

Two-Dimensional Crystal Growth and Stacking of Bis(phthalocyaninato) Rare Earth Sandwich Complexes at the 1-Phenyloctane/Graphite Interface

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Initial stages of two-dimensional crystal growth of the double-decker sandwich complex $\text{Lu}(\text{Pc}^*)_2$ [$\text{Pc}^* = 2,3,9,10,16,17,23,24\text{-octakis(octyloxy)phthalocyaninato}$] have been studied by scanning tunneling microscopy at the liquid/solid interface between 1-phenyloctane and highly oriented pyrolytic graphite. High-resolution images strongly suggest alignment of the double-decker molecules into monolayers with the phthalocyanine rings parallel to the surface. Domains were observed with either hexagonal or quadrate packing motifs, and the growing interface of the layer was imaged. Molecular resolution was achieved, and the face of the phthalocyanine rings appeared as somewhat diffuse circular features. The alkyl chains are proposed to be interdigitating to maintain planar side-by-side packing.

Introduction

Molecular orientation and position in a crystalline thin film can affect physical and chemical properties of the components. Ordered crystalline thin films may enable us to control precisely the orientation and position on the molecular scale. To attain our eventual goal of coupled single-molecular devices, recognition and manipulation of individual molecules in ordered thin films must be achieved. Sandwich complexes of phthalocyanines and porphyrins are promising candidates for nanodevices such as molecular switches^{1,2} and synthetic molecular motors,^{3,4} due to their unique photophysical and redox properties.

The development of scanning tunneling microscopy (STM) has enabled the imaging and positional control of individual molecules such as phthalocyanines.⁵ Lippel et al. obtained the first STM images showing the internal structure of isolated molecules of copper phthalocyanine on the Cu(100) surface.⁶ Hipps et al. succeeded in recognizing individual molecules in the mixed phase of copper and cobalt phthalocyanines.⁷ These measurements were conducted in ultrahigh vacuum (UHV) on vapor deposited films, which has proven to be a useful technique to produce ordered crystalline thin films on solid surfaces. Organic macromolecules, being more readily decomposed by

heat, cannot be applied by this technique. Pulse injection methods can be used to deposit separated macromolecules onto well-ordered metal surfaces in UHV, and STM can then be used to visualize these molecules,⁸ though ordered epitaxial thin films of macromolecules are not obtained with this technique.

For observation under solution and ambient conditions, highly oriented pyrolytic graphite (HOPG) is a suitable substrate because it offers an inert, well-ordered two-dimensional surface on an atomic scale. The physical properties of liquid-crystal molecules make it possible to immobilize them on HOPG surfaces, allowing high-resolution images to be obtained by STM. Foster and Frommer observed liquid crystals of alkylcyanobiphenyls.⁹ Rabe and Buchholz observed *n*-alkanes and their derivatives, which form mesomorphic phases around room temperature.¹⁰ Flynn and co-workers have observed ordered layers of a number of heteroatom-functionalized hydrocarbons, and have determined the orientation and chirality of the molecular layers.¹¹

In general, the orientation and position of molecules are retained when crystalline thin films are heated mildly (annealed). When thin films are further heated to the melting point, all long-range order is abruptly lost and the crystalline thin films are transformed into an isotropic two-dimensional gas phase. However, not all crystalline thin films show such simple behavior. When some particular structural features are present in the molecule, the melting process occurs stepwise; the molecules possess one or more intermediate states between ordered crystalline phases and the disordered two-dimensional gas phase. Such an intermediate state is called a mesophase.¹² The ordering of crystalline thin films of macromolecules can be achieved by utilizing the mesophase. Therefore, utilizing a low-energy technique to form a thermally unstable mesophase

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of molecules presents a means of forming ordered thin films at a surface, but how can this be done?

