

Supporting information

A facile synthesis of linear benzene-fused bis(tetrathiafulvalenes) compounds and their application for organic field-effect transistors

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Experimental section

General Chemicals were purchased from Fluka, Lancaster and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. 1,3,5,7-tetrathia-s-indacene-2,6-dithione (**4**)¹ and 1,3-dithiole-2-thione **6 (a–c)**² were synthesized according to the literature. Melting points were measured with a WRR melting point apparatus. ¹H-NMR spectra were obtained on a Bruker DMX-300 NMR Spectrometer using tetramethylsilane as internal standard. Mass spectra were recorded on AEI-MA50-MS spectrometer for EI MS and Bruker BIFLEX III Mass Spectrometer for MALDI-TOF-MS. Elemental analyses were performed on a Carlo-Erba-1160 elemental analyzer. FT-IR spectra were determined using a Pekin-Elmer Tensor 27 spectrometer. Electronic absorption spectra were measured on a Jasco V570 UV-vis spectrophotometer. TGA-DTA measurements were carried out on a Universal V2.6D TA instruments under a dry nitrogen flow, heating from room temperature to 500 °C, with a heating rate of 10 °C/min. DSC analyses were performed on a Universal V4.1D TA instruments under a dry N₂ flow, heating from room temperature to the onset decomposition temperatures of **1–3**, respectively. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. X-ray diffraction (XRD) measurements were carried out with a 2-kW Rigaku X-ray

diffraction system.

Synthetic Details

Synthesis of 1,3,5,7-tetrathia-s-indacene-2,6-dione (**5**)

A mixture of 1,3,5,7-tetrathia-s-indacene-2,6-dithione (**4**) (1.22 g, 4.2 mmol), Hg(AcO)₂ (5.3 g, 16.8 mmol) and 50 mL toluene was stirred under reflux for 12 h. The reaction mixture was fast hot filtered through a G3 funnel which was covered by a layer of silica gel, and the silica gel layer was washed by hot toluene for several times. When the most solvent of the combined filtrate was removed, put the residues in the refrigeratory and stayed for 2 h. Filtered and dried in vacuum, afforded **5** (0.94 g, 86.7%) as white solid: MS(EI), 258 (M⁺, 100%).

Synthesis of 2,6-bis(4,5-dithiobutyl-1,3-dithiol-2-ylidene)benzo[1,2-*d*:4,5-*d'*]bis-[1,3]dithiole (**1**)

A mixture of **5** (0.4 g, 1.55 mmol), **6a** (3 g, 8.1 mmol) and P(EtO)₃ (15 mL) was refluxed for 24 h under a nitrogen atmosphere at 120°C. The mixture was cooled to room temperature and 30 mL anhydrous methanol was added. The precipitate was filtered and washed with methanol and ether, respectively. Recrystallization from chloroform gave **1** (0.46 g, 38%) as orange crystals: Mp 195–196°C; ¹H-NMR (CDCl₃) δ 0.93 (t, *J* = 7.08 Hz, 12H, –CH₃), 1.40–1.50 (m, 8H, –CH₂–), 1.60–1.67 (m, 8H, –CH₂–), 2.80–2.85 (t, *J* = 7.02 Hz, 8H, –CH₂–S), 7.08 (s, 2H, Ph-H); MS (EI) *m/z* 782, 784 (M⁺, 100, 55%), 725 (M⁺ – C₄H₉), 668 (M⁺ – 2C₄H₉), 611 (M⁺ – 3C₄H₉), 555 (M⁺ – 4C₄H₉); FT-IR (KBr, cm⁻¹) ν 3056, 2957, 2926, 2867, 1633, 1556, 1494, 1445, 1417, 1376, 1332, 1301, 1268, 1224, 1102, 860, 859, 773, 718, 639; Elemental analysis (%) calcd. for C₃₀H₃₈S₁₂, C 45.99, H 4.89; Found C 45.77, H 4.93.

