

Self-Assembly of PcOC8 and Its Sandwich Lanthanide Complex Pr(PcOC8)₂ with Oligo(Phenylene-ethynylene) Molecules

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Received: April 28, 2005; In Final Form: August 25, 2005

Self-assemblies of octakis(octyloxy) phthalocyanine (PcOC8) and its sandwich lanthanide complex, substituted praseodymium bis(phthalocyanine) (Pr(PcOC8)₂), with oligo(phenylene-ethynylene) (OPE) have been investigated by scanning tunneling microscopy (STM) on a highly oriented pyrolytic graphite (HOPG) surface. The assemblies were prepared by dissolving the molecules in phenyloctane solution. It was found that both PcOC8 and Pr(PcOC8)₂ can form 4-fold or 6-fold symmetrical adlayers on HOPG. The intramolecular structure of Pr(PcOC8)₂ molecule was revealed by a high-resolution STM image. When OPE molecules are added into phenyloctane solvent, Pr(PcOC8)₂ molecules prefer to form an ordered adlayer at the top of the OPE adlayer, while PcOC8 molecules adsorb on HOPG surface directly and form separated domains with OPE. These results may be helpful to construct surface assemblies and develop molecular electronic devices in the future.

Introduction

Self-assembling is a natural, spontaneous, and effective process in the formation of materials and living organisms. Currently, this technique is widely employed in supramolecular architecture, materials science, crystal engineering, and surface nanostructure. In particular, two-dimensional self-assembly on a solid surface is paid special attention because scientists and industrialists are aware that the “top-down” approach reaches its practical and theoretical limit when they attempt to make nanometer- and subnanometer-scale electronic devices.¹ A potential approach is the so-called “bottom-up” technique in which atoms or molecules are used to assemble a nanometer-scale device. Self-assembling is a powerful method in the “bottom-up” technique. Through a self-assembling process, functional molecules can self-assemble into a well-defined monolayer with various patterns. By accurately controlling the self-assembled monolayer (SAM), the development of electronic devices is expected. Therefore, researchers are working hard in the field related to building, addressing, and controlling SAMs and trying to achieve molecular-based devices.^{2,3} On the other hand, exploring the relationship between molecules and molecular adlayer structures is also becoming an important issue in self-assembly research,^{4,5} which is considered to be a prerequisite for the realization of tunable SAMs.

Phthalocyanines have been industrially used in gas sensors, optoelectronic, and microelectronic devices owing to their appealing photophysical, electronic, and electrochemical properties as well as their chemical and physical stability.^{6–11} The adlayer of phthalocyanine has been intensively studied by using STM in ultrahigh vacuum,^{12–15,22} ambient conditions,^{16–21} and electrolyte solution.^{23,24} As a result, it is known that these molecules easily form ordered SAMs and the central metal atoms in phthalocyanine molecules appear in high or low

contrast in STM images, depending on their different d-orbit occupation.^{12–15} Qiu et al. reported the adlayer structure of copper(II)-2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (CuPcOC8) on highly oriented pyrolytic graphite (HOPG) and investigated the molecular contrast variation in the adlayer with the change of bias polarity.¹⁶ Recently, the study on multicomponent adlayers of phthalocyanines with other molecules have been reported.^{17–21} It is found that molecules can form defined adlayers with different structures in different arrangements of phthalocyanines and other molecules. Although separated domains were seen, the overlapped structure phthalocyanines site over the adlayer by other atoms or molecules, was also reported.^{19, 21}

Coordination complexes are an important class of compounds. Recently, attention has been paid to metal bis(phthalocyanine)s (MPc2), especially lanthanide bis(phthalocyanine)s coordination complex (LnPc2), because of their intrinsic semiconducting, nonlinear optical, and electrochromic properties.^{25–27} The morphology of LB films of substituted YbPc2 at the air/water interface with phase change was observed by Brewster angle microscopy (BAM), and the YbPc2 molecular orientation in LB films was determined with polarized UV–vis spectra.²⁸ The effect of the ratio of ytterbium bisphthalocyanine to stearic acid on the morphology of LB films was investigated by using atomic force microscopy, micro-Raman imaging, resonance Raman scattering, surface-enhanced resonance Raman scattering, and surface-enhanced Raman scattering.²⁹ The results show that phase separation is more apparent when the sample included more stearic acid, and there is no interaction between stearic acid and YbPc2 molecules at the molecular level.²⁹ Lutetium and thulium bis(phthalocyanine)s (LuPc2 and TmPc2) were used to fabricate thin-film field-effect transistors, which are mainly used in liquid crystal displays.³⁰ The behaviors of field effect in the transistors were observed only when no defects existed in the inorganic insulating layer. The effect of lanthanide ion and side-chain length on the thermal properties of substituted lanthanide bis(phthalocyanine)s are being investigated by Guillon's group.³¹ All the lanthanide bis(phthalocyanine)s

