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Molecular orientation dependent interfacial dipole at the F$_{16}$CuPc/CuPc organic heterojunction interface

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In situ synchrotron-based near-edge x-ray absorption fine structure measurements and photoemission spectroscopy have been used to investigate the effect of molecular orientation on the interfacial dipole and the energy level alignment at the interfaces of organic heterojunctions comprising copper-hexadecafluoro-phthalocyanine (F$_{16}$CuPc) on both standing-up and lying-down copper(II) phthalocyanine (CuPc) thin films. It is found that F$_{16}$CuPc thin films adopt the same molecular orientation of the underlying CuPc thin films. An interfacial dipole of 0.45 eV forms at the interface of lying-down F$_{16}$CuPc/CuPc on highly ordered pyrolytic graphite. In contrast, a much larger interfacial dipole of 1.35 eV appears at the interface of standing-up F$_{16}$CuPc/CuPc on octane-1-thiol terminated Au(111). © *2008 American Institute of Physics*.
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Energy level alignment and the interfacial dipole formation at the organic-electrode or organic heterojunction interface play key roles in determining the performance of organic electronic devices, including organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells.[1,2] Intensive research efforts have focused on the understanding of electronic structures near organic/inorganic or organic/organic interfaces,[1–4] and the engineering of the interface properties to improve device performance via various surface modification schemes.[5–9] Another important factor that affects device performance is the molecular orientation near the interfaces, which is mainly governed by molecule-substrate interfacial interactions or the electronic structure of substrates.[10,11] Many organic electronic devices such as OLEDs, ambipolar OFETs, or organic solar cells, frequently incorporate multiplicity of tailored organic layers with predefined molecular orientation. However, how the molecular orientation affects the interfacial dipole and the energy level alignment at the organic heterojunction interface is less understood.

In this letter, *in situ* synchrotron-based near-edge x-ray absorption fine structure (NEXAFS) measurements and photoemission spectroscopy (PES) are used to evaluate the effect of molecular orientation on interfacial dipole formation and the energy level alignment at organic heterojunction interfaces comprising copper-hexadecafluoro-phthalocyanine (F$_{16}$CuPc) on copper(II) phthalocyanine (CuPc) with well-defined molecular orientations. Figure 1(a) shows the molecular structures of both molecules. This particular organic heterojunction has promising applications in ambipolar OFETs.[12–14] We report the formation of orientation dependent interfacial dipoles at the F$_{16}$CuPc/CuPc interface.

In situ PES and NEXAFS measurements were carried out at the SINS beamline of the Singapore Synchrotron Light Source.[8,9,15] A monolayer of octane-1-thiol self-assembled monolayer (C8-SAM) was formed by spontaneous adsorp-
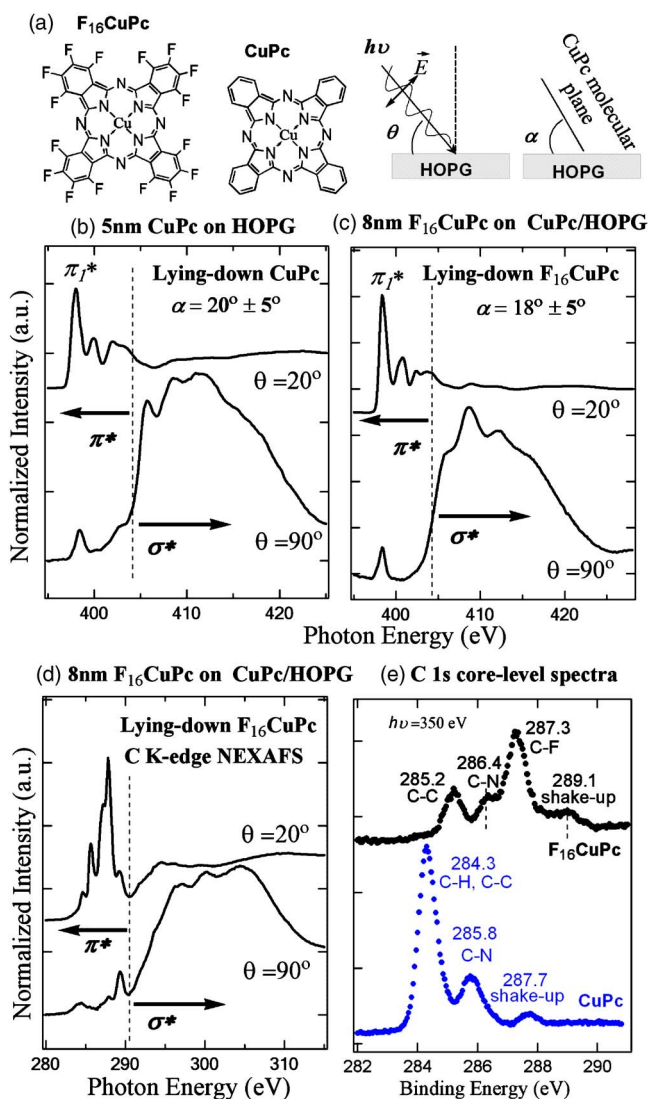
FIG. 1. (Color online) (a) Molecular structure of F$_{16}$CuPc and CuPc. Angle-dependent N *K*-edge NEXAFS spectra for (b) 5 nm CuPc on HOPG, (c) 8 nm F$_{16}$CuPc on CuPc on HOPG, and (d) corresponding C *K*-edge NEXAFS spectra of 8 nm F$_{16}$CuPc on CuPc on HOPG. (e) C 1*s* core-level spectra of 5 nm CuPc on HOPG and 8 nm F$_{16}$CuPc on CuPc on HOPG.

