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Synthesis and properties of pyrrolo[3,4-*c*]pyrrole-1,3-dione based polymer semiconductors and their performance in organic thin film transistors

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Pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (1,3-DPP) was used as a building block to construct copolymers with a quaterthiophene unit. The resulting conjugated polymers showed rather high LUMO (the lowest unoccupied molecular orbital) levels of ca. -3.5 eV, compared to the polymers based on the well-known pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)dione (1,4-DPP) isomeric structure. These polymers exhibited promising p-channel charge transport performance with hole mobility up to 0.013 cm^{2}V^{-1}s^{-1} in organic thin films transistors.

Introduction

Conjugated polymers for organic thin-film transistors (OTFTs)[1-4] and organic photovoltaic (OPVs)[5-8] have attracted tremendous attention in recent years. Recently, the use of electron-donating and electron-accepting units to form donor-acceptor (D-A) copolymers proved to be successful to shorten the distance between neighbouring polymer chains for more efficient charge hopping, leading to enhanced charge carrier mobility.[9-11] As the most successful electron-acceptor building block, diketopyrrolopyrrole (DPP), or more precisely, pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1,4-DPP as shown in Fig. 1), has been extensively investigated for the development of high-performance small molecules and polymeric semiconductors for OTFTs and OPVs.[1, 9, 12-21] Another diketopyrrolopyrrole isomer, pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (2,5-DPP in Fig. 1), was investigated, which showed promising mobility up to 0.03 cm^{2}V^{-1}s^{-1} in OTFTs and power conversion efficiency up to 5.1% in OPVs.[22] The third DPP isomer, pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (1,3-DPP in Fig. 1), was recently used as a building block for polymers for OPVs,[23] but the charge transport property of the polymers based on 1,3-DPP is still unknown. In this study, we designed and synthesized two copolymers comprising this 1,3-DPP building block and quaterthiophene for OTFTs. We found that these polymers showed dramatic differences in their optoelectronic properties from the ones based on the 1,4-DPP isomer. In OTFT devices, both new polymers showed characteristic p-channel charge transport behaviour with hole mobility in the order of 10^{-2} cm^{2}V^{-1}s^{-1}.

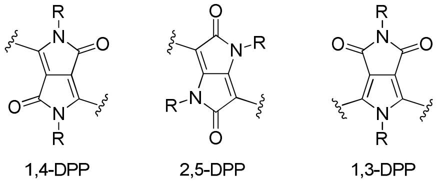
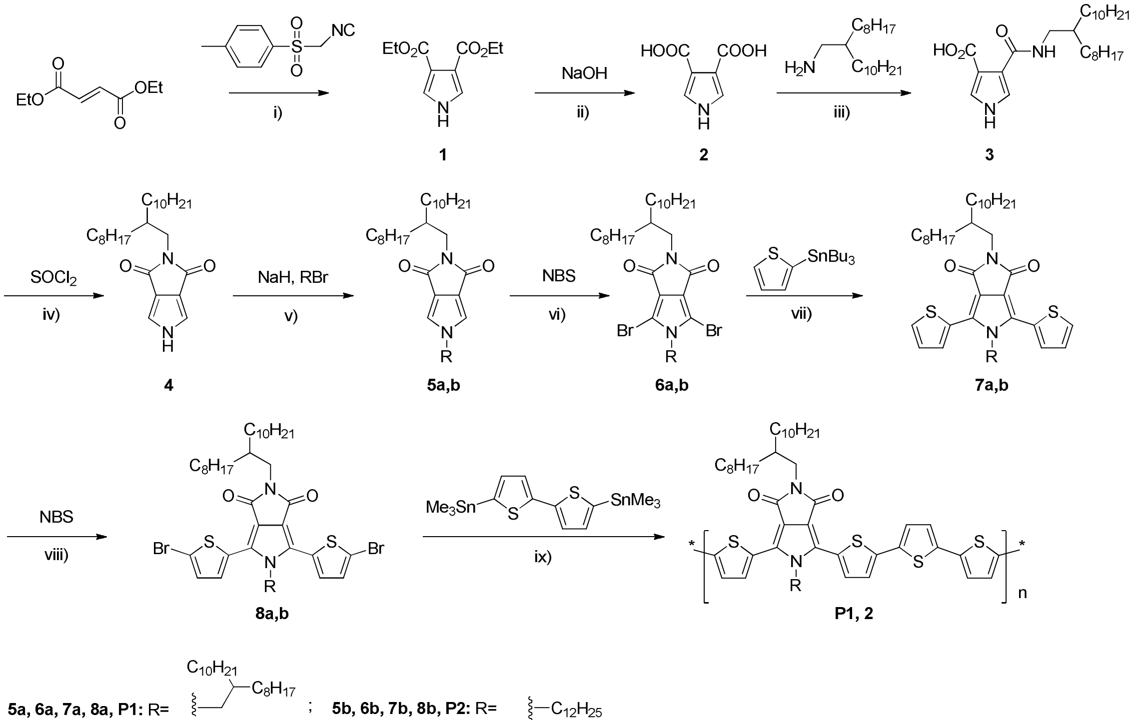


Fig. 1 Chemical structures of three DPP isomers: pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1,4-DPP), pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (2,5-DPP), and pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (1,3-DPP).

