

Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

## Promoting Phototransistor Performance by Utilizing Solution Epitaxy Templated Organic Semiconductor Films

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### Experimental

#### Materials

Highly n-doped silicon wafers with a 300 nm thermal oxide layer as the dielectric layer ( $C_i=10 \text{ nF}\cdot\text{cm}^2$ ) were chosen as the substrates (purchased from the Si-Mat company). The wafers were ultrasonically cleaned for 15 min with acetone, ethanol, and deionized water in sequence (purchased from Sinopharm Group) and then dried with nitrogen before being put in an oven for 30 min at 80 °C. Organic alkane  $\text{C}_{32}\text{H}_{66}$  (>98%) was purchased from Alfa Aesar company. Chlorobenzene (>99.8%) was purchased from Sigma-Aldrich Chemie GmbH, and the organic semiconductor molecules dif-TES-ADT (>98%) was purchased from Lumtec company. All materials were used directly without further purification.

#### Film deposition and device fabrication

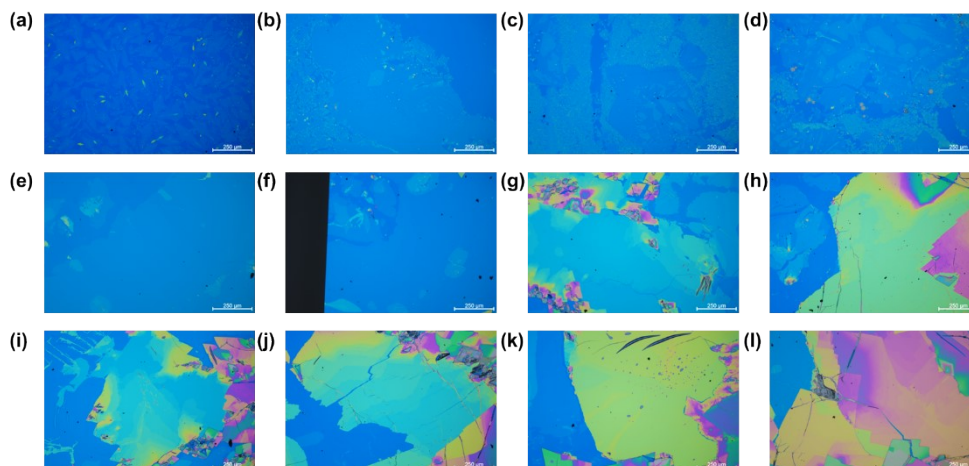
For template layer fabrication, 25 mL deionized water was added into a petri dish, serving as the substrate for crystal growth. As chlorobenzene solution of  $\text{C}_{32}\text{H}_{66}$  with different concentrations was dripped onto still water surface, the solvent rapidly disperses across the water surface due to surface tension. After several hours, as the solvent gradually evaporates,  $\text{C}_{32}\text{H}_{66}$  molecules start to coalesce and form aggregates

through  $\pi$ - $\pi$  interactions, eventually evolving into micron-sized two-dimensional (2D) crystals of organic semiconductors (2DCOS). Keep adding the solution of identical concentration onto the water surface, utilizing micron-sized 2D molecular crystals as “seed crystals” and allow for an extended waiting period of tens of hours to facilitate the gradual epitaxial growth of small 2D OSCs molecular crystals. Upon solvent evaporation, crystals with dimensions ranging from hundreds of microns to even millimeters ultimately obtained. The prepared substrate was inserted at a certain angle just below the crystal on the water surface. As the water slowly evaporates, the crystal gradually falls onto the substrate. Under the action of nitrogen flow, the residual water between the crystal and the substrate is removed, and finally the  $C_{32}H_{66}$  crystal is successfully transferred to the substrate.

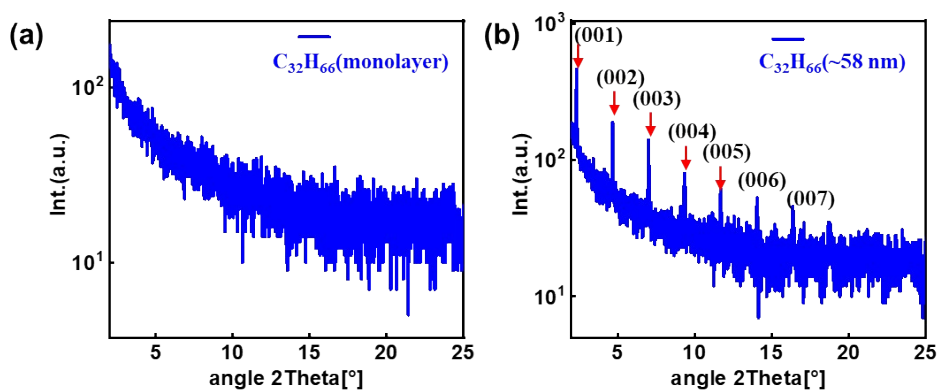
For OFET fabrication, dif-TES-ADT molecules were first deposited on the template layer at room temperature, with a sublimation temperature of 120 °C and a deposition rate of 0.5-1 nm/min using an equipment developed by Shenyang ultra-high vacuum application technology research institute with a vacuum below  $10^{-4}$ - $10^{-5}$  Pa. 40 nm Au electrodes were then deposited on top of dif-TES-ADT films by using thermal evaporator in Glove box (MIKROUNA Company) through a shadow mask with a 50  $\mu$ m channel length.

