

## Supporting Information

### **New Sulphur Bridged Neutral Annulenes. Structure, Physical Properties and Application in Organic Field-Effect Transistors**

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## Materials and Methods

The solvents and reagents: diethyl ether/hexane/tetrahydrofuran (THF) (Na-benzophenone ketyl), dichloromethane (DCM)/acetophenone/alkyl halides (CaCl<sub>2</sub>), acetone (K<sub>2</sub>CO<sub>3</sub>), diisopropylamine/pyridine (KOH pellets), dimethylformamide (molecular sieves) were adequately dried as specified and drawn under N<sub>2</sub> atmosphere using hypodermic glass syringes. Titanium tetrachloride (TiCl<sub>4</sub>) was distilled before use. Low boiling reagents were invariably distilled over 4Å molecular sieves. Freshly prepared *n*-BuLi (2.1 N in hexane) was titrated against diphenylacetic acid<sup>1</sup> before use. Reactions were run under a blanket of dry nitrogen gas in round-bottomed flasks, sealed with rubber septum (Aldrich). Organometallic reagents were transferred using cannula. The low temperature (0°C) was achieved by using ice-flakes.

### Synthesis of 5,16-dihydro tetrathia[20]annulene 9 derivatives

To a suspension of zinc dust (54.15 mmol) in dry THF (200 ml) was added TiCl<sub>4</sub> (27 mmol, 1M in DCM) under nitrogen with stirring over 30 min. The reaction mixture was refluxed for 1 h, and then a solution of appropriate dialdehyde **8** (2.61 mmol) (Scheme 1, manuscript) and pyridine (43.57 mmol) in 200 ml of anhydrous THF was added through a cannula over 45 min to the gently refluxing suspension. After refluxing under nitrogen for 16 h, the dark reaction mixture was cooled to room temperature and quenched with aqueous K<sub>2</sub>CO<sub>3</sub> (10%, 50 ml). The resulting mixture was filtered through Celite. Filtrate was washed with water, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent evaporated under reduced pressure. The corresponding products **9** were purified by flash chromatography using silica gel-G (60-120 mesh) and mixtures of ethyl acetate/hexane as eluent. The following products have been prepared.

#### 5,16-Diphenyl-5,16-dihydrotetrathia[20]annulene (9a)

Yield 74%; Light green solid; m.p. 208-210°C (DCM); (Found C, 73.05; H, 4.06; S, 22.68. C<sub>34</sub>H<sub>24</sub>S<sub>4</sub> requires C, 72.85; H, 4.28; S, 22.85%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3030 and 1630;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 5.74 (2H, s, *meso*-CH), 6.48-6.49 (4H, m, 4 x CH), 6.60-6.65 (4H, m, 4 x CH), 6.80-6.82 (4H, m, 4 x CH), 7.24-7.26 (2H, m, ArH), 7.27-7.33 (8H, m, ArH);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 48.2, 123.5, 125.6, 127.0, 128.4, 128.5, 128.5, 138.5, 142.8 and 149.1; *m/z* (FAB) 561 (M<sup>+</sup>+1).

#### 5,16-Bis(*p*-tolyl)-5,16-dihydrotetrathia[20]annulene (9b)

Yield 82%; Light green solid; m.p. 214-216 °C (DCM); (Found: C, 73.56; H, 4.56; S, 21.89. C<sub>36</sub>H<sub>28</sub>S<sub>4</sub> requires C, 73.47; H, 4.76; S, 21.77%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2170 and 1490;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 2.36 (6H, s, 2 x Me), 5.74 (2H, s, *meso*-CH), 6.49-6.59 (4H, m, CH), 6.60-6.64 (4H, m, ArH), 6.80-6.82 (4H, m, ArH), 7.22-7.31 (8H, m, ArH).  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 21.4, 48.3, 48.4, 123.7, 123.8, 125.8, 128.7, 128.7, 128.8, 128.9, 137.1, 138.8, 140.3, 140.5, 149.7 and 149.8;  $m/z$  (FAB) 589 (M<sup>+</sup>+1).

