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ARTICLE TYPE

Modulation of the Properties of Pyrrolo[3,4-c]pyrrole-1,4-dione Based Polymers Containing 2,5-Di(2-thienyl)pyrrole Derivatives With Different Substitutions on the Pyrrole Unit

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In this study, four new pyrrolo[3,4-c]pyrrole-1,4-dione (DKPP)-based polymers, P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA), and P(DKPP-TPTI), containing *N*-alkyl-2,5-di(2-thienyl)pyrrole (TPT) derivatives with four different substituents such as hydrogen, ester, amide, and imide groups on the 3,4- position of the pyrrole unit were prepared to tune the properties of the polymers. Opto-electrical studies showed that the incorporation of electron withdrawing substituents such as ester, amide and imide groups instead of hydrogen on the pyrrole backbone of the polymers increased the band gaps significantly from 1.31 eV to 1.42 eV, 1.37 eV and 1.37 eV, respectively, and reduced the highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) energy levels from -4.96 eV/-3.65 eV to -5.24 eV/-3.82 eV, -5.17 eV/-3.80 eV and -5.35 eV/-3.98 eV, respectively. Organic field effect transistors (OFETs) made from these polymers indicated that the incorporation of electron withdrawing functional groups on the polymer backbone reduced the hole mobility. Polymer solar cells (PSCs) prepared with the polymers as an electron donor offered higher power conversion efficiency (*PCE*) for the polymer containing hydrogen on TPT backbone, but the polymers incorporating electron withdrawing substituents on the TPT backbone showed a significantly higher open circuit voltage (V_{oc}) though the *PCE* was relatively lower.

Introduction

The recent progress of polymer solar cells (PSCs) has revealed them to be the most promising green energy production technique because of their high solar to electrical energy conversion efficiency via the easy device fabrication at low-cost to large area.^{1–3} The photoactive layer of the PSCs are usually made from an interpenetrating network of electron donating π -conjugated polymers and electron accepting fullerene derivatives. Numerous π -conjugated polymers^{4–9} and fullerene derivatives^{10–12} have been reported for PSCs over the last decade. Note that the polymer and fullerene derivatives used in the photoactive layer of PSCs, the device structure and its preparation conditions are crucial factors determining the performance of PSCs. In this instance, chemists are looking forward to developing highly efficient donor or

acceptor materials and physicists are working more on the device optimization of PSCs to improve the *PCE* further. Currently, single junction PSCs made from single donor and acceptor materials offer the maximum *PCE* in the range of 8–9.5%,^{13–18} whereas multijunction or tandem PSCs prepared with two different donor and acceptor materials provide a relatively higher *PCE* of 9–11.5%.^{1,19–21}

Since 2010, the authors have been involved in the preparation of highly efficient 2,5-di(2-thienyl)pyrrole (TPT)-based polymeric donor materials for PSCs.^{22–29} In the beginning of these studies, TPT was utilized as an electron donor unit and TPT-based polymers containing electron rich indenofluorene,²² 2,5-dioctyloxyphenylene²³ and 3-octylthiophene²³ or electron accepting benzothiadiazole,^{24–26} thiophene-benzothiadiazole-thiophene (TBT),^{27,28} and thiadiazoloquinoxaline (DQ)²⁹ were developed for PSCs. The opto-electrical and photovoltaic studies showed that the properties of TPT-based polymers varied considerably according to the electron rich or deficient units incorporated in their main chain. Although, all polymers showed poor photovoltaic performances (~1–2%) due mainly to the lower open circuit voltage (V_{oc} ~ 0.4–0.5 V) and fill factor (*FF* ~ 30–40%).^{22–29} The V_{oc} and *FF* are dependent mainly on the highest occupied molecular orbital (HOMO) energy level and carrier mobility of electron donating polymers. In an effort to lower the HOMO level as well as to improve the mobility of

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TPT-based polymers, more recently we incorporated electron accepting imide groups on the 3,4-position of pyrrole of TPT unit (pyrrolo[3,4-c]pyrrole-1,3-dione (TDPPDT)) and copolymerized it with electron rich benzodithiophene (BDT and BDTT) derivatives to afford structurally new donor-acceptor (D-A) large band gap polymers, namely P(BDT-TDPPDT) and P(BDTT-TDPPDT).^{30–32} The chemical structures of P(BDT-TDPPDT) and P(BDTT-TDPPDT) are presented in Fig. 1. As expected, the HOMO energy levels of the polymers P(BDT-TDPPDT) and P(BDTT-TDPPDT) were found to be 0.2–0.4 eV deeper than those of TPT-based polymers incorporating TPT as the donor unit.^{22–29}

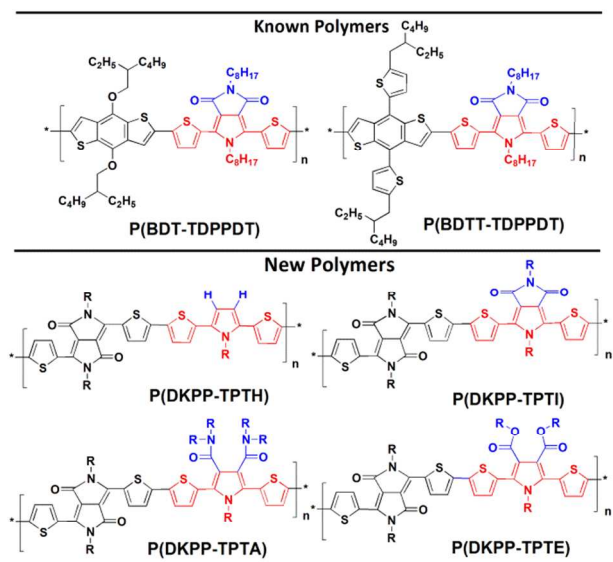


Fig. 1 Structures of known polymers P(BDT-TDPPDT), P(BDTT-TDPPDT) and new polymers prepared in this study.

The PSC made from a blend of P(BDT-TDPPDT):PC₇₀BM gave a record *PCE* of 6.74% with a greatly improved open-circuit voltage (V_{oc}) of 0.86 V, a short-circuit current (J_{sc}) of 10.94 mA/cm² and a fill factor (*FF*) of 71%. The PSC prepared from a blend of P(BDTT-TDPPDT):PC₇₀BM also exhibited a high *PCE* of 6.57% with V_{oc} , J_{sc} and *FF* of 0.90 V, 10.12 mA/cm² and 72%, respectively. Although P(BDT-TDPPDT) and P(BDTT-TDPPDT) exhibit a wide band gap ($E_g \sim 2.11$ and 2.04 eV, respectively), still they produce a high *PCE* in single layer PSCs.^{30–32} The incorporation of an imide group on the TPT backbone was found to improve the V_{oc} and *FF* significantly and consequently, the *PCE* of TPT-based polymers. To improve the *PCE* of P(BDT-TDPPDT), electron deficient thiophene-based imide functionalized thieno[3,4-c]pyrrole-4,6-dione (TPD) unit was incorporated randomly in the P(BDT-TDPPDT) main chain to offer a random polymer.³³ Interestingly, the PSC made from the random polymer was found to give an enhanced *PCE* of 7.03 % with a relatively higher J_{sc} (~ 11.52 mA/cm²) compared to the PSC prepared from P(BDT-TDPPDT).³³

The recently reported alternating polymer, P(DKPP-TPD), containing pyrrole-based lactam functionalized pyrrolo[3,4-c]pyrrole-1,4-dione (DKPP) and TPD units displayed a narrow band gap (1.42 eV) and high *PCE* (5.3%).³⁴ Just changing the TPD in P(DKPP-TPD) with TDPPDT is expected to offer a freely

soluble polymer via the incorporation of alkyl groups on the pyrrole as well as imide nitrogen of the TDPPDT unit. The solubility of the polymer is also essential for PSCs owing to its solution processability. In addition, P(DKPP-TPD) is an acceptor-acceptor (A–A) type of polymer, and the photovoltaic performance of A–A polymer is usually lower than that of donor-acceptor (D–A) polymers. TDPPDT is a relatively weak electron acceptor unit compared to TPD due to the intrinsic electron-rich character of pyrrole on DPPD unit. Consequently, the polymerization of pyrrole-based imide functionalized pyrrolo[3,4-c]pyrrole-1,3-dione (TDPPDT)^{32,33} unit with its structural isomer, such as DKPP, might offer a lower band gap polymer than P(DKPP-TPD) due to the improved internal charge transfer between the donor-acceptor units along with better solubility. In this study, polymer P(DKPP-TPTI) containing DKPP and TDPPDT was prepared. In addition, to clarify the effect of substituents on the properties of polymers, three more polymers containing DKPP and TPT derivatives with hydrogen, esters and amides on the 3,4-position of pyrrole unit were prepared. The molecular structures of new polymers are presented in Fig. 1. This paper reports the synthesis, opto-electrical, charge transport and photovoltaic properties of four new DKPP-based polymers containing TPT units with different substituents on the pyrrole unit.

