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Conjugation-Length Dependent Interplay Between Charge Transfer and Locally Excited States in Sequence-Defined Donor–Acceptor Substituted Oligo(Phenylene Ethynylene)s

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ABSTRACT

Oligo(*para*-phenylene ethynylene)s (OPEs) serve as well-defined model compounds to understand electronic effects in conjugated macromolecules. Here, we report a sequence-defined series of OPEs capped with a di-*tert*-butylcarbazole (DtBCz) donor and a triphenyltriazine (Trz) acceptor to investigate how the donor–acceptor distance along a conjugated OPE backbone governs charge-transfer properties. Using an iterative synthetic strategy, the OPE length was extended stepwise, providing a molecularly highly defined platform to investigate length-dependent excited-state evolution. The lowest excited-state character was examined by steady-state absorption and photoluminescence spectroscopy, Lippert–Mataga analysis, time-resolved photoluminescence (TRPL) spectroscopy, transient absorption (TA) spectroscopy, and quantum-chemical calculations. Shorter OPE sequences (**PE0** and **PE1**) exhibit stronger charge-transfer (CT) dominant behavior, reflected by clear donor–acceptor coherence in transition-density analyses and pronounced solvatochromism. With increasing OPE length (**PE2** and **PE3**), locally excited (LE) contributions become more prominent, leading to hybridized LE and CT (HLCT) states which is further supported by TA and TRPL spectroscopy. The observed CT-to-HLCT evolution highlights the importance of precise backbone length control for rationally tuning excited-state properties in conjugated macromolecules.

1 | Introduction

The control over intramolecular charge transfer (CT) versus locally excited (LE) character in the singlet excited state is a decisive factor governing photophysical properties like emission color, photoluminescence efficiency, and excited-state lifetime [1, 2]. In π -conjugated organic donor–acceptor systems, this balance is modulated not only by the “strength” of the respective electron donor and acceptor, but also by their relative spatial arrangement

[3, 4] and the effective conjugation length that mediates electronic coupling between them [5–8].

In the early 2010s, the concept of hybridized local and charge transfer (HLCT) states was proposed to describe excited states in which the transition characteristics of LE and CT are closely combined and mutually compatible [9, 10]. They are attractive for the design of organic emitters aiming for higher electroluminescence and exciton utilization efficiency than conventional fluorophores

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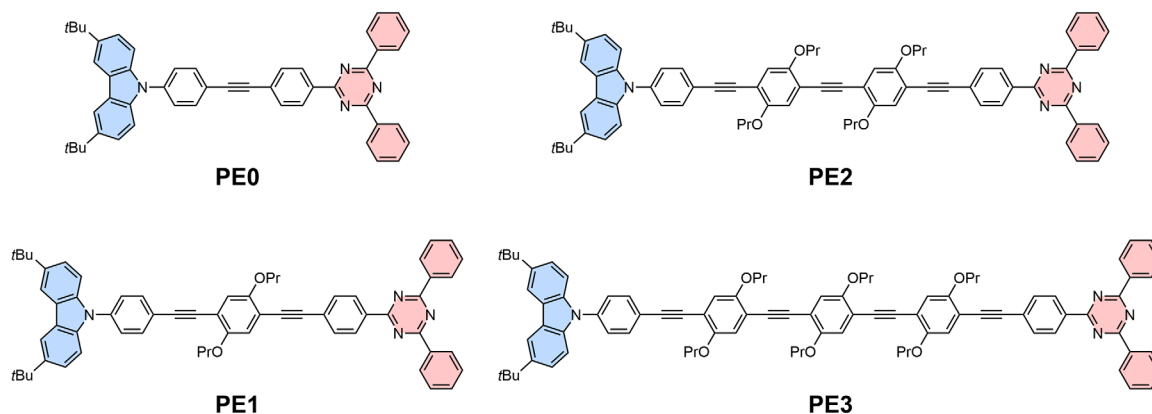


FIGURE 1 | Chemical structures of target compounds **PE0–PE3** investigated in this work.

[11–13]. Many reported HLCT emitters rely on an extended conjugated scaffold to tune the LE/CT balance [14, 15]. However, studies that identify the exact donor–acceptor distance at which hybridized character emerges are still lacking. Such investigations are therefore essential to deepen the fundamental understanding, which may aid the development of HLCT emitters.

Sequence-defined conjugated oligomers offer a suitable platform for addressing such questions. Their structural precision allows parameters, such as conjugation length and spatial separation of functional units, to be varied systematically without introducing dispersity-related ambiguity [16]. Among other conjugated structural motifs, oligo(*para*-phenylene ethynylene)s (OPEs) are especially attractive in this context. Owing to their nearly ideal one-dimensional “molecular wire” structure, OPEs have been employed to investigate distance-dependent charge transfer processes [17–20]. Importantly, if sample purity is only confirmed by NMR spectroscopic analysis, synthetically typically occurring homocoupling side products may be underestimated [21]. Therefore, truly monodisperse and thoroughly purified oligomers are required to establish the desired structure–property relationships.

This work aims to provide a systematic approach to investigate how the conjugation length and thus the distance between the same donor (D) and acceptor (A) units in D-OPE-A systems impact the CT and LE excited state characteristics of the investigated sequence-defined oligomers. Thus, four new sequence-defined macromolecules, denoted as **PE0–PE3**, were synthesized, in which OPE segments of varied lengths connect a di-*tert*-butylcarbazole (DtBCz) donor and a triphenyltriazine (Trz) acceptor (Figure 1). In addition to characterization typically applied to organic molecules, size-exclusion chromatography (SEC) was employed to assess the purity of the samples before photophysical experiments [21]. The electronic structures and excited-state characteristics of all molecules were evaluated by quantum-chemical calculations. Furthermore, steady-state photoluminescence (PL) solvatochromism analysis was used as an experimental indicator to identify hybridized excited-state behavior, since HLCT states exhibit a two-slope linear correlation in a Lippert–Mataga plot [9, 10, 15, 22]. Finally, transient absorption (TA) and time-resolved photoluminescence (TRPL) spectroscopy were employed to understand the excited-state dynamics across the series.