Synthesis of 2,6-bis(4,5-dithiohexyl-1,3-dithiol-2-ylidene)benzo[1,2-*d*:4,5-*d'*]bis-[1,3]dithiole (**2**)

A mixture of **5** (0.22 g, 0.85 mmol), **6b** (2 g, 5.5 mmol) and P(EtO)₃ (10 mL) was refluxed for 24 h under a nitrogen atmosphere at 120°C. The mixture was cooled to room temperature and 30 mL anhydrous methanol was added. The precipitate was filtered and washed with methanol and ether, respectively. Recrystallization from toluene gave **2** (0.40 g, 52%) as orange crystals: Mp 170–171°C; ¹H-NMR (CDCl₃) δ 0.89 (t, *J* = 6.69 Hz, 12H, –CH₃), 1.29–1.43 (m, 24H, –CH₂–), 1.58–1.68 (m, 8H, –CH₂–), 2.79–2.84 (t, *J* = 7.26 Hz, 8H, –CH₂–S), 7.07 (s, 2H, Ph-H); MS (EI) *m/z* 894,

896 (M^+ , 100, 65%), 809 ($M^+ - C_6H_{13}$), 724 ($M^+ - 2C_6H_{13}$), 639 ($M^+ - 3C_6H_{13}$), 554 ($M^+ - 4C_6H_{13}$); FT-IR (KBr, cm^{-1}) ν 3058, 2955, 2924, 2852, 1633, 1555, 1496, 1462, 1441, 1415, 1377, 1332, 1303, 1263, 1208, 1102, 895, 847, 772, 723, 638; Elemental analysis (%) calcd. for $C_{38}H_{54}S_{12}$, C 50.96, H 6.08; Found C 50.89, H 6.07.

Synthesis of 2,6-bis(4,5-dithiooctyl-1,3-dithiol-2-ylidene)benzo[1,2-*d*:4,5-*d'*]bis-[1,3]dithiole (3)

A mixture of **5** (0.4 g, 1.55 mmol), **6c** (3.43 g, 8.1 mmol) and $P(EtO)_3$ (15 mL) was refluxed for 24 h under a nitrogen atmosphere at 120°. The mixture was cooled to room temperature and 30 mL anhydrous methanol was added. The precipitate was filtered and washed with methanol and ether, respectively. Recrystallization from toluene gave **3** (0.60 g, 38.5%) as orange crystals: Mp 158–159 °C; 1H -NMR ($CDCl_3$) δ 1.02 (s, 12H, $-CH_3$), 1.42–1.55 (m, 40H, $-CH_2-$), 1.78 (s, 8H, $-CH_2-$), 2.97 (s, 8H, $-CH_2-S$), 7.19 (s, 2H, Ph-H); MS (MALDI-TOF) m/z 1006 (M^+); FT-IR (KBr, cm^{-1}) ν 3059, 2956, 2923, 2851, 1643, 1556, 1496, 1464, 1439, 1413, 1377, 1332, 1294, 1265, 1197, 1102, 895, 845, 771, 722, 638; Elemental analysis (%) calcd. for $C_{46}H_{70}S_{12}$, C 54.82, H 7.00; Found C 54.48, H 6.76.

References

1. P. Wolf, K. Müllen and M. Przybylski, *Chimia.*, 1986, **40**, 200.
2. K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mørk, G. J. Kristensen and J. Becher, *Synthesis.*, 1996, 409.

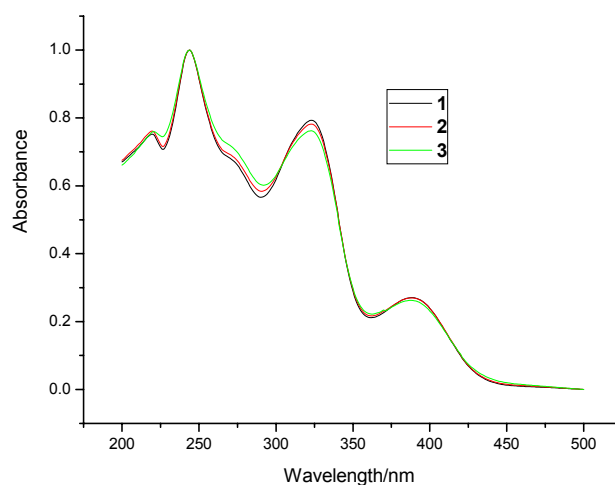


Fig. 1. UV-vis spectra of **1–3** in CH_2Cl_2 , in which $\lambda_{max} = 220, 244, 323, 344$ nm, respectively.

