Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 18950

www.rsc.org/materials

PAPER

Diketopyrrolopyrrole-based semiconducting polymer bearing thermocleavable side chains†

Bin Sun,[ab] Wei Hong,[ab] Hany Aziz[bc] and Yuning Li*[ab]

Received 14th June 2012, Accepted 12th July 2012
DOI: 10.1039/c2jm33818a

The synthesis of a diketopyrrolopyrrole (DPP)-based semiconducting polymer bearing thermocleavable side chains is described. This polymer can be converted into a native semiconductive polymer by thermal annealing at 200 °C. The resulting side chain-free polymer showed a good p-type semiconductor performance in organic thin film transistors.

Introduction

π-Conjugated polymer semiconductors have attracted much attention in recent years as active materials in organic thin film transistors (OTFTs),[1] organic photovoltaics (OPVs),[2] *etc.* Their excellent solution processability and mechanical robustness allow for fabrication of various low-cost, large-area, and flexible organic electronic products such as displays, radio-frequency identification (RFID) tags, memory devices, and solar cells. To be solution-processable, polymer semiconductors require the incorporation of a large portion of solubilizing side chains to oppose the strong aggregation tendency of polymer backbones from solution. For instance, the hexyl side chains in poly(3-hexylthiophiophene) (P3HT) constitute of up to ~51% of the polymer mass. The non-conjugated side chains would separate the semiconductive aromatic polymer backbones and intrinsically reduce the overall charge carrier transport performance. Labile side chain groups, which provide the needed solubility and can be chemically[3] or thermally[4,5] removed under mild conditions, have been used to substitute both small molecular and polymeric semiconductors to achieve a higher density of the aromatic components *via* a post-deposition treatment. For example, cyclohexadiene[4a] and *N*-sulfinylamide[4b] were used to form soluble pentacene precursors, which can undergo thermally activated retro Diels–Alder reactions to recover the native semiconductive pentacene after solution deposition. Fréchet *et al.* used thermally decomposable secondary ester groups as terminal substituents for oligothiophenes.[4c,d] After thermal annealing, the resulting oligothiophenes possessed shorter terminal groups and showed good performance in OTFTs. The same research group reported a polythiophene having tertiary ester side chains, which could result in a polythiophene with the carboxylic acid side chains upon heating at 210 °C.[5a] To form a completely side chain-free (native) polythiophene, a higher temperature of 310 °C was required to remove the carboxylic acid groups.[5c,d] Bao *et al.* recently found that the secondary or tertiary alkyl groups on the nitrogen atoms of quaterrylene diimides could be removed at elevated temperatures (~350 to 400 °C) with the chromophore intact.[4e] After thermally removing the side chains, the resulting quaterrylene diimide showed a significant increase in mobility in OTFTs. Holdcroft *et al.* reported polythiophenes having side chains comprising acid-sensitive tetrahydropyran (THP) groups.[3] In the presence of a trace amount of acid and at an elevated temperature, the THP groups were readily detached to form a closer polymer chain packing due to the shortened side chains.[3a] The THP group was also found thermocleavable at ~300 °C.[5a,e]

Here we report a novel polymer semiconductor, **PDQT-tc**, which has 2-octyldodecanoyl side chains that can be completely thermally removed at a low temperature of ~200 °C to form a side chain-free conjugated polymer **PDQT-n**. Our results show that this native conjugated polymer is a promising semiconductor for OTFTs and other organic electronics.

