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Graphical Abstract

Synthesis and properties of perylene diimide dyes bearing unsymmetrical

and symmetrical phenoxy substituents at bay positions

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ABSTRACT

Perylene diimide dyes bearing symmetrical and unsymmetrical phenoxy substituents at the bay positions (N,N'-diethylhexyl-1-bromo-7-pentafluorophenoxy-substituted perylene diimide and 1,7-diphenoxy-substituted perylene diimide) were prepared. ¹H NMR analysis indicated that these compounds contain a small quantity of the 1,6-regioisomer, and yield intramolecular hydrogen bonds. Furthermore, their photophysical, electrochemical, aggregation, and thermal properties were studied. It was found that their photophysical properties, structure, aggregation, and thermal stability in the solid state depend on the structure of the phenoxy substituent.

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1 Introduction

Perylene diimide derivatives (PDIs) are promising and versatile candidates for use in organic photo-electronic applications due to their commercial availability, low cost, and electronic, optical, and charge transport properties, which can be tuned via careful functionalization.¹ In particular, PDIs form an appealing class of n-channel semiconductors for organic field effect transistors, and as electron-acceptor components in organic solar cells.²

To date, two strategies have been exploited for the design of new functional PDIs: (1) substitution on the imide nitrogen atoms,³ and (2) substitution at the 1, 6, 7, or 12 positions, known as the bay positions.⁴ Substitution on the imide nitrogen atoms maintains the planarity of the perylene core, which usually exhibits indistinguishable absorption and emission properties due to nodes in the HOMO and LUMO levels on the imide nitrogens reducing coupling between the perylene diimide units.⁵ Substitution in the bay positions therefore leads to distortion of the perylene core, thus altering the photo-physical properties of the PDIs.⁶

1,7-Diphenoxy-substituted PDIs are among the most widely utilized PDI scaffolds due to their facile synthesis via dibromination and nucleophilic displacement.⁷ However, synthesis of PDIs bearing a single phenoxy moiety is difficult, due to the higher nucleophilic ability of the phenol and the phenol derivatives.⁸ To date, only 1-bromo-7-alkoxyl perylene diimides, prepared by the nucleophilic substitution of one 1,7-dibromo unit with an alkyl alcohol (using K₂CO₃ as base), have been discussed.⁹ However, the presence of a bromine atom at a

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bay position is important in the design of unsymmetrical PDIs.¹⁰ The introduction of an electron withdrawing group on the phenol moiety can decrease its nucleophilic ability, thus giving unsymmetrical phenoxy-substituted PDIs.

We, herein, present the synthesis and the characterization of four PDIs from a range of phenol derivatives (see Scheme 1). Structural effects of the nucleophile on the resulting products will be discussed, and their photophysical and electrochemical properties will be investigated.

2 Results/Discussion

2.1 Preparation of PDIs

A series of phenoxy-substituted PDIs were synthesized from perylene-3,4,9,10-tetracarboxylic dianhydride 1 in three steps according to the route depicted in Scheme 1. Dibromo perylene-3,4,9,10-tetracarboxylic dianhydride was first prepared by the I₂catalyzed bromination of perylene-3,4,9,10-tetracarboxylic dianhydride 1 in 96% sulfuric acid. This reaction yielded the crude product 2, which was a mixture of 1,7- and 1,6-dibromo perylene dianhydride, along with a trace of 1,6,7-tribromo perylene dianhydride. The crude product was insoluble in commercial organic solvents, and so was subjected to imidization without characterization or further purification. Imidization of 2 with 2-ethylhexylamine in propionic acid at reflux vielded BrPDI and 3. The resulting product mixture was subjected to silica gel column chromatography using CH₂Cl₂ as eluent. **BrPDI** was obtained and characterized by ¹H NMR spectroscopy and FTIR spectrophotometry. Two groups of signals with

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different intensities were observed in the aromatic region of the ¹H NMR spectrum indicating the presence of 1,7- and 1,6regioisomers in the product (Figure 1, **BrPDI**). Two wellresolved doublets and a singlet were observed in the region between 8.6 ppm and 9.4 ppm. Integration of the doublets at 9.50 and 9.43 ppm revealed that the 1,7- and 1,6-regioisomers were present in a 97:3 ratio in the product. The mixture was subsequently treated with *p*-fluorophenol (PF), *p-tert*-butylphenol (BO), and pentafluorophenol (DF) in the presence of a K₂CO₃ catalyst to afford symmetrical PDIs. In addition, ¹H NMR spectroscopic data indicated that the 1,7- and 1,6-regioisomers were also present in **PFPDI**, **DFPDI**, and **BOPDI**, respectively (Figure 1).



