Electronic Supplementary Information (ESI)

Thin Film Field-effect Transistors of 2,6-diphenyl Anthracene (DPA)

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Table of Contents

Experimental Section

Reference

Experimental Section

Materials and synthesis

All reagents and chemicals were obtained from commercial sources and used without further purification.

2,6-Diol-anthracene: To a 100 mL two neck round bottom flask fitted with magnetic bar, was added sodium borohydride (2.4 g, 62.5 mmol) and 1M sodium carbonate solution (60 mL). 2,6-dihydroxyanthracene-9,10-dione (1.2 g, 5 mmol) was added in small portions which resulted in colorless gas evolution. After gas evolution stopped, the whole system was heated up to 80 ^{o}C for 30 min. It was then transferred to a 500 mL baker fitted with magnetic bar and slowly acidified with 3M HCl (60 mL) and then filtrated and dried. The filtrate was washed on a filter with acetone and the solution was evaporated under reduced pressure to afford brown solid 0.72 g (68% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 9.69 (s, 2H), 8.19 (s, 2H), 7.87 (d, 2H), 7.18 (d, 2H), 7.12 (dd, 2H). MS (EI): m/z 210 (M^+).

2,6-Diyl bis(trifluoromethanesulfonate)-anthracene: To a 50 mL two neck round bottom flask charged with magnetic bar was added crude product 1 (420 mg, 2 mmol), then protected under argon, dry dichloromethane (8 mL) and triethylamine (1.4 mL). After cooling to -20 ^{o}C, triflic anhydride (0.82 mL, 5 mmol) was slowly added dropwise via syringe. The mixture was stirred for 2 h and then warmed up to room temperature. Dichloromethane (10 mL) was added and the mixture was washed with water (10 mL × 3) and brine (10 mL × 3). The organic layer was separated, dried over Na_2SO_4 and evaporated under reduced pressure, the crude product was purified by column chromatography (silica, petroleum / dichloromethane) to afford white yellowish solid (550 mg, 58%yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] 8.41 (s, 2H), 8.03 (d, 2H), 7.89 (d, 2H), 7.40 (dd, 2H). MS (EI): m/z 474 (M^+).

2,6-Diphenylanthracene, DPA: To a 100 mL flask, 474 mg (1 mmol) 2, 268 mg (2.2 mmol) phenylo boric acid and $Pd(PPh_3)_4$ 63 mg (0.05 mmol) was added under argon. Then 2 mL ethanol, 8 mL toluene and 2mL 2M K_2CO_3 aqueous solution was added. The whole system was heated to 90 ^{o}C and kept overnight. Then the whole system was filtered, the filtrate was washed with triethylamine, dichloromethane, water and ethanol successively, and then further purified by sublimation. DPA was obtained as a yellow solid in a yield of 85% (280 mg). ^{1}H-

NMR (400 MHz, $CDCl_3$): δ [ppm] 8.50 (s, 2H), 8.21 (s, 2H), 8.10 (d, 2H), 7.78 (m, 6H), 7.52 (t, 4H), 7.40 (m, 2H). MS (EI): m/z 330 (M^+). Elemental analysis calculated for C26H18: C 94.51, H 5.49. Found: C 94.48, H 5.45.

Instrument Descriptions and Experimental Details.

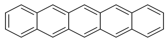
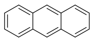
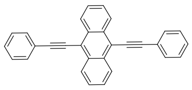
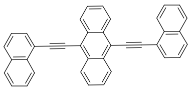
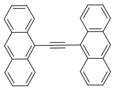
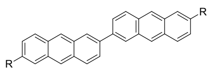
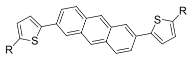
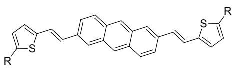
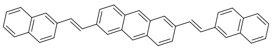
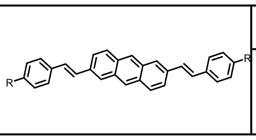
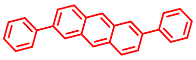
^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer in deuterated chloroform with tetramethylsilane (TMS) as an internal reference. All chemical shifts were reported relative to TMS at 0.0 ppm. TGA was carried out on a Perkin Elmer TGA7 under nitrogen. CV was run on a CHI660C electrochemistry station in THF solution using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte at a scan speed of 100 mVs^{-1}, and glassy carbon was used as the working electrode and Pt wire as the counter electrode and ferrocene as inner standard. The UV-vis spectra were obtained on a Jasco V-570 UV-vis spectrometer with solution concentration of 1×10^{-5} mol/L. X-ray diffraction measurement was performed in reflection mode at 40 kV and 200 mA with Cu Ka radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer. The films were imaged in air using a Digital Instruments Nanoscope III atomic force microscope operated in tapping mode.