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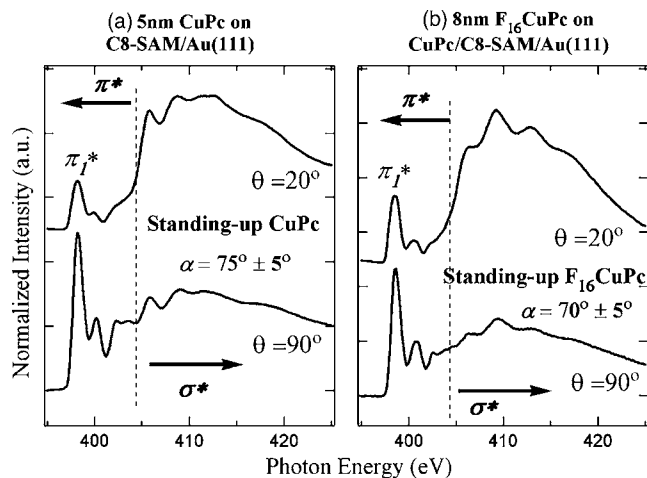
FIG. 2. (a) Angle-dependent N K-edge NEXAFS spectra for the 5 nm CuPc on C8-SAM/Au(111), (b) are the N K-edge NEXAFS spectra after deposition of 8 nm of F_{16}CuPc on CuPc.

tion on Au(111)/mica substrates (SPI, U.S.A.) in 3 ml of 1 mM solution in a N_2 environment for 48 h, using absolute ethanol as the solvent.[16] F_{16}CuPc and CuPc (Sigma-Aldrich) were *in situ* deposited from two K cells in the main analysis chamber of the SINS beamline (for F_{16}CuPc) and the preparation chamber (for CuPc) onto substrates of highly ordered pyrolytic graphite (HOPG) and C8-SAM/Au(111) held at room temperature. Prior to the deposition, F_{16}CuPc was pu-

rified twice via vacuum sublimation (Creaphys GmbH). The deposition rates for both molecules (0.1 nm/min for F_{16}CuPc and 0.2 nm/min for CuPc) were calibrated by monitoring the attenuation of the Au $4f_{7/2}$ peak intensity before and after the deposition on a sputter-cleaned poly-Au sample.[17]

For F_{16}CuPc and CuPc monolayers on HOPG, both molecules adopt the lying-down configuration with their extended π-plane parallel to substrate surface, arising from the directional interfacial π-π interactions between π electrons in HOPG and those in F_{16}CuPc and CuPc.[18,19] Figure 1(b) shows the nitrogen K-edge NEXAFS spectra of 5 nm CuPc on HOPG as a function of the p-polarized synchrotron light incidence angle θ. The first three sharp absorption peaks (397–404 eV) in Fig. 1(b) are assigned to the excitations from N 1s core level to individual π^* states, and the broad absorption peaks at higher photon energy (404–415 eV) are transitions to the σ^* states.[8,9] The intensity I of the π_1^* resonance is related to the tilt angle α of the CuPc molecular plane with respect to the substrate plane and the synchrotron light incidence angle θ by[20]