RESULTS AND DISCUSSION

Scheme 1 outlines the synthesis of 1,3-DPP monomers and their copolymers with quaterthiophene **P1** and **P2**. Diethyl 1*H*-pyrrole-3,4-dicarboxylate (**1**) and 1*H*-pyrrole-3,4-dicarboxylic acid (**2**) were prepared in 55% and 87% yields, respectively, according to the literature methods.[24] Branched 2-octyldodecan-1-amine was then reacted with **2** to obtain 4-((2-octyldodecyl)carbamoyl)-1*H*-pyrrole-3-carboxylic acid (**3**) (90% yield), which was ring-closed in refluxing thionyl chloride to form (2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (**4**) (62% yield). Two types of side chains, 2-octyldodecyl and dodecyl, were incorporated at the 5-position of **4** using the respective alkylbromide. The resulting 2,5-disubstituted **5a** and **5b** were then brominated at the 4,6-positions to form compound **6a** and **6b** using *N*-bromosuccimide (NBS). Stille coupling reaction of **6a** and **6b** with 2-tributylstannylthiophene produced compounds **7a** and **7b**, which were further brominated with NBS to afford the monomers **8a** and **8b**, respectively. The target polymers **P1** and **P2** were synthesized via Stille coupling polymerization with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene. The crude polymers were purified by Soxhlet extraction using acetone to remove oligomers. **P1** showed excellent solubility and could be dissolved completely with refluxing hexane with 98.7 % yield. **P2** with one branched 2-octyldodecyl side chain and one shorter straight dodecyl side chain is insoluble in hexane, but could be easily dissolved in chloroform with 94.3 % yield. Gel permeation chromatography (GPC) with chloroform as an eluent and



Scheme 1 Synthetic route to 1,3-DPP monomers and polymers **P1** and **P2**: i) THF / r.t.; ii) ethanol / H_2O / reflux; iii) THF / reflux to r.t.; iv) DMF / r.t.; v) DMF / r.t.; vi) DMF / r.t.; vii) toluene / $Pd_2(dba)_3$ / P(*o*-tolyl)$_3$ / 110 °C; vii) DMF / r.t.; ix) chlorobenzene / $Pd_2(dba)_3$ / P(*o*-tolyl)$_3$ / 130 °C.

polystyrene as standards at a column temperature of 50 °C was used to determine the molecular weights of both polymers. The number average molecular weight (M_n) / the polydispersity index (PDI) are 37.8 kDa / 2.13 for **P1** and 40.7 kDa / 2.05 for **P2**. Both polymers showed very good thermal stability with a 5% weight loss at 412 °C for **P1** and 415 °C for **P2**, as determined by thermal gravimetric analysis (TGA) (ESI).

To reveal their absorption characteristics, **P1** and **P2** were measured in dilute chloroform solutions, showing the wavelength of maximum absorption (λ_{max}) at 473 nm and 497 nm, respectively (Fig. 2a). The red-shift (~24 nm) in λ_{max} for **P2** with respect to **P1** most likely resulted from the more coplanar backbone of **P2** due to the less steric effect of its straight dodecyl substituent on the neighbouring thiophenes than that of the bulkier 2-octyldodecyl in **P1**. In the solid state, the λ_{max}'s of **P1** and **P2** red-shifted to 483 and 526 nm, respectively. Notice that a small shoulder appeared in the absorption curve of the **P2** film. The larger red-shift in λ_{max} from solution to film for **P2** (29 nm) than that for **P1** (10 nm) as well as the appearance of a shoulder in **P2** suggest that the polymer chains in **P2** are more ordered due to the less steric effect of the straight side chain in **P2**. As a result, the optical band gap of **P2** (1.92 eV) is narrower than that of **P1** (2.02 eV), calculated from the absorption onset of the as-spun films. The observation of reversible oxidative cycles obtained by cyclic voltammetry (CV) suggests that both polymers are stable in the oxidation processes (Fig. 2b). The reductive processes are also reversible, but the currents are much weaker relative to those in the oxidative processes. By using the onset oxidative potentials, the highest occupied molecular orbital (HOMO) levels were calculated to be -5.54 eV and -5.40 eV for **P1** and **P2**, respectively. The lowest unoccupied molecular orbital (LUMO) levels were estimated using the HOMO levels by CV and the optical bandgaps by UV-vis to be -3.52 eV and -3.48 eV, respectively. The UV-vis absorption and the electrochemical properties of **P1** and **P2** dramatically differ from those of their analogous polymers PDQTs based on 1,4-DPP and quarterthiophene (λ_{max} = 777 nm in solution and 790 nm in film; E_{HOMO} / E_{LUMO} = -5.2 eV / - 4.0 eV).[13] Although data of the **P2**'s analogous polymer based on 2,5-DPP and quaterthiophene are unavailable due to its poor solubility, other 2,5-DPP polymers showed similar UV and CV properties to those of **P2**.[22] Therefore the 1,3-DPP building block seems more resembling the 2,5-DPP isomer, and thus a weaker electron acceptor than the 1,4-DPP isomer.

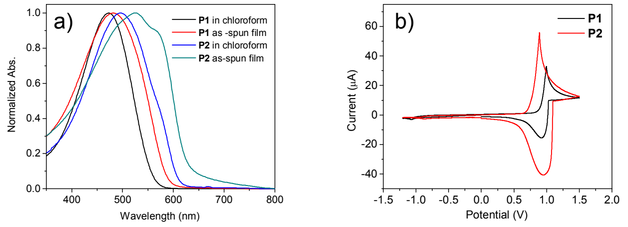


Fig. 2 UV-vis absorption spectra of (a) **P1** and **P2** in chloroform solutions and in thin films; (b) Cyclic voltammograms of as-spun **P1** and **P2** thin films measured in anhydrous CH_3CN solution using Bu_4NPF_6 as the electrolyte, ferrocene as the reference.

