

Synthesis and Properties of Novel Polymers Based on PD Electron-withdrawing Unit^{*}

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Abstract In this article, we designed and synthesized a series of 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydropyrimidine-4,6(1H, 5H)-dione (PD) unit based polymers (PFTDT, CZTDT, PHTDT and THTDT) for the first time. In these polymers, fluorene, 2,7-carbazole, phenothiazine and thiophene are employed as electron-donating groups and PD as electron-withdrawing group. TGA measurements demonstrated that these polymers possess good thermal stability (all above 377 °C). Very broad absorption spectrum was also obtained from the polymer THTDT (300–850 nm). CV characterization found that these polymers owned low highest occupied molecular orbital (HOMO) energy levels (–5.39 eV for THTDT, –5.49 eV for CZTDT and –5.78 eV for PFTDT) except for PHTDT (–5.17 eV). The geometry and electronic properties of PFTDT, CZTDT, PHTDT and THTDT were investigated by means of theoretical calculation. All the above advantages demonstrate that PD based polymers could be candidates for electronic devices.

Keywords: PD unit; Polymer; Low bandgap; Low HOMO energy level.

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INTRODUCTION

Polymer solar cells (PSC) are considered as one of the most potential ways to address the growing global energy crisis. Owing to their advantages of low-cost, easy fabrication, light weight, being mechanically flexible and being suitable for large-area production, PSC have attracted more and more attentions^[1–5]. According to the simulated results by Dennler *et al.*, power conversion efficiency (PCE) as high as 15% can be achievable for a polymer tandem cell with optimized materials combination^[6]. Recently, PCE over 10% has been reported by Yang *et al.*^[7]. Many effective methods have been employed to improve the PCE of photovoltaic devices^[8–11]. Among them, building donor-acceptor (D-A) polymers or small molecules has been proved to be one of the most efficient manners^[12–16].

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The intramolecular charge transfers (ICT) from the electron-donating moiety to the electron-withdrawing moiety inside a D-A molecule can efficiently extend the absorption spectrum of the molecule for matching well with the solar spectrum^[12]. Furthermore, incorporation of functional moieties with varied electron-donating ability will bring different degrees of ICT to the conjugated system and thus provide a means to tune the optical band gap, electrochemical properties and energy levels for achieving low band gap, good air stability and high open circuit voltage (V_{oc}) polymers or small molecules^[12–14].

In our previous work, we have successfully designed and synthesized a novel electron-withdrawing moiety PD by Knoevenagel reaction^[17, 18]. Organic small molecule 8TPDC8 based PD unit, 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione, displayed promising properties and performance. Such as good thermal stability (5% weight-loss temperatures of 394 °C), relatively broad absorption range (from 300 nm to 900 nm), good air stability and high open circuit voltage of 0.92 V. Thus, due to such important advantages of PD unit above, we designed and synthesized a series of novel polymers (PFTDT, CZTDT, PHTDT and THTDT) based on PD moiety in this article. As for these polymers, they possess the advantages of high molecular weight and viscosity. Also they possess excellent film-forming ability which could contribute to the control of morphology of these polymer films. Therefore, we could easily achieve the ideal size of phase separation which benefits the transportation of excitations^[5]. In these D-A polymers, classical electron-donating groups of fluorene, 2,7-carbazole, phenothiazine and thiophene are employed as electron-donating moieties due to their high carrier mobility, strong electron-donating ability and good air stability while PD is employed as electron-withdrawing moiety. The symmetrical combination of PD group with two thiophene units (note as TDT) assured long conjugated length and better coplanarity, which could enhance the intermolecular interactions, electronic delocalization and further reduce the band gap of these polymers.

In order to investigate thermal, optical and electrochemical properties of these polymers, thermogravimetric analysis (TGA), UV-Vis absorption spectrum, cyclic voltammetry (CV) and theoretical calculation were carried out. TGA measurement demonstrates that these polymers possess good thermal stability (the decomposition temperatures all above 377 °C). Very broad absorption spectra were also obtained from these polymers (300–700 nm for PFTDT, CZTDT and PHTDT, 300–850 nm for THTDT). CV characterization finds that these polymers own the low HOMO energy levels (–5.39 eV for THTDT, –5.49 eV for CZTDT and –5.78 eV for PFTDT) except for PHTDT (–5.17 eV), which indicates that these polymers possess excellent air stability. Considering above advantages (good thermal stability, broad absorption spectra and low HOMO energy level), these polymers could be the candidates for electronic devices.

