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Alternating Copolymers Consisting of Dialkoxylated Naphthalene along with Either Dithiophenylated 1,4-Dioxopyrrolo-[3,4*c*]-pyrrole or 5*H*-thieno[3,4-*c*]pyrrole-4,6-dione: Synthesis and Photo-Electrochemical Properties

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Recently, research has rapidly progressed on the development of bulk heterojunction polymer solar cells that use low band-gap polymers (*p*-type semiconducting polymers or electron donors) blended with (6,6)-phenyl-butyric acid methyl ester (PCBM, a *n*-type organic molecule or an electron acceptor) in the active layers, and their power conversion efficiency (PCE) has been increased over 8%.[1] One approach to further improve the performance of polymer solar cells is through the use of new conjugated polymers with ideal properties such as low band-gap, high charge mobility, and appropriate energy levels of the highest/lowest molecular orbital (HOMO/LUMO).

Low band-gap polymers have been developed which allow polymer solar cells to harvest more sunlight. Low band-gap polymers for use in solar cells have been synthesized from many different types of electron-rich and electron-poor monomers.[2] One strategy for obtaining low band-gap polymers is to synthesize alternating copolymers by combining appropriate electron-rich monomers with electron-poor monomers (so-called "push-pull" architecture).

The charge mobility of active layers in polymer solar cells has been increased using various methods such as thermal annealing[2b] and the use of additives. The energy difference between the HOMO level of the *p*-type polymer and the LUMO level of PCBM is closely related to the open-circuit voltage (V$_{oc}$) of a solar cell, which increases as the HOMO/LUMO difference increases. Thus, *p*-type conjugated polymers with low (or deep) HOMO levels are preferred. The energy levels of the HOMO/LUMO of *p*-type polymers can be tuned by combining appropriate electron-rich monomers with electron-poor monomers.

Dialkoxynaphthalene (DN) is planar and can form intermolecular π-π stacks, leading to high charge mobility.[3] Alternating polymers based on DN that contain benzodithiadiazole, thiazolothiazole, bithiophene, and (*Z*)-2,3-di(thiophen-2-yl)acrylonitrile units have been used to fabricate solar cells. The PCEs of solar cells fabricated using these *p*-type polymers were in the range of 0.06-2.90%. Diketopyrrolo[3,4-*c*]pyrrole (DPP) is a strong electron acceptor that can lower the HOMO level. Some DPP-containing conjugated

polymers exhibited high hole mobilities, up to 2×10^{-3} cm^2/V·s, and PCEs up to 6.5%.[4] Thieno[3,4-*c*]pyrrole-4,6-dione (TPD) is also a strong electron acceptor, and some TPD-containing conjugated polymers were reported to have deep HOMO levels, leading to a high V$_{oc}$ and the highest reported PCE of 7.30%.[5]

A DPP-naphthalene polymer (PDPP-TNT) with a thiophene spacer between the DPP and naphthalene units has been reported to have a PCE of 4.7%.[6] A DPP-containing polymer analog (PDPP-TDNT) is also interesting since alkoxy substituents can tune the HOMO/LUMO levels by increasing the electron-donating properties of the naphthalene moiety.[4d] Various TPD-containing polymers have been reported, but there have been no reports regarding TPD-DN alternating polymers with thiophene spacers (PTPD-TDNT). In this paper, PDPP-TDNT and PTPD-TDNT are described with respect to their synthesis and photo-electrochemical properties.