$$I(\theta) \propto 1 + \frac{1}{2}(3\cos^2\theta - 1)(3\cos^2\alpha - 1).$$

Using the intensity ratio $R(\pi_1^*) = I(90°)/I(20°)$, we estimate the average tilt angle α for 5 nm CuPc on HOPG to be $20° \pm 5°$. Figure 1(c) shows the angle-dependent N K-edge NEXAFS spectra of 8 nm F_{16}CuPc on 5 nm CuPc (lying
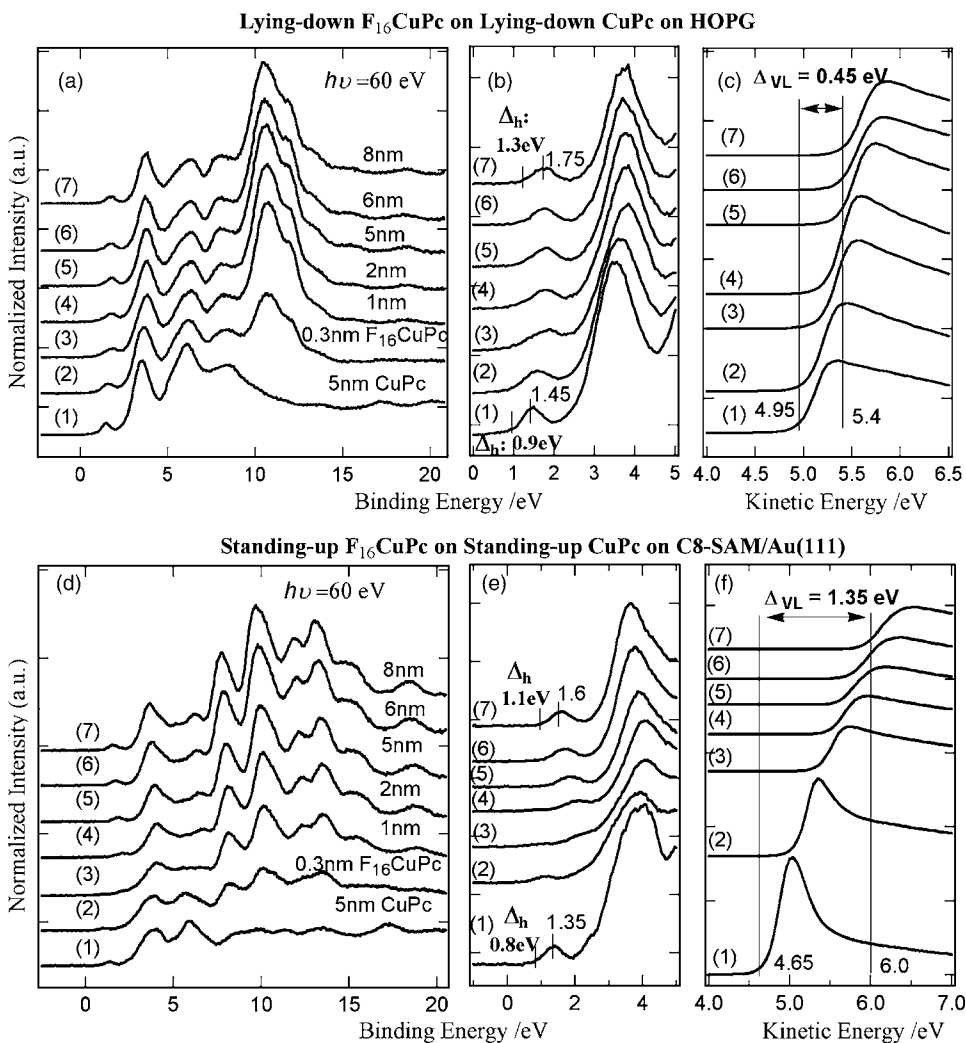
FIG. 3. Synchrotron PES spectra during the deposition of F_{16}CuPc on [(a)–(c)] 5 nm CuPc (lying down) on HOPG and [(d)–(f)] 5 nm CuPc (standing up) on C8-SAM/Au(111): [(a) and (d)] valence band spectra at the low-binding energy part, and [(b) and (e)] corresponding near the E_F region spectra from panels a and d, and [(c) and (f)] PES spectra at the low-kinetic energy part (secondary electron cutoff). All spectra are measured with photon energy of 60 eV. All binding energies are relative to the Fermi level position of the electron analyzer.

down) on HOPG. The average tilt angle α of F16CuPc was estimated to be $18° \pm 5°$, indicating that $F_{16}CuPc$ molecules lie flat on the lying down CuPc thin film. The C K-edge NEXAFS spectra of 8 nm $F_{16}CuPc$ on 5 nm CuPc on HOPG [Fig. 1(d)] shows similar angular dependence, confirming the flat-lying geometry of $F_{16}CuPc$ on the lying-down CuPc thin film. Figure 1(e) shows the C 1s core-level spectra of 5 nm CuPc on HOPG and 8 nm $F_{16}CuPc$ on CuPc, revealing the different carbon species (C–H, C–C, C–N, or C–F) in both molecules.