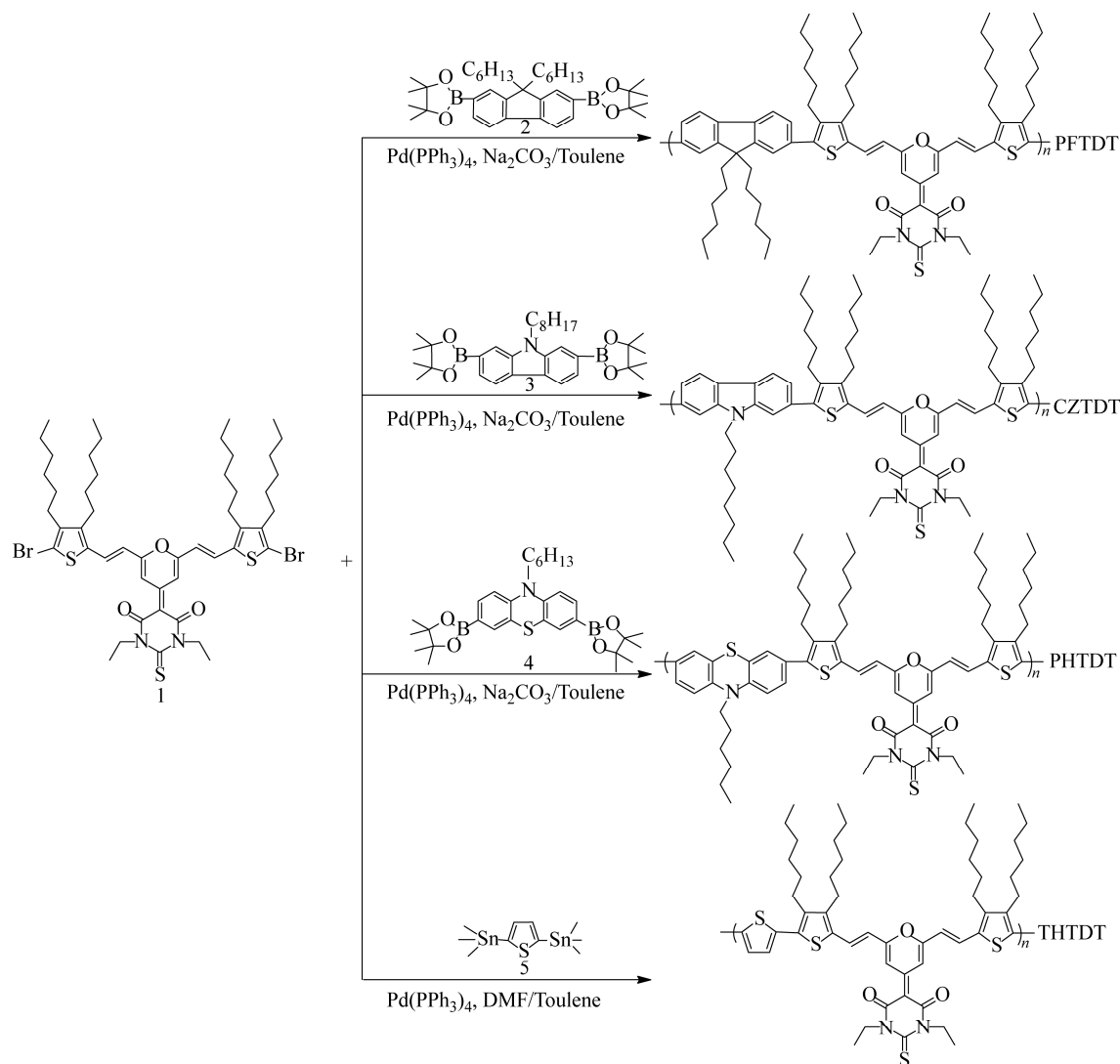
EXPERIMENTAL

All reagents and chemicals were purchased from commercial sources (Aldrich and across) and used without further purification unless specifically stated. All solvents were distilled over appropriate drying agents prior to use and were purged with nitrogen. Synthesis of monomers 1, 2, 3, 4 and 5 was according to our previous works and other literatures^[14, 19–21].

General Procedures of Polymerization

The synthesis routes of PFTDT, CZTDT, PHTDT and THTDT are shown in Scheme 1. Suzuki coupling reaction was employed to synthesize PFTDT, CZTDT and PHTDT. As for the synthesis procedures, monomer 1, 2 (or 3, 4) and $(PPh_3)_4Pd(0)$ (2 mol% with respect to the monomer) were dissolved in a mixture of toluene (6 mL) and 2 mol/L K_2CO_3 aqueous (4 mL, 3:2 volume ratio). Then the solution was stirred under the N_2 atmosphere and refluxed with vigorous stirring at 85 °C for 72 h. The resulting solution was then poured into water and was extracted with chloroform. The extracted solution was then poured into methanol and followed by washing with water. The precipitated solid was washed by methanol and acetone for 24 h in a Soxhlet apparatus to remove the residual monomers, low molecular weight polymers and catalyst, respectively. The soluble fraction is then collected *via* extraction with chloroform for 24 h. The chloroform solution is then concentrated to precipitate the polymers. Stille coupling reaction was used to synthesize THTDT (shown in Scheme 1), Monomer 1, 5 and

(PPh_3) $_4$ Pd(0) (2 mol% with respect to the monomer) were dissolved in a mixture of toluene (8 mL) and *N,N*-dimethyl-formamide (2 mL, 4:1 volume ratio). The solution was stirred under the N_2 atmosphere and refluxed with vigorous stirring at 120 °C for 24 h. The processing steps are similar to the former.



