

Synthesis and Photovoltaic Properties of Conjugated D–A Copolymers Based on Thienyl Substituted Pyrene and Diketopyrrolopyrrole for Polymer Solar Cells

Ning Wang,¹ Xichang Bao,¹ Yan Yan,² Dan Ouyang,¹ Mingliang Sun,^{2,3} V. A. L. Roy,² Chun Sing Lee,² Renqiang Yang¹

¹CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

²Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Tat Chee Ave, Hong Kong

³Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, China

Correspondence to: R. Yang (E-mail: yangrq@qibebt.ac.cn)

Received 10 July 2014; accepted 16 August 2014; published online 8 September 2014

DOI: 10.1002/pola.27378

ABSTRACT: A new donor-acceptor conjugated copolymer (PDTPyDPP), comprising 2,7-di-2-thienyl-4,5,9,10-tetrakis(hexyloxy)pyrene as a donor and diketopyrrolopyrrole (DPP) as an acceptor, was synthesized. PDTPyDPP showed good solubility in common organic solvents, broad visible absorption from 300 to 900 nm, and a moderate hole mobility up to $6.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The power conversion efficiency of the photovoltaic device based on the PDTPyDPP/PC₇₁BM photoactive layer

reached 4.43% with 0.66 V of open-circuit voltage (V_{oc}), 10.52 mA cm⁻² of short-circuit current (J_{sc}) and 64.11% of fill factor. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 3198–3204

KEYWORDS: charge transfer; conjugated polymers; diketopyrrolopyrrole; photovoltaic; pyrene; structure-property relations

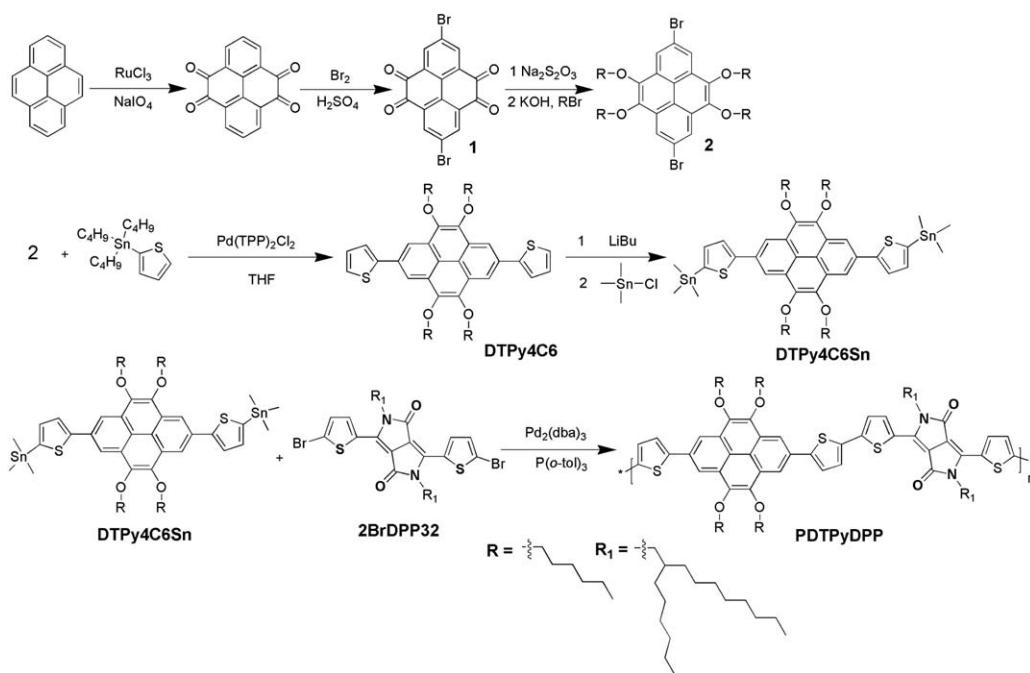
INTRODUCTION Polymer solar cells (PSCs) have been extensively studied in recent years, owing to their low cost, light weight, and flexibility.^{1–7} Recently, PSCs based on conjugated polymers and fullerene derivatives have shown a remarkable breakthrough, the power conversion efficiencies (PCEs) over 8% have been obtained.^{8–10} In PSCs, the bulk heterojunction device structure, in which the active layer consists of nanoscale bicontinuous phase-separated electron donor and acceptor components, has been proven to be the most successful structure.^{11,12} As for the active layer materials, many research efforts have been devoted to design and synthesis novel polymer donor materials with good solubility, broad absorption, optimized energy levels and high mobility.^{13–15} The conjugated polymers with alternating electron-rich units (D) and electron-deficient segments (A), known as D–A structured polymers,^{16–18} are one of the most efficient structures. Therefore, many electron-rich and electron-deficient building blocks have been used in the design and synthesis of novel D–A copolymer photovoltaic materials. Among various donor units in the D–A copolymers, pyrene is a completely planar electron-rich moiety, and has prominent optical and electronic properties such as high quantum yield, good thermal stability and strong propensity to form π stack

aggregation.^{19,20} Some conjugated polymers^{21–24} or small molecules^{25,26} containing pyrene moieties have been prepared and showed excellent performance in organic electronics. For example, Hwang and coworkers reported that the incorporation of the pyrene units to the donor-acceptor (D–A) conjugated polymer backbone would improve the hole mobility and decrease the highest occupied molecular orbital (HOMO) energy level of the copolymer, which resulted in a highest PCE of 5.04% obtained.²¹ However, diketopyrrolopyrrole (DPP) is a strong electron-deficient segment with two electron-deficient carbonyl groups. DPP-based conjugated polymers have shown intense absorption in near infrared region and excellent performance in photovoltaic devices.^{27–30}