Scheme 1. Synthetic pathway to PDI derivatives.



Figure 1. ¹H NMR (400 MHz, CDCl₃) spectra of **PFPDI** (R = 86:14); **BOPDI** (R = 80:20); DFPDI (R = 90:10); **SFPDI** (R = 88:12); and **BrPDI** (R = 97:3). R = ratio of 1,7- to 1,6-regioisomers.

Nucleophilic substitution of a single 1,7-dibromo unit was attempted to prepare the monophenoxy PDIs (**SFPDI**, **SPFPDI**, and **SBOPDI**) using either a K₂CO₃ or triethylamine catalyst, but only 1-bromo-7-pentafluorophenol perylene diimide (**SFPDI**) was obtained. This is likely due to the *p*-tert-butylphenol being easily converted into a *p*-tert-butylphenol ion when treated with either K₂CO₃ or triethylamine, as the resulting oxide anion (O[¬]) is a much stronger nucleophile than neutral oxygen itself (O). As a result, reaction of *p*-tert-butylphenol with 1,7-dibromo-PDI produced diphenoxy PDIs. The introduction of a fluorine atom to the phenol moiety can destabilize the oxide anion (O[¬]), which aids in forming only the monophenoxy PDI. In addition, the presence of additional fluorine atoms can result in a decrease in interactions between the PDIs and silica gel, resulting in facile purification by silica gel column chromatography.

The presence of C-H…O hydrogen bonds between the 1,7oxygen and the 6,12-hydrogen atoms in BOPDI, PFPDI, and DFPDI molecules was supported by analysis of the proton chemical shifts of bay protons 6 and 12 (Figure 1 and Table 1). The shifts of the 6, 12-bay protons were observed between 9.44 and 9.61 ppm for BOPDI, PFPDI, and DFPDI, while those of the parent Br-substituted PDI (BrPDI) were observed at 9.48 ppm. Figure 1 shows how the chemical shifts corresponding to the aromatic protons of PDIs shift downfield with an increase in the electronegativity of the oxygen atom of the phenoxy groups (DFPDI->PFPDI->BOPDI), suggesting the presence of C-H...O hydrogen bonds.¹¹ Concomitant to the involvement of the H6 and H12 protons in hydrogen bonding, the H2 and H8 protons located in direct proximity to the respective phenoxy substituents shifted to higher fields. Further evidence was found in the shifts of bay protons 6 and 12 adjacent to the pentafluorophenol and Br moieties in SFPDI, respectively. The chemical shifts corresponding to the H6 aromatic protons (9.65 ppm) move downfield compared to that of H12 (9.26 ppm), suggesting the formation of an intramolecular C6-H6...O hydrogen bond in SFPDI. The H8 protons (8.08 ppm), located in close proximity to the phenoxy substituents, were also displaced to higher fields. It was therefore clear that the substituent-induced distortion of the perylene core may be restrained through the presence of such hydrogen bonds, especially for the 1,7diphenoxy-substituted PDIs.

Table 1. ¹H NMR (400 MHz) chemical shifts for perylene core protons (CDCl₃, 298 K)

dye	H ₆ , H ₁₂ /ppm (doublet)	H ₅ , H ₁₁ /ppm (doublet)	H ₂ , H ₈ /ppm (singlet)
BOPDI	9.61 (d, <i>J</i> =8 Hz)	857 (d, <i>J</i> =8 Hz)	8.34
PFPDI	9.54 (d, <i>J</i> =8 Hz)	8.60 (d, <i>J</i> =8 Hz)	8.27
DFPDI	9.44 (d, <i>J</i> =8 Hz)	8.68 (d, <i>J</i> =8 Hz)	8.15
SFPDI	H ₆ : 9. 65 (d, J=8 Hz); H ₁₂ : 9.26 (d, J=8 Hz)	H ₅ : 8.71 (d, J=4 Hz); H ₁₁ : 8.69 (d, J=4 Hz)	H ₂ : 8.99; H ₈ : 8.09
BrPDI	9.48 (d, <i>J</i> =8 Hz)	8.69 (d, <i>J</i> =8 Hz)	8.93

