## Article

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# Visible-Light Mediated Synthesis of AzaBenzannulated Perylenediimide-Based Light Harvesting Dyads

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**Abstract** An intramolecular imine photocyclization has been explored for grafting on the bay region of perylenediimide (PDI) different electro- and photoactive chromophores to reach new AzaBenzannulated-PDI (AzaBPDI) dyads. Triphenylamine (TPA), fluorene (Fl), perylenemo-noimide (PMI) and perylenediimide (PDI) units have been successfully assembled to AzaBPDI using this straightforward one-pot synthesis starting from the easily accessible 1-aminoPDI. This original procedure was compared to the well-known Pictet-Spengler reaction and appears to be an attractive alternative in terms of versatility and efficiency with higher yields obtained. The optical and electrochemical properties of these molecular systems demonstrated large absorption capabilities in the visible range, good accepting abilities with low-LUMO levels and efficient electronic interactions between chromophoric units such as energy or electron transfers. In addition, with their large dihedral angle estimated by theoretical calculations, those dyads should present interesting applications in various organic optoelectronic devices. In particular, the PMI-AzaBPDI and PDI-AzaBPDI dyads presenting low-LUMO levels, a broad absorption in the visible range and a twisted

conformation make them good candidates as Non-Fullerene Acceptors (NFAs) in organic solar cells (OSCs).

## Introduction

Perylenediimide (PDI) derivatives have emerged as one of the most important classes of dyes and pigments<sup>1</sup> thanks to their outstanding chemical, thermal and photochemical stabilities,<sup>2</sup> strong electron acceptor capabilities and semiconducting behaviour. Because of their absorption properties and high quantum yield of fluorescence emission, PDI based materials have received much attention for their utilization in photoinduced electron and/or energy transfer processes to construct light-harvesting arrays and artificial photosynthetic systems.<sup>3</sup> In addition, over the last decade, PDI derivatives, and in particular three dimensional PDI-based multimers (Figure 1a), have been intensively studied in Organic Solar Cells (OSCs) as a promising class of Non-Fullerene Acceptors (NFAs).<sup>4</sup> The PDI multimerization or decoration can be achieved by means of linkage at the imide, bay or ortho positions. For reasons of synthetic accessibility, electro- and photoactive counterparts are usually introduced by condensation of a primary amine onto anhydride functionality, most often at the imide position and more rarely on its bay region.<sup>5</sup> Functionalization at the bay region is commonly achieved through pallado-catalyzed cross-coupling reaction or nucleophilic substitution starting from 1-bromoPDI derivative.<sup>6</sup> The latter being not easily accessible from a synthetic point of view, other strategies have recently emerged starting from more largely scalable 1-nitroPDI.<sup>7</sup> We have recently demonstrated that 1-nitroPDI could be engaged in Suzuki-Miyaura reaction to synthesize PDI multimers in good yields, making it an attractive alternative to 1-bromoPDI.<sup>8</sup> This nitrated derivative can also be reduced into 1-aminoPDI by catalytic hydrogenation, opening new synthetic possibilities (Figure 1b).<sup>9</sup> In particular, Z. Wang and co-workers,<sup>10</sup> and later the group of

F. Würthner,<sup>11</sup> exploited 1-aminoPDIs to prepare a library of mono and bis-AzaBenzannulated Perylenediimides (AzaBPDI) *via* a Pictet-Spengler type reaction, unfortunately in moderate yields. On the other hand, C. Cheng, Y. Xiao and coll. reported an alternative pathway towards the synthesis of bisazacoronene bisimides involving the oxidative photocyclization of an aliphatic imine grafted on the bay of perylene tetraester core, an approach that required several subsequent steps before reaching the desired diimide derivative.<sup>12</sup> Very recently, we have reported a straightforward procedure directly on the diimide scaffold for the synthesis of AzaBPDI and AzaBPDI dimers in high yields and proved its large scope. This methodology relies on a one-pot three steps sequence starting from 1) a condensation between 1-aminoPDI and an aldehyde, 2) followed by the visiblelight-promoted photocylization of the corresponding imine and 3) its subsequent oxidative re-aromatization by DDQ.<sup>13</sup> With the aim of exploiting our procedure, we have been interested in synthesizing original AzaBPDI dyads by attaching electro- and photoactive electron-rich triphenylamine (TPA) or fluorene (FI) species and electron-poor perylenediimide (PDI) or perylenemonoimide (PMI). We present herein the synthesis of those core-extended AzaBPDIs derivatives, in addition to electronic and photophysical properties of these light-harvesting dyads.



Figure 1. Structure of a) PDI and b) AzaBPDI, and synthetic strategies for their multimerization.