OFET devices were fabricated in top-contact geometry. Thin films were deposited under vacuum on OTS-modified Si/SiO_2 substrates and 20 nm thick gold source and drain electrodes were deposited successively using the shadow masks with width-to-length ratio (W/L, 240μm/30μm) of cal. 8/1. Organic semiconductors were deposited under a pressure of about 4.0×10^{-4} Pa determined by a quartz crystal monitor. OFET characteristics were obtained at room temperature in air on a Keithley 4200 SCS and Micromanipulator 6150 probe station. And the mobility was calculated by using the equation: $I_{DS} = (W/2L)C_i\mu(V_G-V_T)^2$.

Measurements of contact resistance.

DPA-thin film devices are fabricated based on OTS-modified Si/SiO_2 substrate with bottom-gate top-contact geometry. The channel lengths are 50 μm, 70 μm, 90 μm with the same channel width of 1.2 mm. Figure S3 shows the relationship between the R_{ON} resistance and channel length at different gate voltages for the DPA-based devices with gold source and drain electrodes. According to the equation in the linear operation regime ($V_{DS} << V_G$), $R_{ON}=R_{ch}+R_c=L/WC_i\mu(V_G-V_T)+R_c$, where R_{ON} is the ON resistance, R_{ch} is the channel resistance and R_c is the contact resistance,[1] the R_c can be extracted by measuring the ON resistance from the linear region of the DPA-FET output characteristics. Since W was constant in the measurement, by extrapolating the relationship of R_{ON} *vs* L at L=0, the calculated R_c value is around 0.1 MΩ.[1b,2] The contact resistance in DPA-thin film transistors is due to the mismatch of the HOMO level of DPA (-5.6 eV) and the work function (-5.1 eV) of gold electrodes as well as structural defects at the interface.

Table S1. Summary of the properties of typical anthracene derivatives in comparison with pentacene. Based on the previous studies, the chemical structure of a novel anthracene derivative, DPA, designed for promising semiconductor candidate is shown in the bottom column.

Molecular structure			HOMO (eV)	Eg (eV)	Mobility (cm^{2}V^{-1}s^{-1})	Reference
Pentacene			-5.1[c]	1.8	1-2.3	3
Anthracene			-5.79[c]	3.9	0.02[b]	4
BPEA			-5.49[c]	2.57	0.03~0.73[b]	5
BNEA			-5.49[c]	2.5	0.01~0.52[b]	5
"H" type molecule			-5.4~-5.5[c]	2.5~2.6	0.2~0.82[b]	6
2-A		R=H	--	--	0.013[a]	7
DH-2A		R=C_6H_{13}	-5.09[c]		0.11[a]	
DTAnt		R=H	--	2.8[c]	0.063±0.06[a]	8
DHTAnt		R=C_6H_{13}		2.8[c]	0.5±0.045[a]	
TVAnt		R=H	-5.42[c]	2.55	0.44[a]	9
HTVAnt		R=C_6H_{13}	-5.2[c]	2.59	0.15[a]	
DNVAnt			-5.54[c]	2.71	0.2[a]	10
DPVAnt		R=H	-5.4[c]	2.6	1.3[a] 4.3[b]	3a, 11
DPPVAnt		R=C_6H_{13}	-5.52[c]	2.59	1.28[a]	
Our target molecule：DPA 			-5.6[c]	3.0	14.8[a]	Our work

[a] Corresponding to thin film FETs, [b] corresponding to single crystal FETs, [c] all the HOMO levels and bandgaps are obtained from experimental results.