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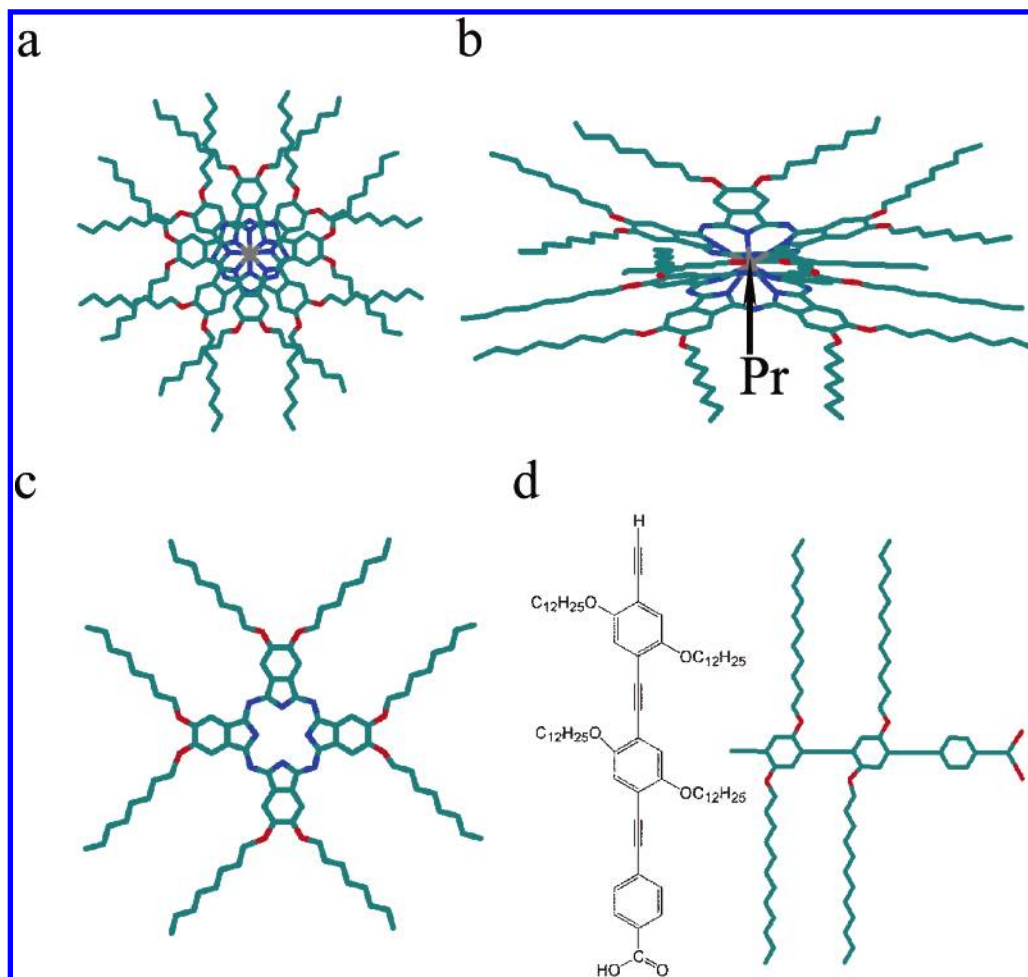


Figure 1. Molecular structures of $\text{Pr}(\text{PcOC8})_2$ (top view (a) and side view (b)), PcOC8 (c) and oligo(phenylene-ethynylene) (d).

molecules they investigated exhibited hexagonal columnar mesophase, and the transition temperature depended on the substituted chain length.³¹ On the other hand, various spectra, such as magnetic circular dichroism and absorption spectra, and theoretical calculation were used to determine the electronic structure and properties of lanthanide bis(phthalocyanine) molecules.^{32–36} These reports show that LnPc2 molecules are sandwich-type compounds in which the lanthanide metal ion (M^{3+}) is 8-fold coordinated to the isoindole nitrogens of the phthalocyanine ring.^{32–36}

Besides phthalocyanines, conjugated polymers such as oligothiophene and oligo(phenylene-ethynylene) (OPE) are another class of semiconductors. These conjugated polymer molecules combine unique optical and electronic properties with the processing advantage and mechanical properties of polymers. Furthermore, the oligo(phenylene-ethynylene) molecule has a remarkable stiffness and linearity along its conjugated backbone that allow it to self-organize into a well-defined structure and makes it a potential molecular template that induces other molecules to assemble into a multicomponent adlayer.^{37–38}

In this paper, a lanthanide bis(phthalocyanine) coordination complex, substituted praseodymium bis(phthalocyanine) ($\text{Pr}(\text{PcOC8})_2$) molecule, and its ligand molecule octakis(octyloxy) phthalocyanine (PcOC8) with OPE molecules were investigated at the liquid/HOPG interface. Figure 1 a–d show the molecular structures of $\text{Pr}(\text{PcOC8})_2$, PcOC8 , and OPE, respectively. Experimental results show that sandwich-like coordination complex $\text{Pr}(\text{PcOC8})_2$ molecules seem to have similar adsorbing behavior with its ligand molecule PcOC8 when a solution contains only PcOC8 and $\text{Pr}(\text{PcOC8})_2$ mol-

ecules. However, the ligand and coordination complex molecules show different adsorption behavior when OPE molecules are included. A phase separation adlayer was observed in the adlayer of PcOC8 and OPE. On the other hand, it is evident that the $\text{Pr}(\text{PcOC8})_2$ molecules always site on the top of OPE adlayer, resulting in an overlayer. These results may be helpful for understanding multicomponent assembling behavior of phthalocyanines and lanthanide bis(phthalocyanine) coordination complex on a solid surface and may have potential in the development of nanoelectronic devices through bottom-up approaches in the future.