The presence of intramolecular C-H···O hydrogen bonds in these molecules was further confirmed by computer simulations. Optimized molecule structures of the PDIs are shown in Figure 2. A weak hydrogen bond was observed between the phenoxy oxygen (O₁, O₂) atom and two hydrogen atoms (H₁, H₂) of the perylene core. The H₁···O₁ distances between the 1,7-oxygen and 1,2-hydrogen atoms are 2.05 Å, 2.05 Å, 2.05 Å, and 2.11 Å for **PFPDI**, **BOPDI**, **DFPDI**, and **SFPDI**, respectively, and the C₅-H₁···O₁ angles are 119.8°, 119.8°, 116.4°, and 115.7° for **PFPDI**, **BOPDI**, **DFPDI**, and **SFPDI**, respectively. These distances and angles are consistent with weak hydrogen bonding according to a previously reported study.¹² Furthermore, the C₁-C₂-C₃-C₄ dihedral angles 13.56°, 13.65°, 15.79°, and 16.57° for **PFPDI**, **BOPDI**, **DFPDI**, and **SFPDI**, respectively are almost equal, indicating that their photophysical properties primary depend on the substituent structures.





Figure 2. Optimized molecular structures of the PDIs.

2.2 Steady-State Absorption and Fluorescence Studies

UV-Vis absorption spectra of the PDIs in CH_2Cl_2 allow important information regarding the molecular structures of the PDIs to be derived (Figure 3). **DFPDI** contains two pentafluorophenol groups, **BOPDI** two *p*-tert-butylphenol groups, and **PFPDI** two *p*-fluorophenoxyl groups at the 1,7positions, while the 1,7-positions in **SFPDI** are occupied by one pentafluorophenol group and a Br atom, respectively. Such structural differences result in different optical properties, reflected in the S_0/S_1 and S_0/S_2 absorption bands.

For example, the $S_0 \rightarrow S_1$ absorption band is red shifted from SFPDI to **DFPDI**, **PFPDI**, and **BOPDI** with λ_{max} moving from 528 nm to 529 nm, 539 nm, and 543 nm, respectively. Such a change in absorption spectra can be caused either by increased conjugation between the substituents and the PDI core,¹³ or by substituent-induced distortion of perylene core.¹⁴ The latter can be ignored in the case of **BOPDI**, **PFPDI**, and **DFPDI** due to the presence of two CH···O hydrogen bonds and almost unanimously dihedral angles. Hence, the spectral changes between **BOPDI**, **DFPDI**, and **PFPDI** are dependent only on the electronic coupling between the electron-rich phenoxy substituents, and the electron-deficient perylene core.¹⁵ In addition, the low energy absorption onset provides the value for optical gap (OG).¹⁶ The optical gap and the wavelength maxima (λ_{abs0-0}) and onsets (λ_{abs}) of the 0-0 transitions are summarized in ST1.

In contrast with the solution spectra, the casting film spectra for **DFPDI**, **SFPDI**, **PFPDI**, and **BOPDI** exhibited a slight redshift and were significantly broader. The 0-0 transitions of the **DFPDI**, **SFPDI**, **PFPDI**, and **BOPDI** occur at shifts of 11, 13, 17 and 16 nm, respectively.



Figure 3. UV-Vis absorption spectra of the PDIs (a) in CH_2Cl_2 , concentration = 10^{-5} M; and (b) in casting films.

