Two-dimensional benzodithiophene and benzothiadiazole based solution-processed small molecular organic field-effect transistors & solar cells

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Benzodithiophene (BDT) and benzothiadiazole (BT) based small molecules have been synthesized through palladium-catalyzed Stille coupling reactions. The molecules with and without the conjugated thiophene side-chain were named as DRTBTTBDTT (2D) and DRTBTTBDT (1D), respectively. These molecules exhibited an optical band gap of around 1.8 eV. Solution-processed thin films of 1D and 2D showed that the conjugated thiophene side-chain oriented to produce a uniform 2D structure, which led to a relatively high hole mobility of $0.016 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and this was one of the highest values for solution-processed small-molecule donors in organic solar cells (OSCs). With proper engineering of energy levels, the organic solar cells based on DRTBTTBDTT (2D) as donors exhibited a high V_{oc} of around 0.9 V.

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1. Introduction

Solution-processed organic semiconductors have attracted significant attention for their potential applications in low-cost electronics such as organic solar cells (OSCs), organic field-effect transistors (OFETs), and mechanically flexible circuits.^{1–3} Currently, tremendous progress has been made on polymeric materials for the fabrication of OFETs with a mobility of over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and OSC devices with power conversion efficiencies (PCEs) up to 9%.^{4,5} More recently, bulk heterojunction (BHJ) OSCs using solution-processed small molecules as donors have attracted huge interest.^{6–8} The small molecule OSC donor materials have numerous advantages, such as relatively simple purification, well-defined structures, no end group contaminants, high charge carrier mobility and less batch-to-batch variation.^{6–9} To date, a PCE of 8%^{10,11} for solution-processed small molecule based OSCs and a mobility of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for OFET devices have been achieved, making

these materials ideal candidates for solution-processed organic electronics.

Regarding recent developments in OSCs, the search for new donor materials with appropriate physical properties such as low band gap, suitable energy levels, high crystallinity, decent solubility, *etc.* has taken centre stage.^{12–14} In this regard, a large number of donor molecules have been extensively investigated with varying degrees of success. Among them, the symmetrical acceptor–donor–acceptor (A–D–A) system represents the most ubiquitous molecular architecture, in which a wide variety of electron-withdrawing groups, such as squaraine,¹⁵ benzotriazole,¹⁶ alkyl cyanoacetate,¹⁷ diketopyrrolopyrrole¹⁸ and iso-indigo¹⁹ are combined with electron-donating oligothiophenes and arylamines. Through a judicious combination of donors and acceptors, the energy levels and band gaps of these chromophores can be easily modulated. There are many examples exhibiting remarkable success with this molecular design. Among the variety of electron deficient acceptors, benzothiadiazole (BT) based conjugated molecules^{20–23} are one of the most important organic semiconductors due to their ease of preparation, excellent stability and electro-optical characteristics.^{22,23} For example, PCEs of OSCs based on BT-containing D–A copolymers have reached 8%;²⁴ and hole mobilities of OFETs based on the BT-containing polymers have been up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²⁵ On the other hand, benzodithiophene (BDT) has a large and planar molecular structure by fusing a benzene with two flanking thiophene units. Some BDT-based small molecules and polymers show great potential in OSCs with enhanced mobility, high PCEs up to 8% and high open-circuit voltage (V_{oc}) attributable to efficient cofacial π – π stacking and a low-lying

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highest occupied molecular orbital (HOMO) level.^{10,26,27} Typically, the hole mobilities of solution-processed OSCs based on small molecules are around $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, including those record-high PCE BDT based molecules, which actually limit the hole transport in OSC devices.^{2,17} Although there are reports on the hole mobility of the BDT based molecule up to $2 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the large band gap (2.7 eV) of the molecules limits the applications in solar cells.²⁸

In this paper, we report the synthesis and characterization of two A-D-A type small molecules DRTBTTBDT and DRTBTTBDTT with benzodithiophene (BDT) and benzothiadiazole (BT) as the D and A segments, respectively (Scheme 1). The electronic properties of DRTBTTBDT (1D) and DRTBTTBDTT (2D) are investigated through typical OFET and BHJ OSC devices. The DRTBTTBDTT (2D) possesses one of the highest hole mobilities of donors for the solution-processed small-molecule organic solar cells.