One answer is to choose a solvent, such as 1-phenyloctane, to control the environment surrounding the molecules without heating. Bai and co-workers showed excellent high-resolution STM images of phthalocyanines with long alkyl chains, e.g., 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyanine and its metal complexes, dissolved in 1-phenyloctane and deposited onto an HOPG surface.¹³ This method was also applied to observe bis(phthalocyaninato) double-decker sandwich complexes by STM. Liu et al. first observed the double-decker complex bis[2,9,16,23-tetrakis(propoxy)phthalocyaninato]lutetium(III) by STM, although they did not mention the solvent used for dilution.¹⁴ Binnemans et al. imaged the double-decker phthalocyanine complex bis[2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyaninato]erbium(III) at the liquid (1-phenyloctane)/solid (HOPG) interface using variable current mode, and proposed a layered structure with the phthalocyanine (Pc) rings parallel to the surface.¹⁵ However, the resolution of the reported STM images^{14,15} was not as good as those for monophthalocyanines reported by Bai and co-workers;¹³ clear molecular and film structures were not apparent. Three-layer Langmuir–Blodgett films of unsubstituted lutetium bis(phthalocyanine) and alkoxy-substituted lutetium bis[2,3,9,10,16,17,23,24-octakis(butyloxy)phthalocyanine] were imaged by Jones et al. in the absence of solvent, and a structure with the rings approximately perpendicular to the surface was proposed, giving a rowlike repeating structure.¹⁶ In this case, the alkoxy chains affected the images adversely, with a more fluid, softer structure being evident. Very recently, Wan and co-workers have reported the STM imaging of mixed adlayers of the praseodymium double-decker phthalocyanine complex $\text{Pr}[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ with oligo(phenylene-ethynylene) on HOPG.¹⁷

In this paper, we demonstrate molecular resolution of a bis(phthalocyaninato) rare earth complex using STM. According to the study by Bai and co-workers,¹⁸ the length of the alkyl side chains directly affects the molecular array spacing and particularly the adsorption stability. Therefore, we have chosen the ligand 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyanine for good adherence to the graphite surface and to induce stable layered structures and hence better resolution STM images.

Experimental Section

The homoleptic bis(phthalocyaninato)lutetium double-decker complex $[\text{Lu}(\text{Pc}^*)_2]$ and heteroleptic triple-decker complex $[\text{Pc}]\text{Y}(\text{Pc}^*)\text{Y}(\text{Pc}^*)$ [Pc = phthalocyaninato; Pc^* = 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninato] were prepared according to published procedures.^{19–22} The complexes were dissolved in 1-phenyloctane. After heating the solution to ca. 80 °C, several drops were applied to freshly cleaved HOPG (ZYA, 10 mm × 10 mm) also at 80 °C. The initial concentrations of the applied solutions were in the range 10^{-5} to 10^{-3} M, although the actual concentrations of the droplets during measurements were unknown because the solvent was continuously evaporating. The clearest images were obtained with 10^{-4} M nominal concentrations. The samples were cooled to room temperature; then, STM observations were carried out on a Solver P47 Pro Probe instrument (NT-MDT, Zelenograd, Russia) with Pt/Ir (90/10) wire tips. The STM images were recorded in constant current mode at various sample bias voltages in the range 0.5–0.6 V, and currents below 0.1 nA. Scanning was carried out at 1–3 Hz for image areas of $(100\text{--}1000\text{ nm})^2$ and 10–20 Hz for higher resolution images. Specific conditions used to obtain the images are given in the figure

captions. The vertical scale of the STM images was calibrated with a monatomic step of the HOPG substrate ($c/2 = 0.34\text{ nm}$) and an evaporated gold film on mica (monatomic step height of 0.235 nm).

Results and Discussion

The structure of the lutetium double-decker phthalocyanine complex $[\text{Lu}(\text{Pc}^*)_2]$ is shown in Figure 1a. Figure 1b shows an STM image from the 1-phenyloctane solution on HOPG. A HOPG substrate step runs from top to bottom through the middle of the image. In the left part of the image, both quadrate and hexagonal close-packed domains are apparent. This image indicates that the surface energy for the quadrate arrangement is comparable to that for the hexagonal arrangement. On the left, we see numerous single and multiple vacancies in the rather ordered layer, while on the right side of the image, there are scattered single, double, and triple features. Moreover, some short protruding scan lines appear in this domain, which indicates that some of the molecules were moved by the STM tip in this region. In the background of this region, a faint regular pattern was observed, which aligned with the isolated protruding features. We propose that the underlying layer is a stable, ordered first monolayer on the graphite. The protruding features on the right side of Figure 1b represent isolated, more mobile double-decker molecules that were lying on top of the first monolayer.