The fluorescence spectra of the PDIs recorded in both solution (CH_2Cl_2) and solid/powder form are shown in Figure 4. As expected from the absorption results, **DFPDI** and **SFPDI** exhibited comparable emission characteristics once again. The emission bands of both **DFPDI** and **SFPDI** were approximate mirror images of their S₀-S₁ absorption bands, with a Stokes shift of approximately 29 nm. Both compounds show maximum emission peak at ~556 nm, with a shoulder peak at 590 nm. The maximum emissions of **PFPDI** and **BOPDI** were observed at 574 nm and 577 nm, respectively, with corresponding Stokes

shift decreased with the introduction of additional fluorine atoms into the phenoxy groups. The powder/solid state emission spectra of **DFPDI**, **SFPDI**, **PFPDI**, and **BOPDI** were largely red-shifted and broadened compared to the solution spectra. Corresponding maxima appeared at 661 nm, 638 nm, 661 nm, and 669 nm, respectively. In contrast with its solution behavior, SFPDI powder exhibited a redshift of 81 nm, which is lowest redshift of all PDIs. This suggests that weak molecular interactions exist in solid SFPDI, as confirmed by X-ray diffraction (XRD) analysis (see Section 2.4).



Figure 4. Fluorescence spectra of PDIs (a) in CH_2Cl_2 , concentration = 10^{-5} M; and (b) as a solid powder. Excitation wavelength: 530 nm.

2.3 Electrochemical properties

The electrochemical properties of **DFPDI** in CH_2Cl_2 at room temperature were investigated by cyclic voltammetry (CV). The CV curve was recorded vs. the Ag/AgCl electrode as reference electrode(Ag/AgCl), using ferrocene as an internal standard (Figure. 5). As expected, **DFPDI** exhibited two typical reversible reduction waves due to the first and second one-electron stepwise reductive process from the perylene core to the corresponding radical anions and dianions (for the **DFPDI** molecule these are **DFPDI**⁻ and **DFPDI**²⁻).¹⁷

The onset reduction potential (E_{onset}) for **DFPDI** is -0.32 eV. According to the empirical formulae $E_{LUMO} = -([E_{onset}]^{red} +$ 4.8 eV)¹⁸ and $E_{HOMO} = E_g^{opt} + E_{LUMO}$, the HOMO and LUMO energy levels of DFPDI were calculated as -6.73 eV and -4.48 eV. The calculated values for the HOMO and LUMO of PFPDI, SFPDI, and BOPDI are summarized in ST2. The first reduction potentials appeared to vary with the introduction of substituted groups. So the HOMO and LUMO energy levels also changed, with the LUMO levels being calculated as -4.32 eV, -4.48 eV, -4.54 eV, and -4.35eV for PFPDI, DFPDI, BOPDI, and SFPDI, respectively. The HOMO and LUMO energy levels for P_3HT were previously reported in the literature to be 5.1 eV and 3.2 eV,¹⁹ and so it is clear that the HOMO and LUMO energy levels of our PDIs are suitable to efficiently drive exciton dissociation at the P₃HT/PDIs heterojunction interfaces. Thus, PFPDI, DFPDI, BOPDI, and SFPDI may be candidates for use as an electron-acceptor component in P₃HT/PDIs systems.



Figure 5. Cyclic voltammograms of **DFPDI** and **BOPDI** recorded in CH_2Cl_2 containing 0.1 M *n*-Bu₄NPF₆ at 0.1 Vs⁻¹.

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To gain insight into the geometrical and electronic structures of the perylene diimide derivatives, we performed density functional theory (DFT) calculations on **DFPDI** using the Gaussian03 package.²⁰ The orbital spatial distributions of the HOMO and LUMO for **DFPDI** are shown in Figure 6, where it is clear that the HOMO and LUMO of **DFPDI** both localize at the central pyrelene core. The theoretical estimation of the HOMO-LUMO gaps for **DFPDI** in vacuo (2.62 eV, B3LYP/6-31G*) are in good agreement with the measured optical bandgaps. Theoretical estimations of other samples are shown in the Supplementary Material (Fig. SF1).



Figure 6. Molecular orbital distributions and energy levels for DFPDI estimated by density functional theory (DFT) calculations.

