Electronic Supplementary Information (ESI)

Self-Assembled Ultrathin Crystalline Polymer Film for High Performance Phototransistors

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Materials and Instruments: The polymer **PQBOC8** used in this work was synthesized according to the literature.[1] Number average molecular weight (M_n) of this polymer is 40.4 kDa and weight average molecular weight (M_w) is 74.7 kDa with a narrow polydispersity of 1.8. P3HT and PBDTTT-C-T were purchased from solarmer materials, Inc. without further purification. The solvent of $CHCl_3$ was purchased from Beijing Chemical Agent Ltd., China and used without further purification. Ultrapure water with a resistivity of 18.2 $M\Omega \cdot cm^{-1}$, produced by using a Milli-Q apparatus (Millipore), was used in all experiments. Transmission electron microscopy (TEM) was performed on a JEM-1011, JEOL operated at 100 kV. The samples were prepared by transferring on a carbon-coated copper grid, and dried under vacuum. The X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu K_α radiation (λ = 1.54050 Å) operated in the 2θ range from 2° to 40° by using the samples transferred onto the SiO_2/Si substrate. UV−vis absorption spectrum was measured on a Shimidazu UV-3600 UV−vis−NIR spectrophotometer. Fluorescence spectrum was recorded by a home-made optical microscopy equipped with a 50 × 0.9NA excitation objective and collected underneath using a liquid-nitrogen-cooled CCD (SPEC-10-400B/LbN, Roper Scientific) attached to a polychromator (Spectropro-550i, Acton). The samples were prepared by dipping onto a cleaned quartz plate, and then dried in oven. Atom force microscopy (AFM) was investigated by Brucker Multimode 8 using tapping-mode with a scan speed of 1Hz. The white light source is an iodine−tungsten lamp with wavelength range from 450 to 750 nm. UV light, blue light and green light are obtained from a xenon lamp through a band-pass filter. The fluorescence decay measured by the ps time-resolved fluorescence spectrometer. The excitation laser pulses (480 nm) were supplied by an optical parametric amplifier, which was pumped by a regenerative amplifier. The detail of the instrument has been described elsewhere.[2]

Fabrication and Characterization of Field-effect Transistors and Phototransistors: The field-effect transistors were fabricated with a bottom-gate top-contact configuration. The substrates were heavily *n*-doped Si wafers covered with 300 nm-thick SiO_2 dielectric (C_i=10 nF cm^{-2}). After cleaned, the substrates were

treated with vaporized octadecyltrichlorosilane (OTS). For spin-coated film transistors, the fabrication process was the same as reported previously. For 2D crystalline film devices, the substrate was dipped in beaker, and then dried in oven at 80℃ to remove water. All devices used gold as source and drain electrodes which thermally evaporated using copper grid as shadow mask. (Channel length =30 μm, channel width = 100 μm). The electrical characteristics were obtained using a Keithly 4200 SCS semiconductor parametric analyzer under ambient condition at room temperature. For phototransistor, light was irradiated on the devices from the semiconductor side. Photoresponsivity (R) and photocurrent/dark-current ratio (P) are important parameters for phototransistor. The R is defined by the following equation:

$$R = \frac{\left(I_{\mathrm{DS,ill}} - I_{\mathrm{DS,dark}}\right)S^{-1}}{P_{\mathrm{inc}}}$$

Where $I_{\mathrm{SD,\,ill}}$ and $I_{\mathrm{DS,\,dark}}$ are the source-drain current under illumination and in dark, respectively. S is the effective area of device. P_{inc} is the power of the incident light per unit area. The P is defined by the following equation:

$$P = \frac{I_{\mathrm{DS,ill}} - I_{\mathrm{DS,dark}}}{I_{\mathrm{DS,dark}}}$$

Where $I_{\mathrm{SD,\,ill}}$ and $I_{\mathrm{DS,\,dark}}$ are the same as previous defined.