2. Results and discussion

2.1. Materials and synthesis

All starting reagents were obtained commercially as analytical reagents and used directly without any purification. Tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) and bis(triphenylphosphine)palladium(II) chloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) were purchased from Acros Organics and used as received. *N,N*-Dimethylformamide (DMF) was purified by vacuum distillation. Toluene and tetrahydrofuran (THF) were dried over sodium with benzophenone as an indicator. All synthetic reactions were performed under argon. 4,7-Dibromo-benzo[1,2,5]thiadiazole (1),²⁹ 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (5)³⁰ and 2,6-bis(trimethyltin)-4,8-bis(5-(2-

ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (6)³¹ were synthesized according to the reported literature studies and characterized by ^1H NMR, ^{13}C NMR and MS. The synthesis routes for DRTBTTBDT (1D) and DRTBTTBDTT (2D) are summarized in Scheme 1.

2.2. Optical properties

The absorption spectra of small molecules in chloroform solution and thin solid film are represented in Fig. 1, and the data are summarized in Table 1. The absorption spectra of DRTBTTBDT and DRTBTTBDTT are found to be similar both in solution and film. DRTBTTBDT and DRTBTTBDTT in diluted chloroform solution show an absorption peak at 508 nm and 511 nm respectively. The molar extinction coefficients for solutions of DRTBTTBDT and DRTBTTBDTT are calculated according to the following equation

$$A = \epsilon bc$$

where ϵ is the molar extinction coefficient, A is the absorbance, b is the thickness of the liquid layer (1 cm) and c is the concentration of solution (here $10^{-5} \text{ mol L}^{-1}$). The calculated maximum molar extinction coefficients of diluted solutions are $123\,000 \text{ L M}^{-1} \text{ cm}^{-1}$ at 508 nm for DRTBTTBDT and $72\,500 \text{ L M}^{-1} \text{ cm}^{-1}$ at 511 nm for DRTBTTBDTT, respectively.

In the film form, the DRTBTTBDT film displays an absorption peak at 588 nm with a shoulder at 612 nm, and the DRTBTTBDTT film displays an absorption peak at 583 nm with a shoulder at 621 nm. The absorption peaks of small molecules in the film exhibit an obvious red-shift in comparison with those peaks in solution, and the aggregate absorption peak of the DRTBTTBDTT ($\lambda = 621$) is found to be higher than that of DRTBTTBDT ($\lambda = 612$), indicating an effective π - π packing in the DRTBTTBDTT molecular thin film. The optical band gaps of DRTBTTBDT and DRTBTTBDTT are estimated to be 1.80 eV and 1.81 eV, respectively. This indicates that the introduction of the conjugated side chain in the benzodithiophene (BDT) core unit does not obviously affect the band gap.

Scheme 1 Synthesis routes of DRTBTTBDT and DRTBTTBDTT.

Fig. 1 UV-vis absorption spectra of DRTBTTBDT and DRTBTTBDTT in chloroform solution and in thin film.

Table 1 Optical and electrochemical properties of DRTBTTBDT and DRTBTTBDTT molecules

Molecular	$\lambda_{\max}$ (nm), in chloroform	$\lambda_{\max}$ (nm), in film	λ_{onset} (nm)	E_g^{opt} (eV)	E_{ox}	HOMO	LUMO
DRTBTTBDT	508	588, 612	685	1.81	0.67	−5.09	−3.28
DRTBTTBDTT	511	583, 621	688	1.80	0.71	−5.13	−3.33

2.3. Electrochemical properties

Cyclic voltammograms of DRTBTTBDT and DRTBTTBDTT were measured on a CHI660D electrochemical workstation to determine the redox potentials of small molecules. A three-electrode cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode was used. The cyclic voltammetry curves are shown in Fig. 2. The redox potential of the Fc/Fc^+ internal reference is found to be 0.38 V vs. SCE. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the molecules is determined by the empirical equation, $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8 - E_{1/2}(\text{Fc}/\text{Fc}^+))$ and $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$, where E_{ox} is the onset of the oxidation potential and E_g is the optical band gap. The onset oxidation potentials of DRTBTTBDT and DRTBTTBDTT are 0.67 V and 0.71 V, thus the corresponding HOMO energy levels are −5.09 eV and −5.13 eV. The LUMO levels of DRTBTTBDT and DRTBTTBDTT are found to be −3.28 eV and −3.33 eV.

