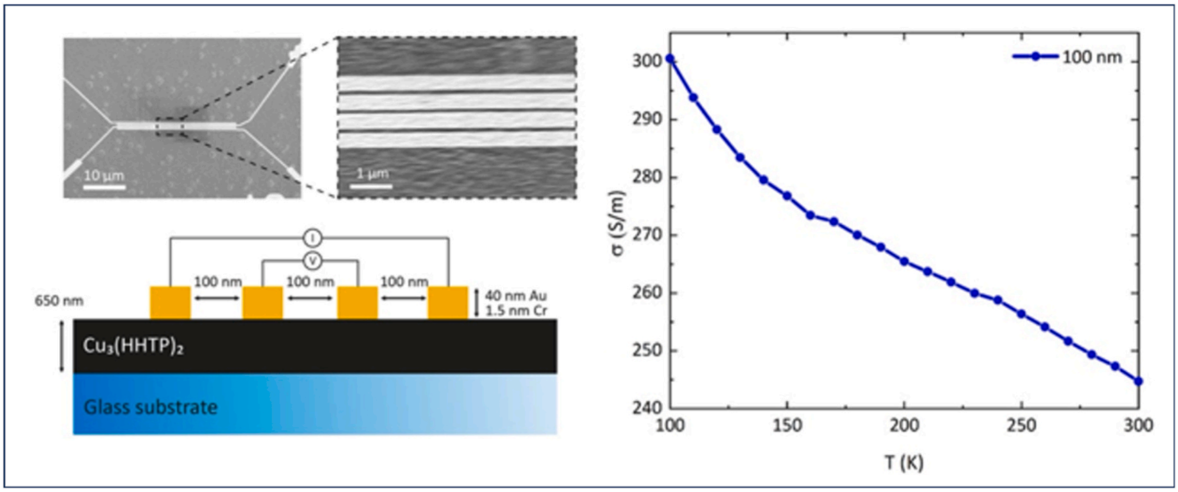

Fig. 7. The SEM images and scheme of high-quality MOF thin films, and the corresponding electrical conductivities. Picture taken from Ref. [6], with permission. Note the increase of conductivity when lowering the temperature, indicative of metallic behaviour.

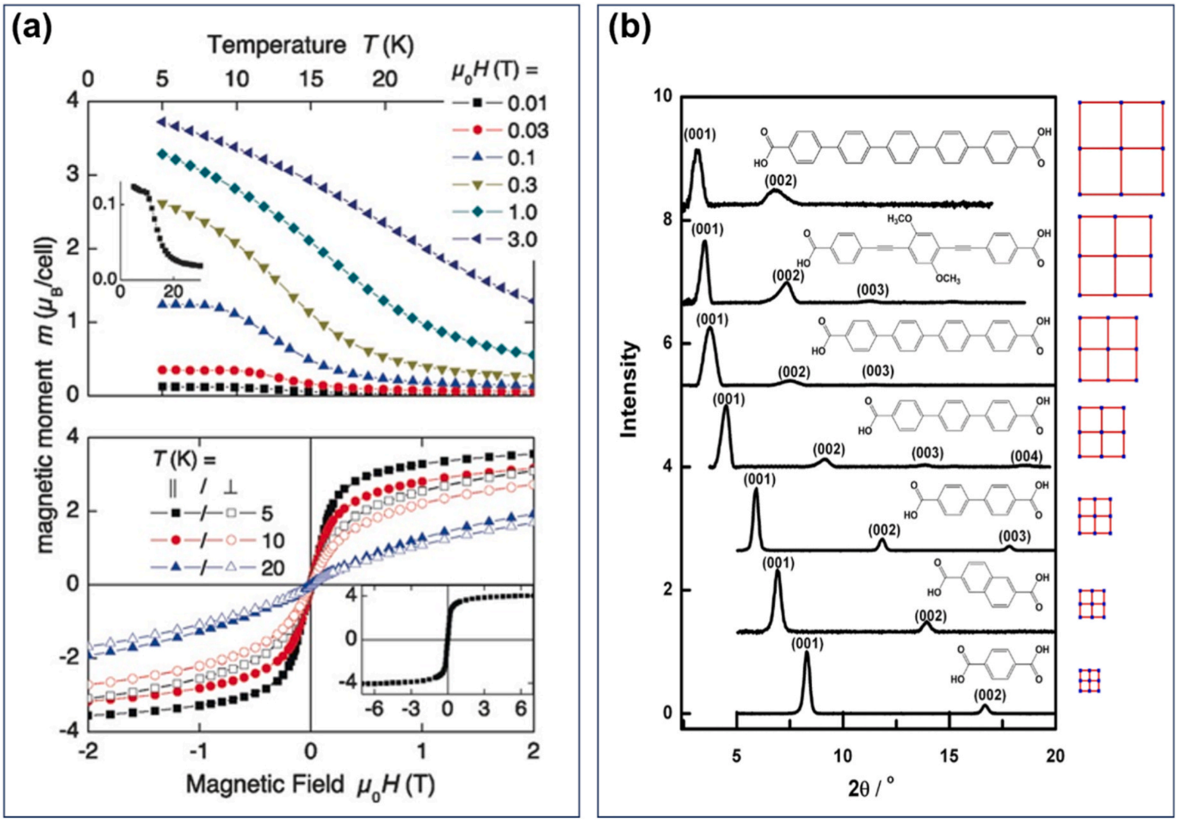

Fig. 8. (a) Magnetic moment and hysteresis of SURMOF-2 measured by temperature for various magnetic fields. Picture taken from Ref. [102], with permission. (b) XRD of a novel series of isoreticular SURMOF-2 analogs. Picture taken from Ref. [103], with permission.

