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Isomers of organic semiconductors based on dithienothiophenes: the effect of sulphur atoms positions on the intermolecular interactions and field-effect performances†

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Index **Page Number**

1. Experimental Section

General procedures and materials Ether(Et_2O) and tetrahydrofuran (THF) for use were freshly distilled from sodium/benzophenone prior to use. Bis(phenylsulfonyl) sulfide was obtained according to the literature method.[1] Concentration of *n*-BuLi (in hexane) was determined by titration with N-oivaloyl-o-toluidine.[2] Column chromatography was carried out on silica gel (300-400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8-mm PTFE vacuum stop-cock, were employed. All starting materials and reagents were commercially available.

NMR spectra were obtained using chloroform-*d*($CDCl_3$),or dimethyl sulfoxide- d_6 (DMSO- d_6) as solvent. The chemical shift references were as follows: (^1H) $CDCl_3$, 7.26 ppm ($CHCl_3$); (^{13}C) $CDCl_3$, 77.00 ppm ($CDCl_3$); (^1H) DMSO-d_6, 2.50 ppm (DMSO); (^{13}C) DMSO-d_6, 39.97 ppm (DMSO-d_6). IR spectra were obtained using an FT-IR instrument, equipped with an ATR sampling accessory. MS analysis was carried out at 70 eV, using a direct insertion technique or a GC insertion. HRMS spectra were recorded on a mass spectrometer equipped with TOF (EI+) or FTMS (ESI). Melting points were obtained on a XT4A (Beijing Sci. & Ins.).

UV-vis spectra were obtained with a double-beam spectrophotometer at room temperature. The AFM topographical images of BP2T films were performed with SPI3800N (Seiko Instruments Inc.) in tapping mode by the probe of 3 N/m using 3 Hz scan rate at environment.

The X-ray crystallographic analyses were performed using crystal of compound **DEP-*bt*-DTT** : the Crystal size 0.23 × 0.18 × 0.15 mm, cell dimensions: $a = 7.4707(12)$ Å; $b = 5.9227(10)$ Å; $c = 42.784(7)$ Å; $\alpha = 90.00\ ^o$; $\beta = 92.760(3)\ ^o$; $\gamma = 90.00\ ^o$; $V = 1890.9(5)$ Å^3; $\rho = 1.407$ mg/cm^3. The X-ray crystal structure analyses were made on a Bruker SMART CCD diffractor, using graphite- monochromated MoKα radiation (λ) 0.7107 Å. The data were collected at 293 K and the structures were refined by full-matrix least-square on F^2. The computations were performed with SHELEX-97 program and refined using full matrix least squares.[3] The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Further details are in the deposited CIFs. The single crystal of **DEP-*bt*-DTT** was obtained by accurately controlling the sublimation temperature.

Synthesis of Dithieno[3,2-*b*:2′,3′-*d*]thiophene(2)

To a solution of **1** (4.6173 g, 14.25 mmol) in anhydrous Et_2O (180 mL), *n*-BuLi (2.56 M, 11.69 mL, 29.92 mmol, 2.1 equiv) was added dropwise at −78 °C. After keeping at −78 °C for 2 h, anhydrous $(PhSO_2)_2S$ (4.70 g, 14.96 mmol, 1.05 equiv) was added, then the reaction mixture was warmed slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O (10 mL), extracted with CH_2Cl_2 (4 ×10 mL), and then washed with H_2O (2 × 150 mL). After drying over $MgSO_4$, the solvent was removed in vacuum. The residue was purified by column chromatography on silica gel with PE (60−90 °C) as eluent to yield **2** (1.7900 g, 63.9%) as a white solid. Mp: 66-67 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 5.2, 2H), 7.29 (d, J = 5.2, 2H). ^1H NMR and melting point is consistent with the previous report.

Synthesis of Dithieno[3,2-*b*:2',3'-*d*]thiophene-2,5-dicarboxaldehyde (3)

n-BuLi (2.57 M, 2.04 mL, 5.24 mmol, 2.5 eq) was added dropwise to diisopropylamine (0.82 mL, 5.76 mmol, 2.75 eq) in anhydrous tetrahydrofuran(15 mL) at 0 °C under argonatmosphere. After keeping at 0 °C for 0.5 h, the prepared LDA solution was transferred by syringe into a solution of **2** (0.4117 g，2.10 mmol) in anhydrous THF (60 mL) at -78 °C. After stirred for 2 h at 0 °C, anhydrous DMF (0.65 mL，8.39 mmol，4.0 eq) was added , then the reaction mixture was warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O(10 mL), extracted with CH_2Cl_2 (4×5 mL), washed with saturated NaCl (40 mL) and water (100 mL) and then the solvent was removed under vacuum. The residue was washed by diethyl ether (3×4 mL) and CH_2Cl_2 (5 mL) to yield **3** (0.4651 g, 87.9%)as a yellow solid. Mp > 300 °C; ^1H NMR (300 MHz, DMSO-d_6) δ10.05 (s, 2H), 8.54 (s, 2H).