Herein, we designed and synthesis a D–A copolymer containing 2,7-di-2-thienyl-4,5,9,10-tetrakis(hexyloxy)pyrene as a donor moiety and DPP as an acceptor unit (Scheme 1). The inclusion of two thiophene spacers at 2, 7 position of pyrene was expected to broaden the absorption and enhance the light harvesting ability of the conjugated polymer. The four hexyloxy side chains at 4, 5, 9, 10 position of pyrene would improve the solubility of the conjugated polymer in common organic solvent. The thermal, optical, electrochemical, and

Additional Supporting Information may be found in the online version of this article.

© 2014 Wiley Periodicals, Inc.



SCHEME 1 Synthesis route of PDTPyDPP.

photovoltaic properties of the polymer were investigated systematically. The polymer exhibited a high decomposition temperature of 350 °C, a broad absorption in the range of 300–900 nm, and a HOMO energy level of -5.16 eV. Finally, the PSC device based on this polymer and [6,6]-phenyl- C_{71} -butyric acid methyl ester ($PC_{71}BM$) showed the best power conversion efficiency (PCE) of 4.43% with an open-circuit voltage (V_{oc}) of 0.66 V, a short-circuit current density (J_{sc}) of 10.52 $mA\ cm^{-2}$ and a fill factor (FF) of 64.11%.

EXPERIMENTAL

Materials

All reagents were bought from commercial sources and were used without further purification. The solvents were purified with standard methods. All air and water sensitive reactions were performed under an argon atmosphere. Silica gel (200–300 mesh) was used for column chromatography. New products were characterized by 1H NMR, ^{13}C NMR, and Atmospheric Pressure Chemical Ionization-Time of Flight (APCI-TOF) high resolution mass spectra (HRMS). Compound **1**,³¹ 2-tributylstannylthiophene,³² were synthesized according to the corresponding literatures.

Characterization

1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-600 spectrometer. APCI-TOF HRMS were performed on Bruker Maxis UHR-TOF (both positive and negative ion reflector mode). The molecular weight and polydispersity were determined by size exclusion chromatography (SEC) analysis using an ELEOS System, with monodisperse polystyrene as standard and THF as eluent at a flow rate of 1.0 $mL\ min^{-1}$ at 35 °C. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were

performed using a TA-Q600 analyzer with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The ultraviolet-visible (UV-vis) spectra were measured on a Varian Cary 50. The electrochemical behaviour of the polymer was investigated by cyclic voltammogram (CV). The CV was performed in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 ; 0.1 M) in acetonitrile. A three-electrode cell consisting of a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode was used. The scan rate was 100 $mV\ s^{-1}$. The polymer solution was dipped on the glassy carbon electrode. The potential of ferrocene/ferrocenium (Fc/Fc^+) was measured to be 0.43 V compared with the Ag/AgCl electrode under the same conditions. It is assumed that the redox potential of Fc/Fc^+ , has an absolute energy level of -4.8 eV under vacuum. Atomic force microscopy (AFM) images were obtained on an Agilent 5400 scanning probe microscope using AC mode.

Fabrication of Photovoltaic Devices

Photovoltaic devices with a layered structure of ITO/PEDOT:PSS/PDTPyDPP: $PC_{71}BM$ blend/Ca (10 nm)/Al (100 nm) were fabricated on ITO coated glass substrates (15 \times 15 mm^2). The ITO coated glasses were cleaned in an ultrasonic bath with detergent, ultra pure water, acetone, and isopropyl alcohol sequentially for 20 min, and then oxygen plasma treated for 20 min. The substrates were spin coated with PEDOT:PSS at 5000 rpm, and dried at 120 °C for 20 min. PDTPyDPP and $PC_{71}BM$ were dissolved in deoxygenated anhydrous *o*-dichlorobenzene (*o*-DCB) in the weight ratios of 1:1, 1:1.5, and 1:2, respectively and stirred overnight in glovebox at 90 °C. An active layer consisting of the blend of PDTPyDPP and $PC_{71}BM$ was then spin coated on PEDOT:PSS. A typical concentration of the PDTPyDPP/

PC₇₁BM blending solution was 24 mg mL⁻¹. Subsequently Ca (10 nm) and Al (100 nm) were thermally evaporated in a vacuum of 2×10^{-4} Pa on top of the active layer as cathode. Photovoltaic performance was characterized under illumination with an AM 1.5G (100 mW cm⁻²) in a nitrogen atmosphere, and the current-voltage curves were recorded using a Keithley 2400 source meter. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency measurement system.

Fabrication of Field-Effect Transistors (FET) Devices

Bottom-gate/bottom-contact transistors were fabricated on Au-patterned SiO₂/Si substrate. After standard cleaning (15 min ultrasonic process in acetone, isopropanol and DI-water, sequentially), 5 mg mL⁻¹ polymer dissolved in chlorobenzene was spin-coated on the substrates at a speed of 1200 rpm for 1 min. Then, substrates were annealed on a hot plate at 120 °C for 30 min before device test. I-V curves were measured by a Keithley 6212 source meter, Agilent 4155C semiconductor parameter analyzer and HP 4284A LCR meter in nitrogen glove-box under dark conditions.