Experimental section

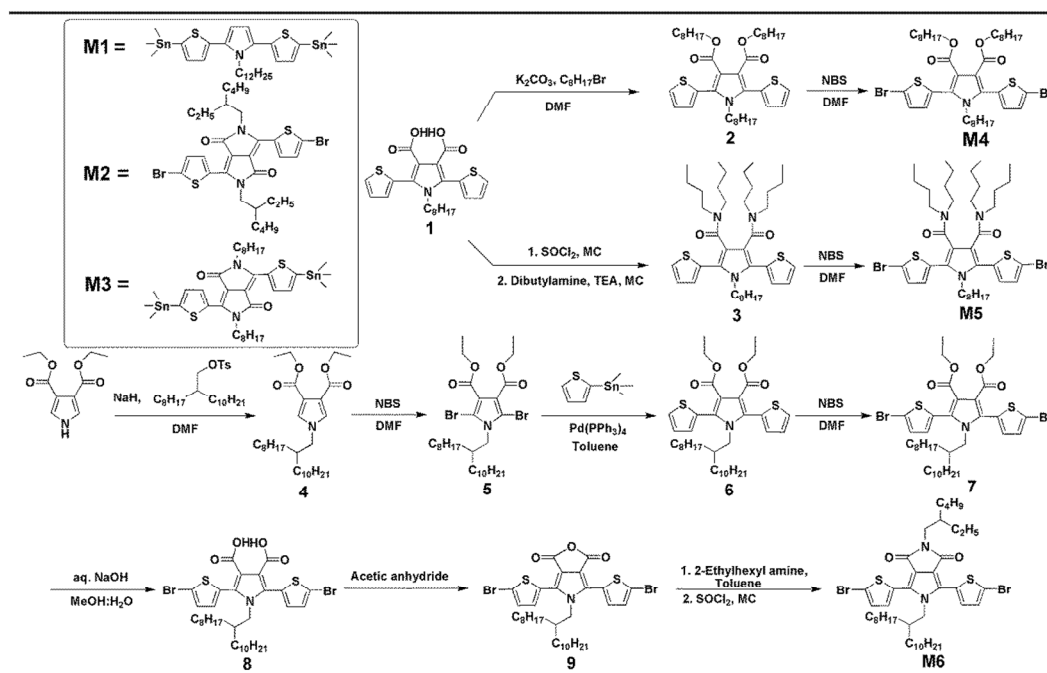
Materials and measurements

All necessary reagents and solvents were obtained from Sigma-Aldrich or TCI chemicals. The reagents were used as received and the solvents were handled in a moisture-free atmosphere. Purification of the compounds was performed by column chromatography (silica gel, Merck Kieselgel 60, 70–230 mesh ASTM). The nuclear magnetic resonance (NMR) spectra were recorded using Varian Mercury Plus spectrometer (300 MHz for ¹H and 75 MHz for ¹³C NMR) and the high resolution fast atom bombardment (FAB) mass spectra were analyzed using a JEOL JMS-700 mass spectrometer. An Agilent 1200 Infinity Series separation module was used to determine the molecular weight of the polymers by gel permeation chromatography (GPC) with chloroform as an eluent at ambient temperature. The GPC instrument was calibrated with the polystyrene standard prior to analysis. Thermogravimetric (TGA) analysis of the polymer was performed on TA instrument Q600-0825 at a heating and cooling rate of 10 °C/min under nitrogen. The UV-visible absorption spectra of the polymers in the solution and film state were recorded on a JASCO V-570 spectrophotometer and a CH Instruments Electrochemical Analyzer was used for cyclic voltammetry (CV) of the polymers. The polymer cast film on the platinum working electrode was immersed in an acetonitrile solution containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄), Ag/AgCl as the reference electrode and platinum wire as a counter electrode and then the measurements were taken. For CV, the instrument was calibrated with the most common ferrocene/ferrocenium ion (Fc/Fc⁺) standard. Atomic force microscopy (AFM) was performed using a Seiko instruments (SPI 3800N-SPA 400).

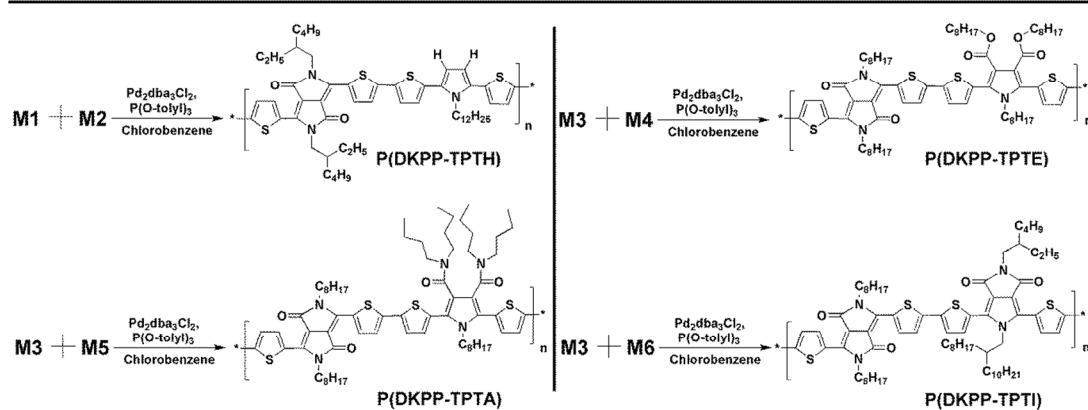
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ARTICLE TYPE



Scheme 1 Synthetic route to monomers.



Scheme 2 Synthetic route to polymers.

5 Device fabrication and characterization of OFETs

Organic field effect transistors (OFETs) were fabricated on highly n-type-doped silicon (Si) substrates with a 200 nm thermally grown silicon oxide (SiO₂) layer. The Si substrates were subjected to the UV-Ozone treatment for 30 min and treated with an octadecyltrichlorosilane (OTS) self-assembled monolayer. The n-type doped Si substrate functions as a gate electrode and the SiO₂ layer acts as a gate dielectric. The CB solution of the polymer (10 mg/ml) was spin-cast on top of the Si substrate (2000 rpm) and then dried at room temperature (RT) for 30 minutes. The source and drain electrodes (Au, 70 nm) were deposited on top of the polymer layer by thermal evaporation in a vacuum ($\sim 2 \times 10^{-6}$ Torr). The channel length (L) and channel

width (W) of the device was 50 μm and 3.0 mm, respectively. The output and transfer characteristics of the OFETs were measured using a Keithley semiconductor parametric analyzer (Keithley 4200). All preparation processes and the characterization of the OFETs were performed inside a N₂-atmosphere glove box. The mobility (μ) was determined using the following equation in the saturation regime:

$$I_{DS,sat} = (-WC_i/2L) (V_{GS} - V_T)^2$$

where C_i is the capacitance per unit area of the SiO₂ dielectric ($C_i = 15 \text{ nF cm}^{-2}$) and V_T is the threshold voltage.

Device fabrication and characterization of PSCs

The PSCs were fabricated with the simple device structure of ITO-coated glass substrate/PEDOT:PSS/polymer/PC₇₀BM/Al.

The pre-cleaned ITO-coated glass substrate was dried overnight in an oven. Subsequently, a 40 nm thickness layer of PEDOT:PSS (Baytron PH) was spin-cast from aqueous solution on ITO-coated glass substrate. The substrate was dried for 10 min at 140 °C in air and then transferred to a glove box to spin-cast the photoactive layer. A solution containing a mixture of polymer:PC₇₀BM (1:1, 1:2 and 1:3 wt%) in dichlorobenzene (DCB) with a concentration of 20 mg/ml was then spin-cast on top of the PEDOT/PSS layer. For the device made with 1,8-diiodooctane (DIO), the polymer:PC₇₀BM blends were dissolved in DCB:DIO (98:2 vol%). The thickness of the photoactive layer was 80 nm and the film was dried for 30 min at RT in a glove box. Subsequently, an aluminium (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum (~3 x 10⁻⁶ Torr). The current density-voltage (*J-V*) characteristics of the PSC devices were measured using a Keithley 2400 Source Measure Unit. The solar cell performance utilized an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 Wm⁻². The spectral mismatch factor was calculated by comparing the solar simulator spectrum with the AM 1.5 spectrum at room temperature.

