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A corannulene-based donor–acceptor polymer for organic field-effect transistors†

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For the first time, the corannulene unit was incorporated directly into the backbone of conjugated polymers. A new donor–acceptor (D–A) copolymer PICBT using imide-fused corannulene as acceptor was synthesized and its performance in organic field-effect transistors (OFETs) was tested. PICBT exhibited ambipolar transporting property with a hole mobility of $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $7.45 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the substrates were treated with octyltrimethoxysilane (OTS). If the substrates were not modified with OTS, PICBT showed lower device performances with a hole mobility of $4.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $1.54 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The device performances are competitive among the amorphous materials. This work paved the way for incorporating the corannulene unit into conjugated materials.

Received 5th October 2014
Accepted 10th October 2014

DOI: 10.1039/c4ra11824c

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Introduction

Conjugated polymers have been extensively used in organic electronic thin film devices due to their good film-forming properties and solution processability.^{1–5} Through prolonged development, the application of donor–acceptor (D–A) copolymers (the third generation semiconducting polymers as named by Heeger)⁶ has proved to be an effective way to improve the device performance of organic electronics.^{7–9} Although D–A copolymers based on electron-deficient blocks such as iso-indigo (IID),^{10,11} naphthalene diimide (NDI),^{12,13} benzobisthiadiazole (BBT),¹⁴ diketopyrrolopyrrole (DPP)^{15,16} and benzodifurandione-based oligo(*p*-phenylene vinylene) (BDOPV)^{17–19} have led to excellent performances, the types of acceptor units are still limited. Because distinct new structures are the basis for further improvement of the conjugated polymers, it is important to develop different acceptor structures. To the best of our knowledge, the bowl-shaped aromatic molecule has seldom been used in conjugated polymers, partly due to the synthetic difficulty.^{20–22} (A fragment of C_{70} , cyclopenta-fused anthracene,^{20,21} has been introduced in conjugated polymers recently, but this unit is essentially a planar structure.)

Corannulene is a bowl-shaped molecule which has 1D columnar convex–concave stacking upon periphery modification.^{23–25} The large π – π overlap may form a channel for efficient charge transport.²³ The spherical shape of fullerene and its derivatives provides the possibility of multi-dimensional charge transport.²⁶ The structural correlation of corannulene with fullerene derivatives makes it extremely attractive and may also partly facilitate its multi-dimensional charge transport. Many efforts have been devoted to develop its efficient synthetic methods^{27,28} and its application in dendrimers,²⁹ molecular tweezers,^{30–32} polymers,²² carbon nanotubes (CNTs),^{33,34} and liquid crystals.^{29,35} Recently, its application in organic electronics has also been proved.^{23–25,36–39} Small-molecule corannulene derivatives were used in OFETs, providing electron mobility of $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole mobility of $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²³

Recent studies suggest that the introduction of electron-withdrawing groups into corannulene may enhance its electron-accepting properties, some can even exceed C_{60} as an effective electron acceptor.^{37,38} Electron-deficient imide-fused corannulene showed a low LUMO level of -3.4 eV ²⁴ and could be potentially used as an excellent electron acceptor. The design strategy of corannulene-based acceptor unit can be described as follows (see Fig. 1): (1) electron-deficient imide group can lower LUMO level and provides a position to introduce alkyl chains. The strong dipole orientation of imide may also lead to better arrangement of corannulene.^{23,24} (2) Long and further branched alkyl chains will both ensure sufficient solubility of the resulted conjugated polymer and may also lead to a closer π – π stacking distance.^{11,40–42} (3) Two bromides in the 4- and 9- positions of imide-fused corannulene unit allow the incorporation of this unit into the backbone of conjugated

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† Electronic supplementary information (ESI) available: TGA, PES, GPC, AFM phase image and NMR. See DOI: 10.1039/c4ra11824c

