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Thickness-Dependent Structural Transitions in Fluorinated Copper-phthalocyanine (F_{16}CuPc) Films

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Small aromatic molecules have emerged as promising candidates for application in organic electronics, because they can be grown in films of high crystalline order, thus, fulfilling one of the key requirements for high charge carrier mobility.[1,2] The detailed knowledge of their film structure is a prerequisite to understand and tailor the transport properties. In particular, the structure and morphology of the first organic layers are known to have a large impact on the charge carrier mobility in organic field effect transistors (OFETs).[2]

The organic molecule F_{16}CuPc (Figure 1a) is receiving increasing attention[3−5] as one of the few molecules that exhibit air-stable n-channel semiconducting behavior.[4a] So far it has been shown that F_{16}CuPc films on SiO_2 form a disordered interfacial layer (of ~6.5 Å) in direct contact with the oxide,[5c] on top of which a well-ordered layered structure is formed.[5] The final layer interspacing concluded from specular X-ray data is 14.3 Å (Figure S1, Supporting Information), evidencing an upright-standing molecular configuration.[5] Although it has been shown that the first layers of upright standing molecules are subject to significant structural relaxations,[5c] the detailed crystal structure of F_{16}CuPc films is still unknown. Instead, the "sister molecule" H_{16}CuPc is often taken as reference.[4]

This work is the first report of the in-plane structure of F_{16}CuPc films, determined from the first monolayer to the multilayer regime by means of in situ grazing incidence X-ray diffraction (GIXD). It discloses a structural transition with thickness, implying large changes in the cofacial stacking of the molecules. The experiments have been performed at the Max Planck Surface Diffraction Beamline of ANKA (Karlsruhe) and at the beamline ID-3 of the ESRF (Grenoble).

Figure 1b shows by GIXD the evolution of the in-plane order in films with increasing thickness (substrate temperature of 195 °C, deposition rate ~3 Å/min.). For the first monolayer (ML), an ordered structure is evidenced by two in-plane reflections that correspond to lattice distances of 14.61 Å ($q = 0.43$ Å^{-1}) and 3.31 Å ($q = 1.90$ Å^{-1}). Because the former is in the range of the lateral molecular dimensions (Figure 1a) and the latter is in the range of the intermolecular spacing between cofacially packed molecules, these peaks have been correlated to the (10) and (01) reflections of a rectangular unit cell, respectively (Figure 1c).[6] This implies that the upright-standing molecules are stacked in columns along the [01] direction, with the molecular planes nearly parallel to the [10] direction. A small tilt angle $\omega = 0°...16°$ may exist between the molecular plane and the [10] direction, depending on the exact molecular orientation, that is, rotation of the molecule around the axis perpendicular to its plane. The formation of this phase is restricted to the first two F_{16}CuPc layers, as evidenced by the saturation in the integrated intensity of the (10) reflection after a nominal thickness of about 2 ML (29 Å). This structure is referred to as β_{bilayer}-structure. With additional coverage, the (01) reflection continues to grow and experiences a shift that implies a contraction of the in-plane lattice parameter b toward a final value of 3.19 Å. The behavior of the integrated Bragg intensity ratio I(01)/I(10) with the film thickness has been analyzed to provide a qualitative explanation of this puzzling structural change of the β_{bilayer}-structure. The very anisotropic molecular structure factor of F_{16}CuPc (Figure 1d) has been exploited to estimate from the ratio I(01)/I(10) the molecular tilt angle ω (Figure 1e). A comparison of the experimentally observed and the calculated I(01)/I(10) ratio for the first 2 ML and for thicker films evidence a reduction in the tilt angle of about 4° upon film growth.[7] Thus, the observed lattice contraction in b is intimately associated with a change in the molecular tilt ω. This calculation has been performed assuming upright standing molecules with their molecular side parallel to the surface (a rotation of the molecule around the normal to the molecular plane leads only to minor changes in the resulting intensity).[8]

Table 1. Unit Cell Parameters for the F_{16}CuPc β_{bilayer}- and β-Structures and the Bulk Structure

	β_{bilayer}	β	bulk[a]
a (Å)	14.61	20.26 ± 0.06	20.018
b (Å)	3.31	4.87 ± 0.04	5.106
γ (deg)	~90	84.1 ± 0.2	90
layer height (Å)	14.1 ± 2.6[b]	14.3 ± 0.05	(14.227)
V/molec (Å^{-3})	682 ± 126	701 ± 7	727

[a] From ref 10, (space group $P2_1/a$, $c = 15.326$, $\beta = 111.83°$) [b] Value taken for the first layer as measured by AFM in ref 5c.

Upon further deposition (above 14 ML), additional Bragg reflections can be distinguished which are related to the growth of a new structure (Figure 1b) referred to as β-structure. The in-plane reflections of this β-structure correspond to an oblique unit cell containing two molecules with the parameters shown in Table 1 (summarizing the β_{bilayer}- and bulk structures). The β-structure consists in columns of cofacially oriented upright-standing molecules with a distance between them of $a/2 = 10.13$ Å. Comparing again the observed lattice spacing of 10.13 Å to the molecular dimensions (Figure 1a), an average tilt angle between the molecular planes and the [10] direction of ~45° is obtained. By analogy to the β-H_{16}CuPc structure,[9] and supported by the presence of two molecules within the unit cell (implying nonequivalent molecular orientations or positions between them), we suggest a configuration of molecules with alternating tilt in adjacent columns (Figure 1f). The columnar stacking has been clearly observed by atomic force microscopy (AFM) on F_{16}CuPc films grown on functionalized SiO_2.[5a] The parameters a, b, and γ, determined from the AFM images, correspond to values of 18.7 Å, 4.5 Å, and 85 degrees,