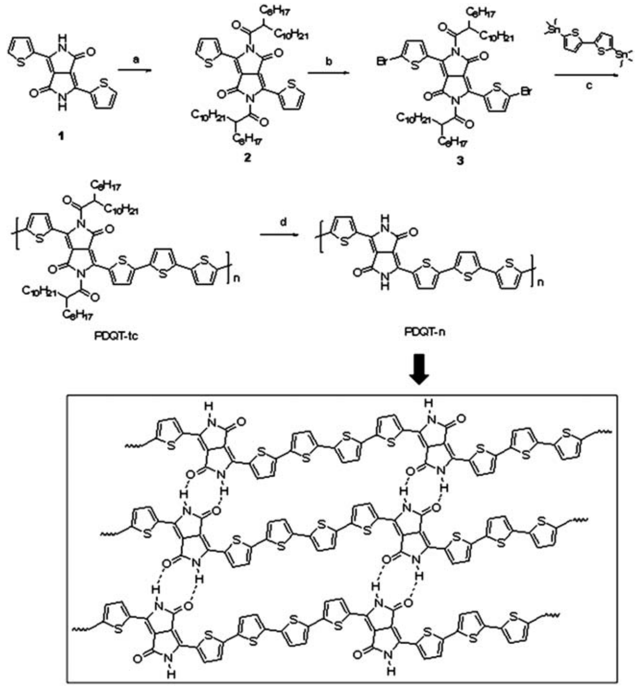
Results and discussion

The key building block for **PDQT-tc** is 2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione or diketopyrrolopyrrole (DPP), which has been an increasingly popular electron acceptor moiety for constructing high mobility donor–acceptor polymers for OTFTs.[6–9] The *tert*-butoxycarbonyl (*t*-BOC) substituted DPP molecule was found to be thermally decomposable at ~180 °C.[10] Very recently a DPP-based copolymer incorporating a *t*-BOC-substituted DPP unit was reported.[11] The *t*-BOC groups in the polymer could be thermally removed at ~200 °C and the resulting polymer showed enhanced electron transport performance. Previously we have developed a high mobility polymer **PDQT**,[6c] which has solubilising 2-octyldodecyl (OD) side chains on the DPP units. In this

---

[a] *Department of Chemical Engineering, University of Waterloo, 200 University Ave West, Waterloo, ON, Canada, N2L 3G1. E-mail: yuning.li@uwaterloo.ca*
[b] *Waterloo Institute for Nanotechnology (WIN), University of Waterloo, 200 University Ave West, Waterloo, ON, Canada, N2L 3G1*
[c] *Department of Electrical and Computer Engineering, University of Waterloo, 200 University Ave West, Waterloo, Ontario, Canada N2L 3G1*

† Electronic supplementary information (ESI) available: NMR, GPC, FT-IR, and AFM data. See DOI: 10.1039/c2jm33818a



Scheme 1 Synthesis of **PDQT-tc** and **PDQT-n**: (a) (i) NaH, NMP, (ii) 2-octyldodecanoyl chloride; (b) NBS, $CHCl_3$; (c) $Pd(PPh_3)_2Cl_2$, toluene, 90 °C; (d) heating at T °C; 200 °C;C under nitrogen.

study, we synthesized a **PDQT** derivative, **PDQT-tc**, which has 2-octyldodecanoyl groups on the nitrogen atoms. The synthesis of **PDQT-tc** is outlined in Scheme 1. 2,5-Dihydro-3,6-di-2-thienyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**1**) was first substituted with 2-octyldodecanoyl groups at two nitrogen atoms by reacting with NaH in *N*-methylpyrrolidone (NMP) followed by addition of 2-octyldodecanoyl chloride, yielding 2,5-bis(2-octyldodecanoyl)-2,5-dihydro-3,6-di-2-thiophen-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**2**) in 10% yield. Bromination of **2** with 2 equivalents of *N*-bromosuccinimide (NBS) gave 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecanoyl)-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**3**) in 65% yield. Stille coupling polymerization of **3** with 5,5′-bis(trimethylstannyl)-bithiophene was conducted in toluene at 90 °C for 24 h in the presence of a catalytic amount of bis(triphenylphosphine)palladium(II) dichloride. The resulting crude polymer was purified by Soxhlet extraction sequentially with acetone and hexane to remove oligomers and other impurities. Extraction with chloroform dissolved the remaining polymer, affording blue solid films after removal of the solvent in a high yield of 92%. The number average molecular weight (M_n) and polydispersity index (PDI) of **PDQT-tc** were determined by gel-permeation chromatography (GPC) to be 24 334 and 3.90, respectively, using chlorobenzene as an eluent and polystyrene as standards at a column temperature of 40 °C.

The thermal decomposition characteristics of **PDQT-tc** were investigated by using thermogravimetric analysis (TGA). The thermal liability of the –N–C(=O)– linkage was demonstrated by heating compounds **2** and **3**. Both compounds started to decompose at ~180 °C, although compound **3** was found to decompose at a slightly faster rate (Fig. 1). Polymer **PDQT-tc** started to lose weight at ~200 °C, while its structural analogue **PDQT**,[6c] which has 2-octyldodecyl side chains, showed a much higher onset thermal decomposition temperature at ~400 °C. A weight loss of ~46% for **PDQT-tc** levelled off at ~350 °C, which is ~10% less than the calculated mass fraction (~56%) of the 2-octyldodecanoyl side chains in **PDQT-tc**. This discrepancy is probably due to trapping of some decomposed side chain fragments in the polymer sample, whereas for the small molecule **3** the decomposed side chains could evaporate readily and its weight loss at ~350 °C is close to the calculated value (~56%).