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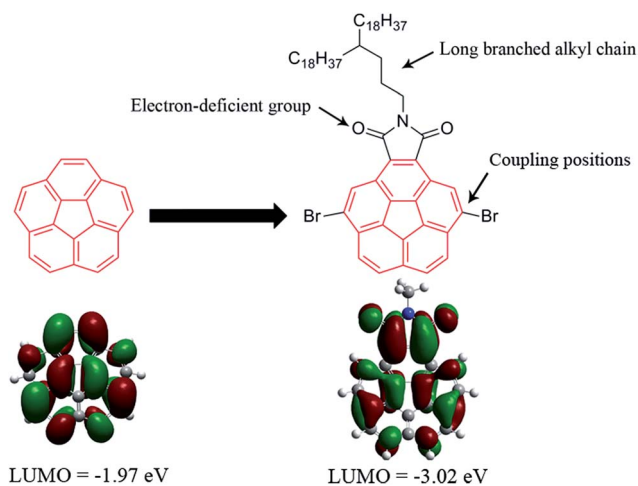


Fig. 1 Design strategy of corannulene-based acceptor unit and calculated energy levels and LUMO of corannulene and imide-fused corannulene at B3LYP/6-311G(d) level.

materials. Connection through these two positions also guarantees the best effective conjugation length and the maximum intrachain charge transfer of those materials.^{36,43}

Herein, we use imide-fused corannulene as acceptor unit in D–A copolymer with 2,2′-bithiophene as donor unit (named as **PICBT**) to investigate its OFET properties. OFET devices were fabricated and **PICBT** showed ambipolar transporting property with hole mobility of $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $7.45 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the substrates were treated with OTS using a top-gate/bottom-contact device configuration. When the substrates were not modified with OTS, **PICBT** showed lower device performances with electron mobility of $1.54 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole mobility of $4.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The device performances are competitive among those amorphous materials.^{44–46}

Results and discussion

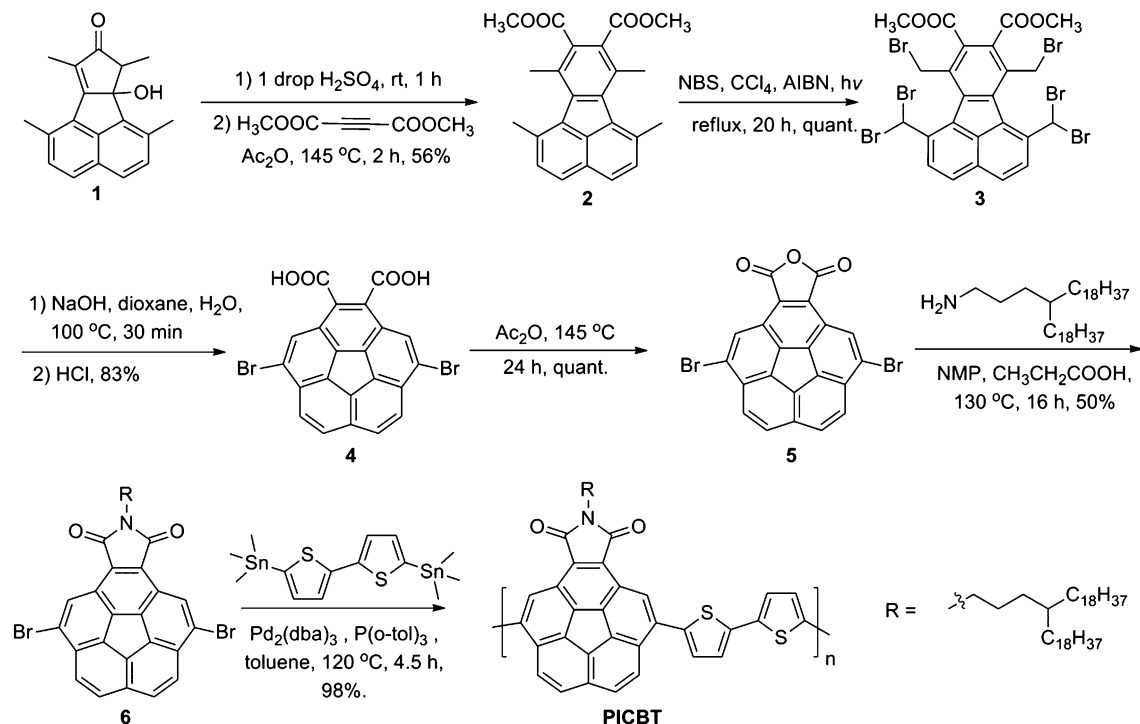
As shown in Scheme 1, the synthesis of polymer **PICBT** started from compound **1**. Compounds **1–4** were synthesized as reported.^{47,48} Compound **1** was dehydrated in acetic anhydride with one drop of sulfuric acid and subsequent Diels–Alder reaction with dimethyl acetylene dicarboxylate to give compound **2**. Radical bromination of compound **2** with AIBN as radical initiator formed compound **3**. The ring closure of compound **3** using a dioxane/water mixture in the presence of NaOH provided compound **4**. In refluxed Ac_2O , dicarboxylic acid **4** was converted to dicarboxylic anhydride **5**. Compound **5** was insoluble in common organic solvents and was used without further purification. An amine with long alkyl chain, 4-octadecyldocosan-1-amine reacted with compound **5** to give compound **6**, thus ensuring sufficient solubility of the resulting polymer. Compound **6** reacted with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene through Stille reaction to form polymer **PICBT**. The number average molecular weights of the polymer **PICBT** was determined as 40.5 kDa with polydispersity index (PDI) of

