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The molecular orientation of the first layers and thin films of differently substituted phthalocyanines on gold substrates is compared. Due to a relatively strong molecule-substrate interaction the orientation is parallel to the sample surface

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for all materials in the first layers. At higher film thickness the orientation is determined by the substituents. Materials with short substituents prefer standing orientation, implying the substituents do not inhibit the intermolecular interactions. Molecules with long substituents are not able to build up the same aggregates, they grow disordered in the upper layers.

Keywords: metal-organic interface; molecular orientation; organic semiconductors; phthalocyanines

INTRODUCTION

In recent years organic semiconducting thin films have become increasingly important for applications in optical and electronic devices such as light emitting diodes or field effect transistors (see, e.g., [1,2]). It has been shown that the ordering and orientation of organic molecules is crucial for device efficiency due to the anisotropy of the transport properties [3,4].

The family of Phthalocyanines is a model system for the entire class of low molecular weight organic molecules and one of the most promising candidates for a variety of applications [5,6] due to their electronic and optical properties, flexibility in functional group substitution, and the very high degree of orientation [7–12] even on ill defined technically relevant substrates [11–13]. In particular the orientation of the interfacial layer may not only affect the charge carrier injection (e.g., due to the overlap of wavefunctions of the metal and the organic molecule [14,15]) but also electronic properties such as the interface dipole for organic polar molecules [16]. In order to access easier coating techniques, efforts have been made to synthesise phthalocyanines with lipophilic substituents for improved solubility [17–19]. These substitutions may significantly affect the molecular orientation and/or the electronic properties of the corresponding interface, e.g., due to altered molecular interactions [20]. In thin films of 10–20 nm thickness of substituted and unsubstituted phthalocyanines a perpendicular molecular orientation has been found [11,12]. Furthermore it has been shown that directly at the interface it may be different. The growth mode depends on the molecule-molecule and the molecule-substrate interactions [13,21].

Long side chains are expected to reduce the degree of order. Optical absorption studies show a weakened π interaction of the aromatic frames of such molecules. In a series of 1–4-alkyl substituted zinc phthalocyanines with chain lengths from zero to ten carbon atoms the spectra show a split Q-band due to aggregation in the solid state.

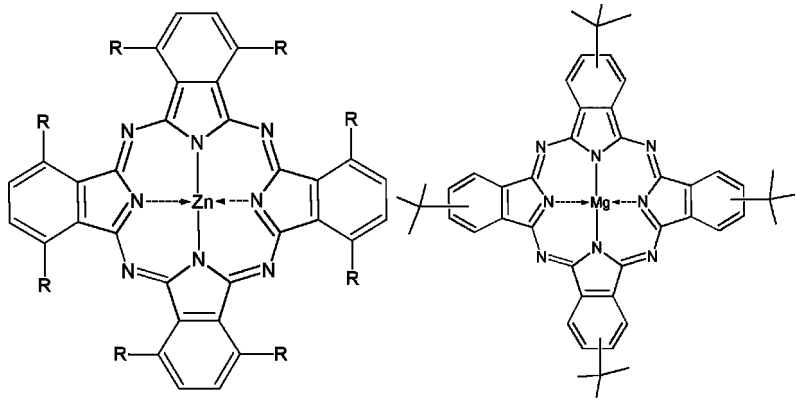

FIGURE 1 Chemical structures of 1,4-octasubstituted zinc phthalocyanines $(But)_8PcZn$ ($R = C_4H_9$), $(Hept)_8PcZn$ ($R = C_7H_{15}$), $(Dec)_8PcZn$ ($R = C_{10}H_{21}$) and 2,3-Tetra *tert*-butyl substituted magnesium phthalocyanine $(t\text{-But})_4PcMg$.

Only the decyl substituted species gives a spectrum similar to the solution spectrum which shows no splitting [22]. Bulky substituents like the *t*-butyl group are commonly used in organic synthesis as spacer, thus an influence on the intermolecular interactions in thin films can be expected as well.

NEXAFS (Near edge x-ray absorption fine structure spectroscopy) [23] was used to investigate changes in the molecular interactions. Two types of molecule were used; 1,4-Octaalkyl zinc phthalocyanines (with n-butyl, n-heptyl and n-decyl substituents), which has chain-like substituents of different lengths, and 2,3-Tetra-(t-butyl) magnesium phthalocyanine as a molecule with bulky substituents (Fig. 1). The investigated films were in the monolayer regime and also reasonably thick films (>5 nm).