### **5,16-Bis(4-chlorophenyl)-5,16-dihydropyridopyrrolo[2,1-b]pyridine (9c)**

Yield 78%; Light green solid; m.p. 218-220 °C (DCM); (Found: C, 65.09; H, 3.42; S, 20.56. C<sub>34</sub>H<sub>22</sub>S<sub>4</sub>Cl<sub>2</sub> requires C, 64.86; H, 3.50; S, 20.35%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2277 and 1530;  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 5.73 (1H, s, *meso*-CH), 5.75 (1H, s, *meso*-CH), 6.65 (4H, s, CH), 6.60-6.67 (4H, m, ArH), 6.83 (4H, s, ArH), 7.14-7.28 (8H, m, ArH);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 47.5, 113.8, 123.3, 123.4, 125.4, 128.4, 128.5, 129.4, 129.5, 138.4, 149.5 and 149.6;  $m/z$  (FAB) 630 (M<sup>+</sup>+1).

### **Synthesis of 5,16-diphenylpyridopyrrolo[2,1-b]pyridine derivatives 10a-c**

To a clear solution of appropriate 5,16-dihydropyridopyrrolo[2,1-b]pyridine **9** (0.89 mmol) in anhydrous toluene (20 ml), was added a solution of DDQ (1.05 mmol) in anhydrous toluene (10 ml). Upon mixing the two solutions, a black precipitates formed immediately. The mixture was stirred for 2 hrs. The black precipitates were filtered and added to 10 ml of hydrazine (95%). After refluxing for 30 min. the mixture was cooled to room temperature, extracted with DCM, evaporated under reduced pressure, and the product was purified by flash chromatography using silica gel-G (60-120 mesh) and DCM as eluent. For preparing sample for micro-analytical analysis, recrystallization was done using combinations of anhydrous DCM and toluene.

### **5,16-Diphenylpyridopyrrolo[2,1-b]pyridine (10a)**

Yield 85%; Purple crystalline solid; m.p. >300°C (DCM); (Found: C, 73.33; H, 3.78; S, 22.78. C<sub>34</sub>H<sub>22</sub>S<sub>4</sub> requires C, 73.11; H, 3.94; S, 22.94%);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3050, 1620 and 1580;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.99 (6H, d, *J* 6.3, ArH), 8.46 (4H, s, ArH), 10.01 (4H, d, *J* 5.2, 4 x CH), 10.40 (4H, d, *J* 4.5, 4 x CH), 11.09 (4H, s, 4 x

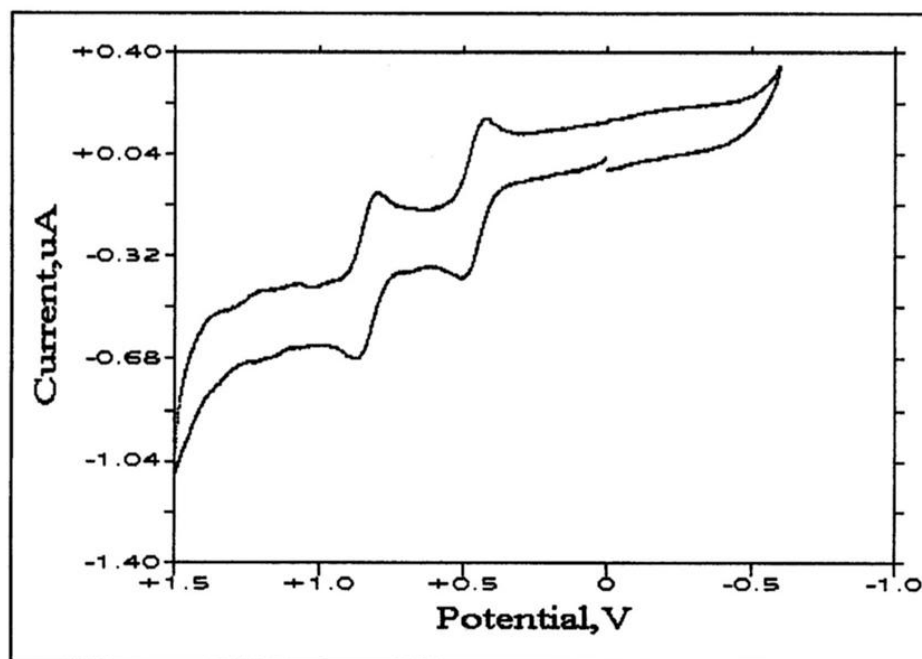
CH).  $\delta_C$  (100 MHz,  $CDCl_3$ +TFA) 121.5, 128.2, 128.6, 128.8, 129.2, 131.7, 132.7, 135.2, 135.7, 136.9, 142.3 and 148.3.  $m/z$  (FAB) 559 ( $M^+$ +1).