In Figure 1c, the growing two-dimensional layer structure is illustrated in the bottom right corner, where isolated single molecules are joining the continuous layer, thus capturing the “two-dimensional crystallization” phenomenon, or filling the vacancies by deposition from solution. Again, this area represents the growth of the second layer of double-deckers, as shown by the regular underlying pattern that is faintly apparent. A higher resolution view of a packed region is shown in Figure 1d, where the key features are visible, namely single and double vacancies and both quadrate and hexagonal packing regions. The almost circular protruding features have a lateral separation of 2.5–3 nm, and the valleys between them have an apparent depth of ca. 0.3 nm. The vacancies appear as deeper holes with apparent depths of 0.9 nm and logically these represent the absence of one molecule from the continuous layer.

Fourier transform power spectra from the STM images of Figure 1b–d are shown in Figure 2a–c, respectively. We did not calibrate the lateral drifts in the images shown in Figure 1b,c, so that the hexagonal lattices indicated by dots in Figure 2a,b are not regular. We calibrated the lateral drift in the image of Figure 1d since we knew the drift vector during the observation ($0.244 \pm 0.005\text{ nm/s}$), measured from consecutive images. The hexagonal lattice in the drift-calibrated STM image was regular, with the lattice constant $2.6 \pm 0.1\text{ nm}$, which was also confirmed by the Fourier transform power spectrum shown in Figure 2c. On the other hand, the quadrate lattice in the drift-corrected image was not regular. We estimated the quadrate lattice $a = 2.5 \pm 0.1\text{ nm}$, $b = 2.7 \pm 0.1\text{ nm}$, and the angle $\theta = 83 \pm 5^\circ$, supposing that the hexagonal lattice was regular. These values are in fairly good agreement with the studies by Bai and co-workers on monomer phthalocyanines¹³ and of Wan and co-workers on the praseodymium double-decker phthalocyanine complex.¹⁷ Moreover, packing densities were calculated from these lattice parameters, 0.167 molecule/ nm^2 for the hexagonal unit cell and 0.149 molecule/ nm^2 for the quadrate unit cell, which indicates that the packing density of the hexagonal unit cell is larger than that of the quadrate unit cell.

The protruding disks, with diameters ca. 1.5–2 nm, are proposed to be the phthalocyanine rings observed from above,