Experiment

Octakis(octyloxy) phthalocyanine was purchased from Aldrich and used without further purification. Praseodymium(III)-bis-octakis(octyloxy) phthalocyanine and oligo(phenylene-ethynylene) were synthesized according to the procedure reported in the literature.^{31,37–38} Phenyl octane was purchased from Aldrich and used as solvent without further purification. The sample of $\text{Pr}(\text{PcOC8})_2$ contains a trace of PcOC8 that was used as a reactant during the synthesis of $\text{Pr}(\text{PcOC8})_2$ molecules. All the investigated molecules were dissolved in phenyl octane. The self-assemblies of the various molecules were prepared by placing a drop of solution containing the assigned molecules in a concentration less than 10^{-4} M on a freshly cleaved HOPG surface. For the preparation of a mixed adlayer, a mass ratio of 1:1 (OPE/ $\text{Pr}(\text{PcOC8})_2$ and OPE/ PcOC8) was used.

All STM experiments were performed on a Nanoscope IIIa scanning tunneling microscope (Digital Instruments Co., CA)

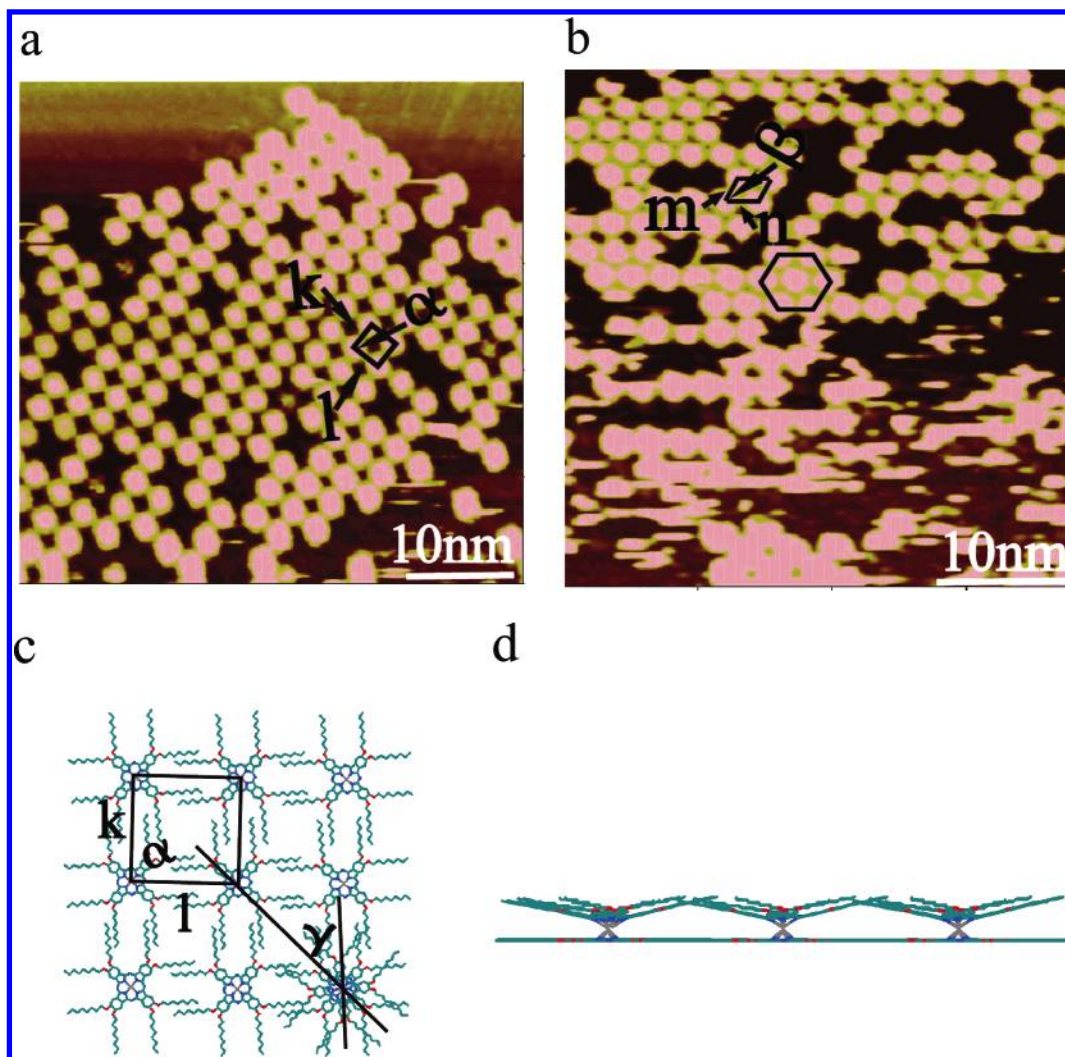


Figure 2. (a) STM image of $\text{Pr}(\text{PcOC8})_2$ adlayer with a 4-fold symmetry. (b) STM image of a quasi-hexagonal symmetry $\text{Pr}(\text{PcOC8})_2$ adlayer. (c) Top and (d) side views of a schematic representation of the $\text{Pr}(\text{PcOC8})_2$ adlayer in (a). Tunneling conditions: (a) 847 mV and 470 pA, and (b) 1.15 V and 506 pA. $\text{Pr}(\text{PcOC8})_2$ molecules were dissolved in phenyloctane in a concentration less than 10^{-4} M.

with mechanically cut Pt/Ir (90:10%) tips. All the STM images given in this paper were collected with constant current mode and used with only flattened processing. The tunneling conditions for each image are given in the figure captions.