EXPERIMENTAL

The measurements were performed at the UE52-PGM beamline at the synchrotron light source BESSY II in Berlin. The energy resolution was set to $\Delta E = 80$ meV at 400 eV. The N1s absorption edge was recorded by collecting the partial electron yield with an applied retarding voltage of 360 V. The raw data were corrected by the photon flux and an additional linear background due to the energy dependent cross sections and were normalised to the same absorption step height

[24]. Soft x-ray photoemission spectra (SXPS) were acquired using a Scienta SES200 hemispherical analyser.

The used substrates were polycrystalline gold foil, which was cleaned by Ar^+ ion sputtering, and a Au(100) single crystal, which was prepared by cycles of sputtering and annealing. The cleanliness was checked by XPS. The organic materials (t-But)$_4$PcMg (mixture of constitutional isomers), (But)$_8$PcZn, (Hept)$_8$PcZn and (Dec)$_8$PcZn (Fig. 1) were evaporated in ultrahigh vacuum (base pressure 1×10^{-9} mbar) with evaporation rates between 0.1 and 1 nm/min. The film thickness was estimated from the XPS intensity ratio of the C1s signal from the overlayer and the attenuated substrate signal [25,26].

RESULTS AND DISCUSSION

Figure 2 shows an angle dependent series of N1s NEXAFS spectra of a (But)$_8$PcZn thin film of about 1–2 nm thickness on gold foil. Utilising the p-polarisation of the synchrotron radiation, the electric field vector can be adjusted from almost perpendicular to parallel to the sample surface by turning the polar angle from grazing incidence ($\theta = 10^\circ$) to normal incidence ($\theta = 90^\circ$). The x-ray absorption process being atom specific [27] excites a core electron into the unoccupied π^* molecular orbital, which consists of $2p_z$ atom orbitals perpendicular to the molecular plane. Consequently, as a result of the selection rules, the maximum N1s-π^* absorption is observed for lying molecules at grazing beam incidence and for standing molecules at normal incidence, respectively [11,12,20,28]. The strong angular dependence of the spectra in Figure 2 distinctly points to predominantly lying molecules, the maximum of the π^* features below 402 eV is observed for $\theta = 10^\circ$. The same results were found for all low coverage films and are summarised in Figure 3. The first layers of the substituted phthalocyanines assume a preferred lying orientation both on single crystalline and polycrystalline gold, unaffected by length or shape of the substituents.

At higher film thickness the molecular orientation is determined by the substitutents. Figure 4 summarises the results of the angle dependent NEXAFS spectra for (But)$_8$PcZn, $\sim$20 nm on Au foil, (Dec)$_8$PcZn, $\sim$20 nm on Au(100), and of (t-But)$_4$PcMg, $\sim$10 nm on Au foil and $\sim$7 nm on Au(100). (But)$_8$PcZn shows preferred standing orientation, which is caused by the dominating intermolecular π-π interaction; the first flat lying adsorption layers work as a weakly interacting substrate [13]. (Dec)$_8$PcZn does not show, as expected, any significant orientation, the long side chains inhibit the ordering due to intermolecular interactions. The 10 nm film of (t-But)$_4$PcMg on gold foil, with its

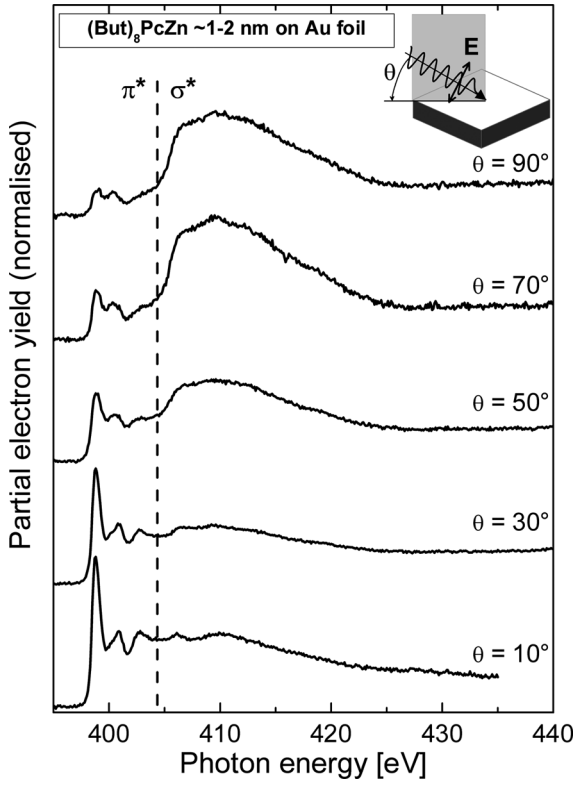

FIGURE 2 N1s x-ray absorption spectra of $(But)_8PcZn$, ~1–2 nm on Au foil. The features below 402 eV represent the N1s-π^* excitations and those above represent the N1s-σ^* excitations. The sketch illustrates the experimental geometry for p-polarised radiation. The observed angular dependence reveals a molecular orientation parallel to the sample surface.