2 | Results and Discussion

2.1 | Synthesis of D-OPE-A Sequences

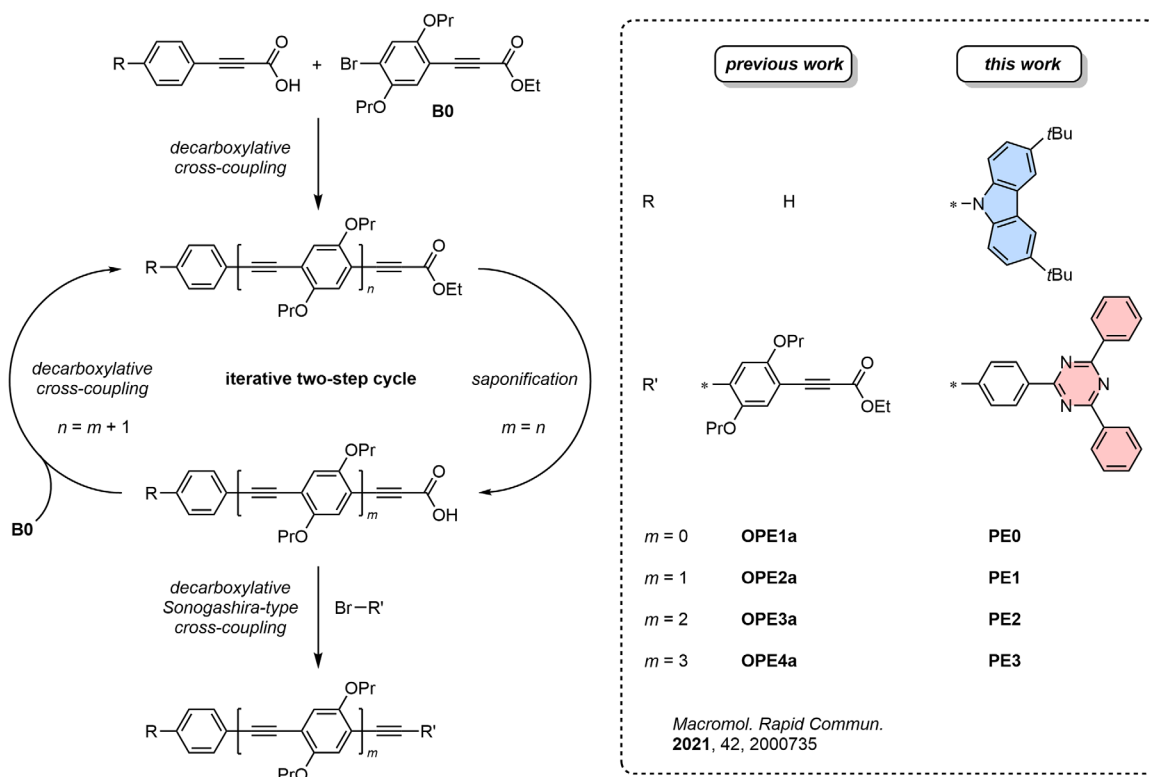
The D-OPE-A molecules depicted in Figure 1 were synthesized in an iterative manner based on a two-step cycle involving decarboxylative cross-coupling followed by saponification (Scheme 1). This modular synthetic strategy enables precise control over the oligomer length and has previously been established for the preparation of **OPE1a–OPE4a** molecules [23].

All synthesized molecules were fully characterized by NMR spectroscopy, IR spectroscopy, and HRMS analysis, as detailed in the Supporting Information. The ^1H NMR spectra of the final products **PE0–PE3** are shown in Figure 2a. The appearance of an additional aromatic resonance at around 7.1 ppm, along with the distinct aliphatic signals in the regions of 4.1–4.0 ppm (OCH_2), 2.0–1.8 ppm (CH_2), and 1.2–1.1 ppm (CH_3), confirmed the successful incorporation of the propoxylated PE units. The integrals of these signals increased proportionally with the oligomer length, while the signals corresponding to the terminal donor and acceptor units remained constant, thus verifying the stepwise elongation of the conjugated backbone.

Further evidence for the high purity of the isolated oligomers is provided by size-exclusion chromatography (SEC) (Figure 2b). Distinct single-peak elution signals were detected for all the members of the series in the retention time range of 17–19 min. The peak maximum shift toward shorter retention times with increasing oligomer length is consistent with the expected increase in hydrodynamic radius, primarily reflecting an increase in molecular size of the rigid, rod-like molecules.

2.2 | Computational Investigation

To understand the electronic structure as a function of the conjugation length within **PE0–PE3**, quantum mechanical calculations were carried out [24, 25]. Ground-state (S_0) geometries of the **PE n** oligomers were optimized at the PBE0-D3/6-31G(d,p) level of theory in the gas phase to probe their intrinsic electronic properties. The propoxy groups were replaced by methoxy groups



SCHEME 1 | Left: iterative synthesis toward sequence-defined OPEs via decarboxylative cross-coupling and saponification reactions. Right: comparison with previous work [23].

