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Low Band Gap Thiophene−Perylene Diimide Systems with Tunable Charge Transport Properties

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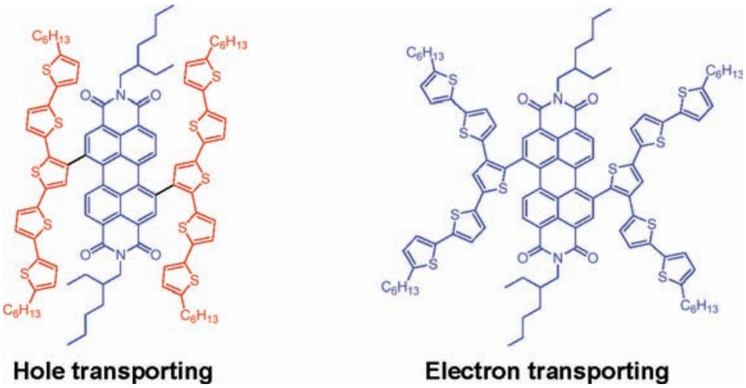
ABSTRACT



Perylenediimide−pentathiophene systems with varied architecture of thiophene units were synthesized. The photophysical, electrochemical, and charge transport behavior of the synthesized compounds were studied. Both molecules showed a low band gap of ∼1.4 eV. Surprisingly, the molecule with pentathiophene attached *via β*-position to the PDI unit upon annealing showed a predominant hole mobility of 1×10^{-4} cm^2 V^{-1} s^{-1} whereas the compound with branched pentathiophene attached *via β*-position showed an electron mobility of 9.8×10^{-7} cm^2 V^{-1} s^{-1}. This suggests that charge transport properties can be tuned by simply varying the architecture of pentathiophene units.

Donor−acceptor conjugated molecules have gained tremendous scientific interest due to their unique optoelectronic properties and have been successfully employed in applications such as organic field effect transistors, light-emitting diodes, and photovoltaic devices.[1] Perylene diimide (PDI) belongs to the class of n-type semiconductors which exhibits high molar extinction coefficients and high electron mobility.[2] Significant research efforts have been focused on the modification of PDI structures to improve their optoelectronic and charge transport properties.[3] The bay substitution of PDI is an easy approach to fine-tune the properties of PDI by modifying its frontier orbital energy levels.[3] Oligothiophenes are a well-known class of donor moieties with excellent

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(1) (a) Roncali, J. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: NewYork, 1998; Chapter *12*. (b) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1685.

(2) (a) Ford, W. E.; Kamat, P. V. *J. Phys. Chem.* **1987**, *91*, 6373. (b) Quante, H.; Geerts, Y.; Müllen, K. *Chem. Mater.* **1997**, *9*, 495. (c) Thelakkat, M.; Pösch, P.; Schmidt, H.-W. *Macromolecules* **2001**, *34*, 7441.

(3) (a) Delgado, M. C. R.; Kim, E.-G.; Filho, D. A. S.; Bredas, J.-L. *J. Am. Chem. Soc.* **2010**, *132*, 3375. (b) Scholz, M.; Schmidt, R.; Krause, S.; Schöll, A.; Reinert, F.; Würthner, F. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *95*, 285. (c) Liang, B.; Zhang, Y.; Wang, Y.; Xu, W.; Li, X. *J. Mol. Struct.* **2009**, *917*, 133. (d) Ahrens, M. J.; Fuller, M. J.; Wasielewski, M. R. *Chem. Mater.* **2003**, *15*, 2648.