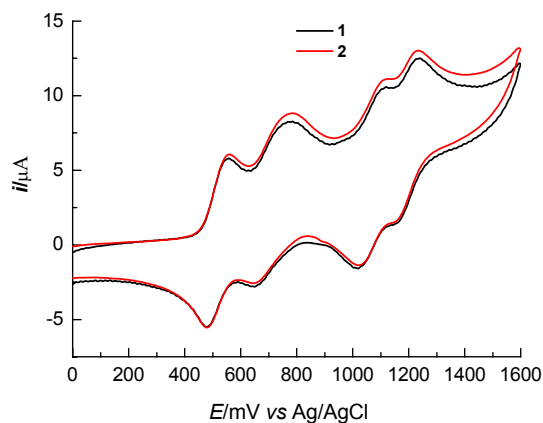


Fig. 2. Cyclic voltammograms of **1** and **2** vs Ag/AgCl in 0.1M/TBAHP/CH₂Cl₂ (50 mV/s)

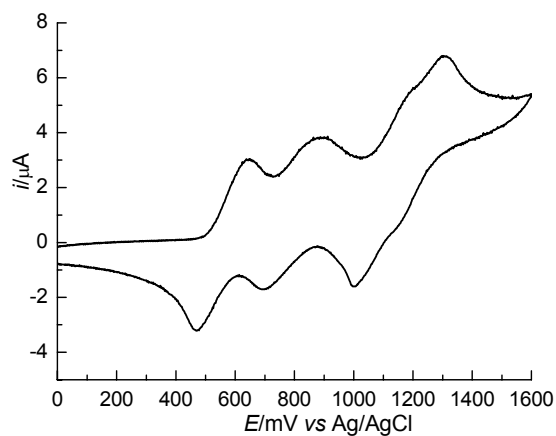


Fig. 3. Cyclic voltammograms of **3** vs Ag/AgCl in 0.1M/TBAHP/CHCl₃ (50 mV/s)

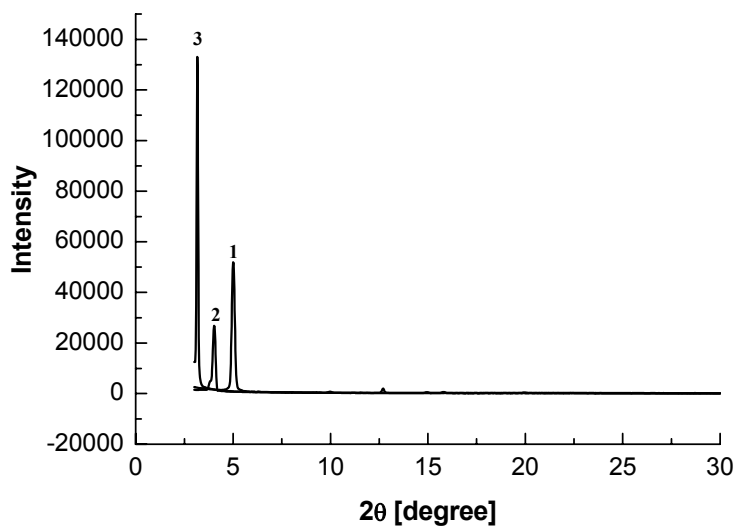


Fig. 4. X-ray diffraction of spin-coating thin films of **1–3** on SiO₂/Si substrate at room temperature.

