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Article

Control of $\pi-\pi$ Interactions in Epitaxial Films of Platinum(II) Octaethyl Porphyrin[†]

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Epitaxial thin films of Pt(II) octaethyl porphyrin were grown on the cleavage surface of graphite and potassium hydrogen phthalate. The structure of the films was characterized by high resolution atomic force microscopy, showing that the two substrates template the growth of two layered phases with dramatic structural differences, strongly influencing π-stacking of adjacent molecules. The impact of these characteristics on the electronic structure of the film phases is illustrated by a thorough optical investigation.

Introduction

Porphyrin derivatives represent stable and versatile π-conjugated planar molecules finding a multitude of applications in opto-electronics. Among them, 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*- porphyrin platinum(II) (PtOEP) is a commercial derivative recently used as active layer in field-effect transistors[1] and solar cells,[2] as dopant in light-emitting diodes,[3] and as absorber for up-conversion photoluminescence.[4] Common to other organic semiconductors, the electric and optical properties of solid phases of PtOEP are dramatically impacted by the molecular arrangement and the intermolecular interactions. Both characteristics are usually dominated by the overlap of π-orbitals, which is responsible for the development of molecular stacks and for the formation of collective electronic states (bands) enabling charge transport and exciton diffusion. Depending on the film growth conditions, the $\pi-\pi$ stacking may develop either along an in-plane direction, or along an out-of-plane one. The former arrangement, when a single azimuthal orientation of crystalline domains can also be selected, is particularly advantageous for the fabrication of thin film transistors, indeed requiring in-plane charge transport; on the contrary, the out-of-plane stacking direction is desirable when a sandwich geometry of electrodes is employed, therefore requiring out-of-plane charge transport, as in the case of photovoltaic cells. When planar molecules are used, as PtOEP, in-plane $\pi-\pi$ stacking is attained for an edge-on molecular arrangement, whereas an out-of-plane $\pi-\pi$ stacking requires a flat-on arrangement. The possibility to control the molecular orientation in thin film phases is therefore fundamental for device optimization; recently, by using low interacting substrates, it has been illustrated how the molecular orientation of PtOEP in thin films can be changed from edge-on to flat-on by increasing the substrate temperature.[1] For the closely related system of copper-phthalocyanines, these two molecular orientations were also observed to coexist when assembled in organic heterostructures at room temperature, possibly due to the structured organic substrate morphology.[5] A different scenario characterizes the assembly of porphyrins on metal surfaces: in these systems, self-assembled monolayers assume always a flat-on geometry,[6] even when an intermediate nonconductive layer is adsorbed on the substrate surface.[7]

Here, we demonstrate that the control of molecular orientation can be achieved with a suitable choice of a crystalline substrate, through the exploitation of organic epitaxy.[8] Epitaxial PtOEP thin films were grown at room temperature on the surface of freshly cleaved highly oriented pyrolythic graphite (HOPG) and potassium hydrogen phthalate (KAP), then their structure fully characterized by high-resolution atomic force microscopy (AFM). HOPG is

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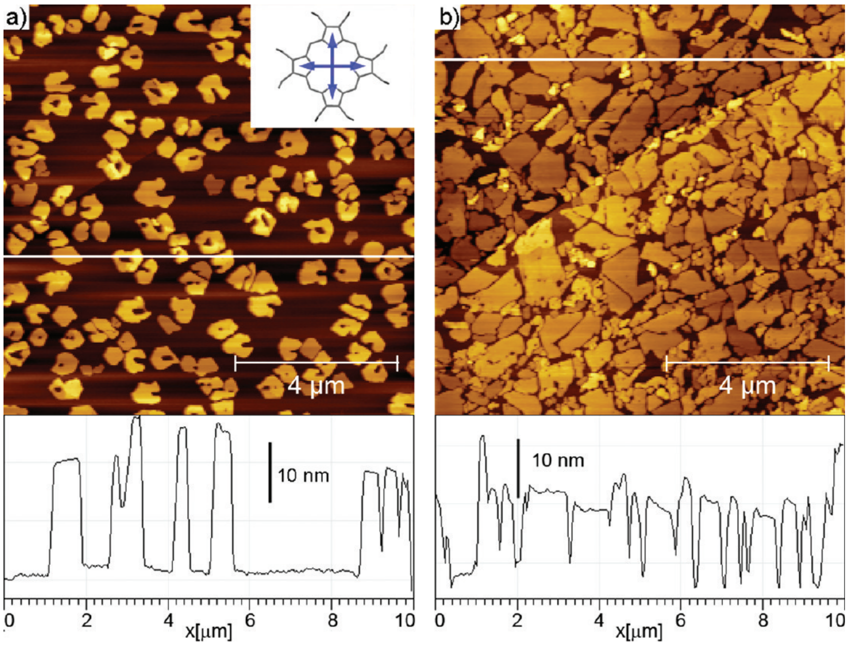

Figure 1. Morphology of PtOEP films grown on HOPG(0001). Nominal thickness is (a) 1 and (b) 4 nm. Below each image, the AFM signal profile along the white horizontal line is reported. The inset in panel a shows the structure of the PtOEP molecule with arrows indicating the orientation of the two transition dipole moments responsible for its optical response.

a very common inorganic conductive substrate whereas KAP is a lamellar organic salt whose (010) surface is used as a paradigmatic organic template for the epitaxial growth of thin films. Oligothiophenes and oligophenyls were demonstrated to assemble in highly ordered epitaxial domains when deposited on KAP by thermal evaporation in vacuum.[8a,9,10] Furthermore, being soluble in water, KAP is potentially useful for the development of organic devices via wet-transfer methods.[1]

Strong differences in the crystal structure of the films are found, either with molecules lying flat on the substrate surface and more than 10 Å far from each other, or arranged edge-on along a precise direction on the substrate surface, less than 4 Å apart from each other. These characteristics determine the optical properties of the PtOEP films, where the shift and splitting of the typical absorption and emission bands of porphyrins is observed to vary with the intermolecular interactions and $\pi-\pi$ overlap in the different crystal structures.