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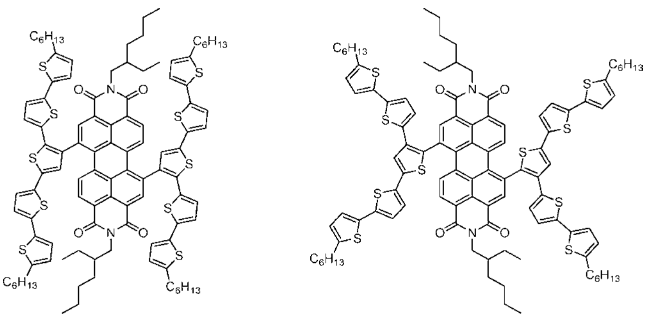
charge transport properties and have been used as the active material in organic electronic devices.[4] Understandably, when considering donor−acceptor systems, oligothiophenes attached to PDI molecules have been the focus of many studies.[5] Among the oligothiophenes, pentathiophene absorbs in the spectral region where the PDI absorption is minimum and the fluorescence of pentathiophene overlaps well with the absorption of PDI, which makes the PDI−pentathiophene pair a favorable system for effective light harvesting and a photoinduced electron transfer process.[6] In our previous work, we studied the effect of substituents on the electron transport properties of bay substituted PDI derivatives.[7] More recently, the color tuning in PDI−terthiophene systems with varied architecture of thiophene units has been reported in the literature.[8] In our work here, unlike the conventional D−A−D systems, we have designed and synthesized D−A−D systems **1** and **2** with restricted conjugation. Hence, they are expected to interact *via* an energy transfer process (pentathiophenes interact well with PDI units)[6] which does not require conjugation. More specifically, we were interested in investigating which of these molecules exhibit low band gap features, while allowing for tuning the charge transport properties.

The structures of the targeted molecules are shown in Figure 1. In molecule **1**, the linear pentathiophene units are attached to the bay position of the PDI moiety *via* the central thiophene unit through a β linkage, leading to a cross conjugated D−A−D system. Whereas in molecule **2** the donor unit (pentathiophene) is cross conjugated and attached to PDI through a central thiophene through an α linkage.

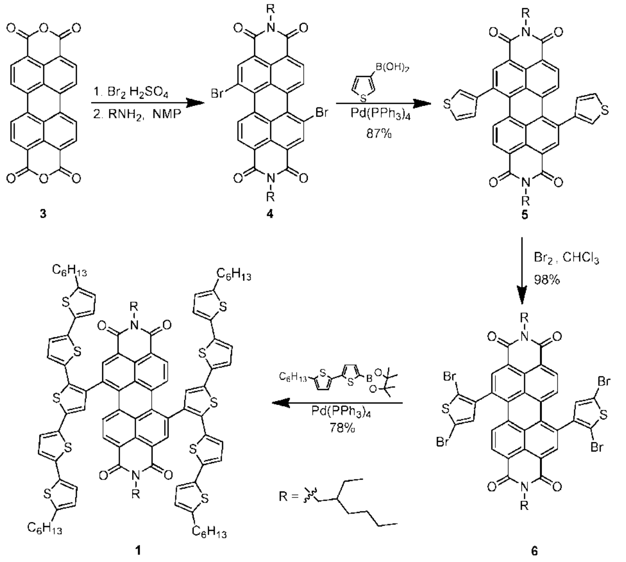


1 **2**

Figure 1. Chemical structure of PDI−pentathiophene compounds **1** and **2**.

Syntheses of target compounds **1** and **2** are depicted in Schemes 1 and 2, respectively. *N*,*N*′-Bis(2-ethylhexyl)-1,7-dibromoperylenediimide (**4**) was synthesized from 3,4,9,10-perylenetetracarboxylic acid anhydride following a procedure reported earlier.[7] The dibromo compound **4** was reacted with 3-thiopheneboronic acid by a Suzuki coupling reaction to get compound **5** in 87% yield. The compound **5** was effectively brominated under $Br_2/CHCl_3$ conditions to obtain the tetrabrominated product **6**. This product upon Suzuki coupling with 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester yielded the target compound **1** in 78% yield (Scheme 1).

Scheme 1. Synthesis of Compound **1**



Compound **2** was obtained from **4** following a similar procedure. In this scheme compound **4** was coupled under Suzuki conditions with 2-thiopheneboronic acid to afford compound **7**,[5a] followed by tetrabromination to obtain compound **8**. Compound **8**, upon a final Suzuki coupling with 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester, yielded the target compound **2** with an overall yield of ∼45% (Scheme 2). The synthesized molecules are highly soluble in common organic solvents such as dichloromethane, chloroform, and THF.

