

Supplementary Information

Face-on stacking and enhanced out-of-plane hole mobility in graphene-templated copper phthalocyanine

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Experimental Methods

AFM and C-AFM

A Veeco Dimension 3100 AFM, Nanoscope V Controller, and Extended TUNA module were used for all atomic force microscope (AFM) and conductive-AFM (C-AFM) measurements. Standard silicon cantilevers were employed for tapping mode imaging (50 N/m nominal spring constant, 350 kHz nominal resonance frequency). Pt-Ir-coated cantilevers (0.2 N/m nominal spring constant, 13 kHz nominal resonance frequency) were used for C-AFM current-voltage measurements with an applied force of 15 nN.

GIXD

Grazing-incidence X-ray diffraction (GIXD) was performed at stations G1 and G2 at the Cornell High Energy Synchrotron Source (CHESS). All GIXD images were background subtracted. GIXD peaks were indexed using methods described elsewhere.¹⁻³ The average tilt angle between the mean plane of the core CuPc atoms and selected planes was calculated using Mercury 3.1 software.

NEXAFS

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy was carried out at the NIST/DOW soft X-ray materials characterization facility at beamline U7A at the National Synchrotron Light Source at Brookhaven National Laboratories. Spectra were pre- and post-edge normalized according to previously published procedures.⁴⁻⁶

To quantify the extent of the orientation of the CuPc by NEXAFS, we first deconvoluted the oriented resonances from the isotropic background by taking the difference between spectra recorded at two different incident angles.⁶⁻⁸ We fit the spectra to a series of Gaussian functions and extracted the integrated intensity associated with the oriented resonances from the pre- and post-edge normalized NEXAFS spectra. Differences between the integrated intensities at different incident X-ray angles provide information on the orientation of the molecules. The ensemble-average molecular orientation can be quantified by the dichroic ratio (*DR*) according to the following equation:⁶⁻⁸

$$DR = \frac{I(90^\circ) - I(0^\circ)}{I(90^\circ) + I(0^\circ)}$$

where $I(\theta)$ represents the integrated intensity of a specific resonance at an X-ray incident angle of θ relative to the substrate surface. We used the C1s to π^* transition at 284.4 eV to calculate the *DR* and extrapolated $I(90^\circ)$ and $I(0^\circ)$ from a fit of integrated intensity versus $\sin^2\theta$ (see Figure S8). $DR > 0$ indicates that the molecules are preferentially oriented upright, $DR < 0$ indicates that the molecule is preferentially oriented parallel to the substrate, and $DR = 0$ indicates a lack of preferential orientation.

Graphene transfer

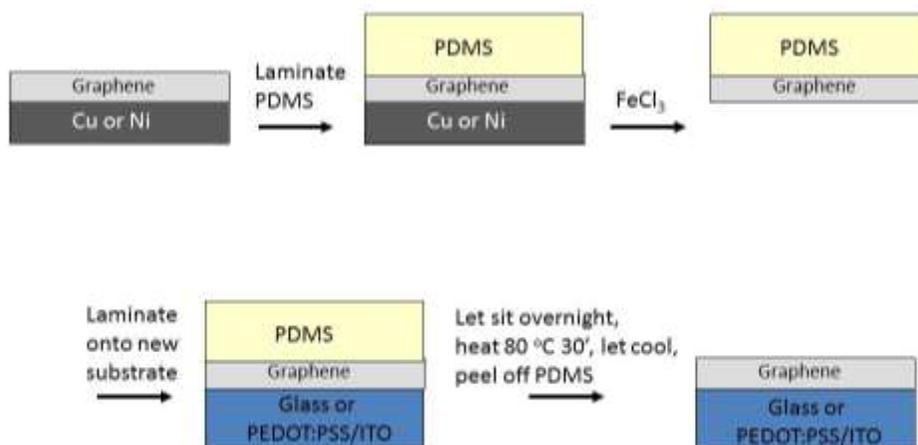


Fig. S1 PDMS transfer: Polydimethylsiloxane (PDMS) elastomer (Dow Corning Sylgard 184) was laminated onto to SLG/Cu or FLG/Ni/Si. The Cu or Ni was then etched in FeCl₃, leaving the graphene attached to the PDMS. The graphene/PDMS was laminated onto glass or PEDOT:PSS/ITO, left to sit overnight, heated for 80 °C for 30 minutes, and left to cool to room temperature. The PDMS was then peeled off, leaving the graphene on the new substrate.