Experimental Section

PtOEP thin films were grown by organic molecular beam epitaxy at a residual pressure of 5×10^{-10} mbar, using a Knudsen-type effusion cell as source; the deposition temperature was 230 °C and films of various thicknesses from 1 to 16 nm were grown at 0.2 nm/min deposition rate. The film nominal thickness was monitored with a quartz crystal microbalance.

AFM images were collected with a Nanoscope V MMAFM (Veeco). Images on microscopic scales were acquired with silicon cantilevers in intermitting contact mode (cantilever force constant, 40 N/m; resonance frequency, 250 kHz), whereas molecular-scale images were collected in contact mode with silicon nitride cantilevers (force constant 0.05 N/m).

X-ray specular scans were performed with an X'Pert Pro (Panalytical) with Cu K_α radiation.

Normal incidence transmission and near-normal incidence reflection measurements were performed in the spectral range from 1.8 to 4.5 eV using a Perkin-Elmer Lambda900 spectrometer, with 1 nm resolution and 2 nm bandwidth; for measurements performed with polarized light a depolarizer and Glan-Taylor polarizers were used. All the measurements have been corrected for the instrumental spectral response.

Photoluminescence (PL) in situ measurements have been performed by using a Nd:YAG CW laser at 532 nm (2.33 eV) as excitation source. Performing the PL measurements in situ permits to avoid the detection of spurious effects related to PtOEP oxidation, particularly effective in altering the sample emission. Emitted light has been detected by a CCD (Spex 2000) equipped with a polychromator (Triax 190 from J-Horiba), with an overall bandpass of 0.05 nm. All the measurements have been done at room temperature, and have been corrected for the instrumental spectral response.

Results

PtOEP/HOPG(0001). PtOEP films on HOPG are characterized by a 3D island morphology (Figure 1). At low nominal thickness, islands are round-shaped and well separated, while, by increasing thickness (and substrate coverage), they grow prevalently laterally, until forming a Voronoi pattern with clear grain boundaries. These films undergo a dewetting process with time, bringing to higher islands and to a decrease of the film coverage. Specular X-ray scans collected on such films present a broad peak at $2\theta = 20.66°$ (see the Supporting Information, Figure S1), corresponding to an interlayer spacing of 4.30 Å, which suggests the formation of molecular layers with the molecular plane parallel to the substrate.

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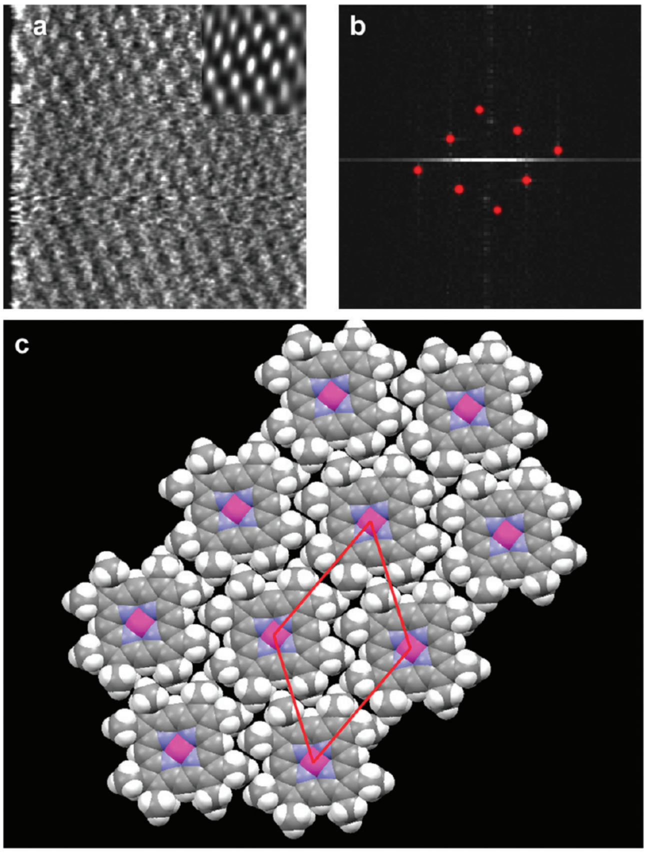

Figure 2. (a) Molecular-scale AFM image (20 × 20 nm^2) collected on an island of a 16 nm thick PtOEP film grown on graphite. Inset: Fourier filtered image. (b) FT of the image contrast. (c) Structural model of PtOEP thin films grown on HOPG(0001). In-plane unit cell parameters are a = 13.5 Å, b = 15.2 Å, γ = 57.6°.

