Terthiophene–Perylene diimides: Color Tuning via Architecture Variation[†]

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N,N'-Bisoctylperylene diimides (PDIs) have been functionalized in the 1,7-position with terthiophenes of varying architecture giving three new donor-acceptor (D-A) compounds of the same molecular weight. Different conjugation lengths, arrangements, and connections of the thiophene units within themselves and toward the PDI core have strong effects on the optical, electronic, and photochemical properties of the D-A compounds. Like jigsaw pieces joined together to give different pictures, the terthiophenes are linked to PDIs to achieve different colors. These insights into tuning color and energy levels can open new possibilities for tailoring chromophores to their desired applications, e.g., organic photovoltaics or organic field effect transistors.

Chemical compounds, which can absorb and reflect light of different wavelengths, stain the world and make it beautiful. To achieve materials in a myriad of colors, organic chemists are still attracted by the design and synthesis of new dyes or pigments where pervlene dyes are key chromophores.^{1,2} Nowadays they are being used not only as pure colorants for aesthetic purposes but also as active components in high technologies, such as organic electronics,^{3,4} biology,⁵ and sensing.⁶ By functionalization using innumerable synthetic pathways, perylenes of various colors can be achieved possessing unique optical and electrochemical properties. Generally, the color of chromophores depends on the structure of the chemicals, which can be tuned by (1) enlargement of the π -system, (2) transition from aromatic to quinoidal structures, (3) polymerization, and (4) introduction of donor-acceptor substituents. Among all these methods, the last one is most efficient because of abundant donors and acceptors.7

In this article, we present three N,N'-bisoctylperylene diimide (PDI) derivatives (1-3, Figure 1) with terthiophene moieties on the perylene core. Thiophene-based materials are well-known as p-type semiconductors and exhibit extraordinary charge transport properties that find broad application in optoelectronic devices.⁸ By coupling two terthiophenes as electron-donating groups in the 1,7-position of PDI, we obtained bay-functionalized PDI compounds for which the first oxidation potential is shifted considerably into the negative direction. Whereas the focus of other research groups so far has mainly been set on varying the chain length of the thiophene moiety,^{9,10} we will compare three PDIs bearing terthiophene units of different architecture in the 1,7-bay positions of the perylene core, displayed in Figure 1. Moreover, due to the variation in the architecture of the three terthiophenes, these terthiophene-PDIs all (Figure 1) have the same molecular weight, consist of a PDI and three thiophene units, but interestingly, are of different color, i.e., bluish green, purple, and dark green, respectively. To our knowledge, this is the first report varying the color of perylene dyes by only changing the arrangement of three thiophenes in the 1,7-positions of the perylene core.

All three compounds were prepared by imidization of 1,7dibromoperylene-3,4:9,10-tetracarboxylic acid dianhydride with n-octylamine as described in literature¹¹ and subsequent metal catalyzed coupling reactions of the N.N'-bisoctyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid diimide with the three different terthiophene moieties (5'-(4,4,5,5-tetramethyl [1,3,2] dioxaborolan-2-yl)-5,5'-bis(trimethylsilyl)-2,2':3',2'-terthiophene^{12,13} (5), 3'-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-5,5"-bis(trimethylsilyl)-2,2':5',2"-terthiophene (7), and 5-(4,4,5,5)tetramethyl[1,3,2]dioxaborolan-2-yl)-2,2':5',2"-terthiophene (9), respectively) under Suzuki conditions followed by removal of the trimethylsilyl groups with tetra-n-butylammonium fluoride (TBAF) in the cases of 1 and 2 (Figure 1). Terthiophene 7 was synthesized starting from 3-bromo-2,5-diiodothiophene (11) and trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)silane (13), which were prepared according to modified protocols (see Supporting Information) described in literature^{14,15} (Scheme 1). Suzuki coupling of 11 with 2 equiv of 13 yielded 3'-bromo-5,5"-bis(trimethylsilyl)-2,2':5',2"-terthiophene (14). Subsequent metal-halogen exchange of 14 with *n*-butyllithium and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2dioxaborolane yielded 3'-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-5,5"-bis(trimethylsilyl)-2,2':5',2"-terthiophene, 7. Detailed information on the synthesis can be found in the Supporting Information.