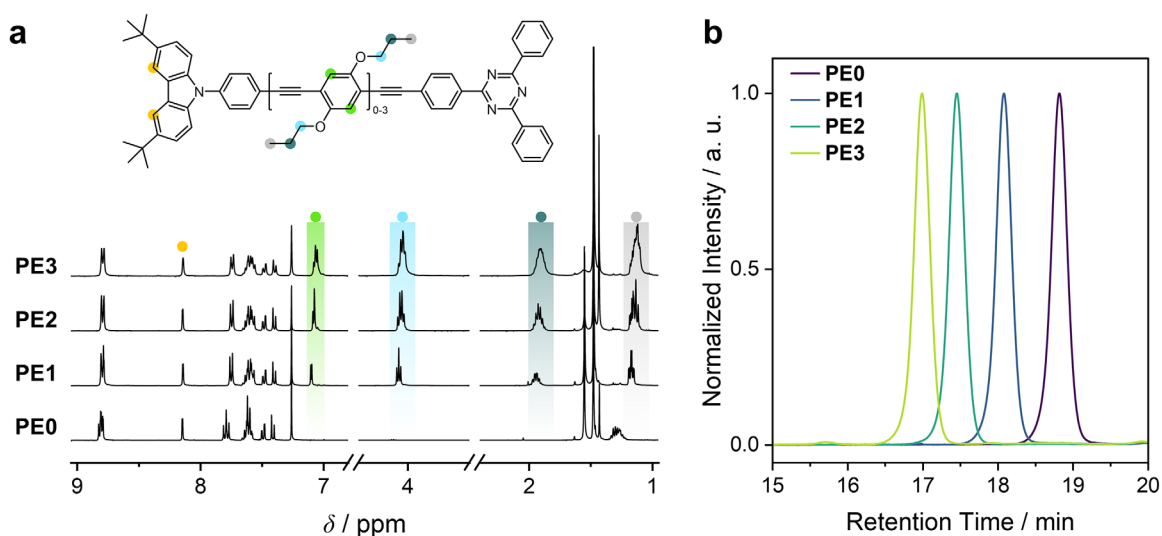


FIGURE 2 | (a) Structure and ^1H NMR spectra of **PE0–PE3** recorded in CDCl_3 . All spectra were normalized to the aromatic signal at 8.17–8.11 ppm, belonging to the DtBCz donor. (b) Normalized SEC traces of **PE0–PE3**.

for computational efficiency. The resulting frontier molecular orbital (FMO) energy levels and the corresponding orbital distributions are shown in Figure 3.

While the lowest unoccupied molecular orbitals (LUMOs) are mainly distributed over the conjugated OPE backbone and their energy levels remain almost consistent across the series, the highest occupied molecular orbital (HOMO) energy levels show

a clear progressive destabilization with n in the **PE n** oligomer series, from -5.45 to -4.99 eV. This trend reflects the increased conjugation introduced by the extended PE units, which generally both destabilizes the HOMO and delocalizes its distribution from the DtBCz donor toward the OPE backbone. Moreover, the alkoxy groups attached to the incorporated PE units exert an additional electron-donating effect, contributing to the delocalization of the HOMO distributions. The resulting HOMO-LUMO gaps (ΔE)

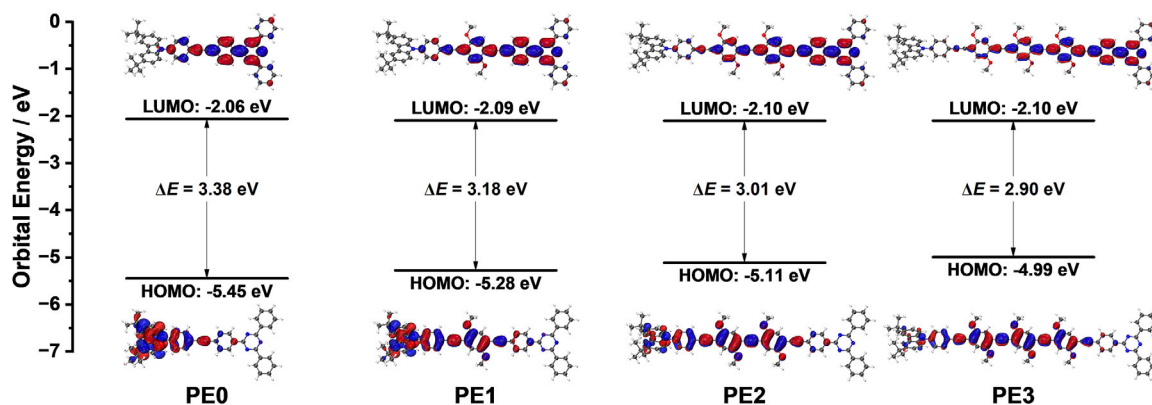


FIGURE 3 | FMO levels of **PE0–PE3** calculated at the PBE0-D3/6-31G(d,p) level of theory. Isovalue = 0.02.

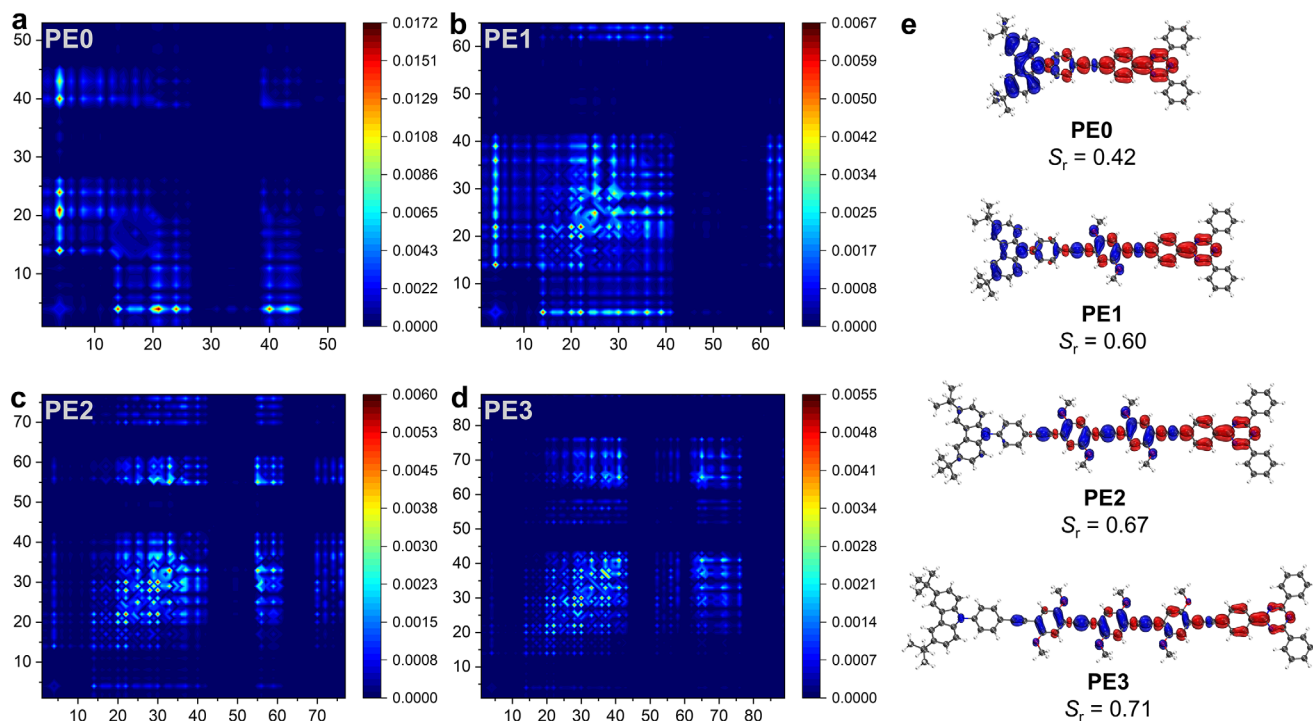


FIGURE 4 | Combined TDA-DFT analysis. (a–d) TDM maps of the $S_0 \rightarrow S_1$ transitions. The x- and y-coordinates correspond to the non-hydrogen atom indices, which are labeled in Figures S28–S31. (e) CDD plots of S_1 states, with blue and red isosurfaces indicating electron depletion and accumulation, respectively. Isovalue = 0.001. The corresponding S_r values are given below each structure.