Synthsis of 2,5-Distyryl-dithieno[3,2-*b*:2',3'-*d*]thiophene (DEP-*tt*-DTT):

Dithieno[3,2-*b*:2',3'-*d*]thiophene-2,5-dicarboxaldehyde (0.3682 g, 1.46 mmol) and benzyl-triphenyl-phosphonium chloride (1.6047 g, 3.65 mmol) were dissolved in 30 mL of anhydrous methanol under argon. With stirring, a solution of potassium tert-butoxide (0.8199 g, 7.31 mmol) in dry methanol (15 mL) was added dropwise in an ice-water bath. Then the solution was kepted at ambient temperature for 0.5 h and heated to reflux for 48 h. After cooling to ambient temperature, the brown yellow product was isolated by centrifugation and washed with alcohol. The crude prpduct was sublimated twice to give bright yellow crystals (186 mg, 31%). Mp > 300 °C ; HRMS (MALDI): m/z: calcd for $C_{24}H_{16}S_3$, 400.04141; found, 400.04086.

Synthesis of Dithieno[2,3-*b*:2′,3′-*d*]thiophene(5)

To a solution of **4** (3.12 g, 12.7 mmol) in anhydrous Et_2O (130 mL), *n*-BuLi (2.49 M, 25.7 mmol, 10.3 mL, 2.02 equiv) was added dropwise at −78 °C. After keeping at −78 °C for 2 h, anhydrous $(PhSO_2)_2S$ (4.19 g, 13.3 mmol, 1.05 equiv) was added, then the reaction mixture was warmed slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O (10 mL), extracted with CH_2Cl_2 (3 ×10 mL), and then washed with H_2O (2 × 100 mL). After drying over $MgSO_4$, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with PE (60−90 °C) as eluent to yield **5** (1.3065 g, 52.3%) as a white solid. From two other reactions on a 3.07 and 3.47 g scale of **4**, 1.3470 g (54.8%) and 1.4781 g (53.2%) of **5** were obtained, respectively. Mp: 52−53 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 5.2, 1H), 7.36 (d, *J* = 5.2, 1H), 7.32 (d, *J* = 5.2, 1H), 7.27 (d, *J* = 5.2, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.2, 137.7, 130.9, 128.2, 125.5, 120.4, 118.6. MS (EI, 70 eV): m/z =195.91(100)[M^+].

Synthesis of Dithieno[2,3-*b*:2',3'-*d*]thiophene-2,5-dicarboxaldehyde (6)

n-BuLi(2.49 M, 3.21 mL, 8.02 mmol, 2.5 eq) was added dropwise to diisopropylamine (1.24 mL, 8.81 mmol, 2.75 eq) in anhydrous tetrahydrofuran(15 mL) at 0 °C under argonatmosphere. After keeping at 0 °C for 0.5 h, the prepared LDA solution was transferred by syringe into a solution of **5** (0.6290 g，3.20 mmol) in anhydrous THF (80 mL) at -78 °C. After stirred for 2 h at 0℃, anhydrous DMF (0.99 mL，12.82 mmol，4.0 eq) was added , then the reaction mixture was warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O(10 mL), extracted with CH_2Cl_2 (4×5 mL), washed with saturated NaCl (40 mL) and water (100 mL) and then the solvent was removed under vacuum. The residue was washed by diethyl ether (3×4 mL) and CH_2Cl_2 (3 mL) to yield **6** (0.6989 g, 86.4%)as a yellow solid. Mp>300 °C. ^{1}H NMR (300 MHz,$CDCl_3$) δ10.00 (s, 1H), 9.97 (s, 1H), 8.07 (s, 1H), 7.98 (s, 1H). ^{13}C NMR(100MHz, DMSO-d_6) δ185.5, 185.1, 153.5, 147.2, 144.5, 143.5, 137.2, 137.1, 132.7, 130.3. MS (EI, 70 eV): m/z =251.89(100)[M$^+$]. HRMS (TOF MS EI+) m/z calcd for [$C_{10}H_4O_2S_3$] 251.9373, found 252.9454 (M+1). IR (KBr): 2957, 2896 (C-H) cm^{-1}, 1609 (C=O) cm^{-1}.

Synthsis of 2,5-Distyryl-dithieno[2,3-b:2',3'-d]thiophene (DEP-*bt*-DTT):

Dithieno[2,3-*b*:2',3'-*d*]thiophene-2,5-dicarboxaldehyde (0.4200 g, 1.66 mmol) and benzyl-triphenyl-phosphonium chloride (1.6083 g, 3.66 mmol) were dissolved in 20 mL of anhydrous methanol under argon. With stirring, a solution of potassium tert-butoxide (0.560 g, 4.99 mmol) in dry methanol (12 mL) was added dropwise in an ice-water bath. Then the solution was kepted at ambient temperature for 0.5 h and heated to reflux for 48 h. After cooling to ambient temperature, the brown yellow product was isolated by centrifugation and washed with alcohol. The crude prpduct was sublimated twice to give bright yellow crystals (238 mg, 35%). Mp > 300 °C ; MS (EI, 70 eV): m/z =400.02(100)[M$^+$]. HRMS (MALDI): m/z: calcd for $C_{24}H_{16}S_3$, 400.04152; found, 400.04086. IR(KBr): ν = 3078.80, 3055.05 (C-H) cm^{-1}, 1595.50 (C=C) cm^{-1}, 947.17 (=C-H) cm^{-1}.