Synthesis of Compound 1

To a solution of pyrene-4,5,9,10-tetraones (13 g, 50 mmol) in 500 mL of 85% H₂SO₄, *n*-bromosuccinimide (NBS) (27 g, 0.15 mol) was added. The mixture was stirred for 4 h at room temperature, and then was poured into 2 L water and stirred overnight. The precipitated was filtered and dried under vacuum to afford compound 1 as pale yellow solid (18.1 g, 86%). ¹H NMR (600 MHz, DMSO-*d*₆) δ (ppm) = 8.35 (s, 4H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ (ppm) = 165.28, 147.65, 139.72, 135.29, 125.75. HRMS (APCI-TOF): [M + H]⁺ Calcd for: C₁₆H₅Br₂O₄ 418.8467; found: 418.8432.

Synthesis of Compound 2

To a solution of compound 1 (8.40 g, 20 mmol) in THF (340 mL) and H₂O (210 mL) were added tetra-*n*-butylammonium bromide (3.22 g, 10 mmol) and Na₂S₂O₃ (18.96 g, 120 mmol). After 15 min, a solution of KOH (16 g, 69.7 mmol) in H₂O (210 mL) was added to the reaction mixture followed by 1-bromohexane (14.85 g, 90 mmol). The red colour reaction mixture was stirred at 100 °C for 4.5 h. The reaction mixture was cooled and extracted with EtOAc (100 mL). The organic layers were separated and the aqueous phase was extracted with EtOAc (3 \times 100 mL). The combined EtOAc extracts were washed with water followed by brine and dried over Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by silica gel flash column chromatography using a mixture of dichloromethane/petroleum ether (1/2, v/v) as an eluent to afford compound 2 as white solid (10.18 g, 13.4 mmol) in 67% yield. ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.54 (s, 4H), 4.32 (t, *J* = 6.72 Hz, 8H), 2.00–1.94 (m, 8H), 1.67–1.60 (m, 8H), 1.46–1.40 (m, 16H), 0.97 (t, *J* = 6.98 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 151.49, 144.27, 138.97, 137.01, 125.34, 74.05, 32.15, 30.64, 26.22, 23.78, 14.17. HRMS

(APCI-TOF): [M + H]⁺ Calcd for: C₄₀H₅₇Br₂O₄ 759.2623; found: 759.2597.

Synthesis of DTPy4C6

Compound 2 (7.61 g, 10 mmol) and 2-tributylstannylthiophene (8.20 g, 22 mmol) were added in a 50 mL three-necked flask. After purging with argon, bis(triphenylphosphine)palladium(II) chloride (350.96 mg, 0.5 mmol) and THF (30 mL) were added. The reaction mixture was stirred at 80 °C for 12 h. After cooling down to room temperature, the products were extracted with chloroform three times, washed with water, and then dried over sodium sulfate. After filtration, the solution was evaporated and the product mixture was purified by silica gel flash column chromatography using a mixture of dichloromethane/petroleum ether (1/1, v/v) as an eluent. Finally, the recrystallization of the product using chloroform/methanol afforded DTPy4C6 as pale yellow solid (5.98 g, 7.79 mmol) in 78% yield. ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.66 (s, 4H), 7.64 (dd, *J*₁ = 3.60 Hz, *J*₂ = 0.98 Hz, 2H), 7.40 (dd, *J*₁ = 5.16 Hz, *J*₂ = 0.98 Hz, 2H), 7.20 (dd, *J*₁ = 5.16 Hz, *J*₂ = 3.60 Hz, 2H), 4.36 (t, *J* = 6.76 Hz, 8H), 2.02–1.96 (m, 8H), 1.71–1.65 (m, 8H), 1.47–1.37 (m, 16H), 0.94 (t, *J* = 7.04 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 151.38, 144.25, 138.46, 137.42, 131.11, 125.18, 124.02, 121.56, 117.23, 73.93, 31.87, 30.64, 26.26, 22.80, 14.14. HRMS (APCI-TOF): [M + H]⁺ Calcd for: C₄₈H₆₃O₄S₂ 767.4238; found: 767.4235.

Synthesis of DTPy4C6Sn

DTPy4C6 (1.53 g, 2 mmol) was added in a 50 mL dry flask. After purging with argon, fresh distilled THF (30 mL) was added. The reaction mixture was cooled down to 0 °C, and *n*-butyllithium (1.6 M in *n*-hexane, 2.6 mL, 4.2 mmol) was added dropwise. After 1 h of stirring at this temperature, the neat trimethylstannyl chloride (1.0 M in *n*-hexane, 4.8 mL, and 4.8 mmol) was added. The solution was allowed to warm to room temperature and stirred for another 12 h, followed by dilution with hexane and washing with brine. The organic layer was collected and dried over anhydrous Na₂SO₄, then, the solvent was removed in vacuum. The recrystallization of the crude product using isopropanol afforded DTPy4C6Sn as pale yellow solid (1.88 g, 1.72 mmol) in 86% yield. ¹H NMR (600 MHz, CDCl₃) δ (ppm) = 8.66 (s, 4H), 7.74 (d, *J* = 3.36 Hz, 2H), 7.28 (d, *J* = 3.36 Hz, 2H), 4.35 (t, *J* = 6.40 Hz, 8H), 2.02–1.95 (m, 8H), 1.73–1.67 (m, 8H), 1.47–1.38 (m, 16H), 0.95 (t, *J* = 6.94 Hz, 12H), 0.45 (s, 18H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) = 151.32, 144.27, 138.46, 136.48, 132.21, 129.18, 125.01, 120.09, 116.46, 73.93, 31.87, 30.64, 26.26, 22.80, 14.14, -8.26. HRMS (APCI-TOF): [M + H]⁺ Calcd for: C₅₄H₇₉O₄S₂Sn₂ 1093.3469; found: 1093.3463.