Scheme 1 Synthesis routes of PFTDT, CZTDT, PHTDT and THTDT

The resulting polymer PFTDT was obtained as a dark green film with a yield of 82%. ^1H -NMR (500 MHz, CDCl_3 , TMS, δ): 8.897 (s, 2H, $-\text{PD}$), 7.759 (m, 4H, Ph and $-\text{vinyl}$), 7.443 (m, 4H, $-\text{Ph}$), 6.716 (d, 2H, $J = 16$ Hz, $-\text{vinyl}$), 4.595 (m, 4H, $-\text{CH}_2$), 2.775 (m, 4H, $-\text{CH}_2$), 2.638 (m, 4H, $-\text{CH}_2$), 2.023 (m, 4H, $-\text{CH}_2$), 1.627 (m, 4H, $-\text{CH}_2$), 1.065–1.476 (m, 50H, $-\text{CH}_2$ and $-\text{CH}_3$), 0.856 (m, 12H, $-\text{CH}_3$), 0.750 (m, 6H, $-\text{CH}_3$). ^{13}C -NMR (150 MHz, CDCl_3 , TMS, δ): 177.568, 161.872, 160.672, 156.534, 151.432, 150.153, 146.993, 142.429, 140.609, 139.841, 133.913, 133.355, 129.717, 128.884, 128.560, 128.532, 128.243, 128.005, 123.428, 120.178, 119.204, 117.636, 112.924, 97.094, 43.380, 31.948, 31.669, 31.604, 31.516, 30.909, 29.820, 29.709, 29.621, 29.539, 27.920, 27.575, 24.935, 23.964, 23.770, 22.693, 22.588, 18.425, 14.018, 12.570. Elem. Anal. Calcd. for $\text{C}_{76}\text{H}_{106}\text{N}_2\text{O}_3\text{S}_3$: C, 76.59; H, 8.96. Found: C, 76.35; H, 9.20.

The resulting polymer CZTDT was obtained as a dark green film with a yield of 79%. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS, δ): 8.935 (s, 2H, —PD), 8.173 (d, 2H, Ph), 7.807 (d, 2H, $J = 15$ Hz, —vinyllic), 7.538 (s, 2H, —Ph), 7.396 (s, 2H, —Ph), 6.765 (d, 2H, $J = 15$ Hz, —vinyllic), 4.631 (m, 4H, — CH_2), 3.721 (m, 2H, — CH_2), 2.840 (m, 4H, — CH_2), 2.727 (m, 4H, — CH_2), 1.972 (m, 4H, — CH_2), 1.694 (m, 4H, — CH_2), 1.231–1.622 (m, 36H, — CH_2 and — CH_3), 0.907 (m, 6H, — CH_3), 0.864 (m, 9H, — CH_3). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , TMS, δ): 177.565, 161.870, 160.694, 156.524, 147.040, 143.135, 142.888, 142.712, 141.113, 140.918, 139.873, 134.099, 133.820, 132.108, 131.908, 129.718, 128.576, 122.436, 120.619, 117.942, 117.596, 112.922, 109.402, 97.075, 43.381, 31.986, 31.810, 31.684, 31.544, 30.974, 29.644, 29.553, 29.463, 29.334, 29.227, 29.130, 27.951, 27.546, 27.471, 24.935, 22.707, 22.598, 18.422, 14.038, 14.007, 12.570. Elem. Anal. Calcd. for $\text{C}_{71}\text{H}_{97}\text{N}_3\text{O}_3\text{S}_3$: C, 75.02; H, 8.60. Found: C, 74.82; H, 8.76.

The resulting polymer PHTDT was obtained as a dark green powder with a yield of 75%. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS, δ): 8.884 (s, 2H, —PD), 7.719 (d, 2H, $J = 15.5$ Hz, —vinyllic), 7.240 (d, 4H, Ph), 6.928 (d, 2H, —Ph), 6.669 (d, 2H, $J = 15.5$ Hz, —vinyllic), 4.615 (m, 4H, — CH_2), 3.921 (m, 2H, — CH_2), 2.750 (m, 4H, — CH_2), 2.528 (m, 4H, — CH_2), 1.897 (m, 2H, — CH_2), 1.609 (m, 4H, — CH_2), 1.257–1.621 (m, 44H, — CH_2 and — CH_3), 0.849–0.932 (m, 15H, — CH_3). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , TMS, δ): 177.547, 161.846, 160.669, 156.534, 146.938, 144.590, 140.717, 139.752, 134.258, 133.859, 133.642, 129.713, 128.711, 128.544, 128.291, 127.988, 127.695, 127.572, 124.392, 117.462, 115.259, 114.723, 112.871, 97.021, 31.894, 31.757, 31.624, 31.459, 31.404, 30.761, 29.545, 29.343, 27.853, 27.257, 26.810, 26.663, 24.810, 22.655, 22.571, 18.412, 14.049, 13.988, 12.557. Elem. Anal. Calcd. for $\text{C}_{69}\text{H}_{93}\text{N}_3\text{O}_3\text{S}_4$: C, 72.65; H, 8.22. Found: C, 74.38; H, 8.98.

The resulting polymer THTDT was obtained as a dark green film with a yield of 86%. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , TMS, δ): 8.926 (s, 2H, —PD), 7.698 (d, 2H, $J = 15.3$ Hz, —vinyllic), 7.239 (d, 2H, —Th), 6.694 (d, 2H, $J = 12.5$ Hz, —vinyllic), 4.625 (m, 4H, — CH_2), 2.764 (s, 8H, — CH_2), 1.625 (m, 8H, — CH_2), 1.481 (m, 8H, — CH_2), 1.361 (m, 22H, — CH_2 , — CH_3), 0.939 (t, 6H, — CH_3), 0.888 (t, 6H, — CH_3). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , TMS, δ): 177.490, 161.759, 160.266, 156.057, 147.207, 140.523, 136.512, 133.956, 133.881, 129.704, 127.848, 127.796, 127.030, 118.237, 113.096, 97.282, 43.355, 31.747, 31.647, 31.573, 30.400, 29.630, 29.535, 28.087, 27.768, 22.676, 18.415, 14.095, 14.030, 12.572. Elem. Anal. Calcd. for $\text{C}_{55}\text{H}_{76}\text{N}_2\text{O}_3\text{S}_4$: C, 70.17; H, 8.14. Found: C, 70.02; H, 9.12.