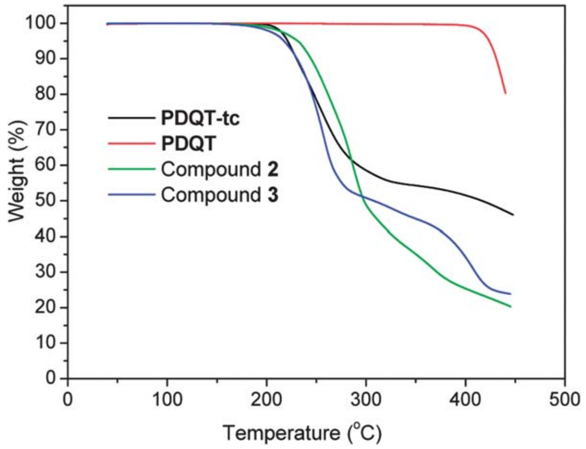


Fig. 1 TGA curves of **PDQT-tc**, **PDQT**, compound **2** and compound **3** at a heating rate of 10 °C min^{-1} under nitrogen.

The chemical structural changes of **PDQT-tc** upon heating were studied by FT-IR spectroscopy. The thin film samples (~63 nm) for FT-IR measurements were prepared by spin coating a **PDQT-tc** solution in chloroform on boron-doped silicon wafer substrates with a (111) orientation and a resistivity of ~10 Ω cm followed by thermal annealing in a glove box for 20 min at various temperatures. It can be clearly seen that the peaks (2922 and 2851 cm^{-1}) representing the side chain C–H groups decreased upon heating at ~200 °C and completely disappeared after heating at 250 °C or higher (Fig. 2: top). It was also observed that the peak at 1598 cm^{-1}, which originated from the N–H vibration, appeared for a film annealed at 200 °C. Extending the annealing time to 3 h, the side chains could be completely removed at 200 °C (Fig. 2: bottom). The thickness of the polymer films with side chains completely removed is ~26 nm, which is ~41% of the thickness (~63 nm) of the films before the thermal treatment (ESI†), in a good match with the calculated value (44%), assuming that the density of the polymer before and after thermal annealing remains similar. As opposed to the trapping of some decomposed side chains observed in the TGA results, the complete elimination of side chains of **PDQT-tc** confirmed by FT-IR is likely due to the easier evaporation of the decomposed side chain fragments in the thin films used for the FT-IR measurements than in the bulk samples used for the TGA. The liberated N–H groups in the resulting **PDQT-n** without side chains are expected to strongly interact with the C=O groups on the DPP units of the neighbouring polymer chains to form intermolecular hydrogen bonding (NH···O),[12] which would help the establishment of tightly held three-dimensional networks of native semiconducting polymer backbones (Scheme 1).

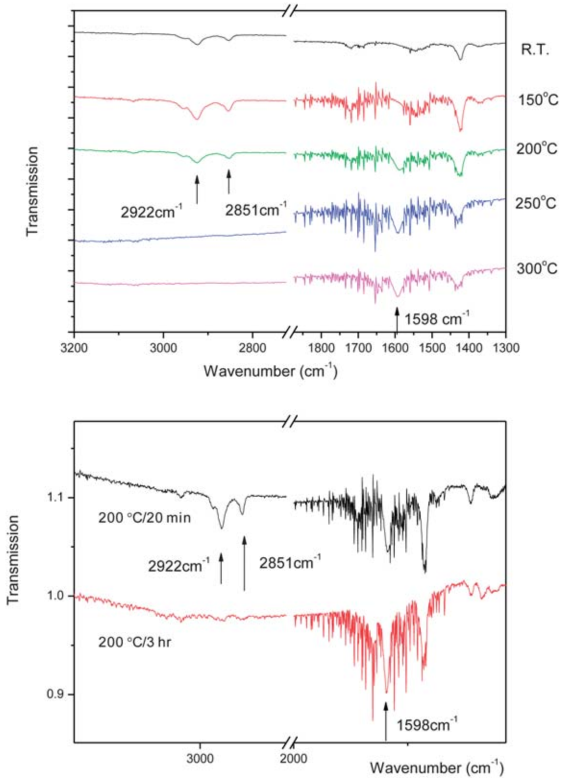


Fig. 2 Top: FT-IR spectra of **PDQT-tc** films on Si wafer annealed at different temperatures for 20 min in nitrogen. Bottom: FT-IR spectra of **PDQT-tc** films on Si wafer at 200 °C for 20 min and 3 h, respectively.