Results and Discussion

The self-assembled monolayer of $\text{Pr}(\text{PcOC8})_2$ was observed after the molecular solution was deposited on the HOPG surface. Figure 2 shows two large-scale STM images of the $\text{Pr}(\text{PcOC8})_2$ molecular adlayer. Repeated experiments demonstrate that $\text{Pr}(\text{PcOC8})_2$ molecules form two adlayer structures, a 4-fold domain and a 6-fold domain, respectively, as shown in Figure 2a and b. Although some molecular defects exist in the adlayer, a self-assembled adlayer with 4-fold symmetries in Figure 2a is extending over the atomically flat HOPG surface with the domain size of several tens of nanometers. On the basis of the adlayer symmetry and intermolecular distance, a unit cell on the 4-fold symmetry adlayer can be determined, which is outlined with black lines in Figure 2a. The lattice parameters in the unit cell are measured to be $k = 2.6 \pm 0.2$ nm, $l = 2.6 \pm 0.2$ nm, and $\alpha = 89^\circ \pm 2^\circ$. These data are very close to the unit cell parameters in former reports on the adsorption of copper(II)-2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (CuPcOC8) on HOPG.^{16,39} The similar structure shows the effect of molecular structure on the adlayer structure

because the ligand in the $\text{Pr}(\text{PcOC8})_2$ molecule has a similar structure to CuPcOC8 . $\text{Pr}(\text{PcOC8})_2$ molecules also form quasi-hexagonal organization, as shown in Figure 2b. A unit cell is outlined in the image. The lattice parameters of the unit cell are measured to be $m = 2.4 \pm 0.2$ nm, $n = 2.5 \pm 0.2$ nm and $\beta = 57^\circ \pm 2^\circ$, respectively. However, the 4-fold symmetry adlayer dominates the assemblies of $\text{Pr}(\text{PcOC8})_2$ molecules, although the assembly in quasi-hexagonal symmetry was occasionally observed. Further experiments are necessary to investigate the origin and transition of the different molecular arrangements.

On the basis of the adlayer symmetry and the results reported in the literature,^{16,39} a schematic representation of the $\text{Pr}(\text{PcOC8})_2$ assembly is illustrated in Figure 2, parts c (a top view) and d (a side view). To see the arrangement of $\text{Pr}(\text{PcOC8})_2$ molecules on the surface clearly, we simplify the molecular model in its top view. Only one $\text{Pr}(\text{PcOC8})_2$ molecule is drawn in the top view of the model (lower-right corner), while the top PcOC8 ligands of other $\text{Pr}(\text{PcOC8})_2$ molecules are cut in Figure 2c. From this model, the molecular arrangement on the HOPG surface is proposed.

Owing to the existence of a trace of PcOC8 molecules with the $\text{Pr}(\text{PcOC8})_2$ coordination complex as a reactant during synthesis, a mixed adlayer consisting of $\text{Pr}(\text{PcOC8})_2$ and PcOC8 molecules was found in the present study. Although the