High-resolution AFM imaging performed on the PtOEP islands on HOPG reveals a pseudohexagonal unit cell with parameters $a = 13 \pm 1$ Å, $b = 14 \pm 1$ Å, and $\gamma = 56 \pm 1°$ (Figure 2). These large parameters are consistent with a structure containing one flat molecule per unit cell. By considering the known triclinic single-crystal structure of PtOEP,[11] one can realize the close similarity of the measured parameters with those corresponding to $(\bar{1}11)$-oriented domains. Indeed, the spacing of molecular layers enclosed in $(\bar{1}11)$ planes is 4.32 Å, while the surface unit cell parameters are a = 13.5 Å, b = 15.2 Å, γ = 57.6°. A structural model of PtOEP films deposited on HOPG(0001) is reported in Figure 2.

The polycrystalline nature of the HOPG substrate prevents a precise experimental determination of the epitaxial relation, which is also complicated by the huge difference between the unit-cell parameters of substrate and overlayer.

The arrangement of PtOEP in a flat-on configuration on HOPG with comparable surface unit cell parameters has been also observed in self-assembled monolayers deposited from solution.[7] This behavior is common to other π-conjugate systems such as oligophenylenes[12] and oligocenes,[13] because of the favorable π-overlap between molecular orbitals and the graphite surface. Nonetheless, after completion of the first monolayer, a transition to a 3D nucleation is often observed, with domains having molecules with upright orientation.[14]

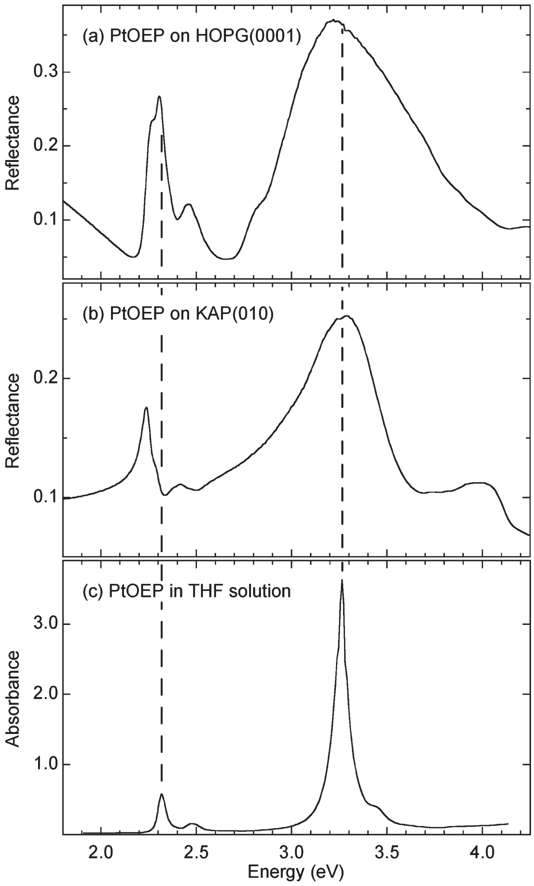

Figure 3. Reflectance spectra of two 16 nm thick films of PtOEP deposited on (a) HOPG and on (b) KAP, as collected at near normal incidence; the absorption spectrum of a 1×10^{-6} M solution of PtOEP in THF is also reported in c, as collected with an optical path of 1 cm. The dotted lines reported in the Figure helps the reader to compare the peak position of the main Q-band and B-band in the spectra of PtOEP films with respect to that of PtOEP in solution.

When the optical behavior of the PtOEP films on graphite is considered, only reflectance spectra can be studied, as graphite is strongly absorbing. Most of the light intensity reaches the film−substrate interface, as the film is very thin, and is reflected back, so that the optical reflectance spectrum can be interpreted as coming from both reflection and absorption. The two transition dipole moments responsible for the PtOEP optical behavior (two equal moments, both within the molecular plane and orthogonal to each other,[15,16] see inset in Figure 1a) give

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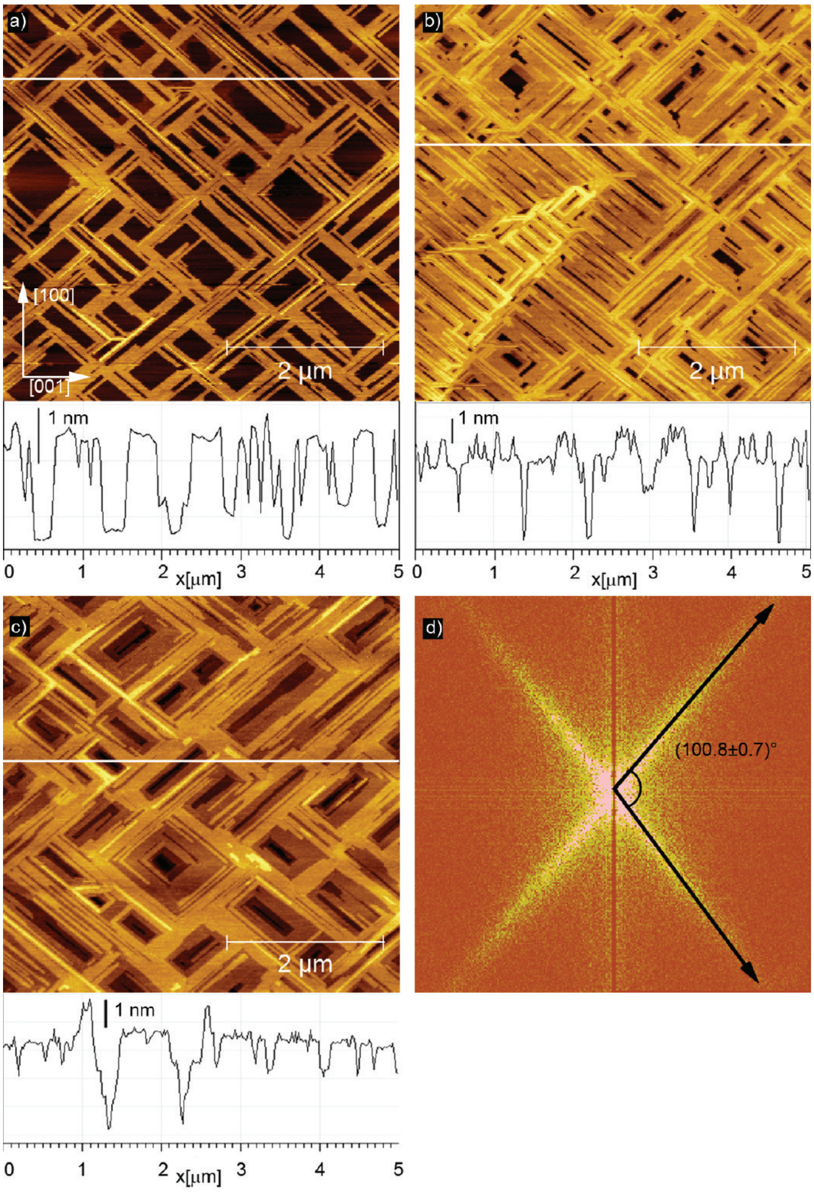

