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1,6-Dinitroperylene Bisimide Dyes: Synthesis, Characterization and Photophysical Properties

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1,6- and 1,7-regioisomers of dinitro-substituted perylene bisimides (**1a**–**1b** and **2a**–**2b**) were synthesized under mild condition in high yields. The 1,6- and 1,7-regioisomers were successfully isolated from the regioisomeric mixture using conventional methods of separation and subsequently characterized by 500 MHz ^{1}H NMR spectroscopy. This is the first time when 1,6-dinitroperylene bisimides (**1a**–**1b**) are obtained in pure form. Furthermore, the photophysical and electrochemical properties of **1** and **2** were found to be almost the same. The nitro functionalities provide stability of *n*-type charge carriers by lowering the LUMO to resist ambient oxidation, which may offer potential applications in air-stable *n*-type organic semiconductors.

Keywords: 1,6-Dinitroperylene bisimide; 1,7-Dinitroperylene bisimide; Organic semiconductors; DFT calculations.

INTRODUCTION

Perylene bisimides (PBIs) and their related derivatives have attracted much attention due to their potential applications in molecular electronic and optical devices, such as organic field-effect transistors (OFETs),[1–3] light-emitting diodes,[4–5] photovoltaic cells,[6–10] LCD color filters,[11–12] photochromic materials,[13–14] molecular wires[15–16] and near-infrared absorbing materials.[17] These molecules are advantageous due to their high photochemical and optical stabilities, ease of synthetic modification and reversible redox properties.[18–38] Furthermore, the electronic characteristics of PBIs can be fine-tuned by the substitution of the conjugated aromatic core. Although organic field-effect transistors (OFETs) have been investigated for many decades, most studies have been focused on developing *p*-type semiconductors, such as pentacene and hexacene.[39–41] For the applications on organic complementary metal-oxide semiconductor (CMOS) circuits, both *p*- and *n*-type semiconductors are required. However, there are several major drawbacks in most organic *n*-type materials, such as their low on/off current ratio, low charge carrier mobility, instability in air, large barriers to electron injection, and poor solubility which hampers processes of film-casting. To date, a promising strategy is to introduce strong electron-withdrawing substituents onto the main π-chromophore by lowering its potential energy level, so that the electron charge carriers are less susceptible to oxidation. Many air-stable *n*-type organic semiconductors based on this method have been reported.[1,42] More recently, cyano-substituted PBIs were prepared with a high electron mobility of 0.1–0.6 cm^2/V·s in air.[1,43] To expand the scope of PBI-based chromophores available for designing systems for *n*-type organic semiconductors, we have synthesized a series of nitro-substituted (1-nitro and 1,7-dinitroperylene bisimides) PBIs,[44–46] since previous studies have used either halogen atoms or cyano substituents as electron-withdrawing groups. Herein, we report the synthesis and characterization of 1,6-dinitroperylene bisimides that are intense red in color and have very similar photophysical and electrochemical properties to the 1,7-dinitroperylene bisimides.

EXPERIMENTAL

Synthesis and characterization: **4a** (or **4b**) (1.8 mmol), cerium (IV) ammonium nitrate (CAN) (4.8 g, 8.8 mmol), nitric acid (8.0 g, 131.1 mmol) and dichloromethane (250 mL) were stirred at 25 °C under N_2 for 50 h. The mixture was neutralized with 10% KOH and extracted with CH_2Cl_2. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent CH_2Cl_2 to afford a mixture of 1,7- and 1,6-dinitroperylene bisimides, and ^{1}H NMR (500 MHz) analysis revealed a 3:1 ratio. Separation of the 1,6 and 1,7 isomers was performed on a preparative HPLC system equipped with a refractive index detector and fitted with a macro-HPLC column (Si, 8 μm, 250 × 22 mm). The eluent was 8:1 hexane/ethyl acetate flowing at 12 mL/min. Two fractions were collected from the column;