synthesized using solvothermal methods has been published to date. Typically, in $(Cu^{++})_2$-carboxylate SBUs, the Cu ions are bonded to carboxylate ions to form paddlewheel (PW) units that exhibit antiferromagnetic (AFM) coupling, and magnetism should not be observed.

However, experimental studies using electron paramagnetic resonance (EPR) and superconducting quantum interference device (SQUID) magnetometer on Cu (1,4-benzenedicarboxylate) (Cu,bdc) and Cu 4-(4-propan-2-yloxycarbonylphenyl)benzoic (Cu,bpdc) SURMOF-2 thin films—where bdc and bpdc denote benzene- and biphenyl-dicarboxylate linkers, respectively—have revealed ferromagnetic ordering with Curie temperatures of approximately 18 K and 22 K. Unlike many other low-dimensional systems, no strong external magnetic fields are required to induce magnetic ordering in these materials. Instead, their FM behavior is intrinsic and appears even in the zero-field limit, as confirmed by SQUID magnetometry.

The surprising presence of ferromagnetism in SURMOF-2 films has been established through a combination of complementary experimental techniques [102]. SQUID magnetometry revealed a sharp increase in magnetization below the respective Curie temperatures, with saturation occurring at low temperatures in low applied fields. This behavior is inconsistent with simple paramagnetism and is a hallmark of long-range magnetic order. EPR spectroscopy provided further insight into the magnetic ground state, showing a pronounced temperature and angular dependence of the resonance field, which disappears above 28 K. The shape and orientation dependence of this signal are consistent with a ferromagnetic resonance (FMR), rather than isolated high-spin paramagnetic species, strongly supporting the existence of ordered FM domains aligned with the film plane. In a second, independent study [104], X-ray magnetic circular dichroism (XMCD) and X-ray resonant magnetic scattering (XRMS) confirmed that the magnetic response originates from the Cu^{2+} ions and revealed anisotropic behavior consistent with the oriented nature of the thin films.

The magnetic behavior observed in these two SURMOF-2 materials could not be explained by earlier structural models for this class of reticular MOFs, which are based on paddlewheel (PW) units. PW units are known to support strong antiferromagnetic coupling between the two Cu^{2+} ions, and materials based on this motif should not show any ferromagnetic behavior.

To resolve this discrepancy, detailed structural and theoretical investigations were conducted for these two SURMOFs. Because conventional X-ray diffraction techniques have limitations when applied to ultrathin films, the researchers employed a novel approach by growing SURMOF-2 using a modified layer-by-layer scheme on spherical magnetite nanoparticles [105] (MagMOFs), enabling the collection of powder X-ray diffraction (PXRD) data suitable for Rietveld refinement. These data revealed a previously unrecognized deviation from the linear paddlewheel-based architecture. Instead, the detailed PXRD analysis showed that the Cu atoms adopt a zigzag configuration, forming zipper-like chains composed of distorted, semi-paddlewheel motifs with alternating Cu–Cu distances of approximately 2.47 Å and 3.85 Å. This unusual motif is not observed in conventional MOFs and had not been considered in prior magnetic models.

Independent confirmation of this atypical formation of quasi-linear Cu^{2+} chains came from a comprehensive set of DFT calculations, performed alongside ab initio Born–Oppenheimer molecular dynamics and simulated annealing [102]. These theoretical investigations confirmed that the dominant Cu–Cu interaction within the chains is ferromagnetic, with a coupling strength of approximately 31 meV per Cu pair. Weaker interactions between more distant neighbors were found to be negligible (<1 meV), suggesting that the system behaves as an assembly of independent 1D magnetic chains. Monte Carlo simulations based on the classical Heisenberg model, using the DFT-derived exchange constants, accurately reproduced the experimental Curie temperatures, providing further support for the validity of the new structural and magnetic model. The DFT calculations also revealed the important role of water molecules in the structure. They mediate coupling between adjacent Cu^{2+} pairs through an almost dissociated water molecule. This linking H_2O also gives rise to a characteristic sharp OH vibration in the IR data, in full agreement with experimental results.

