1,7-Dinitroperylene bisimides: facile synthesis and characterization as *n*-type organic semiconductors

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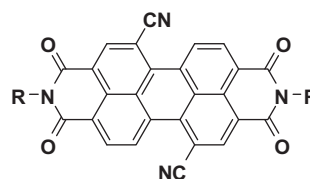
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ABSTRACT

1,7-Dinitroperylene bisimides (**1a–1b**) and 1-nitroperylene bisimides (**2a–2b**) were synthesized under mild condition in high yields, and were characterized by FT-IR, ^{1}H NMR, UV–vis, HRMS spectra, cyclic voltammetry, and thermogravimetric analyses. These compounds are stable up to 260 °C according to thermogravimetric analyses. They undergo two quasi-reversible one-electron reductions in THF at modest potentials. The nitro functionalities provide stability of *n*-type charge carriers by lowering the LUMO to resist ambient oxidation.

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Derivatives of perylene-3,4:9,10-tetracarboxylic acid bisimides have attracted much attention due to their applications in molecular electronic devices, such as organic field-effect transistors (OFETs),[1] photovoltaic cells,[2] light-emitting diodes,[3] and light-harvesting arrays.[4] The advantages of organic materials rely on their structural diversity and tunability through molecular design. Although organic thin film transistors (OTFTs) have been investigated for many years, most studies have been focused on developing *p*-type semiconductors, such as pentacene[5,6] and oligothiophenes derivatives.[7] For the applications on organic complementary metal-oxide semiconductor (CMOS) circuits, both *n*- and *p*-type semiconductors are required.[8] However, there are some major drawbacks in most organic *n*-type materials, such as their low charge carrier mobility, low on/off current ratio, instability in air, large barriers to electron injection,[9] and poor solubility which hampers processes of film-casting. Many *n*-type organic semiconductors with high electron mobility have been reported in the literatures, for example, (a) naphthalene and perylene bisimides derivatives,[10] (b) fullerene (C_{60}) and its derivatives,[11] (c) perfluorohexyl oligothiophenes (DFH-*n*T),[12] (d) tetracyanoquinodimethane (TCNQ), and 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TCNNQ),[13] etc. The OTFT devices fabricated with some of the previous *n*-type materials without strong electron-withdrawing substituents were air sensitive. The electron charge carriers were easily trapped by oxygen, leading to device degradation upon exposure to air. The development of new *n*-type organic semiconductors with both high mobility and good stability in air is a current challenge. 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. Several air-stable *n*-type organic semiconductors based on this concept have been reported.[14] More recently, cyano-substituted perylene bisimides (**PDI-CN₂** and **PDI-FCN₂**, Fig. 1) were prepared with an electron mobility of 0.1–0.6 cm^2/V s in air.[15] In this study, a series of *n*-type organic semiconductors based on perylene bisimides modified with strong electron-withdrawing nitro groups are prepared. By changing the number of the nitro substituents, the trend of molecular energy level can be investigated.

The chemical structures of compounds **1a**, **1b**, **2a**, **2b** and their synthetic routes are shown in Scheme 1. By controlling the reaction time, both mono- and di-substituted nitroperylene bisimides
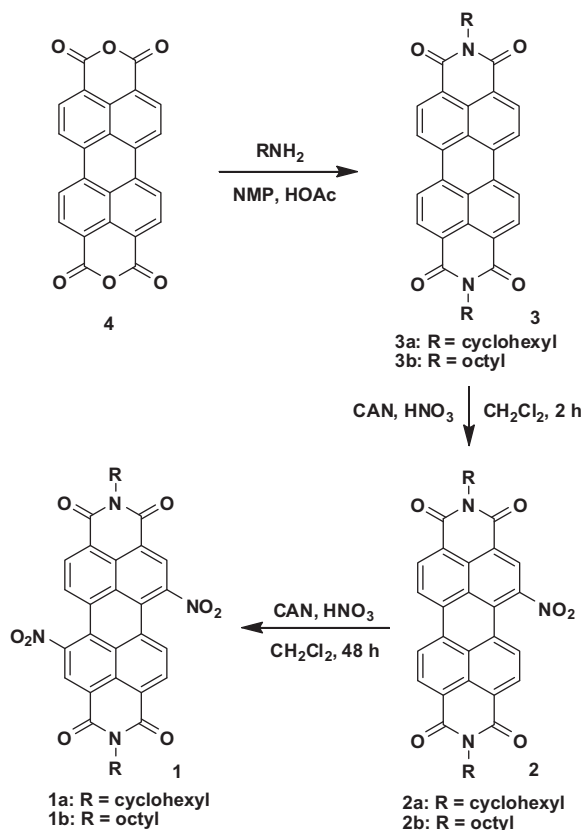
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PDI-CN₂ : R = cyclohexyl

PDI-FCN₂ : R = *n*-CH₂C₃F₇

Figure 1. The structures of **PDI-CN₂** and **PDI-FCN₂**.