Both **3** and **2** consist of linear terthiophenes based on $\alpha - \alpha$ connection of the three thiophene units. For **3**, the terthiophene and the PDI core are joined via the α -position of the terminal thiophene. In **2**, however, it is the middle thiophene unit of the terthiophene chain that is linked to the PDI core via its β -position. Different from **3** and **2**, **1** comprises two branched terthiophene units within the terthiophene building block. The terthiophene itself is α -linked to the PDI core at the middle thiophene unit.

To investigate their different intramolecular charge transfer (ICT) characters caused by the terthiophenes, the absorption

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Figure 1. Synthesis scheme of the terthiophene substituted perylenedicarboximides 1-3: (a) Pd(PPh₃)₄, K₂CO₃, toluene, H₂O, ethanol, 80 °C, 3 days; yields 47%, 30%, 44%, respectively; (b) TBAF, THF, 30–40 min, RT-40 °C; yield 78%; (i) NIS (*N*-iodosuccinimide); (ii) 1 = BuLi, 2 = 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane; (iii) Pd₂(dba)₃CHCl₃/HP(tBu)₄BF₄/K₃PO₄; (iv) 1 = Mg, diethyl ether, 2 = 2,3-dibromothiophene, [Ni(dppp)Cl₂]; (v) Bu₄NF, THF.

and fluorescence emission spectra of 1-3 were measured and are displayed in Figure 2. Going from $2 \rightarrow 1 \rightarrow 3$, a monotonic decrease of the absorption coefficient and a red shift of the absorption onset are observed, which indicates varying donor strength due to the different architectures of the three terthiophenes. Whereas the branched terthiophene compound (1) and the linear α -connected terthiophene compound (3) both show broad, structureless, and intense low-energy charge transfer absorption bands (transition from the ground state S₀ to the excited charge transfer singlet state S₁) with a maxima at $\lambda =$ 591 and 610 nm, respectively, this S₀ \rightarrow S₁ band has almost vanished in the linear β -connected terthiophene compound (2).^{16,17} This effect corresponds to the decreasing length of the α -conjugated oligothiophene around the PDI core (3 > 1 > 2). **3** possesses three α -connected thiophenes, resulting in the longest conjugation, which is also reflected in the bathochromically shifted absorption maximum. This red shift is noticeably smaller for **1** with only two α -conjugated thiophenes around the PDI core. **2** with the β -connected terthiophene on the other hand shows a hypsochromic shift ($\lambda_{max} = 512$ nm) that is due to the lack of conjugation (β -connected with PDI core) between the PDI core and the terthiophene moiety. The even hypsochromic shift of the absorption maximum of **2** compared to a naked PDI ($\lambda_{max} = 526$ nm for *N*,*N*'-bis(1-heptyloctyl)-3,4:9,10-perylenetetracarboxdicarboximide),¹⁸ however, results from the electronic S₀ \rightarrow S₂ transition.

Regarding the fluorescence emission, **1** and **3** show emission bands of different intensities at $\lambda_{max} = 738$ and 782 nm,



Figure 2. (a) Absorption spectra (in CH₂Cl₂) and (b) fluorescence emission spectra (in toluene) of 1–3; excitation wavelengths according to the legend (x = λ_{ex} , c = 2 × 10⁻⁵ mol/L). (c) Absorption spectra of 1–3 in toluene after sunlight irradiation and (d) fluorescence emission spectra in toluene of 1 before and after sunlight irradiation ($\lambda_{ex} = 400$ nm): *, before sunlight irradiation; **, after sunlight irradiation, not further purified.