## **Results and discussion**

The synthesis started from 1-nitroPDI **1** which is prepared nearly quantitatively in multigram scale without requiring more purification than a simple precipitation.<sup>8a</sup> In contrast to the preparation of 1-bromoPDI which requires a fastidious purification by column chromatography,<sup>14</sup> the introduction of the nitro electron-withdrawing group on the PDI backbone enables the selective mononitration over dinitration.<sup>15</sup> Catalytic hydrogenation of 1-nitroPDI **1** in the presence of H<sub>2</sub> along with Pd/C catalyst in THF afforded 1-aminoPDI **2**.<sup>9c</sup> The assembly of the dyads was performed by combining 1-aminoPDI **2** with functionalized aldehydes, so-called 4-formyltriphenylamine (TPA-CHO) **3**, 2-fluorene carboxaldehyde (Fl-CHO) **4**, 1-(4-formylphenyl)perylenediimide (PDI-CHO) **5** and 9-(4-formylphenyl)perylenemonoimide (PMI-CHO) **6**. Conditions to prepare the imine intermediate require the use of trifluoroacetic acid in dry solvent (CH<sub>2</sub>Cl<sub>2</sub> or DMF) under argon atmosphere and

depend on the amount of introduced aldehyde. For the preparation of dyads 7 and 8, the imine condensation was achieved using 3 equivalents of aldehyde 3 and 4, respectively, in CH<sub>2</sub>Cl<sub>2</sub> at 50 °C for 1-2 h in the presence of a catalytic amount of TFA. The syntheses of dyads 9 and 10 using 1.1 equivalent of precious compounds 5 and 6, respectively, required the heating of the reaction in DMF at 130 °C overnight with an excess of TFA, and in the presence of activated molecular sieves (MS) 3Å to trap water formed during the condensation. After dilution in a significant volume of CH<sub>2</sub>Cl<sub>2</sub>, the cyclization was performed under exposure to visible light at room temperature for 1-2 h until complete conversion of the Schiff base into cyclized intermediate. A stoichiometric addition of DDQ allowed its fast conversion into AzaBPDI based architecture, typically in 5 to 30 min relying on the solubility of the material. The reaction sequence was particularly easy to follow when colourless aldehyde 4 was used: the blue solution of amine 2 turned to purple after completion of the imine formation, progressed to green during the photocyclization, and finally gave a yellow colour after the re-aromatization (see S.I., Figure S24). Using TPA-CHO 3, prepared according to literature,<sup>16</sup> or commercially available Fl-CHO 4, donor-acceptor systems were obtained in 77% for AzaBPDI-TPA 7 and 84% for AzaBPDI-Fl 8. For the preparation of dyads 9 and 10, the 4formylphenyl moiety was grafted onto PDI<sup>8a</sup> and PMI<sup>17</sup> following methods developed in our group. The syntheses were then carried out with amine 2 to afford dyads 9 and 10 in 69% and 79% yields, respectively. The reaction using benzaldehyde to prepare compound 11<sup>3a</sup> was also performed in 83% yield as a reference for further electrochemical and spectroscopic studies. Remarkably, this original visible-light mediated procedure (Method A) afforded target compounds in significantly higher yields than the conditions inspired by the Pictet-Spengler reaction (Method B). The latter were investigated by stirring 1-aminoPDI 2 and the aldehyde derivatives at 130°C in anhydrous DMF, in the presence of an excess of triflic acid and activated MS 3Å to thermically cyclize the iminium intermediate. Subsequent oxidation, carried out by treatment with oxygen or DDQ, gave dyads 7 (46% yield), 8 (35%), 9 (25%) and 10 (41%) in moderate yields (Scheme 1). All dyads were characterized by <sup>1</sup>H NMR, HRMS and <sup>13</sup>C NMR in the case of compound 7 and 8. The low solubility of 9 and 10 prevented the acquisition of a satisfying <sup>13</sup>C spectra, even at high temperature in deuterated tetrachloroethane. For evaluating their performance as NFA in OSC devices, the cyclohexyl chains will be further replaced by swallow-tailed highly solubilizing substituents to ensure high processability and appropriate film morphology.



Scheme 1. Synthesis of AzaBPDI-based dyads 7, 8, 9 and 10. For 11, dyads 7 and 8 using Method A : 1) 3 equiv. of aldehyde, CH<sub>2</sub>Cl<sub>2</sub>, 50 °C, 2 h. For dyads 9 and 10: 1) 1.1 equiv. of aldehyde, DMF, 130 °C, overnight. The yields given in grey within parentheses correspond to those obtained through the Pictet-Spengler type reaction (Method B : see experimental section).

The optical properties of PDI-based materials were analyzed in CHCl<sub>3</sub> solutions by steady-state UV-Vis absorption and fluorescence spectroscopy and data are depicted in Table 1. PDI **5**, PMI **6** and AzaBPDI **11** in CHCl<sub>3</sub> solutions were used as references. PDI reference **5** presents the three