2. NMR , MS and HRMS spectra

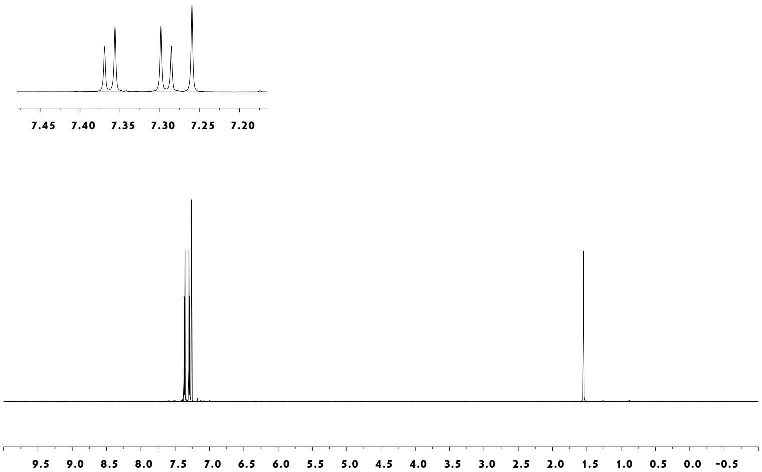


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**

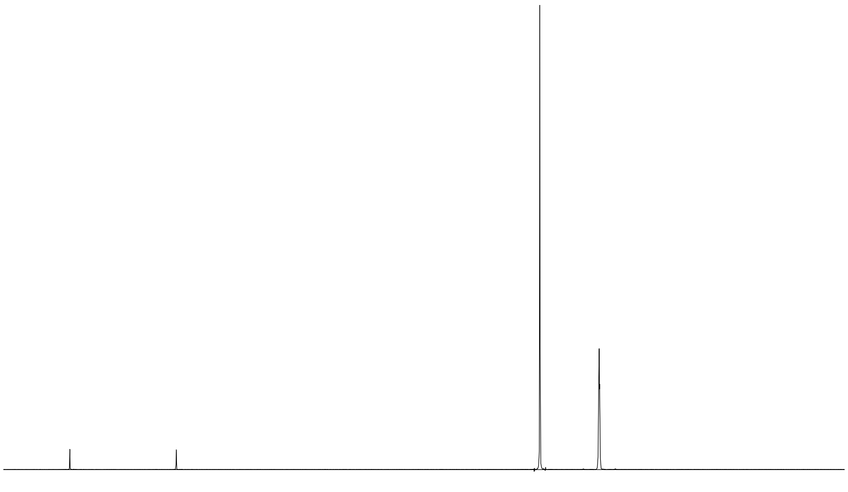
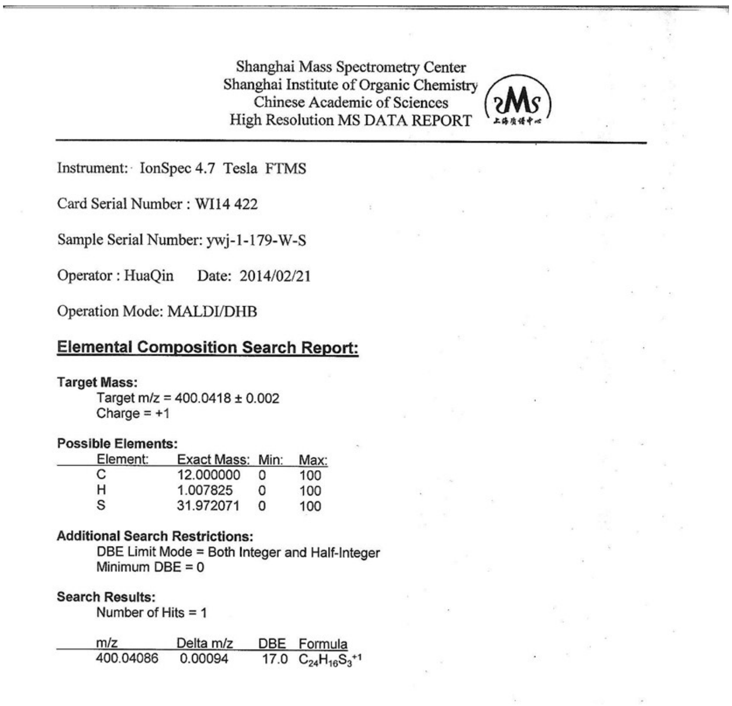


Figure S2. ^{1}H NMR (300 MHz, DMSO-*d*6) spectrum of **3**



Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI14 422

Sample Serial Number: ywj-1-179-W-S

Operator : HuaQin Date: 2014/02/21

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 400.0418 ± 0.002
Charge = +1

Possible Elements:

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H	1.007825	0	100
S	31.972071	0	100

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 1

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Figure S3. HRMS spectrum of **DEP-*tt*-DTT**

