Electronic Supplementary Information (ESI)

Enhancing field-effect mobility and maintaining solid-state emission by incorporating 2,6-diphenyl substitution to 9,10-bis(phenylethynyl)anthracene

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Experimental section：

Sample preparation

Single crystal samples for quantum efficiency measurements of the compounds were prepared by drop-casting (THF for DP-BPEA, CH2Cl2 for α-phase BPEA, chlorobenzene for β-phase BPEA)[1] on 1 cm^2 quartz plates. Single crystals for OFETs were grown by physical vapor transport (PVT) directly on OTS (octadecyltrichlorosilane) treated SiO_2/Si.

X-ray crystal structure analysis

High-quality single crystals of **DP-BPEA** were grown from saturated THF solution at room temperature for X-ray analysis. X-ray diffraction intensity data were collected on a Rigaku Pilatus 200k diffract meter with confocal monochromator Mo K\α radiation under 113 K (Table S1).

Density Functional Theory (DFT) calculation

All the density functional theory (DFT) calculations in this work were done by the Gaussian 09 package. For transfer integrals and reorganization energies, the site-energy overlap correction method and adiabatic potential energy surface method were adopted respectively, where the DFT calculations were obtained at the B3LYP/6-31G(d) level. For excited states, CAM-B3LYP hybrid functional was used, and the basis set size was increased to 6-31+G(d, p). The excitation energy of S1 was obtained as the energy of the first singlet electronic excitation calculated by time-dependent density functional theory (TD-DFT), and the excitation energy of T1 was the difference between the ground state energy of molecules with triplet and singlet multiplicity, both in fully optimized geometry.

Electrochemical analysis

Cyclic voltammetry measurements were performed in 0.1 M electrolyte solution (Bu_4NPF_6) in CH_2Cl_2 with sample concentration of 10^{-3} M at room temperature in N_2 atmosphere, using a Pt disk as a working electrode, Ag/AgCl as a reference electrode and Pt wire as an auxiliary electrode. Ferrocene was added to the analyzed solution at the end of the measurement as an internal reference.

Photophysical studies of solution sample

UV-vis absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1 cm quartz cell for solution samples. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55spectrofluorometer for solution samples. And 1×10^{-5} M THF solution was used for monomers measurements. The relative fluorescence quantum yields of the solutions were measured using fluorescein as a reference ($\Phi = 0.79$).

Photophysical studies of crystalline sample

Absolute quantum yield measurement (LabSphere®, FluoroMax-4, HORIBA Jobin Yvon, PLQY (PL quantum yield) software package) was used for crystalline sample. Emission spectra including the scattering region of excitation light were measured for both blank and samples, and these spectra were corrected with instrumental factors to calculate the quantum yield. PL image was obtained using Olympus inverted fluorescence microscope IX83 with CCD camera. Fluorescent mapping was conducted on laser scanning confocal microscope for the same crystal.

Modification of SiO_2 wafer with OTS

The substrate was a heavily doped n-type Si wafer with a 300 nm thick SiO_2 layer. The substrates were cleaned with deionised water, piranha solution (H_2SO_4:H_2O_2 = 7:3), deionised water and isopropanol successively. OTS modification: The clean wafers were dried under vacuum at 90°C for 0.5 h in order to eliminate moisture. After cooling to room temperature, one drop of OTS was placed on the wafer. This system was then heated up to 120 °C for 2 h under vacuum. After cooling down to room temperature, the wafers were washed by n-hexane, chloroform and isopropanol successively, and then blow-dried by N_2 and ready for use.

AFM and TEM study of single crystal samples

AFM image of single crystal was obtained by using a Digital Instruments Nanoscope III atomic force microscope in air. TEM and SAED measurements were carried out on a JEM 1011 (Japan).

Fabrication of thin film transistors

Thin film transistors (TFTs) were fabricated in bottom-gate top-contact (BGTC) configuration. Thin films of DP-BPEA were grown at room temperature by vacuum deposition (8×10^{-4} Pa) with a deposition speed of 0.1-0.5 $Å s^{-1}$ on OTS treated SiO_2 (300 nm)/Si substrate. TFTs characteristics were recorded by a Keithley 4200 SCS and Micromanipulator 6150 probe station in a clean and shielded box in air.

Fabrication of single crystal transistors

Single crystal devices were fabricated using the "organic ribbon mask" technique.[1] The channel width is the width of the as grown crystals of DP-BPEA, and the channel length is the width of the ribbon mask.

Material Synthesis

2,6-Dibromoanthracene-9,10-dione and 2,6-diphenylanthracene-9,10-dione was synthesized as we previously reported.