The X-ray diffractometry (XRD) measurements of the as-spun film and the films annealed at 150 and 200 °C are shown in Fig. 3. The as-spun film showed a diffraction peak at $2\theta = \sim 4.40°$, which corresponds to a *d*-spacing of 20.1 Å. This peak is considered to reflect the inter-lamellar distance as observed for **PDQT**.[6c] The much weaker diffraction intensity for **PDQT-tc** is probably due to the presence of the C=O groups on the 2-octyldodecanoyl side chains, which interfere with the molecular ordering. The primary peak of the thin film annealed at 150 °C became intensified, resulting from the improved molecular ordering by the thermal annealing. After annealing at 200 °C for 3 h, this diffraction peak completely disappeared. This is due to the elimination of the side chains, which results in the shortening of the interlayer distance. It is also noted that the diffraction intensity in the broad range from ~15 to 30° increased, which is possibly the result of formation of the amorphous phase. The atomic force microscopic (AFM) images in Fig. 4 show that the **PDQT-tc** film annealed at 150 °C (without removal of side chains) is quite smooth (with an RSM roughness of 0.89 nm), which is comprised of small nanograins (~20 to 30 nm). After removal of side chains by annealing at 200 °C for 3 h, the nanograins in the resulting **PDQT-n** film are connected to form nanofibers. The film becomes rougher (with an RSM roughness of 1.42 nm) and has large gaps (~10's to 100's nm) between domains.

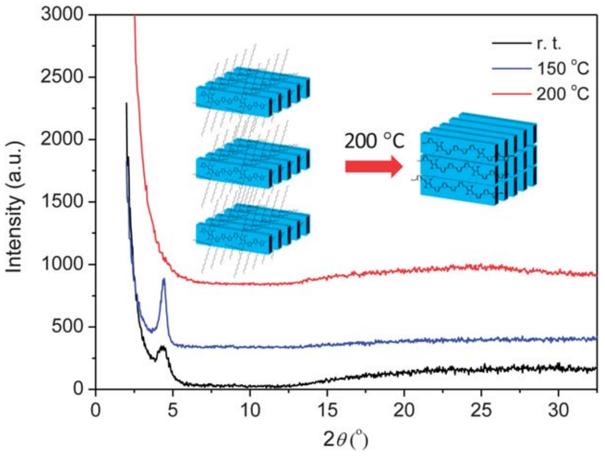


Fig. 3 XRD diagrams obtained from **PDQT-tc** thin films on DTS-treated SiO_2/Si substrates annealed at 150 °C for 20 min and 200 °C for 3 h in nitrogen along with one of the as-spun thin film (r. t.).

The side chain-free **PDQT-n** films are insoluble in any solvents for NMR analysis. To indirectly elucidate the chemical structure of **PDQT-n**, compound **2** was thermally decomposed at 250 °C for 20 min in a sealed vial on a hotplate. The mixture after heating was analyzed using ^{1}H NMR, which unambiguously showed that **2** was completely decomposed and the new peaks that appeared in the aromatic region are identical to the peaks of the known compound **1** with free N–H groups (ESI†). The thermal decomposition of compound **2** to form compound **1** was also investigated using FT-IR, which confirmed that the removal of the side chains and the appearance of the N–H groups started at ~200 °C (ESI†). Therefore, it is reasonable to assume that **PDQT-tc** was converted into the side chain-free native conjugated polymer **PDQT-n** as proposed in Scheme 1.

The UV–Vis absorption spectra of **PDQT-tc** in chloroform solution and of thin films are shown in Fig. 5. In solution, **PDQT-tc** exhibited an absorption maximum (λ_{max}) at 762 nm. The as-spun thin film showed a λ_{max} at a longer wavelength of 800 nm, suggesting an improved coplanarity of the polymer backbone and chain packing order. Thermal annealing at 150 °C led to a further red-shift in the λ_{max} to 820 nm. As the annealing temperature was increased to 200 °C, the absorption peak of the resulting **PDQT-n** film significantly blue-shifted to 772 nm. This dramatic change suggests the shortening of the effective π-conjugation length of the polymer chains, which is probably the direct result of the formation of a less ordered, amorphous phase where the polymer backbones are rather twisted. The strong interchain hydrogen bonding between the C=O and the N–H

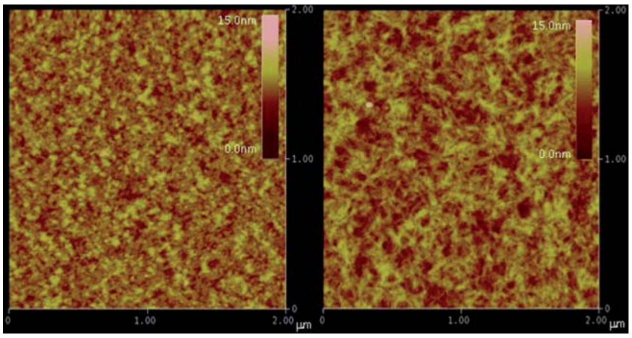


Fig. 4 AFM images (2 µm × 2 µm) of **PDQT-tc** thin films annealed at 150 °C for 20 min (left) and 200 °C for 3 h (right) in nitrogen. The root mean square (RMS) roughness of the films is 0.89 nm (left) and 1.42 nm (right).

