Oligothiophene-Functionalized Perylene Bisimide System: Synthesis, Characterization, and Electrochemical Polymerization Properties

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The novel perylene bisimides functionalized with oligothiophene substituents in the bay position of the perylene core *N*,*N*′-di(2-ethylhexyl)-1,7-di(thiophen-2-yl)perylene-3,4,9,10-tetracarboxylic acid bisimide (**2a**), *N*,*N*′-di(2-ethylhexyl)-1,7-di[(2,2′)bithiophen-5-yl]perylene-3,4,9,10-tetracarboxylic acid bisimide (**2b**), and *N*,*N*′-di(2-ethylhexyl)-1,7-di[(2,2′;5′,2″)terthiophen-5-yl]perylene-3,4,9,10-tetracarboxylic acid bisimide (**2c**) have been synthesized and fully characterized. As compared to the unsubstituted perylene bisimide (**3**), the UV−vis absorptions of **2a**−**c** undergo a bathochromic shift along with considerable band broadening and a less pronounced vibronic fine structure. Moreover, efficient intramolecular electron transfer between the oligothiophene-donor and perylene-acceptor leads to remarkable fluorescence quenching of the perylene core. Cyclic voltammetry measurements of these compounds were performed and corresponding polymers from the monomers **2b** and **2c** were prepared by electrochemical polymerization. Both oligomers and polymers possess a facile reductive process, and their oxidation potential can be tuned by variation of the number of thiophene groups. These properties make them promising materials for optoelectrical devices such as molecular switches, solar energy harvesters, and supercapacitors for energy storage.

Introduction

In recent years, donor−acceptor conjugated complexes or oligomers have attracted intense scientific investigation due to their unique optical and electrical properties with potential applications in many fields such as molecular electronics, optoelectronics, and artificial photosynthetic systems.[1] Perylene bisimides represent a class of highly thermostable n-type semiconductors with relatively high electron affinity and excellent transport property. More and more attention has been focused on the modification of perylene bisimide structures through high-yield synthetic routes to improve their chemical and physical properties.[2] These molecules and their derivatives have been used not only as building blocks for electronics and optoelectronics devices such as organic light-emitting diodes,[2f,g,3] light-harvesting arrays,[4] photovoltaic cells[5] but also for studying the photoinduced energy and electron-transfer process.[6]

Thiophenes or oligothiophenes are commonly employed as electron-donating moieties with various substitution patterns, which often represent the best choice because they are electron-rich subunits with special intrinsic physical properties and numerous chemical transformations. Thiophene-based electronic materials are of much interest due to their environmental and thermal stability and potential applications in many fields such as electrical conductors, nonlinear optical devices, solar cells, energy storage batteries, and field-effect transistors.[7] Although much research has been investigated in the systems based on oligothiophene as the donor or perylene as the acceptor, few papers were reported on the oligothiophene−perylene system. The donor−acceptor sys-

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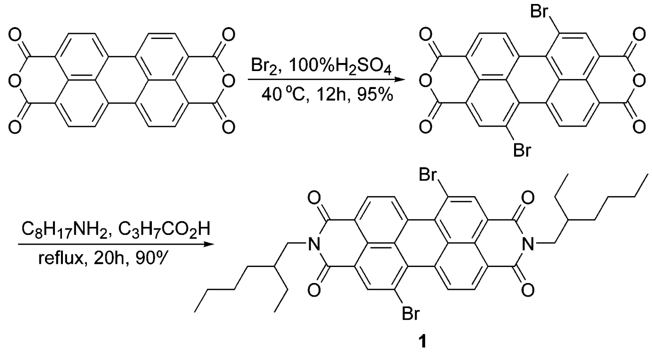
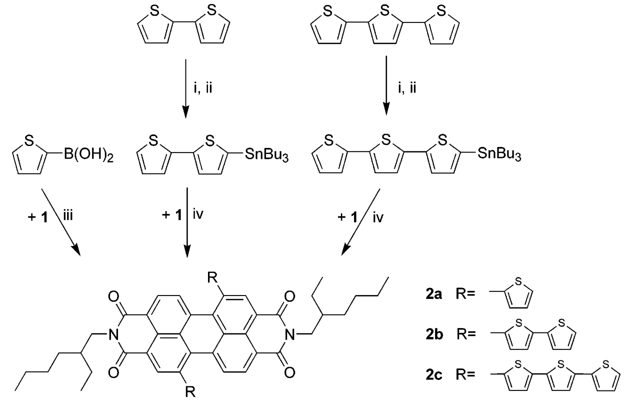
tems will play important roles in artificial photosynthetic systems, molecular switches, and photovoltaic cells.[1f−i,5g,8] On the other hand, conjugated polymers with easy p- and n-doping processes have attracted much interest due to their unique optical properties and intrinsic conductivity. The polymers using functionalized thiophene as the repeated units have been studied intensively, and many instances of their p-doping process have been well documented.[9] However, only limited work has been reported on those that exhibit an easy n-doping process because of its intrinsic difficulty.[10] The polymers with good p- and n-cyclability properties are necessary for application in polymeric supercapacitors for energy storage.[11] One approach to design these polymers is the use of donor and acceptor monomers with regular arrangements in the repeated units to control the energies of the π-system's effective high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) levels, which determine the polymer's p-doping and n-doping properties.[9c,d,12] Therefore, the band gap can be tuned significantly.

