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Organic dyads and triads based on the triphenylene-rylenediimide couple: Molecular design, self-organization, and photo-physical properties

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Highlights

• Dyad and triad discotic mesogens were synthesized by Sonogashira coupling/DBU-promoted cyclization reactions tandem.

• Fluorescence quenching is observed for all compounds due to photo-induced electron transfer between donors and acceptors.

• The compounds exhibit hexagonal and rectangular columnar mesophases over broad temperature ranges.

Abstract

Liquid-crystalline D-A dyads and A-D-A triads, based on the chemical association of electron-donor (D) triphenylene discogens and electron-acceptor (A) perylene/benzoperylene diimides, have been synthesized by the Pd-catalyzed Sonogashira coupling/DBU-promoted cyclization reactions tandem. These molecular heterojunctions spontaneously self-organize into columnar hexagonal
(Col\textsubscript{hex}) or/and rectangular (Col\textsubscript{rec}) mesophases, over broad temperature ranges including room temperature, with the antagonist moieties segregated into alternated homo-molecular (homolithic) stacks within mixed columns. Their intramolecular electron and energy transfers have been studied by UV/Vis absorption and fluorescence emission spectroscopies. Due to photo-induced electron transfer between donor and acceptor units, fluorescence quenching is systematically observed for all the dyads and triads. This study further reveals that perylenediimide is a stronger electron acceptor than the larger benzoperylenediimide building block. Density function theory calculations of their molecular structures and HOMO-LUMO energy levels and gaps support the experimental results and demonstrate that these donor-acceptor systems have potential applications in various optoelectronic devices.

1. Introduction

In many organic-based optoelectronic devices, such as photovoltaic solar cells (PSCs) and light emitting diodes (OLEDs), the active materials usually consist of electron-donor and acceptor molecules (for PSCs), and electron- or hole-transporter moieties (for OLEDs) [1]. Such types of molecular materials could play an essential role in future organic electronic devices, as, for instance, ambipolar semiconductors [2]. According to the devices' structure and active materials, organic solar cells can be categorized into bilayer solar cells, bulk heterojunction solar cells, and molecular heterojunction solar cells [3]. Of interest are the molecular heterojunctions, which consist of chemically linked electron-donor (D)/-acceptor (A) moieties via alkyl spacers, as the ideal device configuration for the photoinduced energy and charge transfer, and for the charge collection and transport in organic photovoltaic solar cells [4], [5], [6]. When an active layer is made of such molecular heterojunctions, one has to ensure that both A and D entities phase separate at the nanometre scale, with ideally, the largest D/A interface [4],[5]. If nanoscale segregation is realized by molecular self-sorting, molecular heterojunctions should be promising supramolecular structures for these applications. Although, as evidenced by the numerous reported attempts in the literature, these molecular heterojunctions do not seem straightforward to design since both entities tend to neutralize each other by mixing rather than by segregating, and their design still remains a timely challenge [4].

π-Conjugated discotic liquid crystals (πDLCs) made of large polycyclic aromatic cores [7], [8], [9] are among the most attractive materials in organic electronics as organic semiconductors. Indeed, πDLCs are outstanding examples of soft self-assemblies: they self-organize with self-healing ability into columnar phases with a large degree of stacking order, and show extraordinary unidirectional charge migration properties [10], [11], [12], [13], [14], [15]. They have potential applications for uses in optoelectronic devices, such as organic field-effect transistors (OFETs) [16], OLEDs [17], [18], [19], or OPSCs [1].

On the one hand, electron-rich triphenylene derivatives (TP) are being widely studied as p-type semiconducting DLCs (for positive charge hopping pathway) because of their natural tendency to stack into columns and to self-assemble into columnar mesophases [20], [21], [22]. On the other hand, electron-deficient perylene bisimides (PI) and related rylene derivatives [23],[24] are among the best n-type organic semiconductors (for electron transport), in replacement of fullerene (C\textsubscript{60}) derivatives [23],[24], but have however been less investigated as discotic liquid crystals essentially due to their low solubility in organic solvents [25], [26], [27]. Introduction of long alkyl groups at either both imide tips or at the ortho/bay positions of the PI cores has
improved drastically their solubility as well as significantly promoted self-assembly in liquid crystal mesophases.

As just mentioned above, and essentially for molecular design considerations, only a few examples of such D–A mesomorphic molecular architectures, mainly triphenylene-rylene molecular heterojunctions, where the n- and p-type entities truly separate in space, have been reported so far [28], [29], [30], [31], [32], [33], [34], [35]. The search for other multi-segregated supramolecular self-assemblies is still essential and therefore highly desirable for the design of efficient ambipolar systems.

Previously, we obtained D-A-D molecules associating triphenylenes and rylenes, in which both electron-donating and accepting species were found to self-segregate into lamello-columnar (LamCol) mesophases, as demonstrated by small-angle X-ray diffraction and STM studies, thus forming distinct electron and hole transport pathways, and showing high electron and hole mobility values [35]. Here, we report on the synthesis, thermal and self-assembly behaviours, and optical properties of triphenylene-rylenebisimide donor-acceptor (D-A) dyads and A-D-A triads, with the inverted topology as previously reported [35]. Thermal gravimetry (TGA), polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and small- and wide-angle X-ray scattering (S/WAXS) revealed that all compounds are highly thermally stable and that they all self-organize into wide-temperature ranges columnar mesophases, including room temperature, with only local-range segregation of the different moieties within mixed columns. The electron and energy transfers between the donor and acceptor have been studied, revealing that perylenediimide is a stronger electron acceptor than the larger benzoperylenediimide building block, in agreement with Density Function Theory (DFT) calculations of their molecular structures, frontier molecular orbitals and energy gaps.