Synthesis

Diethyl 1-octyl-2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (2). Potassium carbonate (K₂CO₃, 0.38 g, 2.70 mmol) and 1-bromoocane (0.70 mL, 4.00 mmol) were added to a stirred solution of compound **1** (0.3 g, 0.70 mmol), which was prepared using a similar procedure reported elsewhere,³² in *N,N*-dimethylformamide (DMF, 10 mL). The mixture was stirred overnight at room temperature (RT) and poured into water (100 mL). The solution was stirred for 30 min and extracted twice with diethyl ether (50 mL). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford pure compound **2** as a colorless liquid. Yield: 0.41 g (89%). ¹H NMR (300 MHz, CDCl₃, δ): 7.47 (dd, 2H), 7.15 (dd, 2H), 7.10 (dd, 2H), 4.10 (t, 4H), 3.77 (t, 2H), 1.36-1.60 (m, 6H), 1.00-1.34 (m, 30H), 0.80-0.92 (m, 9H); ¹³C NMR (75 MHz, CDCl₃, δ): 164.6, 130.6, 130.5, 128.9, 128.1, 127.1, 117.4, 65.3, 32.1, 31.9, 29.5, 29.4, 29.0, 28.8, 26.5, 26.2, 22.9, 22.8, 14.3; HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₈H₅₇NO₄S₂, 655.3729; found, 655.3729.

Diethyl 2,5-bis(5-bromothiophen-2-yl)-1-octyl-1H-pyrrole-3,4-dicarboxylate (M4). *N*-Bromosuccinimide (NBS) (0.18 g, 1.00 mmol) was added in one portion to a stirred solution of compound **2** (0.30 g, 0.46 mmol) in 10 mL of DMF at RT. The solution was stirred for 12 h and then poured into water (200 mL). The solution was extracted twice with diethyl ether (50 mL) and the combined organic layer was washed once with brine and dried over anhydrous Na₂SO₄. The solvent was removed and the compound was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford the pure product **M4** as a colorless liquid. Yield: 0.39 g (93%). ¹H NMR (300 MHz, CDCl₃, δ): 7.06 (d, 2H), 6.90 (d, 2H), 4.10 (t, 4H), 3.77 (t, 2H), 1.36-1.60 (m, 6H), 1.00-1.34 (m, 30H), 0.80-0.92 (m, 9H); ¹³C NMR (75 MHz, CDCl₃, δ): 164.3, 132.1, 131.1, 130.1, 127.8, 118.1, 114.9, 65.3, 32.1, 31.9, 29.5, 29.4, 29.0, 28.8, 26.5, 26.2, 22.9, 22.8, 14.3; HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₈H₅₅Br₂NO₄S₂, 811.1939; found, 811.1941.

N³,N³,N⁴,N⁴-Tetrabutyl-1-octyl-2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxamide (3). Thionyl chloride (10 mL) was added to a stirred solution of compound **1** (0.3 g, 0.70 mmol) in dry methylene chloride (MC, 30 mL) at RT and heated under reflux for 1 h. The solution was then cooled to RT and the solvent was removed by rotary evaporation. The residue was dissolved in MC (30 mL) and cooled to 0 °C. Subsequently, dibutylamine (3.0 mL) was added slowly at 0 °C. The solution was stirred for 3 h and poured into water. The organic layer was then separated. The aqueous solution was extracted once again with MC (50 mL) and the combined organic layer was washed with 2 N HCl, brine and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford pure compound **3** as a light yellow liquid. Yield: 0.43 g (93%). ¹H NMR (300 MHz, CDCl₃, δ): 7.45 (dd, 2H), 7.15 (dd, 2H), 7.08 (dd, 2H), 4.00 (s, 2H), 2.90-3.40 (m, 8H), 1.00-1.60 (m, 28H), 0.70-1.00 (m, 15H); ¹³C NMR (75 MHz, CDCl₃, δ): 166.1, 130.6, 130.5, 128.9, 128.1, 127.1, 117.4, 49.2, 44.7, 31.9, 31.3, 30.8, 29.7, 29.1, 29.0, 26.5, 22.8, 20.4, 20.2, 14.3, 14.1, 13.9; HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₈H₅₉N₃O₂S₂, 653.4049; found, 653.4049.

2,5-Bis(5-bromothiophen-2-yl)-N³,N³,N⁴,N⁴-tetrabutyl-1-octyl-1H-pyrrole-3,4-dicarboxamide (M5). NBS (0.18 g, 1.00 mmol) was added in one portion to a stirred solution of compound **3** (0.30 g, 0.46 mmol) in 10 mL of DMF at RT. The solution was stirred for 12 h and then poured into water (200 mL). The solution was extracted twice with diethyl ether (50 mL) and the combined organic layer was then washed once with brine and dried over anhydrous Na₂SO₄. The solvent was removed and the compound was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford the pure product **M5** as a colorless liquid. Yield: 0.38 g (90%). ¹H NMR (300 MHz, CDCl₃, δ): 7.02 (d, 2H), 6.92 (d, 2H), 4.00 (s, 2H), 2.90-3.40 (m, 8H), 1.00-1.60 (m, 28H), 0.70-1.00 (m, 15H); ¹³C NMR (75 MHz, CDCl₃, δ): 165.9, 133.1, 130.3, 130.0, 123.7, 120.4, 113.8, 49.2, 44.7, 31.9, 31.3, 30.8, 29.7, 29.1, 29.0, 26.5, 22.8, 20.4, 20.2, 14.3, 14.1, 13.9; HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₈H₅₇Br₂N₃O₂S₂, 809.2259; found, 809.2265.

Diethyl 1-(2-octyldodecyl)-1H-pyrrole-3,4-dicarboxylate (4). A solution of diethyl 1H-pyrrole-3,4-dicarboxylate (1.90 g, 9.00 mmol) in 40 mL of DMF was added drop wise to a stirred mixture of sodium hydride (NaH) in 60% dispersed oil (0.40 g, 10 mmol) in DMF (10 mL) at RT under an argon atmosphere. The mixture was then stirred for 10 min and 2-octyldodecyl 4-methylbenzenesulfonate (5.40 g, 12 mmol) in DMF (10 mL) was then added drop wise. The reaction mixture was stirred overnight at RT and poured into water (100 mL) and stirred for another 1 h. The aqueous layer was extracted twice with diethyl ether (50 mL) and the combined organic layer was washed once with brine. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford pure product **4** as a colorless liquid. Yield: 3.50 g (79%). ¹H NMR (300 MHz, CDCl₃, δ): 7.15 (s, 2H), 4.28 (q, 4H), 3.71 (d, 2H), 1.70-1.78 (m, 1H), 1.16-1.40 (m, 38H), 0.88 (t, 6H); ¹³C NMR (75 MHz, CDCl₃, δ): 163.6, 128.3, 116.2, 60.4, 54.5, 39.7, 32.1, 32.0, 31.8, 31.3, 30.0, 29.9, 29.8, 29.7, 29.5, 29.4, 26.5, 22.9, 14.6, 14.3; HRMS (ESI) *m/z*: [M +

$[H]^+$ calcd for $C_{30}H_{53}NO_4$, 491.3975; found, 491.3975.

Diethyl 2,5-dibromo-1-(2-octyldodecyl)-1H-pyrrole-3,4-dicarboxylate (5). NBS (2.70 g, 15.20 mmol) was added in one portion to a stirred solution of compound **4** (3.40 g, 6.90 mmol) in DMF (50 mL) at RT. The solution was stirred for 1 h and then poured into water (200 mL). The solution was extracted twice with diethyl ether (50 mL) and the combined organic layer was washed once with brine and dried over anhydrous Na_2SO_4 . The solvent was removed and the compound was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford pure product **5** as a colorless liquid. Yield: 4.35 g (97%). 1H NMR (300 MHz, $CDCl_3$, δ): 4.29 (q, 4H), 3.94 (d, 2H), 1.90-2.00 (m, 1H), 1.16-1.40 (m, 38H), 0.87 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 163.1, 117.7, 107.6, 61.2, 52.5, 38.4, 32.1, 32.0, 31.8, 31.3, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.6, 22.9, 22.8, 14.4, 14.3; HRMS (ESI) m/z : $[M + H]^+$ calcd for $C_{30}H_{51}Br_2NO_4$, 647.2185; found, 647.2191.