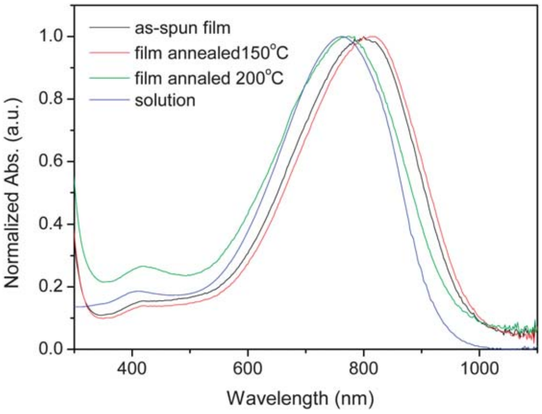


Fig. 5 UV–Vis spectra of the **PDQT-tc** chloroform solution and thin films on glass substrates without annealing (as-spun), annealed at 150 °C for 20 min, and annealed at 200 °C for 3 h in nitrogen.

groups of the native conjugated backbones in the **PDQT-n** film might have segregated the π–π stacks during the elimination of the side chains. The resulting backbone-only polymer **PDQT-n** would have very strong intermolecular interactions, which inhibit any chain motion to reorganize the polymer chains into ordered crystalline structures.

PDQT-tc was tested in bottom-gate, top-contact OTFT devices. A heavily p-doped silicon wafer with a ~200 nm thermally grown SiO_2 layer was used as the substrate, where the conductive silicon functions as the gate electrode and the SiO_2 layer as the dielectric. The SiO_2 layer was modified with dodecyltrichlorosilane (DTS) prior to use. A **PDQT-tc** solution in chloroform was spin coated on the substrate at 1500 rpm for 60 s to form a ~60 to 70 nm polymer thin film, which was subjected to thermal annealing at 200 °C for 3 h in a glove box to form a ~30 nm **PDQT-n** thin film. Then the source-drain electrode pairs were deposited on top of the polymer thin film by thermal evaporation of silver through a shadow mask to form OTFT devices with a channel width (W) of 4 mm and a channel length (L) of 100 μm. For comparison, OTFT devices using **PDQT-tc** annealed at 150 °C for 20 min (without eliminating the side chains) were fabricated. All devices were encapsulated with a TiO_x top layer,[9] which was deposited by spin coating a precursor solution and then annealing at 80 °C for 20 min. The devices were characterized in air in the dark.

As shown in Fig. 6, the device with **PDQT-tc** annealed at 150 °C showed typical hole transport characteristics under the hole accumulation mode. The hole mobility in the saturation regime is 0.096 $cm^2 V^{-1} s^{-1}$ with a current on-to-off ratio of 8.6×10^5. The mobility value is about one order of magnitude lower than that of **PDQT**, probably due to the poor crystallinity of the **PDQT-tc** thin film. The device having the **PDQT-n** film obtained by annealing a **PDQT-tc** film at 200 °C for 3 h also showed a typical hole transport behaviour. The hole mobility of this device is 0.078 $cm^2 V^{-1} s^{-1}$, slightly lower than that of the device annealed at 150 °C. However, if the amorphous nature of the **PDQT-n** film is taken into account, the charge transport of this polymer is quite efficient. It will be our next subject of study to maintain the crystallinity and the π–π stacking during the thermal elimination of the side chains by fine-tuning the heating profile. Thermal removal of side chains under a high pressure[4e] will also be used to improve the quality and the crystallinity of the final polymer thin films.

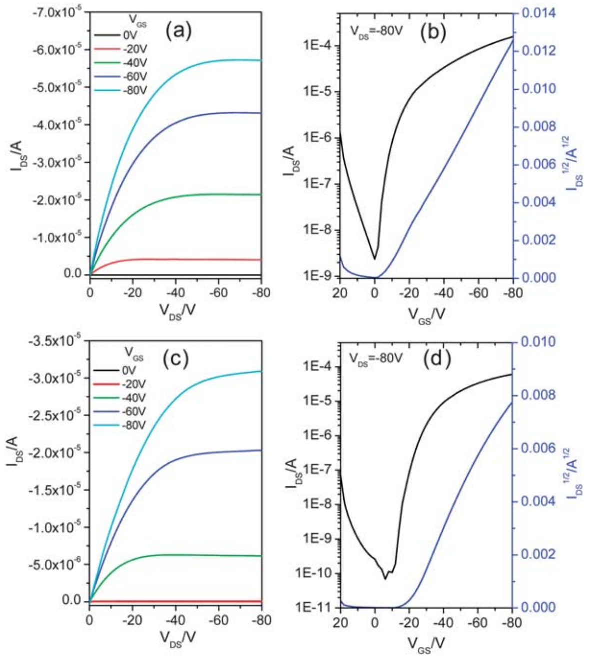


Fig. 6 Output and transfer curves of an OTFT device with a **PDQT-tc** thin film annealed at 150 °C for 20 min (a and b) and an OTFT device with **PDQT-n** obtained by heating a **PDQT-tc** thin film at 200 °C for 3 h in nitrogen (c and d). Device dimensions: channel width (W) = 4 mm; channel length (L) = 100 μm.