3.5, by high temperature gel permeation chromatography using polystyrene as standard and 1,2,4-trichlorobenzene as eluent at 150°C (Fig. S1†). The polymer exhibited great thermal stability with a decomposition temperature at 447°C (5% loss) (Fig. S2†).

The UV-vis absorption (Fig. 2) of **PICBT** was investigated in CHCl_3 ($1 \times 10^{-5} \text{ M}$), in thin film and in annealed thin film. Dilute solution of **PICBT** showed two absorption bands at $\sim 351 \text{ nm}$ and $\sim 516 \text{ nm}$. Band I was attributed to typical intramolecular charge transfer (ICT) absorption from donor to electron-deficient imide-fused corannulene core.⁴⁹ The conformational change of individual polymer and intermolecular interactions may influence the absorption of polymers.⁵⁰ But no obvious shift between absorption maximum of **PICBT** in solution and that in thin film was observed. This phenomenon indicates that polymer molecules may have strong intermolecular interactions, and may form some pre-aggregates in diluted solution.^{17,51} Annealing also had little influence on the absorption spectra of **PICBT**. The bandgap of **PICBT** was calculated to be 1.98 eV from the onset absorption of **PICBT** in thin film.

In cyclic voltammetry (CV) measurement in thin film, **PICBT** showed two reversible reduction peaks and one reversible oxidation peak, as shown in Fig. 2. Two reversible reduction peaks may be attributed to the reduction of imide-fused corannulene core.²⁴ The HOMO and LUMO levels of **PICBT** were estimated to be -5.42 eV and -3.31 eV from the onset of reduction and oxidation peaks. The bandgap between HOMO and LUMO is 2.11 eV, which is consistent with optical bandgap. Photoelectron spectroscopy (PES) (Fig. S3†) was used to further confirm the accuracy of HOMO level of **PICBT**, providing a HOMO level of -5.65 eV . DFT calculation performed on B3LYP/6-311G(d) level revealed that the HOMO orbitals of **PICBT** well delocalized over the conjugated chain, and the LUMO orbitals mainly localized on acceptor units.