Diethyl 1-(2-octyldodecyl)-2,5-di(thiophen-2-yl)-1H-pyrrole-3,4-dicarboxylate (6). A solution of compound **5** (4.35 g, 6.70 mmol) and 2-(trimethylstannyl)thiophene (4.20 g, 17.00 mmol) in toluene (60 mL) was purged with argon for 45 min, and $Pd(PPh_3)_4$ (4 mol %) was then added. The stirred solution was heated under reflux in an argon atmosphere for 24 h. The solvent was then removed completely using a rotary evaporator. The residue was dissolved in ethyl acetate (100 mL) and washed with a brine solution, and then dried over anhydrous Na_2SO_4 . The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford compound **6** as a light yellow color liquid. Yield: 4.05 g (92%). 1H NMR (300 MHz, $CDCl_3$, δ): 7.45 (d, 2H), 7.00-7.20 (m, 4H), 4.14 (q, 4H), 3.82 (d, 2H), 0.80-1.40 (m, 45H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 164.6, 130.9, 130.7, 129.5, 128.0, 127.1, 117.5, 60.7, 49.9, 37.9, 32.1, 32.0, 31.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 22.9, 22.8, 14.3, 14.2; HRMS (ESI) m/z : $[M + H]^+$ calcd for $C_{38}H_{57}NO_4S_2$, 655.3729; found, 655.3731.

Diethyl 2,5-bis(5-bromothiophen-2-yl)-1-octyl-1H-pyrrole-3,4-dicarboxylate (7). NBS (2.40 g, 13.5 mmol) was added in one portion at RT to a stirred solution of compound **6** (4.00 g, 6.10 mmol) in 50 mL of DMF. The solution was stirred overnight and then poured into ice-water (150 mL). The solution was extracted twice with diethyl ether (50 mL) and the combined organic layer was washed once with brine and dried over anhydrous Na_2SO_4 . The solvent was removed and the compound was purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford pure product **7** as a light yellow liquid. Yield: 4.70 g (95%). 1H NMR (300 MHz, $CDCl_3$, δ): 7.06 (d, 2H), 6.89 (d, 2H), 4.18 (q, 4H), 3.81 (d, 2H), 0.80-1.50 (m, 45H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 164.1, 132.0, 131.2, 130.1, 128.0, 117.9, 114.9, 60.7, 49.9, 37.9, 32.1, 32.0, 31.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 22.9, 22.8, 14.3, 14.2; HRMS (ESI) m/z : $[M + H]^+$ calcd for $C_{38}H_{55}Br_2NO_4S_2$, 811.1939; found, 811.1941.

2,5-Bis(5-bromothiophen-2-yl)-1-octyl-1H-pyrrole-3,4-dicarboxylic acid (8). An aqueous sodium hydroxide (2.20 g in 20 mL water, 55.00 mmol) solution was added to a stirred solution of compound **7** (4.50 g, 5.55 mmol) in a methanol:THF (60 mL:30 mL) mixture. The solution was heated to 60 °C and stirred overnight. Methanol was then removed completely by

rotary evaporation and the remaining residue was dissolved in water (100 mL). The aqueous solution was extracted once with ethyl acetate (50 mL) and the organic layer was discarded. A 2N HCl solution was then added drop wise to the stirred aqueous solution until it became acidic. The aqueous layer was then extracted three times with ethyl acetate (50 mL) and the combined organic layer was washed once with water and dried over anhydrous Na_2SO_4 . The solvent was removed and the solid material was washed with hexane to afford pure product **8** as an off-white solid. Yield: 4.00 g (95%). 1H NMR (300 MHz, $CDCl_3$, δ): 7.09 (d, 2H), 6.86 (d, 2H), 3.75 (d, 2H), 0.80-1.50 (m, 39H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 167, 135.4, 132.9, 130.9, 127.6, 116.6, 113.6, 60.7, 49.9, 37.9, 32.1, 32.0, 31.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 22.9, 22.8, 14.3, 14.2; HRMS (ESI) m/z : $[M + H]^+$ calcd for $C_{34}H_{47}Br_2NO_4S_2$, 755.1313; found, 755.1315.

4,6-Bis(5-bromothiophen-2-yl)-5-octyl-5H-furo[3,4-c]pyrrole-1,3-dione (9). The solution of compound **8** (3.90 g, 5.14 mmol) in acetic anhydride (60 mL) was stirred at 70 °C for 10 h. Acetic anhydride was completely removed and the residue was dissolved in ethyl acetate (100 mL). The organic solution was washed once with an aqueous sodium bicarbonate solution (5 %) and the organic layer was then dried over anhydrous Na_2SO_4 . The solvent was removed and the solid material was washed with hexane to afford pure product **9** as a yellow solid. Yield: 3.30 g (87%). 1H NMR (300 MHz, $CDCl_3$, δ): 7.36 (d, 2H), 7.18 (d, 2H), 4.29 (d, 2H), 1.50-1.70 (m, 1H), 0.80-1.50 (m, 38H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 158.8, 131.9, 131.3, 129.3, 128.0, 117.9, 116.4, 60.7, 49.9, 37.9, 32.1, 32.0, 31.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 22.9, 22.8, 14.3, 14.2; HRMS (ESI) m/z : $[M + H]^+$ calcd for $C_{34}H_{45}Br_2NO_3S_2$, 737.1208; found, 737.1206.

4,6-Bis(5-bromothiophen-2-yl)-2,5-diethylpyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (M6). 1-Aminooctane (0.80 mL, 4.80 mmol) was added drop wise via syringe to the ice cold solution of compound **9** (3.25 g, 4.40 mmol) in anhydrous toluene (60 mL) in an argon atmosphere. The solution was stirred for 1 h at 0 °C, warmed slowly to RT and then heated under reflux for 10 h. Toluene was removed completely and the residue was washed with hexane. The remaining residue was then dissolved in dry MC (60 mL) and cooled to 0 °C. Thionyl chloride (20 mL) was then added in one portion to the stirred solution and heated to 40 °C. After 30 min, the solution was removed completely by rotary evaporation. The paste mass was dissolved in MC (50 mL) and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 . The solvent was concentrated and the residue was then purified by column chromatography (silica gel, hexane:ethyl acetate, 90/10, v/v) to afford the pure product **M6** as a yellow solid. Yield: 3.05 g (82%). 1H NMR (300 MHz, $CDCl_3$, δ): 7.34 (d, 2H), 7.11 (d, 2H), 4.20 (d, 2H), 3.44 (d, 2H), 1.54-1.68 (m, 1H), 1.68-1.80 (m, 1H), 0.80-1.40 (m, 52H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 164.3, 131.2, 130.8, 130.6, 127.0, 119.4, 115.2, 51.3, 42.2, 38.7, 38.2, 32.2, 32.1, 31.0, 30.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 28.9, 26.1, 24.2, 23.2, 22.9, 22.8, 14.4, 14.3; HRMS (ESI) m/z : $[M + H]^+$ calcd for $C_{42}H_{62}Br_2N_2O_2S_2$, 848.2619; found 848.2621.

General synthetic procedure for synthesis of the polymers. A flame dried three neck round bottom flask containing a solution of the respective distannyl (0.40 mmol) and dibromo (0.40 mmol) monomers shown in Scheme 2 in chlorobenzene (20 mL) was

purged well with argon for 30 min. Subsequently, $\text{Pd}_2(\text{dba})_3$ (14 mg) and $\text{P}(\text{o-tol})_3$ (30 mg) were added and the entire mixture was heated under reflux in argon for 24 h. The solution was cooled to RT and the solution was added drop wise to methanol (250 mL) with constant stirring. The precipitated polymer was then allowed to settle. The precipitates were filtered and subjected to Soxhlet extraction with methanol and acetone for 24 h. The resulting polymer was dissolved in chloroform (20 mL) and filtered. The polymer was again precipitated by adding methanol (250 mL). The precipitates were filtered and dried under vacuum to afford the pure polymer as a blue solid.

P(DKPP-TPTH): Yield: 0.32 g (87%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.97 (d, 2H), 7.29 (s, 2H), 6.90-7.26 (m, 4H), 6.30-6.44 (m, 2H), 3.90-4.40 (m, 6H), 1.94 (s, 2H), 1.20-1.80 (m, 36H), 0.80-1.00 (m, 15H).

P(DKPP-TPTE): Yield: 0.42 g (89%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.96 (d, 2H), 7.27-7.40 (m, 4H), 7.13 (d, 2H), 3.80-4.30 (m, 10H), 1.80 (s, 4H), 1.00-1.60 (m, 56H), 0.70-1.00 (m, 15H).

P(DKPP-TPTA): Yield: 0.39 g (82%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.96 (d, 2H), 7.27-7.40 (m, 4H), 7.16 (d, 2H), 4.10 (s, 6H), 3.00-3.50 (m, 8H), 1.00-1.90 (m, 52H), 0.60-1.00 (m, 21H).