Herein, we introduced the oligothiophene groups to the perylene core for the first time by the Suzuki or Stille coupling reaction. Thus, we obtained three oligothiophene−perylene−oligothiophene triads with a π-conjugated system, in which oligothiophene groups act as the electron-donor and the perylene bisimide as the electron-acceptor. The optical and electrochemical properties of the triads were carefully investigated. As compared to the unsubstituted perylene bisimide (**3**), the UV−vis absorptions of **2a**−**c** undergo a bathochromic shift along with considerable band broadening and a less pronounced vibronic fine structure. Moreover, the fluorescence quenching of the perylene core was observed possibly due to the efficient intramolecular electron transfer between the oligothiophene-donor and perylene-acceptor induced by excitation of the electron acceptor perylene bisimide chromophore. Furthermore, the typical perylene core emission on excitation of the oligothiophene accounts for the singlet−singlet energy transfer from the oligothiophene to the perylene core. In the cyclic voltammetry, **2a**−**c** have

Scheme 1. Synthetic Route to Compound 1



Scheme 2. Synthetic Route to Compounds 2a, 2b, and 2c[a]



[a] (i) n-BuLi, THF, −78 °C, 1 h; (ii) $(n\text{-Bu})_3SnCl$, THF, room temperature, 6 h; (iii) cat, $Pd(PPh_3)_4$, THF, K_2CO_3 (1 M aq), reflux, 24 h; (iv) cat, $Pd(PPh_3)_2Cl_2$, dry DMF, 60−70 °C, 24 h.

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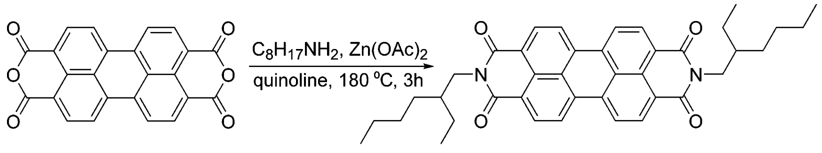
Scheme 3. Synthetic Route to Compound 3



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a relatively high reduction potential because of the presence of the perylene bisimide moiety, and their oxidation potential can be tuned by variation of the thiophene moieties. Furthermore, **2b** and **2c** can be electrochemically polymerized to produce low band-gap conducting materials. The characterization of the poly(**2b**) and poly(**2c**) film by electronic absorption and cyclic voltammetry was also presented.

Results and Discussion

Synthesis and Characterization of the Monomers. The synthetic approach of the necessary precursor **1** is outlined in Scheme 1. Condensation of 1,7-dibromoperylene tetracarboxylic acid anhydride[13] with 2-ethylhexylamine in refluxing propionic acid gave *N*,*N*′-di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide as a deep red solid in a yield of 90%.[2e,g] Subsequent reaction to synthesize **2a**−**c** is showed in Scheme 2. For **2a**, using the palladium-catalyzed Suzuki coupling reaction, **1** reacted with 2-thiopheneboronic acid under refluxing for 24 h in the deaerated solvent of aqueous K_2CO_3 solution and tetrahydrofuran (THF). The purple solid obtained was purified by column chromatography in a good yield of 88.6%. Compounds **2b** and **2c** were synthesized through an analogous two-step procedure: first, tributyl-[2,2′]bithiophen-5-yl-stannane or tributyl-[2,2′;5′,2″]terthiophen-5-yl-stannane was prepared by the reaction of bithiophene or terthiophene with 1 equiv of butyllithium followed by treatment with tributyltin chloride.[14] The raw products were then reacted with **1** through the palladium-catalyzed Stille coupling reaction in dry *N*,*N*-dimethylformamide (DMF) at 60−70 °C for 48 h. After purification by silica gel column chromatography, **2b** and **2c** were obtained as black solids in good yields of 83.3% and 82.4%, respectively. Due to the presence of the flexible alkyl substituents and the oligothiophene groups in the bay position of the perylene core, all compounds exhibit excellent solubility in common organic solvents such as dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$), toluene, and THF. Thus, characterization such as MALDI-TOF mass spectroscopy, elemental analyses, and NMR spectroscopy, especially the ^{13}C NMR spectroscopy, is easily accomplished. In ^1H NMR spectra, the alkyl resonances in **2a**, **2b**, and **2c** are almost the same as those in a reference compound, *N*,*N*′-di(2-ethylhexyl)perylene-3,4,9,10-tetracarboxylic acid bisimide (**3**, mentioned below) because the oligothiophene moieties have little correlation with alkyl groups. Yet the chemical shifts of protons at the 5-, 6- or 11-, 12-positions assigned to the perylene backbone in **2a**, **2b**, and **2c** undergo upfield shifting relative to those of compound **3**. The significant shifting is attributed to the shielding effect caused by the close proximity of the thiophene moieties. The chemical shifts of α-thiophene or *β*-thiophene protons are found as specific doublet and pairs of doublet signals bearing the same intensity in the range of 7.0−7.5 ppm.