Scheme 1. The synthetic routes of **2a–2b** and **1a–1b**.

can be obtained. The synthesis starts from an imidization of perylene bisanhydride (**4**) by reacting with either cyclohexylamine or octylamine. The cyclohexyl end-capping groups increase the steric bulkiness to the periphery of molecule, so that the solubility can be improved without inducing a detrimental effect on the packing of molecules during the formation of solid thin films.[16] The mono-nitration can be achieved by a reaction of perylene bisimides (**3a–3b**) with cerium (IV) ammonium nitrate (CAN) and HNO_3 (or H_2SO_4) under ambient temperature for 2 h,[17] giving **2a–2b** in high yields of ca. 90%. The presence of a single nitro substituent can be verified by the presence of seven signals at δ 8.1–8.8 ppm in ^{1}H NMR spectrum and the strong absorption at 1539 cm^{-1} in FT-IR
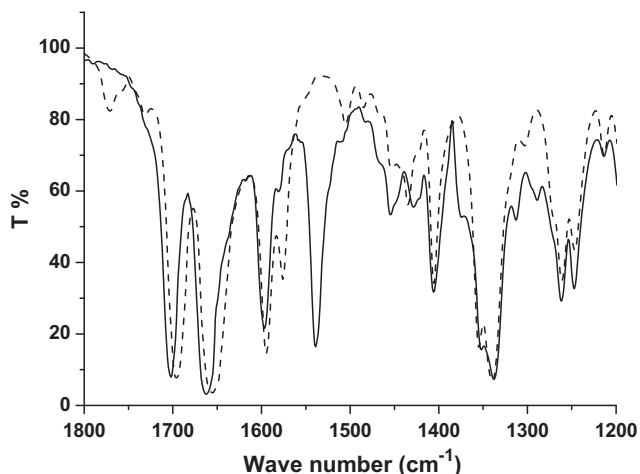
spectrum, corresponding to an asymmetrical stretching of the nitro group (Fig. 2).[18]

Further nitration of **2a–2b** using the same reagents at ambient temperature for 48 h gave **1a–1b** (1,7-dinitro) in 60% yield.[19] Among the products, a 3:1 mixture of regioisomers (nitrated at the 1,7- or 1,6-positions) were observed by ^{1}H NMR spectroscopy, a situation analogous to the result of bromination described previously by Rybtchinski and co-workers.[20] Pure 1,7-regioisomer (**1a** or **1b**) can be obtained through repetitive crystallizations.

The steady state absorption spectra of **1a–3a** in THF are shown in Figure 3, where those of **1b–3b** can be found in the Supplementary data. The longest wavelength absorption bands of **1a–3a** appear at 515, 518, and 520 nm, respectively. These peaks are assigned to the π–π^* transitions localized on the perylene core (Fig. 4).[21] The vibronic progressions at 450–525 nm diminish gradually with an increasing number of the nitro groups (Supplementary data). The phenomenon can be explained by the decrease of molecular rigidity due to enhanced steric hindrance induced by the nitro groups.

To gain insight into the electronic properties of **1a–3a**, **1b–3b,** and **PDI-CN$_2$**, quantum mechanical calculations were performed using density functional theory (DFT) at the B3LYP/6-31G** level.[22] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1a** are shown in Figure 4. The HOMO in **1a** 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 1. The results indicate that both the HOMO and LUMO energy levels decrease as the number of nitro groups increase. The calculated LUMO energy levels of **1a** are similar to those of **PDI-CN$_2$**. It is believed that these nitro-substituted derivatives should be air-stable n-type organic semiconductors, quite like their cyano-counterparts, that is, **PDI-CN$_2$** and **PDI-FCN$_2$**.