P(DKPP-TPTI): Yield: 0.44 g (91%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.98 (s, 2H), 7.66 (s, 2H), 7.27-7.40 (m, 4H), 4.40 (s, 2H), 4.11 (s, 4H), 3.49 (s, 2H), 0.60-2.00 (m, 84H).

Results and discussions

Synthesis and characterization

Schemes 1 and 2 show the synthetic route for new monomers and polymers, respectively. Monomers **M1**³⁰ and **M2**³⁵ were prepared according to the known literature procedures and monomer **M3** was purchased (Cat # IN1346, purity ~ 98%) from Suna Tech Inc. On the other hand, new monomers, such as **M4**, **M5** and **M6** were synthesized as described in the experimental section. All four new polymers, P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI), were prepared via the Stille polycondensation between the respective monomers shown in Scheme 2. The weight average molecular weights (M_w) of the polymers estimated by GPC analysis were 1.54×10^4 g/mol, 2.61×10^4 g/mol, 2.63×10^4 g/mol, and 3.47×10^4 g/mol with a polydispersity (PDI) of 1.68, 1.72, 1.86, and 2.37, respectively. The solubility of the polymers was good in chlorinated solvents, such as chloroform, chlorobenzene and dichlorobenzene. In particular, polymers P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI) exhibited better solubility than P(DKPP-TPTH). The 5% weight loss temperatures of the polymers determined by TGA were 300 °C, 280 °C, 270 °C, and 330 °C, respectively.

Optical Properties

The absorption spectra of polymers P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI) measured in a chloroform solution and as a thin film on glass are displayed in Fig. 2. The maximum absorption peak of P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI) was observed at 659 nm, 634 nm, 650 nm, and 658 nm, respectively, in solution, and 702 nm, 655 nm, 671 nm, and 700 nm, respectively, in the film state. All four polymers shifted their

absorption bands to red in the film compared to those in solution, which suggests that the π - π stacking of the polymers is enhanced in the film state. The optical band gaps (E_g) of P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA), and P(DKPP-TPTI) were calculated from the onset absorption wavelength in the film state to be 1.31 eV, 1.42 eV, 1.37 eV, and 1.37 eV, respectively. As expected, copolymerization of the TPT derivatives with the DKPP unit produced low band gap polymers compared to P(BDT-TDPPDT) and P(BDTT-TDPPDT).^{31,32}

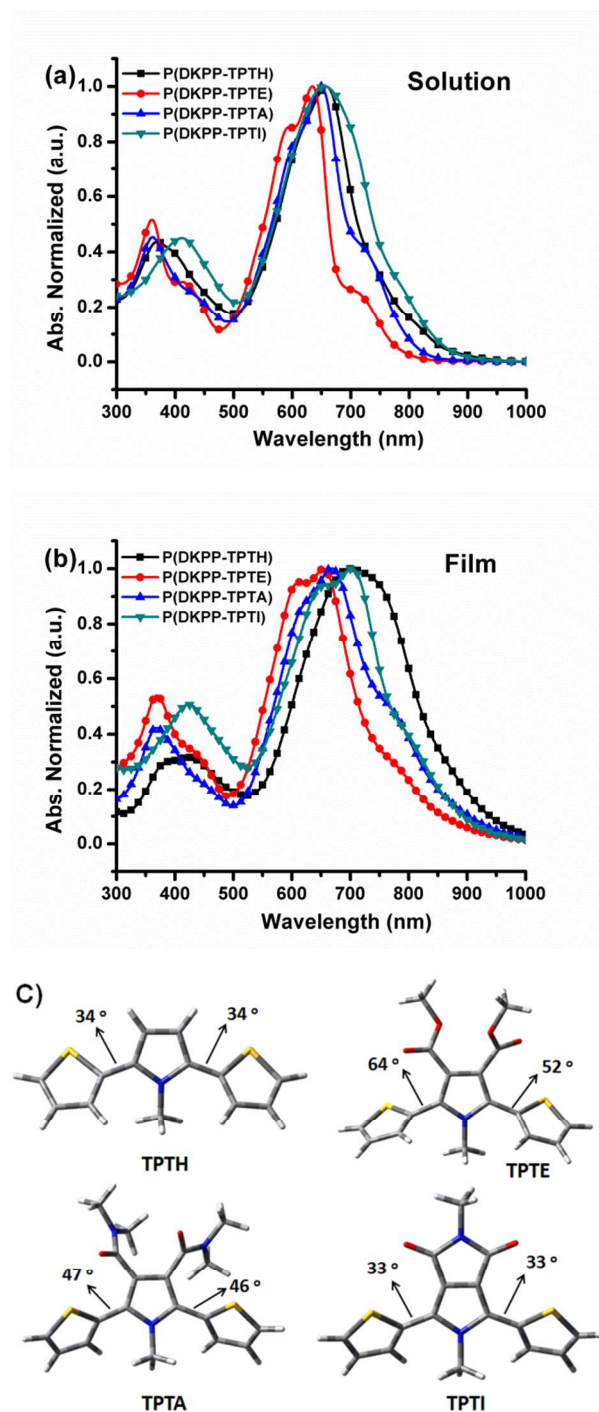


Fig. 2 UV-visible absorption spectra of polymers in chloroform (a), as thin film (b) and the optimized structures of TPT derivatives (c).

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Table 1 Polymerization Results, Thermal, Optical and Electrochemical Properties of Polymers.

Polymer	M_w^a ($\times 10^4$ g/mol)	PDI ^a	TGA ^b (°C)	λ_{max} in solution (nm) ^c	λ_{max} as film (nm) ^d	E_g (eV) ^e	HOMO (eV) ^f	LUMO (eV) ^g
P(DKPP-TPTH)	1.54	1.68	300	659	702	1.31	-4.96	-3.65
P(DKPP-TPTE)	2.61	1.72	280	634	655	1.42	-5.24	-3.82
P(DKPP-TPTA)	2.63	1.86	270	650	671	1.37	-5.17	-3.80
P(DKPP-TPTI)	3.47	2.37	330	658	700	1.37	-5.35	-3.98

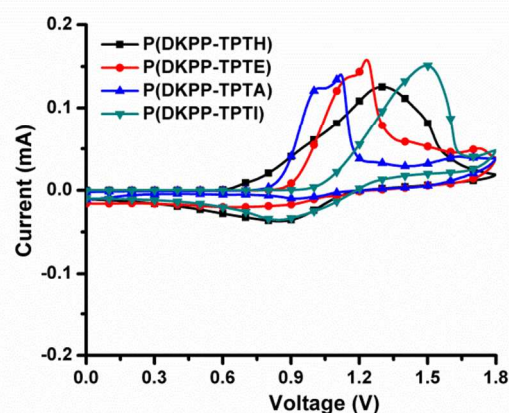
^a Weight average molecular weight (M_w) and polydispersity (PDI) of the polymers were determined by GPC using polystyrene standards. ^b 5 % weight loss temperature measured by TGA under N_2 . ^c Measurements in chloroform solution. ^d Measurements in thin film were performed on the glass substrate. ^e Band gap estimated from the onset wavelength of the optical absorption in thin film. ^f The HOMO level was estimated from cyclic voltammetry analysis. ^g The LUMO level was estimated by using the following equation: LUMO = HOMO + E_g .

The incorporation of electron withdrawing groups on the pyrrole backbone of the polymers (P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI)) is expected to decrease the polymer planarity and reduce the internal charge transfer (ICT) from the donor to acceptor unit and consequently produce a blue shift in the absorption band compared to polymer P(DKPP-TPTH) containing hydrogen on pyrrole backbone. The planarity of the TPT units shown in Fig. 2c, i.e., TPTH, TPTE, TPTA and TPTI containing hydrogen, ester, amide, and cyclic imide functional groups on the 3,4-position of pyrrole unit, respectively, was found to be in the order, TPTI>TPTH>TPTA>TPTE, from their optimized structures (see Fig. 2c). The incorporation of a cyclic imide group on the pyrrole group of the TPT unit (TPTI) showed similar dihedral angles, whereas the incorporation of acyclic amide (TPTA) or ester groups (TPTE) showed higher dihedral angles between the thiophenes and pyrrole compared to that of the TPT unit containing hydrogen on their backbone (TPTH). Consequently, the absorption maximum of the polymers was found to be in the order of P(DKPP-TPTE)>P(DKPP-TPTA)>P(DKPP-TPTI)>P(DKPP-TPTH). Note that P(DKPP-TPTI) showed a blue shift in the absorption band compared to P(DKPP-TPTH) though TPTI exhibited similar planarity to that of TPTH. The presence of an electron withdrawing imide group on the TPT backbone of P(DKPP-TPTI) is expected to decrease the ICT from TPTI to DKPP compared to that from TPTH to DKPP, which leads a blue shift in the absorption band. The latter results suggest that both the planarity and the electron accepting ability of the substituents on the TPT unit have a significant effect on the absorption of the final polymers. Similar trends have also been observed for TPT-based polymers and organic dyes containing substituents on the pyrrole backbone of the TPT unit.^{36–38} Optical studies of the new polymers suggest that the incorporation of electron withdrawing substituents such as, ester, amide and imide groups on the TPT unit alter the absorption of the final polymers significantly. The absorption maxima and optical band gaps of the polymers are summarized in Table 1.