To evaluate the OFET performance of **PICBT**, TG/BC devices were fabricated. The architecture of TG/BC device was often used for ambipolar and n-type polymer due to its good injection characteristics and encapsulation effect that can protect semiconductor layer from ambient atmosphere.¹² A polymer solution (3 mg mL^{-1} in ODCB) was spin-coated on OTS-treated substrates, followed by thermal annealing at 200°C for 30 min. Before electrode evaporation, CYTOP solution (CTL809M : CT-solv180 = 3 : 1) was spin-coated onto the polymer layer to form a dielectric layer. A 70 nm Al layer was evaporated as gate electrodes. **PICBT** showed with hole mobility of $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a threshold of 66 V and a current on/off ratio of 10^4 (evaluated at $V_D = -20 \text{ V}$) and electron mobility of $7.45 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a threshold of 52 V and a current on/off ratio of 10^4 (evaluated at $V_D = 20 \text{ V}$) (Fig. 3). We also found that the polymer spin-coated on substrates without OTS treatment showed ambipolar transporting property with electron mobility of $1.54 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a threshold of 64 V and a current on/off ratio of 10^3 (evaluated at $V_D = -20 \text{ V}$) and hole mobility of $4.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a threshold of 70 V and a current on/off ratio of 10^3 (evaluated at $V_D = -20 \text{ V}$). All device performances were summarized in Table 1. OTS-treated substrates may lead to better arrangement of **PICBT** in thin



Scheme 1 Synthetic route of PICBT.

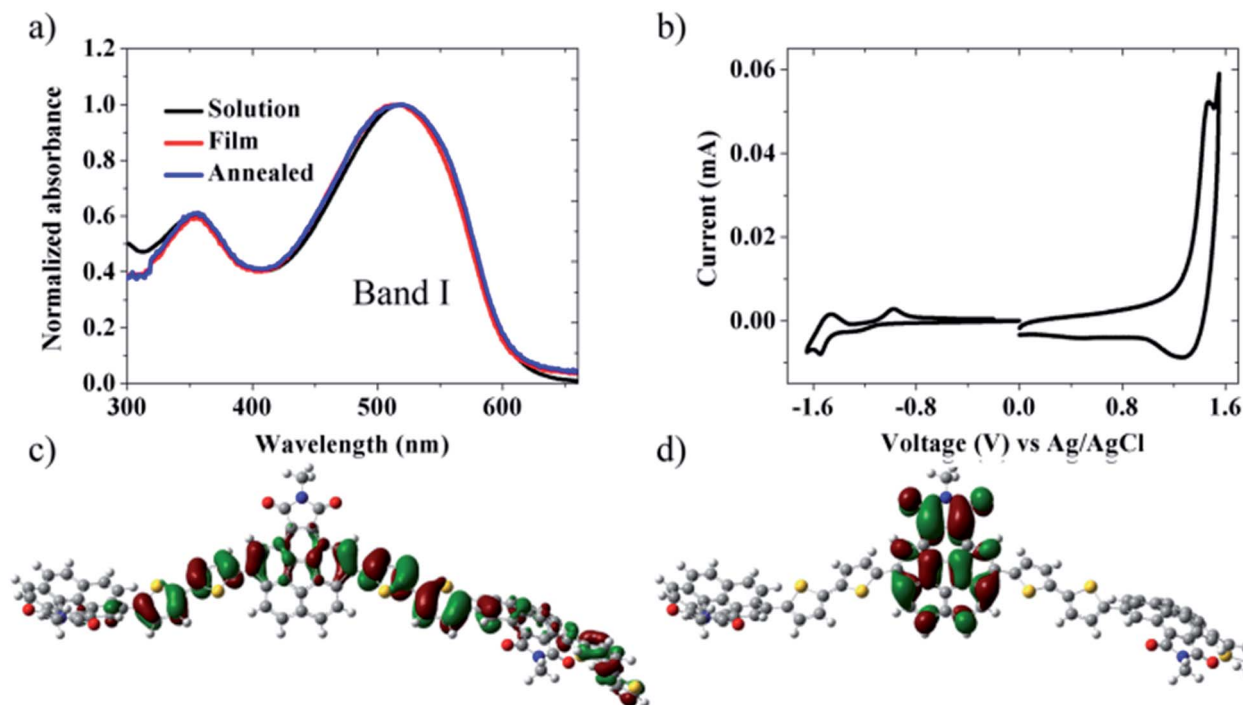


Fig. 2 (a) Normalized absorption spectra of PICBT in CHCl_3 (10^{-5} M), in thin film, and in annealed film (at 200 °C for 30 min). (b) Cyclic voltammogram of PICBT in thin film (scan rate: 50 mV s^{-1}). (c) and (d) HOMO and LUMO of PICBT.