2. Results and Discussion

2.1. Design, synthesis and characterization

In order to improve the solubility of both the discotic fragments in organic solvents and to promote the formation of low-transition temperatures columnar mesophases (including room temperature) with TP-PI dyad and TP-PI2 triad (and their benzoperylenediimide homologs, BP), two bulky forked chain fragments were grafted on either tip of the PI core, whilst the TP periphery was decorated by 5 and 4 octyloxy chains, for the dyads and triads, respectively. A flexible spacer, connecting the TP entity at one or two of the vacant position(s) with one of the bay positions of the PI unit, was set sufficiently long to allow their spatial separation. The perylene-containing compounds (TP-PI and TP-PI2, Scheme 1) were synthesized in one step by palladium-catalyzed Sonogashira cross-coupling reaction between bromoperylene bisimide and mono- or di-alkynyl triphenylene precursors, respectively (PI-Br, TP-1 and TP-2, Scheme 1) in 50–55% yields. Subjecting TP-PI and TP-PI2 to the strong base diazabicyclo[5.4.0]undec-7-ene (DBU), promoted intramolecular cyclization, leading to the corresponding benzoperylene derivatives (TP-BP and TP-BP2, Scheme 1) in 70 and 55% yields, respectively.
Scheme 1. General synthetic scheme, molecular structures, yields and nomenclature of electron donor-acceptor (D–A) dyads (TP-PI, TP-BP) and A-D-A triads (TP-PI2, TP-BP2).

The branched chain perylene bisimide PI was synthesized in high yield (85%) using a classical procedure (Supplementary Information, Scheme S1). Bromation of PI performed with 1 equivalent of bromine yielded, after purification by chromatography, the isomerically pure compound, PI-Br, in 43% yield. Both the mono- and di-alkynyl triphenylene discogens, TP-1 and TP-2, were synthesized by the Williamson ether reaction between 2-hydroxy-3,6,7,10,11-
pentakis(octyloxy)triphenylene and 2,7-dihydroxy-3,6,10,11-tetrakis(octyloxy)triphenylene [36], respectively (Scheme S2), and 10-undecyn-1-yl p-toluenesulfonate (Scheme S3).

The intermediates were characterized by $^1$H NMR and all the final target molecules were characterized by $^1$H NMR, $^{13}$C NMR, HRMS and elemental analysis (see Supplementary Information, Figures. S1–S23). The results revealed the good purity of the compounds and the good agreement with the expected molecular structures.

2.2. Thermal stability, mesomorphism, supramolecular organization

As expected, this specific molecular design promotes the self-organization of the D-A structures into room-temperature columnar mesophases. The thermal stability and mesomorphic behaviour of the D-A and A-D-A compounds were first investigated by POM, TGA and DSC (results summarized in Table S1), prior to the structural characterization of the mesophases by S/WAXS. The excellent thermal stability of the dyads and triads was confirmed by thermal gravimetric analysis (TGA in dynamic mode, Figure 1). Indeed, in all 4 cases, the decomposition temperatures (considered at the onset of the 5% weight loss) are all remarkably higher than 350 °C. Accordingly, no sign of decomposition could be detected by POM in the mesomorphous temperature interval, even in the isotropic state, and the transition temperatures were fully reproducible on subsequent heating-cooling cycles.

As evidenced by POM, the four target compounds revealed fluid and birefringent textures (Figure 1) typical of liquid crystalline mesophases, but not characteristic, from room temperature onwards. These observations thus did not permit their unequivocal assignment, except for TP-PI, whose texture exhibits in addition large homeotropic zones, corresponding to columns of stacked molecules oriented perpendicular to the untreated glass substrates, a good indication of the formation of a columnar hexagonal phase (Col$_{hex}$). No structural change could be observed on further heat-cool cycles, suggesting the presence of one single mesophase per compound only, as also confirmed by DSC analysis (Figure 1); crystallization was not observed for any of them up to below −50 °C. Both the dyads TP-PI and TP-BP exhibit a similar thermal behaviour with only one endotherm detected by DSC, corresponding to the clearing temperature, at ca. 130 and 141 °C on heating, respectively (Table S1). These transition temperatures are perfectly reversible on cooling, with almost no delay in the mesophase reformation (Table S1). The triads TP-PI2 and TP-BP2 also displayed only one endotherm, with higher isotropization temperatures than their corresponding dyads. A substantial increase of the mesophase stability was found for the BP-containing triad with respect to the PI triad, from 181 and up to 230 °C on heating, respectively.