**5,16-Bis(*p*-tolyl)tetrathia[22]annulene (10b)**

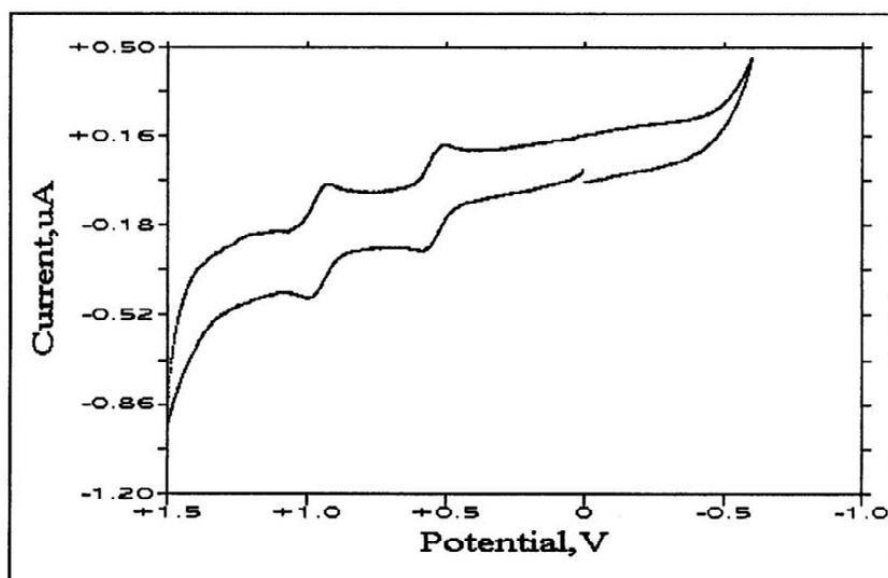
Yield 80%. Purple crystalline solid; m.p.  $\square$  300 °C (DCM); (Found: C, 73.64; H, 4.72; S, 21.76.  $C_{36}H_{26}S_4$  requires C, 73.72; H, 4.44; S, 21.84%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3590, 3000 and 1620.  $\delta_H$  (400 MHz,  $CDCl_3$ ;  $Me_4Si$ ) 1.25 (6H, s,  $CH_3$ ), 7.98 (3H, d,  $J$  8.2, ArH), 8.40 (4H, d,  $J$  7.8, ArH), 9.98 (5H, d,  $J$  9.9, ArH), 10.40 (4H, d,  $J$  4.8, ArH), 11.09 (4H, s, CH).  $m/z$  (FAB) 587 ( $M^+$ +1).

**5,16-Bis(4-chlorophenyl)tetrathia[22]annulene (10c)**

Yield 82%; Purple crystalline solid; m.p.  $\square$  300 °C (DCM); (Found: C, 65.32; H, 3.36; S, 20.72.  $C_{34}H_{20}S_4Cl_2$  requires C, 65.07; H, 3.19; S, 20.41%);  $\nu_{max}$  (KBr)/ $cm^{-1}$  3590, 3000 and 1620.  $\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 7.99 (4H, s, ArH), 8.41 (4H, d,  $J$  3, ArH), 10.00 (4H, m, ArH), 10.42 (4H, s, ArH), 11.11 (4H, s, CH).  $m/z$  (FAB) 626 ( $M^+$ -1).



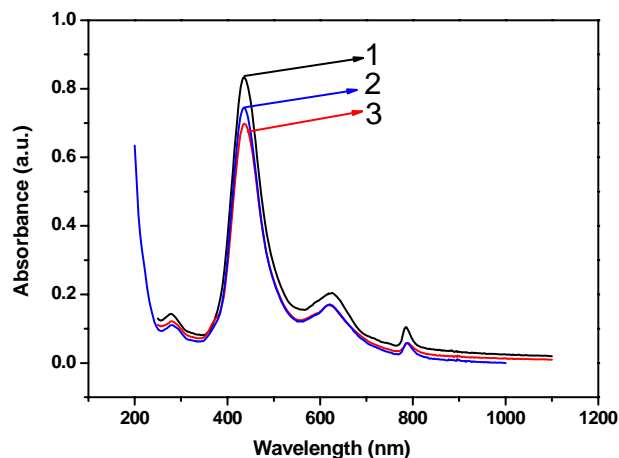
**Figure S1.** Cyclic voltammogram for **10b** (DCM, electrolyte tetrabutylammonium hexafluorophosphate; working electrode: Pt; reference electrode: Ag/AgCl;  $80 \text{ mVs}^{-1}$ ).