Electrochemical Properties

Cyclic voltammetry (CV) was performed on each polymer in a three electrode electrochemical system, as mentioned in the experimental section. The CV curves of the polymers are presented in Fig. 3. The highest occupied molecular orbital

(HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the polymers were estimated using the following standard equations, $E_{\text{HOMO}} = [-(E_{\text{ox,onset vs. Ag/AgCl}} - E_{\text{ferrocene vs. Ag/AgCl}}) - 4.8]$ eV and $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$, respectively. The value, 4.8 eV, represents the energy level of ferrocene below the vacuum level, $E_{\text{ferrocene vs. Ag/AgCl}}$ is 0.46 V, and $E_{\text{ox,onset}}$ is the onset potential values of the polymers in volts for oxidation processes against the Ag/AgCl reference electrode. The calculated HOMO/LUMO levels of polymers P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA), and P(DKPP-TPTI) were -4.96 eV/-3.65 eV, -5.24 eV/-3.82 eV, -5.17 eV/-3.80 eV, and -5.35 eV/-3.98 eV, respectively, from the estimated $E_{\text{ox,onset}}$ (0.62 V, 0.90 V, 0.83 V, and 1.01 V, respectively) and band gaps of the polymers. The energy levels of the polymers confirmed that the incorporation of electron withdrawing substituents on polymer backbone lowers their HOMO/LUMO levels significantly. In particular, the incorporation of a cyclic imide group on the pyrrole backbone of the TPT unit showed more pronounced effect than the incorporation of an acyclic ester or amide groups in terms of lowering the HOMO/LUMO levels of the polymers.

**Fig. 3** Cyclic voltammograms of polymers.

The electrochemical studies of the polymers show that the HOMO levels of polymers P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI) were found to be deeper than that of P(DKPP-TPTH). Consequently, those polymers are expected to provide a

higher V_{oc} than P(DKPP-TPTH) because the V_{oc} is defined as the energy difference between the HOMO and LUMO levels of polymer and PC₇₀BM.^{24,25} On the other hand, although P(DKPP-TPTI) is expected to offer higher V_{oc} than all other polymers, it may show poor photovoltaic performance because of the very low energy difference (~ 0.32 eV) between the LUMO levels of P(DKPP-TPTI) and PC₇₀BM.^{24,25} The HOMO and LUMO energy levels of the polymers are included in Table 1.

Organic field effect transistors characteristics

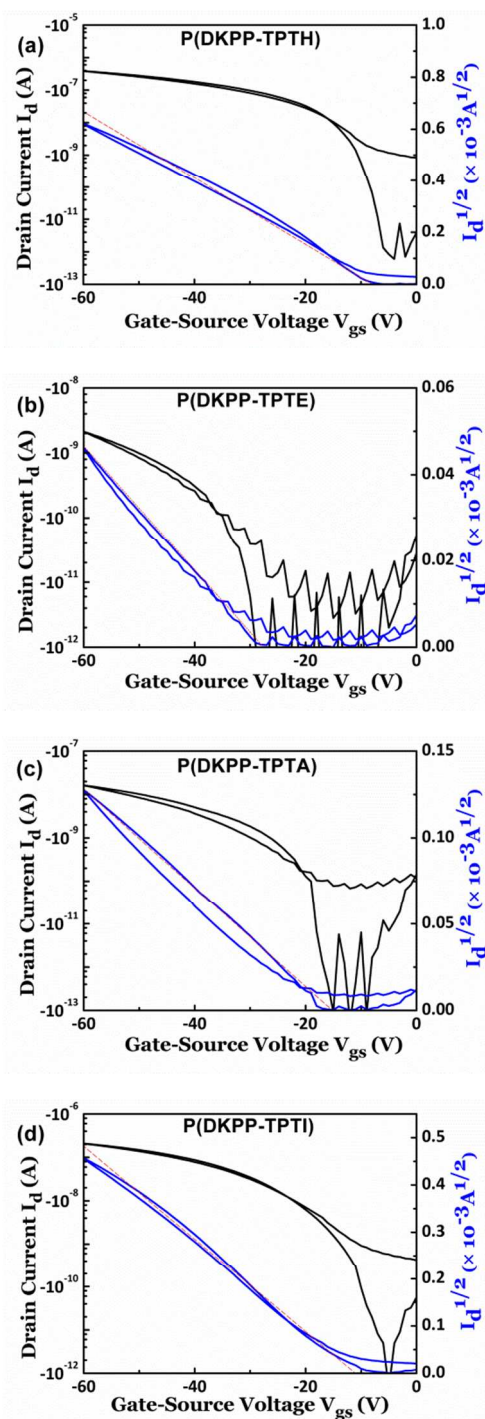


Fig. 4 Typical current-voltage characteristics (drain-source current, I_D , versus drain-source voltage, V_{DS}) of polymers at different voltage.

The field-effect mobility (μ) of polymers P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA), and P(DKPP-TPTI) was estimated from the OFETs characteristics shown in Fig. 4 to be $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $5 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The hole mobility of the polymers was decreased significantly when the electron withdrawing groups were introduced to the pyrrole backbone of the polymers. In addition, the mobility of each polymer increased as the planarity of polymer backbone was enhanced (see Fig. 2c). Therefore, the planarity of the polymers might affect the carrier mobility, and consequently, polymers P(DKPP-TPTH) and P(DKPP-TPTI) have a similar hole mobility, but polymers P(DKPP-TPTE) and P(DKPP-TPTA) containing sterically hindered substituents on the polymer backbone showed lower mobility. All four polymers were typically amorphous according to XRD, as shown in Fig. S1. Consequently, the mobility of the polymers related to crystallinity might be ignored. This paper reports the preliminary OFET device results and the values are expected to improve by working more on the device fabrication.

Photovoltaic properties

The photovoltaic properties of the polymers were examined by preparing PSCs with each of polymers P(DKPP-TPTH), P(DKPP-TPTE), P(DKPP-TPTA), and P(DKPP-TPTI) as an electron donor and PC₇₀BM as an electron acceptor at three different donor:acceptor ratios (1:1 wt%, 1:2 wt% and 1:3 wt%). The device configuration of the PSCs is ITO/PEDOT:PSS/polymer:PC₇₀BM/Al. The device optimization results for each polymer are shown in Fig. S2–Fig. S5 and Table S1–Table S4. The device structure and energy levels of materials used in the PSCs are displayed in Fig. 5a. Among the PSCs prepared, the maximum photovoltaic performance was obtained for the PSCs made with the donor: acceptor blends of P(DKPP-TPTH):PC₇₀BM (1:2 wt%), P(DKPP-TPTE):PC₇₀BM (1:2 wt%), P(DKPP-TPTA):PC₇₀BM (1:3 wt%) and P(DKPP-TPTI):PC₇₀BM (1:3 wt%). The $J-V$ curves of the PSCs made from the abovementioned blends are shown in Fig. 5b and their results, such as the open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) are summarized in Table 2.

The $J-V$ curves of the PSCs were measured under the illumination of an AM 1.5 G (1000 W m^{-2}) solar simulator. The PSC made from the P(DKPP-TPTH):PC₇₀BM (1:2 wt%) blend offered a maximum PCE of 2.63% with a V_{oc} of 0.56 V, J_{sc} of 7.98 mA cm^{-2} , and FF of 59%, whereas the PSCs prepared from the P(DKPP-TPTE):PC₇₀BM (1:2 wt%), P(DKPP-TPTA):PC₇₀BM (1:3 wt%) and P(DKPP-TPTI):PC₇₀BM (1:3 wt%) blends gave a relatively lower PCE of 0.90% ($V_{oc} \sim 0.75 \text{ V}$, $J_{sc} \sim 3.92 \text{ mA cm}^{-2}$, and $FF \sim 31\%$), 0.70% ($V_{oc} \sim 0.66 \text{ V}$, $J_{sc} \sim 3.00 \text{ mA cm}^{-2}$, and $FF \sim 35\%$) and 0.91% ($V_{oc} \sim 0.81 \text{ V}$, $J_{sc} \sim 2.26 \text{ mA cm}^{-2}$, and $FF \sim 50\%$), respectively.