Results and Discussion

PDPP-TDNT and PTPD-TDNT were synthesized by the Suzuki coupling reaction, as shown in Scheme 1. After polymerization, the conjugated polymers were purified by Soxhlet extraction using acetone, hexane, and chloroform, and the chloroform fraction was collected. The chemical structures of the polymers were confirmed by ^{1}H NMR. The number- and weight-average molecular weights (M_n/M_w) of PDPP-TDNT and PTPD-TDNT were 30,000/80,000 and 5,700/7,400, respectively. PDPP-TDNT was soluble in common organic solvents while PTPD-TDNT initially obtained from the polymerization was not readily soluble and about half the initial polymer was discarded after the Soxhlet extraction. The soluble fraction contained only oligomers and low molecular weight polymers. Molecular weights of *p*-type organic materials can affect their optical properties since an absorption spectrum of a polymer can be red-shifted compared to that of a corresponding oligomer even though electrochemical properties may be similar.[7] More importantly, molecular weights can significantly affect morphologies of
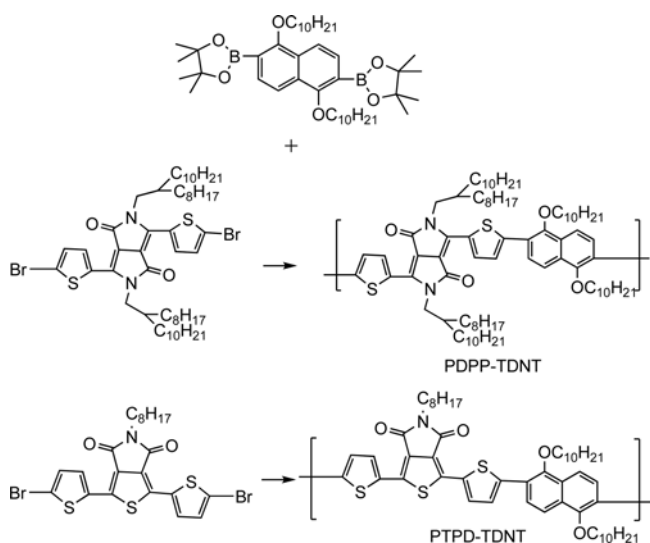
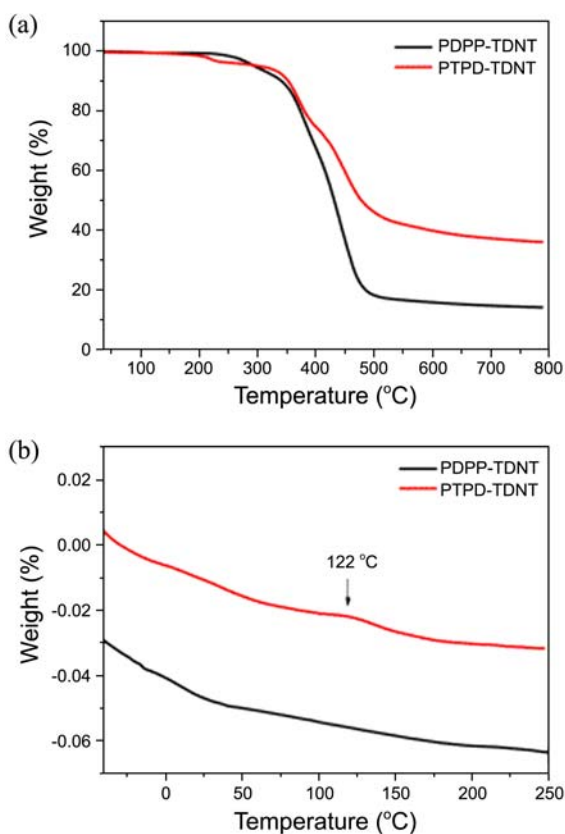**Scheme 1.** Synthesis of PDPP-TDNT and PTPD-TDNT.

Figure 1. TGA curves (a) and DSC traces (b) of PDPP-TDNT and PTPD-TDNT.

active films of the *p*-type material and PCBM. For example, composite films prepared form PCBM and a polymer of thieno[3,4-*b*]thiophene and alkylthiophene units showed a larger charge carrier density and a higher solar cell efficiency than the low molecular weight oligomer counterpart.

The low molecular weight of PTPD-TDNT was a result of the low solubility of the polymer, probably because the TPD moeity has a linear octyl group compared to the DPP moiety of PDPP-TDNT, which has two bulky alkyl chains. TGA
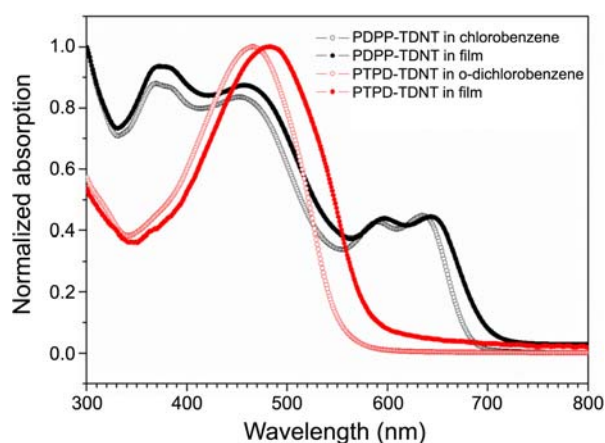

Figure 2. UV-visible absorption spectra of PDPP-TDNT and PTPD-TDNT in solution and film.

data of PDPP-TDNT and PTPD-TDNT revealed that a 5% weight loss due to thermal degradation occurred at around 350 ℃ and 340 ℃ respectively, in a nitrogen atmosphere (Fig. 1). However, the initial weight loss of PTPD-TDNT occurred at about 230 ℃, which can be attributed to some oligomers existing in the soluble fraction. DSC data for PDPP-TDNT revealed that the polymer is amorphous in nature since no thermal transition was detected at temperatures ranging from −80 ℃ to 250 ℃. PTPD-TDNT, on the other hand, exhibited a glass transition at 122 ℃.