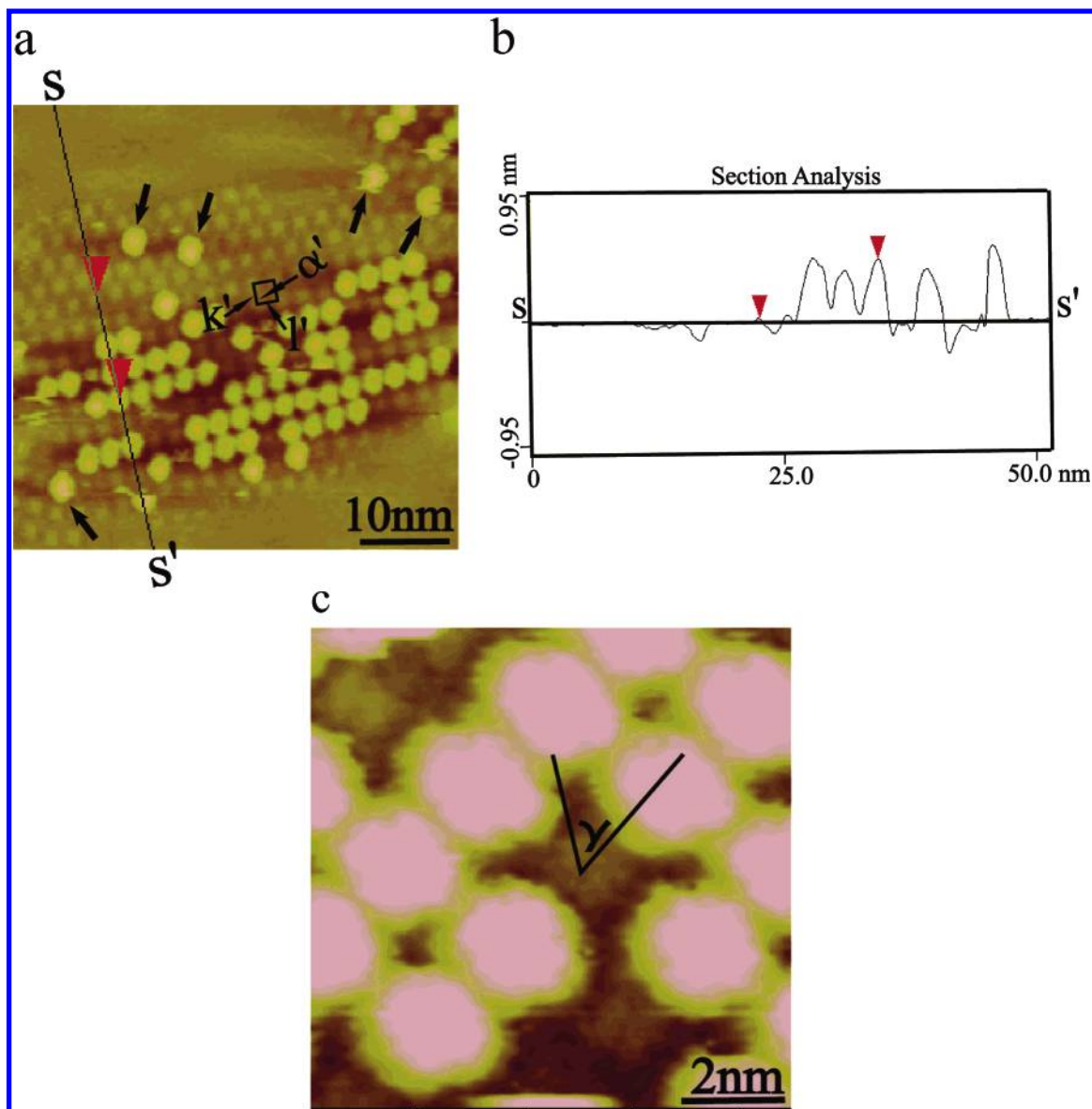


Figure 3. (a) STM image showing a coadsorbed adlayer of $\text{Pr}(\text{PcOC8})_2$ and PcOC8 . (b) Cross-sectional profile along $S-S'$ line in (a). (c) An expanded STM image of $\text{Pr}(\text{PcOC8})_2$ molecules coadsorbed with a PcOC8 . Tunneling conditions: (a) 921 mV and 552 pA, and (c) 834 mV and 559 pA.

remained reactant molecules are not good for synthesis, they are useful for the study of coadsorption. Figure 3a is a typical large-scale STM image in which PcOC8 molecules (low-contrast spots) and $\text{Pr}(\text{PcOC8})_2$ molecules (high-contrast spots) are observed simultaneously. It can be seen from the image that the both $\text{Pr}(\text{PcOC8})_2$ molecules and PcOC8 molecules form well-defined adlayers, although molecular defects of $\text{Pr}(\text{PcOC8})_2$ are corresponded. A careful observation found that, although the adlattice by bright spots form almost the same structure as that by dark spots and the two lattices match very well, several individual bright spots indicated by arrows in the image are obviously mismatched with the dark spots. This fact demonstrates that the bright spots correspond to $\text{Pr}(\text{PcOC8})_2$ molecules rather than the overlapping of PcOC8 molecules. Figure 3b is a cross-sectional profile along a molecular row indicated by line $S-S'$ in Figure 3a, showing the difference of corrugation heights. Between PcOC8 and $\text{Pr}(\text{PcOC8})_2$, the corrugation height difference is measured to be 0.4 ± 0.2 nm.

A previous result showed a monolayer of CuPcOC8 formed on the HOPG surface.^{16,39} In the present research, a unit cell for PcOC8 molecular adlayer can be induced from the STM

image. A square for the unit cell is outlined in Figure 3a. The parameters are determined to be $k' = 2.5 \pm 0.2$ nm, $l' = 2.5 \pm 0.2$ nm, and $\alpha' = 90^\circ \pm 2^\circ$, which are very close to the previous reports of CuPcOC8 on HOPG.^{16,39} $\text{Pr}(\text{PcOC8})_2$ assembly in the mixed adlayer also shows a 4-fold symmetry, which is similar to that of the pure $\text{Pr}(\text{PcOC8})_2$ adlayer.

Figure 3c is a higher-resolution STM image showing the details of the molecular adlayer. The square shape of an individual $\text{Pr}(\text{PcOC8})_2$ molecule can be discriminated in this image. Intriguingly, there exists a PcOC8 molecule in this scanning area. From the large-scale STM image in Figure 3a, it is found that PcOC8 molecules and $\text{Pr}(\text{PcOC8})_2$ molecules have the same orientation on the HOPG surface. Therefore, the ligand at the bottom layer of a $\text{Pr}(\text{PcOC8})_2$ coordination complex molecule should take the same orientation on the HOPG surface. An angle γ marked in Figures 3c and 2c between the top ligand and the bottom ligand in a $\text{Pr}(\text{PcOC8})_2$ molecule can be determined. The value is measured to be $47^\circ \pm 2^\circ$, consistent with results reported in the literature.^{31–33,36} It is noteworthy that the detail of a $\text{Pr}(\text{PcOC8})_2$ molecule, such as alkyl chains, cannot be seen as clearly as that for a CuPcOC8 molecule in

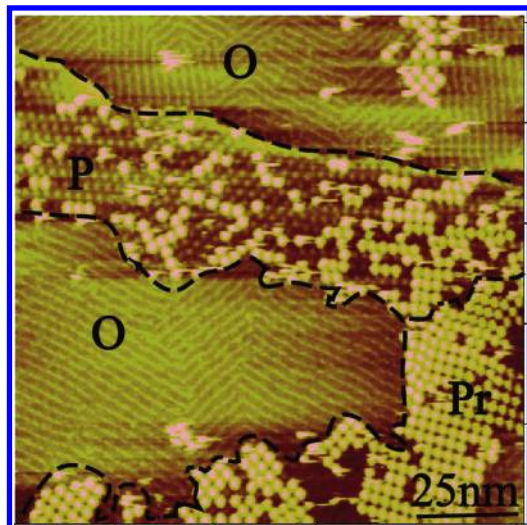


Figure 4. STM image of an adlayer with $\text{Pr}(\text{PcOC8})_2$, PcOC8 , and OPE molecules. Tunneling conditions are 853 mV and 426 pA. $\text{Pr}(\text{PcOC8})_2$ with PcOC8 and OPE molecules were dissolved in phenyloctane in a concentration less than 10^{-4} M.