Owing to their excellent solubility in common organic solvents, **P1** and **P2** showed very good film formation property as shown in the atomic force microscopy (AFM) images in Fig. 3. All **P1** thin films are very smooth and didn't change markedly by thermal

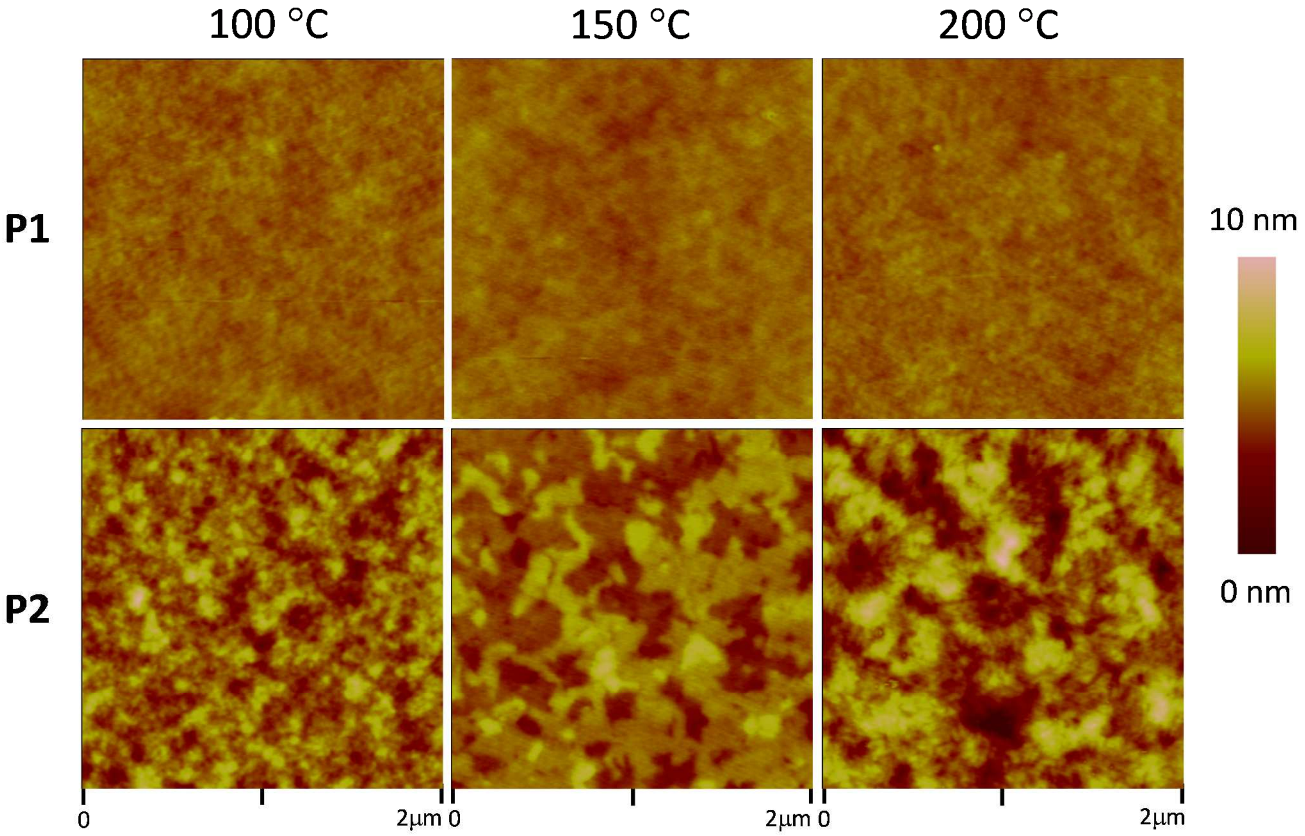


Fig. 3 AFM images (2 μm × 2 μm) of **P1** and **P2** thin films (~50-60 nm) spin coated on silicon substrate annealed at 100, 150 and 200 °C under nitrogen.