characteristic absorption bands of the PDI core at 533, 498 and 465 nm, associated with the  $0 \rightarrow$  $0, 0 \rightarrow 1$  and  $0 \rightarrow 2$  vibrational modes of the perylene core, respectively (Figure 2 d).<sup>18</sup> In comparison, the UV-Vis spectrum of AzaBPDI 11 exhibits a blue shift with a maximum band at 485 nm. The latter was juxtaposed with the dyads spectra (in orange in Figure 2). The UV-Vis spectrum of dyad 7 compared to that of reference 11, displays a hypsochromic shift accompanied by a broad and very weak band from 500 to 650 nm, presumably an intramolecular charge transfer band (ICT) such as for its PDI-TPA analog.<sup>19</sup> The absorption profil of AzaBPDI-Fl 8 exhibits an enlargement of the bands, as previously observed for AzaBPDI attached with donor units,<sup>13</sup> suggesting electronic interaction at the ground state between the two photoactive units. On the contrary, the spectra of AzaBPDI-PDI 9 and AzaBPDI-PMI 10 correspond to the linear combination of the two units spectra. Indeed, dyads 9 and 10 absorb between 400 and 550 nm with distinct peaks at 430 and 476 nm characteristic of the AzaBPDI chromophoric unit and 520 and 533 nm for PMI and PDI units, respectively. UV-Vis spectra of thin films show a red-shift of the absorption maxima for compound 9 and 10, and their coverage of the visible spectrum is extended beyond 600 nm (see S.I., Figure S21). All together, the optical properties of dyads 9 and 10 demonstrate that they could be of particular interest for applications of as NFAs in OSCs.

Regarding the fluorescence properties, the parent chromophoric units AzaBPDI **11**, PDI-CHO **5** and PMI-CHO **6** display very high quantum yields ( $\Phi_{fl}$ ) from 0.9 to 1. When attached to the second unit, the quantum yield of dyads strongly varied according to their molecular design. While AzaBPDI-PDI **9** displays a good yield  $\Phi_{fl} = 0.88$ , the fluorescence of AzaBPDI-TPA **7** or AzaBPDI-PMI **10** is quasi-totally quenched with  $\Phi_{fl} = 0$  and 0.04, respectively, suggesting the presence of intramolecular quenching mechanisms. Considering that into dyads **9** and **10**, the chromophoric units do not electronically interact at the ground state, in addition with the complementarity of the spectral properties of AzaBPDI and PMI/PDI, intramolecular energy transfer (EnT) processes within dyads **9** and **10** were investigated using steady-state fluorescence spectroscopy (Figure 3).



**Figure 2.** UV-Vis absorption spectrum of AzaBPDI **11** juxtaposed with that of a) AzaBPDI-TPA **7**; b) AzaBPDI-Fl **8**; c) AzaBPDI-PDI **9**, PDI-CHO **5**; d) AzaBPDI-PMI **10**, PMI-CHO **6** in CHCl<sub>3</sub>. Molar extinction coefficients were determined from five different concentrations (10<sup>-5</sup>-10<sup>-6</sup> M).

Compound	$\lambda_1^{max}(nm)$	$\mathcal{E}_1/10^4 (M^{-1} cm^{-1})$	$\lambda_2^{max}(nm)$	$\mathcal{E}_2/10^4 (M^{-1} cm^{-1})$	$\lambda_{em}^{max}(nm)$	${\it I}\!$	$E_{0-0}^b(eV)$
PDI-CHO 5	533	4.2	498	2.9	570	0.95	2.25
PMI-CHO 6	520	3.7	495	3.7	555	1.00	2.31
AzaBPDI-TPA 7	465	5.7	435	4.1	-	0.00	-
AzaBPDI-Fl 8	481	3.1	434	3.1	554	0.55	2.45
AzaBPDI-PDI 9	535	4.2	476	6.0	583	0.88	2.23
AzaBPDI-PMI 10	520	3.7	476	6.0	563	0.04	2.28
AzaBPDI 11	476	5.6	446	3.1	489	0.90	2.58

**Table 1.** UV-Vis absorption  $(10^{-5} \text{ M})$  and emission  $(10^{-6} \text{ M})$  data of references 5, 6 and 11, dyads 7, 8, 9 and 10 in CHCl<sub>3</sub>.

<sup>a</sup> Determined with Rhodamine 101 ( $\Phi_{\rm fl}$  = 1 in MeOH).<sup>20</sup>

<sup>b</sup> Determined by the intersection  $\lambda_{0-0}$  of the normalized absorption and emission spectra according to  $E_{0.0} = 1240/\lambda_{0-0}$ .

The complementary spectral properties of AzaBPDI and PDI/PMI units depicted in Figure 2a, suggests that a Förster Resonance type Energy Transfer mechanism,<sup>21</sup> can occur within dyads **9** and **10** as the emission spectrum of AzaBPDI **11** perfectly overlaps with the absorption spectra of PDI **5** and PMI **6**. In this respect, AzaBPDI units can act as an energy donor and PDI/PMI units as energy acceptors. Moreover, the donor and acceptor units absorb and emit at distinct wavelength and can be selectively excited. Hence, the efficiency of the energy transfer  $\Phi_{EnT}$  can be quantified using steady-state techniques following two methods.<sup>22</sup>



**Figure 3.** a) Complementary normalized absorption and fluorescence spectra of PDI-CHO 5, PMI-CHO 6 and AzaBPDI 11. Fluorescence emission spectra of b) AzaBPDI-PDI 9 and d) AzaBPDI-PMI 10 by selective excitation of donor AzaBPDI ( $\lambda_{exc} = 430$  nm) and acceptor PDI/PMI ( $\lambda_{exc} = 500$  nm); Fluorescence excitation ( $\lambda_{emis} = 620$  nm) and absorption spectra normalized on  $\lambda_{max}$  acceptor of c) AzaBPDI-PDI 9 and e) AzaBPDI-PMI 10.