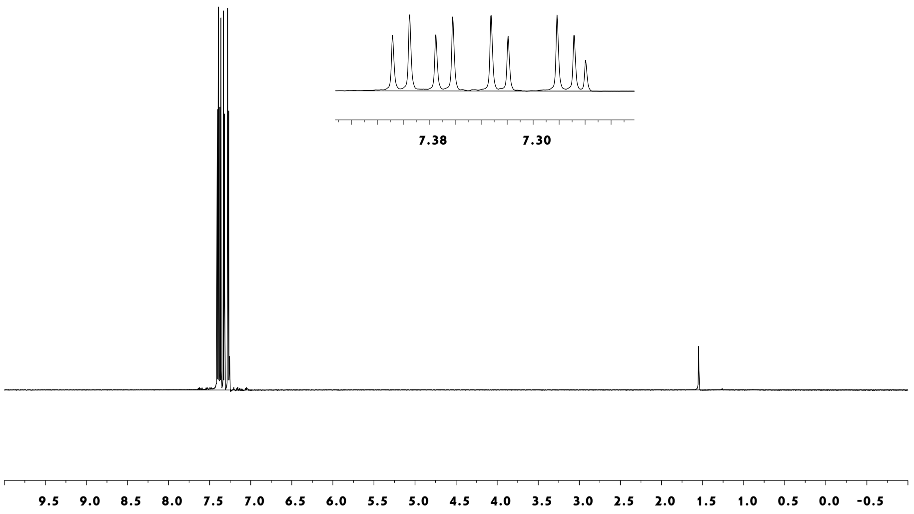


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**

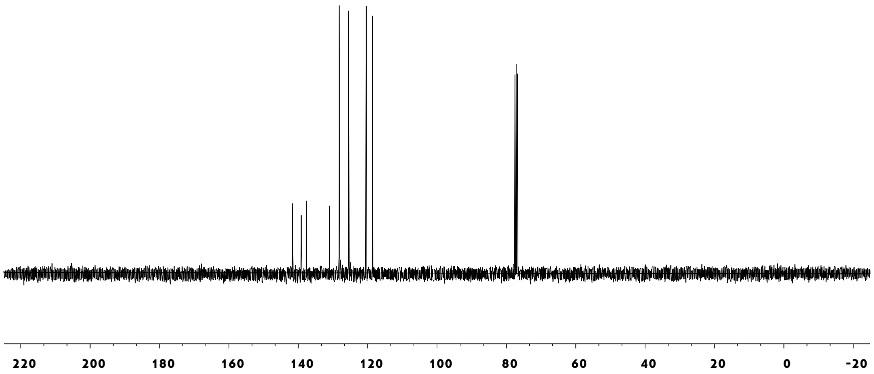


Figure S5. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **5**

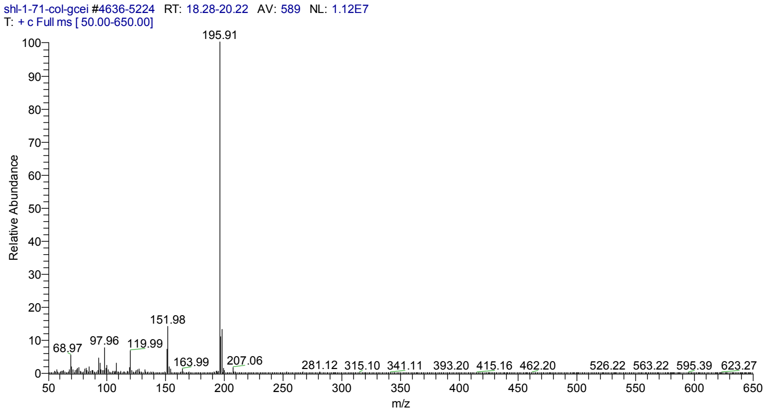


Figure S6. MS spectrum of **5**

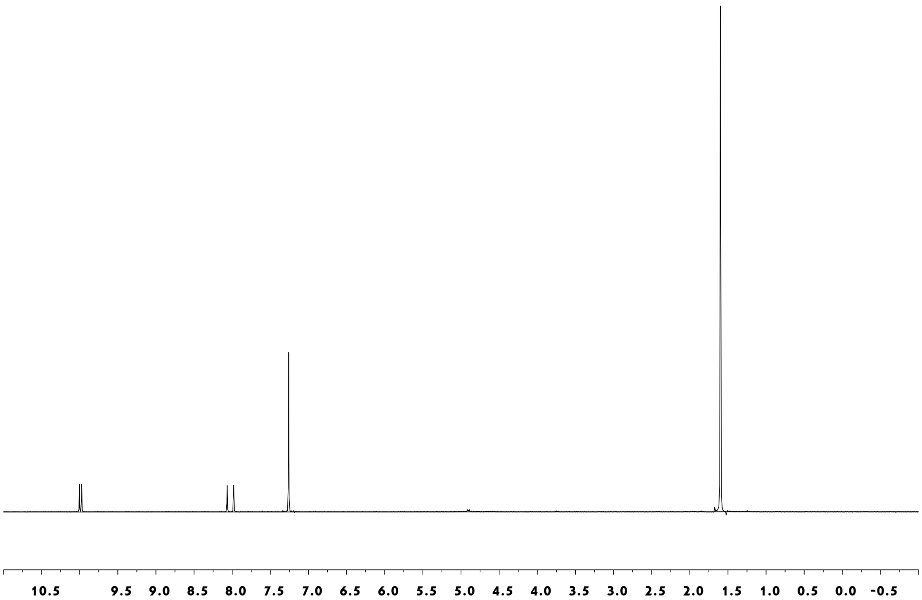


Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **6**

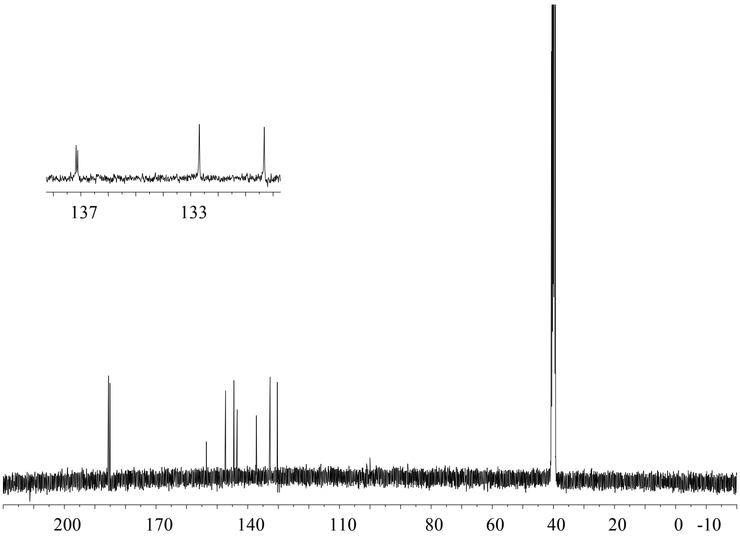


Figure S8. ^{13}C NMR (100 MHz, DMSO-*d*6) spectrum of **6**

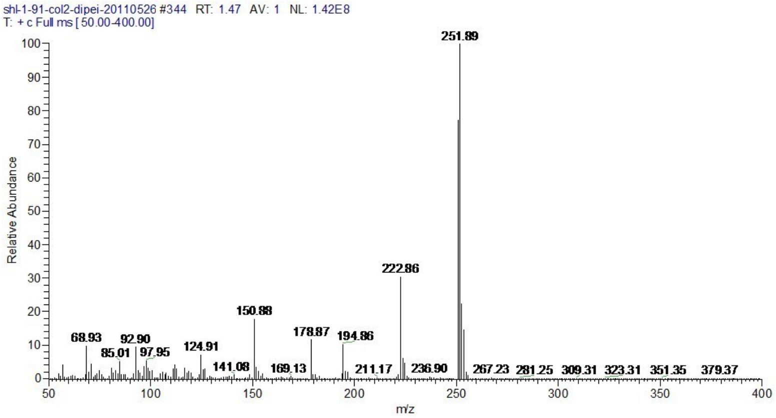


Figure S9. MS spectrum of **6**

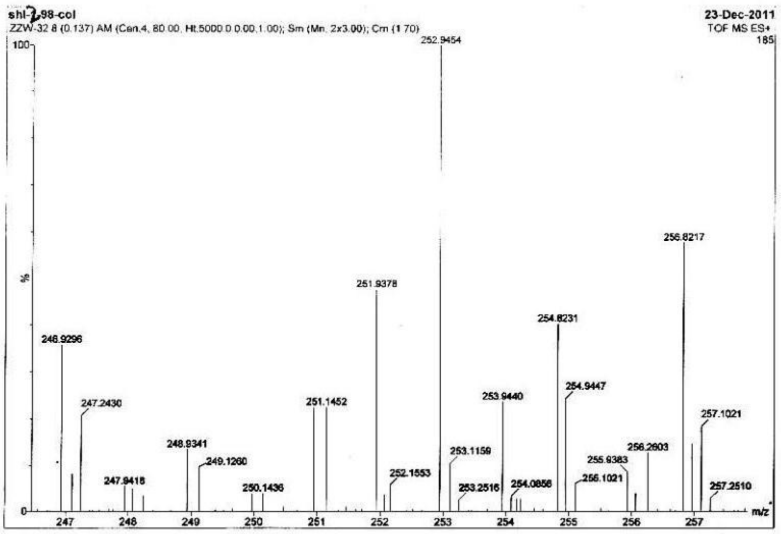


Figure S10. HRMS spectrum of **6**

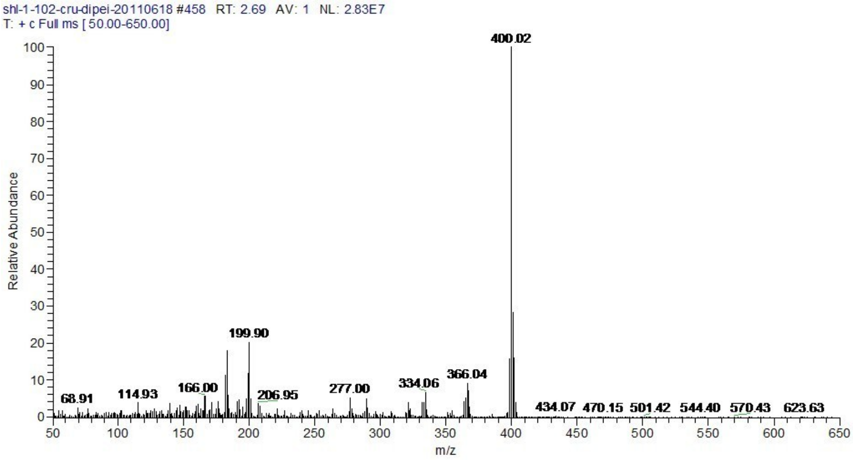
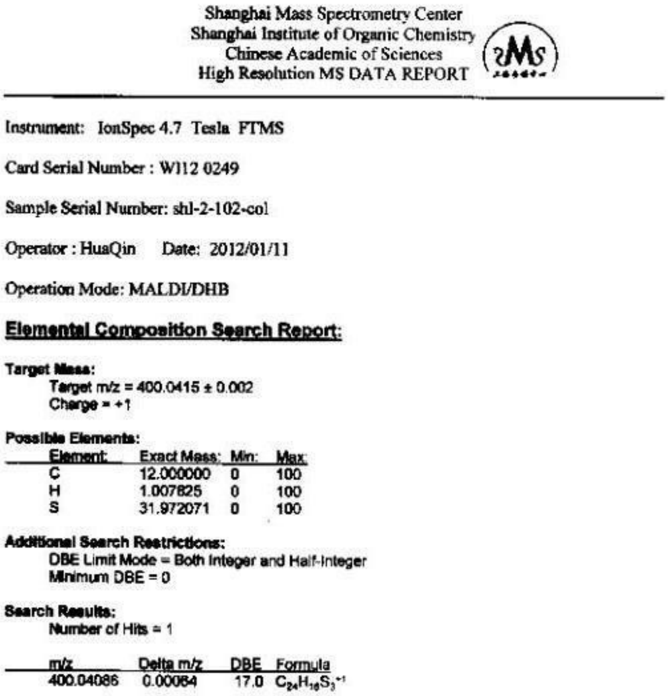


Figure S11. MS spectrum of **DEP-*bt*-DTT**



Shanghai Mass Spectrometry Center
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: IonSpec 4.7 Tesla FTMS

Card Serial Number : WI12 0249

Sample Serial Number: shl-2-102-col