As already previously noted with other structurally related alkyne-containing compounds [35], TP-PI2 exhibited partially heating-induced polymerization above 200 °C if maintained at this temperature for prolonged periods of time, and with evidences of irreversible thermal behaviour after repeated DSC heat-cool treatments and the observation of small domain-formation in POM texture.
Figure 1. Representative optical photomicrographies (POM, on cooling from the isotropic liquid) of the D-A dyads and A-D-A triads in the mesophases: TP-PI at 115 °C in Col_{hex}, TP-BP at 126 °C in Col_{rec}, TP-PI2 at 153 °C in Col_{rec}, TP-BP2 at 230 °C in Col_{rec}. Thermal gravimetry curves (TGA, dynamic mode), heating rate 10 °C min^{-1}, under N_{2}; the 5% weight loss temperatures were 402, 395, 397 and 395 °C for TP-PI, TP-BP, TP-PI2, and TP-BP2,
Thus, the triads show higher phase transition temperatures and mesophase stability than the dyads, as well as the BP derivatives with respect to the PI systems. This tendency can be understood by the enhancement of π-π interactions upon the change of the molecular structures and the increase conjugation (dyads→triads:+50,+90 °C, PI→BP:+10,+50), hence stronger packing cohesion in columns, and therefore the increase of the thermal stability and phase transition temperatures. Furthermore, mesomorphism was strongly promoted by chemically connecting both types of molecular species. As far as the precursory fragments are concerned indeed, only the mono-functional discogen TP-1 was mesomorphous, exhibiting a Col$_{hex}$ mesophase with a narrow, though low, temperature range (Cr 50 Co$_{hex}$ ∼ 61 Iso/Iso 58 Co$_{hex}$ ∼ 28), whereas both the di-functional TP-2 (Cr 61 Iso/Iso 33 Cr) and PI-BR (Cr 132–134 Iso) melted directly in the isotropic liquid without showing any mesophase (Figures S24–S25).

The mesophases’ structures were investigated by S/WAXS and the representative X-ray patterns of TP-PI, TP-BP, TP-PI2 and TP-BP2, recorded on cooling from the isotropic liquid at room temperature are shown in Figure 2a, and the structural and geometrical data are reported in Table 1. The assignment to p6mm Co$_{hex}$ mesophase for TP-PI suggested by POM was confirmed by the presence of only one single sharp and intense small-angle reflection, indexed as (10). In the wide-angle range, two additional signals were observed: i) the intense semi-diffuse peak, at around 3.5 Å, arising from the regular distance between triphenylene or perylene rings, respectively, piled into columns (h$_{TP}$ ≈ h$_{PI}$ ≈ h$_{PP}$, a priori undifferentiated), with a correlation length, ξ ≈ 40 Å, corresponding to molecular stacks of ca. 11 mesogens, and ii) the strong and broad scattering with a maximum in the 4.5–5.0 Å range, due to liquid-like lateral distances between molten chains (h$_{ch}$). Due to the sole presence of the intense small-angle reflection (10), a square symmetry could also have been suggested, but this possibility was disregarded as incompatible with the dimensions of the dimer, too large to be accommodated within the lattice without a significant tilt with respect to the symmetry plane (For a Colsqu at T = 25 °C, Α$_{squ}$ = 18.78 Å, Z = 1, γ = 90°, Α$_{squ}$ = 352.8 Å$^2$, h$_{mol}$ = 4.27 Å, ψ = 35–40°).

The S/WAXS patterns of the other 3 compounds showed two intense diffraction peaks in the small-angle region, indexed as the fundamental reflections (20) and (11) of a rectangular lattice, plus additional very weak diffraction peaks corresponding to the (31) and (02) indexations (Table S2). Similarly, the semi-diffuse peak at ca. 3.5 Å (ξ ∼ 30-55 Å, ca. stacks of ca. 9–16 mesogens on average) and the broad scattering at ca. 4.5 Å correspond, as above, to the stacking of the TP, PI/BP aromatic cores and to the average lateral distances between molten chains, respectively. The mesophase is the same for the three compounds and could be safely assigned to as rectangular columnar mesophase (Col$_{rec}$) with the c2mm planar symmetry.

The major changes in mesophases’ structural parameters consist in the larger lattice elongation in the triad architecture, imposed by the larger proportion of the non-symmetrical rylene mesogens (PI and BP) and to the loss of the preferential orientation in the particular case of the TP-PI dyad (whose lattice parameters hardly change with temperature). In the Col$_{hex}$ phase, the lath-shaped PI have no preferential orientation likely due to mismatch of chains’ substitution patterns (Figure 2c) leading to overall
circular columns, whilst in the Col\textsubscript{rec} phase of TP-BP, TP-PI2 and TP-BP2, the rylene cores align preferentially along defined directions (along the a-lattice axis), causing the elongation doubling and the symmetry breaking of the lattice to rectangular symmetry c2\textsubscript{2}mm (solid line frames, Figure 2b). The elongation markedly increases with temperature, which is the logical consequence of the lower degree of stretching of the alkyl spacers connecting column walls. The lattice area on the contrary just follows the normal volume expansion with temperature, resulting in quite constant molecular slice thicknesses ($h_{\text{mol}} = 3.52–3.85$ Å, Table 1), obtained as the ratio between half a dyad or a third of a triad volume with the average cross-section of one column, A/Z). These average values are slightly, but significantly, above the face-to-face stacking distances directly determined from wide-angle scattering maxima ($h_{\pi}$), which might either come from slightly out-of-plane tilted mesogens (by $18 \pm 5°$, $\psi$, Table 1) and/or from orientational fluctuations. The detailed analysis of the mesophases' geometrical parameters (lattices' parameters and areas, Table 1) reveals that both the Col\textsubscript{hex} (TP-PI) and Col\textsubscript{rec} (TP-PI2, TP-BP, TP-BP2) phases are therefore constituted of one single (Col\textsubscript{hex}) and two (Col\textsubscript{rec}) columns per lattice, respectively, composed of a priori undifferentiated triphenylene/rylene mesogenic stacks, thus ruling out the formation of multicolumnar superlattices [30]. This implies that both mesogens somehow periodically distribute along the columns.