Synthesis of PDTPyDPP

DTPy4C6Sn (218 mg, 0.2 mmol) and 2BrDPP32 (178 mg, 0.2 mmol) were dissolved in 8 mL toluene. The mixture was purged with argon for 30 min, then Pd₂(dba)₃ (4 mg) and P(*o*-tol)₃ (8 mg) were added. After being purged with argon for another 30 min, the reaction mixture was heated to 100

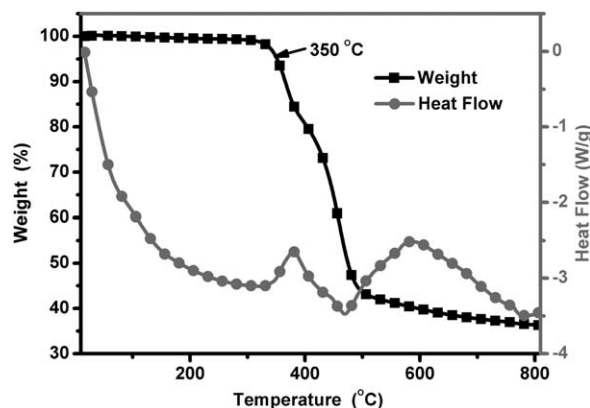


FIGURE 1 TGA and DSC curves of PDTPyDPP.

°C and stirred for 12 h under an argon atmosphere. Then the mixture was cooled down to ambient temperature and the polymer was precipitated by the addition of 150 mL methanol. The crude product was then subjected to Soxhlet extraction with methanol, hexane, and chlorobenzene. The polymer recovered from chlorobenzene was precipitated by the addition of 150 mL methanol. Then the product was dried under vacuum for 1 day to give the target polymer PDTPyDPP as a dark solid (242 mg, yield 75.6%, $M_n = 14.5$ kDa, PDI = 1.4). $^1\text{H NMR}$ (600 MHz, CDCl_3), δ (ppm) = 9.50–7.35 (br, 12H), 5.0–3.5 (br, 12H), 2.5–1.1 (br, 80H), and 1.1–0.5 (br, 24H).

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis of the monomer and the target polymer is depicted in Scheme 1. 2,7-Dibromo-4,5,9,10-tetra-hexyloxy-pyrene (compound **2**) was prepared conveniently via reductive alkylation with $\text{Na}_2\text{S}_2\text{O}_3$ and 1-bromohexane according to the modified procedure reported previously.³¹ DTPy4C6 was synthesized by the Stille coupling reaction between compound **2** and 2-tributylstannylthiophene. Then it was stannated with trimethyltinchloride to produce the monomer DTPy4C6Sn. 2BrDPP32 was commercial available. Finally, the D–A structured polymer (PDTPyDPP) was synthesized via Stille coupling polymerization between DTPy4C6Sn and 2BrDPP32 in the presence of $\text{Pd}_2(\text{dba})_3$ catalyst and tri(*o*-tolyl)phosphine ligand with a yield of 75.6%. The synthesized polymer was characterized by $^1\text{H NMR}$ (Supporting Information Fig. S1) and the number-average molecular weight (M_n) was measured by SEC to be 14.5 kDa with a polydispersity index (PDI) of 1.4. PDTPyDPP can be dissolved in common organic solvent such as chloroform, chlorobenzene, and 1,2-dichlorobenzene.

Thermal Stability

The thermal properties of the polymer PDTPyDPP were measured by TGA and DSC. As shown in Figure 1, TGA indicates that PDTPyDPP has good thermal stability and the decomposition temperature (T_d) at 5% weight loss is about 350 °C. DSC reveals that there is no apparent thermal transi-

tion for the polymer before 350 °C. The high decomposition and thermal transition temperatures prevent the deformation and degradation of the polymer film when the active layer was annealed, indicating sufficient thermal stability for PSCs application.³³

Optical Properties

The absorption spectra of PDTPyDPP in 1,2-dichlorobenzene and in film are shown in Figure 2. A maximum peak at 700 nm with two shoulder peaks at 778 and 643 nm was observed in the spectrum of the polymer in 1,2-dichlorobenzene solution, meanwhile, two peaks at 422 and 367 nm were showed in short wavelength region. Compared with the weak absorption for the π – π^* transition in the 300–500 nm range, the intense absorption in the range of 550–900 nm was attributed to the intramolecular charge transfer (ICT) from electron-donating units (pyrene and thiophene) to electron-withdrawing unit (DPP) in the conjugated main chain.³⁴ In the solid film, the peak of maximum ICT absorption was at 715 nm, which was red-shifted by 15 nm in comparison with their solution absorption. Interestingly, the solid absorption spectrum demonstrates a more pronounced shoulder peak at long wavelength (797 nm) and a weaker shoulder peak at short wavelength (653 nm), which indicates an increased interchain π – π^* stacking for planar polymer chain in the solid state. The optical band-gap of the polymer was estimated as 1.33 eV from the onset of the UV-vis absorption in the thin film.