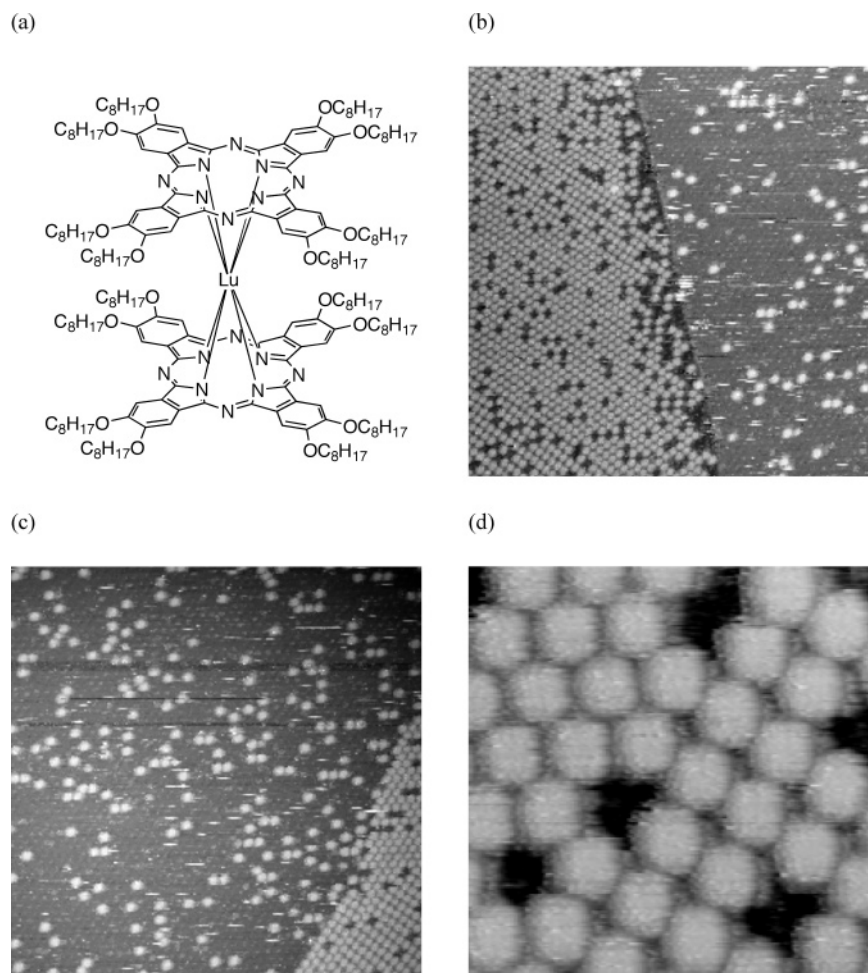


Figure 1. (a) Structure of $\text{Lu}[\text{Pc}(\text{OC}_8\text{H}_{17})_2]$ double-decker molecules; (b–d) STM images of the double-decker complex on HOPG obtained at sample bias of +0.524 V and $I = 0.058$ nA: (b and c) $100 \text{ nm} \times 100 \text{ nm}$ and (d) $16 \text{ nm} \times 16 \text{ nm}$.

i.e. the double-deckers stack side-by-side in the layer(s) with the rings parallel to the HOPG surface. This interpretation was adopted by Binnemans et al.,¹⁵ who also found a spacing of ca. 3 nm for their octakis(dodecyloxy) system, but our images are clearer, especially in the much larger areas of ordered domains that we observed. The regions of the surrounding alkyl chains were diffuse, and we could not resolve any details at the edges, only the valleys with apparent depths of 0.3 nm. Both quadrate and hexagonal monolayer patterns have been observed for the $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ complexes of octakis(octyloxy)phthalocyanine.¹³ Our observed lateral separations are similar to those reported by Bai and co-workers for these single layer complexes and the corresponding uncomplexed ligand (2.6–2.7 nm), although their images showed submolecular detail, including partial impressions of the interdigitated alkyl chains.¹³ The similar packing patterns and intermolecular distances suggest that the alkyl chains attached to the phthalocyanines are similarly interdigitated for the double-decker complexes. The dimensions of the double-decker molecule have been estimated by molecular modeling with use of the Spartan 02 program. The diameter of the Pc ring is about 1.5 nm. The diameters and separations of the protruding disks in our images are therefore consistent with a rather close-packed, strongly interdigitated model. Given that both rings of the double-decker complex are adorned with eight alkoxy chains, there should be a strong driving force to pack in layered arrangements.

We also observed the heteroleptic triple-decker molecule $[\text{Pc}]\text{Y}(\text{Pc}^*)\text{Y}(\text{Pc}^*)$ [Pc = phthalocyaninato; Pc^* = 2,3,9,10-

16,17,23,24-octakis(octyloxy)phthalocyaninato] by the same method. The packing structure observed in the STM image was not ordered and the image quality was similar to that reported by Binnemans et al.,¹⁵ though we did observe the stacking in the triple-decker molecule at the boundaries of partially ordered domains, similar to the effects seen in Figure 1d. Moreover, we attempted to image the corresponding europium complex without significant success, as the monolayers were even less stable, and we also tried unsuccessfully to obtain images from single crystals of the gadolinium triple-decker molecules. Presumably, the conductivity of the crystals was too low for sufficient tunneling.