UV-visible absorption spectra for PDPP-TDNT and PTPD-TDNT are shown in Figure 2. The absorption maxima of PDPP-TDNT occurred at 369, 453, 591, and 635 nm in chlorobenzene and at 379, 458, 597, and 643 nm in film. Absorption maxima of PTPD-TDNT in solution and film occurred at 466 and 483 nm, respectively. The absorption onsets of PDPP-TDNT and PTPD-TDNT films in the lower energy region occurred at 700 and 583 nm, indicating that the optical band-gaps (E_g^{opt}) of the polymers are 1.77 and 2.13 eV, respectively. PDPP-TDNT showed a much broader absorption range than PTPD-TDNT, but its absorption intensity at longer wavelengths (550-700 nm) was much weaker than at shorter wavelengths (below 550 nm). On the other hand, the absorption pattern of PDPP-TNT was reported to be reversed from PDPP-TDNT, which absorbed much more intensely at 500-800 nm than at 300-500 nm.[6] The absorption in the longer wavelength region can be attributed to intermolecular charge transfer between the electron-rich and electron-poor units in the polymer chain. This comparison suggests that the low absorption intensity of PDPP-TDNT in the longer wavelength region may result from less efficient charge transfer between the DNT and DPP moieties through the thiophene spacer due to the bulky alkoxy substituents on the naphthalene ring.[3a] This less efficient charge transfer can be seen in the electron-state-density distribution of the HOMO and LUMO of PDPP-TDNT and PTPD-TDNT analogues[7] as shown in Figure 3. As shown in the figure, the charge transfer was more evident in PTPD-TDNT than PDPP-TDNT, wherein there is a clear charge transfer from DN to the TPD moiety of PTPD-TDNT. On the other hand, the
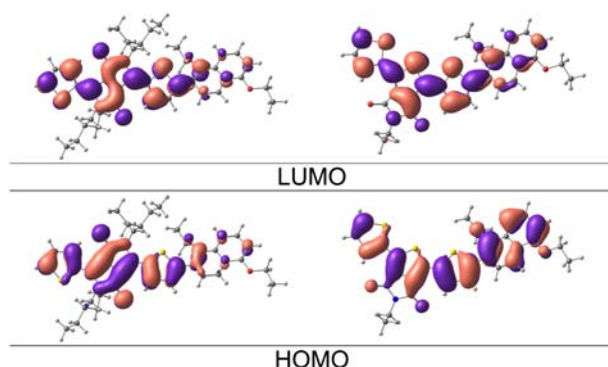
Figure 3. HOMO and LUMO spatial distribution of PDPP-TDNT (left) and PTPD-TDNT (right) calculated using B3LYP/6-31G(d) theoretical methodology in gas phase without symmetry constraints.

electron distribution of PDPP-TDNT for both HOMO and LUMO is mostly situated at DPP.

The oxidation and reduction behaviors of the polymers are shown in Figure 4. The onsets of oxidation and reduction potentials of PDPP-TDNT and PTPD-TDNT are $1.30/-0.83$ and $1.01/-1.02$ eV, indicating that the HOMO/LUMO levels of the polymers are $-5.70/-3.57$ eV and $-5.42/-3.27$ eV, respectively. Accordingly, the electrochemical band-gaps (E_g^{ec}) of PDPP-TDNT and PTPD-TDNT are 2.13 eV and 2.15 eV, respectively (Table 1). The HOMO level and E_g^{ec} of PDPP-TNT were reported to be -5.29 and 1.99 eV, respectively.[6] These results indicate that our PDPP-TDNT has a larger E_g^{ec} but a deeper HOMO level compared to the reported PDPP-TNT. It has been reported that electron-releasing substituents such as alkoxy groups on electron-donor units can tuned the HOMO level of the resulting conjugated polymers.[4b] The larger E_g^{ec} of PDPP-TDNT compared to that of PDPP-TNT may be caused by the alkoxy substituents since the bulky substituent can cause the benzoid form to be more favorable than the quinoid form by twisting the polymer main chain, leading to a reduction in the effective conjugation length of the polymer. There is a discrepancy between the E_g^{opt} and E_g^{ec} (1.77 *vs* 2.13). A similar result was also reported for PDPP-TNT, which was attributed to the exciton binding energy of the polymer.[6]