Electrochemical Properties

Electronic energy levels of the polymers are crucial for their application in PSCs. To evaluate the redox behaviours of the synthesized conjugated polymer, the electrochemical property of PDTPyDPP was measured by CV with 0.1 M Bu_4NPF_6 as the supporting electrolyte. As shown in Figure 3, the polymer film exhibited an irreversible reduction wave in the negative potential range and a quasi-reversible wave in the positive potential range (vs. Ag/AgCl). The HOMO and lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymer film were estimated from the onset potentials according to the equation HOMO

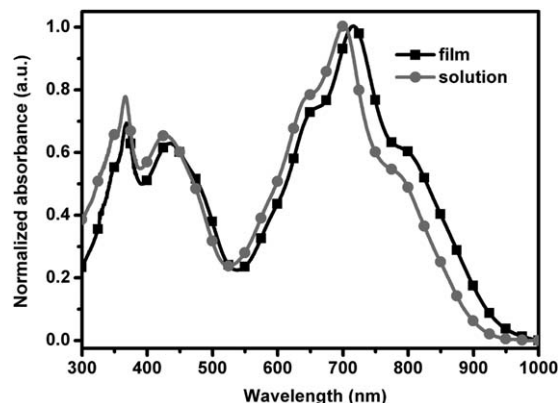


FIGURE 2 Normalized UV-vis absorption spectra of PDTPyDPP in 1,2-dichlorobenzene solution and in the thin solid film.

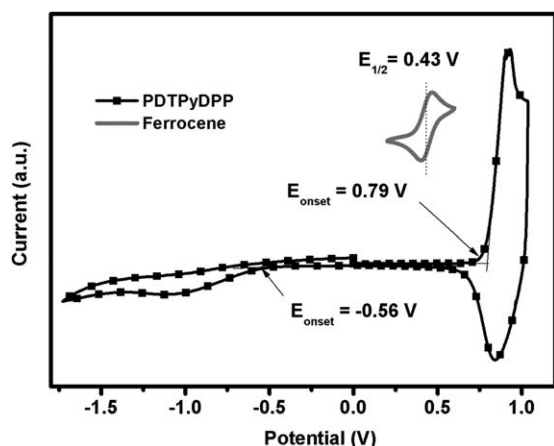


FIGURE 3 CV of PDTPyDPP.

(LUMO) = $-[(E_{\text{ox/red}}^{\text{onset}} - E_{\text{foc}}) + E_{\text{ref}}]$ (eV), where E_{foc} is the potential of the external standard, the ferrocene/ferrocenium ion (Foc/Foc⁺) couple, and E_{ref} is the reference energy level of ferrocene (4.8 eV below the vacuum level; the vacuum level is defined as zero). The HOMO and LUMO energy levels of PDTPyDPP calculated in this way are -5.16 and -3.81 eV. The energy band-gap calculated from the HOMO and LUMO levels is 1.35 eV, which is consistent with the optical band gap (1.33 eV) estimated from absorption onset in the thin film.

Polymer Solar Cell Performance

Photovoltaic property of PDTPyDPP was investigated with a device structure of ITO/PEDOT:PSS/PDTPyDPP:PC₇₁BM/Ca/Al under the illumination of AM 1.5G at 100 mA cm⁻². The devices fabrication conditions, such as the weight ratio of polymer to PC₇₁BM, and the amount of the 1,8-diiodooctane (DIO) additive were carefully optimized. As shown in Table 1 and Figure 4(a), the V_{oc} values kept almost stable while the ratio of PDTPyDPP to PC₇₁BM increased from 1:1 to 1:1.5, and then to 1:2, however, the device showed the highest J_{sc} and FF values at 1:1.5, and the PCE of the device reached 3.45%, with $V_{\text{oc}} = 0.66$ V, $J_{\text{sc}} = 8.01$ mA cm⁻², and FF = 64.95%. To further investigate the effect of processing additive on the performance of devices, the PDTPyDPP/

TABLE 1 Device Performance of the Copolymer

Ratio ^a	Solvent	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
1:1	<i>o</i> -DCB	0.66	7.89	61.32	3.18
1:1.5	<i>o</i> -DCB	0.66	8.01	64.95	3.45
1:2	<i>o</i> -DCB	0.66	7.42	61.29	2.99
1:1.5	<i>o</i> -DCB + 1.0%DIO	0.67	8.97	64.81	3.90
1:1.5	<i>o</i> -DCB + 1.5%DIO	0.66	10.52	64.11	4.43
1:1.5	<i>o</i> -DCB + 2.0%DIO	0.65	9.99	59.67	3.87
1:1.5	<i>o</i> -DCB + 2.5%DIO	0.67	9.58	60.07	3.83
1:1.5	<i>o</i> -DCB + 3.0%DIO	0.66	9.00	59.51	3.55

^a The weight ratio of the PDTPyDPP to PC₇₁BM.