2.4. Field-effect transistor (FET) characteristics

Bottom-gate/top-contact OFETs based on DRTBTTBDT (1D) and DRTBTTBDTT (2D) have been fabricated using conventional techniques (see the Experimental section). The performance of devices with various annealing temperatures (RT, 80 °C, 100 °C and 150 °C) was measured under a nitrogen atmosphere in a glovebox and was summarized in Table 2. Both the carrier mobility and the on/off ratio increased with the annealing temperature.

Large mobility values of 0.004 and 0.016 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and threshold voltage (V_T) values of around −2 and −6 V respectively with an on/off ratio of 10^3 were obtained when the annealing

temperature was 100 °C. A further increase in the annealing temperature negatively influences the device performance. Fig. 3 shows a standard p-type transfer and output characteristics of devices with annealing at 100 °C for 30 minutes. It can be seen that the output curves of the devices exhibited standard linear and saturation regimes. The mobility was calculated at the saturation region of the transfer curves.

In order to understand the variation of OFET performance of 2D (DRTBTTBDTT) and 1D (DRTBTTBDT) due to annealing, XRD studies have been carried out. Fig. 4 shows the TM-AFM topographies of 20 nm-thick 2D (DRTBTTBDTT) and 1D (DRTBTTBDT) films on SiO_2 surfaces with various annealing temperatures. As the annealing temperature increases, significant changes in the morphology have been observed. From RT to 100 °C, the grain size enlarges obviously and achieves the highest value of around 0.35 and 0.42 nm respectively. However, when the temperature reaches to 150 °C, an incontinuous film morphology (Fig. 4D) is obtained which is harmful for the charge transport. Additionally, the root-mean-square (RMS) roughness versus annealing temperature is listed in Table 3. In comparison, 2D (DRTBTTBDTT) containing the conjugated thiophene side-chain is more inclined to grow smoothly with a uniform film morphology, leading to a relatively high mobility up to 0.016 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Moreover, the best annealing temperature is found to be 100 °C which is suitable for the fabrication of flexible OFETs devices based on plastic substrates.

From the XRD spectrum (Fig. 5), DRTBTTBDT and DRTBTTBDTT films display a sharp diffraction peak at $2\theta = 4.7^\circ$ and 3.7° respectively, indicating film crystallization. In fact, for 2D (DRTBTTBDTT), there is a diffraction peak at $2\theta = 7.4^\circ$, however, it is not prominent in Fig. 5 due to the strong diffraction peak at $2\theta = 3.7^\circ$. A higher peak intensity is achieved for samples with 100 °C annealing temperature due to enhanced molecular orientation influenced by the thermal annealing process. All the above results are consistent with electrical characteristics.

The carrier mobility is influenced by many parameters, especially crystallinity and orientation of the semiconductor film.^{32,33} From AFM images in Fig. 4, the grain sizes of two kinds of small molecular materials are found to be similar when the annealing temperature is 100 °C. However, the RMS shows obvious difference in Table 3. Compared with 1D (DRTBTTBDT), a smooth film of 2D (DRTBTTBDTT) displays less intergrain voids and better intergrain connection, which is good for the charge transport in the active layer resulting in higher carrier mobility. In terms of molecular orientation, due to relatively high device performance, molecules may have a face-to-face structure with pi-pi interaction in the horizontal direction. However, it is hard to obtain single crystals for these small molecules to further confirm the orientation.

Fig. 2 Cyclic voltammograms of DRTBTTBDT and DRTBTTBDTT molecules.