**Figure S2.** Cyclic voltammogram for **10c** (DCM, electrolyte tetrabutylammonium hexafluorophosphate; working electrode: Pt; reference electrode: Ag/AgCl;  $80 \text{ mVs}^{-1}$ ).

### Physical properties of thin films of **10a-c**

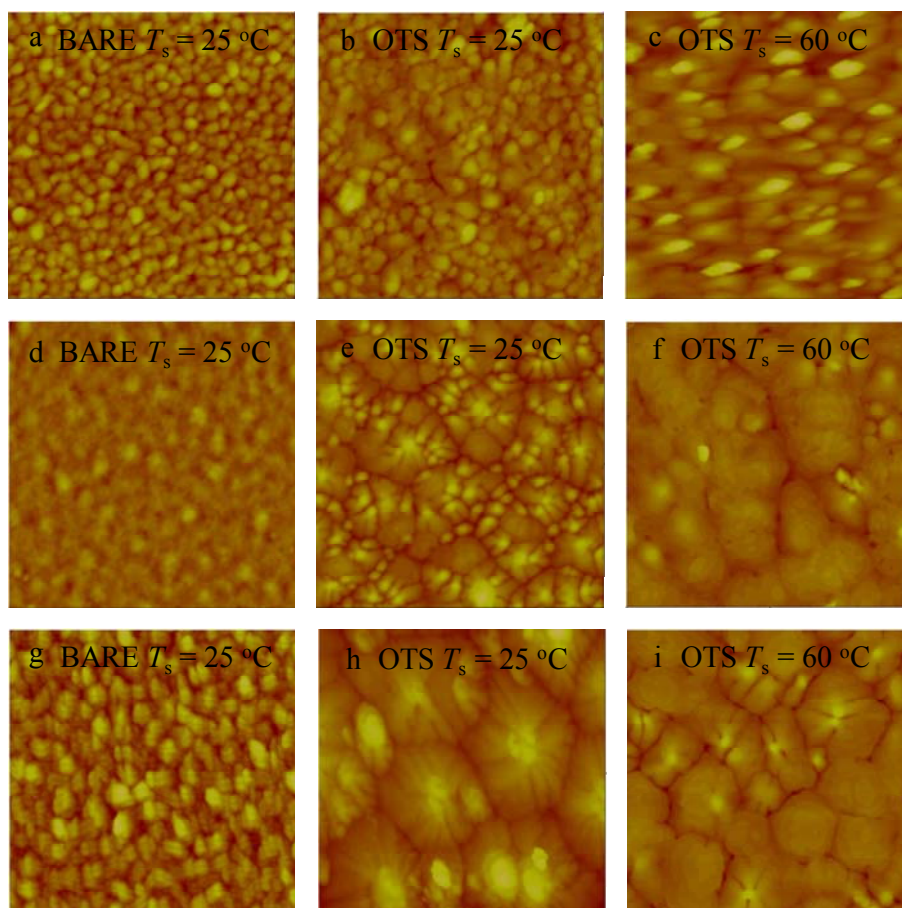
The UV-vis absorption spectra of **10a-c** thin films are shown in Fig. S3.