2,6-Diphenyl-9,10-bis(phenylethynyl)anthracene (DP-BPEA). To a 250 mL round-bottom flask containing 100 mL anhydrous THF, ethynylbenzene 2.85 g (27.88 mmol) was added and the stirring system was placed in an ice-water bath, then 7.8 mL (15.6 mmol 2M) *n*-BuLi was added slowly and this mixture was stirred for 1 h at 0 ^{o}C. Then 2,6-diphenylanthracene-9,10-dione 1.8 g (5 mmol) was added quickly, and the mixture was stirred overnight. Stannous chloride dihydrate 2.83 g (12.5 mmol) and 12.5 mL 10% HCl was added to the mixture which was stirred for another 7 h. Then the whole system was extracted with chloroform (60 mL × 3) and the combined organic layer was washed with saturated brine solution, dried over anhydrous Na_2SO_4 and concentrated. The final DP-BPEA was obtained after silica chromatography (eluent: petroleum ether/dichloromethane) with a yield of 56% (1.48 g). ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 8.93 (2 H, s), 8.79 (2 H, d, J = 9.0), 7.98 (2 H, d, J = 9.0), 7.89 (4 H, d, J = 7.7), 7.81 (4 H, d, J = 7.9), 7.55 (4 H, t, J = 7.5), 7.46 (8 H, t, J = 8.0). MS (EI) m/z: 530 (M^+). Anal. calcd for $C_{42}H_{26}$ (%): C: 95.06, H: 4.94. Found: C: 94.79, H: 5.18.

Table S1. Crystal Data and Structure Refinement for *DP-BPEA* (CCDC1526493)

Empirical formula	C42H26
Formula weight	530.63
Temperature	113.0 K
Wavelength	0.71075 Å
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 17.727(13) Å □α = 90° b = 3.932(3) Å □β = 111.119(16)° c = 20.797(15) Å □γ = 90°.
Volume	1352.2(18) $Å^3$
Z	2
Density (calculated)	1.303 mg/m^3
Absorption coefficient	0.074 mm^{-1}
F(000)	556
Crystal size	0.16×0.14 × 0.12 mm^3
Theta range for data collection	3.5° to 27.5°
Index ranges	-22 ≤h≤ 22, -5 ≤k≤ 4, -27≤l≤ 25
Reflections collected	12339
Independent reflections	3057 [R(int) = 0.0889]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.991 and 0.988
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3057 / 0 / 190
Goodness-of-fit on F2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0612,
R indices (all data)	R1 = 0.1023,
Largest diff. peak and hole	0.365 and -0.267 e.$Å^{-3}$

Table S2. Transfer integrals (T) and reorganization energies (R) of BPEA and DP-BPEA along b-axis.

	T (meV)	R (meV)
BPEA	56.2	141.4
DP-BPEA	71.5	128.3

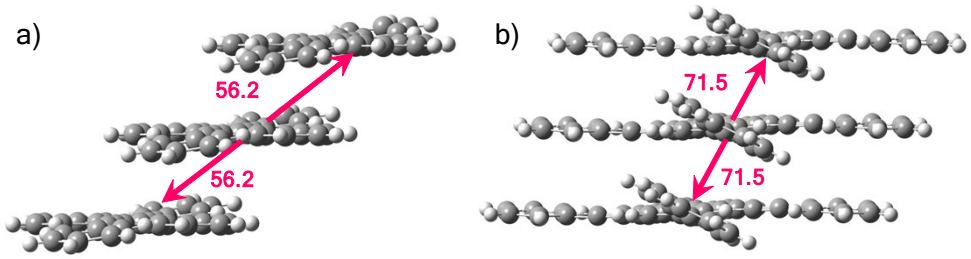

Figure S1 Calculated transfer integrals of BPEA (a) and DP-BPEA (b) along b-axis.

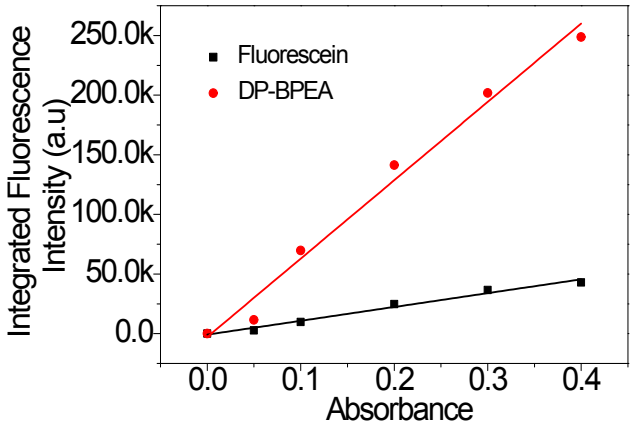

Figure S2. Fluorescent quantum efficiency of DP-BPEA solution. The efficiency of DP-BPEA solution was measured in comparison with fluorescein. THF was used as solvent for the two compounds and the excite wavelength was fixed at 440 nm, ΦF of 79% was reported for fluorescein, and a 5 times stronger fluorescence was obtained for DP-BPEA under the same condition, thus the Φ_F of DP-BPEA was estimated as 100%.