Characterization

The elemental analysis was carried out with a Thermoquest CHNS-Ovelemental analyzer. The gel permeation chromatographic (GPC) analysis was carried out with a Waters 410 instrument (2414 differential refraction detector, styragel HT6E column) with tetrahydrofuran as the eluent (flow rate: 1 mL/min, at 35 °C) and polystyrene as the standard. TGA was performed on a Perkin Elmer Pyris 1 analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10 K/min. DSC was performed under nitrogen flushing at a heating rate of 10 K/min with a NETZSCH (DSC-204) instrument. The X-ray diffraction (XRD) was measured by an instrument of X'Pert PRO. The fluorescence spectra were performed by a RF-5301PC. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured using a Bruker AVANCE-500 NMR spectrometer and a Varian Mercury-300 NMR spectrometer, respectively. UV-Visible absorption spectra were measured using a Shimadzu UV-3600 spectrophotometer. Electrochemical measurements of these derivatives were performed with a Bioanalytical Systems BAS 100 B/W electrochemical workstation. Atomic force microscopy (AFM) was carried out using a NanoScope IIIa Dimension 3100 system.

RESULTS AND DISCUSSION

Material Synthesis and Characterization

All the polymers are soluble in common organic solvents (e.g., chloroform and chlorobenzene) at room temperature. Molecular weights and polydispersities of the resulting polymers were determined by GPC analysis with the weight average molecular weight (M_w) of 8.8–46.2 kg/mol and polydispersity index (PDI, M_w/M_n) of 1.55–2.23. Table 1 summarizes the polymers' data including molecular weights, PDI, and 5% weight loss

temperature. The observed low M_w of THTDT is mainly caused by the excellent coplanarity of thiophene units, and thus strong rigidity of polymer THTDT. Furthermore, the introduction of no alkylation thiophene should be another reason for the low M_w of THTDT.

Table 1. Polymer data of PFTDT, CZTDT, PHTDT and THTDT

	M_n^a (kg/mol)	M_w^a (kg/mol)	PDI	T_d^b (°C)
PFTDT	13.3	22.9	1.72	389
CZTDT	13.2	21.4	1.62	397
PHTDT	20.7	46.2	2.23	377
THTDT	5.8	8.8	1.55	378

^a Calculated from GPC (eluent: THF; polystyrene standards);

^b Temperature of 5% weight loss at a heating rate of 10 K/min under nitrogen

Thermal Properties

These polymers exhibited relatively good thermal stability when they were heated at the rate of 10 K/min under the N_2 atmosphere. As shown in Fig. 1(a) and Table 1, the decomposition temperatures (T_d) of the polymers are in the range of 377–397 °C. The excellent thermal stability of the polymers is adequate for the fabrication of organic solar cells or other electronic devices. DSC was also performed to investigate the thermal property of these polymers. The endothermic peak attributed to the glass transition temperatures (T_g) of PFTDT, CZTDT, PHTDT were observed at 80, 91 and 125 °C respectively, demonstrating that these polymers are amorphous. The amorphous polymers possess isotropic optical properties and excellent film-forming ability, which increases the absorption cross section for the incident light as well as the charge transport efficiency through the active layer. The reason why THTDT does not possess T_g is that it lacks the alkyl chain (there is no alkyl chain in the thiophene unit) and has the better coplanarity compared with other polymers.

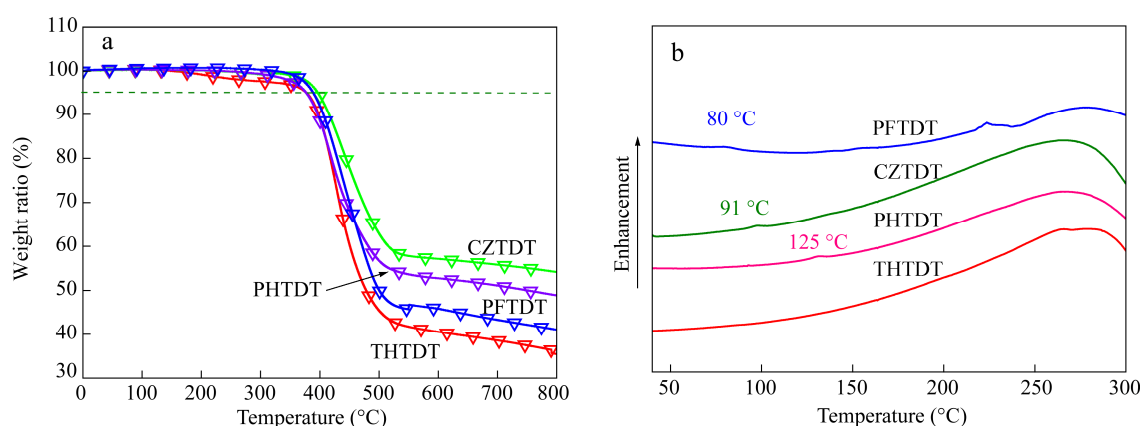


Fig. 1 Thermal properties of PFTDT, CZTDT, PHTDT and THTDT: (a) TGA curves and (b) DSC curves (The measurements were performed under nitrogen atmosphere at a heating rate of 10 K/min.)