bulky substituents shows a molecular orientation similar to the $(But)_8PcZn$ film with its short chain substituents. No additional effect of the different shape of the substituent could be observed, the *t*-butyl group does not interfere with the intermolecular interactions. However, from the NEXAFS data the 7 nm thick film on the single crystal substrate seems to be completely disordered. This indicates a complicated growth mode with a transition/intermediate layer between the flat lying thin film and the thicker 10 nm film. Further evidence for this is seen in SXPS measurements of the C1s core levels at various excitation energies. With the synchrotron radiation adjusted to an energy of 320 eV, the emitted C1s electrons have a kinetic energy of

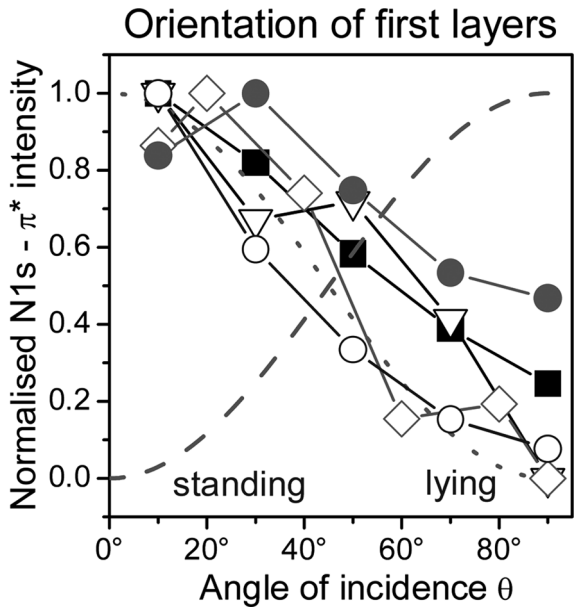

FIGURE 3 Angle dependence of the N1s-π^* excitation intensities in ultrathin films of 1–2 nm thickness (filled rectangles: $(But)_8PcZn/Au$ foil; spades: $(Hep)_8PcZn/Au(100)$; triangles: $(Dec)_8PcZn/Au(100)$; filled circles: $(t\text{-But})_4PcMg/Au$ foil; circles $(t\text{-But})_4PcMg/Au(100)$). The expected intensity profiles for standing and lying molecules are indicated by dashed and dotted lines. For all materials a lying orientation is preferred.

approximately 45 eV and thus an inelastic mean free path in the range of the molecule diameter [26]. Only the uppermost layer of the sample is probed, while higher excitation energies provide bulk data. Figure 5 shows the C1s spectra of $(t\text{-But})_4PcMg$ on Au foil (a) and on single crystalline Au (b). The C1s signal can be described by three components, the benzene ring ("aromatic") at 284.5 eV and the N-neighbouring component ("pyrrole") at 285.7 eV, which are both well known from unsubstituted phthalocyanines [29,30], and a third component at 285.2 eV due to the substituents ("aliphatic"). The latter increases with surface sensitivity, thus these substitutents are closer to the surface than the phthalocyanine frame, which is the case for standing molecules. This behaviour was found both for polycrystalline and single crystalline substrate, while the C1s spectrum of the 1–2 nm thick film (inset in Fig. 5b) is unaffected. On both substrates