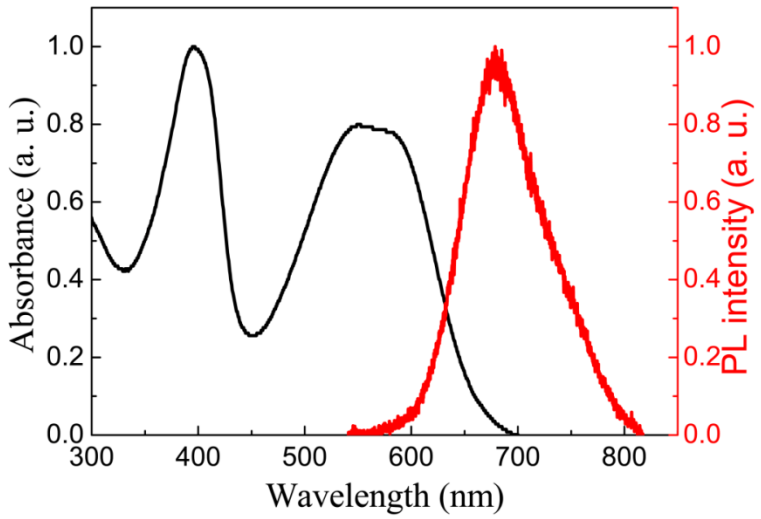

Fig. S1. Absorption and photoluminescence (PL) spectra of **PQBOC8** in solid state.

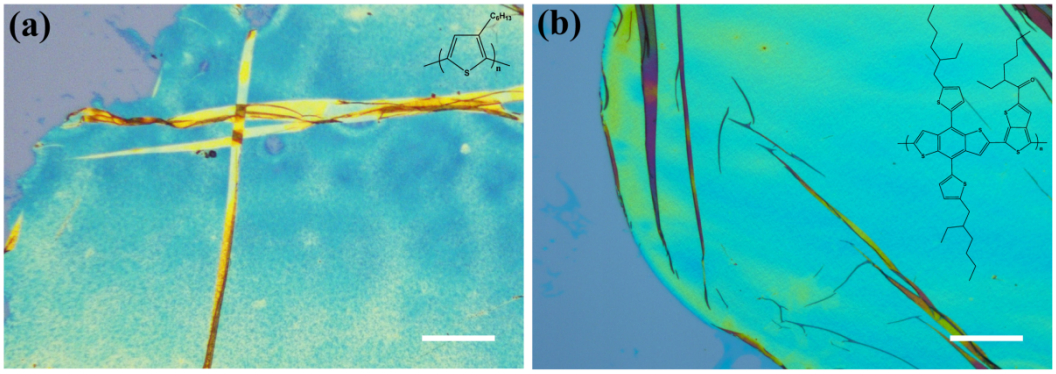

Fig. S2. The 2D films of P3HT (a) and PBDTTT-C-T (b) prepared by $CHCl_3$/water interface method. Scale bars represent 50 μm.

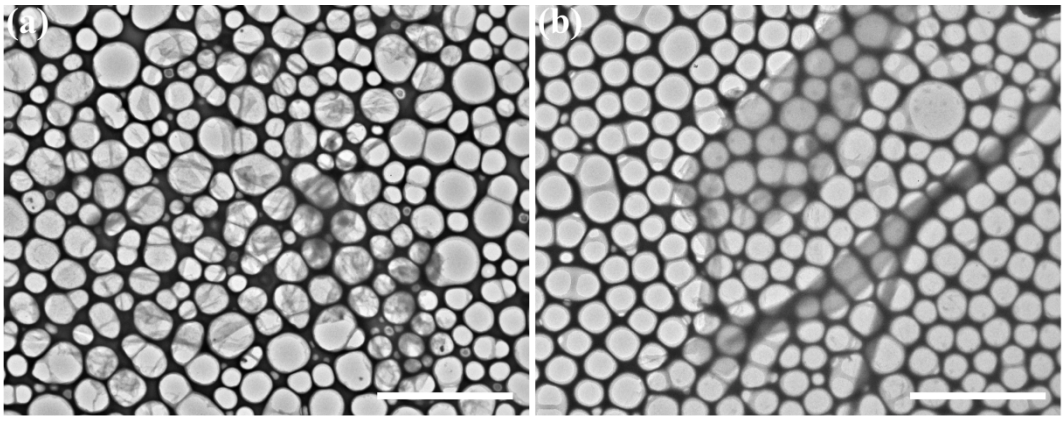

Fig. S3. The growing process of 2D film at the interface of $CHCl_3$/water. (a) before $CHCl_3$ evaporation; (b) after $CHCl_3$ totally evaporation. Scale bars represent 10 μm.