high-resolution STM images.¹⁶ The flexibility and stability of the alkyl chains in the ligand at the top layer of a $\text{Pr}(\text{PcOC8})_2$ molecule may be responsible for this image difference. The alkyl chains in a CuPcOC8 molecule can adsorb directly on the HOPG surface. The stable adsorption results in an image showing the detailed structure of the molecule.

On the basis of the experiment results, it is concluded that $\text{Pr}(\text{PcOC8})_2$ molecules have similar assembly behavior to PcOC8 due to similar molecular structures between the ligands of $\text{Pr}(\text{PcOC8})_2$ and PcOC8 molecules. Therefore, although a coadsorption of $\text{Pr}(\text{PcOC8})_2$ and PcOC8 exists in self-assembly, no phase separation is observed. However, when OPE molecules were added into the solutions containing $\text{Pr}(\text{PcOC8})_2$ and PcOC8 , different adsorption behavior was found in the molecular assemblies.

Figure 4 is a large-scale STM image showing the adlayer by $\text{Pr}(\text{PcOC8})_2$, PcOC8 , and OPE molecules with different contrasts. Three domains can be seen in the image, as indicated by Pr, P and O. From the chemical structures and features in STM images, the domain Pr is composed of $\text{Pr}(\text{PcOC8})_2$. The domain O is composed of OPE molecules. From a higher-resolution STM image (not shown here), the structure of the OPE adlayer is the same as that reported in the literature.³⁸ In the domain P, although several bright spots of $\text{Pr}(\text{PcOC8})_2$ can be observed, the PcOC8 adlayer is clearly resolved. The three kinds of molecules can be corresponded in different domains.

To understand the details on the coadsorption, we prepared an adlayer with PcOC8 and OPE molecules. Figure 5 is a typical STM image showing the coadsorbed adlayer. From this image, we can understand that the two molecules form a well-ordered adlayer on the HOPG surface. The OPE molecules show the same structure as that reported in the literature.³⁸ The bright lines and low-contrast bands are attributed to the backbone and the side alkane chains of OPE molecules. The PcOC8 molecules mainly form a hexagonal pattern similar to that in MPcOC8 adlayers.^{16,39} The molecules exist in solitary domains, resulting in a separated phase. The molecules directly bond at the HOPG surface. No overlay was found.

When $\text{Pr}(\text{PcOC8})_2$ molecules were mixed with OPE molecules, a new adlayer appears. Figure 6 is a large-scale STM image showing the adlayer feature. There are bright spots corresponding to $\text{Pr}(\text{PcOC8})_2$ molecules in the image. Several

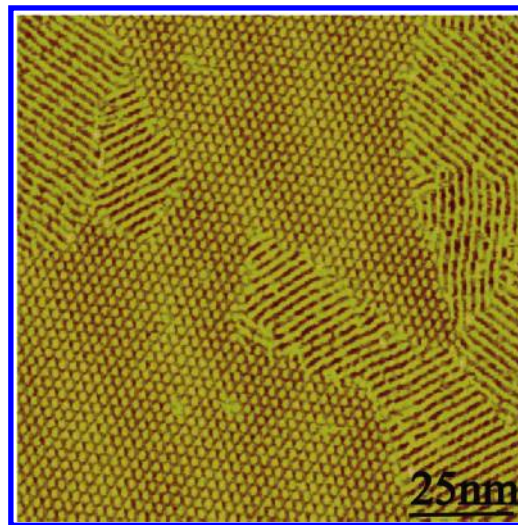


Figure 5. STM image of an adlayer by the coadsorption of PcOC8 and OPE molecules. Tunneling conditions are 710 mV and 679 pA. PcOC8 and OPE molecules were dissolved in phenyloctane in a concentration less than 10^{-4} M.

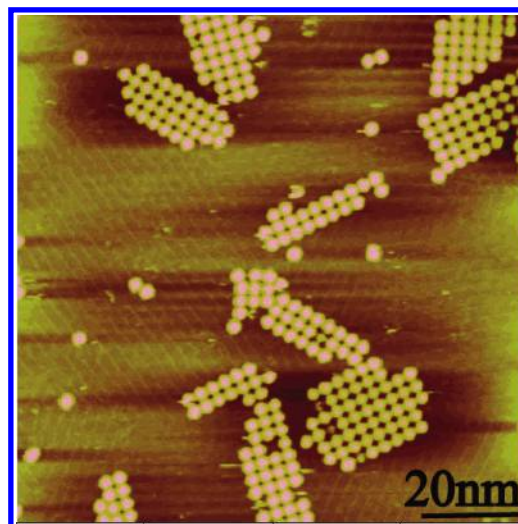


Figure 6. Large-scale STM image of $\text{Pr}(\text{PcOC8})_2$ and OPE molecular adlayer. Tunneling conditions are 894 mV and 500 pA. $\text{Pr}(\text{PcOC8})_2$ and OPE molecules were dissolved in phenyloctane in a concentration less than 10^{-4} M.