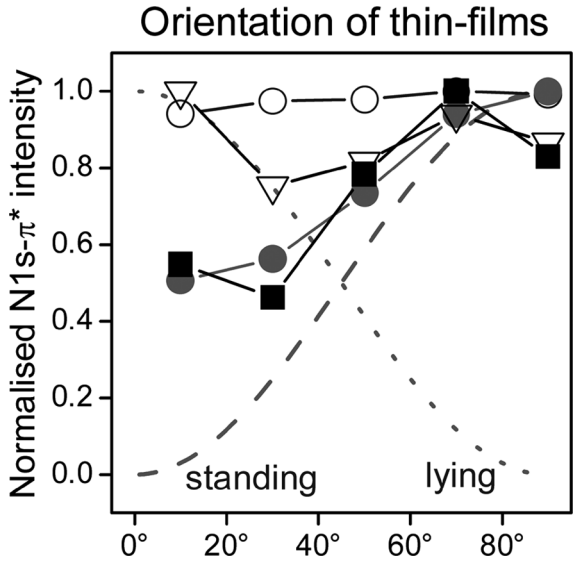

FIGURE 4 Angle dependence of the N1s-π^* excitation intensities in thin films of 7–20 nm thickness (filled rectangles: $(But)_8PcZn$, 20 nm/Au foil; triangles: $(Dec)_8PcZn$, 20 nm/Au(100); filled circles: $(t\text{-But})_4PcMg$, 10 nm/Au foil; circles $(t\text{-But})_4PcMg$, 7 nm/Au(100)). The materials with short substituents preferredly assume standing orientation, regardless of the substitutentś shape, while $(Dec)_8PcZn$, with long substitutents, grows disordered. The data for the 7 nm of $(t\text{-But})_4PcMg$ represent a disordered intermediate layer.

the $(t\text{-But})_4PcMg$ molecules are lying in the first layers and standing in the upper layers with an intermediate layer of disordered molecules. The thickness of this intermediate layer can be roughly estimated to 5–6 nm, just below the thickness of the examined thin film.

SUMMARY

The molecular orientation of phthalocyanines with chain-like substituents of different length and with bulky substituents in evaporated thin films on gold substrates has been investigated. The first layers assume lying orientation for all materials, while at higher film thickness the orientation depends on the substituents. The materials with short substituents prefer standing orientation due to intermolecular

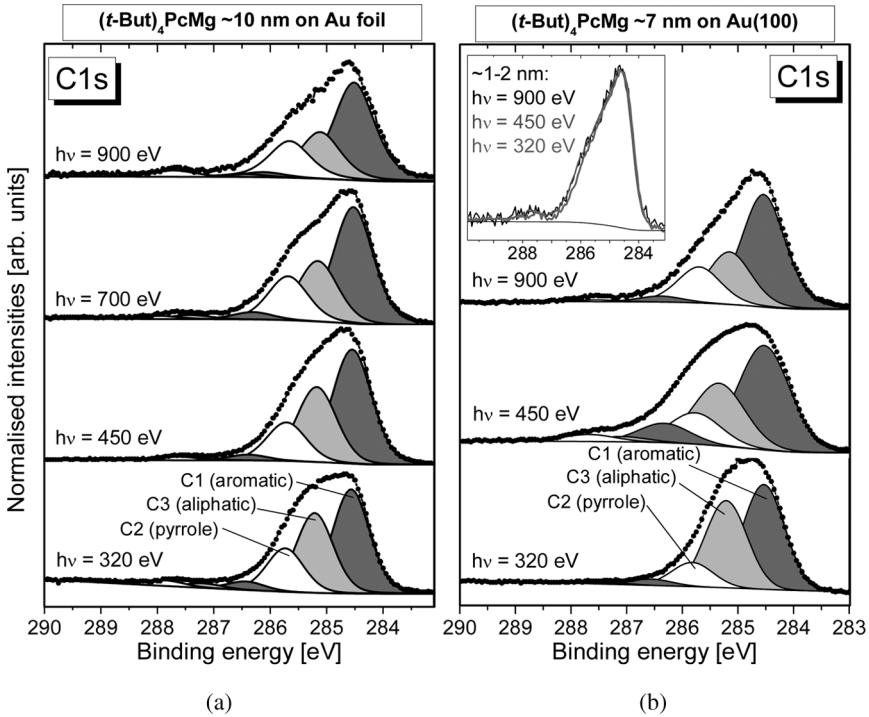

FIGURE 5 Energy dependent x-ray photoemission spectra of the C1s level of $(t\text{-But})_4$PcMg. At 320 eV the probing depth is in the range of the molecule diameter. Here the signal component from the aliphatic substitutents is at its highest value, showing they are above the phthalocyanine frame for both the 10 nm thick film on Au foil and the 7 nm thick film on Au(100). The inset in (b) represents the energy independence for the 1–2 nm layer with lying molecules.

interactions with an intermediate transition layer. The materials with long substituents grow disordered due to inhibited intermolecular interactions.

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