All three polymers, P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI), incorporating electron withdrawing substituents on the pyrrole backbone showed similar performance, but their performance was relatively lower than that of polymer P(DKPP-TPTH) containing hydrogen on the pyrrole backbone. Polymer P(DKPP-TPTH) is a donor-acceptor (D-A) type of polymer because it composed of electron rich TPT and electron deficient DKPP units, whereas polymers, P(DKPP-TPTE), P(DKPP-

TPTA)

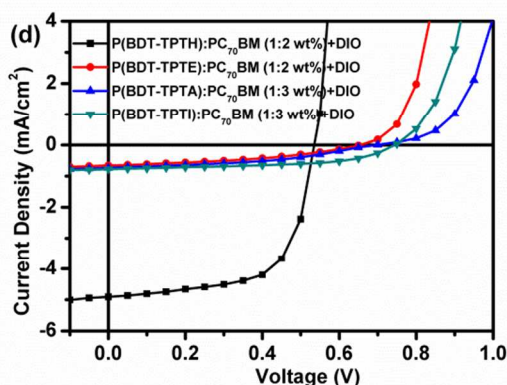
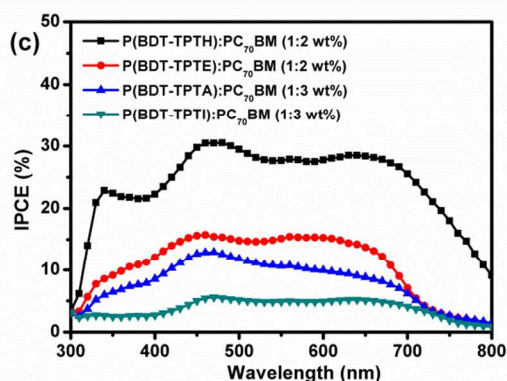
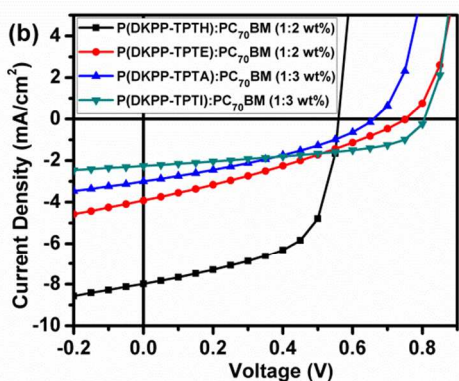
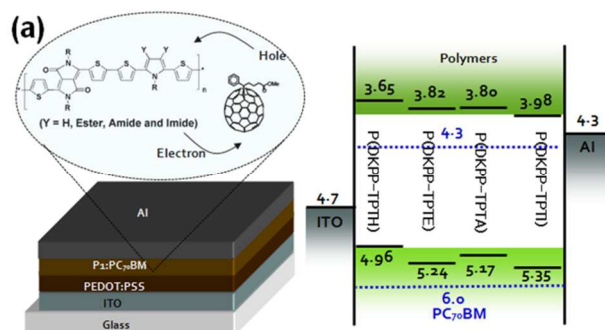


Fig. 5 (a) device structure and energy levels diagram of PSCs. (b) J - V characteristics of the PSCs prepared without DIO. (c) IPCE spectra of

PSCs prepared without DIO. (d) J - V characteristics of the PSCs prepared with 2 vol% DIO.

Table 2 Photovoltaic Properties of the Polymer Solar Cells Prepared by Using the Configuration of ITO/PEDOT:PSS/Polymer:PC₇₀BM/Al.

Polymer:PC ₇₀ BM ratio	J_{sc} (mA/cm ²) ^a	V_{oc} (V) ^b	FF (%) ^c	PCE (%) ^d
P(DKPP-TPTH):PC ₇₀ BM (1:2 wt%)	7.98	0.56	59	2.63
P(DKPP-TPTH):PC ₇₀ BM (1:2 wt%)+DIO	4.91	0.54	63	1.68
P(DKPP-TPTE):PC ₇₀ BM (1:2 wt%)	3.92	0.75	31	0.90
P(DKPP-TPTE):PC ₇₀ BM (1:2 wt%)+DIO	0.66	0.66	40	0.17
P(DKPP-TPTA):PC ₇₀ BM (1:3 wt%)	3.00	0.66	35	0.70
P(DKPP-TPTA):PC ₇₀ BM (1:3 wt%)+DIO	0.74	0.70	41	0.21
P(DKPP-TPTI):PC ₇₀ BM (1:3 wt%)	2.26	0.81	50	0.91
P(DKPP-TPTI):PC ₇₀ BM (1:3 wt%)+DIO	0.78	0.75	54	0.32

^a Short-circuit current density. ^b Open-circuit voltage. ^c Fill factor. ^d Power conversion efficiency.

and P(DKPP-TPTI), are expected to be acceptor-acceptor (A-A) type polymers because the presence of electron withdrawing substituents on the pyrrole unit make TPT a weak acceptor unit. In general, the photovoltaic performance of A-A type polymers^{34,39-42} offered a relatively lower PCE than D-A type polymers¹³⁻¹⁸ though the opto-electrical properties of A-A type polymers are good. However, A-A type polymers had not previously attracted a great deal of attention but they have recently attracted interest for PSCs^{34,39-42} and thin film transistor applications.⁴³⁻⁴⁸

The V_{oc} of the PSCs made from the polymers was in the order of P(DKPP-TPTI) > P(DKPP-TPTE) > P(DKPP-TPTA) > P(DKPP-TPTH), and the estimated HOMO energy levels of the polymers were also found to be deeper in the same order. On the other hand, the J_{sc} values were expected to be in the order of P(DKPP-TPTH) > P(DKPP-TPTI) > P(DKPP-TPTA) > P(DKPP-TPTE) according to the absorption spectra of the polymers, but the actual J_{sc} values were in the order of P(DKPP-TPTH) > P(DKPP-TPTE) > P(DKPP-TPTA) > P(DKPP-TPTI). Usually, the J_{sc} values are correlated with the light harvesting ability and carrier mobility of the polymer, charge separation at D-A interface and charge collection at their respective electrodes.^{34,49,50} Although P(DKPP-TPTI) exhibits better absorption and mobility than P(DKPP-TPTE) and P(DKPP-TPTA), the low energy difference (~ 0.3 eV) between the LUMO levels of P(DKPP-TPTI) and PC₇₀BM might lower the charge separation and collection³⁴ and consequently, produce a lower J_{sc} than P(DKPP-TPTE) and P(DKPP-TPTA). On the other hand, the lower J_{sc} values obtained for P(DKPP-TPTE) and P(DKPP-TPTA) compared to that of P(DKPP-TPTH) might be due to their lower mobility and the morphological differences of the photoactive layers.

The decreased J_{sc} values of the PSCs made from polymers P(DKPP-TPTE), P(DKPP-TPTA) and P(DKPP-TPTI) compared to that of P(DKPP-TPTH) were confirmed by the incident photon to current efficiency (IPCE) spectra of the PSCs shown in Fig. 5c. The IPCE spectra of the PSCs were measured in the range, 300–800 nm, and the PSC made from the P(DKPP-TPTH):PC₇₀BM (1:2 wt%) blend displayed a broad photoresponse from 300 nm to over 800 nm. On the other hand, the PSCs made from the P(DKPP-TPTE):PC₇₀BM (1:2 wt%), P(DKPP-TPTA):PC₇₀BM (1:3 wt%) and P(DKPP-TPTI):PC₇₀BM (1:3 wt%) blends displayed relatively narrow responses between 300 nm to 750 nm with lower IPCE maxima

compared to that of the P(DKPP-TPTH)-based PSC. These results suggest that the incorporation of electron withdrawing substituents on the TPT-based polymer backbone decrease the electron donating ability to PC₇₀BM significantly due to their blue shifted absorption band and lower LUMO level, but at the same time, produce a higher V_{oc} due to the deeper HOMO levels of the polymers.

Sometimes the processive additives, such as DIO and 1-chloronaphthalene improve the PSC device performance significantly due to the improved surface morphology of the

photoactive layer. To examine the additive influence on the performance of the PSCs, the PSCs were prepared from the P(DKPP-TPTH):PC₇₀BM (1:2 wt%), P(DKPP-TPTE):PC₇₀BM (1:2 wt%), P(DKPP-TPTA):PC₇₀BM (1:3 wt%), and P(DKPP-TPTI):PC₇₀BM (1:3 wt%) blends along with 2 vol% DIO. Unfortunately, all four PSCs showed lower PCE s than the device prepared without DIO. The corresponding $J-V$ curves of the PSCs are shown in Fig. 5d and their photovoltaic parameters are included in Table 2.