annealing. In contrast, small grains are observed for the **P2** thin film annealed at 100 °C. At an annealing temperature of 150 °C, the grains have grown notably and become well interconnected. The 200 °C-annealed **P2** thin film, however, showed more isolated grains with larger grain boundaries. To study the chain ordering of these polymers, we used both reflection and transmission X-ray diffractometry (XRD) techniques. As shown in Fig. 4, the reflection XRD of the **P1** thin films showed no peaks at the annealing temperatures of 100, 150, and 200 °C, indicating that all these **P1** films are amorphous. This is due to the two bulky branched side chains on the 1,3-DPP unit, which impede the self-assembly of polymer chains to form ordered structures. The **P2** film annealed at 100 °C exhibited a peak at 2θ = 4.23°, which corresponds to a d-spacing of 2.1 nm. Since there are no other diffraction peaks, the polymer chains presumably adopted a layer-by-layer lamellar packing motif, which has been frequently observed for other crystalline conjugated polymers.[25, 26] As the annealing temperature increased to 150 °C, the primary peak intensified significantly and the peak shifted slightly to 2θ = 4.35°, which corresponds to a d-spacing distance of 2.03 nm. A small secondary peak also appeared at 2θ = 8.63°. This manifests that the polymer chains are packed much more orderly with the aid of thermal annealing at this temperature. Upon annealing at a higher temperature of 200 °C, a precipitous drop in the intensity of the primary peak was observed, indicating the reduced crystallinity and chain ordering of the polymer film. To elucidate the in-plane chain packing, we measured the 150 °C-annealed polymer thin films using transmission XRD (Fig. 4c). As expected, **P1** showed a broad peak around 2θ = ~20° (d = 0.44 nm), which represents the typical van der Walls distance for an amorphous polymer. On the other hand, the 150 °C-annealed **P2** thin film showed a distinct peak at 23.68°, corresponding to a π-π stacking distance of 0.376 nm. The XRD data fully agree with the AFM images observed for the morphological evolution of the polymer thin films with the annealing temperature.

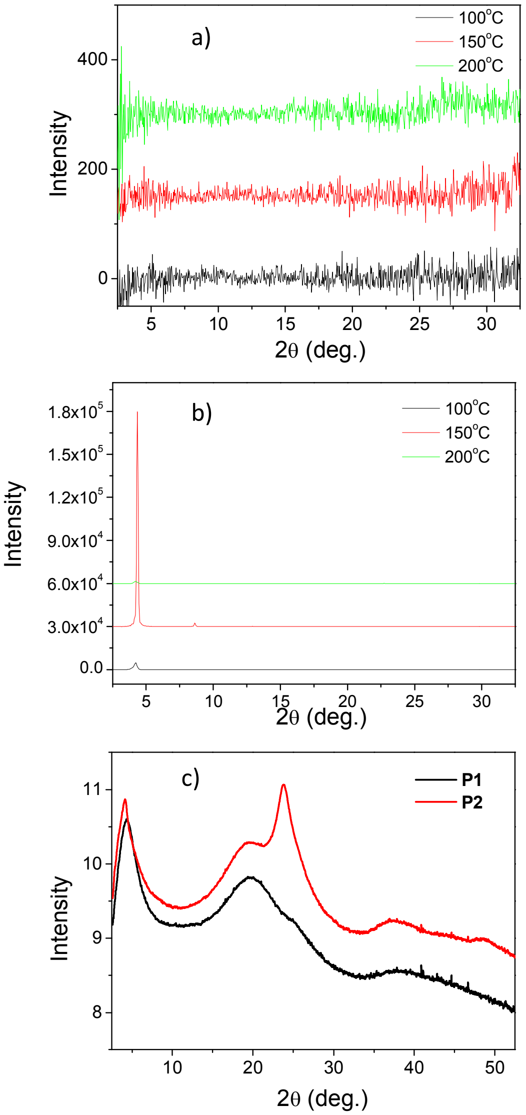


Fig. 6 XRD diagrams obtained from spin-coating **P1** (a) and **P2** (b) thin films on silicon substrates, and transmission diagram (c) of 150 °C-annealed **P1** and **P2** films.

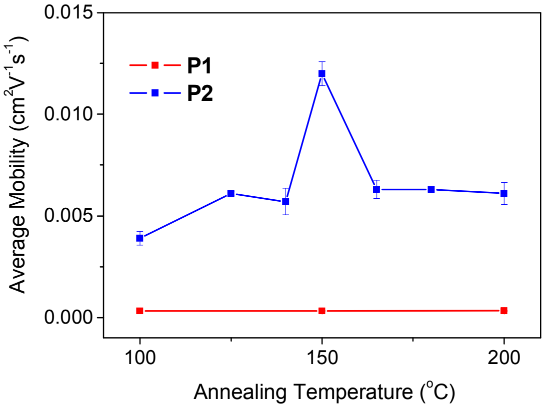


Fig. 4 Mobility variations of **P1** and **P2** thin films versus annealing temperature.

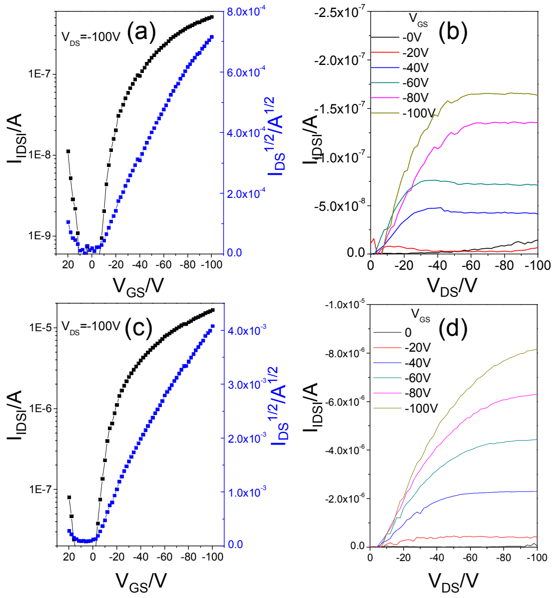


Fig. 5 Transfer and (left) output (right) curves of typical OTFT devices using a 150 °C-annealed **P1** (a and b) and **P2** (c and d) thin films.