Table 2 OFET device performances of DRTBTBBDT and DRTBTBDDT annealing at (RT, 80, 100 and 150 °C)

T (°C)	DRTBTBBDT (1D)				DRTBTBDDT (2D)			
	RT	80	100	150	RT	80	100	150
μ_p (cm ² V ⁻¹ s ⁻¹)	4.3×10^{-4}	1.6×10^{-3}	4.3×10^{-3}	2.1×10^{-4}	1.2×10^{-3}	7.1×10^{-3}	1.6×10^{-2}	5.1×10^{-4}
$-V_{Th}$ (V)	12	7	2	10	5	10	6	12
On/off ratio	10–10 ²	10 ²	10 ³	10–10 ²	10 ²	10 ²	10 ³	10–10 ²

Fig. 3 I_D versus V_G transfer characteristics (A and B) and output characteristic I_{DS} versus V_{DS} at different V_{GS} (C and D) of the small molecule OFETs. **Fig. 4** AFM images of the molecule films annealed at different temperature DRTBTBBDT (up) and DRTBTBDDT (down).**Table 3** AFM image root-mean-square (RMS) of the molecule films annealed at different temperatures

Molecule	RMS at RT (nm)	RMS at 80 °C (nm)	RMS at 100 °C (nm)	RMS at 150 °C (nm)
DRTBTBBDT	4.52	3.10	1.62	0.62
DRTBTBDDT	0.74	0.33	0.43	0.56

2.5. Solar cell characteristics

Bulk heterojunction OSCs were prepared with a device structure of ITO/PEDOT:PSS/small molecule:PC₆₁BM/Ca/Al, and tested under a simulated AM 1.5 G illumination of 100 mW cm⁻². The blends of DRTBTBBDT and PC₆₁BM at different weight ratios of 1 : 1, 2 : 1, 3 : 1 and 4 : 1 were used to optimize the device performance. Current density *versus* voltage

Fig. 5 XRD patterns of DRTBTBBDT (a) and DRTBTBDDT (b) based pristine films and 100 °C annealed films.

(J - V) curves are shown in Fig. 6 and the detailed device parameters are summarized in Table 4. Finally, the PCE of 1.01% for the DRTBTBBDT was obtained with an open-circuit voltage (V_{oc}) of 0.70 V, a short circuit current density (J_{sc}) of 4.15 mA cm⁻², and a fill factor (FF) of 35%, when the device was fabricated at a donor-acceptor weight ratio of 3 : 1 in chloroform at a concentration of 10 mg ml⁻¹ and spun cast at 1000 rpm.

The blends of DRTBTBDDT (2D) and PC₆₁BM at different weight ratios of 1 : 2, 1 : 1, 2 : 1, 3 : 1 and 4 : 1 have also been used to investigate their respective device performance. 2D-conjugated small molecule DRTBTBDDT based devices show relatively high photovoltaic performances than 1D molecule devices under the same conditions (donor : PCBM = 1 : 1). The reason is that the 2D-conjugated small molecules show relatively high V_{oc} (Table 4) and high hole mobility (Table 3).

Fig. 6 J - V curves of the OSCs based on DRTBTBBDT:PC₆₁BM and DRTBTBBDTT:PC₆₁BM under the illumination of AM 1.5G, 100 mW cm⁻².

Table 4 Device performance of the small molecules

Molecular	DA Ratio	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
DRTBTBBDT:PCBM	1 : 1	0.76	1.19	31	0.29
DRTBTBBDT:PCBM	2 : 1	0.70	3.07	34	0.73
DRTBTBBDT:PCBM	3 : 1	0.70	4.15	35	1.01
DRTBTBBDT:PCBM	4 : 1	0.69	3.58	34	0.84
DRTBTBBDTT:PCBM	1 : 2	0.89	2.07	29	0.54
DRTBTBBDTT:PCBM	1 : 1	0.88	1.63	29	0.43

The high V_{oc} can be explained in accordance with the band structure of OPVs based on the two organic materials (DRTBTBBDT and DRTBTBBDTT) and PC₆₁BM (Fig. 7),^{34,35} the offset between the HOMO of the small molecule and LUMO of PC₆₁BM is around 1.2 eV which leads to a relatively high V_{oc} . 2D small molecule based devices with a high D : A ratio, such as 2 : 1, 3 : 1 or 4 : 1, are not shown in the manuscript due to their inferior film quality and the respective devices show no performance.