Conclusions

We have studied the initial stages of two-dimensional crystal growth of the homoleptic double-decker complex $\text{Lu}[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2$ at the liquid/solid interface of 1-phenyloctane and HOPG. The complex formed a stable, ordered monolayer, upon which we observed the growth of a second layer, with regions of quadrate and less frequently hexagonal close-packed order. The lateral spacing indicated the molecules were layering with the planes of the macrocycles parallel to the HOPG surface. Neither the internal structures nor the details of the alkoxy chains on the phthalocyanines were observed in this study. The tunneling current during our STM measurements was near the limit of our apparatus. Recently, we observed the internal structure of double-decker molecules with STM at tunneling currents less than a few pA.²³ Control of the ordered arrange-

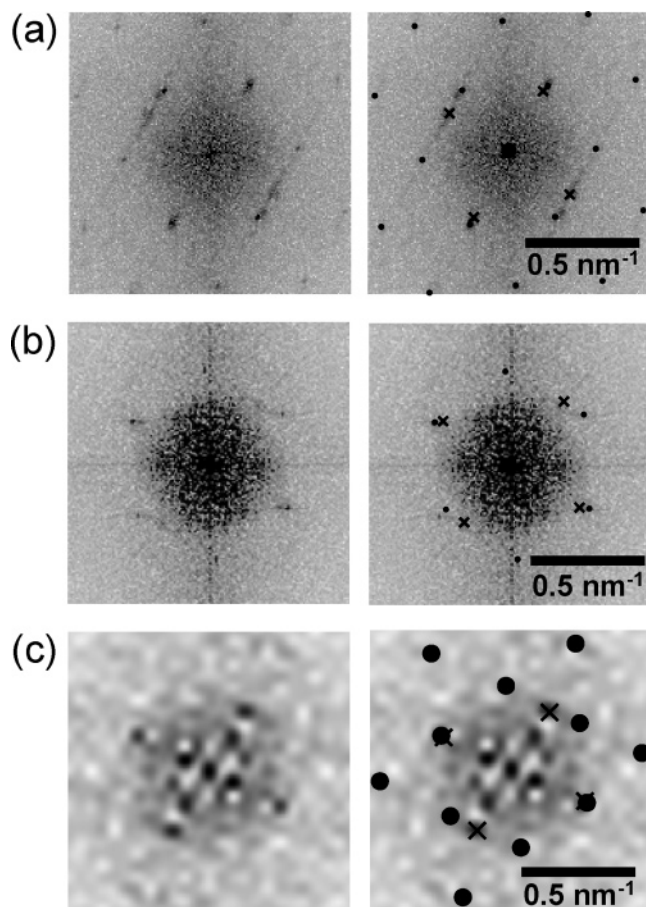


Figure 2. Fourier transform power spectra from the STM images in Figure 1: (left) power spectra and (right) power spectra with dot marks indicating hexagonal lattice and \times marks indicating quadrate lattice. Power spectra (a) from Figure 1b, (b) from Figure 1c, and (c) from Figure 1d.

ments of double-decker or triple-decker phthalocyanine molecular thin films may enable future applications such as molecular information storage²⁴ and molecular phase memory.²⁵