The cyclic voltammograms of **3a**, **2a,** and **1a** with no, mono and di-nitro substituents are illustrated in Figure 5. These chromophores undergo two quasi-reversible one-electron reductions in THF at modest potentials. Table 2 summarizes the optical absorption peaks obtained in THF solutions and the LUMO energy levels estimated from cyclic voltammetry (CV) for **1a–3a**, **1b–3b**, and **PDI-CN$_2$**.[22] It appears that the first reduction potential is shifted toward more positive values with increasing number of substituted nitro groups, while the LUMO energy level decreases along the trend. The LUMO levels of compounds **3a** (**3b**), **2a** (**2b**), and **1a** (**1b**) are estimated to be −3.98 (−3.99), −4.25 (−4.26), and −4.35

Figure 2. FT-IR spectra of **3a** (dashed line) and **2a** (solid line).
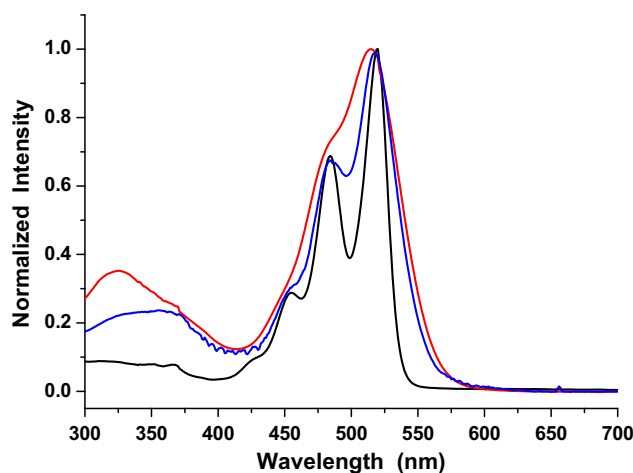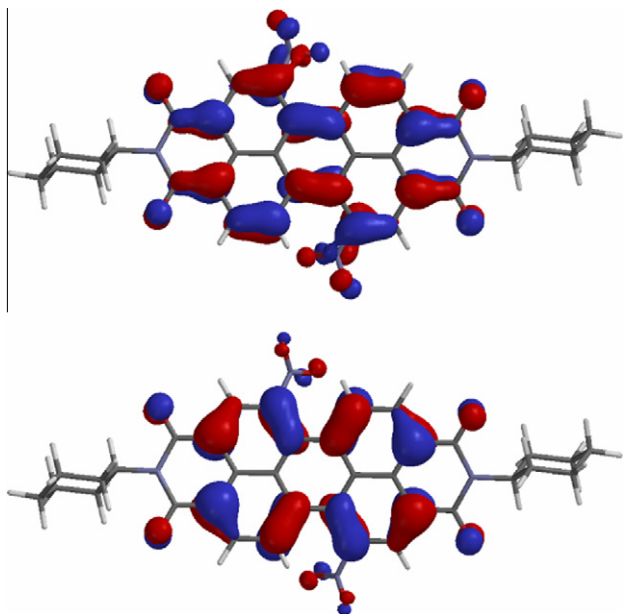

Figure 3. Normalized absorption spectra of **3a** (black line), **2a** (blue line) and **1a** (red line) in THF solution (2×10^{-4} M).

**Figure 4.** The HOMO (bottom) and LUMO (top) of **1a** calculated at by DFT at B3LYP/6-31G** level.

Table 1
Calculated and experimental parameters for perylene bisimide derivatives **1a–3a**, **1b–3b**, and **PDI-CN₂**

Compound	HOMO[a] (eV)	LUMO[a] (eV)	E_g[a] (eV)	E_g[b] (eV)
3a	−5.94	−3.46	2.48	2.38
3b	−5.97	−3.49	2.48	2.39
2a	−6.25	−3.84	2.41	2.39
2b	−6.29	−3.84	2.45	2.39
1a	−6.57	−4.11	2.46	2.40
1b	−6.61	−4.13	2.48	2.41
PDI-CN₂[c]	−6.52	−4.09	2.43	2.34