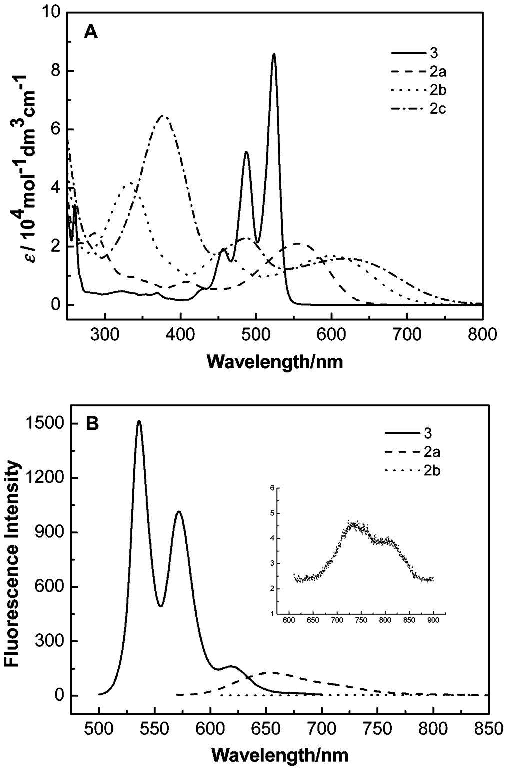

Figure 1. Electronic absorption spectra of compounds **3**, **2a**, **2b**, and **2c** (A) and fluorescence spectra of **3**, **2a**, and **2b** (2.0×10^{-5} M) (B) in CH_2Cl_2. The inset shows the amplificatory fluorescence spectra of **2b**.

To investigate the influence of the oligothiophene moieties on the optical and electrochemical properties of perylene bisimide, we synthesized compound **3** as a reference by the reaction of perylene tetracarboxylic acid anhydride with 2-ethylhexylamine in quinoline with acetate zinc as catalyst (Scheme 3).

Optical Properties of the Monomers. Figure 1A shows the electronic absorption spectra of **2a**−**c** and the reference compound **3** recorded in CH_2Cl_2. Increasing the number of thiophene substituents in the bay position of the perylene core alters significantly the characteristic absorption. The longest absorption bands assigned to the electronic S_0−S_1 transition (a transition dipole moment along the long molecular axis)[15] undergo a bathochromic shift of the maximum

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absorption from 524 nm (**3**) to 557 (**2a**), 601 (**2b**), and 621 nm (**2c**), respectively, along with considerable band broadening and a less pronounced vibronic fine structure. Moreover, the lower absorption bands assigned to the electronic S_0-S_2 transition (a transition dipole moment perpendicular to the long molecular axis) of **2a**−**c** evolve at 408, 458, and 487 nm, respectively. These results stem from the donor substituents in the bay position of the perylene core,[16] the enlargement of π-conjugation because of appending oligothiophenes,[17] and the loss of planarity and rigidity of the perylene bisimide chromophore.[18] The absorptions below 400 nm mainly come from the oligothiophene groups, which undergo a substantially bathochromic shift relative to those of thiophene, bithiophene (302 nm), and terthiophene (354 nm), respectively. The continuous bathochromic shifts result from the formation of a highly extended π-delocalized system through the perylene core,[19] and the remarkable increase of absorption intensity reflects the corresponding increases in the number of thiophene units in the oligomers.

Figure 1B shows the fluorescence emission spectra of **3**, **2a**, and **2b** at the same concentration in CH_2Cl_2 excited at 490, 560, and 600 nm, respectively. As compared to compound **3**, the triad **2a** displays a sharp drop of the fluorescence intensity. In the case of **2b**, only a very weak signal-to-noise ratio is observed for the emission (Figure 1B inset), while for **2c**, no fluorescence is detected in the visible region. It demonstrates that the presence of oligothiophene dramatically quenches the fluorescence of the perylene core in the solvent. The phenomenon of the fluorescence quenching might be attributed to the efficient intramolecular electron transfer between the electron-donor oligothiophene moieties and the electron-acceptor perylene core induced by excitation of the electron acceptor perylene bisimide chromophore.[1h,i,6c,20] The further experimental proof femtosecond transient absorption spectroscopy will be carried out, and a full explanation will be reported in due course. In these systems, energy transfer is also detected by the following experiment. Excitation of the thiophene at 290 nm resulted in the typical perylene core emission, indicating the singlet−singlet energy transfer from thiophene to the perylene core (representative example of **2a**, Supporting Information).[1h,i,6c,21]

Electrochemistry of Monomers and Electrochemical Polymerization. Further insight into the electronic properties of these compounds was investigated by cyclic voltammetry at room temperature. Thiophene or functionalized thiophene can be easily oxidized and subsequently deposited as electroactive polymer films on the working electrode surface. So the cathodic scan was carried out first to avoid the contamination of electrode surface. Table 1 lists the redox potentials of triads **2a**−**c** together with the reference compound **3** for comparison. Figure 2A shows the representative cyclic voltammetry of **2b**.