Compared to other low-dimensional magnetic materials, the magnetic behavior of SURMOF-2 is remarkable. While 1D magnetic order is notoriously difficult to stabilize due to thermal fluctuations, the SURMOF-2 system exhibits a robust FM phase without requiring large external fields or high-pressure conditions. Materials such as $CrSb_2$, Co chains on Pt(111), and Fe-MOF-74 have shown 1D magnetic features, but typically only under constrained conditions or high magnetic fields. In contrast, SURMOF-2 thin films offer a unique combination of synthetic accessibility, structural tunability, and intrinsic ferromagnetism. The ability to systematically vary interchain spacing via linker length—without affecting intrachain coupling—makes these systems ideal for studying the dimensional crossover between 1D and quasi-2D magnetic behavior.

An additional advantage of MOFs, and particularly SURMOF-2 systems, lies in their porosity, which enables the incorporation of guest molecules. This opens up new avenues for designing hybrid magnetic systems in which guest–host interactions can modulate the magnetic properties. Recent studies [104] have demonstrated that loading SURMOF-2 films with metallocene molecules such as nickelocene leads to partial alignment of the guest spins due to proximity-induced polarization from the ferromagnetically ordered Cu chains. In contrast, when bulkier metallocene derivatives like isopropyl-substituted manganocene were introduced, no polarization of the guest spins was observed, indicating the importance of spatial proximity for magnetic exchange. Importantly, these guest molecules did not disrupt the magnetic ordering of the host framework, underscoring the robustness of the magnetic lattice and the potential for multifunctional design.

Taken together, these findings position SURMOF-2 thin films as a new class of tunable low-dimensional magnetic materials. They combine the advantages of modular synthesis, intrinsic ferromagnetism at accessible temperatures, and structural porosity that allows for host–guest interactions. These attributes are unmatched among traditional inorganic 1D or 2D magnets and suggest a promising future for MOFs in spintronic applications, data storage, and quantum materials research. Future studies will likely focus on exploring additional members of the SURMOF-2 series, fine-tuning interchain coupling through linker design, and integrating these systems into device architectures to probe their electronic transport properties under spin-polarized conditions.

4.4. Diffusion and mass transport properties

For some of the main applications of MOFs—gas storage, separation, and catalysis—the diffusion of guest molecules into the MOF is of crucial importance. Therefor the accurate determination of the diffusion coefficients of guest molecules within these materials is essential for understanding and optimizing their performance. To date, various techniques have been employed to measure diffusion in MOFs, including nuclear magnetic resonance (NMR)-based methods [106], quasi-elastic neutron scattering (QENS) [107], and interference microscopy [108]. Each of these techniques provides complementary insights into molecular mobility over different time and length scales, contributing to a more comprehensive understanding of transport phenomena in these porous materials. However, the availability of SURMOFs allows for much more straightforward measurements using a quartz crystal microbalance (QCM). Using this approach, the diffusion of guest molecules into MOFs can be studied in a much more straightforward fashion. In a paper by Zybaylo and coworkers [109], the homogeneous structure and well-defined thickness of the SURMOFs enabled the analysis of QCM data using a Fickian diffusion model to determine the diffusion constant. The effectiveness of this approach was illustrated by examining the diffusion of pyridine within the HKUST-1 ($Cu_3(BTC)_2$) MOF. At room temperature, the diffusion coefficient is found to be 1.5×10^{-19} m^2 s^{-1}. By assuming a Fickian diffusion process governed by a hopping mechanism, we estimate a binding energy of 0.78 eV for pyridine interacting with Cu^{2+} sites in the HKUST-1 framework. This value aligns well with high-level ab initio quantum chemistry calculations (Fig. 9a) [109].

Whereas the diffusion inside the MOF material is governed by the size and the chemical nature of the windows connecting the MOF pores, for entering the MOF particle from the surrounding phase, gas or liquid, one often finds that a surface barrier needs to be overcome. In a study by Heinke and coworkers (Fig. 9b) [40], these phenomena were studied for a prototype MOF material, HKUST-1, using MOF thin films supported on a quartz crystal microbalance (QCM). This paper highlights the variations in mass transfer rates of cyclohexane and ferrocene indiffusion among different samples of the same material and the impact of surface barriers on molecular uptake.

The study used a QCM to quantitatively analyze surface barriers in MOFs, showing that they are not intrinsic features but are created by exposure to air or water vapor. Different thicknesses of MOF films are studied to understand the importance of surface barriers, with results indicating that mass transfer is controlled by intra-crystalline diffusion rather than surface barriers in pristine films. The research emphasizes the significance of clean synthesis and storage conditions for achieving MOFs with high mass transfer rates, shedding light on the critical role of surface barriers in MOF applications.

In a subsequent paper, it was demonstrated that in some cases the defects formed at the outer surface of the MOF can be healed (Fig. 9c) [110]. This was shown for the case of water-induced corrosion of the MOF layers exposed to the exterior. MOFs exhibit reversible architecture, enabling extended crystalline frameworks, making them suitable for diverse applications. The interaction with guest molecules in MOFs is crucial, with reduced uptake rates limiting performance. Surface barriers in MOFs can hinder the uptake of guest molecules, affecting diffusion coefficients significantly. The study specifically examines the HKUST-1 MOF, showcasing how exposure to water vapor can impact its structure and performance. Experimental methods such as QCM sensors and spectroscopic measurements are utilized to analyze the behavior of MOFs in different conditions.