accordingly decrease from 3.39 to 2.89 eV, indicating a red-shifted trend with increasing chain length.

Furthermore, excited-state calculations were performed using time-dependent density functional theory within the Tamm-Dancoff approximation (TDA-DFT). The following analysis focuses on the first excited singlet state (S_1), which is most relevant to the steady-state optical properties discussed below. In this context, atom-based transition density matrix (TDM) maps of the $S_0 \rightarrow S_1$ transitions and charge density difference (CDD) contours between S_0 and S_1 were generated using Multiwfn (Figure 4) [26, 27].

As shown in Figure 4a, the TDM map of **PE0** contains strong off-diagonal contributions between the nitrogen atom of the D π BCz donor (index 4, Figure S29) and parts of the Trz acceptor (indices 21–26 and 40–45, Figure S29), indicating a characteristic CT transition [28]. For **PE1–PE3** (Figure 4b–d), this donor–acceptor coherence becomes less and less pronounced. Indeed, with increasing conjugation length, the diagonal contributions increase progressively, indicating growing LE character [28]. Simultaneously, distinct off-diagonal contributions from the inserted PE segments, e.g., indices 20–43 in **PE3** (Figure S32), are identified, which may suggest a coexistence of LE and CT contributions characterizing its S_1 state. A similar trend is

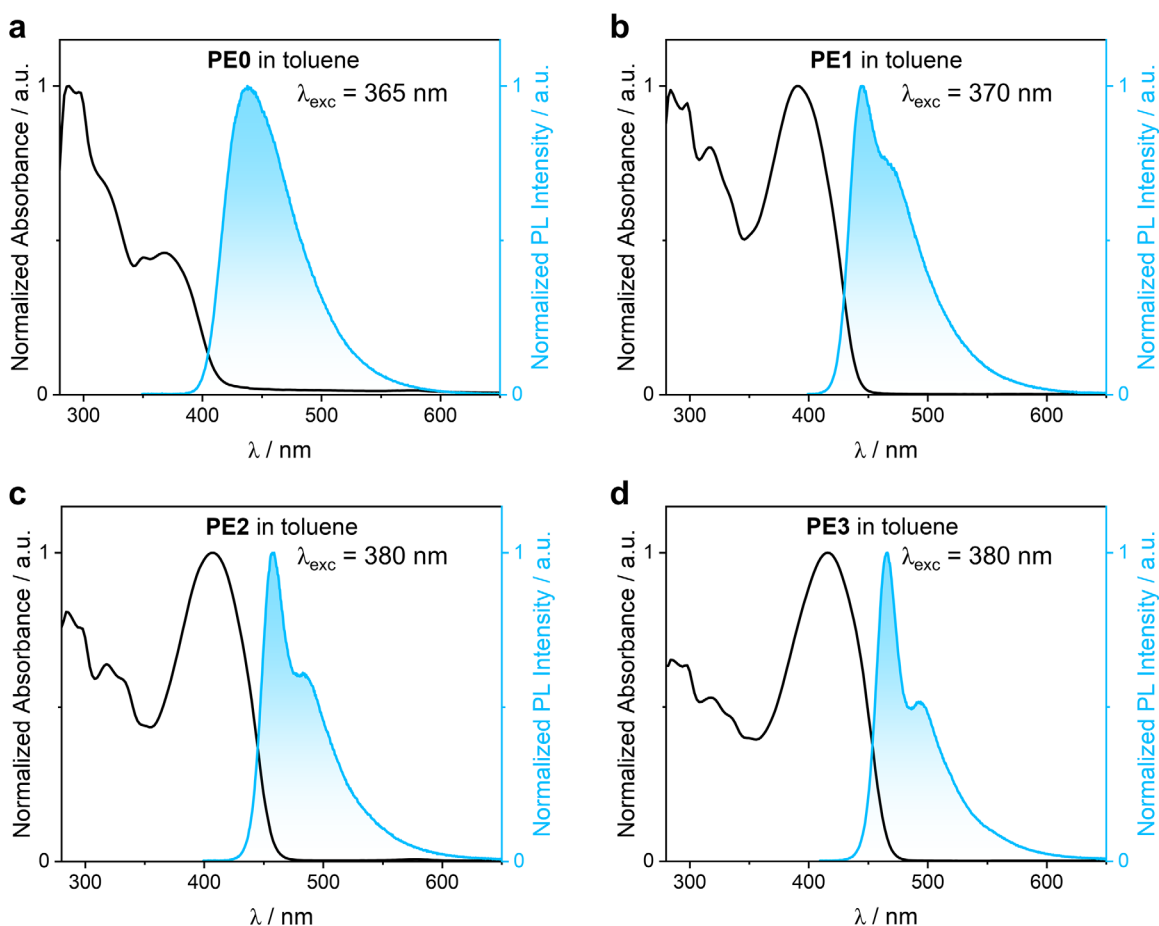


FIGURE 5 | Normalized UV-vis absorption and photoluminescence spectra of **PE0–PE3** (a–d) in 10 μM solution of toluene. Excitation wavelengths (λ_{exc}) were chosen based on the respective lowest-energy absorption maxima.

obtained from the CDD analysis (Figure 4e). From **PE0** to **PE3**, the contribution of the DiBCz donor to the $S_0 \rightarrow S_1$ transition gradually decreases, while the electron-density redistribution becomes increasingly delocalized over the extended PE backbone. The transition character was further quantified using the hole-electron density overlap index (S_r) [29, 30]. Based on the S_r values, the transition character is conventionally assigned as CT (0–0.40), HLCT (0.40–0.75), and LE (0.75–1) [31–33]. At the applied level of theory, **PE0** lies close to the CT range with an S_r value of 0.42, whereas **PE1–PE3** fall within the HLCT range, tending toward its upper region.