![Figure 2](image.png)

Figure 2. (a) Representative S/WAXS patterns of dyads/triads at room temperature (and 70 °C for TP-PI2). (b,c) Symmetries and geometrical local-range representations of the columnar arrangements exhibited (b, Col\textsubscript{rec}; c, Col\textsubscript{hex}) by dyads and triads combining triphenylene (TP, pink discs) and side-attached rylene (PI or BP, blue rectangles). Solid frame: hexagonal (grey)
and rectangular (black) lattices; dotted frame (see text). (d) Schematic representation of the supramolecular arrangement in domains of the various columnar phases: for the Col_{rec} phase, TP and PI/BP columnar homo-molecular stacks alternate while preserving the orientation of the PI/BP stacks; for the Col_{hex} phase, the blue tiles (PI/BP) are freely orientated to yield time-averaged discoid shape (not represented). The dashed red curves represent the permutation of the columnar domains. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Therefore, this simple molecular design did not permit, as demonstrated by the non-formation of superlattices (S/WAXS), to obtain the desired so-called “double-cable” mesophases, consisting of separate columns purely made of TP units alternating with columns solely constituted of PI/BP species, an essential condition for the fabrication of OPV devices. A contrario, the columns of both Col_{hex} and Col_{rec} phases appear undifferentiated at the macroscopic level, with the apparent homogeneous mixing of TP and rylenes along the columns (i.e. complete loss of differentiation between TP and PI/BP fragments). Despite that individual mesogenic rylene diimides and triphenylenes self-organize into columnar stacks with rather similar stacking distances ($h_{TP} \approx h_{PI/BP} \approx h_{\pi}$) [21],[26], their intrinsic chemical nature, shape and the symmetry of the chains’ substitution pattern (here, TP has C$_3$-type chains’ pattern, and PI, a C$_2$-type) are substantially different rendering their complete intimate mixing by CT interactions in single mixed stacks highly doubtful. Indeed, such a homogeneous stacking of TP and PI (BP) units would likely cause thermodynamically-unfavorable interactions between alkyl chains of the TP mesogens and the core of the PI units, and would foster their self-sorting assembly into uniform and distinct homolithic columns [37]. In order to support the hypothesis of mixed columns of alternating blocks, DSC experiments (supported by POM) were performed on 1:1 and 1:2 M mixtures of their single components TP-1 and TP-2 with PI and BP model compounds, respectively. It was found that overall these compounds phase segregate and still behave almost as individual components (Figure S26) [38]. Hence, the supramolecular arrangement of the dyads and triads must be somehow a compromise between both extreme situations i.e. uniform A-B-A-B … intimate mixing in one single column versus complete phase separation into two distinct segregated columns (A-A-A … or B-B-B …). It is proposed based on the above arguments that the various molecules self-assemble into some kind of mixed D/A columns, made of the alternation of short-range homolithic D- or A-stacks. The apparent loss of differentiation at the molecular scale is most likely consequent to the periodic permutation of entire groups of identical mesogens, within stacks of mesogens, with an average of about 10–15 identical mesogens per stack (Figure 2d) and at larger scale between neighboring columnar domains. These permutations would be facilitated by the partial erasing of the shape differences between the two types of mesogens by the lateral chains of the TP compounds on the one hand, and the long aliphatic spacers and the bulky ramified chains at the rylene tips, on the other hand.
Table 1. Structural and geometrical parameters of the dyads and triads mesophases, at various temperatures.

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<th>T°</th>
<th>Phase</th>
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<th>ρ^{c}</th>
<th>χ_{ch}^{d}</th>
<th>n_{mes}^{e}</th>
<th>a^{f}</th>
<th>b^{f}</th>
<th>A[2]^{j}</th>
<th>a/b\sqrt{3}</th>
<th>h_{mol}^{g}</th>
<th>h_{c} (Å)^{h}</th>
<th>Ψ^{i}</th>
<th>A_{core}^{j}</th>
<th>D_{cyl}^{k}</th>
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<td>TP-PtI</td>
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<td>3</td>
<td>47.02</td>
<td>18.14</td>
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<td>3.57</td>
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<tr>
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<td>3</td>
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<td>18.05</td>
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<td>112.9</td>
<td>12.00</td>
<td>23.99</td>
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*aTemperature (°C) of experiment; bMesophase type; cMolecular volume (Å³) and density (g.cm⁻³) calculated by additivity of partial elementary volumes; dAliphatic volume fraction (χ_{ch} = V_{ch}/V_{mol}, χ_{core} = 1 - χ_{ch}, n_{mes}: number of mesogens per molecule (n_{mes} = 2 for dyads and 3 for triads); eLattice parameters (Å), areas (Å²) and number of columns (Z) per lattice: i) Col_{hex}: b = a_{hex} (a = b√3), γ = 120°, A = a_{hex}²sinγ, Z = 1 column per lattice; with rectangular coordinates: b = b_{rec}, a = a_{rec} = b√3, γ = 90°A = b×a, Z = 2; ii) Colec: a = a_{rec}, b = b_{rec}, γ = 90°A = b×a, Z = 2; elongation of the columnar lattice in the a-axis (a_{rec}) direction with respect to hexagonal geometry; fColumnar slice thickness h_{mol} = (V_{mol}/n_{mes})/(A/Z) in Å; gFace-to-face π–π stacking distance (Å) from scattering maximum from S/WAXS pattern, and □, correlation length (Å) determined by Debye-Scherrer formula; hOut-of-plane tilt angle (°) of mesogenic cores inside columns; iCross-sectional area of columnar cores (Å²): A_{core} = (1-χ_{ch})A/Z; j Diameter (Å) of equivalent circular cross-sectional area A_{core}, D_{cyl} = √(4×A_{core}/π) for TP moieties; kColumn area (Å²) per chain: σ_{cyl} = πD_{cyl}²h_{mol}/n_{ch}, where n_{ch} = 6 for the dyads and the triads (chains around TP part); mChain packing ratio: q = σ_{cyl}/σ_{ch}, σ_{ch} being the cross-sectional area (Å²) of a molten chain.
From a geometrical point of view, the mesogens can therefore be averaged to pseudo-disc-shaped units of dimensions defined by the columnar section and the average molecular slice thickness, $h_{mol}$ (Table 1). The average area needed by the peripheral chains is perfectly compatible with the interface area offered by the non-tilted stacked mesogens, since the mean ratio $q_{cyl}$ (Table 1) between required and available areas does not deviate from unity [39]; the chains are therefore fully stretched in the plane and densely packed in this case, which suggest that the deficiency of chains around the PI/BP units is well compensated by the lateral TP chains from neighboring columns (Figure 2d). The absence of a three-dimensional order in the mesophases also implies the variation of homolithic stacks periodicity along the columns, but still remains more or less matched (mirrored) with the surrounding neighboring columns (Figure 2d). This compensation process and the chemical connection between both entities likely disturbs the free rotation, even more for the triads, stabilizing the rectangular symmetry more efficiently. The proposed supramolecular model (Figure 2d) is further consistent with the relative mesophase stability (i.e. temperature range) observed in this series of compounds.