Experimental

Instrumentation and materials

All materials were purchased from Sigma-Aldrich and used without further purification. 3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1**)[13] and 5,5′-bis(trimethylstannyl)bithiophene[14] were synthesized according to the literature. NMR data were collected on a Bruker DPX 300 MHz spectrometer with chemical shifts relative to tetramethylsilane (TMS, 0 ppm). FT-IR spectra were performed on an FTIR-8400S (Shimadzu) Fourier Transform Infrared Spectrophotometer. UV–Vis spectra were recorded on a Thermo Scientific GENESYS™ 20 Spectrophotometer. XRD diagrams of polymer thin films (~100 nm) on the DTS-modified Si/SiO_2 substrate deposited by spin-coating polymer solutions in chloroform were obtained with a Bruker D8 Advance powder diffractometer using standard Bragg-Brentano geometry with Cu Kα radiation ($\lambda = 1.5406$ Å). Gel-permeation chromatography (GPC) measurements were performed on a Waters Breeze HPLC system using chlorobenzene as an eluent with polystyrene as standards at a column temperature of 40 °C. Thermogravimetry analysis (TGA) was conducted on a TGA Q500 (TA Instruments) at a heating rate of 10 °C min^{-1} under nitrogen. AFM images were performed on polymer thin films on a DTS-modified SiO_2/Si substrate using a Dimension 3100 Scanning Probe Microscope. The polymer thin films (~30 to 40 nm) were deposited by spin-coating polymer solutions in chloroform and optionally annealed at different temperatures.

Synthesis of 2-octyldodecanoic acid

Sulphuric acid (10 g, 98%) was diluted with water (75 mL) and added to a solution of 2-octyl-1-dodecanol (30 g) in dichloromethane (60 mL). To this mixture was added drop-wise 1 M potassium permanganate solution (15 mL) over 1 h and then this mixture was stirred for an additional 3 h. The mixture was filtered to remove precipitated manganese dioxide, washed with water, and treated with 2 M NaOH (400 mL). The solution was washed with hexane, neutralized with 2 M HCl, and extracted with ethyl acetate three times. The combined organic phase was dried over anhydrous Na_2SO_4. Distillation under a reduced pressure gave a colourless liquid (23 g, 74%). ^{1}H NMR ($CDCl_3$) 2.38–2.35, 1.59–1.54, 1.47–1.43, 1.26, 0.90–0.85.

Synthesis of 2-octyldodecanoyl chloride

2-Hexyldecanoic acid (82 mmol, 21 g) was added drop-wise into thionyl chloride (80 mL). The reaction mixture was refluxed for 3 h and the excess thionyl chloride was removed at 70 °C *in vacuo* to leave a brown liquid (22.3 g, ~100%), which was used in the next step without further purification. ^{1}H NMR ($CDCl_3$): 2.76–2.71, 1.70, 1.53, 1.24, 0.88–0.84.

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

3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1**) (1.2 g, 4 mmol) was dissolved in anhydrous *N*-methyl-2-pyrrolidone (NMP) (25 mL) at 60 °C. Then the solution was cooled down to room temperature, and sodium hydride (0.36 g, 9 mmol) was added. The reaction mixture was stirred for 0.5 h at 60 °C before 2-octyldodecanoyl chloride (3.3 g, 10 mmol) was added into the reaction mixture. After stirring for 24 h at 60 °C, the reaction mixture was cooled down to room temperature and poured into DI water (500 mL), and extracted with ethyl acetate three times. The organic layer was washed with brine and DI water to remove NMP. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After evaporating the solvent, the residue was purified by column chromatography on silica gel with a mixture of ethyl acetate and hexane (1 : 6, v/v) as an eluent to give the title compound as a dark purple solid. Yield: 0.35 g (~10%). ^{1}H NMR ($CDCl_3$): 8.28 (2H, *d*, $J = 3.0$ Hz), 7.62 (2H, *d*, $J = 3.9$ Hz), 7.19–7.16 (2H, t, $J = 4.5$ Hz), 3.89–3.77 (2H, *m*), 1.90–1.70 (4H, m), 1.70–1.54 (4H, m), 1.50–1.10 (56H, *m*), 0.95–0.80 (12H, *m*).