2.3 | Steady-State Photophysics

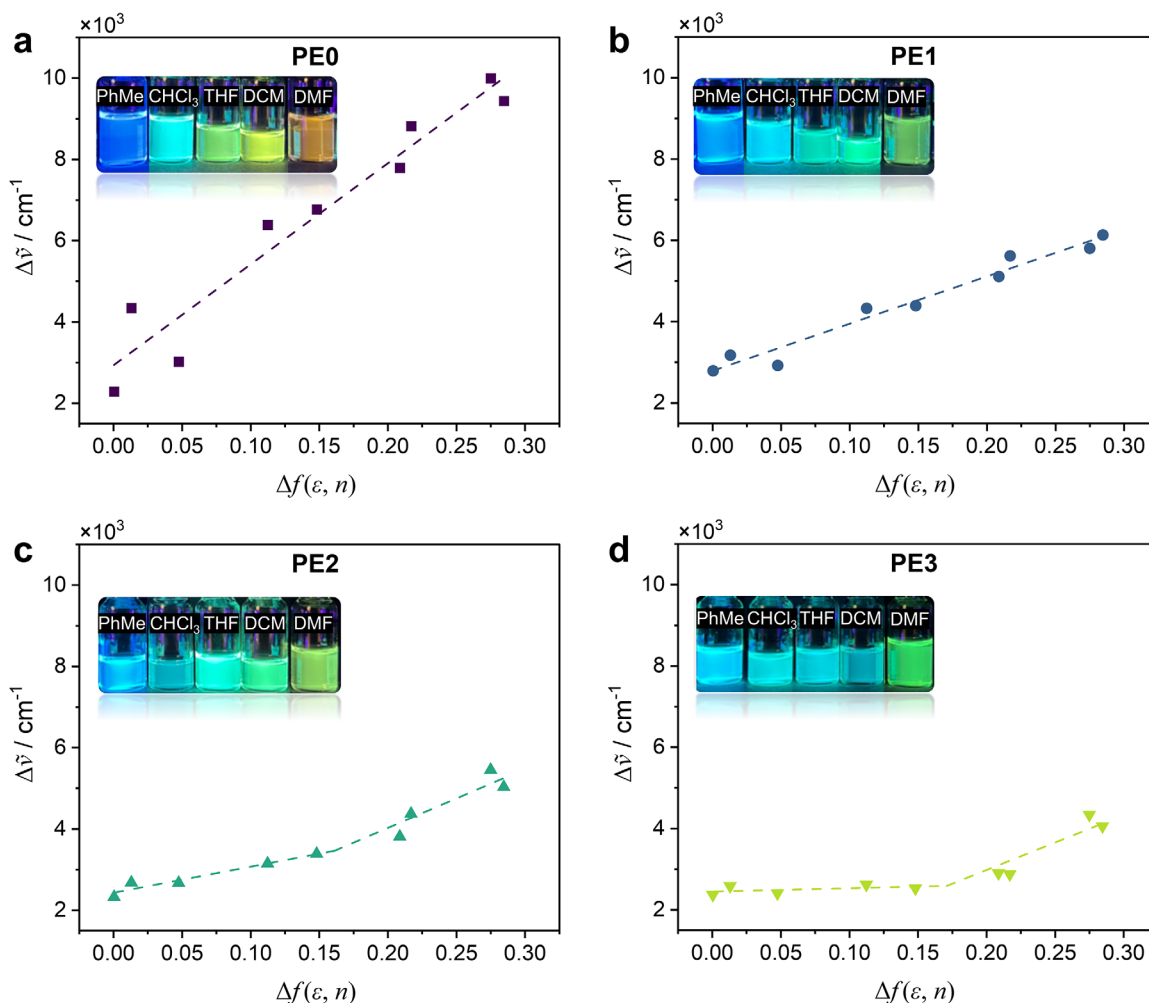
The steady-state optical properties of the **PE n** oligomers were first investigated in toluene solution. All molecules have high photoluminescence quantum yields (Φ_{PL}) exceeding 95%. Figure 5 presents the UV-vis absorption and steady-state PL (SSPL) spectra, while key spectral features are summarized in Table 1. From **PE0** to **PE3**, the lowest-energy absorption band increased in intensity with respect to the higher-energy bands, reflecting enhanced π -electron delocalization along the conjugated backbone. The peak position red-shifted from 368 to 416 nm, consistent with the progressive narrowing of the HOMO-LUMO gap, as predicted by TDA-DFT calculations (Figure 3). A corresponding

red-shift was also observed in the SSPL spectra, with the emission maxima shifting gradually from 438 to 466 nm across the series. The narrowing of the PL bands from **PE0** to **PE3** (Figure 5), with the bandwidth at 1/e (36.7%) of the maximum intensity decreasing from 82 to 56 nm (Table 1), is accompanied by a more clearly resolved vibronic structure. These spectral changes are consistent with an increasing LE character upon extension of the PE bridge.

To better understand the conjugation-length dependent solvatochromism behavior of the **PE n** oligomers, their steady-state photophysical properties were further investigated in aprotic solvents of different polarity (Figures S25 and S26 and Table S1). The Stokes shifts $\Delta\bar{\nu}$ were plotted against the Lippert-Mataga orientation polarizability Δf (Figure 6). Detailed calculations are described in the Supporting Information. Linear fits were applied to the data, and the resulting slopes (m) with the coefficients of determination (R^2) are summarized in Table S2. The high R^2 values for **PE0** (0.95) and **PE1** (0.99) confirm good linear correlations between Δf and $\Delta\bar{\nu}$ throughout the tested solvents. In this regard, both **PE0** and **PE1** exhibit CT-like excited-state character. In contrast, **PE2** and **PE3** are better described by a two-slope linear fit. Here, chloroform ($\Delta f = 0.15$) was used as an empirical breakpoint, separating the data into low- and high- Δf regions. However, due to the limited number of data points in each segment, the individual linear fits should be

TABLE 1 | Summary of steady-state optical spectroscopy feature in toluene.