On Au(111), CuPc adopts a lying down configuration due to the strong interfacial interactions between the metal d bands and conjugated π system (d-π interaction).[8] However, by terminating Au(111) with SAMs, the d-π interface interaction is minimized, causing CuPc to stand up on the substrate.[8,9] Figure 2(a) shows the angle-dependent N K-edge NEXAFS spectra of 5 nm CuPc on C8-SAM/Au(111), clearly revealing the standing-up configuration of CuPc thin film on the passivated Au(111) with average tilt angle α of $75° \pm 5°$. After depositing 8 nm $F_{16}CuPc$ on the standing-up CuPc thin film on C8SAM/Au(111), $F_{16}CuPc$ maintains a similiar standing-up orientation ($\alpha = 70° \pm 5°$) with that of the underlying CuPc, as indicated by the angle-dependent NEXAFS spectra in Fig. 2(b).

The orientation dependent interfacial dipole formation and energy level alignment at the $F_{16}CuPc/CuPc$ interfaces have been investigated by PES. Figure 3 shows the evolution of PES valence band spectra at the low-binding energy region [Figs. 3(a), 3(b), 3(d), and 3(e)] and spectra at the low-kinetic energy region [Figs. 3(c) and 3(f)] after the sequential deposition of $F_{16}CuPc$ on both the lying-down and standing-up CuPc thin films. The hole injection barriers (Δ_h) can be measured from the energy difference between the substrate Fermi level and the highest occupied molecular orbital leading edge (linear extrapolation of the low-binding energy onset),[1–3] and are summarized in Figs. 3(b) and 3(e) for different films.

For 8 nm lying-down $F_{16}CuPc$ on the lying-down CuPc, a work function change (vacuum level shift) by 0.45 ± 0.05 eV is observed, as shown in Fig. 3(c). This work function change most likely originates from the interfacial charge transfer involving electron transfer from the donorlike CuPc layer to the acceptorlike $F_{16}CuPc$ top layer, leading to an electron accumulation layer in $F_{16}CuPc$ and electron depletion layer in CuPc.[3,14] In contrast, a much larger work function change by 1.35 ± 0.05 eV forms at the interface of 8 nm standing-up $F_{16}CuPc$ on the standing-up CuPc thin film, as shown in Fig. 3(f). The work function changes ($\Delta\phi$) at the $F_{16}CuPc$-CuPu interfaces can be understood via the equation $\Delta\phi = n_{pair}\phi_{pair}$, where n_{pair} is the area density of the $F_{16}CuPc$-CuPc charge transfer pairs at the interfaces and ϕ_{pair} is the charge transfer induced by a single $F_{16}CuPc$-CuPc pair. From a simple model, n_{pair} for σ-$F_{16}CuPc$ on σ-CuPc is roughly twice of that for λ-$F_{16}CuPc$ on λ-CuPc, where σ denotes the standing-up configuration and λ represents the lying-down configuration. Such orientation dependence in n_{pair} gives rise to the observation that $\Delta\phi$ at the interface of σ-$F_{16}CuPc$ on σ-CuPc is much larger than that at the interface of λ-$F_{16}CuPc$ on λ-CuPc. The charge transfer (ϕ_{pair}) induced by a single $F_{16}CuPc$-CuPc pair is largely governed by the degree of intermolecular interaction or the molecular orbital coupling between $F_{16}CuPc$ and CuPc. As compared to

the π-π interaction at the interface of λ-$F_{16}CuPc$ on λ-CuPc, the relatively stronger C–F$\cdots$H–C interaction dominates the interface of σ-$F_{16}CuPc$ on σ-CuPc,[21] leading to the larger charge transfer (ϕ_{pair}) of a single $F_{16}CuPc$-CuPc pair, thereby resulting in the orientation dependent work function changes ($\Delta\phi$) observed at the $F_{16}CuPc$-CuPc interfaces.

In conclusion, the molecular orientation of $F_{16}CuPc$ on both standing-up and lying-down CuPc thin films has been investigated by *in situ* NEXAFS. It is found that $F_{16}CuPc$ adopts the same molecular orientation as the underlying CuPc film. *In situ* PES revealed that orientation dependent interfacial dipoles form at the $F_{16}CuPc/CuPc$ interfaces: a small work function change or weak interfacial dipole of 0.45 eV at the interface of the lying-down $F_{16}CuPc/CuPc$, and a much larger interfacial dipole of 1.35 eV at the interface of the standing-up $F_{16}CuPc/CuPc$. This detailed understanding of molecular orientation dependent interfacial dipole formation and energy level alignment at the organic heterojunction interfaces has promising implications in improving the performance of organic electronic devices, in particular, the $F_{16}CuPc/CuPc$ based ambipolar OFETs.

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