The absorption spectra of **1** and **2** in solution (chloroform) are shown in Figure 2. Both **1** and **2** showed two absorption maxima with a weak low energy absorption band around 650 nm. The absorption spectrum of α-linked **2** is blue-shifted compared to the β-linked compound **1**. This may be due to the branched nature of the thiophene segment, which prevents the effective conjugation of the pentathiophene unit.[9] The peak around 500 nm can be assigned to the PDI-based transition. The high energy peak at 426 nm for **1** and 340 nm for **2** can be assigned to the thiophene centered transition (terthiophene $\lambda_{max} = 354$ nm, pentathiophene $\lambda_{max} = 428$ nm),[10] and the weak low energy absorption to the thiophene−PDI charge transfer band.[11] While PDI itself exhibits

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[4] (a) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999. (b) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev* **2009**, *109*, 1141.

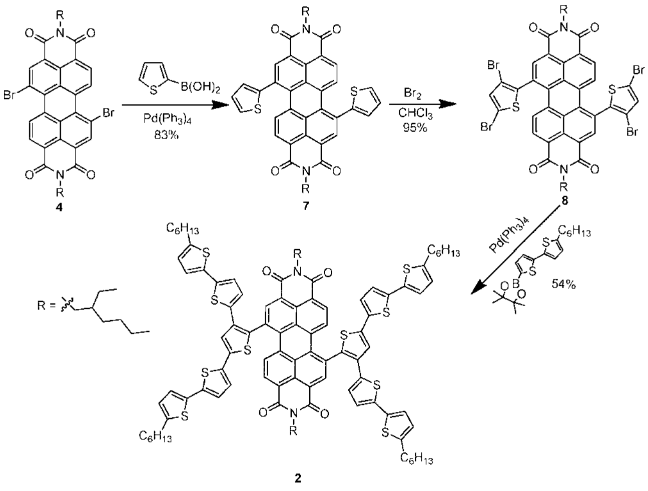
[5] (a) Chen, S.; Liu, Y.; Qiu, W.; Sun, X.; Ma, Y.; Zhu, D. *Chem. Mater.* **2005**, *17*, 2208. (b) Huang, J.; Fu, H.; Wu, Y.; Chen, S.; Shen, F.; Zhao, X.; Liu, Y.; Yao, J. *J. Phys. Chem. C* **2008**, *112*, 2689.

[6] Fujitsuka, M.; Harada, K.; Sugimoto, A.; Majima, T. *J. Phys. Chem. A* **2008**, *112*, 10193.

[7] (a) Vajiravelu, S.; Ramunas, L.; Vidas, G. J.; Valentas, G.; Vygintas, J.; Valiyaveettil, S. *J. Mater. Chem.* **2009**, *19*, 4268. (b) Sivamurugan, V.; Kazlauskas, K.; Jursenas, S.; Gruodis, A.; Simokaitiene, J.; Grazulevicius, J. V.; Valiyaveettil, S. *J. Phys. Chem. B* **2010**, *114*, 1782.

[8] Wonneberger, H.; Ma, C.-Q.; Gatys, M. A.; Li, C.; Bäuerle, P.; Müllen, K. *J. Phys. Chem. B* **2010**, *114*, 14343.

Scheme 2. Synthesis of Compound **2**



significant fluorescence ($\Phi_F = 0.95$),[5b] neither **1** nor **2** exhibits any fluorescence. This is attributed to the possible photoinduced intramolecular electron transfer between the oligothiophene moiety and the perylene core.[6]

The electrochemical properties were investigated by cyclic voltammetry. Both compounds **1** and **2** showed ambipolar redox behavior (Figure S2). During the positive potential sweep, **1** and **2** showed two reversible oxidation peaks corresponding to the oxidation of thiophene units.[12] In the negative potential regime, two characteristic reversible reduction waves of the PDI moiety were observed. The HOMO and LUMO energy levels were determined from oxidation and reduction onset potentials, respectively, and their values are summarized in Table 1.

Interestingly, **1** and **2** possess similar energy gaps (E_g) of 1.38 and 1.36 eV respectively, even as the positions of HOMO and LUMO levels were different. In compound **1**, the HOMO energy level resembles that of pentathiophene while the LUMO level resembles that of PDI due to the effective decoupling of these two functionalities.[12,13] This is supported by the calculated frontier molecular orbitals by density functional theory (Figure 3).