2.4 Powder X-ray diffraction studies

The structures of the PDI powders were investigated by X-ray diffraction (XRD) analysis. As shown in Figure 7, in the low angle range, the XRD pattern of BOPDI shows two clear diffraction peaks at $2\theta = 4.32^{\circ}$ (2.04 nm) and 5.56° (1.58 nm), which correspond to the diffractions from the (100) and (010) planes, respectively.²¹ The peak at 24.80° corresponding to a distance of 3.50 Å can be attributed to the π - π stacking distance of the adjacent perylene diimide.²² In contrast with **BOPDI**, the XRD data of DFPDI displays a greater number of sharp diffraction peaks between 3-30°, with the diffraction peaks from the (100) planes appearing at $2\theta = 5.00^{\circ}$ (1.76 nm). In addition, diffraction peaks can be seen at 24.39° (0.331 nm), which can be attributed to the π - π stacking distance of PDI rings between the adjacent molecules. The d value of the (001) planes and the distance between the adjacent PFPDI molecules are comparable with those of DFPDI. This indicates that the solid state structure of 1,7-diphenoxy-substituted PDIs is dependent on the substituent group at the para-position of the phenoxy group. This is supported by comparing DFPDI and PFPDI, because where the same atom is present on the *para* position of the phenoxy group, a similar structure is observed. In the case of BOPDI, the presence of a large para substituent results in the distances of the (100) plane and π - π stacking increasing. The XRD diagram of SFDPI shows two wide diffraction peaks at $2\theta = 4.61^{\circ}$ (1.93 nm) and 23.80° (3.70 Å). The former may be related to the (100) planes, while the latter may be related to the π - π stacking distance of the adjacent perylene diimide. The wider diffraction peaks in SFPDI powder indicate that the molecular order degree in the solid decreased compared with other symmetrical PDIs, such as BOPDI, DFPDI, and PFPDI.

Finally, thermogravimetric (TGA) analysis was carried out on all four PDIs under a nitrogen atmosphere, and the thermograms are shown in Figure 8. It is clear that the thermal stability of the 1,7diphenoxy-substituted PDIs depend on the identity of the phenoxy substituents, where the 5% weight loss temperatures for **PFPDI**, **BOPDI**, **DFPDI**, and **SFPDI** were 436 °C, 422 °C, 405 °C, and 373 °C, respectively. In contrast to the other PDIs, **SFPDI** exhibited a lower thermal stability due to its structural asymmetry.



Figure 7. X-ray diffraction patterns of the PDI powders: (a) **BOPDI**, (b) **DFPDI**, (c) **PFPDI**, and (d) **SFPDI**,



Figure 8. TG curves of PFPDI, BOPDI, DFPDI, and SFPDI

3 Conclusion

We successfully synthesized a series of 1,7-diphenoxy-PDIs (perylene diimide derivatives) equipped with different substituents on one or more positions of their phenoxy moiety, and investigate the impact of structure on their photophysical, electrochemical. aggregation, and thermal properties. Intramolecular hydrogen bonds were found to restrain rotation of the PDI core. The photophysical and electrochemical properties of these species therefore depended on the quantity, position, and characteristics of the phenoxy substituents. In addition, the 1bromo-7-pentafluorophenoxy PDIs were obtained successfully via optimized reaction conditions. It is expected that our study will be useful for the development of new PDIs for use in organic photo-electronic applications.

3 Experimental Section

3.1 Materials and instrument

¹HNMR and ¹³C NMR were recorded on Bruker 400 MHz spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal reference. Infrared measurement with the KBr pellet technique was performed within the 400 to 4000 cm⁻¹ on a Perkin-Elmer spectrum 100 spectrophotometer. MS analysis was performed using an LTQ-Orbitrap XL mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an APCI ion source in the positive ion mode (scan range 150-2000 m/z). Electronic absorption spectra is performed with a Perkine Elmer Lambda 35 spectrophotometer in dichloromethane

solution and cast films. Fluorescence spectra were measured on PE LS-55 system in dichloromethane solutions and solid powder. The X-ray powder diffraction data was carried out on powered samples via Rigaku D/max-2500/PC diffraction using monochromator Cu K_a (λ =1.54 Å) over the 20 range of 2 to 50°.TGA was done with TA thermal analysisystem at heating rate 10°C/min under a N₂ environment.