Figure 4. Morphology of PtOEP films epitaxially grown on KAP(010). Nominal thicknesses are (a) 1, (b) 2, and (c) 8 nm. (d) Typical FT of height images is reported. Below each image, a cross-sectional profile as taken along the white lines is reported.

rise to the two main bands typical of porphyrins, i.e., the so-called B-band (or Soret band) and the Q-band, present at about 3.2 and 2.2 eV in the spectrum reported in Figure 3a, slightly red-shifted with respect to the corresponding peaks in the absorption spectrum of PtOEP in THF solution, also reported for comparison (Figure 3c). In the latter spectrum, the typical solution response is observed, with the B-band at 3.28 eV and the multiple Q-band between 2.3 and 2.5 eV. All the bands of the film are broader and the Q-band presents more resolved components.

PtOEP/KAP(010). At very low nominal thickness (Figure 4a), the morphology of PtOEP films is characterized by the presence of tabular domains elongated along two almost orthogonal directions, displaying specular symmetry with respect to KAP[100] and KAP[001]. The height of the domains is uniformly 2.02 ± 0.06 nm (see sectional profile), indicating the onset of a three-dimensional nucleation. Indeed, as the width of a PtOEP molecule is ca. 1.5 nm, the height of the domains is indicative of a multilayer structure, possibly with two molecular layers with molecules tilted by ca. 42° to the substrate surface. Further deposition brings to overgrowth of layers having 1.05 ± 0.03 nm height (Figure 4b, c), displaying the same preferential growth directions as the lower layer. Such an overgrowth preserves its layer-by-layer characteristics up to a nominal thickness of 16 nm (not shown here), giving rise to a hopperlike morphology. The Fourier transform (FT) of the AFM images shows enhanced intensities along two reciprocal directions forming an angle of 100.8 ± 0.7° (see Figure 4d). X-ray specular scans performed on a 16 nm-thick film show peaks at 2θ = 8.01, 2θ = 16.06, and 2θ = 24.09°, corresponding to an interlayer spacing of 1.11 nm (see the Supporting Information, Figure S2). This spacing, which well-compares with that estimated with AFM, is indicative of a layered

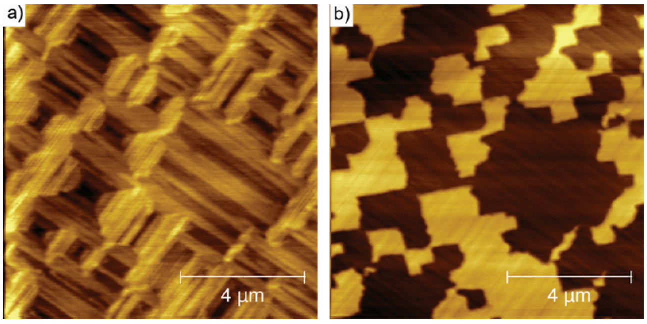

Figure 5. Transverse shear microscopy (TSM) image of PtOEP films (thickness 8 nm) epitaxially grown on KAP(010). (a) Contact-mode height image and (b) TSM contrast.

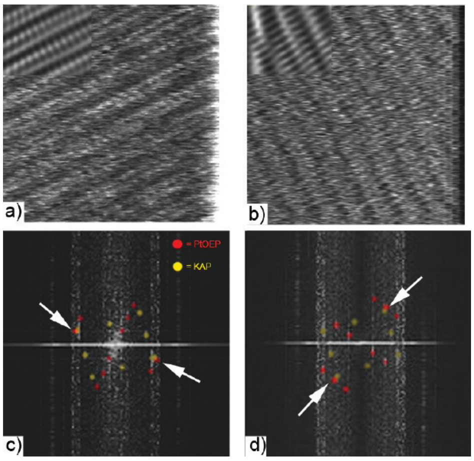

Figure 6. (a, b) Molecular resolution AFM images (15×15 nm^2) of the two domains of PtOEP epitaxially grown on KAP(010). Insets: Fourier filtered images. (c, d) Corresponding FTs superimposed with that of the substrate. White arrows indicate coincident reciprocal lattice vectors.

structure with molecules edge-on, slightly tilted toward the substrate.