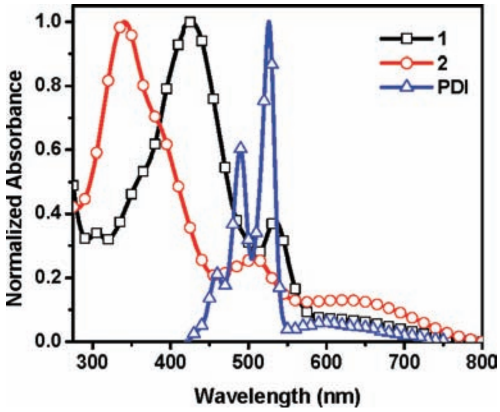


Figure 2. Absorption spectra of PDI−pentathiophene compounds **1**, **2**, and PDI in chlorofom at room temperature.

Table 1. Optoelectronic Properties of Compounds **1** and **2**

compd	λ^a_{max} (nm)	E^b_{oxid} (V)	E^b_{red} (V)	HOMO^c (eV)	LUMO^d (eV)	E_g^e (eV)
1	426, 534	0.64, 0.51	−1.08, −1.38	−5.18	−3.80	1.38
2	340, 508	0.74, 0.61	−1.01, −1.20	−5.29	−3.93	1.36

[a] Recorded in chloroform. [b] Versus Ferrocene in 0.1 M Bu$_4$NPF$_6$ in dichloromethane, platinum disk as working electrode with a scan rate of 100 mV s^{-1}. [c] Calculated using the relationship $E_{HOMO} = -(E_{oxi}^{onset} + 4.8)$. [d] Calculated using the relationship $E_{LUMO} = -(E_{red}^{onset} - 4.8)$. [e] Electrochemical.

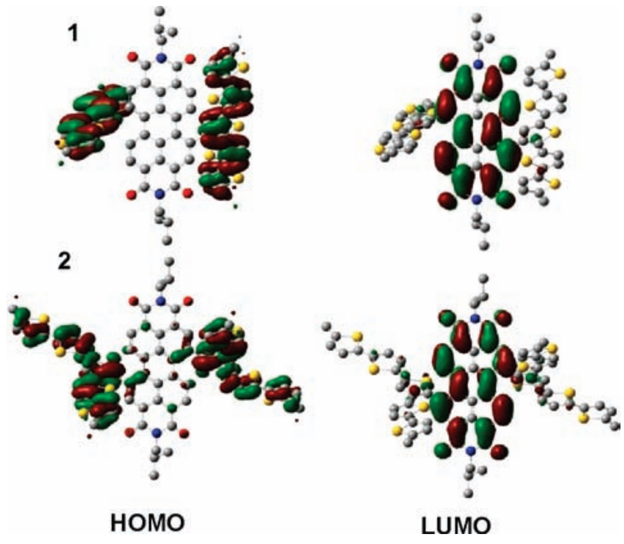


Figure 3. Optimized geometric structure of compounds **1** and **2** and their frontier orbitals were calculated by density functional theory (DFT) at the BLYP/3-21G level.

On the other hand, the HOMO and LUMO energy levels are both lowered in the case of **2**. We resorted to DFT calculations to rationalize this experimental observation. The DFT calculations showed a subtle distribution of HOMO lobes on the PDI units and LUMO lobes on the thiophene units, which is not present in compound **1** (Figure 3). We speculate that, in the absence of an alternate explanation, this leakage in electron density stabilizes the frontier molecular orbitals in **2**.

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(9) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C.; Gies, A.; Nonides, W. *J. Am. Chem. Soc.* **2004**, *126*, 8735.

(10) (a) Oliva, M. M.; Pappenfus, T. M.; Helby, J. H.; Schwaderer, K. M.; Johnson, J. C.; McGee, K. A.; Filho, D. A. S. F.; Bredas, J. -L.; Casado, J.; Navarrete, J. T. L. *Chem.—Eur. J.* **2010**, *16*, 6866. (b) Becker, R. S.; de Melo, J. S.; Maçanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683.

(11) Zhan, X.; Tan, Z.; Zhou, E.; Li, Y.; Misra, R.; Grant, A.; Domercq, B.; Zhang, X.-H.; An, Z.; Zhang, X.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem* **2009**, *19*, 5794.

(12) Zen, A.; Bilge, A.; Galbrecht, F.; Alle, R.; Meerholz, K.; Grenzer, J.; Neher, D.; Scherf, U.; Farrell, T. *J. Am. Chem. Soc.* **2006**, *128*, 3914.