To evaluate their charge transport performance, we used these two polymers as channel semiconductors in bottom-gate, bottom-contact OTFT devices. Gold source and drain electrode pairs (with a channel length of 30 μm and a channel width of 1 mm) were deposited on heavily n-doped Si wafer (as the gate) with a 300 nm-thick top SiO_2 insulating layer (as the dielectric), using a conventional photolithography technique. Prior to use, the SiO_2 surface in the channel region was passivized with dodecyltrichlorosilane (DDTS). Then a polymer thin film (~30-50 nm) was deposited by spin-coating a polymer solution in chloroform, followed by thermal annealing at different temperatures on a hot plate in a glove box. After cooling to room temperature, the devices were analysed in the same glove box in the absence of light. Devices based on the **P1** thin films annealed at 100, 150, and 200 °C showed almost the same hole transport characteristics with mobility up to 3.2×10^{-4} $cm^2V^{-1}s^{-1}$ (current on-to-off ratios of $\sim10^3$). Devices based on the **P2** thin films were investigated in more detail with finer annealing temperature intervals at 100, 130, 140, 150, 160, 180, and 200 °C, since the crystallinity and morphology of **P2** were found to be very sensitive to the annealing temperature, particularly around 150 °C, as discussed previously. As can be clearly seen in Fig. 5, the average mobility increases from 3.9×10^{-3} $cm^2V^{-1}s^{-1}$ for the 100 °C -annealed film to 1.2×10^{-2} $cm^2V^{-1}s^{-1}$ for the 150 °C-annealed film, then decreases as the annealing temperature is beyond 150 °C. This trend is in agreement with the change in crystallinity revealed by the XRD and AFM results. The maximum mobility is 1.3×10^{-2} $cm^2V^{-1}s^{-1}$ (on-to-off ratios of $\sim5\times10^4$) for a device with a 150 °C-annealed **P2** film (Fig. 6a,b). The mobility values are similar to those achieved for the 2,5-DPP based polymers.[22] The dramatic difference in mobility between **P1** and **P2** suggests that the side chains have a significant impact on the charge transport performance of these 1,3-DPP polymers, that is, the incorporation of a straight side chain at the 5-position of 1,3-DPP helps increasing the chain ordering and thus the charge transport of the resulting polymer. We will optimize the side chains and copolymerize 1,3-DPP with other comonomer building blocks to further improve the chain ordering and the charge transport performance of this class of polymers**.**

Experimental

Materials and Characterization

All chemicals were purchased from Sigma Aldrich and used without further purification. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with chemical shifts relative to tetramethylsilane (TMS, 0 ppm). Thermo Scientific GENESYS[20] Spectrophotometer was used to collect UV-vis spectra. Cyclic voltammetry (CV) data were obtained with a DY2111 potentiostat using an Ag / AgCl reference electrode, a Pt wire counter electrode, and a Pt foil working electrode in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a scan rate of 50 mVs^{-1}. Ferrocene was used as a reference, which has a highest occupied molecular orbital (HOMO) of -4.8 eV.[28] AFM profiles were recorded on polymer thin films spin coated on the dodecyltrichlorosilane (DDTS)-modified SiO_2 / Si substrates using a Dimension 3100 scanning probe microscope. The same samples were measured by a Bruker D8 Advance powder diffractometer with standard Bragg-Bretano geometry using Cu Kα radiation (λ = 1.5418 Å). Transmission XRD measurements were conducted on a Bruker Smart 6000 CCD 3-circle D8 diffractometer with a Cu RA (Rigaku) X-ray source (λ = 1.5418 Å) using polymer flakes stacked between two Mylar substrates. Gel-permeation chromatography (GPC) measurements were performed on a Waters SEC system using chloroform as an eluent and polystyrene as standards at 50 °C. The thermogravimetry analysis (TGA) was conducted on TGA Q500 (TA Instruments) at a heating rate of 10 °Cmin^{-1} under nitrogen. Elemental analysis (EA) was performed on Elementar Vario EL Cube elemental analyser.

OFETs fabrication and characterization

A bottom-gate, bottom-contact OTFT structure was adopted for evaluating **P1** and **P2**. Heavily n-doped Si wafer with a 300 nm-thick SiO_2 layerwas used as the substrate, where the conductive Si layer and the SiO_2 layer function as the gate and the dielectric, respectively. The source / drain electrode pairs were deposited using the conventional photolithography to obtain the defined device dimensions with a channel length (*L*) of 30 µm and a channel width (*W*) of 1 mm. The substrate was cleaned using an ultrasonic bath with de-ionized (DI) water, rinsed with acetone and isopropanol and then merged in a DDTS solution (3% in toluene) for 15 min. The polymer films with a thickness of ~30-50 nm were deposited on the substrate by spin coating a polymer solution in chloroform (10mg / mL) at 3000 rpm for 40s and subsequently annealed at 100, 150 or 200 °C for 20 min. All devices were characterized in nitrogen atmosphere in the absence of light using an Agilent B2900A Semiconductor Analyzer.

Synthesis

Synthesis of diethyl 1*H*-pyrrole-3,4-dicarboxylate (1)[24]

A solution of *p*-toluenesulfonylmethyl isocyanide (20.0 g, 102 mmol) and diethyl fumarate (17.6 g, 102 mmol) in anhydrous THF (100 mL) was added dropwise into a suspension of potassium *t*-butoxide (23.0 g, 205 mmol) in anhydrous THF (200 mL) under argon atmosphere at room temperature. The mixture was then stirred for overnight. Saturated aqueous NaCl (100 mL) and THF (100 mL) were added into the mixture. The organic layer was separated, dried over Na_2SO_4 and filtrated. After removal of solvent from the filtrate, a dark red residue was obtained, which was then dissolved in methanol again. With slow addition of water, a white precipitate formed. The solid was washed with excess water and then dried to give the product. Yield: 11.6 g (53.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.35 (d, *J* = 2.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 6H).