Table 1. Redox Potentials of Triads 2a−c and Reference Compound 3[a]

	OTM	$P^0 \leftrightarrow P^{1-}$	$P^{1-} \leftrightarrow P^{2-}$	band gap	
compd	E_{pa} (V)	E_{pc}/E_{pa} (V)	E_{pc}/E_{pa} (V)	$E_g{}^b$ (eV)	$E_g{}^c$ (eV)
2a	1.53	−0.63/−0.53	−0.85/−0.72	1.88	1.97
2b	1.33	−0.59/−0.51	−0.79/−0.70	1.68	1.73
2c	1.12	−0.61/−0.53	−0.79/−0.70	1.51	1.63
3	>1.70	−0.66/−0.56	−0.89/−0.75		2.31

[a] E_{pa} = peak anode potential, E_{pc} = peak cathode potential, OTM = oligothiophene moiety, P = perylene. Potentials vs Ag/AgCl, working electrode Pt, 0.1 M $Bu_4NPF_6-CH_2Cl_2$, scan rate 50 mV/s. [b] Electrochemical band gap. [c] Optical band gap.

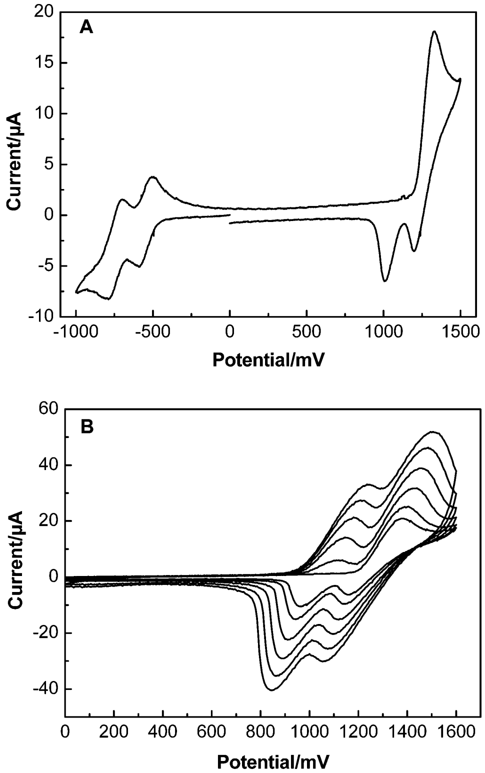

Figure 2. Cyclic voltammograms of **2b** (1 mM) (A) and repeated potential scans (B) in 0.1 M $Bu_4NPF_6-CH_2Cl_2$, scan rate 50 mV/s.

In the cathodic scan region, triads **2a**−**c** all give rise to two reversible reduction waves, which reflect the first and the second one-electron stepwise reductive process of the perylene cores. Although the reduction potential values are sensitive to the properties of electron donating or electron withdrawing appending to the perylene bisimide position,[22] we found that oligothiophene substituents in the bay position of perylene bisimide do not significantly affect the first reduction potential as compared to that of **3**. The result is in agreement with the system when the bay position was substituted with *N*-cycloalkylamines, such as *N*-pyrrolidine

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reported by Zhao et al.[16] Furthermore, the potential difference between the first and the second one-electron reduction waves is obviously reduced with the increase of the π-conjugation from **2a** to **2c**. The phenomenon is consistent with the result observed by Bard's group in the perylene, terrylene, and quaterrylene bisimide system.[23]

In the anodic scan region of the compounds, no oxidation potential is observed for reference **3** due to the solvent-limited potential in our experiments. So the irreversible oxidation peak of **2a** observed at 1.53 V can be attributed to the oxidation of thiophene moieties. For **2b** and **2c**, the oxidation potentials observed at 1.33 and 1.12 V are attributed to the oxidation of bithiophene and terthiophene moieties, respectively, which is progressively reduced as compared to that of **2a**. The result shows that the oxidation potentials decrease with the increasing of the thiophene units, which is in agreement with related studies on substituted and unsubstituted thiophene previously reported by other authors.[9h,24] From the second scan (Figure 2B shows the representative repeated potential scans of **2b**), the appearance and growth of the new broad peaks at a diminished potential relative to the bithiophene and terthiophene moiety indicate the presence of a species grafted onto the electrode with a more extended conjugation that can be assigned to the oxidation of the newly formed polymer in the first cyclic voltammetric scan. The gradually increased current response and new broad peak observed at lower potential are typical characteristics of conducting polymer formation on the electrode surface.[9i,24,25] Accordingly, in the first reverse scan of the cyclic voltammogram, the reduction peaks, located at 1.20 and 1.01 V for **2b**, 1.01 and 0.77 V for **2c**, can be attributed to the reduction of the conductive polymers formed on the electrode surface from the oxidized conductive state to the neutral state.[25e,f] The two-step reductive processes have been observed in other conjugated conducting polymers such as alkoxy-substituted di-2-thiophenylene polymers. The phenomenon can be attributed to ion transport phenomena or sequential reduction of bipolaron initially to polaron and then to neutral polymer.[9f,26] However, in the case of **2a**, because of the decrease of the electronic density on the α-position due to the electron-withdrawing effect of perylene bisimide,[25a] the feature of cyclic voltammetry has no changes and no film forms on the electrode surface during the subsequent cycles.