(13) Li, C.; Schöneboom, J.; Liu, Z.; Pschirer, N. G.; Erk, P.; Herrmann, A.; Müllen, K. *Chem.—Eur. J.* **2009**, *15*, 878.

Next, we were interested in analyzing the charge transport characteristics of these molecules. Bottom contact field effect transistors were fabricated by spin coating the compounds from 1 wt % solution in chlorobenzene on prepatterned substrates. Thermal annealing was carried out under an inert atmosphere at 80 °C for 1 h. The channel width and channel length of the transistors were 10 mm and 5 μm, respectively. Output characteristics of these transistors are as shown in Figure 4. The charge transport properties are summarized in Table 2. In as cast films, **1** showed ambipolar behavior with an electron mobility of 2.23×10^{-7} cm^2 V^{-1} s^{-1} and hole mobility of 6.85×10^{-6} cm^2 V^{-1} s^{-1}. The compound **2** showed only electron transport behavior which is expected for the PDI-based systems, with an electron mobility of 6.21×10^{-7} cm^2 V^{-1} s^{-1}.

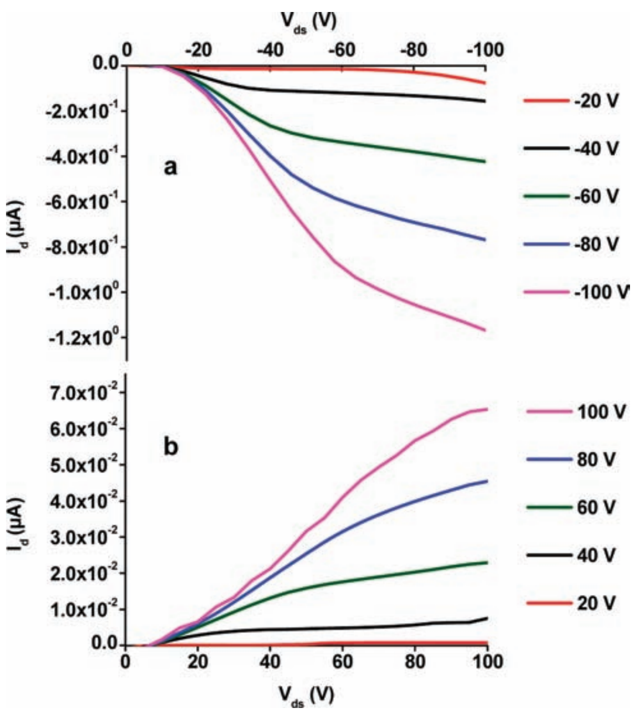

Figure 4. Output characteristics of bottom contact field effect transistors (a) **1** and (b) **2** at $W/L = 2000$.

Table 2. Mobility Data of Compound **1** and **2**

		mobility (cm^2 V^{-1} s^{-1})	
compd	charge	beforeannealing	afterannealing
1	hole	6.85×10^{-6}	1.04×10^{-4}
	electron	2.23×10^{-7}	9.13×10^{-8}
2	electron	6.21×10^{-7}	9.83×10^{-7}

The PDI−thiophene-based systems generally show electron transporting behavior.[14] The predominantly hole transporting feature of **1** is unusual for PDI-based systems. In compound **1** the PDI unit is buried between the pentathiophene chains which are not in plane with the PDI unit (Figures 3 and S4). As a result of this, the interaction of PDI units with adjacent molecules is likely to be restricted and the mobility is dominated by thiophene units. Upon annealing, the hole mobility of **1** increases to 1.04×10^{-4} cm^2 V^{-1} s^{-1} and the electron mobility decreases to 9.13×10^{-8} cm^2 V^{-1} s^{-1}, which is attributed to the better ordering of pentathiophene units terminated with hexyl chains resulting in a more effective isolation of PDI units. Annealing has marginal effect on the transport behavior of **2**.

The low electron mobility of **2**, compared to other reported systems,[11] can be attributed to the branched nature of the side chain, which is expected to affect the packing of the molecules.

In summary, we have synthesized highly stable and soluble PDI−thiophene systems with varied thiophene architecture. Such variations provide the ability to tune the charge transport properties, while retaining the advantage of lowering the band gap. Photovoltaic studies of these molecules are currently underway in our laboratory.

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Supporting Information Available: Experimental procedures, cyclic voltammograms, AFM images of all compounds, and BLYP calculated structures of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 7246.