

SUPPORTING INFORMATION

Intrinsic and Extrinsic Parameters for Controlling the Growth of Organic Single-Crystalline Nanopillars in Photovoltaics

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Methods

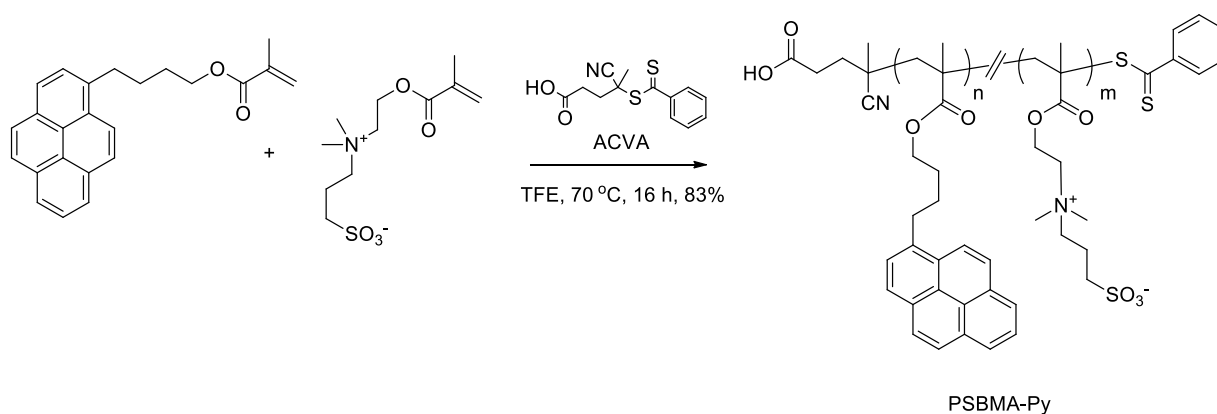
Graphene film. The graphene was synthesized by chemical vapor deposition on copper foil at 1000 °C with methane as the carbon-containing precursor.¹ After growth, the graphene was transferred onto a silicon/silicon oxide substrate for morphology study or ITO glass substrate for OPV characterization. The details of the transfer technique can be found in previous report.¹ Note that it is important to thermal treat the transferred graphene film in inert gas atmosphere before used to further remove any polymer residue introduced during transferring.² Nanoimprint lithography of graphene employed previously described techniques and materials using a polyPFPE perfluoropolyether mold.^{3,4}

Crystallization. The crystallization and growth of organic single-crystalline vertical NPs were performed in a customized organic vapor deposition system with vacuum of 45 mTorr, with substrates positioned 5 cm above the source. The organic semiconductors for crystallization were used without further purification. The graphene film transferred on to silicon wafer (1 cm²) was used as growing substrates. The systematic studies were carried out separately on different samples.

Morphology and crystallographic characterization. Organic NPs were characterized by SEM (Magellan 400 made by FEI). Imaging was typically performed with electron energy of 5 keV. Grazing-incidence X-ray diffraction was performed at the Stanford Synchrotron Radiation Light source on beamline 11-3 with a photon energy of 12.73 keV. The incidence angle of the incident beam was set to 0.1°. The diffraction intensity was detected on a 2D image plate (MAR-345). HRTEM images were taken using a Titan G2 FEI at UCLA.

Fabrication of Patterned Graphene Substrates. The silicon wafer with graphene layer was washed several times using DI water and ethanol. After thorough cleaning and drying, a 180 nm

polyvinylpyrrolidone lift-off layer was spin coated on the graphene. We used 2.6 wt. % of polyvinylpyrrolidone in ethanol as spin coating solution (2500 rpm, 40 sec). The film was dried at 80 °C on a hot plate for 30 sec. A 12.5 wt. % solution of UV curable Norland Optical Adhesive 81 in propylene glycol monomethyl ether acetate (PGMEA) solution was spin coated on the PVP layer (3000 rpm, 45 sec). Immediately after spin coating, the PDMS mold having micro and nano sized pillar / hole features was carefully placed on the spin coated photoresist. The entire assembly was then placed in Nanonex Nanoimprinter (NX2000) for UV nanoimprinting (365 nm) for 3 minutes. Afterwards, the patterned substrate was anisotropically etched with O₂ plasma for 60 sec (Trion Phantom III etcher, 20 mT, ICP 20 W, RIE 35 W, O₂ 35 sccm) to etch thorough the lift-off layer and the graphene, exposing the oxide underneath the graphene. The photoresist was removed by dissolving the lift-off layer in DI water in an ultrasonic bath for 20 minutes. The substrate was then cleaned again with DI water, ethanol and dried under N₂.