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

2,5-Bis(2-octyldodecanoyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]-pyrrole-1,4(2*H*,5*H*)-dione (**2**) (1.1 g, 1.24 mmol) was dissolved in chloroform (50 mL) and NBS (0.441 g, 2.48 mmol) was added. After stirring for 24 h at room temperature in the absence of light, the solvent in the reaction mixture was removed and the residue was purified with column chromatography on silica gel using a mixture of dichloromethane and hexane (1 : 4, v/v) as an eluent. A dark purple solid was obtained (0.85 g, 65%). ^{1}H NMR ($CDCl_3$): 8.17 (2H, *d*, $J = 4.2$ Hz), 7.14 (2H, *d*, $J = 4.2$ Hz), 3.88–3.76 (2H, *m*), 1.90–1.70 (4H, *m*), 1.70–1.54 (4H, *m*), 1.45–1.10 (56H, *m*), 0.95–0.80 (12H, *t*, $J = 6.36$ Hz).

Synthesis of poly(2,5-bis(2-octyldodecanoyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione-alt-2,2′-bithiophene) (PDQT-tc)

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2 octyldodecanoyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**3**) (0.2470 g, 0.236 mmol) and 5,5′-bis(trimethylstannyl)-bithiophene (0.1160 g, 0.236 mmol) were charged in a 50 mL flask. After degassing and refilling argon for 3 times, toluene (12 mL) and bis-(triphenylphosphine)palladium(II) dichloride (4.8 mg) were added and the reaction mixture was stirred at 80 °C for 1 h, and 90 °C for 23 h. Then 0.5 mL of bromobenzene was added and stirred at 90 °C for an additional 3 h. The mixture was then poured into stirring methanol (200 mL). The solid was filtered off and further purified by Soxhlet extraction using acetone and hexane, and then dissolved with chloroform. A dark blue solid was obtained (227 mg, 91.5%). GPC: $M_n = 24\,334$; PDI = 3.90.

Fabrication and characterization of OTFT devices

A top contact, bottom-gate OTFT configuration was used to evaluate the polymer semiconductors. A heavily p-doped Si wafer with a thermally grown SiO_2 layer (~200 nm) having a capacitance of ~17 nF cm^{-2} was used as a substrate, where the conductive Si layer functions as the gate electrode and the SiO_2 layer as the dielectric. After cleaning sequentially with DI water, acetone, and isopropanol in an ultrasonic bath, the substrate was cleaned by O_2 plasma. Subsequently, the substrate was merged in a dodecyltrichlorosilane (DTS) solution in toluene (10 mg mL^{-1}) at 70 °C for 20 min. The substrate was then washed with toluene and dried under a nitrogen flow. A **PDQT-tc** solution in chloroform (5 mg mL^{-1}) was spin coated on the substrate at 1500 rpm for 60 s, resulting in a ~30 to 40 nm thick **PDQT-tc** thin film. A more concentrated **PDQT-tc** solution (10 mg mL^{-1}) was used to deposit a ~70 nm thick polymer film, which was annealed at 200 °C for 3 h on a hotplate in a glove box, resulting in a **PDQT-n** film with a thickness of ~30 nm. Subsequently, the source/drain electrode pairs were deposited on the polymer film by thermal evaporation of silver through a shadow mask. Finally, the device was encapsulated by TiO_X (ref. 9) and annealed at 80 °C for 20 min under nitrogen. The OTFT devices have a channel length (L) of 100 μm with a channel width (W) of 4 mm. The devices were characterized in air using an Agilent 4155C Semiconductor Analyzer. The field effect mobility was calculated according to the previously employed method.[6a]

Conclusions

We have presented a novel polymer semiconductor with side chains thermally cleavable at a low temperature of 200 °C. The complete cleavage and removal of the insulating 2-octyldodecanoyl side chains were verified with TGA, FT-IR, and NMR data. The liberated N–H groups on the polymer backbone are expected to form intermolecular hydrogen bonding with the C=O groups on the neighbouring polymer chains to establish three-dimensional charge transport networks. The resulting side chain-free conjugated polymer is proven an active p-type semiconductor material for OTFTs, exhibiting a hole mobility of up to 0.078 cm^2 V^{-1} s^{-1}. The resulting side chain-free polymer thin film is morphologically very stable, resistant to any solvents, and has a favourable band gap for light harvesting, which may also be a useful electron donor material for stable organic photovoltaics.

Acknowledgements

The authors thank the financial support provided by the Teledyne-DALSA-NSERC Industrial Research Chair Program Grants, and Dr Jianfu Ding of the National Research Council Canada for the GPC measurements.

Notes and references

1 (*a*) G. Horowitz, *Adv. Mater.*, 1998, **10**, 365; (*b*) C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99; (*c*) H. E. Katz, *Chem. Mater.*, 2004, **16**, 4748; (*d*) S. Allard, M. Forster, B. Souharce, H. Thiem and U. Scherf, *Angew. Chem., Int. Ed.*, 2008, **47**, 4070; (*e*) B. S. Ong, Y. Wu, Y. Li, P. Liu and H. Pan, *Chem.–Eur. J.*, 2008, **14**, 4766; (*f*) H. Sirringhaus, M. Bird, T. Richards and N. Zhao, *Adv. Mater.*, 2010, **22**, 3812.