Synthesis of 1*H*-pyrrole-3,4-dicarboxylic acid (2)[24]

To a solution of NaOH (4.69 g, 118 mmol) in 50 v % aqueous ethanol (47 mL) was added compound **1** (3.17 g, 15.0 mmol), which was then heated to reflux for 2 h. Before cooling down, the mixture was added to water and then acidified with 10% HCl solution to pH 4~5. The white precipitate was filtrated, washed with water and dried to give a white solid. Yield: 2.02 g (86.9%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.21 (s, 2H), 7.65 (d, *J* = 2.9 Hz, 2H).

Synthesis of 4-((2-octyldodecyl)carbamoyl)-1*H*-pyrrole-3-carboxylic acid (3)

Compound **2** (0.944 g, 6.08 mmol) and *N*,*N*'-dicyolohexylcarbodiimide (1.51 g, 7.30 mmol) was dissolved in anhydrous THF (15 mL) under argon atmosphere. The mixture was refluxed with stirring for 2 h before cooling down to room temperature. The precipitate (*N*,*N*'-dicyclohexylurea) was filtered off and washed with THF. Under argon atmosphere, 2-octyldodecan-1-amine was added dropwise into the filtrate with stirring. The reaction mixture was stirred overnight at room temperature, poured into DI water and extracted with ethyl acetate three times. The combined organic layer was dried over Na_2SO_4 and filtered. After evaporating the solvent, the resulting solid was washed with dilute HCl and dried. This solid was used in the next step reaction without further purification. Yield: 2.61 g (98.7%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.87 (s, 1H), 8.96 (s, 1H), 7.64 (s, 1H), 7.48 (s, 1H), 1.19 (s, 30H), 0.81 (d, *J* = 2.0 Hz, 7H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.90, 165.39, 128.37, 124.59, 116.12, 115.65, 31.59, 31.51, 29.58, 29.55, 29.29, 29.26, 29.18, 28.99, 28.95, 26.22, 22.39, 14.23.

Synthesis of 2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (4)

To a solution of compound (**3**) (1.78 g, 4.08 mmol) in anhydrous *N*,*N*-dimethylformamide (DMF) (5 mL) was added thionyl chloride (0.9 mL) at 0 °C under argon atmosphere. After stirring overnight at room temperature, the solution was poured into an ice / water mixture and extracted with ethyl acetate three times. The organic layers were combined and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (1 : 2, v : v) as an eluent to give a yellow solid. Yield: 1.05 g (62.0%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.10 (d, *J* = 2.5 Hz, 2H), 3.45 (d, *J* = 7.3 Hz, 2H), 0.87 (dd, *J* = 6.7, 4.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.04, 121.27, 115.71, 42.23, 36.90, 31.81, 31.79, 31.34, 29.92, 29.54, 29.52, 29.46, 29.24, 29.20, 26.20, 22.57, 22.56, 14.01. HRMS (M+H)$^+$ Calc. for $C_{26}H_{45}N_2O_2^+$: 417.3481; found: 417.3485.

Elemental analysis: Calc. for $C_{26}H_{44}N_2O_2$: C 74.95, H 10.64, N 6.72%; found: found: C 75.01, H 10.40, N 6.66%.

Synthesis of 2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (5a)

Sodium hydride (67.2 mg, 2.80 mmol) was added to a solution of compound **4** (1.05 g, 2.53 mmol) in anhydrous DMF (10 mL) and the mixture was stirred at room temperature for 2 h. To this mixture was added 9-(bromomethyl)nonadecane (1.10 g, 3.04 mmol) and the solution was stirred overnight at room temperature. After removing the solvent, the product was purified using chromatography on silica gel (hexane : dichloromethane (DCM) = 1 : 1, v : v) to give a yellow oil. Yield: 1.21 g (69.3%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (s, 2H), 3.81 (d, J = 6.7 Hz, 2H), 3.42 (d, J = 7.2 Hz, 2H), 1.78 (d, J = 23.4 Hz, 2H), 0.87 (d, J = 6.4 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.91, 121.15, 118.53, 54.46, 42.11, 39.67, 36.92, 31.77, 31.71, 31.40, 31.08, 29.92, 29.69, 29.51, 29.45, 29.41, 29.36, 29.21, 29.18, 29.10, 26.23, 22.53, 22.51, 13.95. HRMS $(M+H)^+$ Calc. for $C_{46}H_{85}N_2O_2^+$: 697.6611; found: 697.6611. Elemental analysis: Calc. for $C_{46}H_{84}N_2O_2$: C 79.25, H 12.14, N 4.02%; found: C 79.64, H 12.30, N 3.89%.