First, emission spectra can be used, by determining the ratio of quantum yield of the acceptor unit by selective excitation of the donor ( $\lambda_{exc} = 430$  nm) affording its sensitized quantum yield, and

direct excitation of the acceptor ( $\lambda_{exc} = 500 \text{ nm}$ ):  $\Phi_{EnT} = \Phi_{fl(A)}^* / \Phi_{fl(A)}$ . According to this strategy, the energy transfer appears to be very efficient, with yields of 95% within dyad **9** and 79% within **10** for its remaining fluorescence. Those results are in agreement with the quenched emission of the donor units when dyads were excited at 430 nm. Besides, these can be confirmed by recording the excitation spectrum of the derivatives at the selective emission wavelength of the acceptor units ( $\lambda_{emis} = 620 \text{ nm}$ ), normalizing it with their absorption on  $\lambda_{max}$  acceptor, and comparing the intensity of the donor at 430 nm:  $\Phi_{EnT} = Exc_{(D)}/Abs_{(D)}$ . Indeed for dyad **9**, an efficiency of 95% was calculated whereas 81% was found for dyad **10**. The quenching of fluorescence in dyad **10** cannot be explained by these experiments and would require further investigations by transient absorption (TA) spectroscopy, to explore various hypotheses such as a photoinduced electron transfer (PET) or the conversion into a triplet state *via* intersystem crossing (ISC).

The electrochemical properties of the four dyads were investigated by cyclic voltammetry (CV) in deaerated CH<sub>2</sub>Cl<sub>2</sub>, or CH<sub>2</sub>Cl<sub>2</sub>/Chlorobenzene (1:1) for lower soluble products, and in the presence of Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte (Figure 4). PDI **5**, PMI **6** and AzaBPDI **11** compounds were used as references to determine the nature of reduced species. As previously reported, AzaBPDI based compounds display slightly lower reduction potentials than PDI derivatives.<sup>11</sup> Dyads **7** and **8** showed the expected two reversible one-electron reduction waves around  $E^{1}_{red} = -1.2$  V and  $E^{2}_{red} = -1.4$  V *vs* Fc<sup>+</sup>/Fc comparable to that of AzaBPDI **11**, corresponding to the successive formation of AzaBPDI<sup>-</sup> and AzaBPDI<sup>2-</sup> species, respectively. A reversible oxidation wave was observed for AzaBPDI-TPA **7** at  $E^{1}_{ox} = +$  0.61 V *vs* Fc<sup>+</sup>/Fc and attributed to the oxidation of the TPA unit, whereas no oxidation waves were detected for reference **11** and an irreversible oxidation wave at + 0.91 V was found for dyad **8** (see S.I., Figure S23).

By comparison with references PMI **5**, PMI **6** and AzaBPDI **11**, we assigned the electrochemical processes for both dyads AzaBPDI-PDI **9** and AzaBPDI-PMI **10**. Compound **9** showed three reversible reduction waves (Figure 4a). The first reduction process of PDI and that of AzaBPDI are overlapping leading to AzaBPDI<sup>-</sup>-PDI<sup>-</sup> species. Following this two-electron process at  $E^{1}_{red} = -1.14 \text{ V} vs \text{ Fc}^{+}/\text{Fc}$ , two one-electron reduction waves are observed at -1.29 and -1.42 V corresponding to the generation of AzaBPDI<sup>-</sup>-PDI<sup>2-</sup> and AzaBPDI<sup>2-</sup>-PDI<sup>2-</sup> species, respectively. AzaBPDI-PMI **10** showed three reversible reduction waves with a first one-electron process at  $E^{1}_{red} = -1.20 \text{ V} vs \text{ Fc}^{+}/\text{Fc}$  corresponding to the formation of AzaBPDI<sup>-</sup>-PMI species (Figure 4b). The second two-electron wave at  $E^{2}_{red} = -1.45 \text{ V}$  arises from the concomitant second reduction of AzaBPDI unit and the first reduction of PMI leading to the AzaBPDI<sup>2-</sup>-PMI<sup>-</sup> species. Finally, the last one-electron reduction wave at  $E^{3}_{red} = -1.92 \text{ V}$  corresponds to the AzaBPDI<sup>2-</sup>-PMI<sup>2-</sup> species. Using the reduction potentials coupled with the optical properties, the molecular orbital frontiers were calculated and are depicted in Table 2.



**Figure 4.** Cyclic voltammograms (CV) in Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M), CH<sub>2</sub>Cl<sub>2</sub> (for **5**, **6** and **11**) or CH<sub>2</sub>Cl<sub>2</sub>/Chlorobenzene (1:1) (for **9** and **10**), 100 mV/s of a) AzaBPDI **11**, PDI-CHO **5** and AzaBPDI-PDI **9**; **b**) AzaBPDI **11**, PMI-CHO **6** and AzaBPDI-PMI **10**.