Optical Properties

The normalized absorption spectra of PFTDT, CZTDT, PHTDT and THTDT in dilute (10^{-5} mol/L) chloroform solution are shown in Fig. 2(a) while those of the thin films are shown in Fig. 2(b). Also the main optical property data are listed in Table 2. The polymer THTDT with the electron-donating of thiophene moiety shows absorption peaks at 334, 421 and 550 nm in dilute solution, which should be attributed to the intrinsic absorption of π - π^* transition of the conjugated polymer backbone and ICT interaction respectively. Similarly, the absorption spectra of other polymers (PFTDT, CZTDT and PHTDT) in dilute solution show two absorption peaks (341 and 533 nm for PFTDT, 346 and 533 nm for CZTDT, 318 and 534 nm for PHTDT). The absorption peaks of 341, 346 and 318 nm should belong to the absorption of π - π^* transition in the conjugated polymer backbone, while the absorption peaks around 533 nm could mainly originate from the ICT interaction between the donor segments of

adjacent thiophene units and the electron-withdrawing unit PD. In order to examine this speculation, we measured the absorption spectrum of the core unit TDT in dilute solution (Fig. 1S). The absorption peak 523 nm of TDT unit proves our speculation and demonstrates that fluorene, 2,7-carbazole and phenothiazine moieties contribute slightly to the ICT interactions (about 10 nm). By contrast, the absorption peak 550 nm of polymer THTDT further testifies that the thiophene unit contributes strongly to the ICT interactions because of its excellent coplanarity. Furthermore, the absorption edge (λ_{edge}) of THTDT (728 nm) is broadened compared with that of PFTDT (634 nm), CZTDT (640 nm) and PHTDT (665 nm), which could be explained by much stronger ICT effect of THTDT than that of PFTDT, CZTDT and PHTDT.

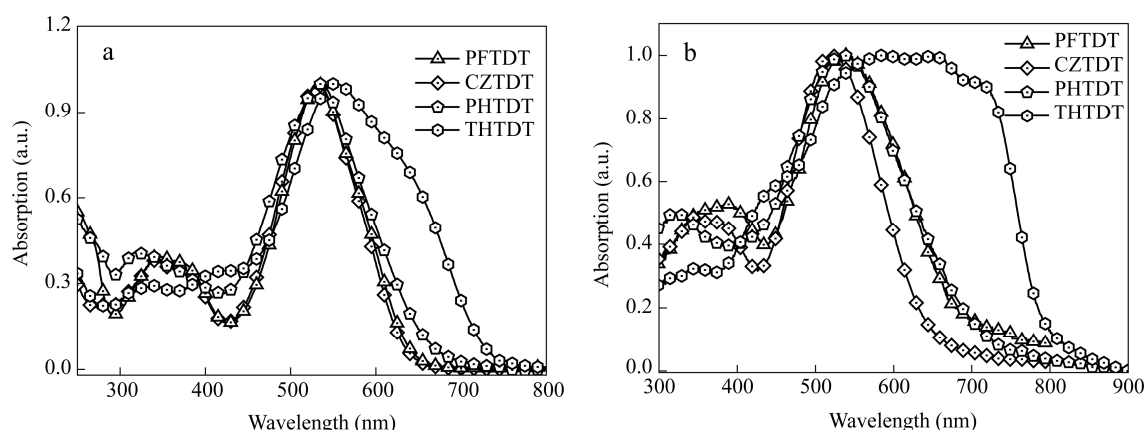


Fig. 2 The normalized absorption spectra of PFTDT, CZTDT, PHTDT and THTDT: (a) in chloroform solutions with the concentration of 10^{-5} mol/L and (b) films spin-coated from a 5 mg/mL chloroform solution

Table 2. Optical and electrochemical data of PFTDT, CZTDT, PHTDT and THTDT

	In solution ^a		In film ^b		$E_{\text{onset}}^{\text{ox}}$ (V)	$E_{\text{onset}}^{\text{red}}$ (V)	Electrochem	Optical ^c
	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	ϵ_{max} ((mol/L) ⁻¹ cm ⁻¹)	λ_{edge} (nm)	$\lambda_{\text{max}}^{\text{abs}}$ (nm)				
PFTDT	532/86400		634	539	1.09/−5.78	−1.19/−3.50	2.28	1.80
CZTDT	533/107200		640	522	0.80/−5.49	−1.18/−3.51	1.98	1.90
PHTDT	534/79100		665	534	0.48/−5.17	−1.18/−3.52	1.75	1.74
THTDT	550/73300		728	584	0.70/−5.39	−1.13/−3.56	1.83	1.56

^a 1×10^{-5} mol/L in anhydrous chloroform;

^b PFTDT, CZTDT, PHTDT and THTDT films were spin-coated from a 5 mg/mL chloroform solution;

^c The optical band gap ($E_{\text{g,opt}}$) was obtained from the films absorption edge.

Figure 2(b) displays the normalized absorption spectra of the polymer films. The absorption spectra are generally similar to those in dilute solution except for THTDT. It should be noted that THTDT displays an absorption peak of 584 nm and an absorption edge of 794 nm, which are 34 and 68 nm red shift respectively compared with those in solution. The red shifts may be caused by the existence of strong π - π stacking in the solid state and thus could broaden their absorption spectra. The very broad absorption range of THTDT (300–850 nm) was very ideal for matching well with solar spectrum. The band gap of PFTDT, CZTDT, PHTDT and THTDT were estimated to be 1.80, 1.90, 1.74 and 1.56 eV respectively, which are calculated from the film absorption edge of these polymers. As expected, THTDT with the strongest intramolecular charge transfer interaction and the best coplanarity exhibits the lowest optical band gap.