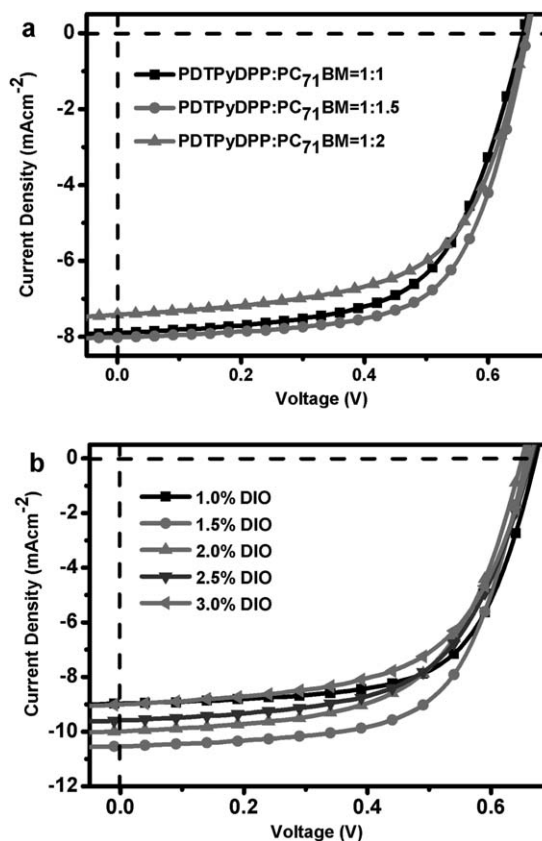


FIGURE 4 J-V characteristics of PSCs based on the PDTPyDPP:PC₇₁BM blend film with (a) different ratios and (b) different amount of DIO as additive when PDTPyDPP:PC₇₁BM = 1:1.5.

PC₇₁BM blend films were prepared at the above optimized composite ratio from *o*-dichlorobenzene solution with addition of 1, 1.5, 2, 2.5, and 3% (volume) DIO as additive, respectively. As shown in Table 1 and Figure 4(b), while 1.5% volume ratio of DIO was used as the additive, the PCE of the PDTPyDPP:PC₇₁BM based device increased to 4.43% with $V_{\text{oc}} = 0.66$ V, $J_{\text{sc}} = 10.52$ mA cm⁻², and FF = 64.11%. We also use PC₆₁BM as acceptor to investigate the device performance of our polymer. As shown in Supporting Information Figure S2 and Table S1, the devices with PDTPyDPP as donor and PC₆₁BM as acceptor showed the best PCE of 1.86%, with $V_{\text{oc}} = 0.63$ V, $J_{\text{sc}} = 5.01$ mA cm⁻², and FF = 58.80%, when the weight ratio of PDTPyDPP to PC₆₁BM was 2:3 with addition of 1.5% DIO as additive.

The photoresponse curve of the optimized device based on PDTPyDPP was investigated, which showed a relatively broad photoresponse range between 300 and 800 nm (Fig. 5). The maximum EQE value of 50% at 460 nm was observed. The integrated J_{sc} from EQE spectrum is 10.01 mA cm⁻², which is consistent with the measured J_{sc} value (10.52 mA cm⁻²).

Hole Mobility

The hole mobility of the polymer is tested by FET device. Figure 6 shows the transfer curve of the FET device based

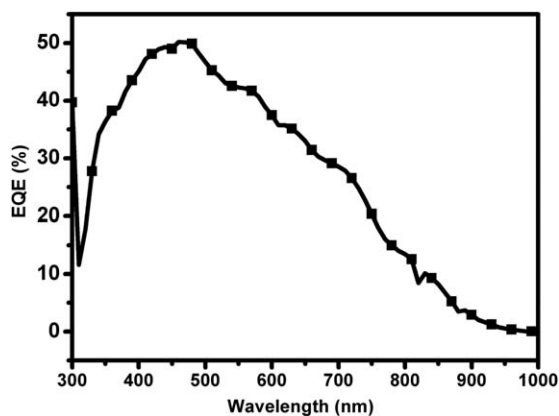


FIGURE 5 EQE curve of device based on PDTPyDPP/PC₇₁BM (1:1.5, w/w) with 1.5% DIO as additive.

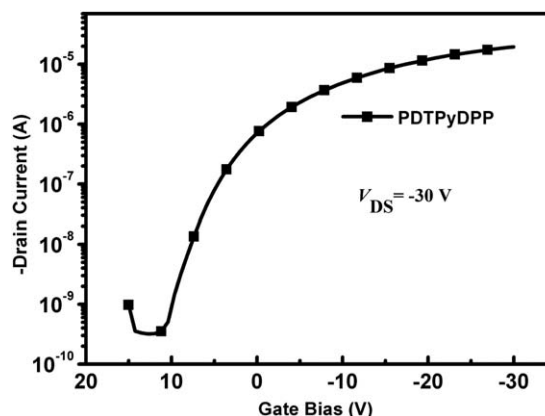


FIGURE 6 I_D versus V_G transfer characteristic of PDTPyDPP based FET device.

on PDTPyDPP. The calculated mobility of the polymer is $6.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with on/off ratio of 1×10^5 and V_{Th} of 8 V for the FET device. Obviously, the high efficiency of the PSC based on PDTPyDPP should be as a benefit of the high hole mobility and broad absorption of PDTPyDPP.

AFM Images

The morphologies of the blend films of PDTPyDPP and PC₇₁BM (1:1.5, w/w) have been investigated by tapping-mode AFM. Figure 7 showed the topographic and phase images of the films with or without DIO additive treatment.