Operator : HuaQin Date: 2012/01/11

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:
Target m/z = 400.0415 ± 0.002
Charge = +1

Possible Elements:

Element	Exact Mass:	Min:	Max:
C	12.000000	0	100
H	1.007825	0	100
S	31.972071	0	100

Additional Search Restrictions:
DBE Limit Mode = Both Integer and Half-Integer
Minimum DBE = 0

Search Results:
Number of Hits = 1

m/z	Delta m/z	DBE	Formula
400.04086	0.00064	17.0	$C_{24}H_{16}S_3^{+1}$

Figure S12. HRMS spectrum of **DEP-*bt*-DTT**

Device Fabrication:

OFETs were fabricated in top contact geometry configuration. A heavily doped, n-channel Si wafer, with a 500 nm thermal oxidation SiO_2 layer as the gate insulator, was used as the gate electrode and substrate. Firstly, the compounds were deposited at different substrate temperature (RT, 60 °C and 70 °C for **DEP-*tt*-DTT**; RT, 60 °C and 70 °C for **DEP-*bt*-DTT**; RT, 70 °C and 100 °C for **DEP-*bb*-DTT**) with the thickness of 15 nm, respectively. Then, with a shadow mask, the source and drain electrodes with thickness of 50 nm were preceded by thermal evaporating Au. The length and width of channel were 200 μm and 6000 μm, respectively. For electrical characterizations, the devices were transferred to a shield box. The transistors output and transfer characteristics were measured with Keithley 4200 under ambient conditions at room temperature. Carrier mobilities (μ) were calculated in the saturation region by the relationship:

$$\mu = (2I_DL)/[WC_i(V_G\text{-}V_T)^2] \qquad (1)$$

where I_D is the source–drain saturation current, C_i is the oxide capacitance (7.5 nF cm^{-2}), V_G is the gate voltage, and V_T is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of V_G *vs* $(I_D)^{1/2}$.

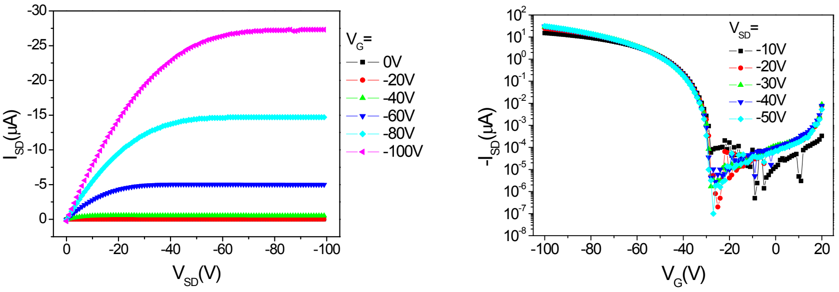


Figure S13. Output and transfer curves of DEP-*tt*-DTT with T_s at RT.

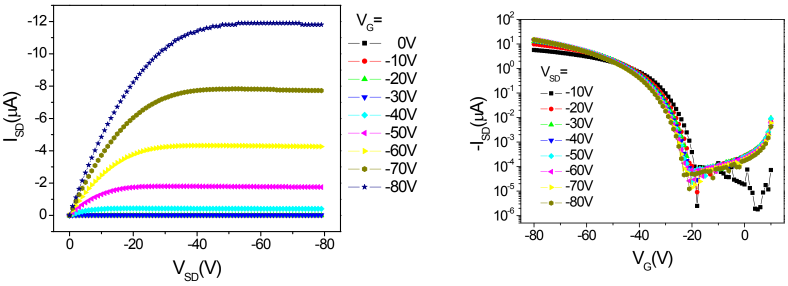


Figure S14. Output and transfer curves of DEP-*tt*-DTT with T_s at 60 °C.