Cyclic voltammetry measurements were performed in solution, under argon atmosphere with a computer controlled CHI600E electrochemical workstation in a three electrode single-compartment cell using platinum electrodes and Ag/AgCl electrode as reference electrode, with Fc/Fc* redox couple as internal standard²³, with a tetrabutyl-ammonium hexafluorophosphate (Bu₄NPF₆) solution (0.1 M) in dichloromethane at a scan rate of 0.1V/s.

3.2 Synthesis of materials

3.2.1 *N*,*N*'-diethylhexyl-1,7-dibromo perylene diimide (**BrPDI**)

Synthesis of *N*,*N*'-diethylhexyl-1,7-dibromo perylene diimide is reported earlier ²⁴. Yield: 80% ; ¹H NMR (400 MHz, CDCl₃,) δ 9.48 (d, 2H, J=8 Hz, Per-H), 8.93 (s, 2H, Per-H), 8.69 (d, 2H, J=8 Hz, Per-H), 4.10-4.20 (m, 4H, N-C<u>H₂</u>), 1.92-1.99 (m, 2H, -C<u>H</u>-), 1.32-1.41 (m, 16H, alkyl-C<u>H₂</u>), 0.93-0.97 (t, 6H, alkyl-C<u>H₃</u>), 0.88-0.91 (t, 6H, alkyl-C<u>H₃</u>), FI-IR (KBr), v: 2960 cm⁻¹, 2927 cm⁻¹, 2858 cm⁻¹, 1703 cm⁻¹, 1658 cm⁻¹, 1591 cm⁻¹, 1434 cm⁻¹, 1392 cm⁻¹, 1328 cm⁻¹, 1236 cm⁻¹, 808 cm⁻¹, 744 cm⁻¹, 684 cm⁻¹.

3.2.2 *N*,*N*'-diethylhexyl-1,7-di(p-fluorphenoxyl) perylene diimide (**PFPDI**)

A mixture of p-fluorophenol (89.6 mg, 0.8 mmol), K₂CO₃ (137 mg, 1.00 mmol) in dry dimethylformamide (50 mL), was stirred for 20 min under argon and subsequently N,N'-diethylhexyl-1,7-dibromo perylene diimide (144.4 mg, 0.20 mmol) was added. The reaction mixture was stirred for 7 h at 80 °C under argon atmosphere. After being cooled to room temperature, the solvent was removed by rotary evaporation. The solid residue was thoroughly washed with several portions of water and dried. The crude product was dissolved in dichloromethane and purified by column chromatography on silica 200-300 using dichloromethane as eluent to afford the regioisomeric mixture of product (**PFPDI**) (113 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 9.54 (d, 2H, J=8 Hz, Per-H), 8.60 (d, 2H, J=8 Hz, Per-H), 8.27 (s, 2H, Per-H), 7.15 (d, 8H, J=8 Hz, Ar-H), 4.02-4.13 (m, 4H, N-CH₂-CH-), 1.86-1.95 (m, 2H, -N-CH₂-CH-), 1.25-1.38 (m, 16H, alkyl-CH₂-CH₃), 0.89-0.93 (t, 6H, alkyl-CH₃), 0.85-0.88 (t, 6H, alkyl-CH₃). ¹³C NMR (100.6 MHz, CDCl₃) δ 163.4, 155.5, 152.6, 148.1, 133.3, 130.1, 129.2, 128.7, 127.4, 124.2, 123.2, 119.1, 54.0, 34.5, 31.4, 29.1, 26.5, 25.4. FI-IR (KBr), 2958 cm⁻¹, 2929 cm⁻¹, 2858 cm^{-1} , 1699 cm^{-1} , 1664 cm^{-1} , 1596 cm^{-1} , 1502 cm^{-1} , 1458 cm^{-1} , 1434 cm^{-1} , 1407 cm^{-1} , 1330 cm^{-1} , 1261 cm^{-1} , 1186 cm^{-1} , 856 cm^{-1} , 810 cm⁻¹,775 cm⁻¹. HRMS (EI) calcd for $C_{52}H_{48}F_2N_2O_6$: M⁺, 835.35 Fount: m/z 835.3561.