All the films were prepared under the same conditions with the optimized photovoltaic devices. As shown in Figure 7(a), the surface root mean square (RMS) roughness for the blend film of PDTPyDPP: PC₇₁BM is 0.80 nm. While the blend films are spin-coated from *o*-dichlorobenzene solution containing 1.5% DIO as additive, the RMS data is greatly increased to 2.07 nm, which indicates that adding DIO as additive in the mixture leads to rougher surface than that of the pristine blend film. Notably, the fibrous networks phase images are observed in the blending films with DIO additive, indicating that a well-ordered interpenetrating network between

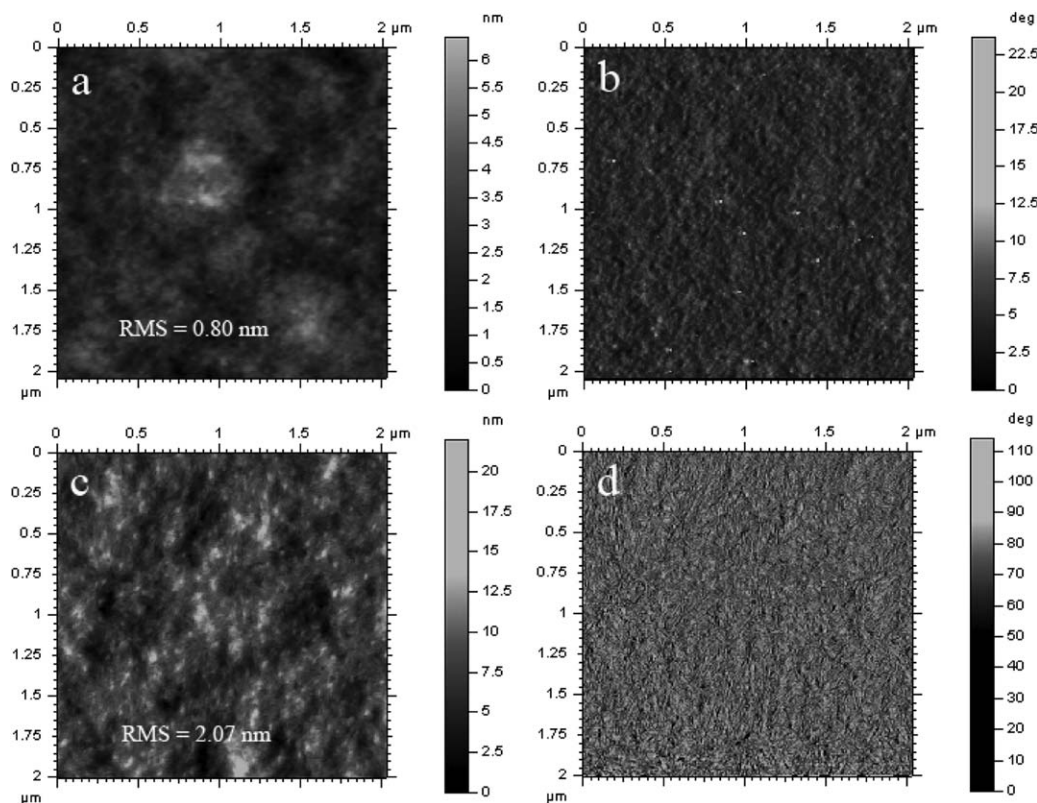


FIGURE 7 AFM topography height (a and c), phase (b and d) images of the PDTPyDPP:PC₇₁BM (1:1.5, w/w) film without (a and b) and with (c and d) 1.5% DIO as additive (scan size: $2 \times 2 \mu\text{m}^2$).

polymer and acceptor is formed [Fig. 7(d)], which would be helpful in the charge collection efficiency in the active layer of the device, finally, resulted in higher J_{sc} (Fig. 4 and Table 1).^{35,36}

CONCLUSIONS

In conclusion, we synthesized a new D-A conjugated copolymer from two easily accessible monomers, pyrene derivative and DPP. The obtained polymer showed broad visible absorption from 300 to 900 nm, a moderate field hole mobility up to 10^{-3} order, a high decomposition temperature of 350 °C, and a HOMO energy level of -5.16 eV. The PSC device based on this polymer and PC₇₁BM gave the PCE of 4.43%, one of the highest efficiencies among pyrene-based polymers. Our preliminary experiment results show that thienyl substituted pyrene with suitable side chains is a promising donor building block in constructing D-A conjugated polymers for the photovoltaic applications.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (21204097, 21274134, 51173199, and 61107090), Ministry of Science and Technology of China (2014CB643501 and 2010DFA52310), Shandong Provincial Natural Science Foundation (ZR2011BZ007), and Qingdao Municipal Science and Technology Program (11-2-4-22-hz).