3. Conclusions

In summary, two novel small molecules, DRTBTBBDT and DRTBTBBDTT with the A-D-A structure and BDT as the central building block have been designed and synthesized. The

2D-conjugated compound DRTBTBBDTT exhibits a relatively smooth and uniform thin film and a high hole FET mobility of 0.016 cm² V⁻¹ s⁻¹ which is among the highest of solution-processed small molecule donors for OSCs. 2D-conjugated small molecule DRTBTBBDTT based devices show relatively higher OSC device performances than those of 1-D molecule devices under the same conditions, due to high V_{oc} and high hole mobility.

4. Experimental

4.1. Measurement

NMR spectra were recorded on a Bruker Avance III 600 spectrometer operating at 600 MHz and were referred to tetramethylsilane. UV-visible absorption spectra were measured on a Hitachi U-4100 spectrophotometer. Cyclic voltammograms were measured on a CHI660D electrochemical workstation at a scan rate of 100 mV s⁻¹ with a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆). X-ray diffraction (XRD) patterns of semiconductor films deposited on SiO₂ with 100 °C annealing were measured by using a Rigaku Smartlab, collecting the diffraction data in a 2 θ range of 3–20° with a step-size of 0.02° (2 θ). The thin film surface morphologies of DRTBTBBDT and DRTBTBBDTT were measured in air using an Atomic Force Microscope (AFM, VEECO Multimode V) working in the tapping mode. Current-voltage (I - V) characteristics of solar cells were measured under the illumination of an AM 1.5 G solar simulator with 100 mW cm⁻² power. A Keithley 6212 source meter, an Agilent 4155C semiconductor parameter analyzer and a HP 4284A LCR meter were utilized to record I - V curves of field-effect transistors in a MBraun nitrogen glovebox under dark conditions.

4.2. Fabrication of field-effect transistor (FET) devices

Bottom-gate/top-contact transistors were fabricated on heavily n-doped silicon substrates (served as the gate electrode) with 300 nm thermal oxide (SiO₂) layers. After standard cleaning (a 15 minute ultrasonic process in acetone, isopropanol and DI-water, sequentially), 5 mg ml⁻¹ small molecules dissolved in chlorobenzene were spin-coated on SiO₂ substrates at a speed of 1200 rpm for 1 min. Then, the substrates were annealed on a hot plate at room temperature (RT), 80, 100 or 150 °C for 30 minutes. Then, a 100 nm-thick gold film was vacuum sublimed as a source/drain electrode on a semiconductor surface through a shadow mask (channel length/width = 30 μ m/1000 μ m) at a rate of 0.2 Å s⁻¹.

4.3. Fabrication of solar cell devices

OSCs were fabricated on pre-patterned indium-tin oxide (ITO) glass with a sheet resistance of 15 Ω sq⁻¹. The ITO glass was ultrasonically cleaned with acetone, toluene, methanol, and isopropyl alcohol subsequently. Oxygen plasma treatment was carried out for 10 min as the final step of substrate cleaning to improve the contact angle just before film coating. Then, a layer of a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film with a thickness of 40 nm was spin-coated on

Fig. 7 Energy level diagram for the OPV device structure using a PCBM acceptor and DRTBTBBDT and DRTBTBBDTT donors.

ITO glass and was dried at 160 °C for 30 min in an oven. The solution of the small molecule with fullerene in chloroform was prepared in a nitrogen-filled glovebox and spin-coated on the top of the ITO/PEDOT:PSS. The typical thickness of the active layer was 100 nm. The typical concentration of the small molecular/PC₆₁BM blending solution used in this study for spin-coating the active layer was 10 mg ml⁻¹. Ca (10 nm) and Al (100 nm) were thermally evaporated in a vacuum of 2×10^{-4} Pa on the top of the active layer as the cathode.