Figure 5 shows that the two domains elongated parallel to different directions give rise to a well differentiated contrast in images collected in transverse shear modality,[17] indicating a different crystallographic orientation. To investigate the in-plane structure of PtOEP films on KAP, we performed molecular-scale AFM measurements. The results are reported in Figure 6, showing high-resolution images collected on the surface of the two domains. The FT of the image contrast is reported below each image and superimposed to the FT of the high-resolution image collected on the bare substrate surface in a region near-by the PtOEP domain. The extracted surface unit cell parameters are $a = 4.9 \pm 0.5$ Å, $b = 13.9 \pm 1.5$ Å, and $\gamma = 97.1 \pm 0.8°$, and the superimposed FTs show a coincidence between KAP(101) and PtOEP(10) (see the Supporting Information, Figure S3). This coincidence between nonprimitive reciprocal lattice vectors identifies a line-on-line registry. Previous studies of the out-of-plane structure of PtOEP thin films deposited on silicon oxide[18] suggested substantial differences with the known single crystal triclinic structure of PtOEP,[11] but close similarities with the known single crystal structure of CuOEP.[19] Our investigation, extending the analysis along the in-plane film directions, definitely substantiates such an attribution. Indeed, the unit cell parameters of the $(1\bar{1}0)$ surface of CuOEP are $a = 4.8$ Å, $b = 14.7$ Å, $\gamma = 95.3°$, whereas the spacing of molecular layers enclosed in $(1\bar{1}0)$ planes is 1.114 nm; all these quantities are fully consistent with those measured by AFM and X-ray diffraction on the PtOEP films on KAP. Hereafter, we will indicate this phase as the film phase of PtOEP, taking the lattice parameters of the $(1\bar{1}0)$ surface of CuOEP as the most accurate ones, coming from X-ray diffraction.

On the basis of this conclusion, Figure 7 reports a structural model for the two PtOEP epitaxial domains growing on KAP(010). The short axis of the PtOEP domains corresponds to the direction of molecular packing, driven by $\pi-\pi$ interactions, which is parallel to the directions of preferential growth of the two domains, enclosing an angle of 101.4° (see FT of AFM morphology, Figure 4d). The molecular plane forms a dihedral angle of 46.1° with the substrate plane, and a dihedral angle of 46.5° with PtOEP(10).

The oriented growth of PtOEP on KAP is driven by the similarity of the KAP(101) spacing and the PtOEP(10) spacing, 5.4 and 4.8 Å, respectively. The 11% mismatch is then still sufficiently low to induce a commensurate growth of the film. However, it is too high to induce a two-dimensional nucleation of the film: this is why the film growth mode is Volmer−Weber. It is interesting to note that the same epitaxial relation can be achieved with domains mirrored with respect to the PtOEP(10) plane. However, consistently with the $p1$ plane symmetry of the contact surface of PtOEP, they are not observed. As a final remark, we note that because the c-axis of KAP is a polar axis, it is expected that the two observed domains are not present with equal population.

Even though PtOEP grows selectively with an edge-on geometry on KAP, this substrate was demonstrated to induce usually the growth of both domains with flat-lying molecules and domains with standing upright molecules. This is the case of, for example, oligothiophenes and oligophenylenes.[8a,9]

To study the optical properties of the PtOEP films deposited on KAP and to compare the optical response of PtOEP growing onto different substrates with the same nominal thickness, the reflectance spectrum of a PtOEP film is reported in Figure 3b: it shows the Q-band at slightly lower energy and the B-band at higher energy with respect to both the spectra of the film on HOPG and that of the solution. Because the KAP substrate is transparent in the spectral range of the typical optical transitions of PtOEP, we have also reported the absorbance spectra of two films of different thickness in Figure 8 for deepening the understanding of the optical properties of PtOEP grown on KAP. In both the film spectra, the

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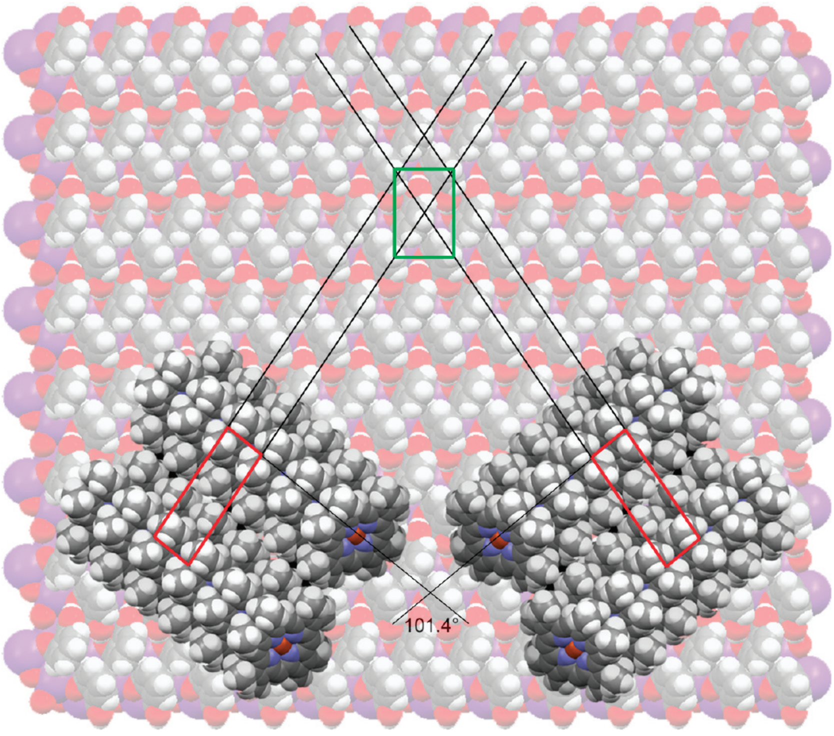

Figure 7. Structural model of PtOEP thin films grown on KAP(010). In-plane unit-cell parameters are a = 4.8 Å, b = 14.7 Å, γ = 95.3°; the surface unit cell of the KAP substrate is also shown.