$\text{Pr}(\text{PcOC8})_2$ domains can be seen. Every domain appears in a 4-fold symmetry, as did the results in Figure 2. The OPE adlayer is also observed in this image around the $\text{Pr}(\text{PcOC8})_2$ molecular domains. From the image characteristics and corrugation height, we assume the $\text{Pr}(\text{PcOC8})_2$ adlayer is overlapped on the OPE adlayer. To further confirm this assumption, a traditional imaging method, using low voltage, high current, and fast scan rate, was employed to remove the molecules at the top layer. If $\text{Pr}(\text{PcOC8})_2$ molecules site on the OPE adlayer, the OPE adlayer will be seen after removing the top $\text{Pr}(\text{PcOC8})_2$ molecules. We chose an area shown in Figure 7a where a $\text{Pr}(\text{PcOC8})_2$ and OPE adlayer exist to make this confirmation. An arrow in the lower part of the image indicates a featured part of the image as a mark to demonstrate the same scanning area. Figure 7a–c is a series of STM images for this process. Figure 7a is the first image recorded before removing second layer molecules, where both OPE and $\text{Pr}(\text{PcOC8})_2$ molecules can be observed. If the $\text{Pr}(\text{PcOC8})_2$ molecules were removed by the STM tip, the lower layer would be imaged. Figure 7b is the image collected after removing $\text{Pr}(\text{PcOC8})_2$ molecules. Compared with Figure 7a, the