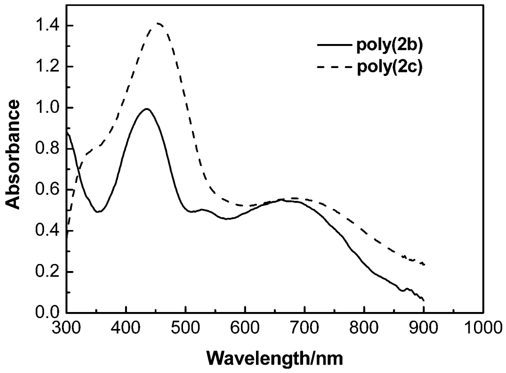

Figure 3. Electronic absorption spectra of neutral poly(**2b**) and poly(**2c**) film deposited on ITO from electrochemical polymerization normalized at the perylene bisimide absorption maximum.

Subsequently, the HOMO−LUMO energy gap of the monomers can be estimated as 1.88, 1.68, and 1.51 eV from the difference between the first oxidation and the first reduction potential obtained from the electrochemical studies. The result is in line with the electronic absorption spectral studies mentioned above and leads to the compounds **2b** and **2c** as the low band-gap precursors for conducting polymers.

The films of poly(**2b**) and poly(**2c**) were prepared for further characterization by repeated potential scans between 0 and +1.6 V (as Figure 2B). The increase of current response indicates the increase of the amount of electroactive polymers deposited on the electrode surfaces. Subsequently, brown films are observed covering the electrode surfaces.

Electronic Absorption and Electrochemistry of the Polymers. Figure 3 shows the electronic absorption spectra of poly(**2b**) and poly(**2c**) films, which had been deposited on the indium tin oxide (ITO) coated glass by cyclic voltammetry. The remarkable bathochromic shift of the absorption and band broadening indicate that they have an extended conjugation system, that is, the formation of the polymers.[25f−h] Evaluating from the absorption edge of the spectra, the optical band gaps of poly(**2b**) and poly(**2c**) are about 1.43 and 1.25 eV (Table 2), respectively, which are much lower than those of the monomers evaluated from the optical absorption or cyclic voltammetry. The narrowing of the band gaps verifies that highly conjugated polymers have generated on the electrode surfaces by electrochemical oxidation.[25f−h] Subsequently, the polymers redox properties were investigated by cyclic voltammetry. The electrochemically deposited films of **2b** and **2c** were washed with CH_2Cl_2 and placed into monomer-free electrolyte CH_2Cl_2 solutions. Figure 4 shows the cyclic voltammetry of the polymers. They both exhibit good and reversible p- and n-doping processes. Moreover, the electrochemical redox processes of the films are very stable with no obvious changes in the features of the cyclic voltammetry during subsequently repeat scanning (over 10 cycles). In the p-doping process, the onset oxidation potential is determined to be 0.96 V for poly(**2b**),

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Table 2. Onset and Peak Potentials of p-Doping and n-Doping Processes of Poly(2b) and Poly(2c) and the Band-Gap Values[a]

	p-doping			n-doping			band gap	
polymer	E_{on} (V)	E_{pa} (V)	E_{pc} (V)	E_{on} (V)	E_{pc} (V)	E_{pa} (V)	$E_g{}^b$ (eV)	$E_g{}^c$ (eV)
2b	0.96	1.29	0.84, 1.01	−0.46	−0.80, −0.94	−0.32, −0.46	1.42	1.43
2c	0.77	1.18	0.55, 0.81	−0.48	−1.02	−0.25	1.25	1.25

[a] Potentials vs Ag/AgCl, working electrode Pt, 0.1 M $Bu_4NPF_6-CH_2Cl_2$, scan rate 50 mV/s. [b] Electrochemical band gap. [c] Optical band gap.

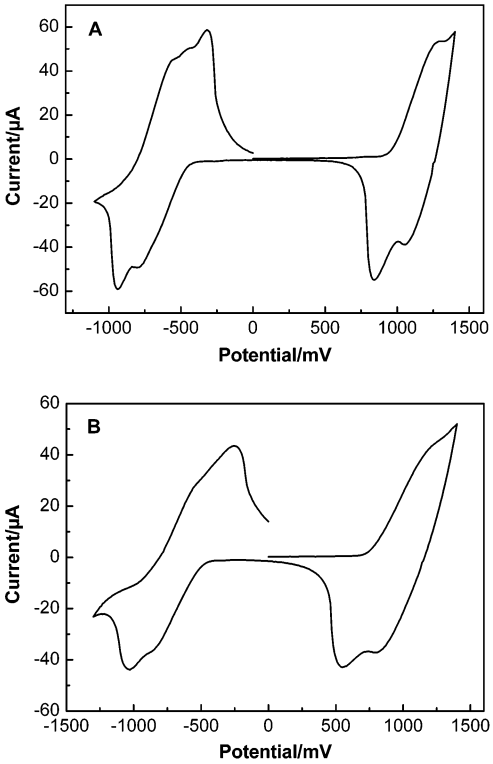

Figure 4. Cyclic voltammetry of poly(**2b**) (A) and poly(**2c**) (B) realized in 0.1 M $Bu_4NPF_6-CH_2Cl_2$, scan rate 50 mV/s.