[a] Calculated by DFT/B3LYP.
[b] At absorption maxima ($E_g = 1240/\lambda_{max}$).
[c] Ref. 15.
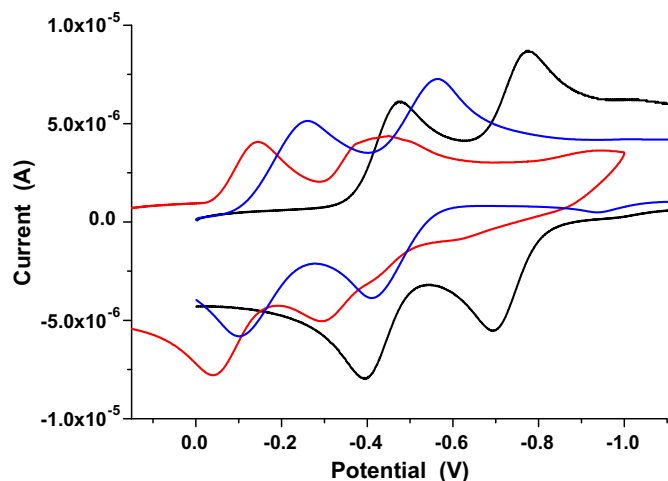
Figure 5. The cyclic voltammograms of **3a** (black line), **2a** (blue line), and **1a** (red line) measured in THF solution, at 200 mV/s.

(−4.35) eV, respectively. Compared to the unsubstituted perylene bisimides **3a**, the LUMO of **2a** is lowered by an amount of 0.27 eV and that of **1a** by 0.37 eV. Both the LUMO and the longest

Table 2
Summary of optical absorption wavelengths, reduction potentials, and LUMO energy levels for perylene bisimide derivatives

Compound	λ_{abs}[a] (nm)/(ϵ (M^{-1} cm^{-1}))	$E_{(1)}$[b] (V)	$E_{(2)}$[b] (V)	LUMO[c] (eV)
3a	520 (68600)	−0.46	−0.76	−3.98
3b	519 (66000)	−0.45	−0.73	−3.99
2a	518 (62400)	−0.19	−0.51	−4.25
2b	518 (58000)	−0.18	−0.49	−4.26
1a	515 (54200)	−0.09	−0.34	−4.35
1b	514 (51000)	−0.09	−0.33	−4.35
PDI-CN₂[d]	530	−0.07	−0.40	−4.37

[a] Measured in THF (2×10^{-5} M).
[b] Measured in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in THF versus SCE.
[c] Estimated versus vacuum level from $E_{LUMO} = -4.44$ eV − $E_{(1)}$.[23]
[d] Ref. 15.
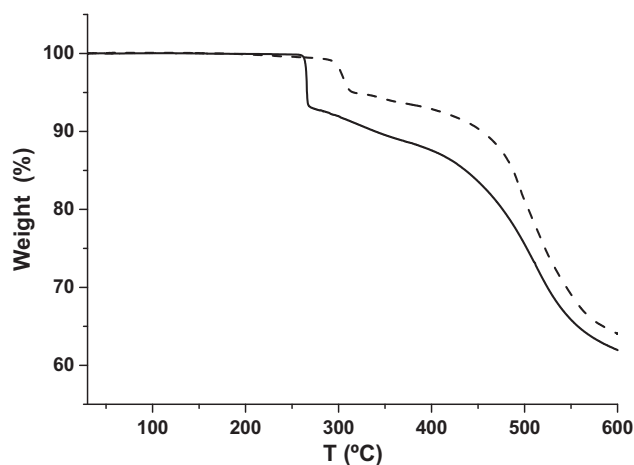
Figure 6. Thermogravimetric analysis graphs for **1a** (solid line) and **2a** (dashed line) in nitrogen atmosphere at normal pressure. Heating rate, 10 °C/min.

absorption maximum of **1a** are similar to the corresponding parameters of **PDI-CN₂**, that is, −4.37 eV and 530 nm. It is apparent that the electrochemical as well as the photophysical properties of **1a** and **1b** are a close resemblance to those of **PDI-CN₂**. The lowering of the LUMOs by multiple nitration suggests an increase of anion stability against oxidation along with an increased number of nitro groups.

Thermogravimetric analysis of compounds **1a** and **2a** are presented in Figure 6. The decomposition temperature of **1a** is 260 °C and that of **2a** is 300 °C, yet both are lower than that of **3a** (~400 °C).[24] The weight loss of about 7% for both **1a** and **2a** is in good agreement with the theoretical calculations of 7.1% and 7.7%, respectively, and is plausibly ascribed to the fragmentation of nitro group. The decomposition of **2a** was further confirmed by FT-IR spectrum. The strong absorption peak at 1539 cm⁻¹, corresponding to the nitro stretching of **2a**, disappeared completely upon heating. The most probable mechanism of fragmentation at high temperature should have started at a C–NO₂ bond scission, because this step has been predicted as the most feasible pathway in a series of nitro-substituted compounds.[25] It also complies well with the relative stability of **3a** > **2a** > **1a**.