Electrochemical Properties

Cyclic voltammetry of the polymer films were performed in anhydrous acetonitrile solution with platinum button working electrode, using tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte at a scan rate of 100 mV/s. Both the platinum wire counter electrode and an Ag/AgNO₃ reference electrode are under

the N_2 atmosphere. Ferrocene/ferrocenium (Fc/Fc^+) was used as the internal standard. The redox potential of Fc/Fc^+ which has an absolute energy level of -4.8 eV relative to the vacuum level for calibration is located at 0.11 V in 0.1 mol/L TBAPF₆/methylene dichloride solution^[22]. So the evaluation of the HOMO and lowest unoccupied molecular orbital (LUMO) energy levels as well as the electrochemical band gap ($E_{g, ec}$) could be done according to the following equations:

$$HOMO(eV) = -e(E_{Ox}^{onset} + 4.69) (eV)$$

$$LUMO(eV) = -e(E_{Red}^{onset} + 4.69) (eV)$$

$$E_{g, ec} = -(HOMO - LUMO) (eV)$$

where E_{Ox}^{onset} and E_{Red}^{onset} are the measured potentials relative to Ag/Ag^+ . The CV curves are showed in Fig. 3 while the relative electrochemical data and calculated energy levels are listed in Table 2. It can be seen that the calculated LUMO energy levels of PFTDT, CZTDT, PHTDT and THTDT are -3.50 , -3.51 , -3.52 and -3.56 eV respectively, which are very similar to each other and our previous reports^[17, 18]. Therefore, we can conclude that the substitution of varied electron-donating ability moiety has almost no effect on the reduction potential. The relatively low LUMO energy levels of the polymers should result from the strong electron-withdrawing ability^[13]. On the other hand, the HOMO energy levels of the polymers PFTDT, CZTDT, PHTDT and THTDT are -5.78 , -5.49 , -5.17 and -5.39 eV respectively, which behave much different. It is clear that the HOMO energy levels rose with the gradually increased electron-donating abilities (fluorene < carbazole < thiophene < phenothiazine).

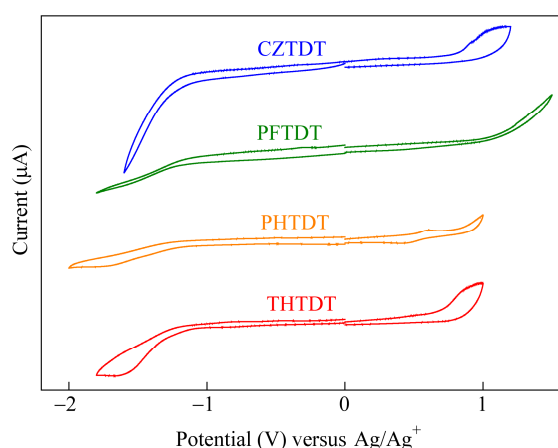


Fig. 3 Cyclic voltammetry curves of PFTDT, CZTDT, PHTDT and THTDT films on platinum electrode in 0.1 mol/L $n\text{-Bu}_4\text{NPF}_6$ in CH_3CN solution, at a scan rate of 100 mV/s

As everyone knows that there are two requests of donor materials energy levels for achieving high performance organic solar cells. One is the HOMO energy level must be low enough, as the open circuit potential (V_{oc}) value for the photovoltaic device is determined by the difference between the HOMO energy level of the donor and LUMO energy level of the acceptor. Therefore, the relatively low HOMO levels of the donor materials can allow a high open circuit voltage (V_{oc}) for the photovoltaic device^[23]. Furthermore, the polymer should also possess good air stability with HOMO energy level being below the air oxidation threshold (~ -5.2 eV)^[24]. Therefore, the relatively low HOMO levels (-5.78 eV for PFTDT, -5.49 eV for CZTDT, -5.17 eV for PHTDT and -5.39 eV for THTDT) of these polymers (except for PHTDT) are beneficial for achieving high V_{oc} values and raising their air stability. The other is that the donor LUMO energy level should be higher than that of the electron acceptor (at least 0.3 eV) considering that the exciton binding energy is assumed to be 0.3 eV^[25].

A complete picture of the band structure of the polymer is presented in Fig. 4. The first dashed line (red) indicates the threshold for air stability, and the second dashed line represents the threshold value for an effective

charge transfer from the polymers to PCBM (-4.3 eV)^[25]. All of the LUMO energy levels of the polymers are in the ideal range for completing an effective charge transfer.

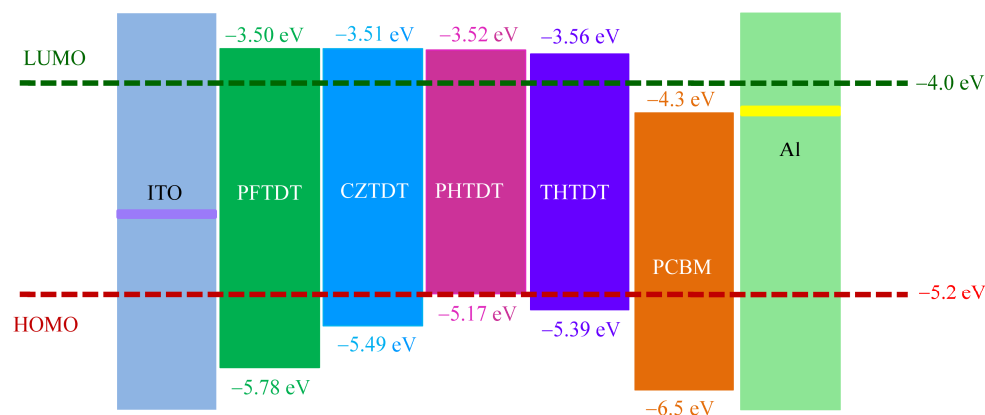


Fig. 4 Band diagram for PFTDT, CZTDT, PHTDT, THTDT and PCBM (The dashed line (-5.2 eV) indicates the thresholds for air stability while the dashed line (-4.0 eV) represents the effective charge transfer energy level from donor to acceptor.)