#### Table 2. Redox potential values

<sup>a</sup> Calculated from  $E^{LUMO}$ = - ( $E^{1}_{red}$  + 4.8) with  $E^{1}_{red}$  being the half-wave potential of the first reduction wave. The LUMO values were calculated with respect to ferrocene (reference energy level = 4.8 eV below the vacuum level). <sup>b</sup> Calculated using the following equation:  $E^{HOMO} = E^{LUMO} - E_{0.0}$ , <sup>c</sup>or using the following equation  $E^{HOMO} = -(E^{1}_{ox} + 4.8)$  with  $E^{1}_{ox}$  being the half-wave potential of the first oxidation wave.

Compounds	<b>E</b> <sup>1</sup> <sub>red</sub> [V vs. Fc <sup>+</sup> /Fc]	E <sup>2</sup> red [V vs. Fc <sup>+</sup> /Fc]	E <sup>3</sup> red [V vs. Fc <sup>+</sup> /Fc]	$E^1_{ox}$ [V vs. Fc <sup>+</sup> /Fc]	E <sup>LUMO</sup> /eV <sup>a</sup>	E <sup>HOMO</sup> /eV
PDI-CHO 5	- 1.05	- 1.24			- 3.75	- 6.00 <sup>b</sup>
РМІ-СНО <b>6</b>	- 1.41	- 1.77			- 3.39	- 5.70 <sup>b</sup>
AzaBPDI-TPA 7	- 1.17	- 1.38		+0.61	- 3.63	- 5.41°
AzaBPDI-F18	- 1.21	- 1.42		+0.91	- 3.59	-5.71°
AzaBPDI-PDI 9	- 1.14	- 1.29	- 1.42		- 3.66	-5.89 <sup>b</sup>
AzaBPDI-PMI 10	- 1.20	- 1.45	- 1.92		- 3.60	- 5.88 <sup>b</sup>
AzaBPDI 11	- 1.16	- 1.38			- 3.64	- 6.22 <sup>b</sup>

Furthermore, DFT calculations were performed on dyads **9** and **10**. In their optimized geometry, the two chromophoric units were found to be almost perpendicular to each other (with dihedral angles of 99° and 79° for **9** and **10**, respectively). This is of great interest as it has been demonstrated that a large dihedral angle into PDI dimers reduces their aggregation and favors their good performance as NFAs in OSCs.<sup>4a, 23</sup> The frontier molecular orbitals of **9** and **10** were also computed (Figure 5 and Calculation reports). For dyad **9**, the HOMO is fully located on the PDI unit with an energy level of –5.85 eV and the LUMO is predominant on the PDI unit as well (-3.41 eV). In contrast, for dyad **10**, the HOMO is centered on the PMI (-5.81 eV) whereas the LUMO on the AzaBPDI (-3.40 eV). Those predictions are in accordance with the experimental findings, and the energetic offset can be presumably attributed to solvents effects as the calculations were performed in gas phase.



Figure 5. Representation of the a) HOMO and b) LUMO of dyad 9 and c) HOMO and d) LUMO of dyad 10 from different points of view, determined by theoretical calculations (see Molecular Calculation Report).

## Conclusion

In conclusion, we have exploited our recently developed visible-light-mediated synthesis of AzaBPDI for preparation of four unprecedented chromophoric dyads in very good yields. This approach was advantageously compared to the well-known Pictet-Spengler type-reaction inspired from reported procedures. Moreover, these results clearly demonstrate that this new procedure can be extended to more complex aldehyde substrates rather than those we initially described. This strategy illustrates that the AzaBPDI unit behaves as an excellent platform for promoting energy

or electron transfer within multichromophoric architectures. Such dyads could also find applications in OLEDs<sup>24</sup> or thermally-assisted delayed fluorescence (TADF) material<sup>25</sup>. Moreover, considering the extension of absorption coverage of dyads **9** and **10** in comparison with PDI dimers described in literature, their incorporation in organic solar cells as non-fullerene acceptors seems promising. These studies are undergoing, in addition with the preparation of more complex AzaBPDI-based architectures using this original synthetic strategy.

## **Experimental section**

**Materials and General Methods.** Thin Layer Chromatography (TLC) was conducted on precoated aluminum sheets with 0.20 mm MerckAlugram SIL G/UV254 with fluorescent indicator UV254. Column chromatography was carried out using Sigma-Aldrich silica gel 60 (particle size 63-200 μm). UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 UV-Vis spectrophotometer using quartz cell (pathlength of 1 cm). Thin-films were prepared by spin-coating 1 % or 0.5% wt/v solutions from CHCl<sub>3</sub> or chlorobenzene onto Corning glass micros slides. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system. Fluorescence was measured on a Shimadzu RF-6000 Spectrophotometer using quartz cell (pathlength of 1 cm). Cyclic voltammetry experiments were carried out at room temperature with a Bio-Logic SAS SP-150 potentiostat. The working electrode is a platinum electrode, the counter electrode a platinum wire and the AgCl/Ag electrode was used as reference. The HOMO/LUMO energy levels calculated were referenced with the energy level of ferrocene (4.8 eV below the vacuum). NMR spectra were recorded using Bruker 300 MHz spectrometer (300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C) and 500 MHz spectrometer (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C). Chemical shifts are reported in ppm (δ) relative