In summary, we have successfully synthesized a new series of nitro-substituted perylene bisimides, that is, 1-nitroperylene bisimides (**2a–2b**) and 1,7-dinitroperylene bisimides (**1a–1b**). These molecules undergo two quasi-reversible one-electron reductions in THF at modest potentials. Their first reduction potential is shifted toward more positive values with an increasing number of substituted nitro groups, and consequently the LUMO energy

level decreases along the trend. 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 field-effect transistors is in progress.

Acknowledgment

Supplementary data

Supplementary data (^{1}H NMR spectra of **1a**–**1b** and **2a**–**2b**; absorption spectra of **1b**–**3b** in THF; absorption spectra of **1a** and **2a** in THF under different concentrations) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.029.

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18. *General procedure for nitration*: **3a** (or **3b**) (1.8 mmol), cerium (IV) ammonium nitrate (CAN) (1.2 g, 2.2 mmol), nitric acid (2.0 g, 31.7 mmol) and dichloromethane (150 ml) were stirred at 25 °C under N_2 for 2 h. The mixture was neutralized with 10% KOH and extracted with CH_2Cl_2. After the solvent was removed, the crude product was purified by silica gel column chromatography with the eluent CH_2Cl_2 to afford **2a** (or **2b**) in 95% yield. *Characterization data*: **2a**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.74 (d, *J* = 7.6 Hz, 1H), 8.62–8.69 (m, 4H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 5.00 (m, 2H), 2.54 (m, 4H), 1.91 (m, 4H), 1.76 (m, 6H), 1.47 (m, 4H), 1.34 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.40, 163.10, 163.00, 162.11, 147.60, 135.32, 132.78, 132.68, 131.20, 131.01, 129.25, 129.21, 128.87, 127.81, 127.40, 126.44, 126.40, 126.34, 126.19, 125.32, 124.59, 124.35, 123.89, 123.52, 54.46, 54.21, 29.06, 29.00, 26.45, 26.41, 25.34, 25.29; IR (KBr): 2928, 2851, 1700, 1659, 1596, 1539, 1401, 1336, 1262, 1245, 1190, 809, 743 cm^{-1}; MS (FAB): *m/z* (relative intensity) 600 (M+H$^+$, 100); HRMS calcd for $C_{36}H_{30}O_6N_3$ 600.2135, found 600.2141. Selected data for **2b**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.73–8.67 (m, 4H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 4.19 (m, 4H), 1.76 (m, 4H), 1.26–1.54 (m, 20H), 0.87 (t, *J* = 6.5, 6H); MS (FAB): *m/z* (relative intensity) 660 (M+H$^+$, 100); HRMS calcd for $C_{40}H_{42}O_6N_3$ 660.3074, found 660.3076.
19. *General procedure for nitration*: **2a** (or **2b**) (1.7 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 48 h. The mixture was neutralized with 10% KOH and extracted with CH_2Cl_2. After the solvent was removed, the crude product was purified by silica gel column chromatography with the 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. The regioisomeric 1,7- and 1,6-dinitroperylene bisimides could not be separated by column chromatography. Regioisomerically pure 1,7-dinitroperylene bisimides was obtained by repetitive crystallization. *Characterization data*: **1a**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.78 (s, 2H), 8.67 (d, *J* = 8.5 Hz, 2H), 8.28 (d, *J* = 8.5 Hz, 2H), 4.99 (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 **1b**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.82 (s, 2H), 8.71 (d, *J* = 8.0 Hz, 2H), 8.30 (d, *J* = 8.0 Hz, 2H), 4.20 (m, 4H), 1.75 (m, 4H), 1.26–1.53 (m, 20H), 0.87 (t, *J* = 6.5, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.97, 161.46, 148.29, 132.57, 130.36, 129.60, 128.67, 127.56, 126.30, 125.58, 124.53, 124.44, 41.06, 31.72, 29.19, 29.10, 27.96, 26.98, 22.55, 13.99; 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.
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