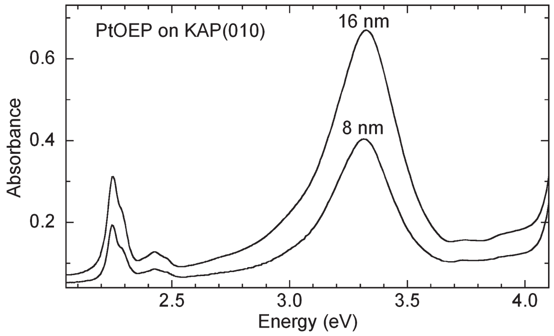

Figure 8. Absorption spectra of PtOEP films of 8 and 16 nm thickness deposited on KAP(010), as measured at normal incidence.

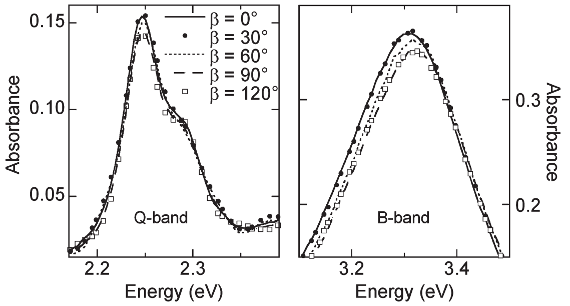

Figure 9. Absorption spectra of a 8 nm thick PtOEP film deposited on KAP(010) in the region of the Q- and B-absorption bands, as measured at normal incidence under linearly polarized light and normalized to the bare KAP spectra collected under the same conditions; the different polarization directions are indicated by the angle β between the light electric field E and the KAP[001] direction.

B-band is broadened and blue-shifted with respect to that of the solution, showing the main peak centered at 3.3 eV, with small shoulders in the low-energy tail. On the contrary, the Q-band is red-shifted, with the strongest components slightly above 2.2 and 2.4 eV, both with high-energy shoulders (with different relative intensity when compared to the spectra of films on HOPG); for both B-band and Q-band, the absorption intensity scales fairly well with film thickness. When compared with the reflectance spectrum of the same sample shown in Figure 3b, a constant 0.02 eV shift of all the main features toward low energy is observed, characteristics of absorption vs reflectance spectra, therefore assessing the full consistency of the experimental results in Figures 3 and 8. Finally, in Figure 9, the two main absorption bands of a 8 nm thick film are reported in details, as collected under light linearly polarized along different directions (labeled by the angle β between the field **E** and the KAP[001] direction). Some anisotropy is clearly observed for both the B-band and the Q-band, both reaching a maximum intensity for β = 0° and β = 30°, giving perfectly superimposed spectra, and the minimum intensity for β = 90° and β = 120°. The directions indicated by β = 15° and β = 105° can therefore be identified as the axes of the optical anisotropy, which do not match with the optical anisotropy axes of KAP, i.e., KAP[001] and KAP[100]. This demonstrates that the two specular crystalline domains, which display specular symmetry with respect to KAP[001] (see Figure 7), are not equally populated.

To corroborate and complete the picture about electronic transitions in the different PtOEP samples, we present in Figure 10 the comparison between the PL spectra of PtOEP in deareated THF solution (dotted line) and of the grown films, as collected in situ under

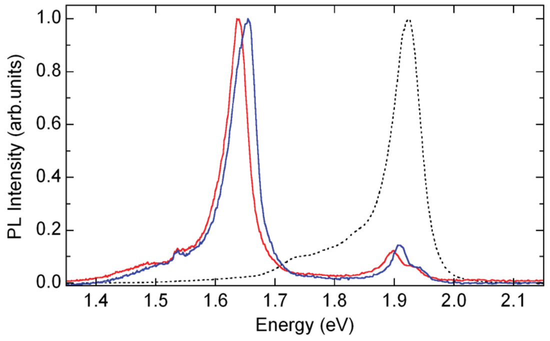

Figure 10. Photoluminescence spectra of PtOEP in THF solution (1×10^{-6} M, dotted line), and of 16 nm thick PtOEP films grown on KAP (red line) and HOPG (blue line). The small peak at 1.55 eV is given by a residual straylight from the pumping laser diodes.

excitation at 2.33 eV in the porphyrin absorption Q-band. In the solution spectrum, it is possible to observe the well-known emissive transition at 1.92 eV attributed to the triplet emission (phosphorescence) from isolated molecules.[16] In both solid samples, a lower-energy emissive transition at about 1.65 eV is detected, which gives the main feature of the PL spectra, in addition to the residual moleculelike emission at about 1.9 eV.