### **Film and device characterization**

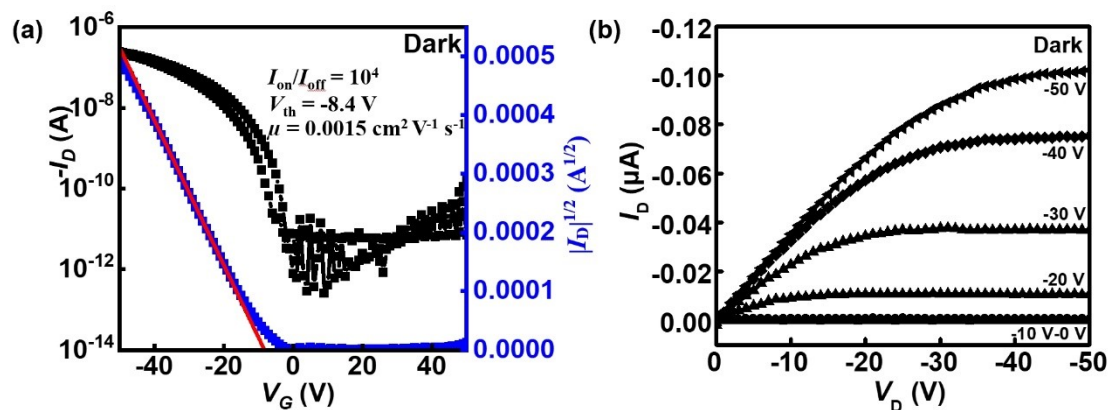
AFM measurements were performed in air by Bruker Dimensional Icon instrument in tapping mode with an  $n^+$ -silicon tip. The XRD patterns were taken in out-of-plane mode with Cu KR radiation ( $\lambda = 1.54056 \text{ \AA}$ ) by using a Bruker D8 Discover (Bruker Instruments) in ambient conditions. The voltage chosen was 40 kV, while the current was set at 40 mA. The selected-area electronic diffraction images were obtained on a FEI TF20 TEM. The UV-vis near-infrared absorption spectra were measured using a Perkin Elmer Lambda 950 spectrophotometer. The electrical and optoelectrical performance of transistors were tested with a 7B Tungsten Probe using a Keithley 4200SCS semiconductor parameter analyser integrated with a high-vacuum probe station (Lake Shore) at room temperature. Monochromatic LEDs of different wavelengths, driven by the commercial illuminant CEAULIGHT CEL-LEDS35, were utilized to illuminate the conductive channels from above. The light power density was measured and calibrated using a PM400 optical power meter from Thorlabs Co., Ltd. The photosensitivity ( $P$ ), photoresponsivity ( $R$ ) and detectivity ( $D^*$ ) of the OPTs were calculated using the following equations, respectively:  $P = I_{\text{ill}} - I_{\text{dark}} / I_{\text{dark}}$ ,  $R = I_{\text{ill}} - I_{\text{dark}} / P_{\text{inc}} A$  and  $D^* = RA^{1/2} (2qI_{\text{dark}})^{-1/2}$ , where  $I_{\text{dark}}$  and  $I_{\text{ill}}$  represent the drain currents measured in the dark and under illumination, respectively, and  $I_{\text{ph}}$  was the difference between  $I_{\text{dark}}$  and  $I_{\text{ill}}$ .  $P_{\text{inc}}$  was the incident light power density, and A was the area of the illuminating channel.