respectively. As the emission bands are in the near-infrared region and very broad without the typical PDI fine structure, these emission bands can be assigned to the intramolecular charge transfer between the terthiophene donor and the PDI acceptor.¹⁹ Moreover, both compounds possess large Stokes shifts (147 and 172 nm, respectively). The emission intensity of 3 is much lower than that of 1. A similar fluorescence quenching in the presence of a thiophene donor was detected by Huang et al. for dithienothiophene-PDI copolymers.²⁰ Moreover, a decrease in the fluorescence quantum yield correlated to an increasing number of α -connected thiophene units in the 1,7-position of PDI was observed.^{9,10} Correspondingly, the quantum yields of 1 and 3 could be determined as 16% and 8%, respectively, using cresyl violet ($\Phi = 54\%^{21}$) as a reference. Compared to the $S_1 \rightarrow S_0$ emission band in 1, the one in 3 is bathochromically shifted. This red shift in emission results just like the red shift in absorption from the longer conjugation. 2 does not show any significant fluorescence. This indicates that the charge transfer state of 2 could be quenched by electron transfer and thus supports the presence of a photoinduced electron transfer (PET) fluorescence quenching mechanism.

Contrary to the absorption where only weak solvent sensitivity is observed (Figure S3: absorption (normalized) of 1 in CH_2Cl_2 , acetone, toluene, and DMSO, Supporting Information), the fluorescence of 1 and 3 is thoroughly quenched in DMSO (Figure S2: fluorescence emission spectra of 1-3 in DMSO, Supporting Information). This solvent effect confirms the assumption that these low energy emission bands in fact result from charge transfer. As all three compounds are symmetrical and according to quantum mechanical calculations (Figure S1: molecular geometries of 1-3, Supporting Information) exhibit no strong dipole (0.82, 1.86, and 2.45 debye for 3, 2, 1, respectively), it is coherent that no obvious solvatochromic absorption is observed. Regarding the fluorescence, the quenching in more polar solvents can be explained by a higher thermodynamic driving force helping the photoinduced electron transfer from the donor to the acceptor moiety.¹³

Due to their different optical behaviors, 1-3 should also exhibit various highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. HOMO and LUMO levels of the three terthiophene-PDI compounds were determined via cyclovoltammetry using the onset potentials and are shown in Table 1. Moreover, the bandgaps were deduced from the cyclovoltammetric results and compared with the optical bandgaps inferred from the onsets of the longest wavelength absorption bands. In general, we can see a good agreement of the electrochemical and optical results. Only 2 shows a much smaller electrochemical than optical bandgap. As the LUMO level is mainly determined by the PDI core and resembles the LUMO level of bay-unsubstituted PDI (LUMO -3.8 eV and HOMO -5.8 eV for N,N'-bis(1-ethylpropyl)-3,4,9,10-perylenetetracarboxylic acid diimide²²), the HOMO is strongly influenced by the donor and the donor-acceptor interactions, respectively. Because of the β -connection of the terthiophene and a strong twist of the donor (D, terthiophene) with respect to the acceptor (A, perylene) plane around the D-Abond, the donor is decoupled in 2 and the HOMO in the D-Acompound is mainly affected by the high HOMO of the terthiophene itself. DFT calculations carried out by Bouzinne et al. resulted in a HOMO level energy of -5.18 eV for a linear terthiophene.²³ It is the same decoupling effect that determines the large optical bandgap as for the orbital partitioning between the HOMO and LUMO the intensity of the intramolecular

TABLE 1: HOMO and LUMO Levels, Band Gap, Absorption and Fluorescence Maxima, and MALDI-TOF Data for 1–3

compound	HOMO _{CV}	LUMO _{CV}	bandgap _{CV}	bandgap _{opt}	$\lambda_{maxAbs(in toluene)}$	$\lambda_{maxEm(in \ toluene)}$	MALDI-TOF before sunlight irradiation	MALDI-TOF after sunlight irradiation ^a
1	-5.7	-3.9	1.8	1.8	593	739	1107	1103
2	-5.5	-3.9	1.6	1.9	509		1107	decomposed
3	-5.4	-3.9	1.5	1.6	608	782	1107	1107





Figure 3. Solution colors (in toluene) and molecular structures of 1-3 before and after light irradiation (suggested structure 4).

charge transition is very low and hence no clear ICT absorption band can be observed. $^{\rm 24}$

For the conjugated thiophene–PDI D–A systems the bandgap diminished with every additional thiophene unit (bandgaps for *N*,*N*'-bis(2-ethylhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide and its thiophene (T)-substituted derivatives: PDI, 2.31 eV; 1T-PDI-1T, 1.97 eV; 2T-PDI-2T, 1.73 eV; 3T-PDI-3T, 1.63 eV).¹⁰ The decreased electrochemical bandgaps of **1** and **3** correspond to the bathocromic shifts in absorption and hence the optical bandgaps. Thus, both decoupling and sizable conjugation, which on first glance seem to be contrary effects, can result in a similarly small bandgap like in **2** and **3**, respectively.