Scheme S1. Synthetic route to polymer PSBMA-Py.

PSBMA-Py was synthesized using a standard reversible-addition fragmentation chain-transfer (RAFT) polymerization procedure. 4-(Pyren-1-yl)butyl methacrylate (122.6 mg, 0.358 mmol), [2-(methacryloyloxyethyl)dimethyl-(3-sulfopropyl)ammonium] hydroxide (900.0 mg, 3.222

mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (9.35 mg, 0.0335 mmol), 4,4'-azobis(4-cyanovaleric acid) (0.94 mg, 0.0033 mmol), and 2,2,2-trifluoroethanol (TFE) (2 mL) were combined in a 10 mL round-bottom flask equipped with a septum and degassed for 30 min (nitrogen purging). The reaction mixture was then immersed in an oil bath preheated to 70 °C, sealed, and stirred for 16 h. The polymerization was quenched by immersing the flask in liquid nitrogen, and the reaction mixture was precipitated in acetone. The precipitate was collected by centrifugation, dried, redissolved in TFE, reprecipitated in acetone, and collected by centrifugation. The crude polymer was then redissolved in saline solution and dialyzed (MWCO = 3.5 kDa) against saline (4 h) and water (4 x 4 h), followed by lyophilization to afford **PSBMA-Py** as a light pink solid (732.0 mg, 86% conversion, 83% yield, **PSBMA-Py** contains ca. 10 mol% of the pyrene-based repeat units). GPC (versus PMMA in TFE): M_n = 24.3 kDa, PDI = 1.1. ^1H NMR (300 MHz, 0.2 M NaCl in D_2O) δ (ppm): 0.94 (s, 3H from the polymer backbone); 1.55-4.68 (m, 2H from the polymer backbone, 16H from SB, 8H from pyrene); 8.01 (sb, 9H from pyrene). ^1H NMR (300 MHz, TFE-d_3) δ (ppm): 0.93 (s, 3H from the polymer backbone); 1.39-4.51 (m, 2H from the polymer backbone, 16H from SB, 8H from pyrene); 7.51 (sb, 9H from pyrene).

Single-carrier only device and OPV fabrication. ITO-coated glass substrates were cleaned using ultra sonication in deionized water, detergent, acetone, 2-propanol and ethanol, and then synthesized graphene was transferred. 0.5 mg/ml in 2,2,2-trifluoroethanol (TFE) of PSBMA-Py solution was spin-coated on graphene/ITO with 500 rpm for 5 sec and then 4000 rpm for 55 sec. For ttb-CuPc hole-only device, ttb-CuPc thin film was deposited onto ITO and graphene-coated ITO glass substrates by technique same as employed in the study, followed by capping the device with top electrodes (10 nm of MoO_3 and 100 nm of Al). For C_{60} electron-only device, PSBMA-Py interlayer was spun-coated on ITO or ITO/graphene substrates before deposition of C_{60} from thermal evaporation, finally finishing device with deposition of top electrodes (10 nm of Ca and 100 nm of Ag). For OPV devices, the PSBMA-Py layer-coated substrates were

introduced in a high vacuum chamber ($< 5 \times 10^{-6}$ mbar) for thermal evaporation. 40 nm of the vertically oriented C_{70} layer was deposited with the evaporation rate of 0.4 nm/s while the conventional thin film C_{70} layer was deposited with 0.1 nm/s. C_{70} ($> 99.0\%$) and DBP (98 %) were purchased from American Dye Sources and Sigma Aldrich, and used as received. Total thicknesses and deposition rates were monitored by a quartz crystal microbalance (QCM). The device fabrication was completed with sequential deposition of DBP (15 nm), MoO_3 (10 nm) and Al (100 nm). The completed devices were annealed using a hot plate with 100 °C for 20 min upon nitrogen atmosphere before measurement. The J-V characteristics were measured using a Keithley 4200-SCS unit in ambient under AM 1.5 conditions using a solar simulator consists of a Xe halogen lamp (Newport) calibrated with a Si reference cell. The device area was 0.05 cm².