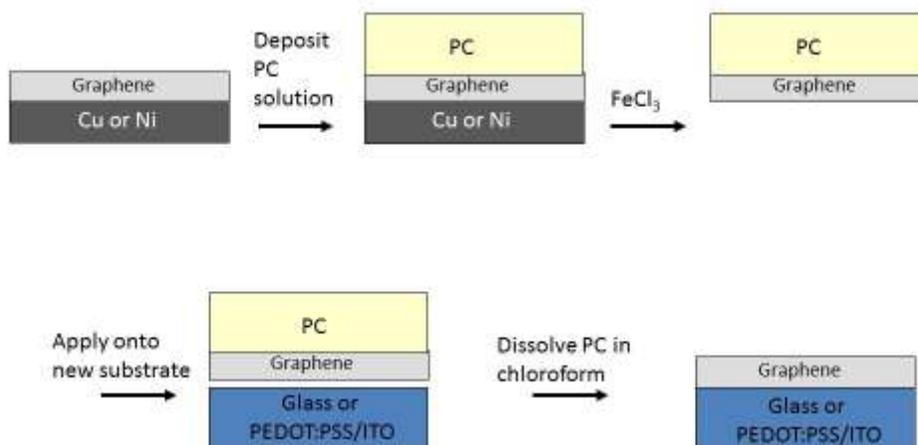


Fig. S2 Polycarbonate transfer: Poly(bisphenol A carbonate) (PC) supplied by Sigma-Aldrich, was dissolved in chloroform at a concentration of 2.5 weight percent. The PC solution was drop-cast onto SLG/Cu or FLG/Ni/Si. The Cu or Ni was then etched in FeCl₃, leaving the graphene attached to the PC. The graphene/PC was placed on top of glass or PEDOT:PSS/ITO and the PC was dissolved in chloroform, leaving the graphene on the new substrate.

Supplementary Data

Transferred graphene morphology

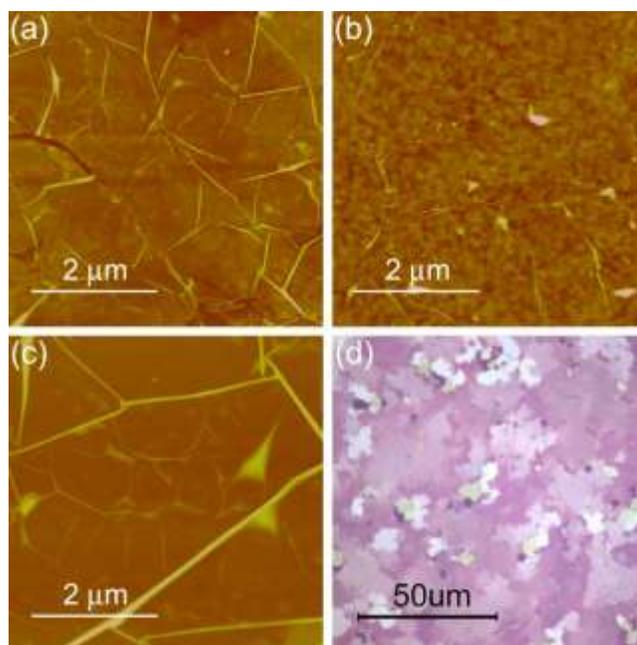


Fig. S3 Atomic force microscope image of SLG transferred onto (a) glass and (b) PEDOT:PSS/ITO (height-range = 50 nm in both images). (c) Atomic force microscope image of FLG transferred onto glass (height-range = 200 nm), and (d) optical micrograph of FLG transferred onto PEDOT:PSS/ITO.

CuPc morphology

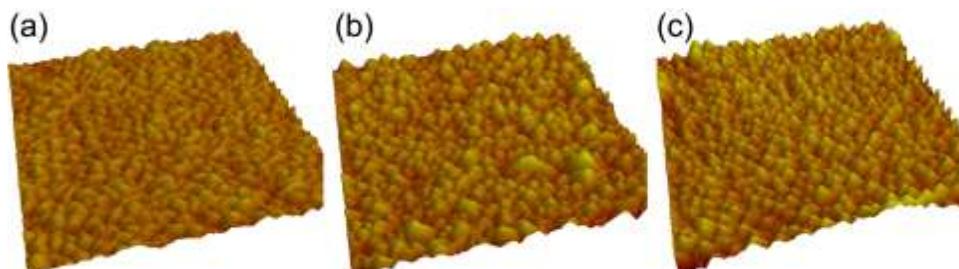


Fig. S4 Atomic force microscope image of CuPc on (a) PEDOT:PSS/ITO, (b) SLG/PEDOT:PSS/ITO, (c) FLG/PEDOT:PSS/ITO. All images 1 μm x 1 μm , 40 nm height.

GIXD

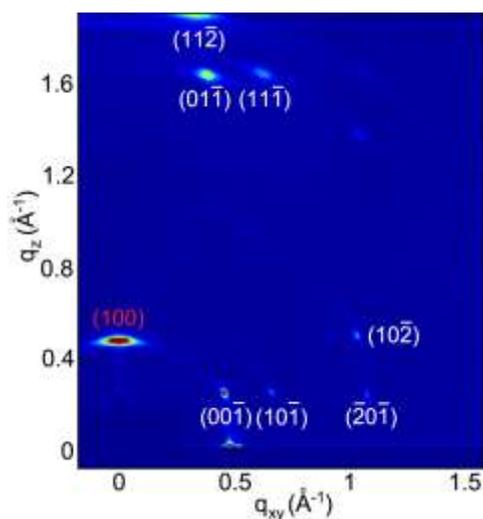


Fig. S5 Grazing incidence X-ray diffraction image for a CuPc film on SLG/glass. The (100) peak, represented in red text, corresponds to (100)-oriented α -phase CuPc; indexed peaks for (01-2)-oriented α -phase CuPc are represented in white text.