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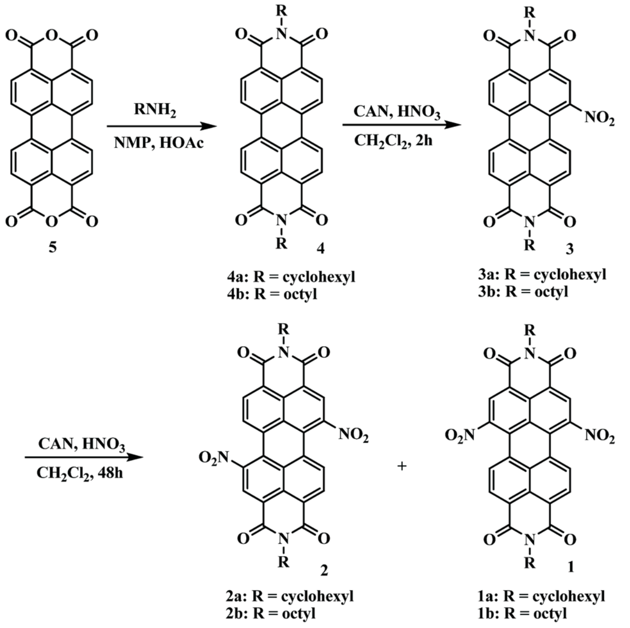
the first was pure 1,6 isomer, and the second was pure 1,7 isomer. Characterization data: **1a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.63 (d, J = 8.0 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 5.01 (m, 2H), 2.52 (m, 4H), 1.90 (m, 4H), 1.74 (m, 6H), 1.46 (m, 4H), 1.36 (m, 2H); MS (FAB): *m/z* (relative intensity) 645 ($M+H^+$, 100); HRMS calcd. for $C_{36}H_{29}O_8N_4$ 645.1985, found 645.1983. Selected data for **1b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.67 (d, J = 8.0 Hz, 2H), 8.32 (d, J = 8.0 Hz, 2H), 4.23 (m, 4H), 1.76 (m, 4H), 1.25~1.55 (m, 20H), 0.88 (t, J = 6.5, 6H); MS (FAB): *m/z* (relative intensity) 705 ($M+H^+$, 100); HRMS calcd. for $C_{40}H_{41}O_8N_4$ 705.2924, found 705.2928. Selected data for **2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 2H), 8.68 (d, J = 8.5 Hz, 2H), 8.28 (d, J = 8.5 Hz, 2H), 5.01 (m, 2H), 2.51 (m, 4H), 1.92 (m, 4H), 1.74 (m, 6H), 1.46 (m, 4H), 1.36 (m, 2H); MS (FAB): *m/z* (relative intensity) 645 ($M+H^+$, 100); HRMS calcd. for $C_{36}H_{29}O_8N_4$ 645.1985, found 645.1981. Selected data for **2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.71 (d, J = 8.0 Hz, 2H), 8.31 (d, J = 8.0 Hz, 2H), 4.20 (t, J = 7.5 Hz, 4H), 1.75 (m, 4H), 1.26~1.53 (m, 20H), 0.87 (t, J = 6.5, 6H); MS (FAB): *m/z* (relative intensity) 705 ($M+H^+$, 100); HRMS calcd. for $C_{40}H_{41}O_8N_4$ 705.2924, found 705.2923.

Scheme I The synthetic routes of **1a**–**3a** and **1b**–**3b**



RESULTS AND DISCUSSION

Scheme I shows the chemical structures of 1,6-dinitro (**1a**–**1b**) and 1,7-dinitroperylene bisimides (**2a**–**2b**) and their synthetic routes. The synthesis starts from an imidization of perylene bisanhydride (**5**) by reacting with either cyclohexylamine or octylamine. The cyclohexyl (octyl) end-capping groups increase the steric bulkiness to the periphery of molecule, so that improves the solubility without inducing a pernicious effect on the packing of molecules during the formation of solid thin films.[3] The mono-nitration can be then achieved by a reaction of perylene bisimides (**4a**–**4b**) with cerium (IV) ammonium nitrate (CAN) and HNO_3 under ambient temperature for 2 h, giving **3a**–**3b** in high yields of ca. 90%. Further nitration of **3a**–**3b** using the same reagents at ambient temperature for 48 h gave 1,6- and 1,7-dinitroperylene bisimides in 80% yield. The regioisomeric 1,6- and 1,7-dinitroperylene bisimides (**1a**–**1b** and **2a**–**2b**) can be separated by high performance liquid chromatography (HPLC). Pure 1,7-regioisomer (**2a** or **2b**) can also be obtained through repetitive crystallizations.

It is to be note that the characteristic signals of the regioisomers **1a** (1,6-) and **2a** (1,7-) in the ^{1}H NMR spectra (Fig. 1), one singlet and two doublets of perylene core protons, exhibit very small differences in the chemical shift values (0.01 and 0.04 ppm for the doublets at 8.26–8.68). However, a convenient unequivocal assignment of the NMR spectrum to the individual regioisomers **1a** (**1b**) and **2a** (**2b**) was performed on the basis of the signal of methanetriyl (methylene) protons next to the imide nitrogen at 5.01 (4.20) ppm. Because of the same chemical environment, both two methanetriyl (methylene) protons of major regioisomer **2a** (**2b**) appear as one common multiplet (triplet) at 5.01 (4.20) ppm, but the signal splits into double multiplets (triplets) for minor regioisomer **1a** (**1b**). In this way, an unambiguous characterization has been made successfully on the basis of 500 MHz ^{1}H NMR.