to the solvent residual signal (CDCl<sub>3</sub>:  $\delta_{\rm H} = 7.26$  ppm,  $\delta_{\rm C} = 77.16$  ppm; Cl<sub>2</sub>CDCDCl<sub>2</sub>:  $\delta_{\rm H} = 6.00$ ppm,  $\delta_{\rm C} = 73.78$  ppm). Coupling constants (J) were given in Hz. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet) and br (broad signal). Carbon spectra were acquired with a complete proton decoupling  ${}^{13}C{}^{1}H$ . MALDI-TOF spectra were performed on a Bruker Daltonics Biflex III using DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix. High resolution mass spectrometry (HRMS-FAB) was performed with a JEOL JMS-700 B/E using *m*-nitrobenzylic alcohol as matrix. Photocyclizations were carried out by introducing the reaction flasks in a homemade photoreactor consisting of a plastic cylinder in which the inside wall was covered by a 1.5 meter white LEDs ribbon (~ 100 LEDs), power of 7 W. The light sources were placed 5 cm away from the reactor. Gaussian (09 revision D.01) was used to perform the DFT calculations. Detailed results for all modelled compounds can be found in the attached "Molecular Calculation Report". Chemicals were purchased from Sigma Aldrich, Acros Organics, Fisher Scientific, Alfa Aesar, Fluorochem, and were used as received. Solvents were purchased from Sigma Aldrich, Fluorochem, or Fischer Scientific while deuterated solvents from Sigma Aldrich. 1-AminoPDI 2 was prepared according to the literature.9c

**Abbreviations**. AzaBPDI : AzaBenzannulatedPerylenediimide; DDQ : 2,3-dichloro-5,6-dicyanobenzoquinone; DFT : density functional theory; DMF: *N*,*N*-dimethylformamide; EnT: energy transfer; Fl : fluorene; HOMO : highest occupied molecular orbital; HRMS : high resolution mass spectrometry; LUMO : lowest unoccupied molecular orbital; NMR : Nuclear Magnetic Resonance; PDI : perylenediimide; PET: photoinduced electron transfer; PMI : perylenemonoimide; rt : room temperature; TFA : Trifluoroacetic Acid; TLC: Thin Layer Chromatography; TPA: triphenylamine. General procedures for syntheses of AzaBPDI based dyads:

**Method A (Light-mediated imine photocyclization)**: 1-AminoPDI **2** (100 mg, 0.18 mmol or 50 mg, 0.09 mmol), aldehyde **3-6** (3 or 1.1 equiv.), and activated molecular sieves (3Å) (if 1.1 equiv. of aldehyde) were placed in a Schlenk flask along with dry solvent (CH<sub>2</sub>Cl<sub>2</sub> or DMF) (0.012 M). The mixture was degassed by bubbling argon for 5 min before the addition of trifluoroacetic acid (around 1 mmol). The mixture was stirred at 50 °C in CH<sub>2</sub>Cl<sub>2</sub> (or 130 °C in DMF) for 1h (to 17 h) using a heating mantle. After cooling down, the reaction mixture was subsequently diluted in CH<sub>2</sub>Cl<sub>2</sub> (400 mL) before being exposed to visible light (white light, 7 W) for ~1h30 until complete disappearance of the imine according to TLC. DDQ (1 equiv.) was then added and the resulting mixture was stirred at room temperature for **5** (compound **7**, **8** and **11**) to 30 min (dyads **9** and **10**) according to the solubility of the material. The solvents were removed under vacuum and the residue was purified on column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/Petroleum Ether (or Et<sub>2</sub>O).

**Method B (Pictet-Spengler type reaction)**: 1-AminoPDI **2** (150 mg, 0.18 mmol), aldehyde **3-6** (6 or 1 equiv), and activated molecular sieves (3Å) were placed in a Schlenk flask along with dry DMF (25 to 45 mL according to the solubility of the aldehyde). The mixture was degassed by bubbling argon for 30 min before the addition of triflic acid (1.8 mmol). The reaction mixture was stirred at 130 °C under argon atmosphere for 3 h using a heating mantle. Subsequently, DDQ (1 equiv) was added and/or the inert atmosphere was replaced by pure oxygen, and the reaction mixture was heated after under reflux for 24 h. The reaction mixture was quenched by addition of water and neutralized with 15% NaOH solution. The organic phase was extracted, washed again two

times with water and brine, dried with MgSO<sub>4</sub> and concentrated. Purification protocol described in Method A was applied.