**Fig. S3** Normalized UV-vis absorption spectra of **10a-c** thin films at room temperature.

### Film morphology

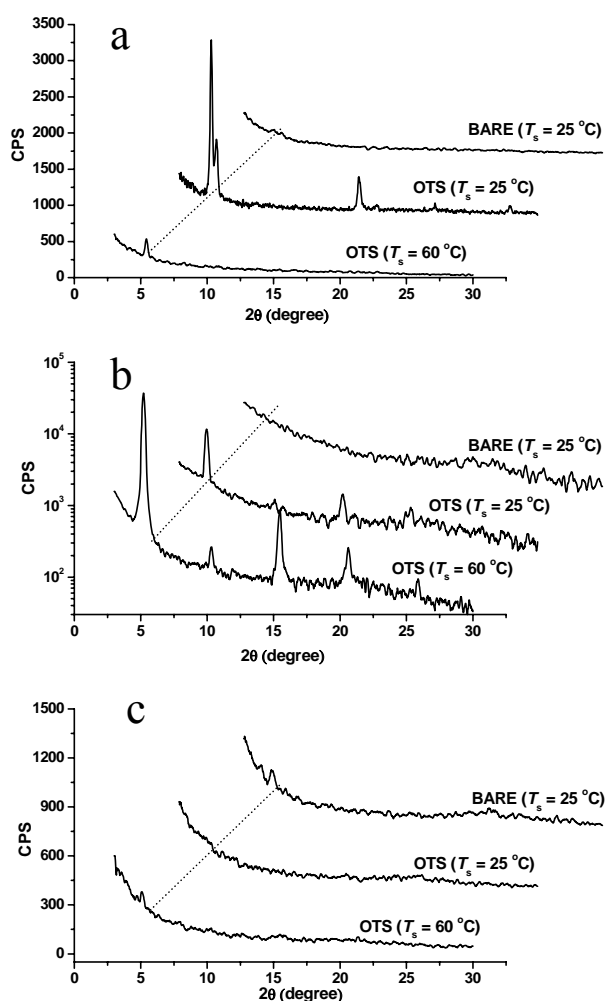
The morphology of 50 nm thick films of **10a-c** deposited on both plain SiO<sub>2</sub>/Si and OTS-treated SiO<sub>2</sub>/Si substrate at various substrate temperature were investigated by AFM (**Fig. S4**). When the substrate temperature was at room temperature (25 °C), the film deposited on SiO<sub>2</sub>/Si substrate was made of small grains. When the substrate was treated with OTS at 25 °C, bigger and interconnected grains were observed and the film became more ordered. When the substrate temperature was increased to 60 °C, the grains became bigger and varied in shape for the film on both SiO<sub>2</sub>/Si and OTS/SiO<sub>2</sub>/Si substrate. However, film discontinuity and large gaps increased as well. As the substrate temperature was increased to 100 °C, the film became cracked and lamellar crystalline grains were observed.



**Fig. S4** AFM images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of 50 nm thick films of **10a**: (a) deposited on  $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 25\ ^\circ\text{C}$ ; (b) deposited on OTS/ $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 25\ ^\circ\text{C}$ ; (c) deposited on OTS/ $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 60\ ^\circ\text{C}$ ; **10b**: (d) deposited on  $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 25\ ^\circ\text{C}$ ; (e) deposited on OTS/ $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 25\ ^\circ\text{C}$ ; (f) deposited on OTS/ $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 60\ ^\circ\text{C}$ ; **10c**: (g) deposited on  $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 25\ ^\circ\text{C}$ ; (h) deposited on OTS/ $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 25\ ^\circ\text{C}$ ; (i) deposited on OTS/ $\text{SiO}_2/\text{Si}$  substrate,  $T_s = 60\ ^\circ\text{C}$ .

## X-ray Diffraction

The X-ray diffraction patterns of the thin films of **10a-c** deposited on SiO<sub>2</sub>/Si and OTS/SiO<sub>2</sub>/Si substrate at various substrate temperatures ( $T_s$ ) are shown in Fig. S5.



**Fig. S5** X-Ray diffraction patterns of the thin films of (a) **10a**, (b) **10b**, (c) **10c** deposited on SiO<sub>2</sub>/Si and OTS/SiO<sub>2</sub>/Si substrate at various substrate temperatures ( $T_s$ ).

