

Supporting Information

C₆-DPA/PMMA binary blend ink for high-performance inkjet-printed organic field-effect transistors

*Yang Liu,^{#a} Chenhuai Yang,^{#a} Ting Jiang,^b Yuanrong Bao,^a Lu Wang,^a Deyang Ji,^{*b} Fangxu Yang,^a Fei Jiao,^{*a} and Wenping Hu^{a,c}*

^a Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China

^b Institute of Molecular Aggregation Science of Tianjin University, Tianjin 300072, China

^c Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

[#] These authors made an equal contribution to this work

^{} Corresponding author, E-mail: jideyang@tju.edu.cn, feijiao@tju.edu.cn*

Materials:

1,2,4-trichlorobenzene and chlorobenzene were purchased from Aladdin (99%). Mesitylene and 1,2-Dichlorobenzene were purchased from Innochem (99%). PMMA (average molecular weight (M_w):550,000) was bought from Alfa, PMMA (M_w :2,480,000) and PMMA(M_w :350,000) and PMMA(M_w :120,000) were bought from Sigma-Aldrich, PMMA (M_w :35,000) was bought from Acros. C₆-DPA were obtained from Luminescence Technology Corp (99%). All materials were used directly without further purification.

OFETs Device Fabrication and Measurement:

The devices were fabricated on SiO₂/Si substrate (China Electronics Technology Group Corporation), the heavily n-doped Si wafer with 300 nm SiO₂ layer was employed as the gate and dielectric layer, respectively. The substrate was cleaned in deionized water, acetone, and isopropyl alcohol for 10 min sequentially in ultrasonic bath, and then cleaned twice with acetone and isopropyl alcohol for 5 min, respectively. Then the silicon substrate was dried by purity nitrogen flow. Each of the inks was stirred for 1 h on 363K to ensure the solute completely dissolved, and was filtered through a 0.22 μm PTFE syringe filter before filling into a DMPLCP-11610 cartridge. Then the blend ink was deposited on the SiO₂/Si substrate using a material inkjet-printer, DMP-2800 (Dimatix). The jetting voltage was 18V and the printing spacing was set to 25 μm. Then the C₆-DPA film was put into oven and crystallized at 40 °C for 60 min. Finally, silver source/drain electrodes were deposited by thermal evaporation through the 200-mesh shadow mask. The vacuum chamber pressure was 1×10^{-6} mbar, the evaporation rate of Ag (50 nm in thickness) was $0.1 \text{A} \cdot \text{s}^{-1}$. The channel length (L) and width (W) are 35 and 90 μm, respectively. The transfer and output I - V curves of the field-effect transistors were measured using a Keithley 4200 CSC semiconductor parameter analyser in air. The field-effect mobility in saturation region of OFETs was calculated from the transfer I - V based on the following equation, $I_{DS} = W\mu C_i (V_G - V_{th})^2/2L$, where I_{DS} is the source–drain current, W and L represent the width and length of the channel, μ stands for the mobility, V_G and V_{th} refer to the gate and threshold voltages, and C_i is the dielectric geometric capacitance, which is 11 nF/cm².

Characterizations:

All the inkjet printing processes were conducted in ambient air with a Dimatix material inkjet printer, DMP-2800. The surface tension of ink and contact angle measurement were made using an OSA100 optical surface analyser. The viscosity of ink was measured on a Brookfield rheometer. POM images were captured by Nikon Eclipse Ci-POL polarized microscope. AFM images were captured by Intelligent mode using a Bruker Dimension Icon in air. Out-of-plane XRD results were obtained using Rigaku SmartLab X-ray diffractometer with highest power of 9 kW. The UV-vis-NIR absorption spectrum of C₆-DPA was obtained on a Shimadzu UV-3600 Plus spectrophotometer.

Table S1 Physical properties of the solvents used.

Solvent	Molecular Formula	Boiling point(°C)	Flash point(°C)	Viscosity (cP)	Surface tension	Solvent
TCB	C ₆ H ₃ Cl ₃	221	112	2.46	39.9	1.45
O-DCB	C ₆ H ₄ Cl ₂	180	66	1.67	38.2	1.30
Mesitylene	C ₉ H ₁₂	164	43	0.85	25.5	0.86
Toluene	C ₇ H ₈	110	4	0.56	28.7	0.87
CB	C ₆ H ₅ Cl	132	29	0.98	33.6	1.11
DMSO	C ₂ H ₆ OS	189	95	2.71	43.1	1.09

Table S2. Density (ρ), surface tension (γ), Viscosity (η), Z values of inks with different blend ratio.