4.4. Synthesis

4-Bromo-7-(5-octyl-thiophen-2-yl)-benzo[1,2,5]thiadiazole (2). 4,7-Dibromo-benzo[1,2,5]thiadiazole (2.94 g, 10 mmol), tributyl-(5-octyl-thiophen-2-yl)-stannane (4.85 g, 10 mmol) and Pd(PPh₃)₂Cl₂ (0.35 g, 0.5 mmol) were dissolved in 60 ml anhydrous degassed toluene. The reaction mixture was heated up to 120 °C and stirred at this temperature overnight under argon. Then the cooled mixture was poured into water and extracted with diethyl ether. The combined organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude residue purified by column chromatography over silica gel with petroleum ether–dichloromethane as the eluent afforded compound 2 as a light red solid (1.43 g, 35% yield).

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.92 (d, 1H), 7.81 (d, 1H), 7.63 (d, 1H), 6.87 (d, 1H), 2.87 (t, 2H), 1.74 (m, 2H), 1.41 (m, 2H), 1.36–1.25 (m, 8H), 0.88 (t, 3H).

¹³C NMR (150 MHz, CDCl₃, δ ppm): 153.80, 151.81, 148.57, 135.84, 132.30, 128.16, 127.47, 125.38, 125.08, 111.53, 31.87, 31.60, 30.30, 29.34, 29.23, 29.15, 22.67, 14.11.

4-(5-Octyl-thiophen-2-yl)-7-(4-octyl-thiophen-2-yl)-benzo[1,2,5]thiadiazole (3). 4-Bromo-7-(5-octyl-thiophen-2-yl)-benzo[1,2,5]thiadiazole (2) (1.43 g, 3.7 mmol), tributyl-(4-octyl-thiophen-2-yl)-stannane (2.2 g, 4.5 mmol) and Pd(PPh₃)₂Cl₂ (0.14 g, 0.2 mmol) were dissolved in 50 ml anhydrous degassed toluene. The reaction mixture was heated up to 120 °C and stirred overnight under argon. Then the cooled mixture was poured into water and extracted with diethyl ether. The combined organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude residue purified by column chromatography over silica gel with petroleum ether and dichloromethane as the eluent afforded compound 3 as a red solid (1.55 g, 80% yield).

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.95 (d, 1H), 7.92 (d, 1H), 7.78 (d, 1H), 7.75 (d, 1H), 7.02 (s, 1H), 6.86 (d, 1H), 2.88 (t, 2H), 2.69 (t, 2H), 1.75 (m, 2H), 1.70 (m, 2H), 1.44–1.26 (m, 20H), 0.89 (t, 6H).

¹³C NMR (150 MHz, CDCl₃, δ ppm): 152.61, 152.58, 147.89, 144.31, 139.07, 136.76, 128.85, 127.46, 126.11, 125.57, 125.21, 124.99, 121.35, 31.91, 31.88, 31.65, 30.67, 30.51, 30.31, 29.48, 29.41, 29.36, 29.30, 29.25, 29.19, 22.69, 22.68, 14.13, 14.12.

4-(5-Bromo-4-octyl-thiophen-2-yl)-7-(5-octyl-thiophen-2-yl)-benzo[1,2,5]thiadiazole (4). 4-(5-Octyl-thiophen-2-yl)-7-(4-octyl-thiophen-2-yl)-benzo[1,2,5]thiadiazole (3) (1.55 g, 2.98 mmol) was dissolved in 60 ml THF at room temperature, and NBS (530 mg, 2.98 mmol) was added slowly. After stirring under light protection overnight, the reaction mixture was poured into ice

water and extracted with chloroform. The organic layer was washed with water and brine and dried with anhydrous Na₂SO₄, then filtered. The solvent was evaporated under reduced pressure. The dark solid was purified by column chromatography with CH₂Cl₂ and petroleum ether as eluent to afford a dark red solid (1.62 g, 90% yield).

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.93 (d, 1H), 7.74 (m, 3H), 6.87 (d, 1H), 2.88 (t, 2H), 2.63 (t, 2H), 1.75 (m, 2H), 1.67 (m, 2H), 1.44–1.28 (m, 20H), 0.88 (m, 6H).

¹³C NMR (150 MHz, CDCl₃, δ ppm): 152.50, 152.36, 148.20, 142.97, 138.73, 136.62, 127.75, 127.69, 126.48, 125.30, 125.08, 124.89, 124.58, 111.18, 31.90, 31.88, 31.64, 30.33, 29.79, 29.69, 29.42, 29.36, 29.31, 29.28, 29.24, 29.18, 22.69, 22.68, 14.13, 14.12.