3.2.3 *N*,*N*'-diethylhexyl-1,7-di(p-tertbutylphenoxyl) perylene diimide (**BOPDI**)

BOPDI was prepared from *N*,*N*'-diethylhexyl-1,7-dibromo perylene diimide and 4-tertbutylphenol as described for the synthesis of **PFPDI**. **BOPDI** shows the brown solid with yield of 80%. ¹H NMR (400 MHz, CDCl₃) δ 9.61 (d, 2H, J=8 Hz, Per-H), 8.57 (d, 2H, J=8 Hz, Per-H), 8.34 (s, 2H, Per-H), 7.46 (d, J=12 Hz, 4H, Ar-H), 7.10 (d, 4H, J=12 Hz, Ar-H), 4.08-4.16 (m, 4H,

N-CH₂-CH-), 1.92-1.97 (m, 2<u>H</u>, -N-CH₂-C<u>H</u>-), 1.28-1.40 (m, 16H, alkyl--C<u>H₂-</u>), 0.93-0.96 (t, 6H, alkyl-C<u>H₃</u>), 0.88-0.91 (t, 6H, alkyl-C<u>H₃</u>). ¹³C NMR (100.6 MHz, CDCl₃), δ 163.5, 155.4, 133.2, 129.1, 128.8, 125.0, 123.8, 123.6, 123.3, 122.3, 121.2, 117.4, 44.3, 37.9, 30.7, 28.7, 24.1, 23.1, 14.1, 10.7. FI-IR (KBr), v: 2958 cm⁻¹, 2929 cm⁻¹, 2858 cm⁻¹, 1669 cm⁻¹, 1656 cm⁻¹, 1595 cm⁻¹, 1504 cm⁻¹, 1406 cm⁻¹, 1330 cm⁻¹, 1263 cm⁻¹, 1215 cm⁻¹, 1175 cm⁻¹, 1014 cm⁻¹, 852 cm⁻¹, 810 cm⁻¹, 557 cm⁻¹. HRMS (EI) calcd for C₆₀H₆₆N₂O₆ : M⁺, 911. 50 Fount: *m/z* 911.5009.

3.2.4 *N*,*N*'-diethylhexyl-1,7-di(pentafluorophenoxyl) perylenete diimide (**DFPDI**)

DFPDI was prepared from *N*,*N*[']-diethylhexyl-1,7-dibromo perylene diimide and pentafluorophenol as described for the synthesis of **PFPDI**. **DFPDI** shows the red solid with yield of 86%. ¹H NMR (400 MHz, CDCl₃) δ 9.44 (d, 2H, J=8 Hz, Per-H), 8.69 (d, 2H, J=8 Hz, Per-H), 8.15 (s, 2H, Per-H), 4.10-4.17 (m, 4H, N-CH₂-CH-), 1.93-1.98 (m, 2H, -CH-), 1.31-1.43 (m, 16H, alkyl-CH₃), 0.95-0.98 (t, 6H, alkyl-CH₃), 0.89-0.92 (t, 6H, alkyl-CH₃). ¹³C NMR (100.6 MHz, CDCl₃) δ 163.3, 162.7, 154.4, 138.3, 133.3, 131.8, 131.2, 129.3, 127.3, 125.1, 124.3, 123.1, 122.7, 121.8, 120.6, 118.5, 44.5, 38.0, 30.7, 28.7, 24.0, 23.0, 14.1, 10.6. FI-IR (KBr), v: 2958 cm⁻¹, 2929 cm⁻¹, 2864 cm⁻¹, 1703 cm⁻¹, 1665 cm⁻¹, 1598 cm⁻¹, 1517 cm⁻¹, 1406 cm⁻¹, 1332 cm⁻¹, 1259 cm⁻¹, 1207 cm⁻¹, 1178 cm⁻¹, 1055 cm⁻¹, 993 cm⁻¹, 810 cm⁻¹. HRMS (EI) calcd for C₅₂H₄₀F₁₀N₂O₆ : M⁺, 979. 28 Fount: *m/z* 979.2802.