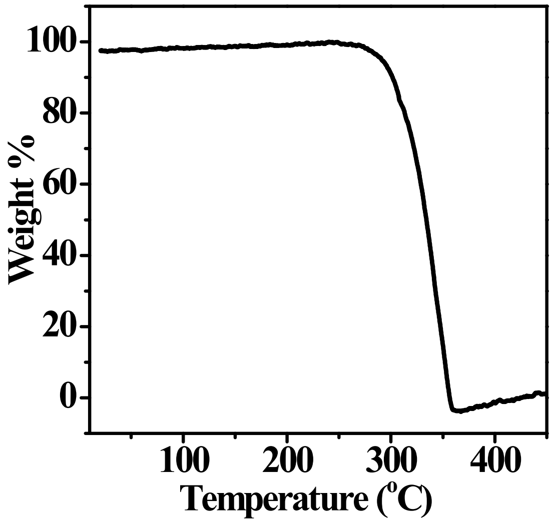


Figure S1. Thermogravimetric analysis of DPA.

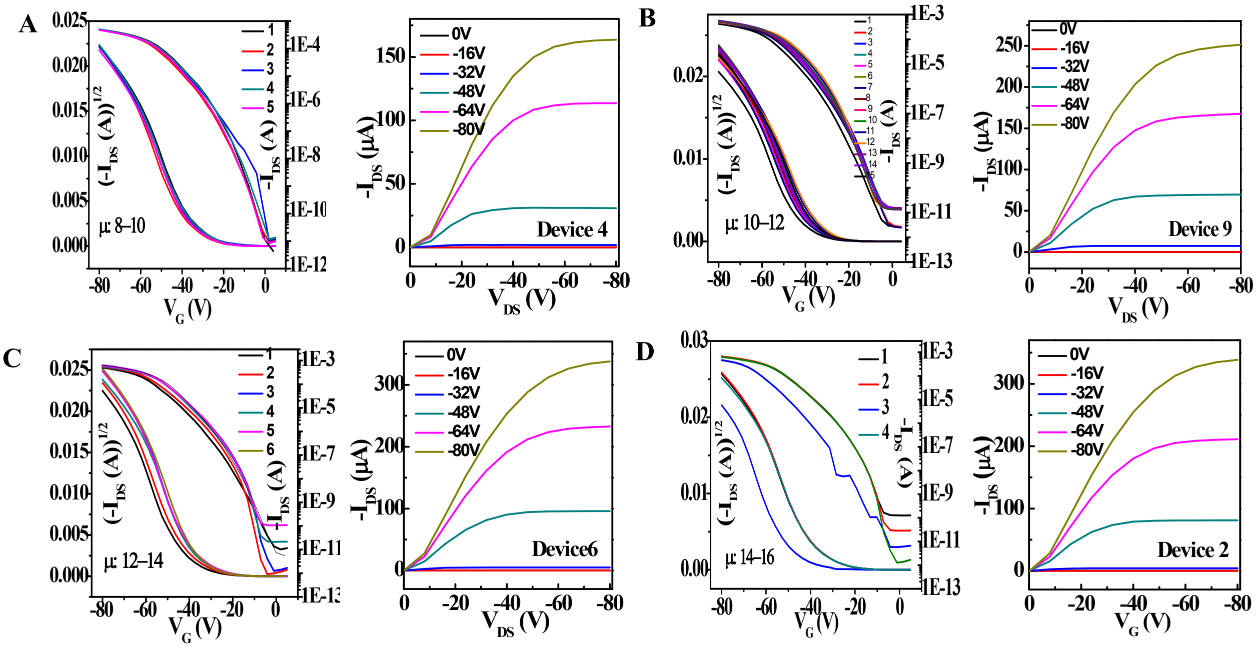


Figure S2. All the transfer and representative output curves of our 30 transistors included in Fig. 4D separated into four groups according to the mobility distribution: (A), mobilities in the region of 8-10 cm^2 V^{-1}s^{-1}, B, mobilities in the region of 10-12 cm^2 V^{-1}s^{-1}, C, mobilities in the region of 12-14 cm^2 V^{-1}s^{-1}, D, mobilities in the region of 14-16 cm^2 V^{-1}s^{-1}.