Along this line, lamello-columnar mesophases with alternating rows of TP and rylene columns were reported for the inverted triads PI-TP2 and BP-TP2, with short spacers (propyl instead of octyl) and octyl end-chains [35]. The fact that even the lattice elongation vanish for the TP-PI is understandable by the conjunction of the longer alkyne spacers and of the dyad stoichiometry. This configuration is intrinsically more favourable to permutation of column segments, since only the triad stoichiometry may realize the ideal separation of components at the nodes and centres of honeycomb lattices [30].

2.3. Photophysical properties

Electronic energy transfer and electron transfer are fundamental and ubiquitous mechanisms in chemistry, physics and biology [40], [41], [42], [43]. Understanding intramolecular energy and electron transfers for these electron-donor/acceptor dyads and triads is important for further molecular designs and extending the potential of these mesomorphic materials [42]. Hexa(alkoxy)triphenylene (TP) and perylene diimide (PI) are both outstanding fluorophores, and the latter exhibits almost 100% fluorescent quantum yield in solution [25]. UV/vis absorption and photoluminescent spectra (Figures 3-4, S28-S29) of the dyads and triads were recorded in dilute solutions (1 x 10^{-6} M in CH2Cl2) and compared to reference compounds PI, BP and TP-1 (the structures of the latter ones are shown in Figure S27). TP-PI/TP-PI2 show similar UV/vis absorption bands with absorption of TP core and PI core peaking at 278, 500, and 538 nm, respectively (Figure 3a). The visible absorption bands of TP-BP/TP-BP2 are blue-shifted by about 63 nm compared to the TP-PI/TP-PI2 pair, due to the change of their aromatic π-conjugation. The A-D-A triads show similar absorption behaviour to the corresponding D-A dyads except that they display stronger bands due to the two acceptors per molecule and more broadened spectra due to the stronger aggregation behaviour. The slight red-shift of TP-PI/PI2 compared to the pure reference compound PI is likely caused by the π-conjugation extension of the alkylnyl-bay-substituted perylenediimide core in the dyad and triad (Figures S28-S29).
Figure 3. (a) Superimposed UV/vis absorption spectra for the 4 dyads/triads (solution concentrations $10^{-6}$ M, solvent: CH$_2$Cl$_2$). (b) Fluorescence spectra of the dyads and triads. (Concentration: $1 \times 10^{-6}$ M, non-normalized intensity, excitation 280 nm, CH$_2$Cl$_2$). See also Figures S26–S27.

The fluorescence of the dyads (Figure 3b) displayed some degree of acceptor-rylenediimide emission when exciting the donor TP unit at 280 nm, due to the intramolecular Forster resonance energy transfer (FRET) from donor-TP’s emission to excitation of acceptor. The triads exhibited no or much weaker fluorescence (Figure 3b), which can be explained by stronger intramolecular Dexter charge/electron transfer (ICT) caused fluorescence quenching [23d].

For better understanding the dominating factor of intramolecular electronic energy and electron transfer of these long spacer-connected dyads and triads, we did comparative study of the fluorescence (Figure 4). The dyads and triads showed very weak fluorescence compared to the emission of reference compounds TP-1, PI and BP, implying that the intramolecular charge transfer is the dominant process over the energy transfer. However, when enlarging and careful analysis of the fluorescent spectra, useful information was collected.
Dyads show stronger fluorescence than triads, and the quenching effect is opposite. This effect could be due to the fact that the A-D-A triads TP-PI2 and TP-BP2 possess two accepting moieties per molecule, showing weaker energy transfer-induced fluorescence, and therefore higher degree of intramolecular electron transfer compared to dyads TP-PI and TP-BP. Further, PI core might be a stronger electron acceptor compared to BP core, because the intramolecular charge-transfer (ICT) induced emission quenching is more complete for TP-PI and TP-PI2.