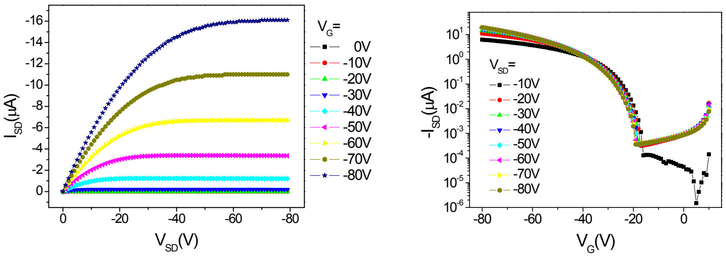


Figure S15. Output and transfer curves of DEP-*tt*-DTT with T_s at 70 °C.

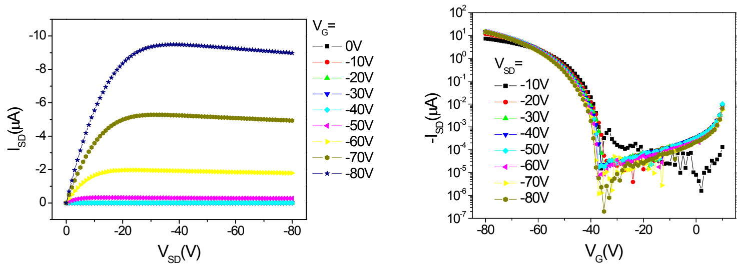


Figure S16. Output and transfer curves of DEP-*bt*-DTT with T_s at RT.

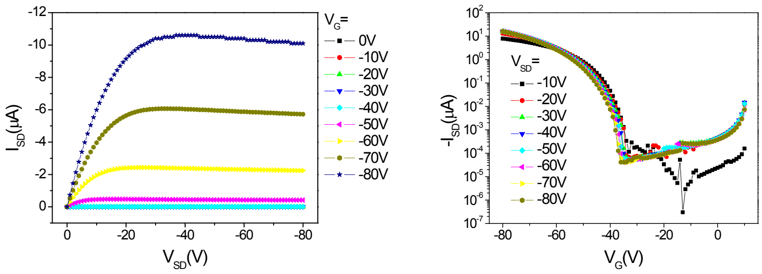


Figure S17. Output and transfer curves of DEP-*bt*-DTT with T_s at 60 ^{o}C.

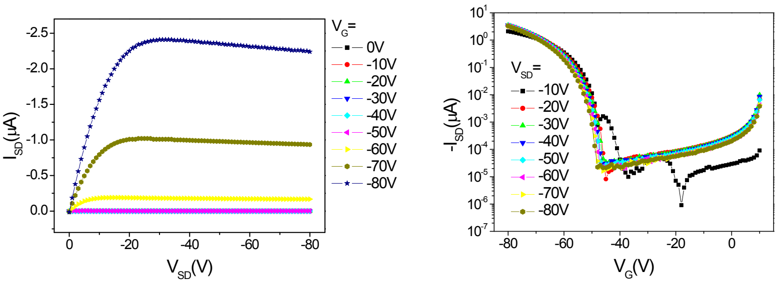


Figure S18. Output and transfer curves of DEP-*bt*-DTT with T_s at 70 ^{o}C.

Theoretical calculations

Theoretical calculations were done at the B3LYP/6-31G(d) level to further understand the effect of the sulfur atom position on the absorption properties and electrochemical characteristics of these CDT derivatives.

The transfer integral (*t*) between neighboring molecular pairs in the crystal structure was calculated based on the direct coupling method [4] with ADF program [5]at the M06-2X/TZ2P level of theory. The hybrid meta exchange-correlation functional

M06-2X was proved to be suitable for describing noncovalent interactions, such as π-π interaction, C-H•••π interaction and so on.[6]

Electrochemical behaviors

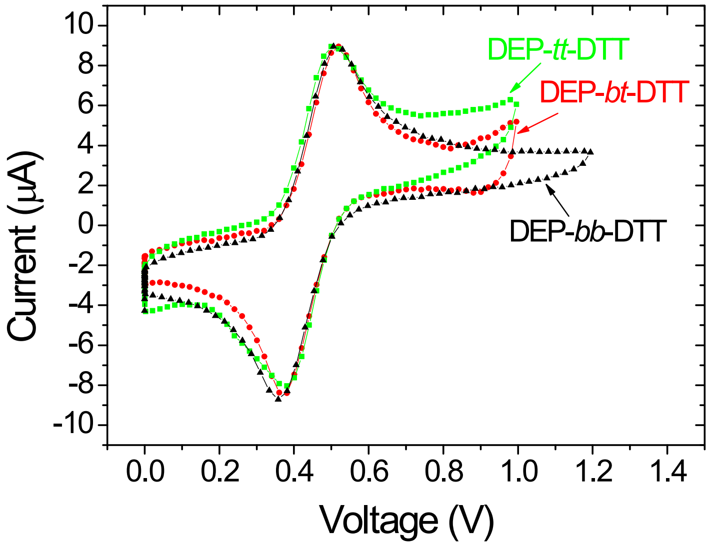


Figure S19. Cyclic voltammetry of **DEP-*tt*-DTT**, **DEP-*bt*-DTT** and **DEP-*bb*-DTT** film.