Blend ratio	4:1	3:1	2:1	1:1	1:2	1:3
(C ₆ -DPA/PMMA)						
(C=4mg/mL)						
ρ [g/mL]	1.45	1.45	1.45	1.45	1.45	1.45
γ [mN/m]	39.90	40.01	39.78	39.94	39.88	40.04
η [cP]	3.19	3.37	3.53	3.64	3.89	4.01
Z	10.94	10.35	9.88	9.58	8.97	8.70

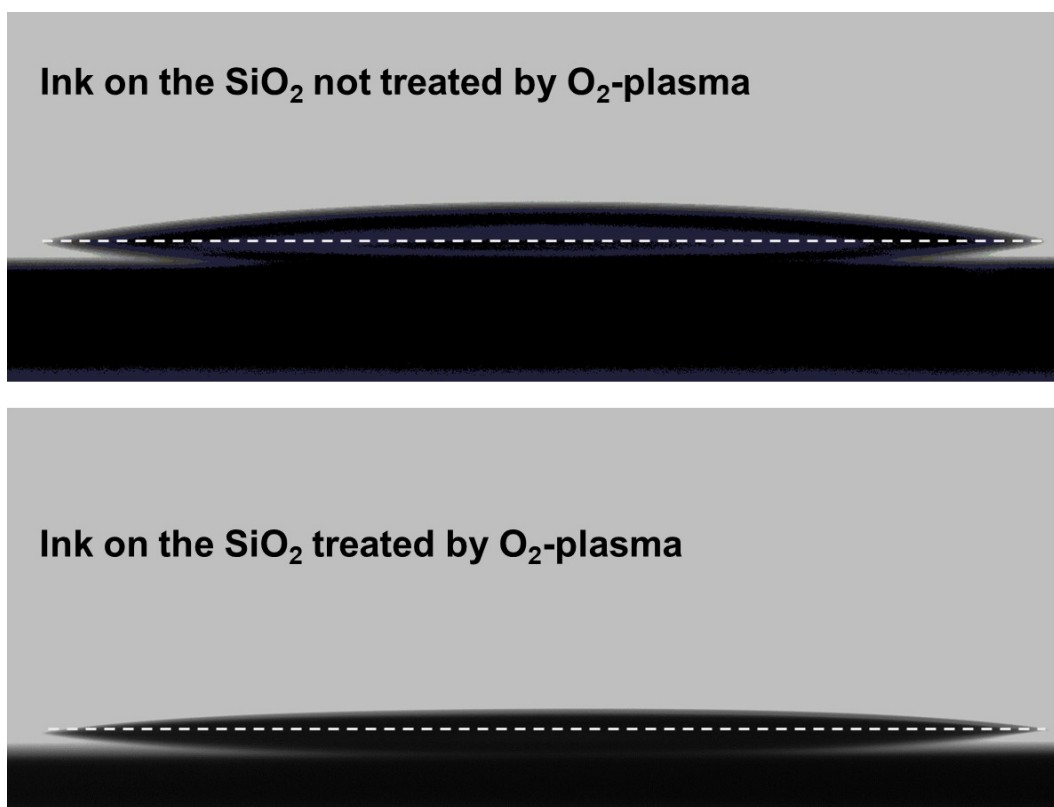


Fig. S1. The contact angle of electronic ink on SiO₂ not treated by O₂-plasma and treated by O₂-plasma, respectively. the dash lines in the figure indicate the boundary of the substrate surface. The ink exhibits better wettability on SiO₂ treated by O₂-plasma.