Synthesis of 5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (5b)

Compound **5b** was synthesized following the similar procedure for compound **5a** using 1-bromododecane instead of 9-(bromomethyl)nonadecane. Yield: 0.840 g (73.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2H), 3.92 (t, *J* = 7.1 Hz, 2H), 3.42 (d, *J* = 7.3 Hz, 2H), 0.87 (dd, *J* = 6.7, 4.3 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.82, 121.24, 117.98, 50.58, 42.04, 36.90, 31.78, 31.75, 31.39, 31.07, 29.89, 29.49, 29.43, 29.37, 29.26, 29.20, 29.16, 28.91, 26.34, 26.21, 22.52, 13.93. HRMS $(M+H)^+$ Calc. for $C_{38}H_{69}N_2O_2^+$: 585.5359; found: 585.5374. Elemental analysis: Calc. for $C_{38}H_{68}N_2O_2$: C 78.02, H 11.72, N 4.79%; found: C 78.62, H 11.68, N 4.83%.

Synthesis of 4,6-dibromo-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (6a)

To a solution of compound **5a (**1.20 g, 1.72 mmol) in DMF (10 mL) was added *N*-bromosuccinimide (NBS) (0.705 g, 3.96 mmol) in absence of light. After stirring at room temperature overnight, the mixture was poured into water (200 mL), extracted with DCM, dried over Na_2SO_4, and filtered. After removing the solvent, the residual was purified using silica-gel column chromatography (hexane : ethyl acetate = 3 : 1, v : v) to give the product as a liquid. Yield: 1.21 g (88.0%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (d, *J* = 7.5 Hz, 2H), 3.42 (d, *J* = 7.1 Hz, 2H), 0.88 (t, *J* = 6.0 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.51, 121.43, 101.28, 51.60, 42.44, 38.34, 36.99, 31.93, 31.92, 31.91, 31.89, 31.84, 31.83, 31.81, 31.81, 31.50, 31.22, 29.95, 29.80, 29.79, 29.65, 29.63, 29.61, 29.59, 29.58, 29.56, 29.54, 29.53, 29.51, 29.49, 29.47, 29.46, 29.44, 29.33, 29.30, 29.28, 29.22, 26.36, 22.66, 22.65, 22.62, 14.08, 14.05, 0.98. HRMS $(M+H)^+$ Calc. for $C_{46}H_{83}Br_2N_2O_2^+$: 855.4801; found: 855.4821. Elemental analysis: Calc. for $C_{46}H_{82}Br_2N_2O_2$: C 64.62, H 9.67, N 3.28%; found: C 64.80, H 9.68, N 3.20%.

Synthesis of 4,6-dibromo-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (6b)

Compound **6b** was synthesized following the similar procedure for compound **6a** using compound **5b** (0.704 g, 1.20 mmol) instead of compound **5a**. Yield: 0.782 g (87.7%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 – 3.97 (m, 2H), 3.42 (d, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 5.8 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.35, 121.30, 100.41, 47.33, 42.28, 36.86, 31.76, 31.38, 29.82, 29.69, 29.50, 29.48, 29.45, 29.35, 29.25, 29.20, 29.17, 29.16, 28.92, 26.28, 26.22, 22.53, 13.93. HRMS $(M+H)^+$ Calc. for $C_{38}H_{67}Br_2N_2O_2^+$: 743.3549; found: 743.3542. Elemental analysis: Calc. for $C_{38}H_{66}Br_2N_2O_2$: C 61.45, H 8.96, N 3.77%; found: C 61.13, H 8.96, N 3.76%.

Synthesis of 2,5-bis(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (7a)

Compound **6a** (1.11 g, 1.29 mmol) and 2-(tributylstannyl)thiophene (1.06 g, 2.85 mmol) were charged to a 25 mL flask. After degassing and refilling argon for 3 times, toluene (8 mL) and $Pd_2(dba)_3$ (32 mg, 0.104 mmol) were added and the reaction mixture was heated to 110 °C and stirred overnight. After cooling down to room temperature, solvent was removed. The liquid was dissolved in hexane and purified by column chromatography on silica gel (hexane : DCM = 2 : 1, v : v) to give a light yellow solid. Yield: 1.08 g (96.8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 3.6, 1.1 Hz, 2H), 7.45 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.14 (dd, *J* = 5.1, 3.7 Hz, 2H), 4.30 (d, *J* = 7.5 Hz, 2H), 3.42 (d, *J* = 7.2 Hz, 2H), 0.85 (dt, *J* = 7.0, 3.6 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.25, 130.06, 129.64, 127.62, 127.53, 127.47, 118.71, 50.90, 42.33, 37.83, 37.02, 31.78, 31.72, 31.54, 30.69, 29.89, 29.56, 29.51, 29.47, 29.44, 29.32, 29.26, 29.21, 29.17, 29.08, 28.15, 26.63, 26.34, 25.71, 22.55, 17.17, 13.96, 13.43. HRMS $(M+H)^+$ Calc. for $C_{54}H_{89}N_2O_2S_2^+$: 861.6365; found: 861.6366. Elemental analysis: Calc. for $C_{54}H_{88}N_2O_2S_2$: C 75.29, H 10.30, N 3.25%; found: C 74.77, H 10.08, N 3.09%.