film,^{52,53} this may be the reason that devices based on OTS-treated substrates had better device performance. The OFET properties based on small-molecule corannulene derivatives also exhibited ambipolar transport without deeper LUMO

level.²³ Imide-fused corannulene derivatives maybe a new type ambipolar materials.

To further explain the device performance of PICBT, we measured the morphologies of annealed polymer films by

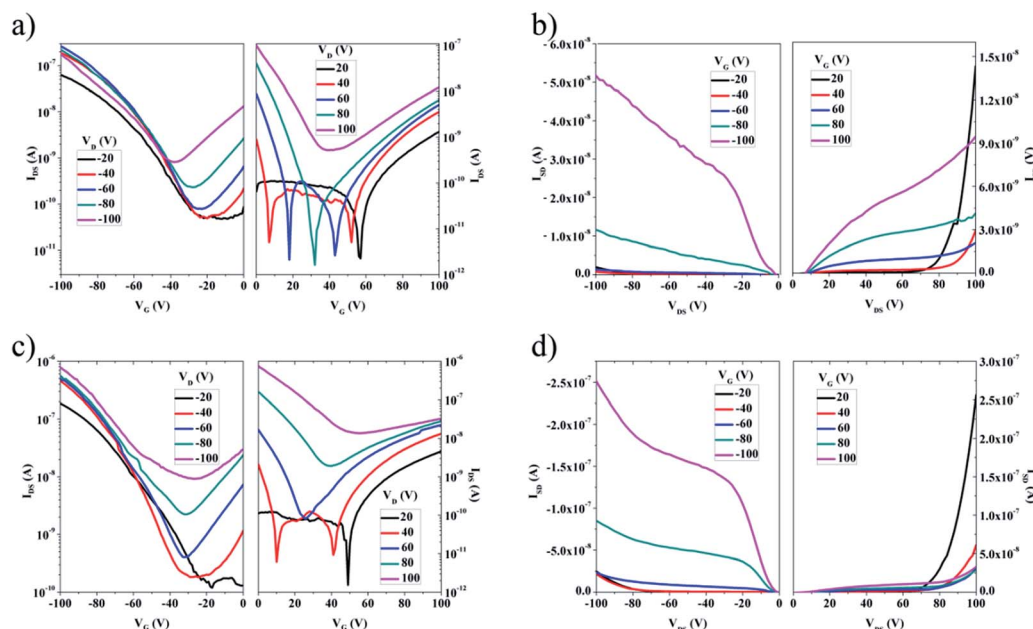


Fig. 3 (a) Transfer and (b) output characteristics of PICBT FET devices (the substrates were without OTS-treatment). (c) Transfer and (d) output characteristics of PICBT FET devices (the substrates were with OTS-treatment).

Table 1 Summary of OFET device performances

Substrates	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_T (V)	$I_{\text{on}}/I_{\text{off}}^a$	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	V_T (V)	$I_{\text{on}}/I_{\text{off}}^b$	d_{spacing}
Bare	4.62×10^{-3}	70	10^3	1.54×10^{-4}	54	10^3	26.9
OTS-treated	0.025	66	10^4	7.45×10^{-5}	52	10^4	26.7

^a Evaluated at $V_D = -20$ V. ^b Evaluated at $V_D = 20$ V.

atomic force microscopy (AFM) and X-ray diffraction (Fig. 4). The surface of polymer film is smooth, with root-mean-square (RMS) of 0.72 nm on bare substrates and 1.0 nm on OTS-treated substrates. Height image showed that no obvious crystallized zones were found on film surface and the film was almost amorphous when the polymer film was on bare

substrates. When the polymer film was on OTS-treated substrates, the morphology didn't show any difference.