and 0.77 V for poly(**2c**), which is higher than those of polythiophene previously reported.[9] The positive shifting of the values can be explained by the electron-accepting effect of the perylene bisimide as the unit of the polymers, and the phenomenon is consistent with the previous reports that the polymers had more positive oxidation potential values when the electron-withdrawing groups such as nitro, cyano attached to the polymers or the pyridine, cyanovinylene groups were used as the repeating unit of the polymers.[10b−d,12b,25a,b] In the n-doping process, the difference reducing between the first and the second n-doping process as compared to that of the monomer **2b** and the merging of the first and the second wave in poly(**2c**) indicate the extended conjugation in the polymers. From the difference of the onset potential between the reductive and oxidative processes, the band gaps of the polymers could be estimated to be 1.42 and 1.25 eV, respectively. The values are relatively low for conjugated conducting polymers with good reversible p- and n-doping processes. In addition, it is consistent with the result from the edge of the absorption mentioned above.

Conclusions

In summary, we have shown a facile approach for the synthesis of donor−acceptor conjugated oligomers **2a**−**c** by Suzuki and Stille coupling reactions in good yields. To our knowledge, this is the first time the oligothiophene moieties have been incorporated in the bay position of the perylene core. Their optical and electrochemical properties are also presented. Due to the incorporation of the electro-donor oligothiophene, the absorption spectra show a remarkable bathochromic shift relative to those of unsubstituted perylene bisimides, and the fluorescence quenching is observed. Cyclic voltammetry results of these compounds indicate that their oxidation potential can be well controlled by variation of the number of thiophene groups and they have facile and reversible reduction potential. Moreover, compounds **2b** and **2c** perform polymerization under current. Due to the presence of electron-withdrawing perylene bisimide in the backbone of the π-conjugated polymers, the electrochemical behavior of the polymers depicts a facile and reversible n-doping characteristic, which endows these materials as good electron-transporting properties. The unique properties they possessed set up a new way for us to design new materials based on perylene bisimide and oligothiophene, which make them potential candidates as intrinsic semiconductors, solar energy harvesters, and some energy conversion systems.

Experimental Section

Materials. 2-Thiopheneboronic acid, [2,2′]bithiophene, and [2,2′;5′,2″]terthiophene were purchased from Aldrich and Acros and were used as received without further purification. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (Aldrich) was recrystallized and dried under vacuum prior to use. Tributyl-[2,2′]-bithiophenyl-5-yl-stannane and tributyl-[2,2′;5′,2″]terthiophen-5-yl-stannane were prepared according to literature procedures.[14] DMF was purified by distillation over phosphorus pentoxide, and dichloromethane was distilled over CaH_2. All reactions were carried out under an atmosphere of nitrogen.

Instrumentation. The ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker DMX 400 NMR spectrometer. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet). ^1H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent resonance as an internal standard. The UV−vis and fluorescence spectra were obtained on a Hitachi U-3010 and Hitachi F-4500 spectrometer, respectively. MS spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III mass spectrometer. The infrared spectra of the compounds-KBr pellets were recorded on a Perkin-Elmer SYSTEM 2000 FT-IR spectrometer. Elemental analyses were carried out on a Carlo-Erba 1160 elemental analyzer.

***N,N′*-Di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic Acid Bisimide (1).** A mixture of 1,7-dibromoperylene tetracarboxylic acid anhydride (1.65 g, 3.0 mmol) and 2-ethylhexylamine (1.55 g, 12 mmol) in propionic acid (90 mL) was heated to refluxing for 12 h. The resulting mixture was cooled and poured into water (200 mL), filtrated, and washed with water until the filtrate reached neutrality. The crude solid was dried at 60 °C under vacuum. After being purified by column chromatography (silica gel) using a mixture of dichloromethane/petroleum ether (1:1) as eluent, the product was obtained (2.08 g, 90% yield) as a deep red solid. Data for **1**, UV−vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4}$) = 524 (5.22), 489 (3.55), 272 nm (2.69 mol^{-1} dm^3 cm^{-1}). IR (KBr, cm^{-1}): υ = 2958, 2929, 2860, 1702 (s, C═O), 1662 (s, C═O), 1591, 1393, 1333, 1239. MS (MALDI-TOF): *m/z* 771.1 (M$^+$ + 1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.43 (d, *J* = 8.2 Hz, 2H, perylene-H), 8.87 (s, 2H, perylene-H), 8.65 (d, *J* = 8.1 Hz, 2H, perylene-H), 4.09−4.19 (m, 4H, −CH_2−N), 1.92−1.96 (m, 2H, −CH−), 1.32−1.42 (m, 16H, −CH_2−), 0.95 (t, 6H, −CH_3), 0.90 (t, 6H, −CH_3). ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 162.81 (C═O), 162.32 (C═O), 137.77, 132.25, 132.18, 129.65, 128.68, 128.06, 126.55, 122.91, 122.48, 120.67, 44.37, 37.87, 30.68, 28.61, 23.98, 23.02, 14.06, 10.55. Anal. Calcd for $C_{40}H_{40}Br_2N_2O_4$: C, 62.19; H, 5.22; N, 3.69. Found: C, 62.30; H, 5.23; N, 3.44.