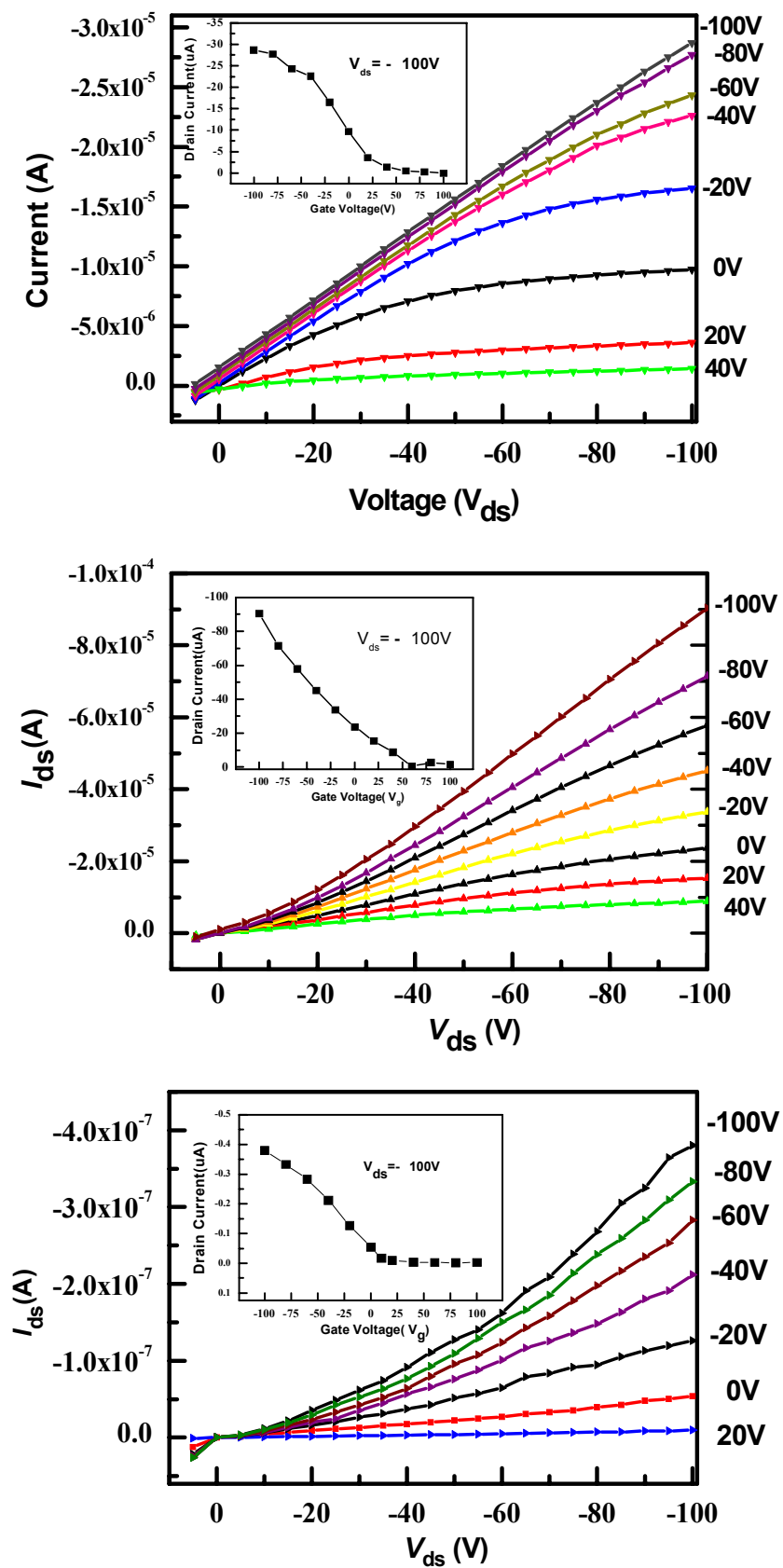
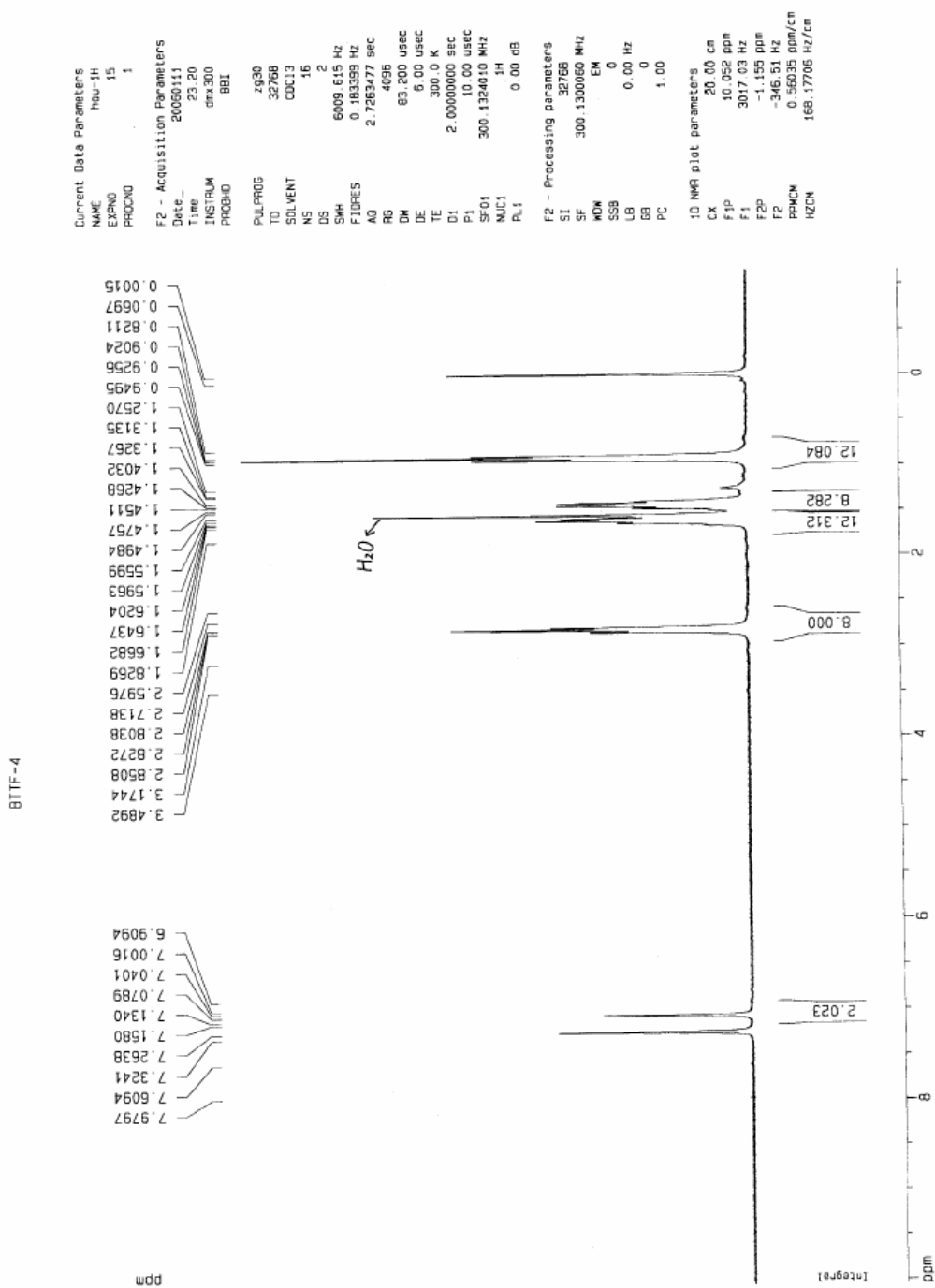
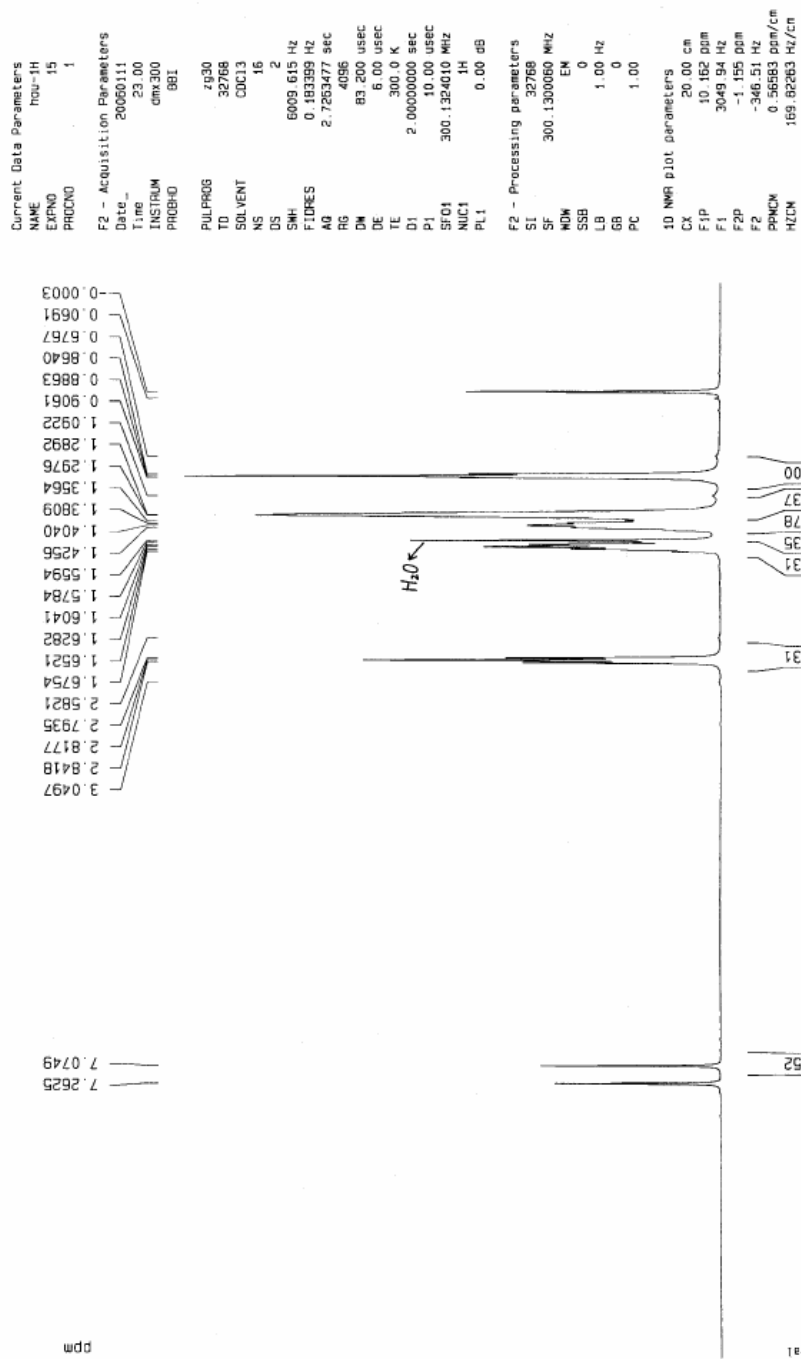


Fig. 5. Drain current versus drain voltage as a function of gate voltage for FETs based on 1–3 (from top to bottom, respectively) at room temperature. In the inset the transfer characteristics of the device at $V_{ds} = -100V$ are shown.

The $^1\text{H-NMR}$ and MS (EI or MALDI-TOF) spectra of **1–3** are given as follows:



BTTF-6



BTTF-8