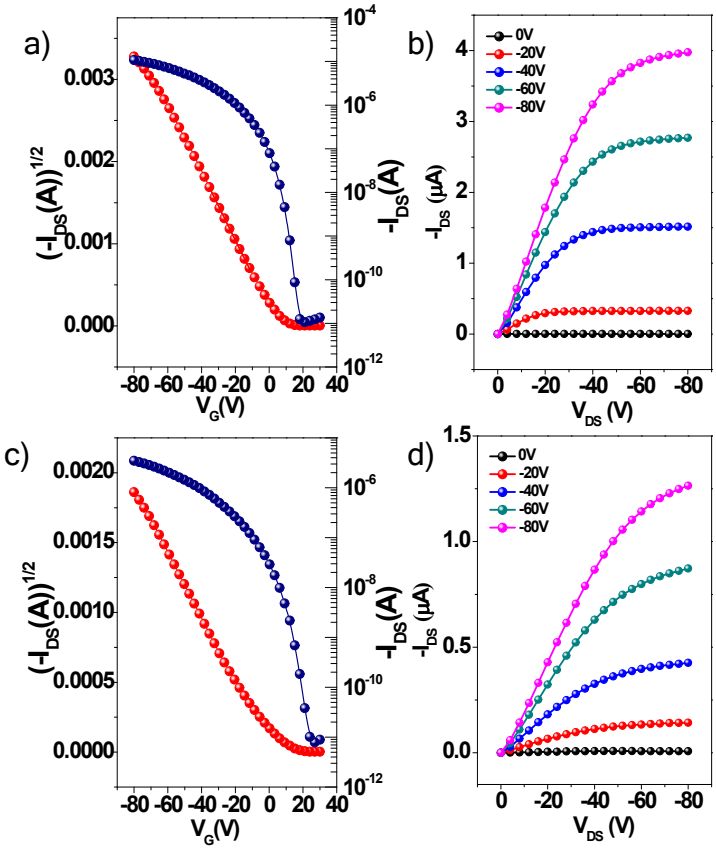

Fig. S3 Transfer and output curves of thin film devices fabricated on OTS-treated (a, b) and bare Si/SiO_2 substrates (c, d).

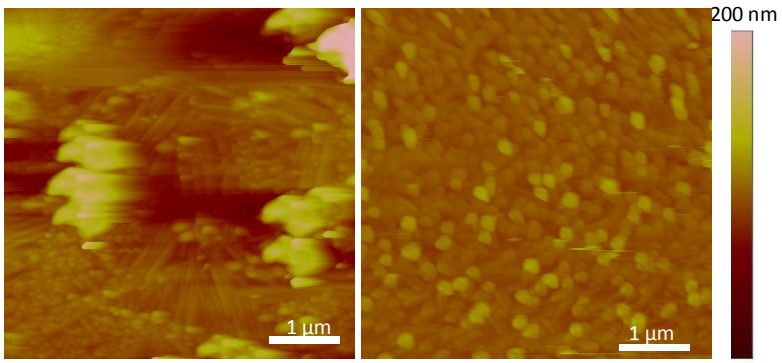

Fig. S4 AFM images of 40-nm DP-BPEA thin films on OTS-treated (left) and bare Si/SiO_2 (right).

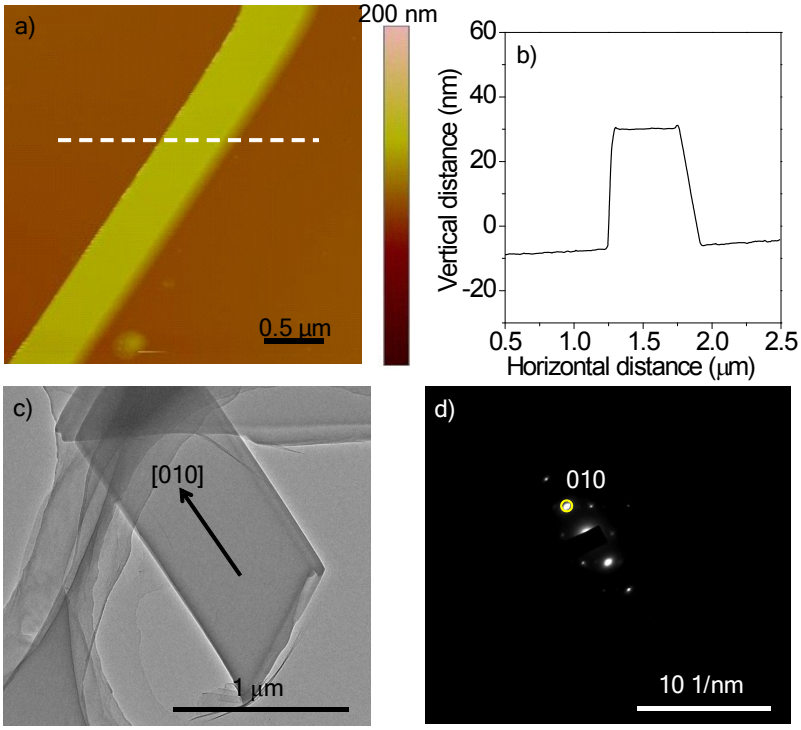

Fig. S5. a) and b) AFM image and heights profile corresponding to the white dot line in a; c) and d) TEM image and corresponding SAED of typical single crystals.

References:

1. L. Jiang, J. H. Gao, E. J. Wang, H. X. Li, Z. H. Wang, W. P. Hu and L. Jiang, *Adv. Mater.*, 2008, **20**, 2735-2740.