***N,N′*-Di(2-ethylhexyl)-1,7-di(thiophen-2-yl)perylene-3,4,9,10-tetracarboxylic Acid Bisimide (2a).** A mixture of 2-thiopheneboronic acid (140 mg, 1.1 mmol), compound **1** (386 mg, 0.5 mmol), and $Pd(PPh_3)_4$ catalyst in 30 mL of 1 M aqueous K_2CO_3 solution and THF (v/v, 1:1) was heated to reflux for 24 h. After being cooled to room temperature, the mixture was extracted with 100 mL of $CHCl_3$ three times. The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography using a mixture of dichloromethane/petroleum ether (1:1) as eluent to give the product as a purple solid (345 mg). Yield: 88.6%. Data for **2a**, UV−vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4}$) = 557 (2.10), 408 (0.80), 286 nm (2.45 mol^{-1} dm^3 cm^{-1}). IR (KBr, cm^{-1}): υ = 2956, 2928, 2861, 1698 (s, C═O), 1658 (s, C═O), 1591, 1403, 1328, 1243. MS (MALDI-TOF): *m/z* 778.4 (M$^+$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.68 (s, 2H, perylene-H), 8.25 (d, *J* = 8.2 Hz, 2H, perylene-H), 8.08 (d, *J* = 8.2 Hz, 2H, perylene-H), 7.50 (dd, J_1 = 1.0 Hz, J_2 = 5.2 Hz, 2H, thiophene-H), 7.32 (dd, J_1 = 1.0 Hz, J_2 = 3.5 Hz, 2H, thiophene-H), 7.19 (dd, J_1 = 3.7 Hz, J_2 = 5.1 Hz, 2H, thiophene-H), 4.11−4.15 (m, 4H, −CH_2−N), 1.94−1.98 (m, 2H, −CH−), 1.31−1.42 (m, 16H, −CH_2−), 0.94 (t, 6H, −CH_3), 0.88 (t, 6H, −CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.49 (C═O), 163.45 (C═O), 143.68, 135.55, 134.46, 133.21, 133.16, 129.61, 129.51, 129.07, 128.71, 128.09, 127.86, 127.37, 122.34, 122.25, 44.39, 38.09, 30.90, 28.72, 24.19, 22.93, 13.84, 10.55. Anal. Calcd for $C_{48}H_{46}N_2O_4S_2$: C, 74.00; H, 5.95; N, 3.60. Found: C, 73.99; H, 6.08; N, 3.70.

***N,N′*-Di(2-ethylhexyl)-1,7-di[(2,2′)bithiophen-5-yl]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (2b).** A mixture of tributyl-[2,2′]bithiophen-5-yl-stannane (501 mg, 1.1 mmol) and compound **1** (386 mg, 0.5 mmol) in 10 mL of dry DMF was added by the catalytic amount of $[Pd(II)(PPh_3)_2Cl_2]$ and stirred at 60−70 °C for 48 h. After removal of the DMF under vacuum, the resulting solid was purified by column chromatography using a mixture of dichloromethane/petroleum ether (2:1) as eluent affording a black solid (393 mg) in 83.3% yield. Data for **2b**, UV−vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4}$) = 601 (1.68), 458 (1.78), 333 nm (4.18 mol^{-1} dm^3 cm^{-1}). IR (KBr, cm^{-1}): υ = 2956, 2930, 2861, 1697 (s, C═O), 1658 (s, C═O), 1591, 1403, 1328, 1243. MS (MALDI-TOF): *m/z* 943.3 (M$^+$ + 1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.60 (s, 2H, perylene-H), 8.27 (d, *J* = 8.2 Hz, 2H, perylene-H), 8.24 (d, 2H, *J* = 8.2 Hz, perylene-H), 7.27 (dd, J_1 = 0.9 Hz, J_2 = 5.1 Hz, 2H, thiophene-H), 7.25 (d, *J* = 3.3 Hz, 2H, thiophene-H), 7.22 (d, *J* = 3.7, 2H, thiophene-H), 7.18 (dd, J_1 = 1.0 Hz, J_2 = 3.6 Hz, 2H, thiophene-H), 7.03 (dd, J_1 = 3.6 Hz, J_2 = 6.3 Hz, 2H, thiophene-H), 4.09−4.16 (m, 4H, −CH_2−N), 1.93−1.94 (m, 2H, −CH−), 1.30−1.40 (m, 16H, −CH_2−), 0.93 (t, 6H, −CH_3), 0.88 (t, 6H, −CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.50 (C═O), 163.46 (C═O), 142.02, 140.43, 136.44, 135.40, 134.30, 132.85, 132.64, 129.70, 129.59, 129.06, 128.38, 127.98, 127.75, 125.25, 124.98, 124.45, 122.24, 122.11, 44.29, 37.89, 30.69, 28.65, 23.98, 23.01, 14.06, 10.58. Anal. Calcd for $C_{56}H_{50}N_2O_4S_4$: C, 71.31; H, 5.34; N, 2.97. Found: C, 71.31; H, 5.57; N, 2.95.