REFERENCES AND NOTES

- 1 G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789–1791.
- 2 P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009–20029.
- 3 J. H. Hou, H. Y. Chen, S. Q. Zhang, R. I. Chen, Y. Yang, Y. Wu, G. Li, *J. Am. Chem. Soc.* **2009**, *131*, 15586–15587.
- 4 H. Tan, X. Deng, J. Yu, J. Chen, K. Nie, Y. Huang, Y. Liu, Y. Wang, M. Zhu, W. Zhu, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1051–1057.
- 5 Y. Z. Lin, Y. F. Li, X. W. Zhan, *Chem. Soc. Rev.* **2012**, *41*, 4245–4272.
- 6 X. Guan, K. Zhang, F. Huang, G. C. Bazan, Y. Cao, *Adv. Func. Mater.* **2012**, *22*, 2846–2854.
- 7 Q. Liu, X. C. Bao, S. G. Wen, Z. K. Du, L. L. Han, D. Q. Zhu, Y. H. Chen, M. L. Sun, R. Q. Yang, *Polym. Chem.* **2014**, *5*, 2076–2082.
- 8 Z. C. He, C. M. Zhong, S. J. Su, M. Xu, H. B. Wu, Y. Cao, *Nat. Photonics* **2012**, *6*, 591–595.
- 9 L. Dou, J. You, J. Yang, C. C. Chen, Y. J. He, S. Murase, T. Moriarty, K. Emery, G. Li, Y. Yang, *Nat. Photonics* **2012**, *6*, 180–185.
- 10 J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Commun.* **2013**, *4*, 1446.
- 11 R. S. Kularatne, H. D. Magurudeniya, P. Sista, M. C. Biewer, M. C. Stefan, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 743–768.
- 12 J.-H. Kim, C. E. Song, H. U. Kim, I.-N. Kang, W. S. Shin, M.-J. Park, D.-H. Hwang, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 4136–4149.
- 13 B. Qi, J. Wang, *Phys. Chem. Chem. Phys.* **2013**, *15*, 8972–8982.
- 14 S. L. Shen, L. Gao, C. He, Z. J. Zhang, Q. J. Sun, Y. F. Li, *Org. Electron.* **2013**, *14*, 875–881.
- 15 H. B. Pan, L. J. Zuo, W. F. Fu, C. C. Fan, B. Andreasen, X. Q. Jiang, K. Norrman, F. C. Krebs, H. Z. Chen, *Org. Electron.* **2013**, *14*, 797–803.
- 16 L. J. Huo, Z. A. Tan, X. Wang, Y. Zhou, M. F. Han, Y. F. Li, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4038–4049.
- 17 X. Zhao, D. Yang, H. Lv, L. Yin, X. Yang, *Polym. Chem.* **2013**, *4*, 57–60.
- 18 P. Shen, H. J. Bin, Y. Zhang, Y. F. Li, *Polym. Chem.* **2014**, *5*, 567–577.
- 19 J. Xiao, X. Xiao, Y. Zhao, B. Wu, Z. Liu, X. Zhang, S. Wang, X. Zhao, L. Liu, L. Jiang, *Nanoscale* **2013**, *5*, 5420–5425.
- 20 S. X. Qu, M. H. Li, L. X. Xie, X. Huang, J. G. Yang, N. Wang, S. F. Yang, *ACS Nano* **2013**, *7*, 4070–4081.
- 21 J. H. Kim, H. U. Kim, I. N. Kang, S. K. Lee, S. J. Moon, W. S. Shin, D. H. Hwang, *Macromolecules* **2012**, *45*, 8628–8638.
- 22 D. S. Yang, K. H. Kim, M. J. Cho, J. I. Jin, D. H. Choi, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1457–1467.
- 23 C. E. Song, I. N. Kang, J. H. Kim, D. H. Hwang, J. C. Lee, T. Ahn, W. S. Shin, S. J. Moon, S. K. Lee, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1512–1519.
- 24 J. H. Kim, S. Lee, I. N. Kang, M. J. Park, D. H. Hwang, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 3415–3424.
- 25 J. W. Mun, I. Cho, D. Lee, W. S. Yoon, O. K. Kwon, C. Lee, S. Y. Park, *Org. Electron.* **2013**, *14*, 2341–2347.
- 26 O. P. Lee, A. T. Yiu, P. M. Beaujuge, C. H. Woo, T. W. Holcombe, J. E. Millstone, J. D. Douglas, M. S. Chen, J. M. J. Fréchet, *Adv. Mater.* **2011**, *23*, 5359–5363.
- 27 R. Zhou, Q. D. Li, X. C. Li, S. M. Lu, L. P. Wang, C. H. Zhang, J. Huang, P. Chen, F. Li, X. H. Zhu, W. C. H. Choy, J. B. Peng, Y. Cao, X. Gong, *Dyes Pigments* **2014**, *101*, 51–57.
- 28 Z. Zeng, Y. Li, J. F. Deng, Q. Huang, Q. Peng, *J. Mater. Chem. A* **2014**, *2*, 653–662.
- 29 J.-H. Kim, C. E. Song, I.-N. Kang, W. S. Shin, D.-H. Hwang, *Chem. Commun.* **2013**, *49*, 3248–3250.
- 30 W. Li, A. Furlan, W. S. C. Roelofs, K. H. Hendriks, G. W. P. van Puijssen, M. M. Wienk, R. A. J. Janssen, *Chem. Commun.* **2014**, *50*, 679–681.
- 31 S.-i. Kawano, M. Baumgarten, D. Chercka, V. Enkelmann, K. Muellen, *Chem. Commun.* **2013**, *49*, 5058–5060.
- 32 Q. Ye, J. Chang, K.-W. Huang, C. Chi, *Org. Lett.* **2011**, *13*, 5960–5963.
- 33 S. Wen, X. Bao, W. Shen, C. Gu, Z. Du, L. Han, D. Zhu, R. Yang, *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 208–215.
- 34 K.-H. Ong, S.-L. Lim, J. Li, H.-K. Wong, H.-S. Tan, T.-T. Lin, L. C. H. Moh, J. C. de Mello, Z.-K. Chen, *Polym. Chem.* **2013**, *4*, 1863–1873.
- 35 Y. Wang, Y. Liu, S. J. Chen, R. X. Peng, Z. Y. Ge, *Chem. Mater.* **2013**, *25*, 3196–3204.
- 36 X. C. Bao, T. Wang, A. L. Yang, C. P. Yang, X. W. Dou, W. C. Chen, N. Wang, R. Q. Yang, *Mater. Sci. Eng. B* **2014**, *180*, 7–11.