Theoretical Calculation

The geometry and electronic properties of PFTDT, CZTDT, PHTDT and THTDT have been investigated by means of theoretical calculation with the Gaussian 09 program package at a hybrid density functional theory (DFT) level^[26]. Becke's three-parameter gradient corrected functional (B3LYP) with a 6-31G** basis was used for full geometry optimization. Figure 5 presents the geometry, the HOMO and LUMO. As for these polymers, all the alkyl chain groups were replaced by H atoms to economize the computation time.

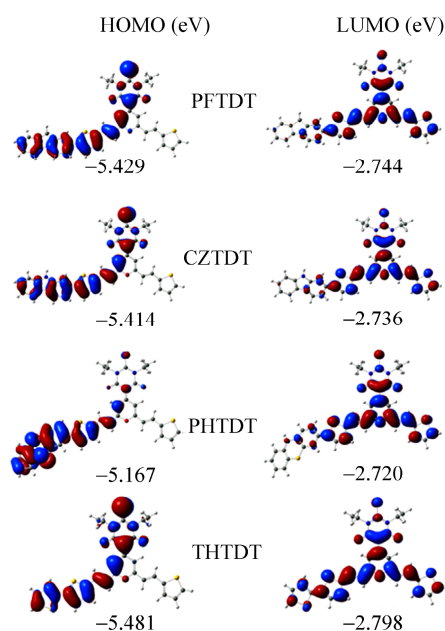


Fig. 5 Molecular orbital surfaces of the HOMO and LUMO of the polymer PFTDT, CZTDT, PHTDT and THTDT obtained at B3 LYP/6-31G** level

In these polymers, there is large contribution to the HOMO from the fluorine, carbazole, phenothiazine and thiophene electron-donating moieties, while the PD electron-withdrawing moiety contributes mainly to the

LUMO, indicating a charge-transfer nature of HOMO→LUMO from the electron-donating units to the electron-withdrawing unit. Furthermore, the calculated HOMO energy levels of these polymers are well consistent with the electrochemical measurement even though the LUMO energy levels exhibit some bias. According to the calculated HOMO and LUMO energies, the band gap of PFTDT, CZTDT, PHTDT and THTDT is 2.69, 2.68, 2.45 and 2.68 eV.

Characterization of Surface Topography

From the AFM images (Fig. 6) we can find that these polymer films exhibit relatively smooth surfaces (0.82 nm for PFTDT, 1.81 nm for CZTDT, 1.21 nm for PHTDT) except THTDT (6.81 nm). So they should own the relatively excellent film-forming abilities. As for THTDT, its relatively rough surface may result from its comparatively better coplanarity, which could easily lead to a certain degree of crystal of this polymer. This result is consistent with the result of DSC measurements. The XRD measurements also suggest that THTDT possesses the highest intensity among these polymers (Fig. 3S).

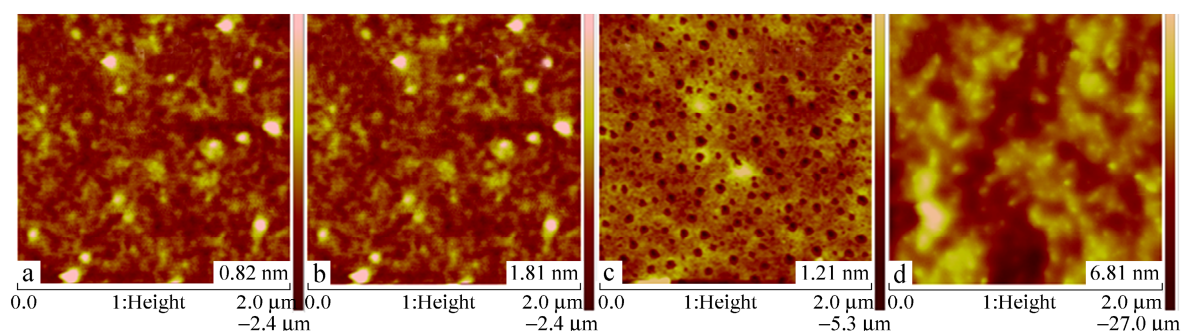


Fig. 6 Topography images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) obtained by tapping-mode AFM showing the morphology of the polymer films spin-coated from chlorobenzene:chloroform (1:1) solutions: (a) PFTDT, (b) CZTDT, (c) PHTDT and (d) THTDT

CONCLUSIONS

In summary, we have designed and synthesized a series of polymers PFTDT, CZTDT, PHTDT and THTDT based on a novel electron-withdrawing unit PD. These polymers demonstrated good thermal stability with the 5% weight loss temperature all above 370 °C. Very broad absorption spectrum (300–850 nm) was also obtained from polymer THTDT. Furthermore, all polymers display relatively low HOMO energy levels (under $-5.20\ \text{eV}$) except for PHTDT ($-5.17\ \text{eV}$), which proves excellent air stability. AFM measurements found that these polymers possess nice film forming abilities. Considering all the above advantages, these polymers could be candidates for organic electronic devices.