2.2.5 *N*,*N*'-diethylhexyl-1-bromo-7-Pentafluorophenoxyl pery lene diimide (**SFPDI**)

SFPDI was synthesised using reaction between *N*,*N*'-diethyl -hexyl-1,7-dibromo perylene diimide and pentafluorophenol by using triethylamine instead of K₂CO₃ as the base. **SFPDI** exhibits brow solid with yield of 65%. ¹H NMR (400 MHz, CDCl₃) δ 9.65 (d, 1H, J=8 Hz, Per-H), 9.26 (d, 1H, J=8 Hz, Per-H) 8.99 (s, 1H, Per-H), 8.71(d, 1H, J=4 Hz, Per-H), 8.09 (s, 1H, Per-H), 4.07-4.18 (m, 4H, N-CH₂), 1.88-1.98 (m, 2H, -CH₂), 1.30-1.41 (m, 16H, alkyl-CH₂), 0.93-0.97 (t, 6H, -CH₂-CH₃), 0.87-0.90 (t, 6H, -CH₂-CH₃). ¹³C NMR (100.6 MHz, CDCl₃) δ 163.3, 154.3, 132.6, 130.6, 129.3, 125.4, 124.2, 122.6, 118.8, 44.5, 38.1, 30.7, 28.7, 24.1, 23.1, 14.1, 10.6. FI-IR (KBr), υ: 2956 cm⁻¹, 2929 cm⁻¹, 2860 cm⁻¹, 1701 cm⁻¹, 1658 cm⁻¹, 1593 cm⁻¹, 1517 cm⁻¹, 1450 cm⁻¹, 1334 cm⁻¹, 1658 cm⁻¹, 1184 cm⁻¹, 1041 cm⁻¹, 995 cm⁻¹, 810 cm⁻¹, 748 cm⁻¹, 696 cm⁻¹, 611 cm⁻¹. HRMS (EI) calcd for C₄₆H₄₀BrF₅N₂O₆ : M⁺, 876.20 Fount: *m*/*z* 876.2002.

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ACCEPTED MANUSCRIPT

Supplementary Material

Synthesis and properties of perylene diimide dyes bearing unsymmetrical and symmetrical phenoxy substituents at bay

positions

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	Molecular structure	HOMO (eV)	LUMO(eV)	
DFPDI	F = F $F = F$	-6.73	-4.48	HOMO→LUMO 2.3308 eV 531.94 nm f=0.7436
PFPDI		-6.78	-4.32	HOMO→LUMO 2.3280 eV 532.57 nm f=0.7315

SF1 Molecular orbital distributions and energy levels for PDIs estimated by density functional theory (DFT) calculations.



PDI λ_{gap} $E_{\rm g}^{\rm opt}$ $\lambda_{abs 0-0}$ \mathcal{E} λ_{PL} Stoks shift $(M^{-1}cm^{-1})$ (nm) (nm) (ev) (nm) (nm) BOPDI 65 600 577 572 2.14 543 34 PFPDI 539 92 000 574 35 567 2.16 DFPDI 529 101 300 557 28 552 2.25 78 100 SFPDI 528 557 552 2.25 29

ST 1 UV-Vis absorption and fluorescence properties of PDIs in dichloromethane at 298 K

ST 2 Fist half-wave reduction and oxidation potentials $E_{red}^{1/2}$ as well as E_{LUMO} and E_{HOMO} values derived for the PDIs from CV

	measurements in CH ₂ Cl ₂ solution.				
				E Y	
dye	$E_{\rm red}^{1/2}$	$E_{\rm ox}^{1/2}$	$E_{\rm LUMO}$ (ev)	$E_{\rm HOMO}$ (ev)	
DFPDI	-0.69	0.93	-4.48	-6.73	
			F	Y	
PFPDI	-0.76	1.58	-4.32	-6.78	
SFPDI	-0.61	1.88	-4.35	-6.84	
BOPDI	-0.66 ^a	1.48	-4.54	-6.99	

a Calculated from $E_{ox}^{1/2}$, and the optical gap E_{g}^{opt} : $E_{red}^{1/2}$ =-(E_{g}^{opt} - $E_{ox}^{1/2}$)