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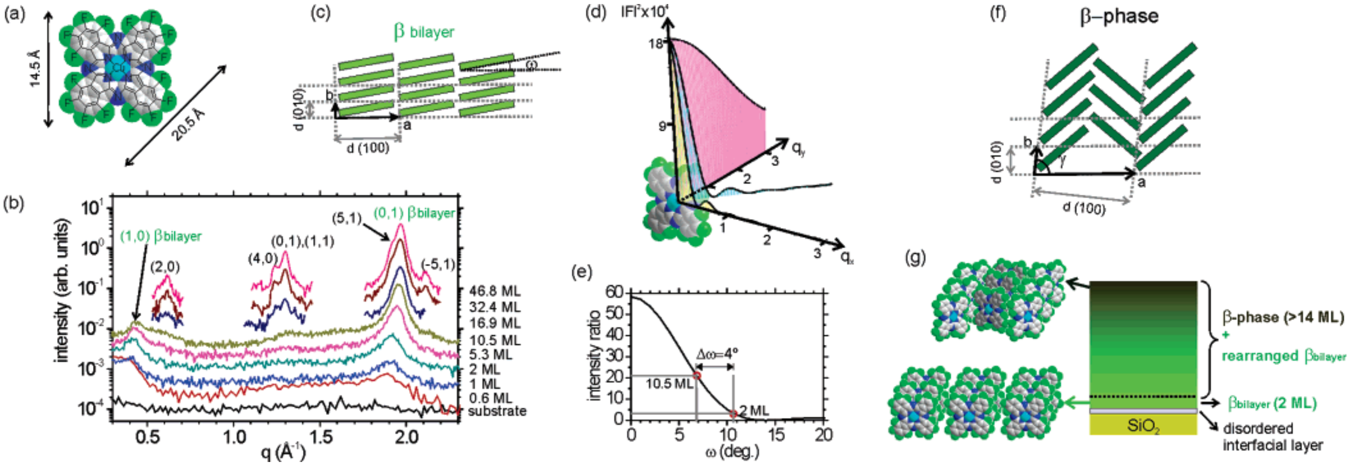

Figure 1. (a) F_{16}CuPc molecule with its dimensions. (b) Evolution of the in-plane structure for increasing coverage. (c) Schematic top-view of the β_{bilayer}-structure (for the first two F_{16}CuPc layers on SiO_2). (d) Squared molecular structure factor along various directions. (e) Ratio between the intensities of the (01) and (10) β_{bilayer}-structure reflections as observed experimentally for different film thicknesses (symbols) and calculated vs the molecular tilt angle ω (line). (f) Schematic top-view of the β-structure. (g) Scheme of the structure of F_{16}CuPc films on SiO_2, including the disordered interfacial film reported in reference 5c.

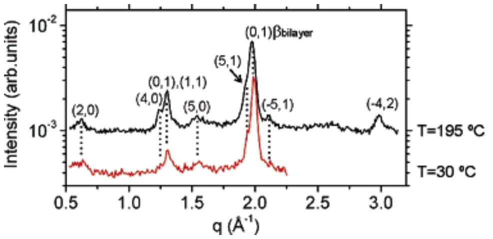

Figure 2. GIXD data for two films grown at 195 °C and at room temperature, with thicknesses of 46.8 and 15 ML, respectively.

respectively, in good agreement with the GIXD structural data (within the AFM error bar of ~10%).

The densities of the β- and β_{bilayer}-structures are rather similar and comparable to that of the bulk structure (see Table 1).

Interestingly, F_{16}CuPc films grown at room temperature exhibit the same structure (Figure 2). This is in strong contrast with the H_{16}CuPc, often considered to be an analogous molecule, which exhibits a metastable α-phase for room-temperature deposition.[11]

In conclusion, the detailed structure of F_{16}CuPc films grown on SiO_2 has been determined by means of in-situ X-ray diffraction, from the first monolayer to thicker films. In contrast to the homologous H_{16}CuPc molecule, the F_{16}CuPc films exhibit the same structure independently from the deposition temperature. We have disclosed a thickness-dependent polymorphism uniquely manifested in the in-plane crystal structure, which implies large differences in the molecular tilt within the cofacial stacking of the molecules (Figure 1g). These structural differences are expected to strongly affect the overlapping of the molecular π-orbitals and thus have important implications in the charge transport of F_{16}CuPc OFETs.

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Supporting Information Available: Specular X-ray data and sample preparation conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) A rectangular unit cell is assumed because the exact angle can not be definitely concluded from only two reflections. The broadness of the reflections indicates a rather low crystallinity of the β_{bilayer}-structure with a correlation length of ~120 Å.

(7) The X-ray intensities have been corrected for the polarization factor. Debye Waller factor (DWF) corrections are estimated to be rather small for these low-order reflections: The thermal DWF (associated with a bulk Debye temperature of 199 K (Bell, N. A.; Brooks, J. S.; Robinson, J. K.; Thorpe, S. C. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3155−3159)) results by way of example into $\exp(-2M) = 0.99$ for the (01) reflection.

(8) Notice that deviations from the assumed rectangular unit cell, or a molecular tilt with respect to the surface normal, could slightly change the absolute values of ω, but would still lead to a similar reduction of the tilt angle.

(9) The analogy to the structure is suggested by the similar anisotropic morphology of F_{16}CuPc and β-H_{16}CuPc.

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