Entry	λ_{abs} [nm] ^a	λ_{PL} [nm] ^a	1/e width of λ_{PL} [nm]	$\Delta\tilde{\nu}$ [cm ⁻¹] ^b
PE0	368 (3.37)	438 (2.83)	82	$4.34 \cdot 10^3$
PE1	390 (3.18)	445 (2.79)	72	$3.17 \cdot 10^3$
PE2	408 (3.04)	458 (2.71)	63	$2.68 \cdot 10^3$
PE3	416 (2.98)	466 (2.66)	56	$2.58 \cdot 10^3$

^aCorresponding energy values in eV are given in parentheses.^bStokes shift $\Delta\tilde{\nu} = \tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{PL}}$.**FIGURE 6** | Lippert-Mataga solvatochromic analysis of **PE0–PE3** (a–d). Dashed lines represent the fitted linear correlations. Insets show photographs of each **PE_n** oligomers in toluene, chloroform, THF, DCM, and DMF under UV excitation (365 nm).

interpreted with caution, particularly for the low- Δf segment of **PE3** ($R^2 = 0.24$). In addition, the Lippert-Mataga model is based on a point-dipole approximation and assumes a spherical solvation cavity, which may be less suitable for larger and more anisotropic molecules [34]. Nevertheless, the overall two-slope behavior remains evident from the broader trend of the data. The segments with smaller slopes indicate an LE-dominant HLCT excited-state, whereas the segments with higher slopes suggest a CT-dominant HLCT excited-state.

2.4 | Transient Absorption Spectroscopy

To elucidate the excited-state dynamics, transient absorption (TA) spectroscopy was carried out for all **PE_n** oligomers in toluene. A full comparison of all TA spectra is shown in Figure 7. Time constants derived from global analysis of the TA measurements are summarized in Table 2. The corresponding decay-associated difference spectra are provided in the Supporting Information (Figure S27).

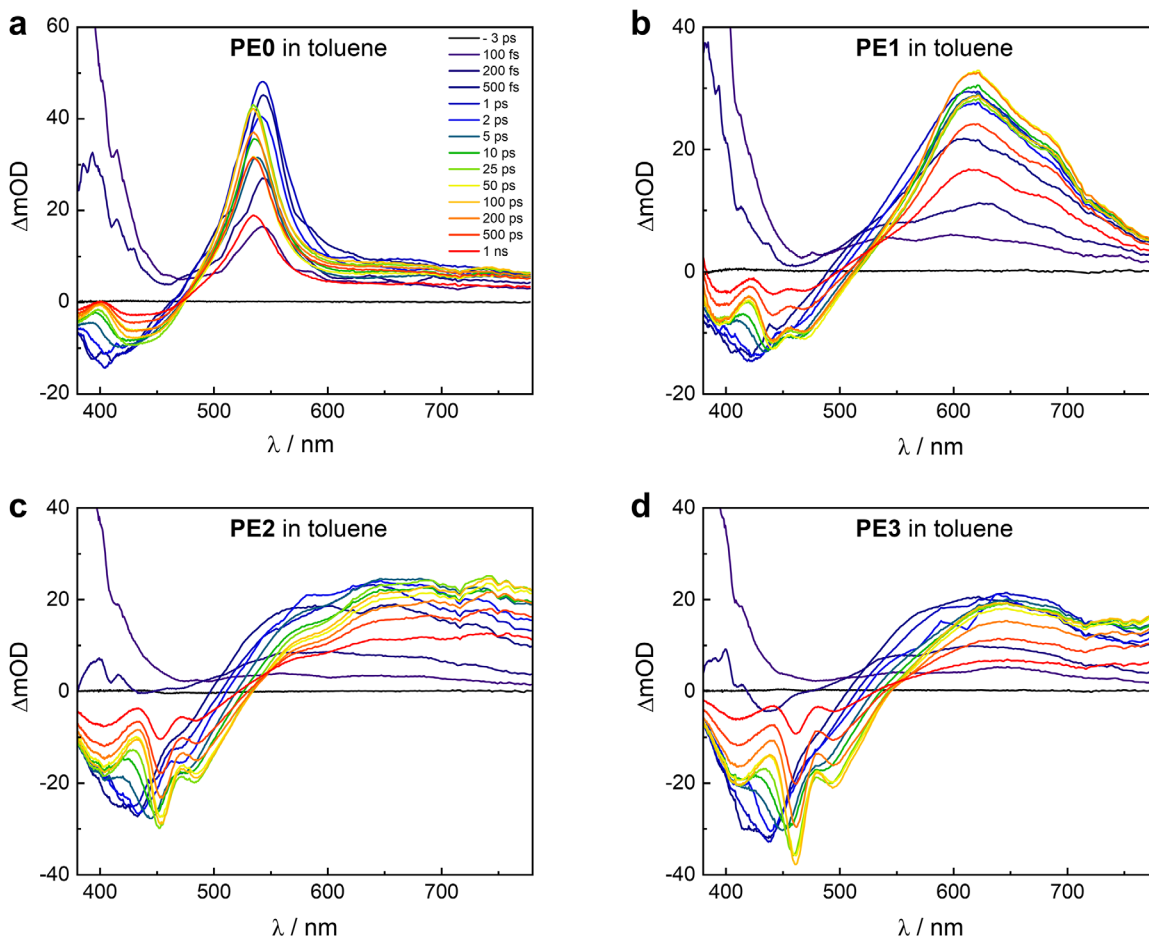


FIGURE 7 | Transient absorption spectra of **PE0–PE3** (a–d) in 25 μM toluene solution, excited by $\lambda_{\text{exc}} = 370$ nm.

TABLE 2 | The time constants of global fitting of TA data for all investigated PE_n molecules in toluene.