4.5. Mechanical properties

MOFs have unique mechanical properties that are important for a number of applications, such as thermoelectric [111], energy storage [112], biomedicine [113], and so on. However, for powder materials the application of common techniques to determine hardness and other mechanical properties is not straightforward.

The availability of high-quality MOF thin films allows for the application of standard indentation methods to determine elastic properties of these framework materials. In a paper published by Bundschuh and coworkers [19], nanoindentation experiments were carried out for HKUST-1 MOF thin films and provided insights into the mechanical behavior of MOFs, allowing for the determination of Young's modulus and other important parameters related to their structural integrity. By analyzing the force-displacement curves and the hardness as a function of the indenter displacement, valuable information about the mechanical response of MOF thin films could be obtained. In addition, Mikhail Krishtab and coworkers [114] reported a relationship of Young's modulus and k-value of MOF-CVD (chemical vapor deposited) thin films for semiconductor device applications. They used an iterative data analysis algorithm proposed by Li and Vlassak [115] to extract the elastic modulus of the MOFs layers. Overview the relevant literatures [19,116–119] about the mechanical properties of some types of MOFs, the average Young's modulus of ZIF, IRMOF-1, MIL-53, and HKUST-1, were about 5.6 Gpa, 3.7 Gpa, 0.55 Gpa, and 10 Gpa, respectively.

Later, the mechanical properties of hybrid MOF-based thin films were studied by combining nanoindentation experiments on single-layer and multilayer stacks composed of mechanically hard indium tin oxide

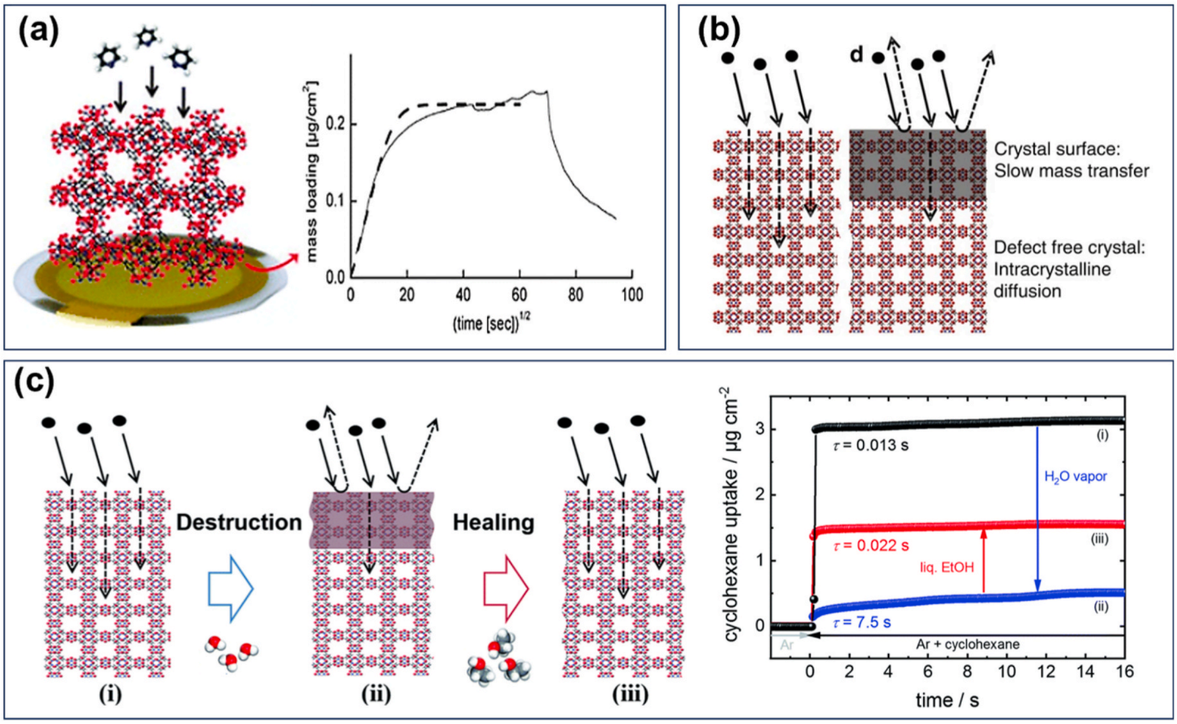

Fig. 9. The scheme of (a) pyridine diffusion within HKUST-1 ($Cu_3(BTC)_2$) MOF, and the data trace of QCM experiment on MOFs. Picture taken from Ref. [109], with permission. (b) The model of the mass transfer in MOFs. Picture taken from Ref. [40], with permission. (c) Preparation of defective HKUST-1 SURMOF and uptake of cyclohexane by pristine HKUST-1. Picture taken from Ref. [110], with permission.