Synthesis of 5-dodecyl-2-(2-octyldodecyl)-4,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (7b)

Compound **7b** was synthesized following the similar procedure for compound **7a** using compound **6b** (0.642 g, 0.865 mmol) instead of compound **6a**. Yield: 0.464 g (71.7%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.9 Hz, 2H), 7.48 (d, *J* = 4.4 Hz, 2H), 7.19 (dd, *J* = 4.9, 3.9 Hz, 2H), 4.40 – 4.25 (m, 2H), 3.45 (d, *J* = 7.2 Hz, 2H), 0.88 (dt, *J* = 6.7, 5.3 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.27, 130.45, 129.20, 127.63, 127.35, 126.81, 118.47, 46.39, 42.31, 37.03, 31.78, 31.54, 30.81, 29.90, 29.51, 29.46, 29.32, 29.21, 29.19, 28.72, 28.15, 26.63, 26.35, 26.13, 22.55, 17.16, 13.97, 13.44. HRMS $(M+H)^+$ Calc. for $C_{46}H_{73}N_2O_2S_2^+$: 749.5113; found: 749.5109. Elemental analysis: Calc. for $C_{46}H_{72}N_2O_2S_2$: C 73.74, H 9.69, N 3.74%; found: C 72.66, H 9.65, N 3.50%.

Synthesis of 4,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (8a)

To a solution of compound **7a** (0.964 g, 1.12 mmol) in DMF (10 mL) was added NBS (0.459 g, 2.58 mmol). The reaction mixture was stirred at room temperature overnight and then poured into water (100 mL). After extraction with DCM, the combined organic phase was dried over Na_2SO_4 and filtered. After removing the solvent, the residual was purified using column chromatography on silica gel (hexane : ethyl acetate = 3 : 1, v : v) to give the product as a liquid. Yield: 1.05 g (91.8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 3.9 Hz, 2H), 7.12 (d, *J* = 3.9 Hz, 2H), 4.20 (d, *J* = 7.5 Hz, 2H), 3.43 (d, *J* = 7.2 Hz, 2H), 0.93 – 0.80 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.92, 130.83, 130.45, 130.25, 126.60, 119.00, 114.86, 31.79, 31.74, 29.50, 29.22, 29.17, 29.12, 22.56, 22.54, 14.00. HRMS $(M+H)^+$ Calc. for $C_{54}H_{87}Br_2N_2O_2S_2^+$: 1019.4555; found: 1019.4539. Elemental analysis: Calc. for $C_{54}H_{86}Br_2N_2O_2S_2$: C 63.64, H 8.50, N 2.75%; found: C 63.94, H 8.47, N 2.78%.

Synthesis of 4,6-bis(5-bromothiophen-2-yl)-5-dodecyl-2-(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (8b)

Compound **8b** was synthesized following the similar procedure for compound **8a** using compound **7b** (0.377 g, 0.500 mmol) instead of compound **7a**. Yield: 0.410 g (90.5%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 3.9 Hz, 2H), 7.14 (d, *J* = 3.9 Hz, 2H), 4.31 – 4.15 (m, 2H), 3.44 (d, *J* = 7.2 Hz, 2H), 0.95 – 0.79 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.09, 130.83, 130.73, 130.54, 126.01, 118.91, 114.90, 46.63, 42.49, 37.14, 31.94, 31.60, 30.99, 30.03, 29.65, 29.60, 29.51, 29.37, 29.33, 28.82, 26.45, 26.20, 22.72, 14.16. HRMS $(M+H)^+$ Calc. for $C_{46}H_{71}Br_2N_2O_2S_2^+$: 907.3303; found: 907.3293. Elemental analysis: Calc. for $C_{46}H_{70}Br_2N_2O_2S_2$: C 60.91, H 7.78, N 3.09%; found: C 61.17, H 7.74, N 3.03%.

Synthesis of P1

To a 25 mL Schlenk flask were added compound **8a** (0.231 g, 0.227 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.112 g, 0.227 mmol) and tri(*o*-totyl)phosphine (5.5 mg, 0.018 mmol). After degassing and refilling argon for 3 times, anhydrous chlorobenzene (5 mL) and tris(dibenzylideneacetone)-dipalladium (4.2 mg, 0.00454 mmol) were added under argon. The flask was sealed and stirred for 60 h at 130 °C. After cooling down to room temperature, the reaction mixture was poured into methanol (100 ml). The precipitated product was collected by filtration and subjected to Soxhlet extraction with acetone and hexane. Yield: 229.4 mg (98.7%) from the hexane extract.

Synthesis of P2

P2 was synthesized using compound **8b** (0.186 g, 0.205 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.101 g, 0.205 mmol), following the similar procedure for **P1**. The precipitated product was collected by filtration and subjected to Soxhlet extraction with acetone, hexane, and chloroform. Yield: 176.2 mg (94.3%) from the chloroform extract.

Conclusions

In summary, we reported the use of another DPP isomer, pyrrolo[3,4-*c*]pyrrole-1,3-dione (1,3-DPP), as a building block to construct π-conjugated polymers as channel semiconductors for OTFTs. Two copolymers based on 1,3-DPP and quaterthiophene units with differed side chain combinations were obtained, which showed dramatically different optoelectronic properties and molecular packing from those of the polymers based on the pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)dione (1,4-DPP) isomer. Charge transport performance of these polymers was evaluated in OTFTs and hole mobility as high as 0.013 cm^{2}V^{-1}s^{-1} was obtained. Our preliminary results indicated 1,3-DPP is a promising building block for constructing polymer semiconductors for printed electronics.

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Notes and references

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Graphical abstract

Pyrrolo[3,4-*c*]pyrrole-1,3(2*H*,5*H*)-dione (1,3-DPP) is used as a building block to construct copolymers for organic thin films transistors.