Entry	τ_1	τ_2	τ_3
PE0	2.2 ps	15 ps	>1 ns
PE1	2.5 ps	9.1 ps	>1 ns
PE2	1.6 ps	15 ps	>1 ns
PE3	1.2 ps	12 ps	867 ps

In toluene, increased initial intensity of the negative features, attributed to ground-state bleaching and stimulated emission [35], was observed as a function of elongation of the conjugated backbone, accompanied by a slight red shift, consistent with the λ_{PL} values of this series (≈ 400 –500 nm). Across the entire series in toluene, the positive excited-state absorption (ESA) signals follow a clear length-dependent trend. **PE0** and **PE1** exhibit well-defined ESA maxima in toluene (**PE0**: 533 nm; **PE1**: 611 nm). Within the first 200 fs, the transient responses are masked by experimental coherence artifacts resulting from the temporal overlap of the pump and probe pulses [36–38]. Following this initial phase, both molecules display a characteristic dynamic red-shift accompanied by spectral narrowing (band sharpening) within the first few picoseconds. This spectral evolution reflects ultrafast excited-state relaxation involving intramolecular vibra-

tional energy redistribution (IVR) [39–41], vibrational cooling, and subsequent structural relaxation within the S_1 state [42, 43]. As the conjugation length extends from **PE0** to **PE3**, the ESA bands broaden progressively and form a flat plateau at longer wavelengths. This behavior may reflect contributions from a denser manifold of coupled vibronic states, together with conformational and structural relaxation effects in the extended OPE backbone [39, 44, 45]. This spectral broadening strongly correlates with the steady-state optical features in toluene, where the emission bandwidth decreases progressively from **PE0** to **PE3** (Table 1). This foreshadows the emergence of a highly structured, LE-dominant backbone contribution. The impact of such an enhanced density of coupled vibronic states on altering IVR pathways within extended molecular bridges has been suggested by the ballistic energy transport models as described in previous studies [39–41, 46].

The time constant τ_1 tracks the early ultrafast excited-state relaxation and exhibits a notable acceleration from **PE0** (2.2 ps) and **PE1** (2.5 ps) down to **PE2** (1.6 ps) and **PE3** (1.2 ps), suggesting the enhanced vibrational coupling in the extended systems [39, 45]. The component τ_2 captures the subsequent geometry relaxation [42, 43], yielding values of 15 ps (**PE0**), 9.1 ps (**PE1**), 15 ps (**PE2**), and 12 ps (**PE3**), influenced by the symmetry of the conjugated pathway [44, 46]. This timescale is consistent with the vibrational cooling and conformational planarization processes occurring in the toluene matrix, leading

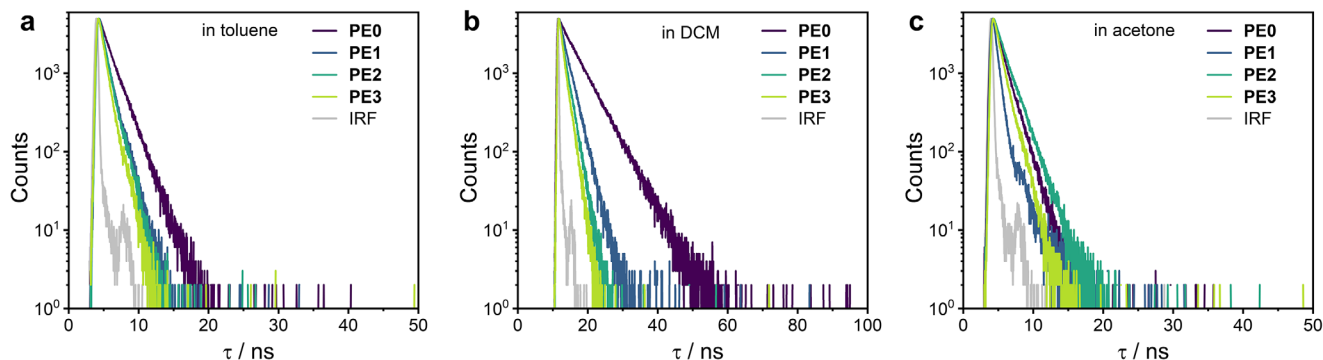


FIGURE 8 | Fluorescence decays of **PE0–PE3** in optically diluted solutions of (a) toluene, (b) DCM, and (c) acetone, obtained from TSCSP measurements, excited by $\lambda_{\text{exc}} = 375$ nm.

to the formation of a fully relaxed S_1 state before electronic population decay takes place [39, 45]. Crucially, the long-lived component τ_3 , which exceeds 1 ns for **PE0–PE2**, supports the strong charge-transfer character introduced by the D–A architecture [44]. This stabilization becomes evident when compared to undecorated OPE structures of similar length, which lack the D–A termini and decay much faster. The longer components τ_3 are in the regime of the rate for (non-)radiative decay of the excited state and may give further insight in its nature. In summary, a trend could be observed: with increasing conjugation length, τ_3 decreases, manifesting in a sub-nanosecond lifetime of 867 ps for **PE3**, indicating a reduced contribution of longer-lived CT character due to increased hybridization with LE admixture. This time-resolved evolution aligns with the two-slope Lippert-Mataga analysis, which identifies an LE-dominated HLCT state for **PE2** and **PE3** in the low- Δf region of non-polar solvents like toluene. This supports the interpretation that the accelerated decay of τ_3 is associated with increased mixing with the faster-decaying LE state, a solvent-modulated excited-state behavior characteristic of intercrossed push-pull systems [15, 9, 10].

2.5 | Time-Resolved Photoluminescence Spectroscopy

Time-resolved PL (TRPL) measurements provided complementary insight into the solvent- and length-dependent excited-state dynamics. Figure 8 presents the TRPL decay profiles measured in toluene, DCM and acetone. The corresponding PL lifetimes, together with the Φ_{PL} values and derived rate constants, are summarized in Table 3.