In summary, two alternating copolymers consisting of DN and DPP or TPD with a thiophene spacer were successfully synthesized. PDPP-TDNT was readily soluble in common organic solvents, but PTPD-TDNT was slightly soluble, thus only the soluble fraction was employed for characterization. This suggested that longer and/or branched alkyl substituents, instead of an octyl group, are required on the TPD moiety in order to obtain soluble polymers. The absorption range of PDPP-TDNT was much broader than that of PTPD-TDNT,
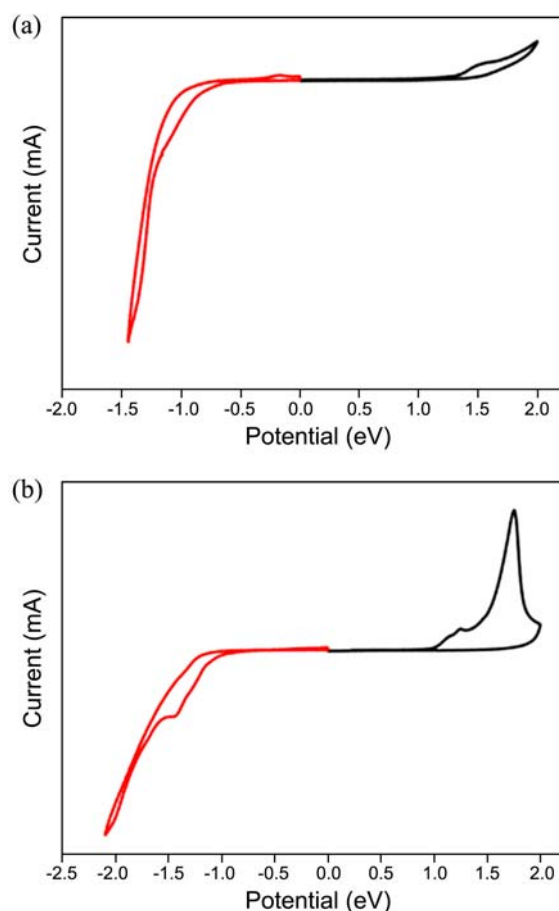

Figure 4. Cyclic voltammogram of PDPP-TDNT in chlorobenzene (a) and PTPD-TDNT in *o*-dichlorobenzene (b).

but narrower than that reported for PDPP-TNT. Furthermore, the absorption intensity of PDPP-TDNT in the long wavelength range was much weaker than that in the shorter wavelength range. Both polymers had larger band-gaps than that of PDPP-TNT. These results can be attributed to the bulky alkoxy substituents, which can twist the polymer main chain. The HOMO level of PDPP-TDNT was deeper than that reported for PDPP-TNT (-5.7 *vs* -5.3 eV). This study clearly indicates that incorporation of appropriate alkoxy substituents on naphthalene moieties can lower the HOMO levels of naphthalene-containing alternating conjugated polymers, but the band-gap of the resulting polymers can become larger, especially when the alkoxy substituents are too large or bulky.

Experimental

2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-

Table 1. Absorption in the visible range and electrochemical properties of PDPP-TDNT and PTPD-TDNT

Polymer	λ_{max} (nm)		λ_{onset} (nm)		E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
	Solution	Film	Solution	Film				
PDPP-TDNT	453, 591, 635	458, 597, 643	682	700	1.77	-5.70	-3.57	2.13
PTPD-TDNT	466	483	553	583	2.13	-5.42	-3.27	2.15

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1,5-decyloxynaphthalene (DN). DN was synthesized from 2,6-dibromo-l,5-didecyloxynaphthalene.[3] IR (KBr) 2923, 2852, 1745, 1590, 1471, 1373, 1288, 1216, 1143, 970, 855, 770, 672 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, 2H), 7.71 (d, 2H), 4.03 (t, 4H), 1.41-1.22 (m, 52H), 0.88 (t, 6H); Calcd: C$_{42}$H$_{70}$B$_2$O$_6$: C, 72.83; H, 10.18. Found: C, 72.87; H, 10.20.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPP). DPP was synthesized from furan-2-carbonitrile with a reported three-step procedure.[6] IR (KBr) 3084, 2922, 2852, 1747, 1657, 1554, 1411, 1362, 1218, 1111, 970, 834, 773, 683 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.62 (d, 2H), 7.22 (d, 2H), 3.91 (d, 4H), 1.88 (m, 2H), 1.21 (m, 64H), 0.86 (m, 12H); Calcd: C$_{54}$H$_{86}$Br$_2$N$_2$O$_2$S$_2$: C, 63.64; H, 8.50; N, 2.75; S, 6.29. Found: C, 63.67; H, 8.62; N, 3.19; S, 6.97.