Discussion

The electronic properties of the crystalline films of PtOEP, determined by the different arrangement of PtOEP molecules with respect to the KAP and HOPG substrate surfaces, as well as by the different structures and intermolecular interactions, can be deduced by analyzing the optical response of the samples. The dependence of the optical behavior of PtOEP thin films on their structure has been inferred also in previous studies, where the characteristics of the porphyrin-related bands are discussed, even if without any precise structural information. For example, Dienel et al.[20] studied the photoluminescence spectra in situ during film growth on KBr, observing the evolution from a moleculelike response with the main peak at 1.91 eV, detected for very thin layers, toward the response of aggregates, where a peak at about 1.6 appears with intensity increasing with thickness. Even if they do not comment on the type of aggregation or the film structure, absorption and emission spectra similar to those of our films on graphite are reported. A very rich and detailed analysis of the optical spectra of thin films deposited on silica is presented, also in comparison with other experimental results, by Kalinowski et al.:[21] they found absorption spectra absolutely equivalent to those of our films grown on KAP, with the same asymmetric shift of B- and Q-bands (also found, for example, in refs 16 and 22, not discussed). In their work, the possible intermolecular distance is obtained from the spectral position of the two main components of the B-band, interpreted within the dipole−dipole model[23] assuming a parallel orientation of the transition dipoles responsible for the main absorption bands.

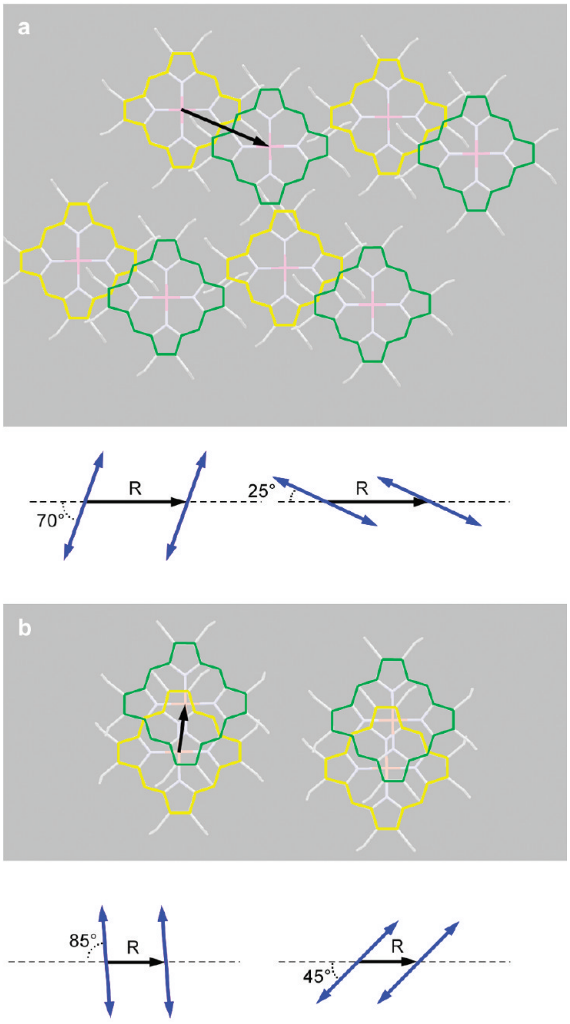

Figure 11. Views along a direction orthogonal to the molecular planes of two adjacent layers (sp^2 C atoms are distinguished in green and yellow colors) in PtOEP films grown on (a) graphite and (b) KAP. The spacing between adjacent molecular planes is (a) 4.32 and (b) 3.40 Å. Below each panel, the arrangements of molecular transition dipole moments responsible for the main absorption bands in PtOEP are illustrated for nearest neighboring molecules belonging to adjacent molecular planes in the solid films; R is the center-to-center distance (R = 8.2 Å and R = 4.8 Å for HOPG and KAP, respectively).

Even though the present study is not aimed at giving a comprehensive and exhaustive description of the optical transitions originating the experimental response, in our case the characteristics of the spectra can be coupled with the precise geometry of π-stacking in the structure of PtOEP films; in Figure 11 the projections of two adjacent molecular layers along a direction orthogonal to the molecular planes, which are parallel to one another, are shown for both structures. Looking at the PtOEP phase grown on HOPG (Figure 11a), the molecules are almost completely segregated; two pairs of sp^2 C-atoms face one another, but the molecular planes are at a distance of 4.32 Å, so that the phase growing on HOPG is expected to have a poor semiconducting behavior and an electronic

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structure with limited differences with respect to that of the isolated molecule. On this basis, the reflectance spectra of the PtEOP film on HOPG in Figure 3 can be interpreted considering a qualitative model where the response of weakly interacting molecules dominates, as already observed in the literature.[20] Considering in details the film structure, the transition moment geometry can be determined (see Figure 11a) and the dipole−dipole model considered adequate for the films on HOPG, as the intermolecular distance is rather large because of their flat-on arrangement (center-to-center distance reaches 8.2 Å). Some effects can therefore be expected on the optical spectra. First, the large center-to-center distance causing a rather weak interaction makes the shift of the transitions of interacting molecules in the crystal (molecularlike contribution) with respect to isolated ones very low. Second, relating the proper crystal response to that of physical dimers of neighboring molecules, a splitting of the molecularlike states into two dimer states, one at higher and one at lower energy, can be expected (crystal-like contribution): the geometry of the dipole arrangement in Figure 11a, showing one dimer nearly J-type, would cause a higher intensity of the lower energy transition. The experimental characteristics of the B-band in Figure 3 match this picture: the most intense peak at about 3.2 eV can be identified as the molecularlike contribution; the lower-energy band component is well-detectable at about 2.8 eV, whereas the high-energy one is detected as a broad shoulder of the main peak centered around 3.5 eV. Looking at the PL results in Figure 10, the shift of the main emission line from the PtOEP in solution to the PtOEP films is of the same order, about 0.3 eV, in full agreement with the above interpretation of the B-band. Finally, also the Q-band shows the same behavior, with the main molecularlike peak at 2.3 eV and a limited crystal-like response, with a well-detectable low-energy component.