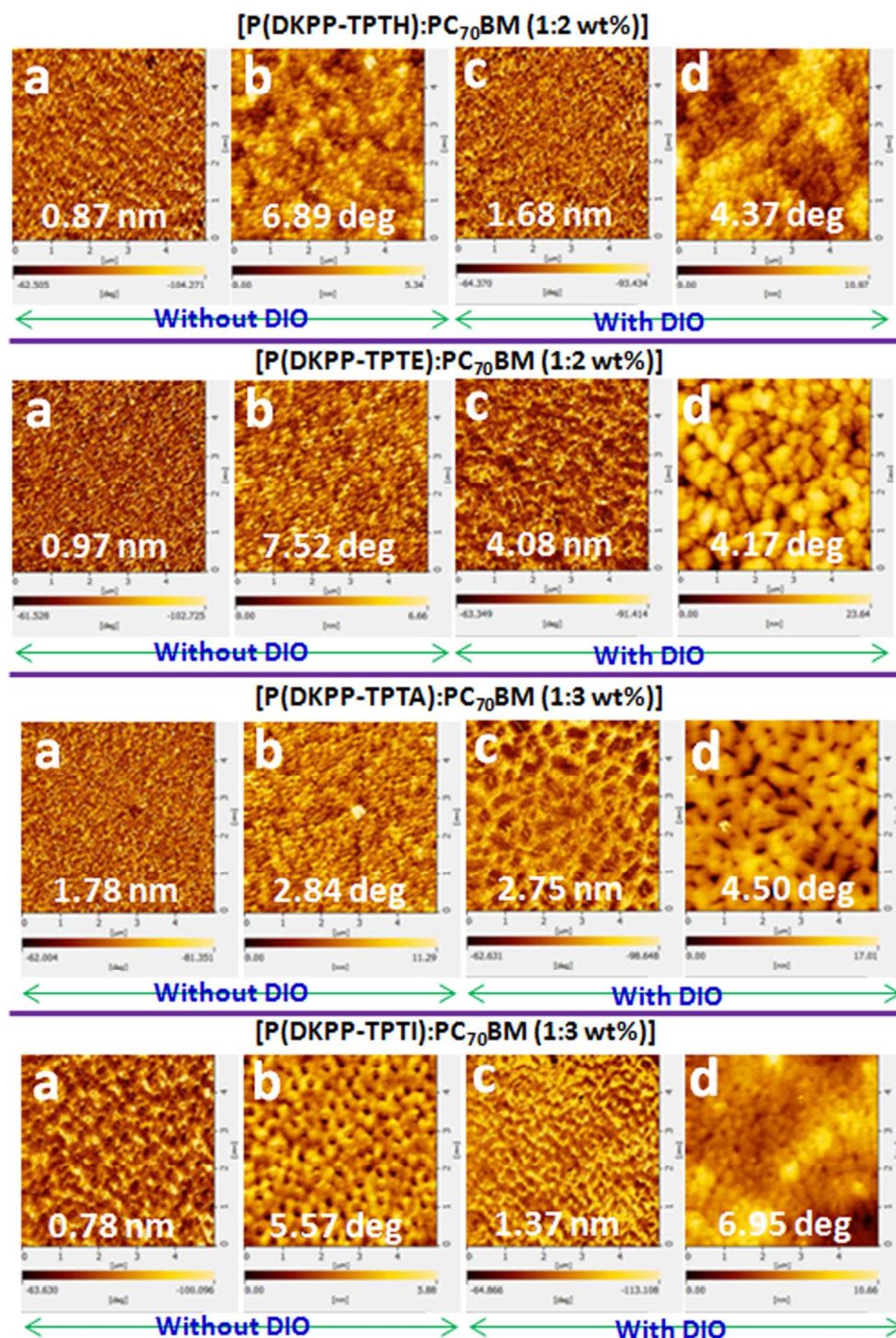


Fig. 6 AFM images (5x5 μ) of polymer:PC₇₀BM blends without (images a, and b) and with DIO (images c and d). Images a and c were obtained in tapping mode, whereas images b and d were obtained from phase mode.

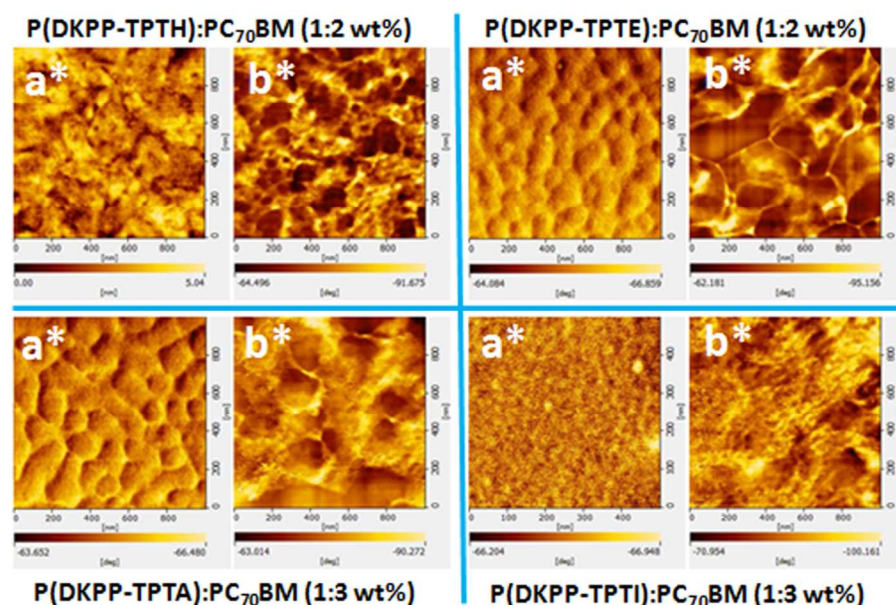


Fig. 7 Phase mode AFM images (1x1 μ) of polymer:PC₇₀BM blends without (image a*) and with (images b*) DIO.

AFM of polymer:PC₇₀BM blends without and with 2 vol% DIO was performed to understand the reason for the decreased *PCE* for the PSCs made with DIO compared to that of the PSCs prepared without DIO as well as to obtain greater insight into the substituent effects on the photoactive layer morphology. AFM images without and with 2 vol% DIO are shown in Fig. 6a,b and Fig. 6c,d, respectively, with their roughness. Fig. 6a,c were obtained in tapping mode, whereas Fig. 6b,d were obtained from phase mode. The AFM images confirmed that the film made with DIO had a poor interpenetrating network between the donor and acceptor molecules as well as a higher root mean square surface roughness than the corresponding films prepared without DIO. Consequently, PSCs made with DIO showed poorer performance than the PSCs made without DIO. To gain more insight into the substituent effect of the TPT unit on the surface morphology of the photoactive layers, 1x1 μ phase mode AFM images were recorded for the films made from the polymer:PC₇₀BM blends without and with 2 vol% DIO and presented in Fig. 7. Interestingly, the films prepared from the P(DKPP-TPTE):PC₇₀BM (1:2 wt%) and P(DKPP-TPTA):PC₇₀BM (1:3 wt%) blends showed the aggregation of PC₇₀BM while P(DKPP-TPTH):PC₇₀BM (1:2 wt%) and P(DKPP-TPTI):PC₇₀BM (1:3 wt%) showed a better interpenetrating network between the donor and acceptor. This shows that each substituent on the TPT unit affects the photoactive layer morphology differently.

Conclusions

Four new polymers were prepared to study the property modulation of pyrrolo[3,4-c]pyrrole-1,4-dione-based polymers via the incorporation of electron rich 2,5-di(2-thienyl)pyrrole or weak electron accepting 2,5-di(2-thienyl)pyrrole containing electron withdrawing ester, amide and imide groups on the 3,4-position of pyrrole. The optical and electrochemical studies

suggest that the incorporation of electron withdrawing substituents such as ester, amide and imide groups on polymer backbone induced a blue shift in absorption and lowered their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels significantly. The organic field effect transistors studies indicated that the polymers containing ester and amide groups on their backbone displayed lower hole mobility than the polymers containing hydrogen and imide groups on their backbone due to the decreased planarity of unit cell. The overall photovoltaic performance of the polymers incorporating electron withdrawing substituents on the polymer backbone was relatively lower than that of the polymer containing hydrogen on the backbone. However, the former polymers resulted in a high open circuit voltage. Overall, it is concluded that the incorporation of any electron withdrawing groups on the 3,4-position of pyrrole-based polymers increases the open circuit voltage of the resulting PSCs significantly.

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Notes and references

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