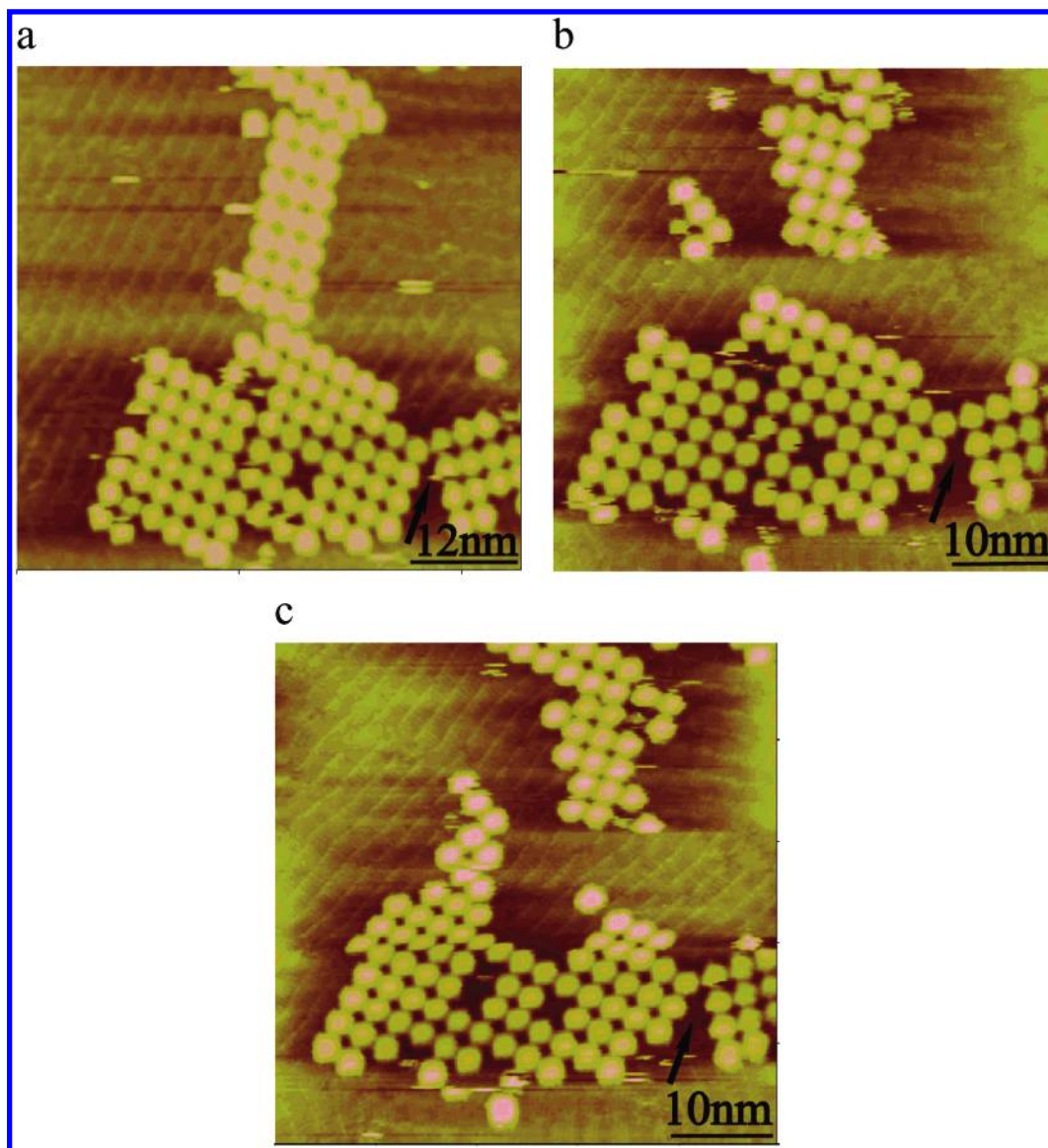


Figure 7. (a) STM image of $\text{Pr}(\text{PcOC8})_2$ and OPE molecular adlayer before removing parts of $\text{Pr}(\text{PcOC8})_2$ molecules. (b) STM image of $\text{Pr}(\text{PcOC8})_2$ and OPE molecular adlayer after removing the $\text{Pr}(\text{PcOC8})_2$ molecules in the middle area. (c) STM image of $\text{Pr}(\text{PcOC8})_2$ and OPE molecular adlayer after removing $\text{Pr}(\text{PcOC8})_2$ molecules in the middle area. Tunneling conditions: (a) 894 mV and 466 pA, (b) 808 mV and 443 pA, and (c) 753 mV and 468 pA. $\text{Pr}(\text{PcOC8})_2$ and OPE molecules were dissolved in phenyloctane in a concentration less than 10^{-4} M.

$\text{Pr}(\text{PcOC8})_2$ molecules in the middle part of the image no longer appear. Now, the lower adlayer is clearly seen, showing the same feature of the OPE adlayer as that in their neighboring area. This result further demonstrates that the $\text{Pr}(\text{PcOC8})_2$ molecules position at the top of OPE adlayer. No phase separation can be found in the coadsorbed adlayer. Figure 7c is another image showing the overlapping adlayer. Although several $\text{Pr}(\text{PcOC8})_2$ molecules diffused back to the middle part of the image, the larger OPE adlayer is resolved.

There is another possibility for the image formation of OPE molecules such as Figure 7b and c. The OPE molecules may diffuse from other parts to the positions where $\text{Pr}(\text{PcOC8})_2$ molecules occupied before they were removed by the STM tip. If this is true, these OPE molecules would adsorb on the HOPG surface and form domains. At least, molecular defects would be observed in the STM image due to a limited diffusion time. However, the OPE molecules adsorbed in the place exposed by removing $\text{Pr}(\text{PcOC8})_2$ molecules are found to be in the same domain as those OPE molecules sited in the area where no $\text{Pr}(\text{PcOC8})_2$ molecules occupied. Furthermore, no domain boundaries or molecular defects can be seen. On the basis of

the above discussion, it can be concluded that the adlayer of $\text{Pr}(\text{PcOC8})_2$ is at the top of the OPE adlayer rather than surrounded by the OPE adlayer. Note that the experiment was done in the presence of $\text{Pr}(\text{PcOC8})_2$ molecules in phenyloctane solvent. During the fast scanning, $\text{Pr}(\text{PcOC8})_2$ molecules in solvent will diffuse and fill the places occupied previously by $\text{Pr}(\text{PcOC8})_2$ molecules on the OPE adlayer. Therefore, most of the $\text{Pr}(\text{PcOC8})_2$ adlayer still remains in the scanning area. However, it can be seen that the molecules near the domain boundary in the middle part of the image are partially removed in Figure 7b and locally recovered in Figure 7c.

The formation of a self-assembly is dependent on the interactions of intermolecule and molecule/substrate. In special cases, the intramolecular interaction also plays an important role. In the present research, owing to the similar chemical structure between PcOC8 and the ligands of $\text{Pr}(\text{PcOC8})_2$, the intermolecular interaction is not enough to induce phase separation. The interaction between a molecule and the HOPG surface dominates the adlayer formation. However, in the system of PcOC8 and OPE, the intermolecular interaction among the same OPE molecules or same PcOC8 molecules is stronger than that

between the different molecules. Therefore, a phase separation adlayer was observed. When Pr(PcOC8)₂ and OPE were mixed together, the interaction between OPE molecules and HOPG substrate is stronger than that between Pr(PcOC8)₂ and HOPG, resulting in a preferential adsorption of OPE. An OPE adlayer was first formed on HOPG surface and then an overlayer of Pr(PcOC8)₂ was observed on the top of the OPE assembly. This discussion is basically a qualitative explanation for the formation of self-assemblies by molecular coadsorption. Theoretical simulation and calculation would supply useful information on the various interactions. The results reported in this paper should be important in constructing multicomponent adlayers on a solid surface and be significant in the study of intermolecular and molecule/substrate reactions.

Conclusion

With scanning tunneling microscopy, the self-assembled monolayers of PcOC8, Pr(PcOC8)₂, and OPE were investigated on a HOPG surface. Pr(PcOC8)₂ formed ordered structures with 4-fold or quasihexagonal symmetries. The angle γ between two ligands in a Pr(PcOC8)₂ molecule was measured to be about $47^\circ \pm 2^\circ$. The mixture of Pr(PcOC8)₂ and PcOC8 molecules formed a coadsorbed adlayer. No phase-separated structure was observed in the coadsorbed adlayer. When Pr(PcOC8)₂ and PcOC8 were mixed with OPE molecules, repeated experimental results showed that the adlayer of Pr(PcOC8)₂ is at the top of the OPE adlayer, while phase separation was seen in the adlayer of PcOC8 and OPE. In this report, the different multicomponent adlayer structures were constructed and analyzed at the sub-molecular level. The results may help us fabricate multicomponent surface nanostructure accurately and may be important in fabricating nanodevices through bottom-up strategy in the future.

Acknowledgment. Financial support from the National Natural Science Foundation of China (20303023 and 20520140277), National Key Project for Basic Research (2002CCA03100 and G2000077501), National Center for Nanoscience and Nanotechnology, and Chinese Academy of Sciences is gratefully acknowledged.

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