For the fluorescence spectra, TP-BP and TP-BP2 were excited at 280 nm (TP part), the emitting spectra of both compounds peaked at 480 nm (BP part), with a very large Stockes shift of 200 nm due to the Forster resonance energy transfer (FRET) mechanism. Both photoluminescent spectra are almost identical and they emit green light (Figure 4). When dyad TP-PI is excited at the excitation wavelength of TP, i.e. 280 nm, the dyad hardly emits, due to stronger electron transfer (ICT) from TP core to PI core; the residual emission of the PI core is due to energy transfer (Figure 4). When the dyad is excited at 488 nm (PI part), it emits weakly, due to the electron transfer from donor TP to acceptor PI, the quenching of the emission dominates. Compared with TP-PI, TP-BP possesses stronger energy transfer and weaker electron transfer between TP and BP cores, i.e. PI core is a stronger electron acceptor.
Figure 4. Fluorescence spectra of: (a) TP-PI (compared with TP and PI, $10^{-6}$ M, CH$_2$Cl$_2$), (b) TP-PI2 (compared with the reference fluorophores TP and PI, $10^{-6}$ M for all, 2. $10^{-6}$ M for PI, CH$_2$Cl$_2$), (c) TP-BP (compared with reference TP and BP, $10^{-6}$M, CH$_2$Cl$_2$), and (d) TP-BP2 (compared with the reference fluorophores TP, PI and BP, $10^{-6}$ M for all, 2.10$^{-6}$ M for BP, CH$_2$Cl$_2$). As PI and BP show too strong emission intensity to suppress others, the insert only shows emission of the other fluorophores.

Table 2. Absorption and fluorescence properties of the dyads and triads.

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<th>Cpd</th>
<th>$\lambda^a$</th>
<th>$\varepsilon^b$</th>
<th>$\lambda_{em}^c$</th>
<th>$\lambda_{em}^d$</th>
<th>$\phi^d$</th>
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<td>7.81</td>
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<td>546 (3.56)</td>
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<td>538</td>
<td>4.18</td>
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<td>480 (7.18)</td>
<td>480 (14.3)</td>
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</tr>
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<td>478</td>
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*a*Maximum absorption wavelengths (nm); *b*Extinction coefficient (×10⁵ L mol⁻¹ cm⁻¹); *c*Emission maxima (nm) with excitation of λex = 280 nm and intensity (×10⁵); *d*Emission maxima (nm) with excitation of λex = 488 nm and intensity (×10⁵); *e*Fluorescence absolute quantum yield (%) at a concentration of 1×10⁻⁶ mol L⁻¹ in CH₂Cl₂ with excitation on rylene diimide moiety.

When TP-PI2 was excited at the TP part or at the PI core separately, no emission was detected in any case (ICT). This triad possesses indeed two acceptor PI cores, therefore stronger photo-induced electron transfer must occur from the donor to the two acceptors, thus completely quenching the emission. However, weak fluorescent emission is still observed for TP-BP2 as BP core is a weaker electron-acceptor.

The fluorescence quantum yields (φ) of these dyads and triads (Table 2) demonstrate quantitatively the emission efficiency of the rylene diimides, while the parent perylene diimide dyes exhibit φ very close to unity (100%) [24c]. The lowered φ values of these dyads and triads plausibly result from the emission quenching caused by intramolecular charge transfer between donor TP and acceptor rylene moieties [23d].

Density functional theory (DFT) was used to study the molecular structures, the HOMO-LUMO energy levels and energy gaps of these dyads and triads (Figure 5, S30-S33), to support the above experimental results. The calculation showed that the molecular structures of the discotic components of the dyads and triads, TP, PI, and BP, are almost planar, which is advantageous for π stacking between the various units to form the discotic columns. The HOMO-1 and HOMO are located on the donor TP core, whilst LUMO and LUMO+1 are located on the acceptor cores of PI and BP; therefore, the photoinduced intramolecular charge-transfer from TP to rylene diimide core is highly possible. The calculated LUMO energy levels of TP-PI and TP-PI2 is lower than that of TP-BP and TP-BP2, proving theoretically the stronger electron affinity of PI than BP, hence the photoinduced electron-transfer of the formers is more complete than the latter, in agreement with the results on photoluminescence.

Finally, DFT calculations show that the HOMO-LUMO energy gaps of the TP-PI and TP-PI2 (Table S3) are narrower than that of TP-BP and TP-BP2, further supporting the experimental results in particular in agreement with the blue-shifted absorption of the benzoperylenediimide (BP) compared to alkynyl-perylene diimide (PI) core. In summary, photoinduced intramolecular charge transfer (ICT) is the paramount feature for these spacer-connected D-A dyads and A-D-A triads.
3. Conclusions

Here four electron-donor/acceptor dyads/triads based on a triphenylene core, as donor (D), and perylene/benzoperylene diimides, as acceptor units (A), both species linked by a long alkyl chain spacer, have been designed and synthesized first by Sonogashira coupling, to bind together TP and PI species, and then by organic base-promoted intramolecular cyclization to yield the benzoperylenediimide-containing systems, in moderate to good yields. Upon heating, all D-A dyads and A-D-A triads show Col$_{hex}$ or a Col$_{rec}$ mesophase, over broad temperature ranges, including room temperature, with the triads showing higher mesophase stability than the dyads. As demonstrated by S/WAXS, the various molecules unfortunately do not entirely segregate in the volume into perfectly distinct single-compound columns but self-assemble into pseudo-mixed D/A columns instead with some alternation of short-range D- or A-stacks within columns. This intermediate situation is likely due to the conjunction of opposite effects through the chemical connection of different molecular structures but having identical stacking periodicities. The rylenediimide compounds have wide absorption bands but weak emission, due to the intramolecular photo-induced electron transfer between TP/PI and TP/BP core. The molecular structures and their HOMO-LUMO energy levels and energy gaps were studied by density functional theory. This analysis is in perfect agreement with the photophysical results and further confirms that TP acts as electron-donor system and that the perylenediimide/benzoperylenediimide core are electron-acceptors.