***N,N′*-Di(2-ethylhexyl)-1,7-di[(2,2′;5′,2′′)terthiophen-5-yl]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (2c).** Tributyl-[2,2′;5′,2′′]terthiophen-5-yl-stannane (591 mg, 1.1 mmol) and compound **1** (386 mg, 0.5 mmol) in 10 mL of dry DMF were added by the catalytic amount of $[Pd(II)(PPh_3)_2Cl_2]$ and stirred at 60−70 °C for 48 h. After removal of the DMF under vacuum, the resulting solid was purified by column chromatography using a mixture of dichloromethane/petroleum ether (3:1) as eluent to give a black solid (456 mg) in 82.4% yield. Data for **2c**, UV−vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4}$) = 621 (1.59), 487 (2.28), 378 nm (6.48 mol^{-1} dm^3 cm^{-1}). IR (KBr, cm^{-1}): υ = 2958, 2927, 2860, 1699 (s, C═O), 1658 (s, C═O), 1591, 1404, 1328, 1243. MS (MALDI-TOF): *m/z* 1106.3 (M$^+$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.61 (s, 2H, perylene-H), 8.29 (d, *J* = 8.2 Hz, 2H, perylene-H), 8.26 (d, *J* = 8.2 Hz, 2H, perylene-H), 7.27 (d, *J* = 3.7 Hz, 2H, thiophene-H), 7.25 (dd, J_1 = 1.1 Hz, J_2 = 5.1 Hz, 2H, thiophene-H), 7.22 (d, *J* = 3.7 Hz, 2H, thiophene-H), 7.20 (dd, J_1 = 1.1 Hz, J_2 = 3.6 Hz, 2H, thiophene-H), 7.09 (d, *J* = 3.6 Hz, 2H, thiophene-H), 7.08 (d, *J* = 3.6 Hz, 2H, thiophene-H), 7.04 (dd, J_1 = 3.5 Hz, J_2 = 5.6 Hz, 2H, thiophene-H), 4.08−4.19 (m, 4H, −CH_2−N), 1.94−1.96 (m, 2H, −CH−), 1.32−1.40 (m, 16H, −CH_2−), 0.94 (t, 6H, −CH_3), 0.89 (t, 6H, −CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.44 (C═O), 163.35 (C═O), 142.11, 140.14, 137.22, 136.76, 135.30, 135.07, 134.10, 132.65, 132.51, 129.57, 129.63, 128.98, 128.56, 127.93, 127.64, 125.09, 124.93, 124.84, 124.42, 124.01, 122.20, 122.10, 44.34, 37.94, 30.74, 28.70, 24.03, 23.07, 14.12, 10.63. Anal. Calcd for $C_{64}H_{54}N_2O_4S_6$: C, 69.41; H, 4.91; N, 2.53. Found: C, 69.22; H, 4.95; N, 2.26.

***N,N′*-Di(2-ethylhexyl)perylene-3,4,9,10-tetracarboxylic Acid Bisimide (3).** A mixture of perylene-3,4,9,10-tetracarboxylic acid anhydride (784 mg, 0.02 mol), zinc acetate (366 mg, 0.02 mol), and quinoline (10 mL) was heated to 180 °C and remained at the temperature for 3 h under nitrogen. After being cooled to room temperature, the reaction mixture was poured into HCl (1 M, 100 mL). The resulting red precipitate (1.11 g) was collected by filtration, washed with water (50 mL) and methanol (50 mL), and then purified by column chromatography (silica gel, CH_2Cl_2). Yield: 90%. Data for **3**, MS (MALDI-TOF): *m/z* 614.4 (M$^+$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.63 (d, *J* = 7.9 Hz, 4H, perylene-H), 8.53 (d, *J* = 8.1 Hz, 4H, perylene-H), 4.11−4.21 (m, 4H, −CH_2−N), 1.97−1.20 (m, 2H, −CH−), 1.35−1.46 (m, 16H, −CH_2−), 0.98 (t, 6H, −CH_3), 0.92 (t, 6H, −CH_3).

General Electrochemistry. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled EG&G potentiostat/galvanostat model 283 at room temperature. For the cyclic voltammetric measurements of monomers, freshly distilled CH_2Cl_2 was used to prepare a solution of **2a**, **2b**, **2c** (1 mM) containing Bu_4NPF_6 (0.1 M) as supporting electrolyte. The same condition was used for reference **3**. **2b** and **2c** polymerized through repeated cycles by cyclic voltammetry contained 5 mM monomer and 0.1 M electrolyte in CH_2Cl_2. After the deposition of the polymers onto the button working electrodes, the films were washed with CH_2Cl_2 and then cycled in a monomer-free electrolyte CH_2Cl_2 solution. A platinum button electrode was polished before each experiment with a 0.05 μm alumina paste, and N_2 bubbling was used to remove oxygen from the electrolyte solutions in the electrochemical cell.

Optical Studies of the Polymers. For the electronic absorption measurement of poly(**2b**) and poly(**2c**) films, the indium tin oxide coated glass was cut into 1 cm × 3 cm pieces, cleaned by sonication in 2-propanol after being washed with detergent, and then rinsed with deionized water and allowed to dry prior to use. The films were deposited onto ITO with the method of polymerization mentioned above. The polymer films were held at nearly 0 V for 5 min to ensure complete reduction to the neutral form before the spectra were obtained.

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Supporting Information Available: NMR spectra, emission spectra of **2a**, and cyclic voltammetry of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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