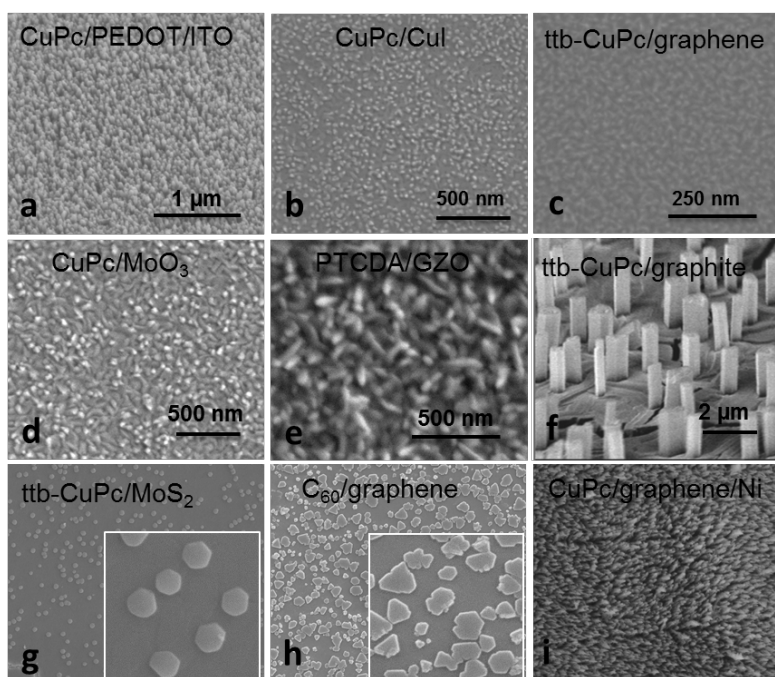


Figure S1 - Surface morphology of organics on common used substrates. (a) CuPc on PEDOT on ITO, (b) CuPc on CuI, (c) ttb-CuPc on graphene, (d) CuPc on MoO_3 , (e) PTCDA on gallium zinc oxide (GZO), (f) ttb-CuPc on graphite, (g) ttb-CuPc on MoS_2 surface, (h) C_{60} on graphene, and (i) CuPc on graphene grown on nickel foil.

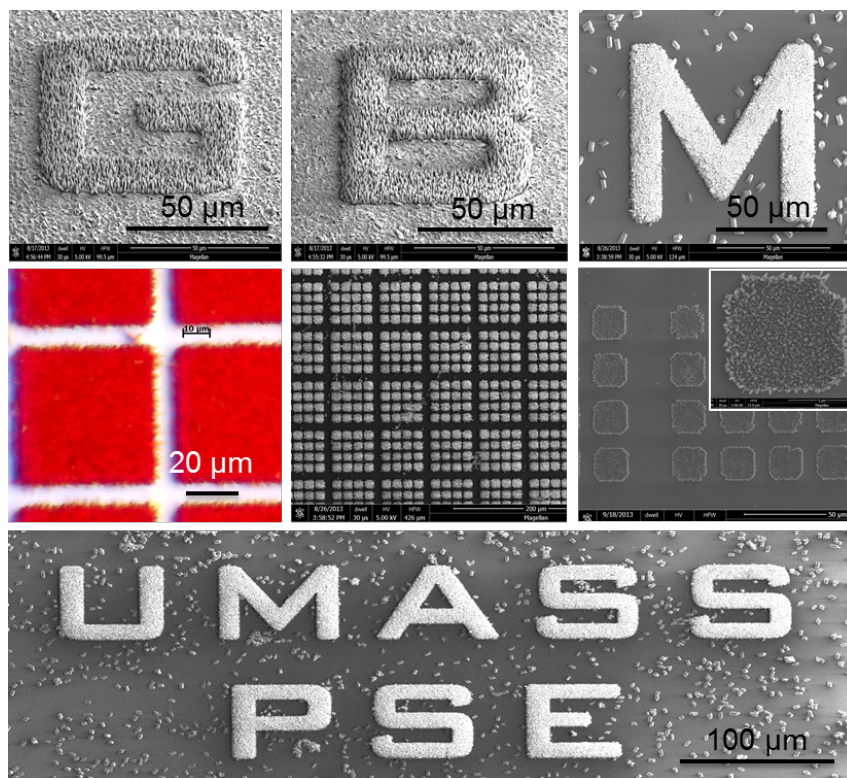


Figure S2 – Additional examples of PTCDA grown on various patterns of graphene.