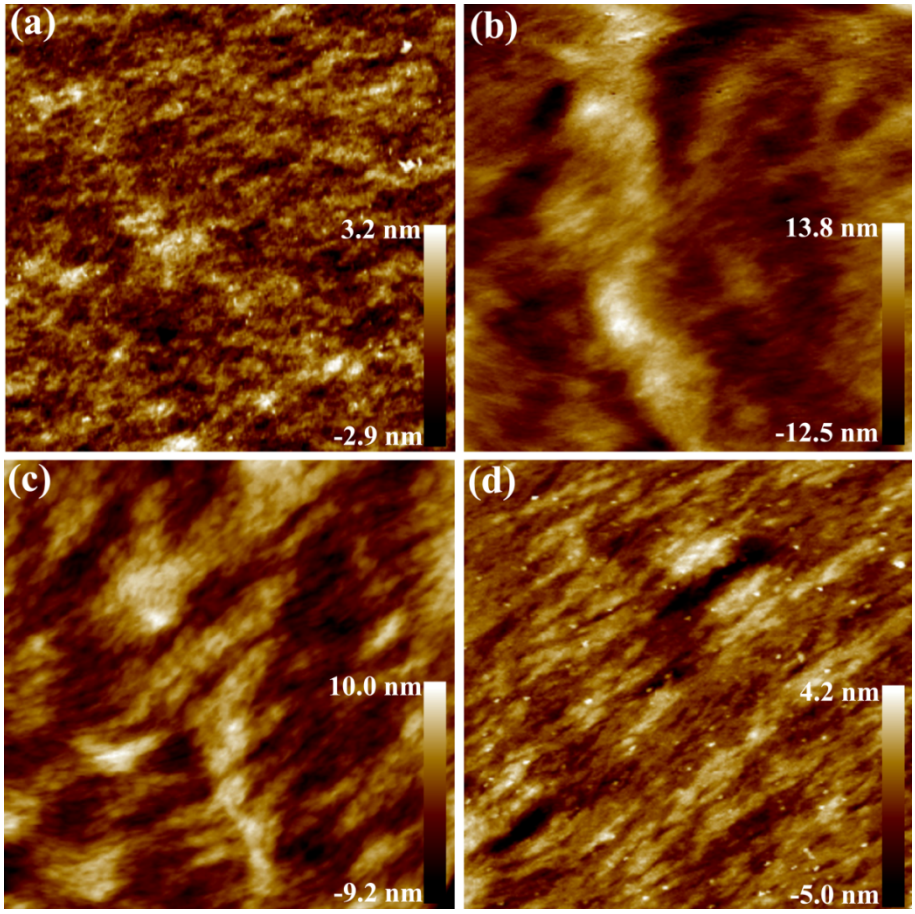

Fig. S4. The AFM height images of 2D crystalline film at the concentration of (a) 0.1 mg mL^{-1}, (b) 0.05 mg mL^{-1}, (c) 0.02 mg mL^{-1}, and (d) 0.005 mg mL^{-1}, respectively, at resolution of 1×1 μm.

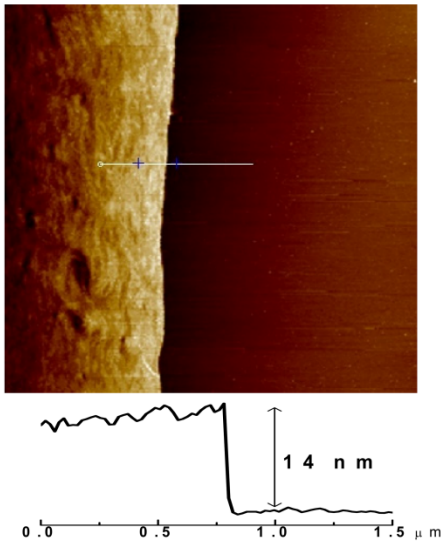

Fig. S5. The AFM height images of 2D crystalline ultrathin film at the concentration of 0.005 mg mL^{-1}.