## FET characteristics

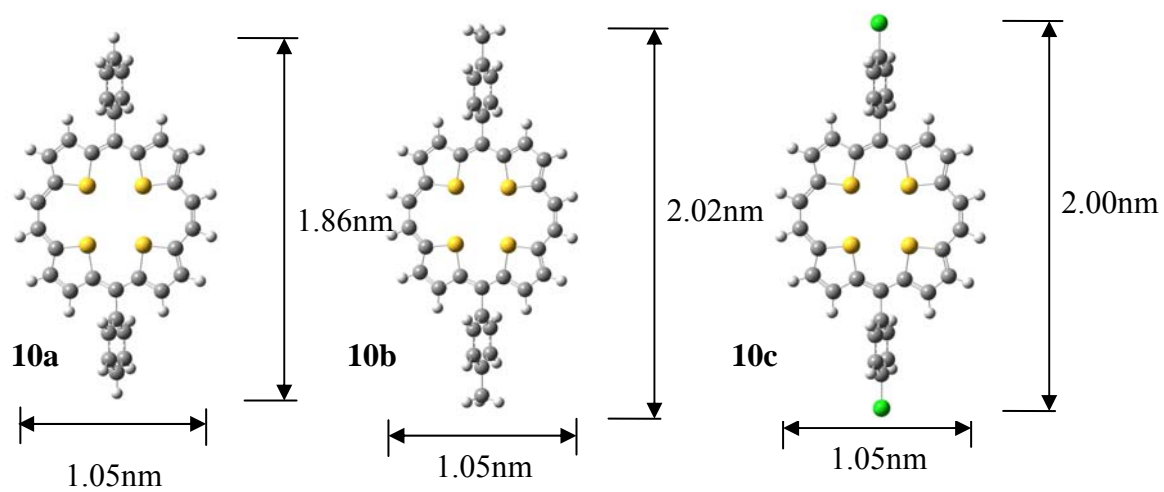
Top contact OFETs based on the thin films were fabricated. The results were summarized in Table 1. Here, the mobilities ( $\mu$ ) were calculated in the saturation regime by the following equation:  $I_D = \mu C_i (W/2L)(V_G - V_T)^2$ , where  $I_D$  is the drain current,  $\mu$  is the field-effect mobility,  $C_i$  is the gate dielectric capacitance,  $W$  and  $L$  are the channel width and length, respectively,  $V_T$  is the threshold voltage. **2** exhibited the best OFET performance. When the SiO<sub>2</sub>/Si substrate was treated with OTS, large improvement in the performance was observed, with the average mobility increased



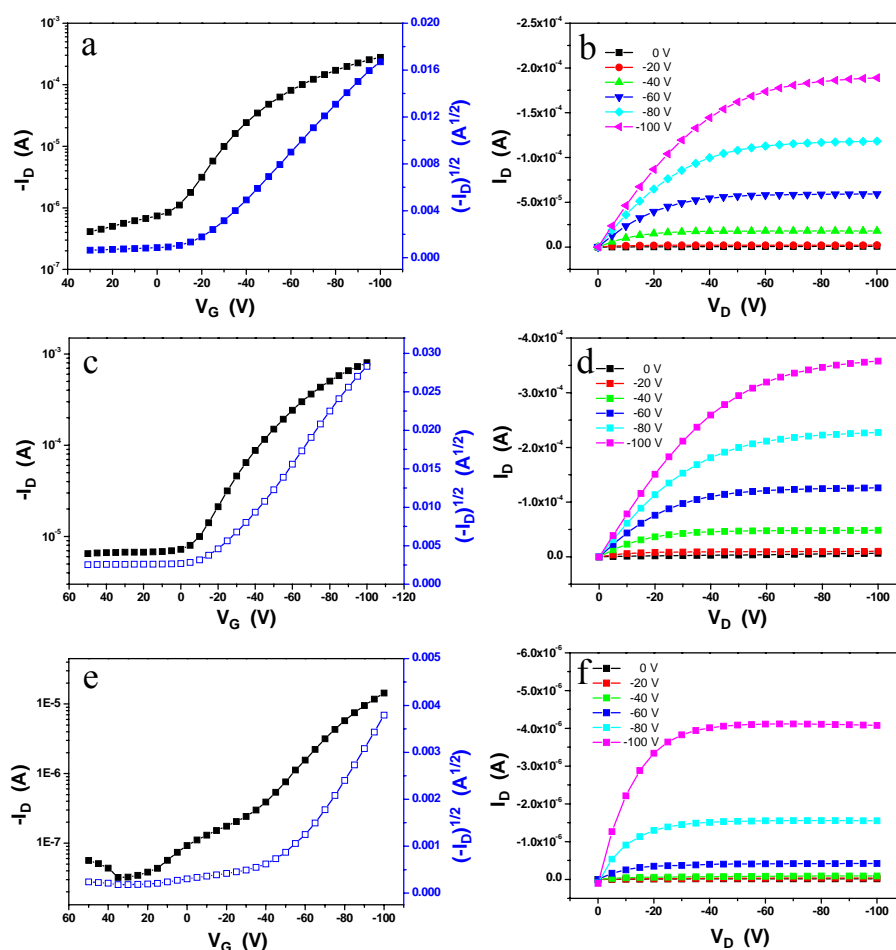
to  $0.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , the maximal mobility as high as  $0.63 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The FET characteristics of **10a-c** are shown in Fig. S7.