Charge transport in polymer films includes intrachain transport and interchain transport⁵⁴ and is usually limited by the most difficult interchain hopping processes.⁵⁵ The increasing of disorder zones may hinder interchain transport

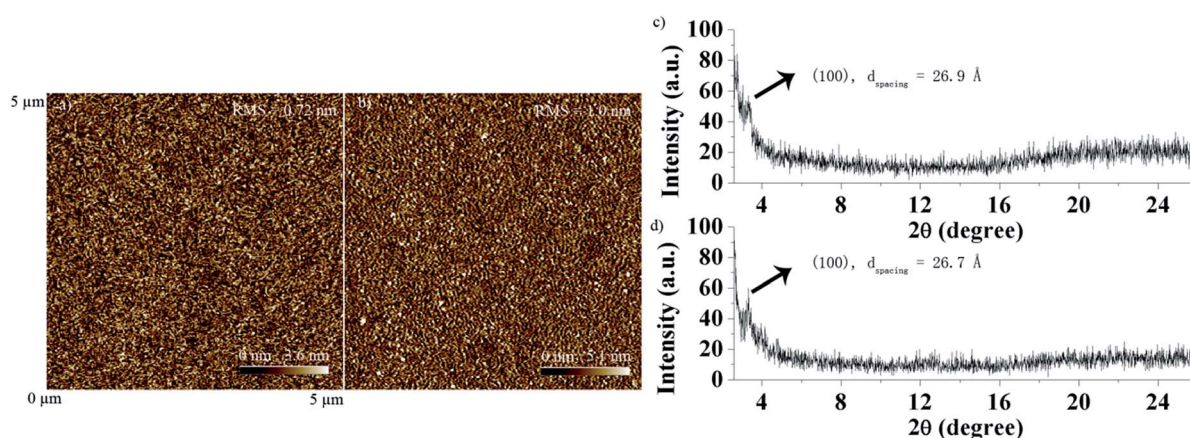


Fig. 4 (a) AFM height images of PICBT on bare substrates and (b) on OTS-treated substrates. (c) X-ray diffraction data of PICBT on bare substrates and (d) on OTS-treated substrates ($\lambda = 1.54$ Å).

and lower charge carrier mobility. On the other hand, XRD diffraction results showed that **PICBT** had only one diffraction peak at 3.30° on bare substrates and 3.28° on OTS-treated substrates corresponding to a d -spacing of 26.9 Å and 26.7 Å, which was attributed to (100) diffraction. Based on present characterization, it is hard to explain the different performance between two substrates based devices. Further research remains important. Although the device performances based on **PICBT** are poor than other D–A polymers with bithiophene as donor^{5,56} but competitive among those amorphous materials.^{44–46}

Conclusions

In summary, we synthesized the first corannulene-based conjugated polymer **PICBT** and measured its organic electronic device performance. **PICBT** provided ambipolar transporting property with electron mobility of $7.45 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole mobility of $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These preliminary results showed that corannulene derivatives can be a promising building block in conjugated materials. Further modification (fluorination, cyanization *etc.*) of the corannulene moiety, the incorporation of other donor units, as well as side chain engineering are currently ongoing and may lead to better arrangement in thin film, thus to achieving better device performance.

Experimental

Materials

All chemical reagents were purchased and used without further purification. Compound **1**⁴⁸ and compounds **2–4**⁴⁷ were synthesized as reported. 19-(3-iodopropyl)heptatriacontane was purchased from Lyn (Beijing) Science & Technology Co., Ltd. and through a standard Gabriel reaction as reported⁵⁷ to give 4-octadecyldocosan-1-amine.