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References and Notes

- (1) Shinkai, S. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001; pp 301–304.
- (2) Jiang, J.; Kasuga, K.; Arnold, D. P. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; pp 113–210.
- (3) van Delden, R. A.; ter Wiel, M. K. J.; Koumura, N.; Feringa, B. L. In *Molecular Motors*; Schliwa, M., Ed.; Wiley-VCH: Weinheim, Germany, 2003; pp 566–567.
- (4) Tashiro, K.; Konishi, K.; Aida, T. *J. Am. Chem. Soc.* **2000**, *122*, 7921–7926.
- (5) Chiang, S. *Chem. Rev.* **1997**, *97*, 1083–1096.
- (6) Lippel, P. H.; Wilson, R. J.; Miller, M. D.; Wöll, Ch.; Chiang, S. *Phys. Rev. Lett.* **1989**, *62*, 171–174.
- (7) Hipps, K. W.; Lu, X.; Wang, X. D.; Mazur, U. *J. Phys. Chem.* **1996**, *100*, 11207–11210.
- (8) Sugiura, K.-i.; Tanaka, H.; Matsumoto, T.; Kawai, T.; Sakata, Y. *Chem. Lett.* **1999**, 1193–1194. Kato, A.; Sugiura, K.-i.; Miyasaka, H.; Tanaka, H.; Kawai, T.; Sugimoto, M.; Yamashita, M. *Chem. Lett.* **2004**, 578–579.
- (9) Foster, J. S.; Frommer, J. E. *Nature* **1988**, *333*, 542–545.
- (10) Rabe, J. P.; Buchholz, S. *Science* **1991**, *253*, 424–427.
- (11) Giancarlo, L. C.; Flynn, G. W. *Acc. Chem. Res.* **2000**, *33*, 491–501. Yablon, D. G.; Wintgens, D.; Flynn, G. W. *J. Phys. Chem. B* **2002**, *106*, 5470–5475. Wintgens, D.; Yablon, D. G.; Flynn, G. W. *J. Phys. Chem. B* **2003**, *107*, 173–179.
- (12) Binnemans, K.; Görrler-Walrand, Ch. *Chem. Rev.* **2002**, *102*, 2303–2345.
- (13) Qiu, X.; Wang, C.; Zeng, Q.; Xu, B.; Yin, S.; Wang, H.; Xu, S.; Bai, C. *J. Am. Chem. Soc.* **2000**, *122*, 5550–5556. Qiu, X.; Wang, C.; Yin, S.; Zeng, Q.; Xu, B.; Bai, C. *J. Phys. Chem. B* **2000**, *104*, 3570–3574. Liu, Y.; Lei, S.; Yin, S.; Xu, S.; Zheng, Q.; Zeng, Q.; Wang, C.; Wan, L.; Bai, C. *J. Phys. Chem. B* **2002**, *106*, 12569–12574.
- (14) Liu, Y.-Q.; Zhu, D.-B.; Ruan, L.-K.; Bai, C.-L.; Yamada, A.; Shigehara, K. *Chin. J. Chem.* **1991**, *9*, 126–130.
- (15) Binnemans, K.; Slevin, J.; De Feyter, S.; De Schryver, F. C.; Donnio, B.; Guillon, D. *Chem. Mater.* **2003**, *15*, 3930–3938.
- (16) Jones, R.; Krier, A.; Davidson, K. *Thin Solid Films* **1997**, *298*, 228–236.
- (17) Yang, Z.-Y.; Gan, L.-H.; Lei, S.-B.; Wan, L.-J.; Wang, C.; Jiang, J.-Z. *J. Phys. Chem. B* **2005**, *109*, 19859–19865.
- (18) Wang, H.; Wang, C.; Zeng, Q.; Xu, S.; Yin, S.; Xu, B.; Bai, C. *Surf. Interface Anal.* **2001**, *32*, 266–270.
- (19) Liu, W.; Jiang, J.; Du, D.; Arnold, D. P. *Aust. J. Chem.* **2000**, *53*, 131–136.
- (20) Jiang, J.; Liu, R. C. W.; Mak, T. C. W.; Chan, T. W. D.; Ng, D. K. P. *Polyhedron* **1997**, *16*, 515–520.
- (21) Jiang, J.; Xie, J.; Choi, M. T. M.; Ng, D. K. P. *J. Porphyrins Phthalocyanines* **1999**, *3*, 322–328.
- (22) Liu, W.; Jiang, J.; Arnold, D. P.; Pan, N. *Inorg. Chim. Acta* **2000**, *310*, 140–146.
- (23) Takami, T.; Ye, T.; Weiss, P. S.; Arnold, D. P.; Sugiura, K.-i.; Jiang, J. Manuscript in preparation.
- (24) Roth, K. M.; Gryko, D. T.; Clausen, C.; Li, J.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. *J. Phys. Chem. B* **2002**, *106*, 8639–8648.
- (25) Takami, T.; Sugiura, K.-i. U.S. Patent 6,762,397, 2004.