(ITO) and mechanically soft, porous HKUST-1 surface-anchored metal-organic frameworks (SURMOFs) [120]. Using precise control over liquid-phase epitaxial growth and magnetron sputtering, the authors fabricated crystalline, continuous thin films with tunable thickness. The study demonstrates that while substrate effects influence indentation responses, the elastic moduli of individual components ($E_{ITO} \approx 96.7$ GPa, $E_{HKUST\text{-}1} \approx 22.0$ GPa) can be effectively decoupled. In multilayer systems, even when the relative thicknesses of ITO and HKUST-1 were kept constant, increasing overall film thickness significantly altered the mechanical resistance, likely due to interface roughness, texture, and size effects. These results underscore the critical role of interface engineering and film architecture in determining the mechanical behavior of MOF-based hybrid thin-film devices, with implications for the design of advanced optical and electronic systems.

In another study, the rigid anchoring of HKUST-1 SURMOFs to their substrates was exploited to determine the Poisson's ratio using X-ray diffraction (XRD) [121]. Because MOFs typically exhibit negative thermal expansion, heating the substrate (Au/Si with positive thermal expansion coefficient) forced the film to expand laterally. This lateral expansion led to a measurable reduction in layer thickness (as determined from the out-of-plane XRD peaks), from which the Poisson's ratio could be derived. Remarkably, even after several heating and cooling cycles, the MOF thin film showed no signs of delamination or damage.

5. Functional devices and applications of MOF thin films

5.1. Dielectric engineering with MOF thin films: enabling tunable plasmonic resonators

Surface plasmon resonances (SPRs), collective oscillations of free electrons in metals, enable novel approaches to engineering structural color. At plasmonic metal-dielectric interfaces, electromagnetic surface waves can be confined to subwavelength dimensions, overcoming the diffraction limit. Metal-insulator-metal (MIM) resonators constitute a particularly promising platform for structural color filtering, leveraging light-matter interactions. Their architecture sandwiches a dielectric spacer between reflective metal films, enabling efficient, scalable, and cost-effective band-pass filtering. Critically, the reflected color of these resonators is tunable through the refractive index and thickness of the dielectric spacer.

The functionality of MIM resonators hinges on the properties of the dielectric components. Conventional inorganic dielectrics (e.g., SiO_2, TiO_2, Al_2O_3, α-Si) offer limited scope for dynamic optical modulation due to their rigid, non-porous structures. While polymers permit analyte diffusion, the tendency toward uneven swelling or collapse compromises reflection quality. Furthermore, dense metal layers inherently prevent analyte access to the dielectric spacer, restricting real-time color tuning and sensing capabilities. Thus, advancing MIM-based sensing requires dielectric materials that enable dynamic color modulation while maintaining structural uniformity under environmental stimuli.

The outstanding optical properties and excellent processability of these precisely tailored MOF thin films render them highly promising as active dielectric layers in advanced photonic device architectures. While MIM filters are capable of manipulating light, achieving dynamic color changes in response to environmental stimuli remains a challenge. By employing a monolithic MOF thin film as the spacer layer, the MIM cavity confines the electromagnetic field to a small volume and surpasses the diffraction limit through subwavelength interference of surface plasmon polaritons, thereby enabling local phase modulation and wavefront control (Fig. 10a) [122]. MOF-based MIM cavities offer high color saturation and brightness, allowing for dynamic optical filtering. Introducing openings into the dense top metal layer enables chemical sensing capabilities (Fig. 10b) [123]. Moreover, sequentially assembling tandem MOFs thin film as dielectric layers (HKUST-1 and ZIF-8), a metal-insulator-insulator-metal (MIIM) with tunable bandwidth has been reported for chemo-sieving sensing(Fig. 10c) [124]. Chemical sensing on the MIIM resonators showed breakthrough enhancement of sensitivity. Compared to the MIM resonator, the MIIM resonator can enhance selectivity for specific analytes up to 92 % with high durability.