In toluene, all compounds exhibit high Φ_{PL} s (95%–99%) and slow non-radiative decay rates, k_{nr} , reflecting efficient radiative emission. Notably, k_{r} increases progressively with increasing OPE length consistently throughout the three investigated solvents. Upon increasing the solvent polarity to DCM, the Φ_{PL} s remain exceptionally high (90%–99%), and the non-radiative decay rates remain slow. This behavior, together with the high Φ_{PL} s and the significant extension of both hole and electron densities onto the OPE bridge, is consistent with substantial LE character being retained within the excited state. In acetone, by contrast, the Φ_{PL} s decrease markedly and k_{nr} increases substantially for all compounds, indicating the activation of additional non-radiative deactivation pathways in this more polar solvent. The

biexponential decay observed for **PE1** in acetone, dominated by a short-lived sub-ns component, is therefore interpreted cautiously as a manifestation of solvent-induced non-radiative deactivation rather than as direct evidence for two emissive excited states. Furthermore, the small calculated S_1 – T_n spin-orbit coupling matrix elements for each of the compounds in the series (Table S4), together with the negligible effect of oxygen removal on the TRPL and SSPL in the example of **PE3** in toluene (Figure S28), suggest that triplet-mediated deactivation is not a major pathway under the investigated condition.

Taken together, the complementary steady-state and time-resolved photophysical data provide important data for assessing the excited-state evolution across the D-OPE-A series. Rather than assigning HLCT character from a single criterion alone, we consider the combination of (i) a solvent-dependent change in the excited-state dipole moment, (ii) simultaneous LE- and CT-type contributions to the excited-state wavefunction, as reflected by the hole-electron analysis, and (iii) retention of efficient radiative coupling in polar media, as reflected by the fast k_{r} . The systematic increase in the hole–electron overlap index from ($S_{\text{r}} = 0.42$) for **PE0** to 0.60, 0.67, and 0.71 for **PE1–PE3**, respectively, together with the increasing k_{r} values, indicate that extending the central OPE spacer does not simply attenuate donor–acceptor coupling, but increasingly incorporates the π -bridge into the emissive excited-state wavefunction. Within this series, **PE2** and **PE3** exhibit the clearest HLCT-type characteristics, as they combine substantial hole-electron overlap with the two-regime Lippert-Mataga behavior and efficient radiative decay retained in polar media. Importantly, the OPE spacer therefore acts not merely as a means of increasing the donor–acceptor distance, but as an electronically active element that modulates both the LE/CT balance and its sensitivity to the surrounding solvent.

3 | Conclusion

In this work, four new D-OPE-A type oligomers (**PE0–PE3**) were synthesized via an iterative strategy combining decarboxylative coupling and saponification reactions. The high purity (>99%) of these oligomers was verified by SEC, ensuring a reliable basis for comparison of their photophysical properties. This is of particular importance in the context of fundamental research on conjugated oligomers, where even minor impurities can interfere with the establishment of structure-property relationships.

TABLE 3 | Summary of fluorescence lifetimes and PLQY of **PE0–PE3** in different solvents together with the derived rate constants.

Entry	τ [ns] ^a			Φ_{PL} ^b			k_{r} [10 ⁸ s ^{−1}]			k_{nr} [10 ⁸ s ^{−1}]		
	in toluene	in DCM	in acetone	in toluene	in DCM	in acetone	in toluene	in DCM	in acetone	in toluene	in DCM	in acetone
PE0	1.64	4.66	1.29	0.95	0.90	0.16	5.8	1.9	1.2	0.31	0.22	6.5
PE1	1.02	2.15	0.71	0.99	0.97	0.13	9.7	4.5	1.9	0.098	0.14	12
PE2	0.93	1.56	1.57	0.98	0.99	0.51	11	6.4	3.3	0.22	0.064	3.1
PE3	0.78	1.24	1.01	0.95	0.99	0.54	13	9.8	5.4	0.26	0.099	4.6

^aDerived from exponential deconvolution fits of fluorescence decays.^bMeasured in non-degassed solvents using an integrating sphere.

Solvatochromism studies combined with computational analysis demonstrated that the character of the lowest excited singlet state (S_1) evolves systematically with the OPE length. UV-vis absorption spectroscopy revealed a growing LE contribution of the excited-state by showing a rise of the π - π^* transition across the series. Consistently, PL investigations showed the gradual decay of CT character. While S_1 of **PE0** and **PE1** are CT-dominated, **PE2** and **PE3** exhibit stronger mixed character of CT and LE. More particularly in the case of **PE2** and **PE3**, the Lippert-Mataga plot indicates a switch between an initially LE-dominated state in non-polar solvents into a CT-dominated state in polar environments.

TA measurements support the progressive shift from CT- toward LE-dominated excited states with increasing OPE length. Following photoexcitation, the early spectral evolution is consistent with rapid excited-state relaxation, particularly involving IVR. As the OPE backbone is systematically extended from **PE0** to **PE3**, the ESA profiles broaden into a less structured plateau, reflecting a denser manifold of coupled vibronic states associated with the increasingly mixed excited-state character. This time-resolved broadening correlates with the steady-state emission band narrowing in non-polar media, where the enhanced density of coupled states within the extended chain reshapes and accelerates the early-stage IVR pathways. The long-lived decay component ($\tau_3 > 1$ ns) for the shorter sequences is consistent with a heavily stabilized charge-transfer character, while the decrease of τ_3 in longer chains tracks the growing LE admixture manifesting in a sub-nanosecond lifetime of 867 ps for **PE3**. TRPL measurements reveal that the OPE-length-dependent evolution of the excited-state character is accompanied by changes in the relative rates of radiative and non-radiative relaxation. In particular, the increasing radiative decay rates with OPE length demonstrate that efficient radiative coupling is retained despite the increasing donor-acceptor separation. Together with the solvent-dependent Lippert-Mataga behavior, hole-electron analysis, and high PL quantum yields, these results support a mixed LE/CT character, with **PE2** and **PE3** exhibiting the clearest HLCT-type signatures.

Overall, this series of sequence-defined macromolecules highlights that the hybridization of LE and CT (HLCT) is a delicate balance that can be precisely tuned through the OPE bridge length in D-OPE-A architectures. Crucially, the OPE spacer acts not merely as a distance-control element, but as an electronically active component that enables tuning of the excited-state character and its solvent responsiveness. These findings establish

π -conjugated spacer length as a molecular design parameter for tuning solvent-responsive excited-state behavior in donor- π -acceptor systems.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

All data generated or analyzed during this study are included in this published article and its Supporting Information file. The TRPL data supporting this publication can be accessed at <https://doi.org/10.17630/8fa64897-4d2b-4fc4-b172-dc9d4fe93a8f>.

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Supporting Information

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