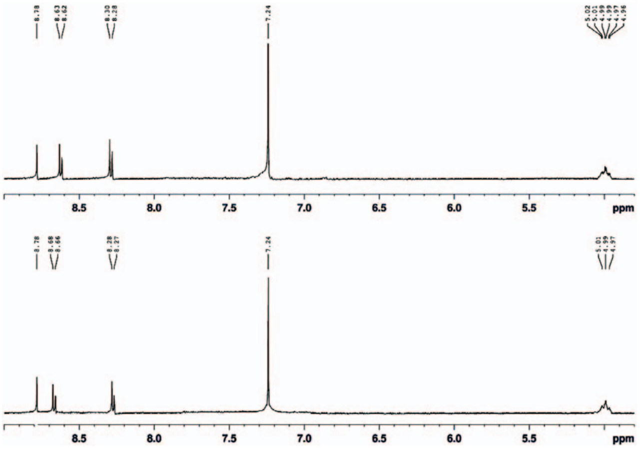


Fig. 1. ^{1}H NMR (500 MHz, $CDCl_3$) partial spectra of regioisomerically pure perylene bisimides **1a** (top) and **2a** (bottom).

Fig. 2 shows the steady state absorption spectra of **1a**–**4a** in THF. The absorption spectra of 1,6-dinitro- (**1a**), 1,7-dinitro- (**2a**) and 1-nitroperylene bisimides (**3a**) are nearly identical with the spectrum of the non-substituted perylene bisimide (**4a**), but they do not exhibit fluorescence. The longest wavelength absorption bands of **1a**–**4a** appear at 514, 515, 518, and 520 nm, respectively. These peaks are assigned to the π–π* transitions localized on the perylene core.[47] In contrast to dipyrrolidinyl-substituted (electron-donating substituted) regioisomers (1,6- and 1,7-),[48] the shapes of the absorption spectra of **1a** (1,6-dinitro) and **2a** (1,7-dinitro) are very similar in the region from about 300 nm to 600 nm. Furthermore, the vibronic progressions at 450–525 nm diminish gradually with an increasing number of the nitro groups, which can be explained by the decrease of molecular rigidity due to enhanced steric hindrance induced by the nitro groups.

The cyclic voltammograms of **1a**–**4a** are shown in Fig. 3. These molecules undergo two quasi-reversible one-electron reductions in THF at modest potentials. Table 1 summarizes the redox potentials and the HOMO and LUMO energy levels estimated from cyclic voltammetry (CV) for **1a**–**4a**. It appears that the first reduction potential is shifted toward more positive values with increasing number of substituted nitro groups, while both the HOMO and the LUMO energy levels decrease with the trend. The HOMO/LUMO energy levels of **1a**, **2a**, **3a**, and **4a** are estimated to be -6.73/-4.33, -6.75/-4.35, -6.64/-4.25, and -6.36/-3.98 eV, respectively. Note that the LUMO energy levels of **1a** and **2a** are quite similar to those of dicyano-substituted PBIs,[44] which may offer potential applications in air-stable *n*-type organic semiconductors.

Table 1. Summary of half-wave redox potentials, HOMO and LUMO energy levels for **1a**–**4a**

Compound	$E_{(1)}{}^{a}$ (V)	$E_{(2)}{}^{a}$ (V)	$E_{\mathrm{HOMO}}{}^{b}$ (eV)	$E_{\mathrm{LUMO}}{}^{b}$ (eV)
1a	-0.11	-0.37	-6.73	-4.33
2a	-0.09	-0.34	-6.75	-4.35
3a	-0.19	-0.51	-6.64	-4.25
4a	-0.46	-0.76	-6.36	-3.98

[a] Measured in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in dichloromethane versus SCE.
[b] Estimated versus vacuum level from $E_{\mathrm{LUMO}} = -4.44 - E_{(1)}$, $E_{\mathrm{HOMO}} = E_{\mathrm{LUMO}} - E_g$.

For deeper insight into the molecular structures and electronic properties of **1**–**4**, quantum chemical calculations were performed using density functional theory (DFT) at the B3LYP/6-31G** level.[49–51] The highest occupied molecular orbitals (HOMOs) and the lowest unoccu-

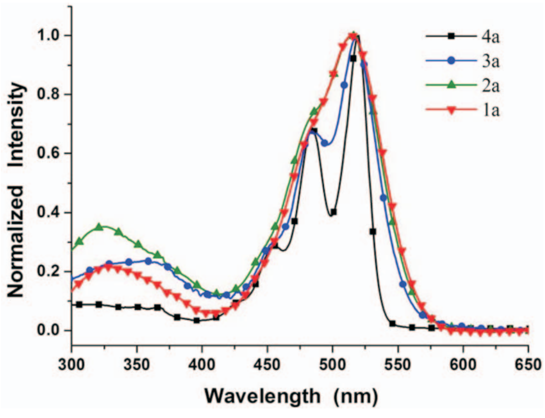


Fig. 2. Normalized absorption spectra of **1a**–**4a** in THF.