In the PtOEP phase grown on KAP, the molecules, arranged in an edge-on orientation, overlap to a fair extent (see Figure 11b), such an overlap determining the intermolecular interaction in the solid and therefore its response. Considering the close similarity of the optical spectra with those discussed in the literature for PtOEP films deposited on SiO_2,[21] one could propose the same interpretation. The B-band could come from a molecular-like transition at 3.0 eV, split by interaction into the two components at 3.3 and 2.7 eV, with the oscillator strength almost completely borrowed by the high-energy component. Nonetheless, knowing the structure, in our case we have to discard this interpretation for at least two reasons: first, the use of the dipole−dipole model for molecules at a distance lower than their size (see Figure 11b) is debatable; second, the presence itself of a molecularlike transition and a lower-energy component at 3.0 and 2.7 eV, respectively, is hard to be observed in the spectrum in Figure 3b, being there only very tiny shoulders. Again, the sketch in Figure 11b permits to get a more convincing and more physical picture, even if qualitative. Also in this case, only two pairs of sp^2 C atoms face one another, but here they make the overall molecular orbital overlap effective, with the molecular plane at a distance of 3.40 Å. It is worth comparing this distance between molecular planes (those comprising the sp^2 C atoms) with the 3.35 Å spacing among layers of sp^2 C atoms in graphite. It is clear that PtOEP grown on KAP represents a phase where the interaction among π-orbitals reaches almost the limit intensity of graphite, even though the overlap integral of π-orbitals is not only a function of the intermolecular distance. For the film phase of PtEOP on KAP therefore the best performance in terms of hole mobility could be envisaged. Indeed, in support to this conclusion, the hole mobility of single crystals of Co-, Cu-, Zn-, and Pd-OEP, isostructural to PtOEP, measured along the stacking direction has been reported, reaching values on the order of 1×10^{-2} cm^2 V^{-1} s^{-1}.[24] The in-plane mobility lowers to 1×10^{-4} cm^2 V^{-1} s^{-1} for thin film devices deposited on silicon oxide,[18] because of the polycrystalline nature of the active layer. However, it is 2 orders of magnitude higher than that measured in devices with an active layer having flat-lying molecules.[1] Note, for example, that for orthorhombic rubrene, a semiconductor crystal that exhibits a record hole mobility of some tens of cm^2 V^{-1} s^{-1}, the spacing of the π-stacking is 3.72 Å,[25] then almost 10% larger than that in the film phase of PtOEP.

The spectra in Figures 3b and 8 can therefore be read as the crystal response, with the proper distribution of the total oscillator strength; the molecularlike peaks are no more observed, so that, e.g., the overall bandwidth of the B-band is limited with respect to the corresponding band of the films on HOPG.

It should be noted, as a last comment, that the stronger intermolecular interaction in the film phase with respect to the phase grown on HOPG is also demonstrated by the PL spectra, where the main emissive state is at lower energy for films on KAP, i.e., it demonstrates a wider splitting of the original molecular state into the crystal states. Also, this splitting agrees well with the crystal structure. Indeed, it is shifted by about 0.3 eV with respect to the emission of the molecules in solution, similarly as for the films on HOPG, which are enhanced by the smaller intermolecular distance and reduced by the nearly H-type alignment of the transition dipole moments.

Conclusions

Exploiting organic epitaxy, crystalline PtOEP films are grown on HOPG and on KAP, finding different structures where different $\pi-\pi$ interactions between the molecules influence the optical behavior. On HOPG, the PtOEP molecules assume a flat-on configuration and assemble in three-dimensional layered domains characterized by a rather weak out-of-plane $\pi-\pi$ interaction; the optical properties of the crystalline films reflect the structural arrangement, showing a molecularlike response, plus some crystal-like contributions. On the contrary, the

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line-on-line registry of PtOEP films grown on KAP drives the formation of a different polymorph, characterized by a stronger in-plane $\pi-\pi$ interaction of edge-on stacked molecules, influencing the spectral position and splitting of the typical porphyrin absorption bands, showing a crystal-like behavior.

Following the organic epitaxy strategy, being the line-on-line registry simultaneously the weakest form of geometric coincidence and a rather common alignment occurring in organic–organic heterostructures, the design of substrates enabling the growth of an overlayer with single-crystalline order could be in principle a quite simple task, this representing an important goal for the optimization of devices requiring high charge mobility along an in-plane direction (e.g., field effect transistors). The surface corrugation of KAP(010) drives the growth of highly ordered phase with a relatively strong $\pi-\pi$ interaction. The point-group symmetry of this surface contains a mirror plane parallel to KAP[001], this originating two mirrored domains of the overlayer. An interesting outlook of this study will be the experimentation of organic substrates with a similar corrugation of KAP, promoting the growth of a high performing phase, but with reduced symmetry, being able to induce the growth of a phase with a single-crystalline order.

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Supporting Information Available: Specular X-ray scans of PtOEP films on KAP and HOPG; high resolution AFM images and indexation of FT images. This material is available free of charge via the Internet at http://pubs.acs.org.