4. Experimental section

All solvents and commercial reagents were used without further purification. The synthesis of the precursors (PI, PI-Br, TP-1, and TP-2, Schemes S1–S3) and characterization (NMR, Figures S1–S19, HRMS, Figures S20–S23) are shown in the supplementary information.
Synthesis of TP-PI To a mixture of PI-Br (442 mg, 0.48 mmol), Cul (2.7 mg, 0.016 mmol), Pd(PPh₃)₂Cl₂ (33.4 mg, 0.048 mmol) and PPh₃ (50.6 mg, 0.098 mmol) in dry toluene (8 mL), a solution of TP-1 (600 mg, 0.58 mmol) in triethylamine (4 mL) was added under a flux of Ar. The mixture was stirred at 80 °C for 24 h. After reaction completion, the organic phase was extracted with CH₂Cl₂, washed with water, and dried over anhydrous MgSO₄. The product was purified by column chromatography (SiO₂, CH₂Cl₂) and crystallized from ethyl acetate-ethanol, yielding a red solid: 0.45 g, 50%. ¹H NMR (CDCl₃, TMS, 600 MHz), δ(ppm): 10.16 (d, J = 8.1 Hz, 1H), 8.58 (s, 1H), 8.52 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 7.9 Hz, 1H), 8.34 (d, J = 7.9 Hz, 1H), 8.08 (dd, J = 8.0, 2.7 Hz, 2H), 7.55 (d, J = 3.6 Hz, 2H), 7.41 (s, 1H), 7.35 (s, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 4.21 (t, J = 6.5 Hz, 2H), 4.18 (t, J = 6.5 Hz, 2H), 4.13 (d, J = 7.3 Hz, 2H), 4.10 (d, J = 7.3 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.6 Hz, 6H), 2.74 (t, J = 6.6 Hz, 2H), 2.02–1.80 (m, 16H), 1.72 (dt, J = 14.6, 7.3 Hz, 2H), 1.62–1.50 (m, 20H), 1.47–1.22 (m, 86H), 0.92–0.89 (m, 15H), 0.83 (t, J = 6.8 Hz, 12H). ¹³C NMR (151 MHz, CDCl₃), δ(ppm): 163.73, 163.52, 163.46, 162.99, 148.69, 148.65, 148.50, 148.42, 148.40, 148.36, 138.51, 134.15, 133.59, 133.39, 133.24, 130.54, 130.39, 130.08, 128.41, 127.52, 126.53, 125.99, 125.84, 123.16, 123.09, 122.96, 122.89, 122.84, 122.77, 122.59, 122.57, 122.38, 122.04, 121.64, 120.45, 106.73, 106.67, 106.59, 106.27, 106.04, 105.96, 102.76, 83.00, 69.54, 69.52, 69.37, 69.21, 69.09, 69.04, 44.58, 36.65, 36.62, 31.89, 31.73, 31.69, 30.11, 30.09, 29.79, 29.78, 29.61, 29.58, 29.55, 29.51, 29.38, 29.33, 29.13, 29.04, 28.68, 28.59, 28.02, 26.51, 26.48, 26.29, 26.26, 26.20, 25.89, 22.71, 22.65, 20.30, 14.13. Elemental Analysis Calcd for C₁₅₂₇H₂₈₂N₂O₁₀ (MW 1872.835): C, 80.17%; H, 9.80%; N, 1.50; Found: C, 79.90%; H, 9.66%; N, 1.71. HRMS (ESI) calcd for [M]+ m/z: 1872.3828 (100%); Found: 1872.3823.

Synthesis of TP-Pl2 TP-PI2 was synthesized and purified as TP-Pl. PI-Br (1.16 g, 1.2 mmol), TP-2 (0.34 g, 0.16 mmol), red solid, 0.48 g, 55%. ¹H NMR (CDCl₃, TMS, 600 MHz), δ(ppm): 9.92 (d, J = 8.1 Hz, 2H), 8.35 (s, 2H), 8.30 (d, J = 8.1 Hz, 2H), 8.21 (d, J = 7.8 Hz, 2H), 8.14 (d, J = 7.8 Hz, 2H), 7.84 (dd, J = 6.9, 1.1 Hz, 1H), 7.10 (s, 2H), 6.98 (s, 2H), 6.82 (s, 2H), 4.08 (d, J = 7.1 Hz, 4H), 4.04 (d, J = 7.1 Hz, 4H), 4.01 (t, J = 6.7 Hz, 4H), 3.97 (t, J = 6.5 Hz, 4H), 3.76 (t, J = 6.4 Hz, 4H), 2.75 (t, J = 6.5 Hz, 4H), 1.99–1.83 (m, 16H), 1.79–1.53 (m, 30H), 1.49–1.22 (m, 130H), 0.94–0.91 (m, 12H), 0.86–0.83 (m, 24H). ¹³C NMR (151 MHz, CDCl₃) δ(ppm): 163.48, 163.26, 163.23, 162.73, 148.21, 148.12, 147.96, 138.27, 133.71, 133.20, 132.94, 132.75, 130.20, 129.96, 129.79, 128.17, 127.29, 126.14, 125.58, 125.53, 122.64, 122.51, 122.44, 122.40, 122.36, 122.34, 122.22, 121.82, 121.45, 120.24, 105.70, 105.55, 105.48, 103.18, 69.08, 68.84, 68.82, 44.55, 44.53, 36.70, 36.67, 31.91, 31.70, 31.67, 30.17, 30.14, 29.84, 29.83, 29.66, 29.54, 29.52, 29.42, 29.39, 29.36, 29.18, 28.97, 28.68, 28.65, 28.63, 28.02, 26.48, 26.45, 26.25, 26.24, 25.90, 22.73, 22.68, 22.66, 20.31, 14.15, 14.14, 14.10. Elemental Analysis Calcd for C₁₉₄H₃₅₂N₄O₁₄ (MW 2748.086): C, 80.42%; H, 9.39%; N, 2.04; Found: C, 79.90%; H, 9.37%; N, 2.17. HRMS (ESI) calcd for [M]+ m/z: 2747.9555 (100%); Found: 2747.9538.