**Table S1.** Detailed performance of OFETs based on **10a-c** thin films.

$T_s=25 \text{ }^\circ\text{C}$	$\mu \text{ (cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$	$I_{\text{on}}/I_{\text{off}}$	$V_T \text{ (V)}$
<b>10a-BARE</b>	$1.07 \times 10^{-4}$	4.05	113
<b>10a-OTS</b>	0.25(0.29)	$1.34 \times 10^3$	-12.9
<b>10b-BARE</b>	$2.03 \times 10^{-5}$	52.7	40.6
<b>10b-OTS</b>	0.44(0.63)	$3 \times 10^2$	-7.47
<b>10c-BARE</b>	$3.01 \times 10^{-5}$	$1.54 \times 10^3$	1.33
<b>10c-OTS</b>	$5.04 \times 10^{-3} (9.68 \times 10^{-3})$	$8.96 \times 10^5$	-49.0
$T_s=60 \text{ }^\circ\text{C}$	$\square\mu \text{ (cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$	$I_{\text{on}}/I_{\text{off}}$	$V_T \text{ (V)}$
<b>10a-BARE</b>	$3.20 \times 10^{-4}$	12.1	56.5
<b>10a-OTS</b>	$1.58 \times 10^{-2}$	$1.48 \times 10^3$	-5.11
<b>10b-BARE</b>	$2.03 \times 10^{-4}$	4.22	90.5
<b>10b-OTS</b>	0.28(0.31)	$1.34 \times 10^3$	-17.6
<b>10c-BARE</b>	$5.22 \times 10^{-5}$	$7.19 \times 10^3$	28.7
<b>10c-OTS</b>	$2.45 \times 10^{-2} (3.16 \times 10^{-2})$	$3.03 \times 10^4$	-50.1



**Figure S6.**



**Fig. S7** Typical transfer (a) and output (b) characteristics of FET devices based on **10a**, with OTS-treated SiO<sub>2</sub>/Si substrate ( $T_s = 25$  °C). Typical transfer (c) and output (d) characteristics of FET devices based on **10b**, with OTS-treated SiO<sub>2</sub>/Si substrate ( $T_s = 25$  °C). Typical transfer (e) and output (f) characteristics of FET devices based on **10c**, with OTS-treated SiO<sub>2</sub>/Si substrate ( $T_s = 60$  °C).

### Experimental:

OFET devices were fabricated in the top-contact device configuration. The substrate was heavily doped, n-type Si gate electrode with a 500 nm thick SiO<sub>2</sub> layer as the gate dielectric. The gate dielectric was treated with octadecyltrichlorosilane (OTS) by vapor deposition method. Subsequently, organic semiconductors were deposited on the substrate by thermal evaporation under a pressure of  $8 \times 10^{-4}$  Pa at a deposition rate gradually increased from  $0.1 \text{ \AA s}^{-1}$  to  $0.4 \text{ \AA s}^{-1}$  at the first 20 nm and then maintained  $0.5 \text{ \AA s}^{-1}$  until the thickness of the film was 50 nm. The deposition rate and film thickness were monitored by a quartz crystal microbalance (ULVAC CRTM-6000). Finally, 20 nm thick gold source and drain electrode were deposited

through a shadow mask. The channel length ( $L$ ) and width ( $W$ ) were 0.11 mm and 5.30 mm, respectively. The FET characteristics were measured at room temperature in air using Keithley 4200 SCS. X-ray diffraction (XRD) measurements were carried out in the reflection mode at RT using a 2-kW Rigaku X-ray diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ ). Atomic force microscopy (AFM) measurements were carried out with a Nanoscope IIIa instrument (Digital Instruments) operating in tapping mode. UV-Vis spectra were recorded on a JASCO V-570 spectrometer.

## Reference

1. W. G. Kofron and L. M. Baclawski, *J. Org. Chem.* **1976**, 41, 1879.