Table S1. OFET properties of 2D films determined at different thickness.

concentration (mg mL^{-1})	thickness (nm)	mobility (cm^2 V^{-1} s^{-1})	$I_{on/off}$	V_T (V)
0.1	22	0.054	10^6	-10
0.05	19	0.060	10^5	-15
0.02	16	0.046	10^6	-14
0.005	14	0.130	10^7	-14

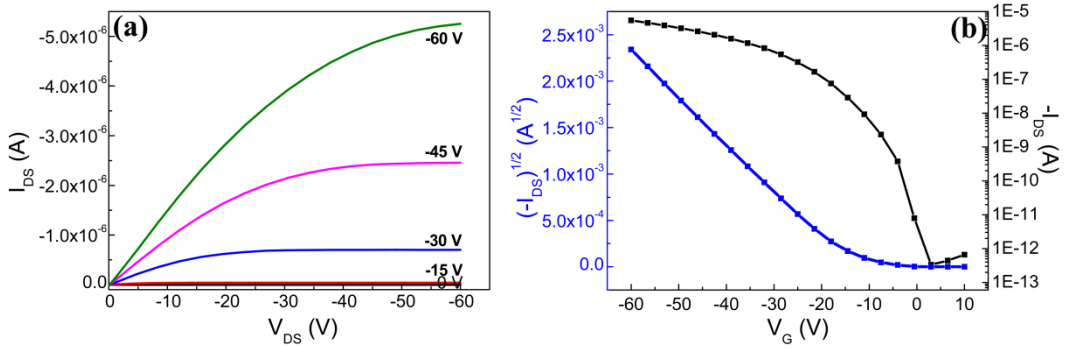

Fig. S6. The output and transfer characteristics of 2D crystalline film at 0.005 mg mL^{-1}.

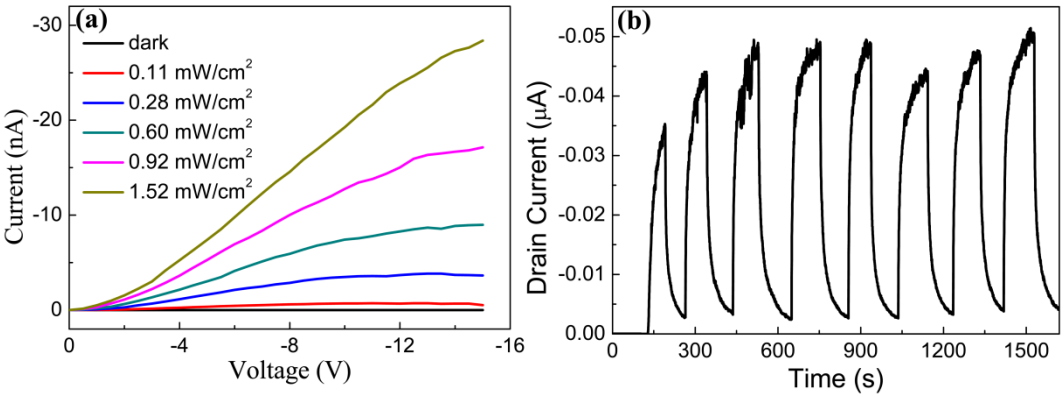

Fig. S7. (a) The output characteristics of 2D crystalline film phototransistor at different light irradiation intensities with a fixed V_G=0 V. (b) The on-off switching behaviors of 2D crystalline film measured at V_G=0 V and V_{DS} = -60 V with white light power density of 0.28 mW cm^{-2}.

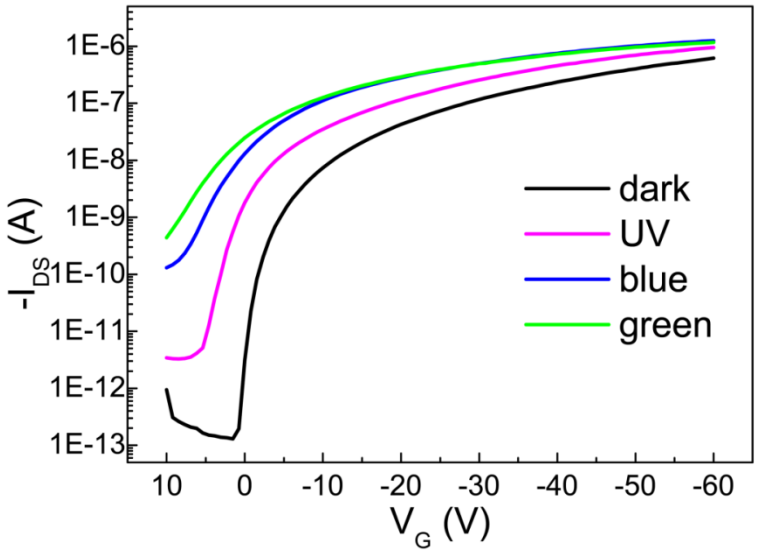

Fig. S8. Transfer characteristics of 2D crystalline film in the dark and under different wavelength light. (The irradiation intensity is 1.38, 0.092, and 0.043 mW cm^{-2} for UV, blue, and green light, respectively.)