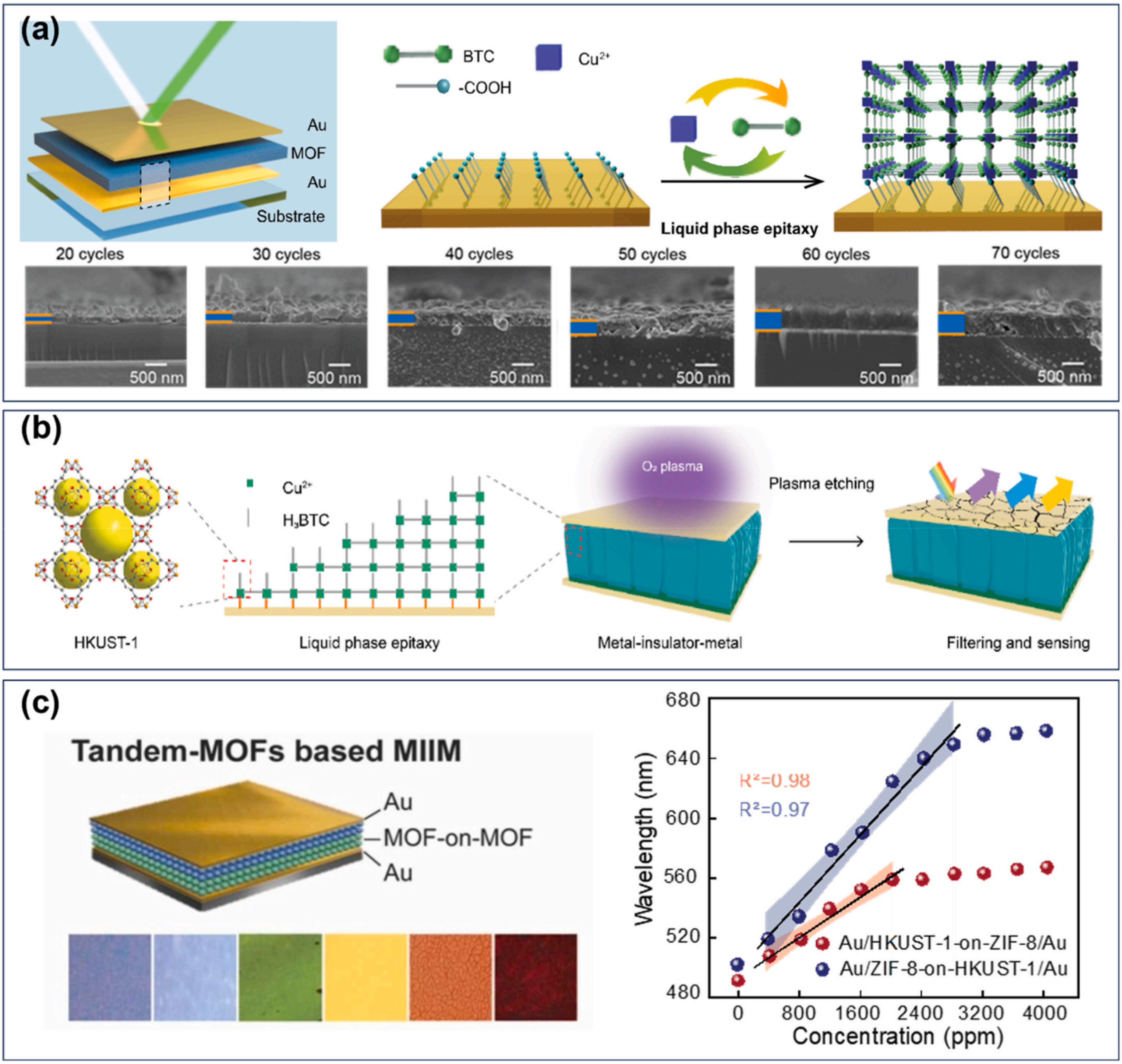

Fig. 10. (a) Scheme of construction of the monolithic MOF-based MIM resonator, and the corresponding SEM images by varying the number of spraying cycles. Picture taken from Ref. [122], with permission. (b) Scheme of plasma etching on the monolithic MOFs-based MIM cavity for developing channels in chemical diffusion. Picture taken from Ref. [123], with permission. (c) Scheme of construction of planar MOFs-based MIM resonator, and methanol sensing on the MOF-on-MOF resonator. Picture taken from Ref. [124], with permission.

5.2. *Gas permeation through MOFs*

Measuring diffusion through MOF particles presents significant challenges due to their small size and the difficulty in isolating pure diffusion processes from interparticle transport effects, grain boundaries, and the occurrence of surface barriers (see above). These complications often obscure intrinsic diffusion properties, making accurate characterization difficult. Mixed-matrix membranes (MMMs), which embed MOF particles in polymer matrices, further complicate the picture. In MMMs, poor interfacial compatibility between the MOF and polymer can lead to non-selective voids or blocked pathways, reducing membrane performance and masking the true transport behavior of the MOF. In contrast, monolithic MOF thin films grown directly on porous substrates offer a well-defined and continuous transport pathway, free from interfacial defects and interparticle diffusion barriers. These supported thin films enable precise measurements of gas transport through the MOF structure itself, providing more reliable data for evaluating and optimizing MOF-based separations.

In a first study of this kind Sanchez and coworkers [125] explored the liquid phase layer-by-layer deposition of ZIF-8 SURMOFs onto porous α-alumina substrates, both with and without a thin gold coating, using a dipping method to fabricate gas-permeable ZIF-8 SURMOF membranes. The presence of a gold layer on the α-Al_2O_3 supports significantly improved the reproducibility, uniformity, and preferred orientation of the resulting ZIF-8 films. In contrast, uncoated substrates often exhibited incomplete coverage and the formation of particle agglomerates, which could hinder their performance in gas separation applications. Characterization by XRD, SEM, and gas permeation experiments revealed that performing 150 deposition cycles yielded thin, continuous ZIF-8 films. However, occasional bare spots were still observed, suggesting that approximately 150 cycles may represent the lower threshold for achieving consistent membrane quality. Application of the Wicke-Kallenbach method for H_2/ethene and ethene/ethane mixtures clearly demonstrated the absence of pin-holes within the SURMOF membranes – the flux through the membrane was independent of applied pressure. Based on these results, such SURMOF-based membranes are suitable for alkane/alkene separation. A later study [126] showed that the experimental results for ethane/ethene separation compared well with computer simulations.