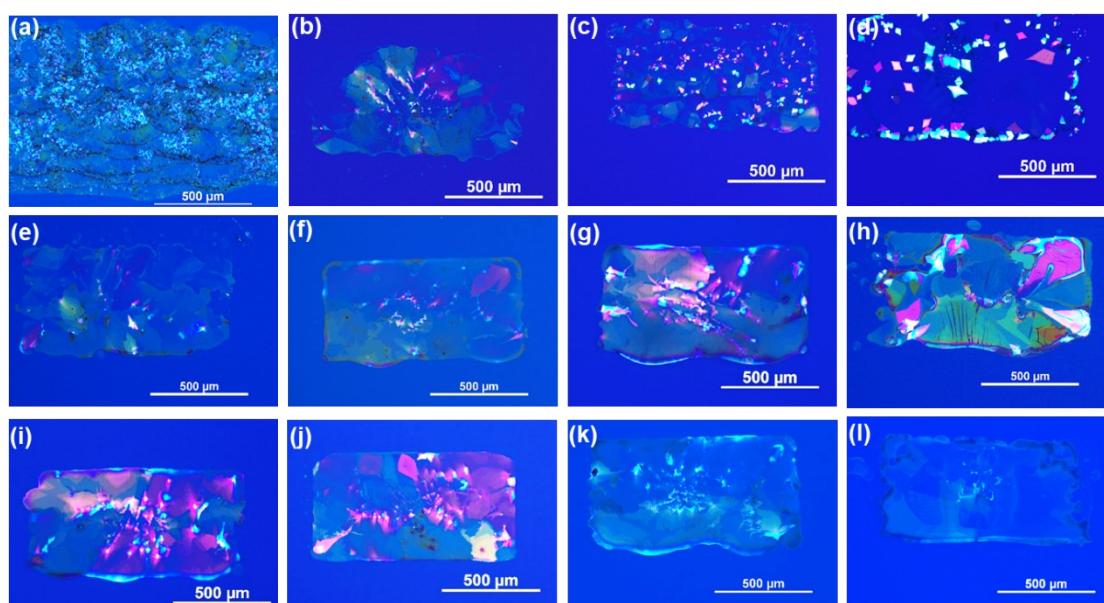


Fig. S2. POM images of the inkjet-printed C₆-DPA thin film in same concentration (4 mg/mL) with 1:1 blend ratio (C₆-DPA/PMMA) and different solvents. (a) CB. (b)

Toluene. (c) o-DCB. (d) Mesitylene. When the above solvent is used, it causes the crystal to have insufficient time to crystallize due to its high boiling point and strong volatility, forming crystal grains or small crystals. POM images of the inkjet-printed C₆-DPA film in different concentration with 1:1 blend ratio (C₆-DPA: PMMA) and TCB as solvent. The existence of coffee ring effect can be clearly seen when the ink concentration $\geq 5 \text{ mg mL}^{-1}$. Most small-molecule OSCs crystallized at the edge of the film, and the crystal was relatively thick. (e) 2 mg mL⁻¹. (f) 3 mg mL⁻¹. (g) 5 mg mL⁻¹. (h) 6 mg mL⁻¹. POM images of the inkjet-printed C₆-DPA film in same concentration (4 mg mL⁻¹) with different blend ratios (C₆-DPA/PMMA) and TCB as solvent. (i)3:1. (j)1:1. (k) 1:2. (l)1:3.

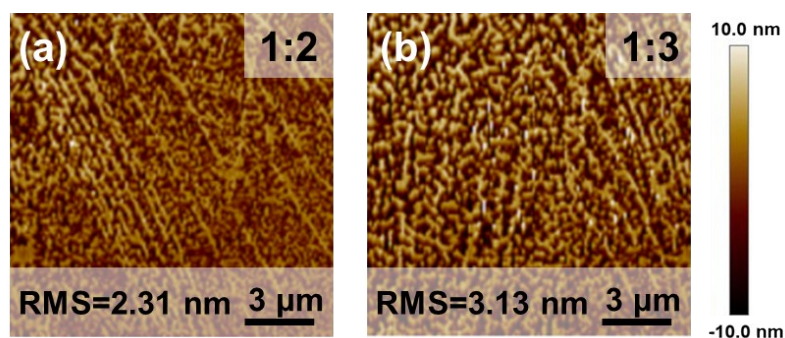


Fig. S3. AFM images of the films based on 1:2 and 1:3 C₆-DPA/PMMA ratios.

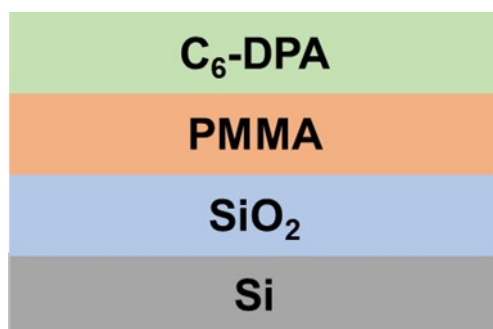


Fig. S4. The schematic diagram of thin film structure.