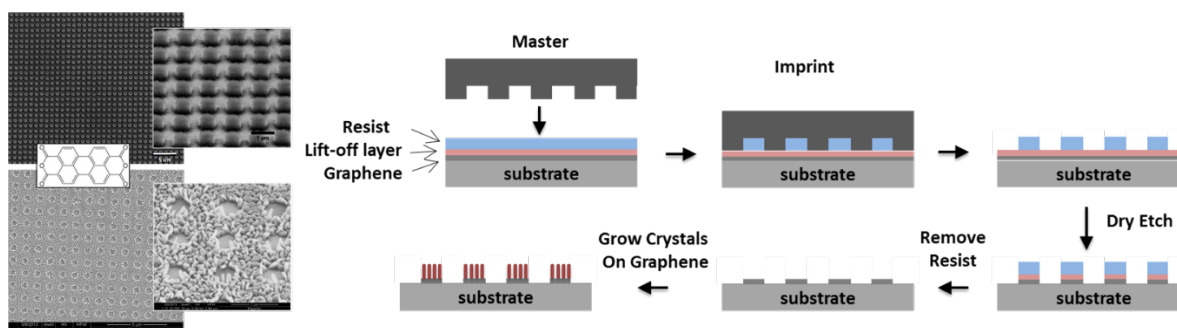


Figure S3 – Process for fabricating patterned domains of graphene for subsequent growth of vertically oriented single-crystalline NPs.