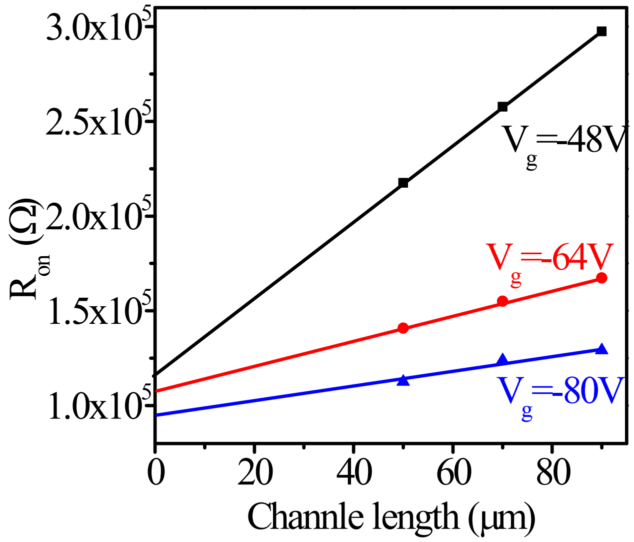


Figure S3. The relationship between R_{ON} resistance and channel length at different gate voltages for DPA transistors.

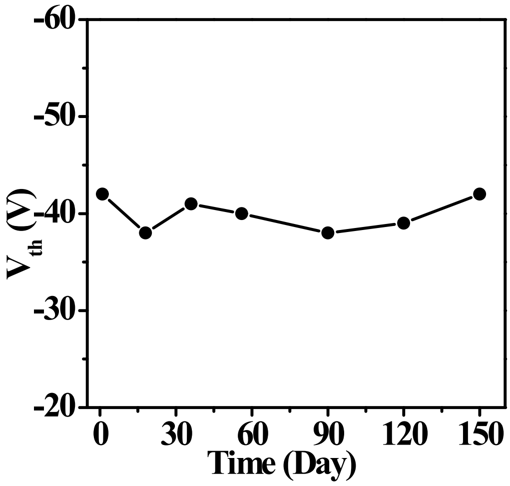


Figure S4. Threshold voltage dependence on time.

Reference

1. (a) B. Stadlober, U. Haas, H. Gold, *et al. Adv. Funct. Mater.* 2007, **17**, 2687-2692. (b) O. Acton, M. Dubey, T. Weidner, *et al.Adv. Funct. Mater.* 2011, **21**, 1476-1488.
2. (a) D. Boudinet, M. Benwadih, Y. B. Qi, *et al. Org. Electron.* 2010, **11**, 227-237. (b) C.-H. Lee, T. Schiros, E. J. G. Santos, *et al. Adv. Mater.* 2014, **26**, 2812-2817
3. (a) H. Klauk, U. Zschieschang, R. T. Weitz, *et al. Adv. Mater.* 2007, **19**, 3882-3887. (b) M. L. Tang, T. Okamoto, Z. Bao, *J. Am. Chem. Soc.* 2006, **128**, 16002-16003..(c) T. W. Kelley, D. V. Muyres, P. F. Baude, *et al. Mat. Res. Soc. Symp. Proc.* 2003, **771**, L6.5.1-L6.5.11.(d) Y.C. Chang, C. Y. Wei, Y. Y. Chang, *et al. IEEE Trans. Electr. Dev.* 2013, **60**,4234-4239.
4. A. N. Aleshin, J. Y. Lee, S. W. Chu, *et al. Appl. Phys. Lett.* 2004, **84**, 5383-5385..
5. C. Wang, Y. Liu, Z. Ji, *et al. Chem. Mater.* 2009, **21**, 2840-2845..
6. L. Jiang, J. Gao, E. Wang, *et al. Adv. Mater.* 2008, **20**, 2735-2740.
7. K. Ito, T. Suzuki, Y. Sakamoto, *et al. Angew. Chem. Int. Ed.* 2003, **42**, 1159-1162
8. H. Meng, F. Sun, M. B. Goldfinger, *et al. J. Am. Chem. Soc.* 2005, **127**, 2406-2407.
9. M.-C. Um, J. Jang, J. Kang, *et al.J. Mater. Chem.* 2008, **18**, 2234-2239.
10. M.-C. Um, J. Jang, J.-P. Hong, *New J. Chem.* 2008, **32**, 2006-2010.
11. (a) H. Meng, F. Sun, M. B. Goldfinger, *et al. J. Am. Chem. Soc.* 2006, **128**, 9304-9305. (b) L. Jiang, W. Hu, Z. Wei, *et al. Adv. Mater.* 2009, **21**, 3649-3653