DRTBTBDT. In a flame-dried two-block flask, compound (4) (0.61 g, 1 mmol), 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b'*]dithiophene (5) (0.3 g, 0.4 mmol) and Pd(PPh₃)₄ (46 mg, 0.04 mmol) were added to 20 ml toluene in an argon atmosphere. The solution was stirred at 120 °C overnight. After cooling to room temperature, the reaction mixture was poured into ice water and extracted with chloroform. The organic layer was dried with anhydrous Na₂SO₄ and filtered. The solvent was evaporated under reduced pressure. The dark solid was purified by column chromatography with CH₂Cl₂:petroleum ether as eluent to afford a dark solid. Then the product was recrystallized with methanol for several times (358 mg, 60% yield).

¹H NMR (600 MHz, CDCl₃, δ ppm): 8.01 (s, 2H), 7.94 (d, 2H), 7.82 (d, 2H), 7.76 (d, 2H), 7.53 (s, 2H), 6.86 (d, 2H), 4.23 (m, 4H), 2.96 (t, 4H), 2.87 (t, 4H), 1.88–1.72 (m, 10H), 1.70–1.24 (m, 56H), 1.07 (t, 6H), 0.98 (m, 6H), 0.88 (m, 12H).

¹³C NMR (150 MHz, CDCl₃, δ ppm): 152.59, 152.54, 148.14, 143.99, 141.82, 138.17, 136.73, 135.76, 132.22, 132.01, 130.77, 129.73, 127.64, 126.41, 125.53, 125.28, 124.93, 124.77, 118.31, 76.04, 40.72, 31.94, 31.89, 31.64, 30.79, 30.54, 30.34, 29.90, 29.81, 29.59, 29.41, 29.37, 29.31, 29.26, 29.20, 23.92, 23.21, 22.71, 22.69, 14.27, 14.13, 11.41.

APCI-MS *m/z*: calculated for C₈₆H₁₁₄N₄S₈O₂ [M]⁺, 1492.3829; found, 1492.6812.

Anal. calcd for C₈₆H₁₁₄N₄S₈O₂: C, 69.21; H, 7.70; N, 3.75; S, 17.19. Found: C, 68.93; H, 7.64; N, 3.74; S, 17.09.

DRTBTBDT. In a flame-dried two-block flask, compound (4) (0.61 g, 1 mmol), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (6) (0.36 g, 0.4 mmol) and Pd(PPh₃)₄ (46 mg, 0.04 mmol) were added to 20 ml toluene in an argon atmosphere. The other procedures are just the same as the DRTBTBDT molecule (357 mg, 55% yield).

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.95 (s, 2H), 7.91 (d, 2H), 7.76 (d, 2H), 7.71 (m, 4H), 7.37 (d, 2H), 6.94 (d, 2H), 6.84 (d, 2H), 2.91–2.84 (m, 12H), 1.76–1.71 (m, 10H), 1.51–1.25 (m, 56H), 0.98 (t, 6H), 0.93 (t, 6H), 0.88 (m, 12H).

¹³C NMR (150 MHz, CDCl₃, δ ppm): 152.56, 152.48, 148.07, 145.77, 141.80, 138.91, 138.19, 137.08, 137.06, 136.93, 136.72, 132.36, 130.72, 127.83, 127.58, 126.31, 125.44, 125.42, 125.24, 124.90, 124.74, 123.22, 121.40, 41.50, 34.34, 32.57, 31.97, 31.88, 31.62, 30.62, 30.32, 29.88, 29.74, 29.54, 29.42, 29.37, 29.26, 29.20, 28.97, 25.73, 23.09, 22.74, 22.68, 14.22, 14.15, 14.12, 10.95.

APCI-MS m/z : calculated for $C_{94}H_{118}N_4S_{10} [M]^+$, 1624.6340; found, 1624.6666.

Anal. calcd for $C_{94}H_{118}N_4S_{10}$: C, 69.49; H, 7.32; N, 3.45; S, 17.74. Found: C, 69.29; H, 7.38; N, 3.42; S, 17.39.

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