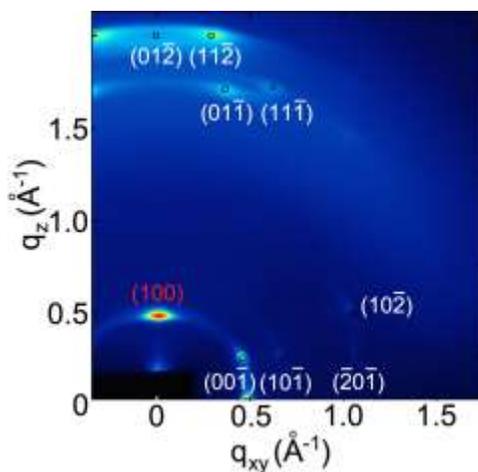


Fig. S6 Grazing-incidence X-ray diffraction image for a CuPc film on FLG/glass, along with simulated peak positions represented by black circles. The (100) peak, represented in red text, corresponds to (100)-oriented α -phase CuPc; indexed peaks for (01-2)-oriented α -phase CuPc are represented in white text.

NEXAFS

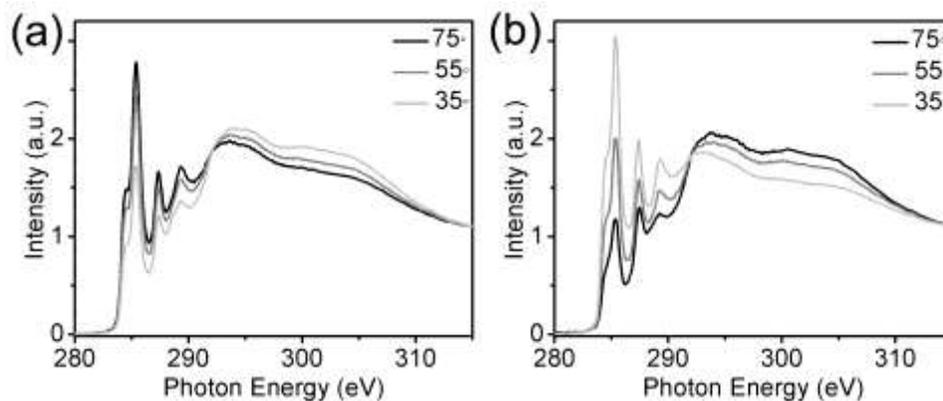


Fig. S7 Near-edge X-ray absorption fine structure spectra collected at three different incident X-ray angles for a CuPc film on (a) PEDOT:PSS/ITO and (b) SLG/PEDOT:PSS/ITO.

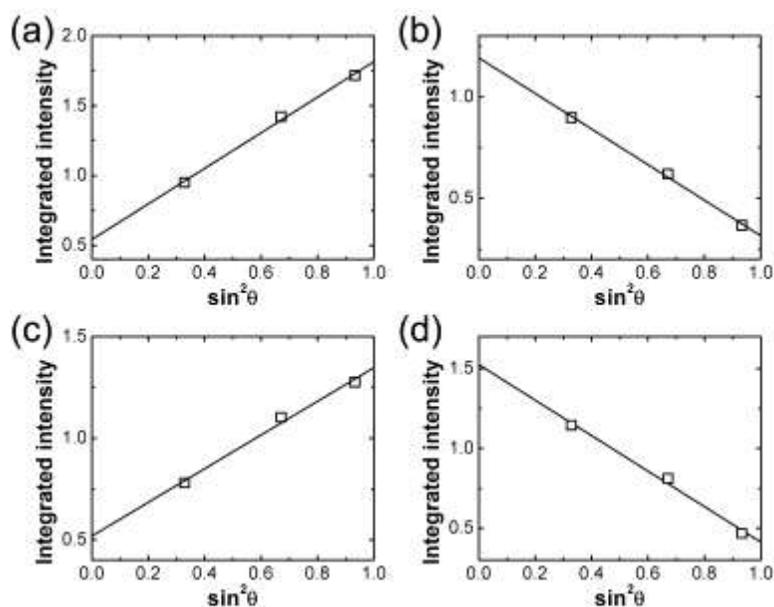


Fig. S8 Integrated intensity of the C1s to π^* transition at 284.4 eV as a function of incident angle for CuPc on (a) glass, (b) SLG/glass, (c) PEDOT:PSS/ITO and (d) SLG/PEDOT:PSS/ITO and the respective linear fits to the data points. A positive slope indicates a preference for edge-on CuPc stacking whereas a negative slope indicates a preference for face-on CuPc stacking.

References

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