Synthesis

Compound 2. Compound **1** (1.08 g, 3.88 mmol) in acetic anhydride (30 mL) with one drop of H_2SO_4 was stirred at room temperature for 1 h under nitrogen atmosphere. Then dimethyl acetylene dicarboxylate (579 mg, 4.07 mmol) was added by syringe. The mixture was heated to 145°C for 2 h. After cooling to room temperature, the mixture was poured to 200 mL of 10% aqueous NaOH. The mixture was extracted with dichloromethane (100 mL) for three times. The organic layer was then washed with water for three times and dried with anhydrous sodium sulfate. After being concentrated through rotary evaporation, the crude product was purified by silica gel chromatography (PE : DCM = 1 : 1) to give compound **2** (814 mg, 56%). ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 3.93 (s, 6H), 2.79 (s, 6H), 2.71 (s, 6H).

Compound 3. Compound **2** (2.8 g, 7.48 mmol), *N*-bromosuccinimide (16.0 g, 89.9 mmol) and AIBN (37.0 mg, 0.226 mmol) were dissolved in tetrachloromethane (100 mL) and the suspension was refluxed for 20 h while irradiating with a 150 W sunlight lamp. The reaction mixture was cooled and all volatiles were removed under reduced pressure. The solid was dissolved

in dichloromethane and washed with water for 5 times. After drying with anhydrous sodium sulfate, the solvent was removed under reduced pressure. The resulting solid was dried at vacuum oven to give compound **3** (6.5 g, quant.). ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, J = 8.5 Hz, 2H), 8.02 (d, J = 8.5 Hz, 2H), 7.52 (s, 2H), 4.99 (s, 4H), 4.03 (s, 6H).

Compound 4. Compound **3** (2.6 g, 3.07 mmol) and NaOH (1.25 g, 31.2 mmol) in dioxane (90 mL) and water (30 mL) was heated to reflux for 30 min. After cooling, the mixture was filtered and acidified with HCl. The precipitate was collected by filtering and washed with water for 3 times. The solid was dried at vacuum oven to give compound **4** (1.25 g, 83%). ^1H NMR (400 MHz, d_6 -DMSO) δ 8.29 (s, 2H), 8.16 (d, J = 8.9 Hz, 2H), 7.97 (d, J = 8.9 Hz, 2H).

Compound 5. Compound **4** (300 mg, 0.605 mmol) in acetic anhydride (10 mL) was heated to 145°C for 24 h under nitrogen atmosphere. The mixture was cooled to room temperature and filtered. The solid was washed with dichloromethane and dried under vacuum to provide compound **5** (290 mg, 100%). Compound **5** was used without further purification.

Compound 6. A solution of compound **5** (143.4 mg, 0.3 mmol), 4-octadecyldocosan-1-amine (181.5 mg, 0.33 mmol) and propionic acid (0.1 mL, 4.0 mmol) in NMP (20 mL) was heated to 130°C for 16 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous NaHCO_3 (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane ($2 \times 20 \text{ mL}$). The combined organic layers were dried, filtered, concentrated through rotary evaporation, and purified by silica gel chromatography (hexanes : dichloromethane = 10 : 1) to give **6** as a yellow solid (178 mg, 50%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.99 (s, 2H), 7.48 (AB, $\Delta\nu$ = 20 Hz, J = 8.8 Hz, 4H), 3.65 (t, J = 6.9 Hz, 2H), 1.74–1.66 (m, 2H), 1.25–1.35 (m, 71H), 0.88 (t, J = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.05, 135.58, 133.11, 132.51, 130.39, 130.31, 130.21, 129.05, 127.47, 127.14, 124.46, 124.03, 38.47, 37.18, 33.59, 31.93, 30.96, 30.15, 29.72, 29.66, 29.57, 26.72, 26.11, 22.69, 14.10. APCI-HRMS calcd. For $[\text{C}_{62}\text{H}_{87}\text{NOBr}_2 + \text{H}]^+$: 1038.5165; found: 1038.5164. Elemental anal. calcd. for $\text{C}_{62}\text{H}_{87}\text{NOBr}_2$: C, 71.73; H, 8.45; N, 1.35%; found: C, 71.68; H, 8.42; N, 1.36%.