The thickness of SURMOFs can be precisely controlled by adjusting the number of liquid-phase epitaxy deposition cycles, which enables the fabrication of high-quality optical multilayers of photonic crystals. In previous works, soft metal-organic thin films (HKUST-1 SURMOF) were combined with hard inorganic metal oxide materials (indium tin oxide, ITO) (Fig. 11a) [60]. Using this approach, a hybrid photonic crystal has been successfully fabricated by stacking MOF and ITO layers, which exhibits high optical quality (achieving reflectivities up to 80 %) and tunable color across the entire visible spectrum.

The incorporation of functional nanomaterials into MOFs has attracted significant attention for advancing practical applications in adsorption/separation, catalysis, and sensing. [128]. In particularly, hybridization with inorganic nanomaterials, such as TiO_2 nanoparticles, can leverage the distinctive physicochemical properties of MOFs to enhance gas molecules adsorption capacity by providing additional active sites. Liu and coworkers demonstrated a strategy for selective chemical sensing on the HKUST-1$\supset$$TiO_2$ Fabry−Pérot (F-P) cavity, and the bandwidth of cavity was modulated by sequentially spray-coating TiO_2 nanoparticles in HKUST-1 thin films via layer-by-layer deposition method (Fig. 11b) [127]. Compared to pure MOFs-based F-P cavity, HKUST-1$\supset$$TiO_2$ thin films significantly enhanced the sensitivity and response time by ≈ 180 % and ≈54 % when exposed to saturated acetone vapors. Dynamic sensing analysis confirmed specific chemical adsorption on the HKUST-1$\supset$$TiO_2$. Molecule dynamics and infrared absorption spectrum revealed the hydrogen-bonding interactions between TiO_2 and the specific oxygen-containing analytes.

5.3. MOF thin films as photoresists: A multifunctional platform for 3D lithographic applications

MOF thin films, and in particular SURMOFs, also exhibit substantial potential as photoresist, as demonstrated in a paper by Wang and coworkers [129]. Utilizing the modularity and post-synthetic tunability of MOFs, the authors introduce a versatile lithographic platform capable of both two-dimensional and three-dimensional patterning with functional chemical specificity. Thin films of crystalline [$Zn_2(N_3\text{-}BPDC)_2(Dabco)$] were grown on Au substrates using liquid-phase epitaxy (LPE), enabling precise thickness control and high crystallinity. Substrate functionalization via self-assembled monolayers allowed for patterned MOF deposition, yielding monolithic films with sub-10 nm roughness and well-defined orientation.

A key advance of this work lies in the use of *post-synthetic modification (PSM)* strategies to induce spatially resolved chemical functionality. Azide–alkyne "click" chemistry was activated either thermally or through photoreduction of Cu^{2+} to Cu^{+}, allowing localized functionalization via UV-irradiation through photomasks. Additionally, the decomposition of azide groups under UV light enabled a complementary *positive photoresist* mechanism. To circumvent cytotoxicity associated with Cu catalysis, *thiol–yne* photochemistry was also implemented as a catalyst-free alternative for functional patterning. In all cases, Infrared Reflection Absorption Spectroscopy (IRRAS), XRD, AFM, and fluorescence imaging confirmed high pattern fidelity, retention of crystallinity, and selective chemical conversion.

Importantly, the study extends beyond planar lithography by introducing *multi-heteroepitaxial growth* to achieve patterned chemical