Synthesis of TP-BP A solution of TP-PI (0.2 g, 0.11 mmol) and DBU (20 mg) in toluene (5 mL) was stirred and heated at 80 °C under Ar for 24 h. After cooling, the reaction mixture was poured into 2 N HCl and extracted with CH₂Cl₂. After removal of the solvents under reduced pressure, the crude product was purified by a column
chromatography on silica gel (CH$_2$Cl$_2$). The product was crystallized from ethyl acetate–ethanol, affording a yellow solid: 0.14 g, 70%. $^1$H NMR (CDCl$_3$, TMS, 600 MHz), δ(ppm): 9.24 (s, 1H), 8.95 (s, 1H), 8.69 (s, 4H), 8.21 (s, 1H), 7.46–7.40 (m, 6H), 4.23 (d, $J = 7.2$ Hz, 4H), 4.13–4.03 (m, 12H), 3.44 (t, $J = 7.7$ Hz, 2H), 2.09–1.85 (m, 16H), 1.66–1.20 (m, 108H), 0.92–0.80 (m, 27H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ(ppm): 163.99, 163.95, 163.90, 163.82, 148.57, 148.50, 141.28, 133.07, 132.28, 131.74, 129.35, 128.50, 128.23, 127.91, 125.99, 125.97, 124.26, 123.03, 123.01, 122.99, 122.97, 122.93, 122.61, 122.45, 122.28, 122.02, 121.99, 121.83, 121.46, 121.29, 106.66, 106.63, 106.56, 106.45, 69.45, 69.39, 69.32, 69.30, 44.84, 44.73, 36.88, 36.80, 33.32, 31.91, 31.89, 31.84, 31.81, 31.78, 31.75, 31.16, 30.18, 29.86, 29.65, 29.57, 29.53, 29.51, 29.48, 29.45, 29.35, 29.26, 29.18, 29.05, 26.60, 26.55, 26.51, 26.24, 26.21, 25.96, 22.70, 22.64, 14.11, 14.10, 14.07. Elemental Analysis Calcd for C$_{125}$H$_{182}$N$_2$O$_{10}$ (MW 1872.835): C, 80.17; H 9.80; N 1.50; Found: C, 79.99; H, 9.95; N, 1.48. HRMS (ESI) calcd for [M]$^+$ m/z: 1872.3828 (100%); Found: 1872.3827.

**Synthesis of TP-BP2 TP-BP2** was synthesized and purified as TP-BP. PI-TP2 (0.2 g, 0.073 mmol), DBU (20 mg), yellow solid, 0.1 g, 55%. $^1$H NMR (CDCl$_3$, TMS, 600 MHz), δ(ppm): 9.10 (s, 2H), 8.75 (s, 2H), 8.42 (d, $J = 7.1$ Hz, 4H), 8.30 (d, $J = 7.1$ Hz, 4H), 8.13 (s, 2H), 6.96 (s, 2H), 6.85 (s, 2H), 6.71 (s, 2H), 4.16 (s, 8H), 4.00 (t, $J = 5.8$ Hz, 4H), 3.83 (t, $J = 5.3$ Hz, 4H), 3.71 (s, 4H), 3.41 (t, $J = 7.1$ Hz, 4H), 2.09–1.22 (m, 176H), 0.92–0.81 (m, 36H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ(ppm): 163.88, 163.77, 163.69, 163.63, 148.13, 148.03, 148.01, 141.16, 132.83, 131.86, 131.32, 129.23, 129.15, 128.46, 128.13, 127.53, 127.52, 127.28, 125.74, 123.99, 122.70, 122.29, 122.26, 122.18, 122.11, 121.75, 121.62, 121.60, 121.23, 121.10, 106.03, 105.62, 105.39, 68.94, 68.83, 44.81, 44.69, 36.93, 36.84, 33.13, 31.95, 31.92, 31.88, 31.80, 31.79, 31.76, 31.73, 30.75, 30.24, 29.91, 29.70, 29.61, 29.55, 29.46, 29.40, 29.37, 29.24, 28.95, 28.94, 28.78, 28.52, 26.60, 26.54, 26.50, 26.22, 26.21, 25.74, 22.72, 22.71, 22.66, 14.14, 14.12, 14.09. Elemental Analysis Calcd. for C$_{184}$H$_{256}$N$_4$O$_{14}$ (MW 2748.086): C, 80.42; H, 9.39; N, 2.04; Found: C, 80.40; H, 9.49; N, 2.02. HRMS (ESI) calcd for [M]$^+$ m/z: 2747.9555 (100%); Found: 2747.9510.

**Supplementary data**

Supplementary data to this article accessible at: https://ars.els-cdn.com/content/image/1-s2.0-S0143720821007774-mmc1.doc

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