REFERENCES

- 1 Krebs, F.C., Sol. Energy Mater. Sol. C., 2009, 93: 394
- 2 Krebs, F.C., Tromholt, T. and Jørgensen, M., Nanoscale, 2010, 2: 873
- 3 Zhou, Y.H., Khan, T.M., Shim, J.W., Dindar, A., Hernandez, C.F. and Kippelen, B.J., Mater. Chem. A, 2014, 2: 3492
- 4 Nielsen, T.D., Cruickshank, C., Foged, S., Thorsen, J. and Krebs, F.C., Sol. Energy Mater. Sol. C., 2010, 94: 1553
- 5 Li, Z.F., Peng, Q., He, P., Wang, Y.L., Hou, Q.F., Li, B.L. and Tian, W.J., Chin. J. Org. Chem., 2012, 32: 834
- 6 Dennler, G., Scharber, M.C., Ameri, T., Denk, P., Forberich, K., Waldauf, C. and Brabec, C.J., Adv. Mater., 2008, 20: 579
- 7 You, J., Dou, L., Yoshimura, K., Kato, T., Ohya, K., Moriarty, T., Emery, K., Chen, C.C., Gao, J., Li, G. and Yang, Y., Nat. Commun., 2013, 4: 1446

- 8 Zhou, Y.H., Fuentes-Hernandez C., Shim J., Meyer J., Giordano, A.J., Li, H., Winget, P., Papadopoulos, T., Cheun, H., Kim, J., Fenoll, M., Dindar, A., Haske, W., Najafabadi., Khan T.M., Sojoudi, H., Barlow, S., Graham, S., Brédas, J.L., Marder, S.R., Kahn, A. and Kippelen, B., *Science*, 2012, 336: 327
- 9 Duan, C.H., Zhang, K., Zhong, C.M., Huang, F. and Cao, Y., *Chem. Soc. Rev.*, 2013, 42: 9071
- 10 Fan, X., Cui, C.H., Fang, G.J., Wang, J., Li, Z.S., Cheng, Z., Long, F.H. and Li, Y.F., *Adv. Funct. Mater.*, 2012, 22: 585
- 11 He, Z.C., Zhong, C.M., Su, S.J., Xu, M., Wu, H.B. and Cao, Y., *Nat. Photonics*, 2012, 6: 591
- 12 Roquet, S., Cravino, A., Leriche, P., Alévêque, O., Frère, P. and Roncali, J., *J. Am. Chem. Soc.*, 2006, 128: 3459
- 13 Wang, Z., Meng, K.G., Zhang, W., Yang, X.J., Deng, S.W. and Li, Y., *Chinese J. Polym. Sci.*, 2010, 28(6): 931
- 14 Li, Y.W., Xue, L.L., Li, H., Li, Z.F., Xu, B., Wen, S.P. and Tian, W.J., *Macromolecules*, 2009, 42: 4491
- 15 Li, Z.F., Bian, J., Wang, Y.L., Jiang, F.Y., Liang, G.J., He, P., Hou, Q.F., Tong, J.H., Liang, Y., Zhong, Z.C., Zhou, Y.H. and Tian, W.J., *Sol. Energ. Mat. Sol. C.*, 2014, 130: 336
- 16 Keshtova, M.L., Marochkina, D.V., Fu, Y.Y., Xie, Z.Y., Geng, Y.H., Kochurovc, V.S. and Khokhlov, A.R., *Chinese J. Polym. Sci.*, 2014, 32(7): 844
- 17 Li, Z.F., Dong, Q.F., Xu, B., Li, H., Wen, S.P., Pei, J.N., Yao, S.Y., Lu, H.G., Li, P.F. and Tian, W.J., *Sol. Energ. Mat. Sol. C.*, 2012, 98: 343
- 18 Li, Z.F., Dong, Q.F., Yao, S.Y., Qian, J.Y., Wang, Y.L., Jiang, F.Y. and Tian, W.J., *J. Mater. Sci.*, 2015, 50: 937
- 19 Li, Y.W., Li, Z.F., Wang, C.Y., Li, H., Lu, H.G., Xu, B. and Tian, W.J., *J. Polym. Sci., Part A: Polym. Chem.*, 2010, 48: 2765
- 20 Li, Q., Liu, L.J., Liu, Z.Y., Li, Z.F., Cheng, W.D., Wen, S.P., Li, P.F., Li, Z.J. and Tian, W. J., *Synth. Met.*, 2011, 161: 731
- 21 Blouin, N., Michaud, A. and Leclerc, M., *Adv. Mater.*, 2007, 19: 2295
- 22 Thompson, B.C., Kim, Y.G. and Reynolds, J.R., *Macromolecules*, 2005, 38: 5359
- 23 Li, Y.W., Xue, L.L., Xia, H., Xu, J.B., Wen, S.P. and Tian, W.J., *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46: 3970
- 24 Leeuw, D.M.D., Simenon, M.M., Brown, J.A.R. and Einerhand, R.E.F., *Synth. Met.*, 1997, 87: 53
- 25 Shirota, Y., *J. Mater. Chem.*, 2005, 15: 75
- 26 Wu, G.L., Zhao, G.J., He, C., Zhang, J., He, Q.G., Chen, X.M. and Li, Y.F., *Sol. Energ. Mat. Sol. C.*, 2009, 93: 108