1,3-Bis(5-bromothiophen-2-yl)-5-octyl-5*H*-thieno[3,4-*c*]pyrrole-4,6-dione (TPD) TPD was synthesized from thiophene-3,4-dicarboxylic anhydride using a reported four-step procedure.[5] IR (KBr) 3031, 2923, 2853, 1744, 1692, 1581, 1542, 1508, 1422, 1364, 1216, 1088, 967, 773, 685, 525 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, 2H); 7.08 (d, 2H); 3.65 (t, 2H, J = 7.6 Hz); 1.67 (m, 2H); 1.25 (m, 10H); 0.87 (t, 3H, J = 7.2 Hz); Calcd: C$_{22}$H$_{21}$Br$_2$NO$_2$S$_3$: C, 44.98; H, 3.60; N, 2.38; S, 16.38. Found: C, 48.87; H, 4.64; N, 2.51; S, 14.83.

Poly(3-(5-(1,5-bisdecyloxynaphthalen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione) (PDPP-TDNT). 2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,5-didecyloxynaphthalene (204 mg, 0.294 mmol), 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (300 mg, 0.294 mmol), Pd(PPh$_3$)$_4$ (17 mg, 0.015 mmol), and tricyclohexyl phosphine (8.25 mg, 0.029 mmol) were added to a reaction flask, and toluene:chlorobenzene (1:1, 15 mL) was added under an argon atmosphere. After the materials dissolved, tetraethyl ammonium hydroxide (1.2 mL) was added. The solution was refluxed for 48 h, followed by end-capping with bromobenzene and phenylboronic acid. After cooling to room temperature, the solution was precipitated in methanol and the filtered product was purified by Soxhlet extraction using acetone, hexane, and chloroform. The chloroform fraction was collected to obtain a dark purple solid (320 mg, 84%). IR (KBr) 3074, 2925, 2854, 1713, 1665, 1540, 1462, 1350, 1232, 1083, 984, 812, 722, 598, 540 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96-7.52 (br m, 8H), 4.15-3.07 (br m, 8H), 2.17-0.94 (br m, 96H), 0.94-0.83 (br m, 12H).

Poly(1-(5-(1,5-bisdecyloxynaphthalen-2-yl)thiophen-2-yl)-3-(thiophen-2-yl)-5-octyl-5*H*-thieno[3,4-*c*]pyrrole-4,6-dione) (PTPD-TDNT). PTPD-TDNT was synthesized using the procedure described above, but with 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,5-didecyloxynaphthalene (236 mg, 0.340 mmol), 1,3-bis(5-bromothiophen-2-yl)-5-octyl-5*H*-thieno[3,4-*c*]pyrrole-4,6-dione (200 mg, 0.340

mmol), Pd(PPh$_3$)$_4$ (19.7 mg, 0.017 mmol), and tricyclohexyl phosphine (9.55 mg, 0.034 mmol). The polymer was obtained as a red solid (130 mg, 44%). IR (KBr) 3413, 2923, 2852, 2320, 1740, 1698, 1652, 1546, 1465, 1365, 1255, 1228, 1052, 983, 799, 751, 722, 600, 502 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) 8.17-7.37 (br m, 8H), 4.14-3.17 (br m, 6H), 2.17-1.25 (br m, 46H), 0.88-0.71 (br m, 9H).

Instrumentation. ^{1}H NMR spectra were recorded using a Varian Gemini-300 (400 MHz) spectrometer. Chemical shifts were recorded in ppm units with TMS as an internal standard. The molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) in CHCl$_3$ with a polystyrene calibration standard. Differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL/min) on a TA Instruments DSC 2920 at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2950 in a nitrogen atmosphere at a heating rate of 10 ºC/min to 800 ºC. UV-visible absorption spectra were recorded using a Varian Cary 1 spectrophotometer. Cyclic voltammograms of polymers were obtained with a solution of tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$, 0.10 M) in acetonitrile at a scan rate of 80 mV/s at room temperature under an argon atmosphere using a Wona-WPG100 in a 3-electrode cell. Polymer films were prepared by dipping platinum wire working electrodes into the polymer solution, which was prepared with a minimum amount of THF, and then air-drying. A platinum wire and an Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively.

Refereneces

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