PICBT. Compound **6** (51.91 mg, 0.050 mmol), 5,5'-bis-(trimethylstannyl)-2,2'-bithiophene (24.59 mg, 0.050 mmol), $\text{Pd}_2(\text{dba})_3$ (1.0 mg, 2 mol%), $\text{P}(o\text{-tol})_3$ (1.3 mg, 8 mol%), and toluene (15 mL) were added to a Schlenk tube. The tube was charged with nitrogen through a freeze–pump–thaw cycle for three times. The mixture was stirred for 4.5 h at 120°C . *N,N'*-Diethylphenylazothioformamide (10 mg) was added and then the mixture was stirred for 0.5 h to remove any residual catalyst before precipitation from CH_3OH (200 mL). The precipitate was filtered through a nylon filter and purified by Soxhlet extraction for 8 h with acetone, 12 h with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL) and filtered off to afford a dark red solid (51 mg, 98%). Elemental anal. calcd: for $(\text{C}_{70}\text{H}_{91}\text{NO}_2\text{S}_2)_n$: C, 80.64; H, 8.80; N, 1.34; found: C, 78.92; H, 8.68; N, 1.32.

Characterization

^1H and ^{13}C NMR spectra were recorded on 400 MHz or 500 MHz Bruker AVANCE III spectrometers. High-resolution mass spectra (HRMS) were recorded on a Bruker En Apex Ultra 7.0T FT-MS mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer under nitrogen atmosphere. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis spectrometer. Cyclic voltammetry (CV) was performed on BASI Epsilon workstation in anhydrous acetonitrile solution of Bu_4NPF_6 (0.1 M). A platinum wire was used as a counter electrode and glassy carbon electrode as a working electrode, all potentials were recorded *versus* Ag/AgCl (saturated) as a reference electrode. The scan rate was 50 mV s^{-1} . Photo-electron spectra (PES) were performed on AC-2 photoelectron spectrometer (Riken-Keiki Co.). Atomic force microscopy studies were recorded on a Agilent 5500 SPM. Density functional theory (DFT) were performed on B3LYP/6-311G(d) level. Gel permeation chromatography (GPC) was performed on Agilent Technologies PL-GPC 220 High Temperature Chromatograph. X-ray diffraction was performed on Rigaku Ultima IV.

OFET device fabrication and measurements

Top-gate/bottom-contact FET devices were fabricated using $\text{n}^{++}\text{-Si/SiO}_2$ (300 nm) substrates. The gold source and drain bottom electrodes were patterned by photolithography on the SiO_2 surface. Acetone, detergent, distilled water and isopropanol were respectively used to clean the substrates in an ultrasonic bath for 10 min. The cleaned substrates were dried under vacuum at 80°C , then modified with OTS as reported.⁵² Polymer solution (3 mg mL^{-1} in 1,2-dichlorobenzene, ODCB) was spin-coated on the substrates with or without OTS-treatment at 1500 rpm for 60 s, followed by thermal annealing at 200°C for 30 min. After polymer thin film deposition, a CYTOP solution (CTL809M : CT-solv180 = 3 : 1) was spin-coated onto the polymer layer at 2000 rpm for 60 s. The CYTOP layer was then baked at 100°C for 1 h to form a dielectric layer. A 70 nm Al layer was thermally deposited on the dielectric layer through a shadow mask under the pressure of $3.2 \times 10^{-4}\text{ Pa}$ to form gate electrodes. The OTFT devices had a channel length (L) and channel width (W) of $5\text{ }\mu\text{m}$ and of $100\text{ }\mu\text{m}$ respectively. All evaluations of the FETs (using Keithley 4200 SCS) were performed in ambient conditions.

Acknowledgements

This work was supported by the National Natural Science Foundation (nos 21102120 and J1210014), Ph.D. Programs Foundation of Ministry of Education (no. 20110121120016), the Fundamental Research Funds for the Central Universities (nos 2012121024 and 2011121014) of China, NFFTS (no. J1310024), and Program for Changjiang Scholars and Innovative Research Team in University.

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