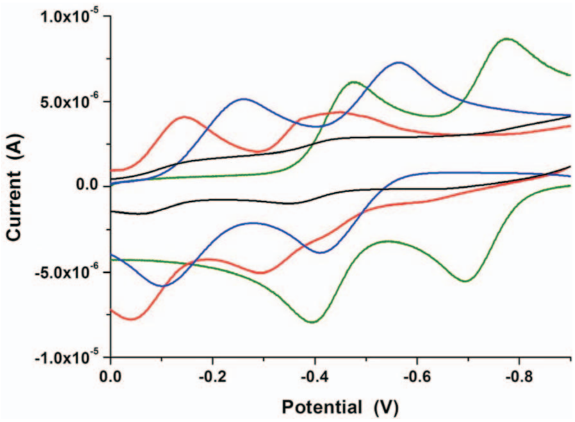


Fig. 3. The cyclic voltammograms of **4a** (green line), **3a** (blue line), **2a** (red line), and **1a** (black line) measured in THF solution, at 200 mV/s.

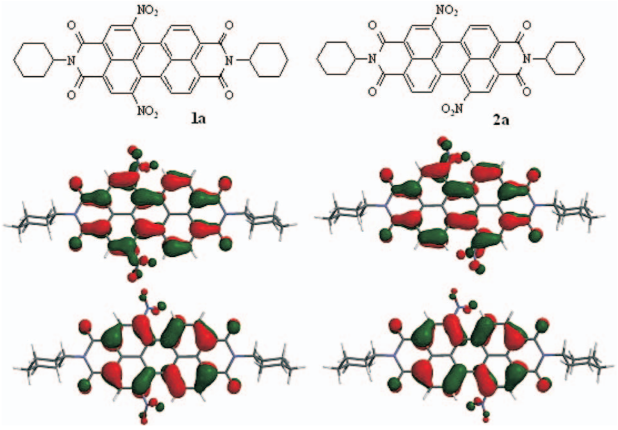


Fig. 4. Computed frontier orbitals of **1a** and **2a**. The upper graphs are the LUMOs and the lower ones are the HOMOs.

Table 2. Calculated (DFT/B3LYP) and experimental parameters

Compound	HOMO[a]	LUMO[a]	E_g[a]	E_g[b]	Twisting angle (°)[a]
1a	-6.55	-4.07	2.48	2.40	17.22, 17.34
1b	-6.58	-4.10	2.48	2.40	17.33, 17.59
2a	-6.57	-4.11	2.46	2.40	17.02, 17.12
2b	-6.60	-4.11	2.49	2.41	17.02, 17.30
3a	-6.25	-3.84	2.41	2.39	7.89, 15.87
3b	-6.29	-3.84	2.45	2.39	7.90, 16.02
4a	-5.94	-3.46	2.48	2.38	0.00, 0.00
4b	-5.97	-3.49	2.48	2.39	0.00, 0.00

[a] TDDFT/B3LYP calculated values.
[b] At absorption maxima ($E_g = 1240/\lambda_{max}$, in eV).

pied molecular orbitals (LUMOs) of **1a** and **2a** are shown in Fig. 4. The HOMO of both **1a** and **2a** is delocalized mainly on the perylene core, while the LUMO is extended from the central perylene core to the peripheral nitro and the bisimide groups. The calculated and experimental parameters are summarized in Table 2. The results reaffirm that both the HOMO and LUMO energy levels decrease as the number of nitro groups increase. In addition, DFT calculations show that the ground-state geometries of the perylene core have different core twist angles, *i.e.*, approximate dihedral angles between the two naphthalene subunits attached to the central benzene ring; these are ~17.2° and ~17.3° for **1a**, ~17.0° and ~17.1° for **2a**, and ~7.9° and ~15.9° for **3a**. The core twist angles of dinitro-substituted PBIs (**1a**–**1b** and **2a**–**2b**) are generally larger than those of mononitro-substituted PBIs (**3a**–**3b**).

CONCLUSION

To conclude, we have successfully synthesized, separated, and characterized 1,6- and 1,7-regioisomers of dinitro-substituted PBIs. The regioisomers of dinitro-substituted PBIs were separated by conventional high performance liquid chromatography. To our best knowledge, this is the first time when 1,6-dinitroperylene bisimides (**1a**–**1b**) are obtained in pure form. Our studies have also shown that these 1,6- and 1,7-isomers can readily be characterized by 500 MHz ^{1}H NMR. Moreover, the photophysical and electrochemical properties of **1a** (**1b**) and **2a** (**2b**) were found to be virtually the same. The nitro functionalities provide a higher stability of *n*-type charge carriers by lowering the LUMO to resist ambient oxidation. Working toward their applications on *n*-type organic semiconductors is in progress.

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