2 (*a*) M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789; (*b*) S. Beaupré, P.-L. T. Boudreault and M. Leclerc, *Adv. Mater.*, 2010, **22**, E1; (*c*) O. Inganäs, F. Zhang, K. Tvingstedt, L. M. Andersson, S. Hellström and M. R. Andersson, *Adv. Mater.*, 2010, **22**, E100; (*d*) G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323; (*e*) B. C. Thompson and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58; (*f*) Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868.

3 (*a*) J. Yu, M. Abley, C. Yang and S. Holdcroft, *Chem. Commun.*, 1998, 1503; (*b*) J. Yu and S. Holdcroft, *Macromolecules*, 2000, **33**, 5073; (*c*) J. Yu, F. P. Orfino and S. Holdcroft, *Chem. Mater.*, 2001, **13**, 526; (*d*) E. Bundgaard, O. Hagemann, M. Bjerring, N. C. Nielsen, J. W. Andreasen, B. Andreasen and F. C. Krebs, *Macromolecules*, 2012, **45**, 3644.

4 (*a*) P. T. Herwig and K. Müllen, *Adv. Mater.*, 1999, **11**, 480; (*b*) A. Afzali, C. D. Dimitrakopoulos and T. L. Breen, *J. Am. Chem. Soc.*, 2002, **124**, 8812; (*c*) A. R. Murphy, J. M. J. Fréchet, P. Chang, J. Lee and V. Subramanian, *J. Am. Chem. Soc.*, 2004, **126**, 1596; (*d*) P. C. Chang, J. Lee, D. Huang, V. Subramanian, A. R. Murphy and J. M. J. Fréchet, *Chem. Mater.*, 2004, **16**, 4783; (*e*) J. H. Oh, W.-Y. Lee, T. Noe, W.-C. Chen, M. Könemann and Z. Bao, *J. Am. Chem. Soc.*, 2011, **133**, 4204.

5 (*a*) J. Liu, E. N. Kadnikova, Y. Liu, M. D. McGehee and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 9486; (*b*) C. Edder, P. B. Armstrong, K. B. Pradob and J. M. J. Fréchet, *Chem. Commun.*, 2006, 1965; (*c*) M. Bjerring, J. S. Nielsen, N. C. Nielsen and F. C. Krebs, *Macromolecules*, 2007, **40**, 6012; (*d*) F. C. Krebs, *Sol. Energy Mater.Sol. Cells*, 2008, **92**, 715; (*e*) J. L. Brusso, M. R. Lilliedal and S. Holdcroft, *Polym. Chem.*, 2011, **2**, 175.

6 (*a*) Y. Li, S. P. Singh and P. Sonar, *Adv. Mater.*, 2010, **22**, 4862; (*b*) P. Sonar, S. P. Singh, Y. Li, M. S. Soh and A. Dodabalapur, *Adv. Mater.*, 2010, **22**, 5409; (*c*) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs and J. Tan, *J. Am. Chem. Soc.*, 2011, **133**, 2198; (*d*) Y. Li, P. Sonar, S. P. Singh, W. Zeng and M. S. Soh, *J. Mater. Chem.*, 2011, **21**, 10829; (*e*) P. Sonar, S. P. Singh, Y. Li, Z.-E. Ooi, T.-J. Ha, I. Wong, M. S. Soh and A. Dodabalapur, *Energy Environ. Sci.*, 2011, **4**, 2288; (*f*) Y. Li, P. Sonar, S. P. Singh, Z. E. Ooi, E. S. H. Lek and M. Q. Y. Loh, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7162.

7 J. S. Ha, K. H. Kim and D. H. Choi, *J. Am. Chem. Soc.*, 2011, **133**, 10364.

8 H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney and I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272.

9 J. D. Yuen, J. Fan, J. Seifter, B. Lim, R. Hufschmid, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2011, **133**, 20799.

10 J. S. Zambounis, Z. Hao and A. Iqbal, *Nature*, 1997, **388**, 131.

11 J. Lee, A. R. Han, J. Hong, J. H. Seo, J. H. Oh and C. Yang, *Adv. Funct. Mater.*, 2012, DOI: 10.1002/adfm.201200940.

12 (*a*) J. Mizuguchi, A. Grubenmann, G. Wooden and G. Rihs, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1992, **48**, 696; (*b*) J. Mizuguchi, *J. Phys. Chem. A*, 2000, **104**, 1817.

13 Y. Li, *US Pat.*, 2009 65766 A1, 2009.

14 I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. M. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 328.