Topographical images and X-ray diffraction partterns

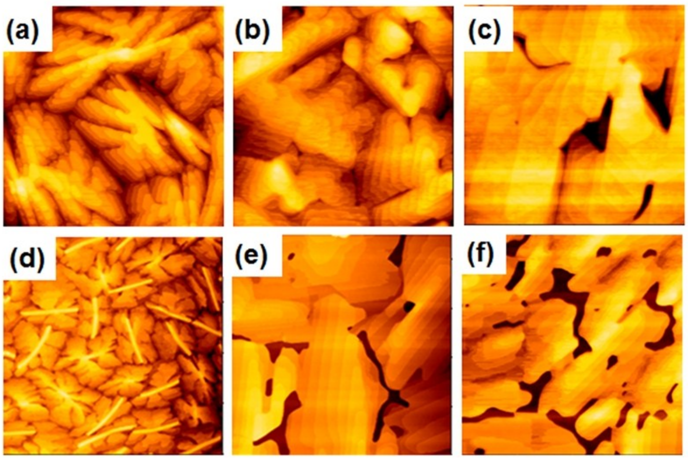


Figure S20. The topographical images films of: (a) **DEP-*bb*-DTT** at T_s of RT, (b) **DEP-*bb*-DTT** at T_s of 70 °C , (c) **DEP-*bb*-DTT** at T_s 100 °C, (d) **DEP-*tt*-DTT** at T_s of RT, (e) **DEP-*tt*-DTT** at T_s of 60 °C and (f) **DEP-*tt*-DTT** at T_s of 70 °C.

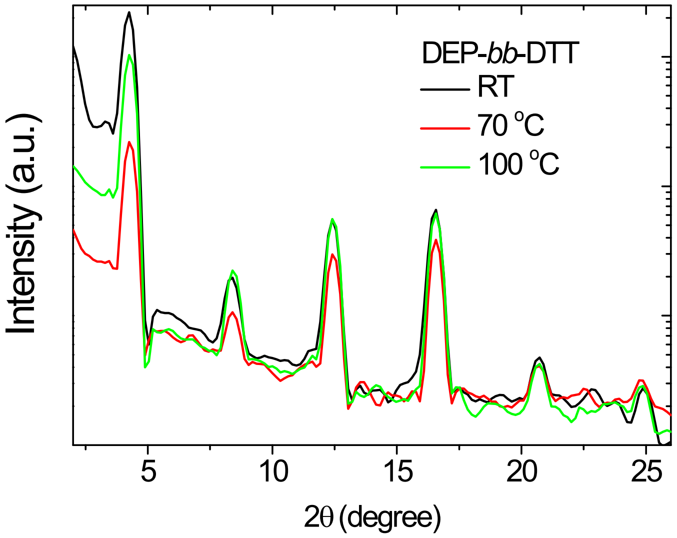


Figure S21. X-ray diffraction patterns of **DEP-*bb*-DTT** films at different substrate temperature.

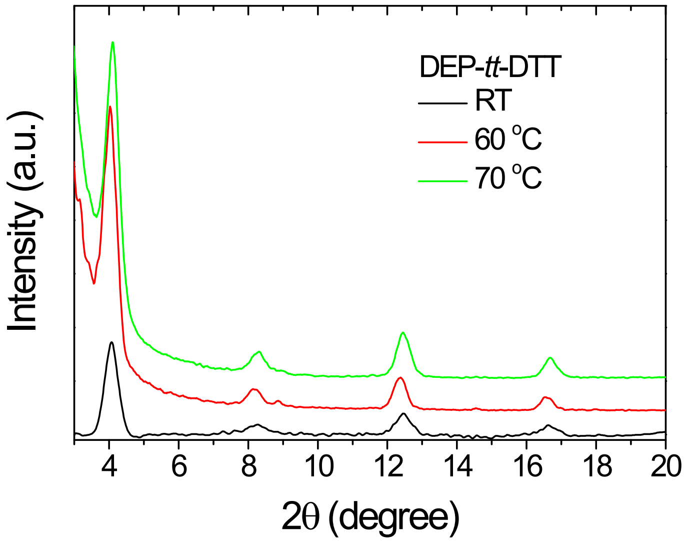


Figure S22. X-ray diffraction patterns of **DEP-*tt*-DTT** films at different substrate temperature.

Reference:

[1] de Jong, F.; Janssen, M. J. *J. Org. Chem*. **1971**, 36, 1645–1648.

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[4] K. Senthilkumar, F. C. Grozema, F. M. Bickelhaupt, L. D. A. Siebbeles, J. *Chem. Phys*. 119 (2003) 9809.

[5] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, J. *Comput. Chem.* 22 (2001) 931.

[6] Y. Zhao, D. Truhlar, Theor. *Chem. Acc.* 120 (2008) 215.