*AzaBPDI-TPA dyad (7).* The compound was prepared according to the general procedures. <u>Method</u> <u>A</u>: Using 1-aminoPDI **2** (100 mg, 0.18 mmol), 4-(diphenylamino)benzaldehyde **3** (145 mg, 0.53 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (step 1/ 15 mL and step 2/ 400 mL). After purification through column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 99:1), and precipitation, AzaBPDI-TPA **7** was obtained (113 mg; 77%) as a brown solid. <u>Method B</u>: Using 1-aminoPDI **2** (200 mg, 0.35 mmol), 4-(diphenylamino)benzaldehyde **3** (574 mg, 2.1 mmol) in dry DMF (30 mL) and DDQ (80 mg, 0.35 mmol) for the re-aromatization step to afford AzaBPDI-TPA **7** (133 mg; 46%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) = 9.32 (s, 1H), 9.11 (s, 1H), 8.71 (d, *J* = 8.1 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.60–8.57 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.42–7.33 (m, 10H), 7.19–7.17 (t, 2H), 5.14–5.09 (m, 2H), 2.69–2.60 (m, 4H), 2.02–1.95 (m, 8H), 1.83-1.80 (m, 2H), 1.57–1.38 (m, 6H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 163.7, 163.6, 163.4, 160.4, 149.8, 147.2, 143.9, 134.2, 133.2, 132.2, 132.2, 131.4, 130.6, 130.2, 129.8, 128.6, 128.4, 127.4, 126.0, 125.8, 125.6, 124.2, 123.5, 123.2, 123.0, 122.6, 122.1, 122.0, 121.9, 121.1, 117.2, 54.7, 54.6, 29.3, 26.8, 25.7, 25.7. HRMS (FAB+) *m/z* : [M]<sup>+</sup> calcd for C<sub>55</sub>H<sub>42</sub>N<sub>4</sub>O<sub>4</sub>: 822.3201; found: 822.3219.

*AzaBPDI-Fl dyad 8*. The compound was prepared according to the general procedures. <u>Method A</u>: Using 1-aminoPDI **2** (100 mg, 0.18 mmol), 2-fluorenecarboxaldehyde **4** (103 mg, 0.53 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (step 1/ 1h30 in 15 mL and step 2/ 400 mL). After purification through column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 99:1), and precipitation, AzaBPDI-Fl **8** was obtained (112 mg; 84%) as a yellow solid. <u>Method B</u>: Using 1-aminoPDI **2** (150 mg, 0.26 mmol), 2-fluorenecarboxaldehyde **4** (408 mg, 2.1 mmol) in dry DMF (30 mL) and pure oxygen for the re-aromatization step to afford AzaBPDI-Fl **8** (70 mg; 35%). <sup>1</sup>H NMR (Cl<sub>2</sub>CDCDCl<sub>2</sub>, 500 MHz, 353 K):  $\delta$  (ppm) = 9.60 (s, 1H), 9.58 (s, 1H), 9.25 (d, *J* = 9.3 Hz, 1H), 9.24 (d, *J* = 9.3 Hz, 1H), 9.11 (d, *J* = 9.1 Hz, 1H), 9.06 (d, *J* = 9.1 Hz, 1H), 8.24 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.7, 1H), 7.53 (t, *J* = 7.5, 1H), 7.46 (t, *J* = 7.5, 1H), 5.21–5.13 (m, 2H), 4.20 (s, 2H), 2.75–2.63 (m, 4H), 2.04–1.80 (m, 10H), 1.53–1.40 (m, 6H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, 353 K, Cl<sub>2</sub>CDCDCl<sub>2</sub>)  $\delta$  (ppm) = 163.8, 163.7, 163.6, 161.3, 144.3, 143.9, 143.8, 143.2, 140.7, 136.6, 134.6, 134.1, 132.5, 130.6, 129.9, 129.1, 129.1, 128.0, 127.5, 127.5, 127.0, 126.3, 126.3, 125.1, 124.0, 123.6, 123.6, 123.2, 123.0, 122.8, 122.6, 121.9, 120.4, 120.0, 99.5, 54.5, 37.2, 29.2, 29.2, 26.5, 26.5, 25.4, 25.4. HRMS (FAB+) *m/z* : [M + H]<sup>+</sup> calcd for C<sub>50</sub>H<sub>38</sub>N<sub>3</sub>O<sub>4</sub>: 744.2866.

*AzaBPDI-PDI dyad (9)*. The compound was prepared according to the general procedures. <u>Method</u> <u>A</u>: Using 1-aminoPDI **2** (50 mg, 0.09 mmol), 1-(4-formylphenyl)PDI<sup>8a</sup> **5** (66 mg, 0.1 mmol) in DMF (step 1/ 17 h in 7 mL) and CH<sub>2</sub>Cl<sub>2</sub> (step 2/ 400 mL). After purification through column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97:3), and precipitation, AzaBPDI-PDI **9** was obtained (75 mg; 69%) as a dark red solid. <u>Method B</u>: Using 1-aminoPDI **2** (150 mg, 0.26 mmol), 1-(4-formylphenyl)PDI **5** (171 mg, 0.26 mmol) in dry DMF (45 mL) and pure oxygen for the rearomatization step to afford AzaBPDI-PDI **9** (54 mg; 25%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) = 9.63 (s, 1H), 9.62 (s, 1H), 9.31 (d, *J* = 8.3 Hz, 1H), 9.30 (d, *J* = 8.3 Hz, 1H), 9.15 (d, *J* = 8.2 Hz, 1H), 9.10 (d, *J* = 8.2 Hz, 1 H), 8.74–8.71 (m, 2H), 8.67–8.65 (m, 2H), 8.62 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 2 H), 7.89 (d, *J* = 8.1 Hz, 2H), 5.11–5.06 (m, 2H), 5.03–4.97 (m, 2H), 2.73–2.64 (m, 4H), 2.62–2.49 (m, 4H), 2.00–1.69 (m, 20H), 1.52–1.37 (m, 12H). Due to the low solubility of compound **9**, <sup>13</sup>C NMR spectrum could not be recorded. HRMS (MALDI) *m/z* : [M]<sup>+</sup> calcd for C<sub>79</sub>H<sub>61</sub>N<sub>5</sub>O<sub>8</sub>: 1207.4520; found: 1207.4520.