As mentioned above, **1** and **3** show substantial charge transfer whereas **2** exhibits strong photoinduced electron transfer. These characteristics can also influence the photochemical stability of the three compounds. To investigate their photochemical stability, solutions in toluene were exposed to sunlight for several days and interestingly all three compounds show different behavior, as presented in Figure 3. Whereas **3** is stable and shows the same mass in MALDI-TOF (Table 1) and the same absorption bands as before (Figure 2), **2** changes color from purple to yellow and, according to MALDI-TOF as well as absorption measurements, is completely decomposed. **1** undergoes a color change from green to red and shows a decrease in mass of 4 according to MALDI-TOF (Figure S5: MALDI of branched terthiophene–PDI **1** before and after sunlight, Supporting Information). The color and the loss of mass indicate the loss of four hydrogens and photoinduced fusion of the terthiophene moiety as it is known in literature for various branched terthiophenes. According to Jayasuriya et al. the 2.2'3',2''-terthiophene always fuses to the benzo[1,2-*b*:3,4-*b'*: 6,5-*b''*]trithiophene, not yielding any other isomers.²⁵ We therefore suggest the formation of **4** according to the structure shown in Figure 3. The fusion of the branched terthiophene leads to a new and more stable chromophore donor, which strongly shifts the optical properties.

Upon fusion, 1 experiences a strong hypsochromic shift of the absorption, the longest wavelength absorption band showing a λ_{max} of only 567 nm (Figure 2). This blue shift can also be observed in the fluorescence of 154 nm to $\lambda_{max} = 584$ nm (Figure 2), hence, fluorescence in the PDI range. The hypsochromic shift in absorption would implicate a rather large bandgap. As the LUMO in the fused product of 1 should remain unchanged as the PDI core is not altered, a larger bandgap would correspond to a more negative HOMO level energy. Molecular geometry calculations (included in the Supporting Information) show a strong twist of the donor and the PDI acceptor, the two planes being almost perpendicular to each other ($\sim 97^{\circ}$), which leads to a stronger decoupling of the donor from the acceptor. A similar case, though even enhanced by the β -connection, is 2, in which we found a strong influence of the donor moiety on the HOMO level energy. In fact, DFT calculations of Taerum et al. predicted the HOMO of terthienobenzene, hence the donor moiety in the fused compound, to be as low as -5.93 eV.²⁶ This corresponds to the result of the larger optical bandgap.

In summary, we showed how different terthiophene architectures can influence optical and photochemical properties of D-A terthiophene-PDIs. The syntheses of three different baysubstituted donor-acceptor terthiophene-PDIs were presented. The target compounds were characterized by UV-vis absorption, fluorescence, and cyclovoltammetric measurements, and their photochemical stability was tested. The optical properties showed that the color can be adjusted and energy levels tuned by variation of conjugation, assembly, and connection of the thiophene moieties within the terthiophene and toward the PDI core. The photochemical stability differs and varies strongly (charge transfer or electron transfer) and photoinduced fusion of the branched terthiophene moiety offers a way to synthesize new chromophores. The tuning of color and energy levels of these terthiophene-PDIs is of vital interest for the potential application in organic electronics, especially for organic photovoltaics, as they show promising absorption in their broadness in the UV-vis region (especially 1 and 3) and their high absorption coefficients (especially 2). The terthiophene-PDIs 1-3 all possess suitable energy levels for the application as the acceptor component in bulk heterojunction cells in combination with P3HT (LUMO, -3.2 eV; HOMO, -5.2 eV). Photovoltaic studies will be performed in the future.

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Supporting Information Available: Measurements and methods, experimental part, molecular geometries, fluorescence spectra in DMSO, absorption spectra of **1** in different solvents, MALDI-TOF spectra of **1** before and after sunlight irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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