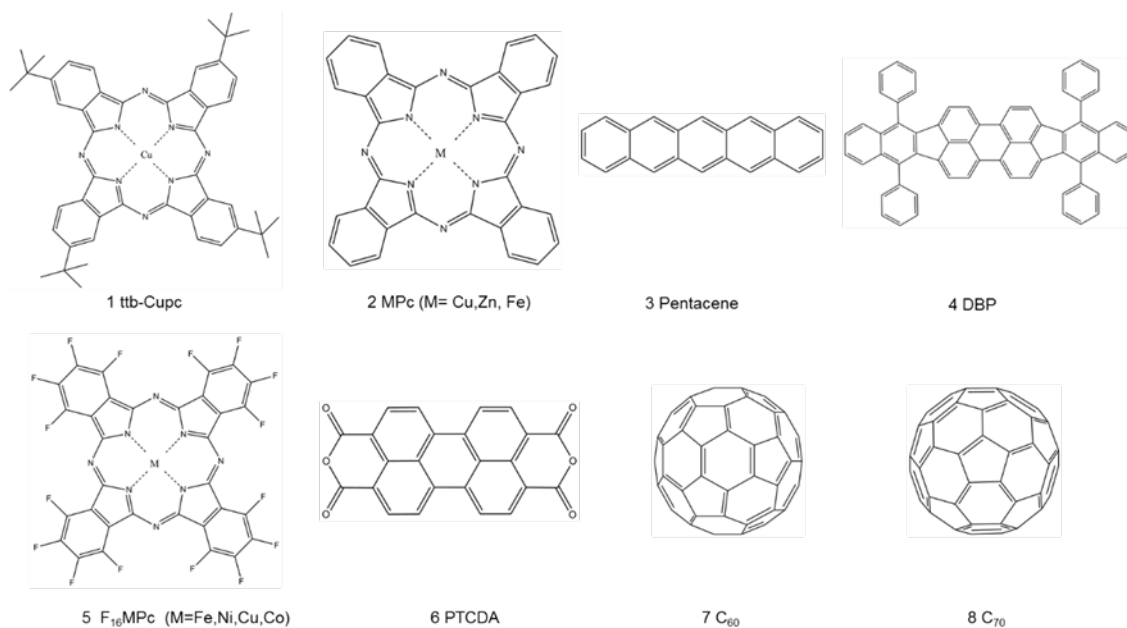


Figure S4- Chemical Structure of molecules studied in this work. *p*-type 1: Copper-tetra-tert-butyl-phthalocyanine (ttb-CuPc), 2: Metal-phthalocyanine (MPc) (M=Cu,Zn,Fe), 3: Pentacene, 4: tetraphenyl dibenzoperiflanthene (DBP). *n*-type 5: Metal-hexadecafluoro-phthalocyanine (F₁₆MPc) (M=Fe,Ni,Cu,Co), 6: Perylene-tetracarboxylic dianhydride (PTCDA), 7: fullerene (C₆₀) and 8: C₇₀.

Table S1- OPV parameters of the best performance devices of ITO/graphene/without or with PSBMA-pyrene interlayer (IL)/C70 (40 nm) thin film (TF) or nanopillar (NP)/DBP (15 nm)/MoO₃ (10 nm)/Al (100 nm). The average values and deviations from 5 devices are written in parentheses.

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
TF, w/o IL	2.50 (2.26±0.24)	0.50 (0.48±0.02)	0.30 (0.28±0.02)	0.34 (0.30±0.04)
NP, w/o IL	3.60 (3.32±0.28)	0.48 (0.45±0.03)	0.34 (0.30±0.04)	0.59 (0.45±0.14)
TF, w/ IL	5.37 (4.92±0.45)	0.84 (0.83±0.01)	0.48 (0.47±0.01)	2.16 (1.92±0.24)
NP, w/ IL	6.24 (5.76±0.48)	0.87 (0.85±0.02)	0.55 (0.51±0.04)	2.85 (2.50±0.35)

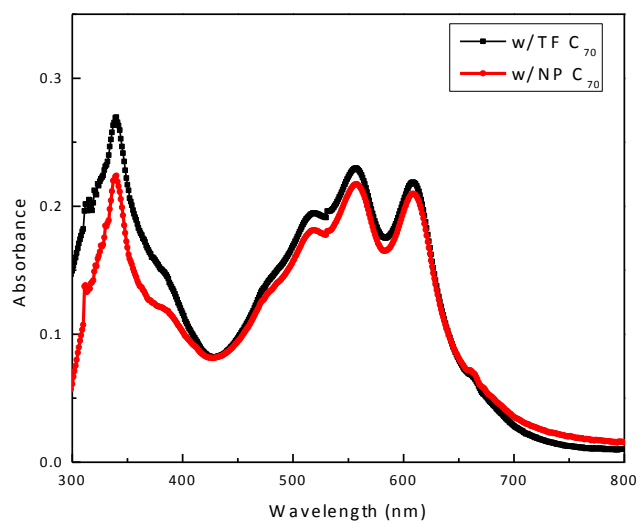


Figure S5-Absorbance of solar cell devices with TF C₇₀ and NP C₇₀.

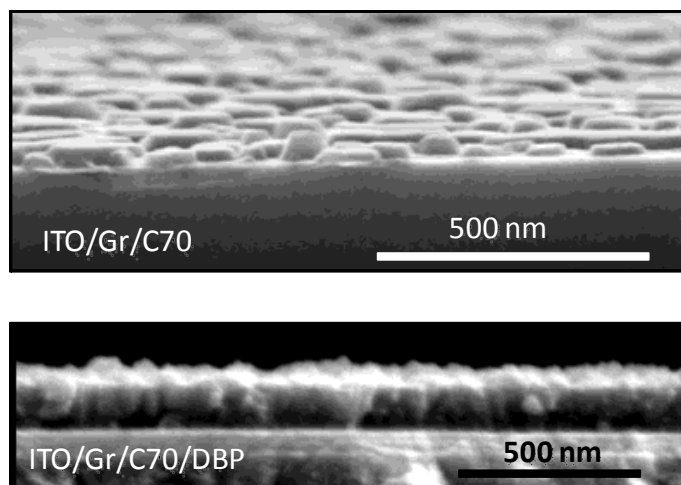


Figure S6-Cross-section SEM of C₇₀ NP (top) and C₇₀/DBP (bottom).

References

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