Supporting information

1. Molecular structures of the contents used in the acrylate mixture:

(1) styrene, (2) ethoxylated bisphenol A diacrylate under tradename of SR-349 from Sartomer, (3) 2,2-Dimethoxy-1,2-diphenylethan-1-one under tradename of IRGACURE 651 from from Ciba, now part of BASF.



(1) styrene



(2) ethoxylated bisphenol A diacrylate



(3) 2,2-Dimethoxy-1,2-diphenylethan-1-one

2. Reactions for normal and oxygen-inhibited polymerization processes.

Chemical reactions for an acrylate-based, free radical polymerization process: initiation, polymerization and termination.

Initiation,

 $Initiator \xrightarrow{hv} R \cdot$ (1)

Polymerization,

$$R \cdot + M \longrightarrow RM \cdot \tag{2}$$

 $RM_n \cdot + M \longrightarrow RM_{n+1} \cdot$ (3)

Termination,

$$RM_n \cdot + RM_m \cdot \longrightarrow RM_{m+n}$$
 (4)

Chemical reactions for an oxygen inhibited polymerization process.

$$Initiator \xrightarrow{hv} R \cdot \tag{5}$$

$$R \cdot + O_2 \longrightarrow ROO \cdot \tag{6}$$

$$RM_n \cdot + O_2 \longrightarrow RM_n OO \cdot$$
 (7)

$$ROO \cdot + RM_n OO \cdot \longrightarrow termination$$
 (8)

where ROO• and RMnOO• are not capable of initiating the polymerization process.

The difference between reaction processes on contacted and uncontacted regions with dissolved oxygen in the acrylate mixture under low incident light intensity can be expressed as the following diagram (9),



3. AFM surface profile of acrylate polymer patterns

The surface profile of the patterned acrylate polymer films has been characterized by AFM. The height profile along with an AFM image is shown in Fig. S1a, indicating that the thickness of the polymer film is quite uniform around 200 nm. More noise can be observed on the edge of the polymer pattern due to a sudden change in the surface profile. An SEM image of a separate acrylate polymer pattern is shown in Fig. S1b as additional visual aid of the uniform acrylate polymer film.



Fig. S1 (a) AFM surface profile of a patterned acrylate polymer film, (b) SEM image of a separate patterned acrylate polymer film.

4. Detailed mobility calculation

From the plot of $ID^{1/2}$ -VG, the slope of the plot is estimated to be 0.000166, giving

$$\frac{\partial \sqrt{\mathbf{I}_D}}{\partial V_G} = 0.000166 \, A^{0.5} / V \,.$$

The dimensions of the transistor is measured with a microscope, giving L = 20 µm and W = 200 µm.

The unit area capacitance of PVP dielectric layer is measured by fabricating capacitors with ITO-PVP-Al structure and the result is $C_i = 4.25 \text{ nF/cm}^2$.

According to equation 5 in the manuscript,

$$\mu = \left(0.000166 \, \frac{A^{0.5}}{V}\right)^2 \times \frac{2 \times 20 \, \mu m}{200 \, \mu m} \times \frac{1}{4.25 \times 10^{-9} \, F \, / \, cm^2} = 1.3 \, cm^2 \, / \, V \cdot s \, .$$

The exceptionally high mobility can be attributed to the smooth electrode edge and PVP dielectric known to have high quality interface with pentacene. Four devices were fabricated as a batch, the mobilities for all devices fall in the range of $1 - 1.3 \text{ cm}^2/\text{V} \text{ s}$.

5. Smooth electrode edge

The electrode edge and the pentacene morphology across the edge were studied by AFM and Fig. S2a and S2b show the AFM images of the electrode edge and the pentacene morphology, respectively.



Fig. S2 AFM images of (a) the edge of an electrode and (b) the morphology of pentacene deposited across the electrode edge.

Fig. S2a shows a smooth electrode edge with an estimated roughness in the range of sub-100 nm, which is similar to the grain size of Au and Fig. S2b shows that the pentacene deposited across the electrode edge possesses a uniform morphology, both of which suggest a good pentacene-electrode interface.

6. Device performance of organic transistors on plastic substrates

The fabrication procedure of the OTFTs on plastic substrates is the same as that of the OTFTs on silicon wafers. The ITO-coated PET substrate is used as substrate with ITO being the gate electrode. The device performance shown in Fig. S3 is similar to that of the devices on silicon wafers. The mobility extracted from Fig. S3

is $1.02 \text{ cm}^2/\text{V}$ s using the same calculation procedure in section 4 and the on/off ratio is slightly above 10^3 .



Fig. S3 (a) ID-VD and (b) ID-VG curves as output and transfer characteristics of the device on plastic substrate, respectively.