Table S2. Phototransistor performances of 2D crystalline film under different wavelength light irradiation.

light source	UV	blue	green
wavelength (nm)	330~350	430~450	540~560
light intensity (mW cm^{-2})	1.38	0.092	0.043
R (A W^{-1})	2.3	454.6	1000
P	5.4×10^{3}	5.0×10^{4}	1.2×10^{5}

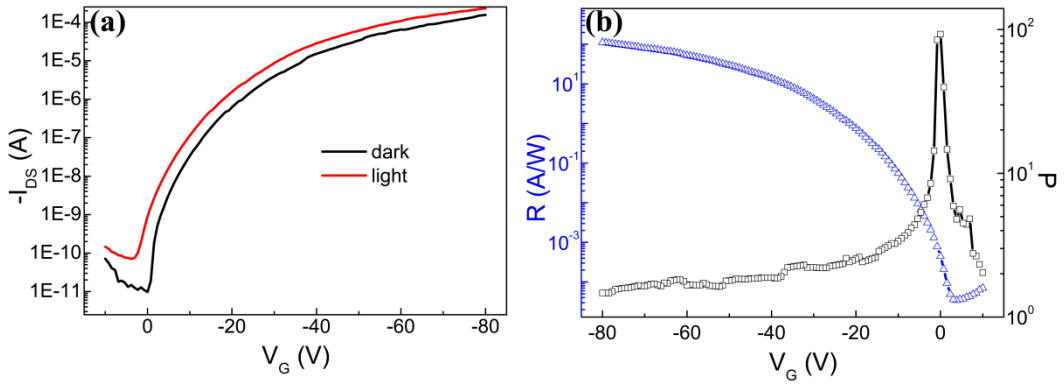

Fig. S9. (a) Transfer characteristic based on spin-coated thin film transistor in the dark and under illumination. (b) Photoresponsivity and photosensitivity under white light power intensity of 0.28 mW cm^{-2}.

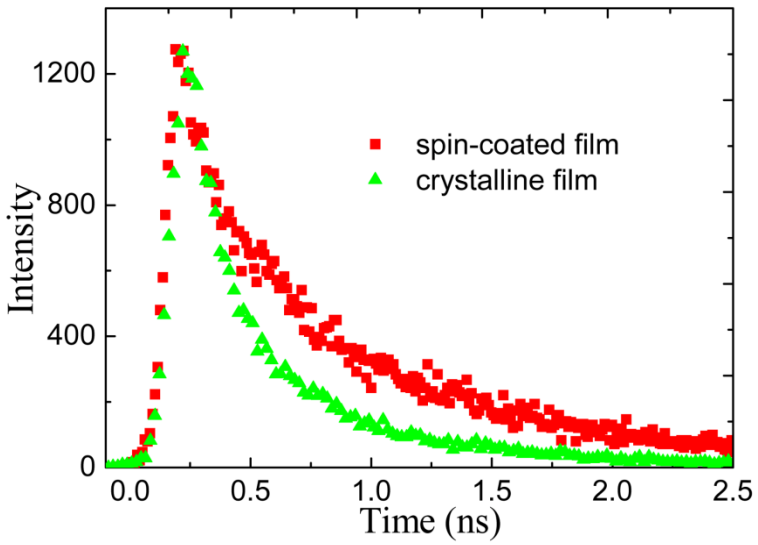

Fig. S10. Time-resolved fluorescence spectra of **PQBOC8** thin film by spin-coated and 2D crystalline film.

For spin-coated film, the apparent time constants are 0.10 ± 0.02 ns and 0.77 ± 0.03 ns with the relative prefactors of 45% and 55%, respectively. For crystalline film, the apparent time constants are 0.11 ± 0.01 ns and 0.56 ± 0.02 ns with the relative prefactors of 72% and 28%, respectively.

1 H. Li, C. Gu, L. Jiang, L. Wei, W. Hu and H. Fu, *J. Mater. Chem. C*, 2013, **1**, 2021-2027.

2 H. Liu, H. Jia, L. Wang, Y. Wu, C. Zhan, H. Fu and J. Yao, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14262-14269.