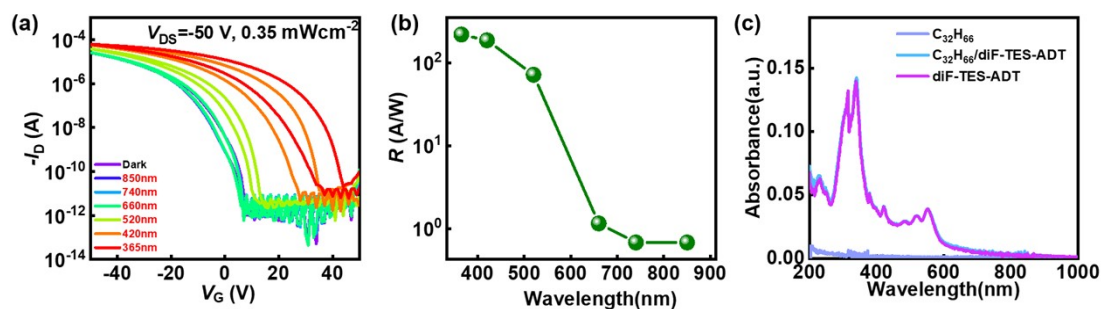
**Fig. S1** Optical micrograph of  $C_{32}H_{66}$  growing on water surface. **(a-d)** Directly drop 25  $\mu$ L solution; **(e-l)**  $C_{32}H_{66}$  films prepared by “solution epitaxy”: **(a, e, i)** 0.5 mg/mL, **(b, f, j)** 1 mg/mL, **(c, g, k)** 1.5 mg/mL, **(d, h, l)** 2 mg/mL. The solvent is chlorobenzene.



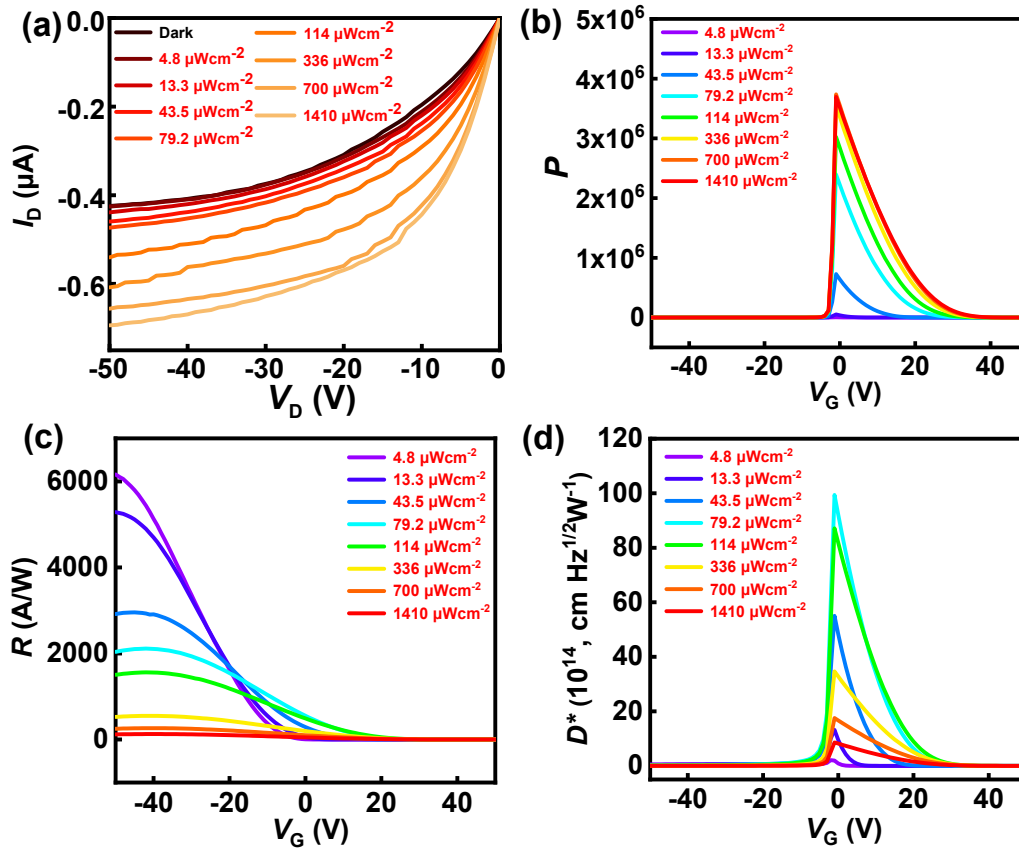
**Fig. S2** Out-of-plane XRD of template layers of  $C_{32}H_{66}$  with different thicknesses: **(a)**  $C_{32}H_{66}$  monolayer; **(b)** 58 nm  $C_{32}H_{66}$  films.



**Fig. S3** (a) transfer and (b) output characteristics of OFETs without  $C_{32}H_{66}$  as the template layer.



**Fig. S4.** (a) The transfer characteristics of diF-TES-ADT OFETs changing with wavelength under a certain illumination power intensity; (b) graph of maximum responsivity of transistors versus incident wavelength. (c) UV-vis absorption spectra of  $C_{32}H_{66}$ , diF-TES-ADT and  $C_{32}H_{66}/diF-TES-ADT$  films.



**Fig. S5** (a) When  $V_G = 0$  V, the output characteristics of OPTs under different illumination power intensity. (b-d) Curves of phototransistor performance parameters changing with gate voltage under different illumination power intensity.