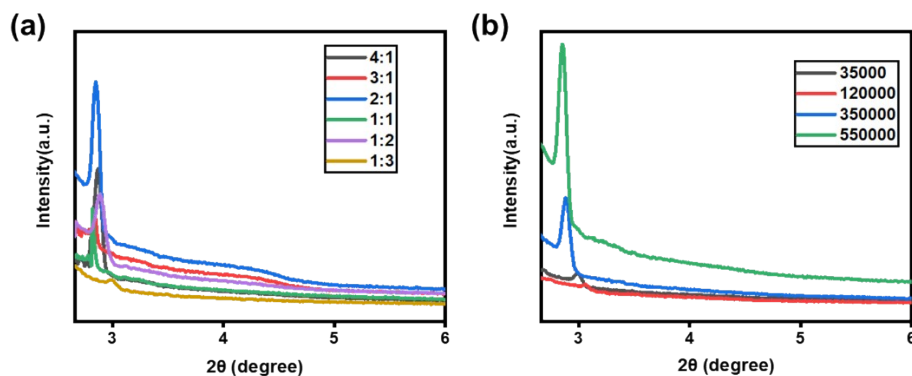


Fig. S5. (a) XRD of the thin films of C_6 -DPA with different blend ratios (C_6 -DPA/PMMA). (b) XRD of the thin films of C_6 -DPA with different molecular weights of PMMA. The intensity of the diffraction peak is positively correlated with the molecular weight of the polymer, however, an ink using a polymer with M_w of 2480000 cannot be printed due to its large viscosity.

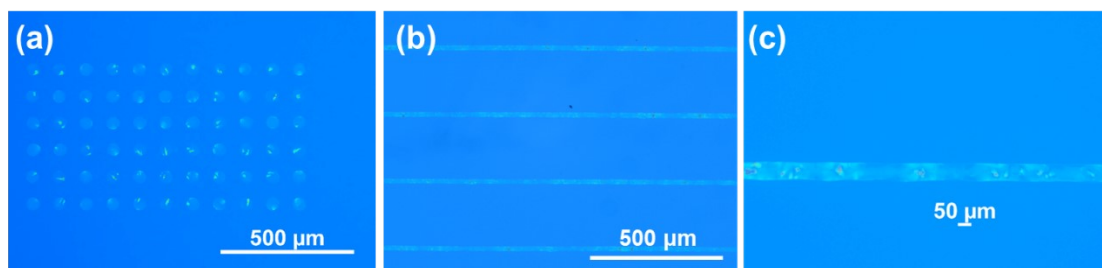


Fig. S6. (a) OM images of inkjet-printed droplets of the blend ink. (b,c) OM images of the printed lines by setting the print spacing to 25 μm .

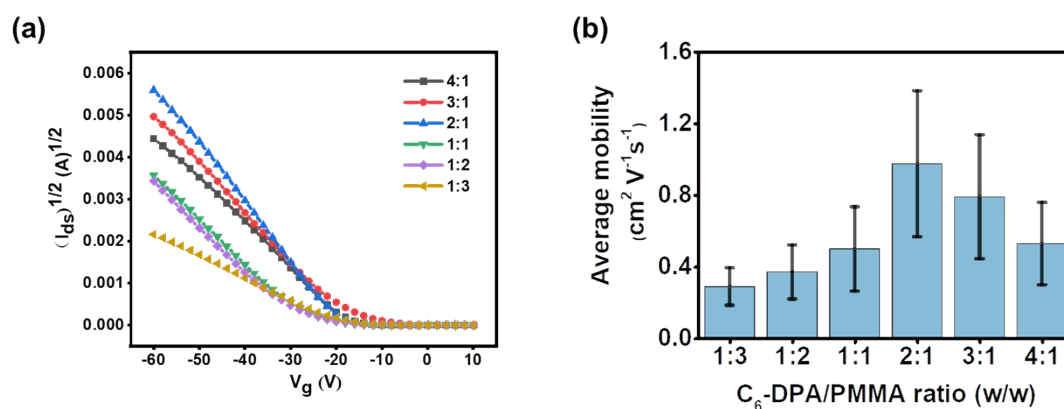


Fig. S7. (a) Transfer characteristics measured for bottom-gate, top-contact transistors with different blend ratios of C_6 -DPA/PMMA (ink concentration is 4 mg mL^{-1}). (b) Field-effect mobility of OFETs with different blend ratios of C_6 -DPA/PMMA (ink concentration is 4 mg mL^{-1}).