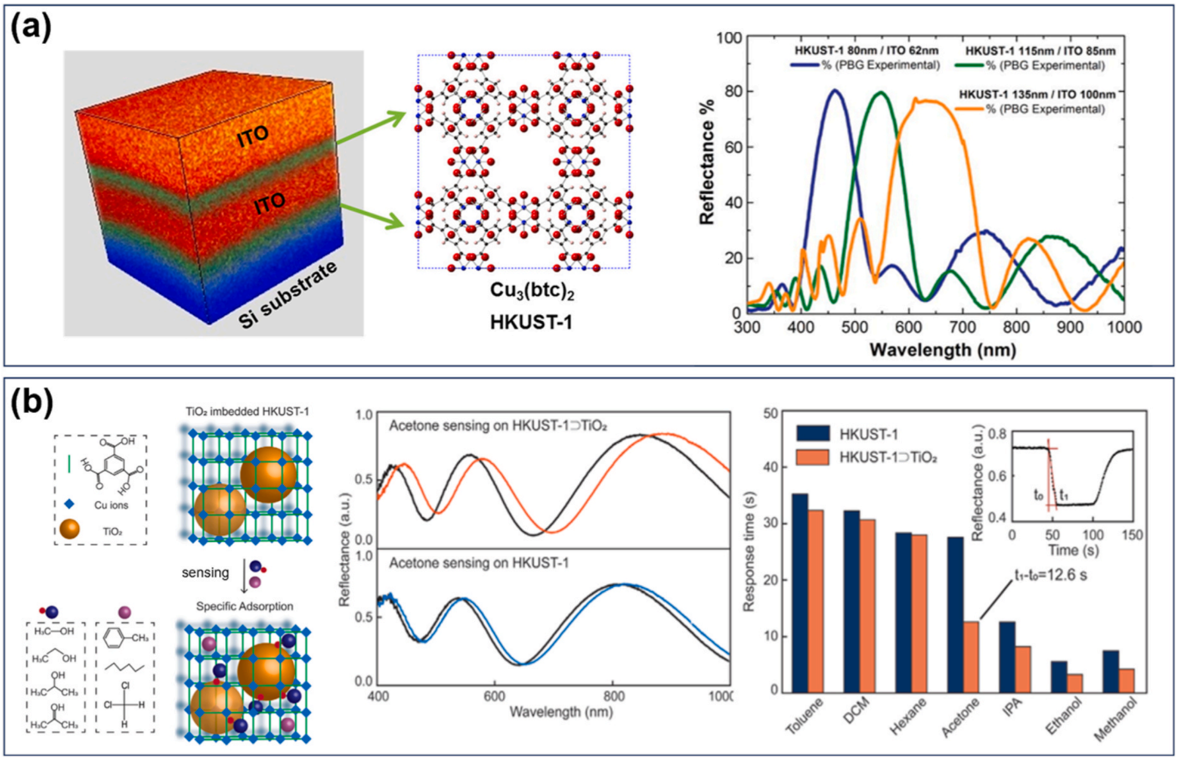

Fig. 11. (a) Scheme of construction of MOFs Bragg reflector, and the corresponding optical sensing reflectance spectrum. Picture taken from Ref. [60], with permission (b) Chemical sensing on MOFs-based Fabry−Pérot cavity by monitoring the change of reflection, and the dynamic behaviors upon exposure to various chemical vapors. Picture taken from Ref. [127], with permission.

functionality in the out-of-plane (z) direction. Layered MOF systems composed of alternating Cu(N_3-BPDC) and Cu(BPDC) domains were fabricated via automated LPE, enabling vertical resolution approaching the unit-cell level. These domains were selectively stained using iodine-tagged click reagents and visualized via backscattered electron SEM, confirming successful 3D patterning.

In a later paper by Drost and coworkers, SURMOFs were also used as resist for E-beam lithography achieving below-10nm resolution [130]. Building on the versatility of MOF thin films as photoresists, this study demonstrates that SURMOFs are also highly effective as resists for focused electron beam induced processing (FEBIP). Using both electron beam induced deposition (EBID) and electron beam induced surface activation (EBISA) with $Fe(CO)_5$ and $Co(CO)_3NO$ precursors, high-resolution nanostructures were fabricated on HKUST-1 and Zn-DPDCPP films. Notably, FEBIP on MOFs enabled chemically selective deposition and the realization of nested-L test structures with line widths below 8 nm—despite a beam diameter >6 nm—highlighting the role of reduced proximity effects and efficient precursor diffusion within the porous matrix. These findings establish SURMOFs as tunable, high-resolution platforms for both photon- and electron-based lithography.

6. Summary and outlook

The development of SURMOFs has transformed MOFs into highly versatile platforms for studying fundamental physical phenomena at well-defined interfaces. Beyond their established roles of MOFs in separation and catalysis, MOF thin films and SURMOFs offer a unique route to explore the intrinsic physical properties of molecular materials under precisely controlled structural, chemical, and environmental conditions. Their modular design enables systematic tuning of key parameters such as pore size, dimensionality, electronic structure, and guest-host interactions—making them an ideal testbed for phenomena ranging from charge transport to exciton dynamics and photonic effects.

One of the most striking recent developments in this field is the discovery of metallic conductivity in SURMOFs fabricated via bottom-up, layer-by-layer techniques. This milestone challenges long-held assumptions about dominance of activated transport in framework materials and opens the door to studying exotic quantum effects—such as correlated electron behavior, low-dimensional magnetism, and topologically nontrivial states—within the framework of crystalline, tunable, and solution-processable molecular solids. These advances highlight the unique role of SURMOFs as a new class of designer quantum materials.

Looking ahead, the integration of high-throughput experimentation, in particular using self-driving laboratories (SDLs) with computational design and AI-driven materials discovery is expected to further accelerate progress. As the interface between molecular architecture and macroscopic function becomes increasingly accessible, SURMOFs are poised to play a central role in the exploration of next-generation materials for quantum devices, energy conversion, and molecular-scale information processing.

CRediT authorship contribution statement

Lejie Tian: Writing – review & editing. **Jianxi Liu:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Christof Wöll:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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