*AzaBPDI-PMI dyad (10).* The compound was prepared according to the general procedures. <u>Method A</u>: using 1-aminoPDI **2** (50 mg, 0.09 mmol), 9-(4-formylphenyl)PMI<sup>17</sup> **6** (59 mg, 0.1 mmol) in DMF (step 1/ 17 h in 7 mL) and CH<sub>2</sub>Cl<sub>2</sub> (step 2/ 400 mL). After purification through column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97:3), and precipitation, AzaBPDI-PDI **10** was obtained (80 mg; 79%) as a brown solid. <u>Method B</u>: Using 1-aminoPDI **2** (100 mg, 0.18 mmol), 9-(4-formylphenyl)PMI **6** (119 mg, 0.18 mmol) in dry DMF (30 mL) and pure oxygen for the re-aromatization step to afford AzaBPDI-PMI **10** (80 mg; 41%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 323 K):  $\delta$  (ppm) = 9.61 (s, 2H), 9.10-9.09 (m, 2H), 9.03 (d, *J* = 9.0, 1H), 8.99 (d, *J* = 9.0, 1H), 8.59 (d, *J* = 8.6 Hz, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.27-8.14 (m, 7H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.54-7.49 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 5.29-5.19 (m, 2H), 2.92-2.88 (m, 2H), 2.77-2.70 (m, 4H), 2.06-1.93 (m, 8H), 1.87-1.80 (m, 2H), 1.59 (br, 4H), 1.45 (m, 2H), 1.33-1.24 (m, 12H). Due to the low solubility of compound **10**, <sup>13</sup>C NMR spectrum could not be recorded. HRMS (FAB+) *m/z* : [M]<sup>+</sup> calcd for C<sub>77</sub>H<sub>58</sub>N4O<sub>6</sub>: 1134.4351; found: 1134.4363.

*AzaBPDI* **11**. The compound was prepared according to the general procedures. <u>Method A</u>: using 1-aminoPDI **2** (100 mg, 0.18 mmol), benzaldehyde (191 mg, 1.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (step 1/15 mL and step 2/ 400 mL). After purification through column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/MeOH 99:1), and precipitation, AzaBPDI **11** was obtained (98 mg; 83%) as a yellow solid. <u>Method B</u>: Using 1-aminoPDI **2** (200 mg, 0.35 mmol), benzaldehyde (222 mg, 2.1 mmol) in dry DMF (30 mL) and pure oxygen for the re-aromatization step to afford AzaBPDI-PMI **10** (79 mg; 34%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) = 9.51 (s, 1H), 9.50 (s, 1H), 9.16–9.14 (m, 2H), 9.04 (d, *J* = 8.2 Hz, 1H), 8.99 (d, *J* = 8.1 Hz, 1H), 7.99–7.97 (m, 2H), 7.76–7.68 (m, 3H), 5.20–5.10 (m, 2H), 2.71–2.59 (m, 4H), 1.98–1.77 (m, 10H), 1.55–1.33 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) = 164.2, 164.0, 164.0, 163.9, 161.5, 144.5, 138.4, 134.9, 134.2, 132.6, 132.5, 131.0, 130.9, 130.0, 129.4, 129.3, 129.2, 128.1, 126.5, 126.4, 124.2, 123.8, 123.7, 123.5, 123.0, 122.9, 122.7, 122.0, 118.6, 54.6, 29.4, 29.4, 26.8, 25.6. HRMS (FAB+) *m/z* : [M + H]<sup>+</sup> calcd for C<sub>43</sub>H<sub>34</sub>N<sub>3</sub>O<sub>4</sub>: 656.2549; found: 656.2529.

**Computational Details.** For dyads **9** and **10**, geometric optimizations followed by frequency calculations have been performed. We chose a hybrid DFT approach, with the B3LYP functional, particularly reliable for geometries and energies. The basis set used is in agreement to an augmented double zeta, 6-31+G(2d,p). The grid used corresponds to the default parameters of the Gaussian09 program. The TD-DFT excited states calculations were set with the same parameters. Although not optimized for TD-DFT, the B3LYP gave a reasonable estimation for singlet states energies. Here, 15 states were computed and all full reports have been included in supplementary information.

### ASSOCIATED CONTENT

## **Supporting Information**

Supporting Information Available: NMR and MS spectra, supplementary spectroscopic data, cyclic voltammetry results.

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## NOTES

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