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Tuning Interactions between Ligands in Self-Assembled Double-Decker Phthalocyanine Arrays

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Controlled assembly of molecular components on surfaces is a crucial step in the development of many molecular-scale devices.[1] Various efforts in synthesis and self-assembly strategies have resulted in increasingly sophisticated supramolecular structures.[2−4] Such structures result from the balance between surface−adsorbate and adsorbate−adsorbate interactions.[4,5] While most studies have focused on controlling 2D structures, a wide range of novel properties, such as molecular rectification,[6] controlled rotary motions,[7] and the potential to address individual molecules, can be introduced into surface structures if additional complexity is incorporated in the surface normal direction.[8] In the formation of such 3D structures, the interactions are no longer restricted to the components in the surface plane; interactions from those elevated from the surface may play important roles as well.

Diverse arrays of surface structures of porphyrin derivatives can be achieved by varying the substituent groups[2] as well as through coadsorption.[9] In addition, by attaching ligands to the center metal, one can grow 3D structures from a 2D template of porphyrins.[10,11] To understand how the additional 3D complexities impact the self-assembly of 3D structures, we have focused our attention on lanthanide sandwich complexes such as double-decker (DD) molecules (Figures 1A and 2A), where parallel porphyrin or phthalocyanine rings are connected by rare earth cations.[12,13] Such structures add additional unique electronic,[14] optical,[15] and redox properties[15] to the rich properties of porphyrin derivatives. In addition, Aida and co-workers demonstrated that DD molecules can behave as redox-modulated rotary machines in the solution phase.[16]

The DD molecules can form highly ordered adlayers on HOPG.[17] Coadsorption of the DD molecule $Pr[Pc(OC_8H_{17})_8]_2$ with metal-free $H_2Pc(OC_8H_{17})_8$ (Chart 1) on graphite leads to random mixing.[18] In this work, we seek to understand how the interactions at different distances from the surface influence the surface structure of DD. By varying the sizes of the top ligands, we observed expansion of the lattice even though the top ligands remain too small to interact directly with each other. We also demonstrate that DD molecules in different local environments adopt significantly different structures. Deliberate control of these interactions can lead to controlled self-assembly of 3D structures from surfaces.

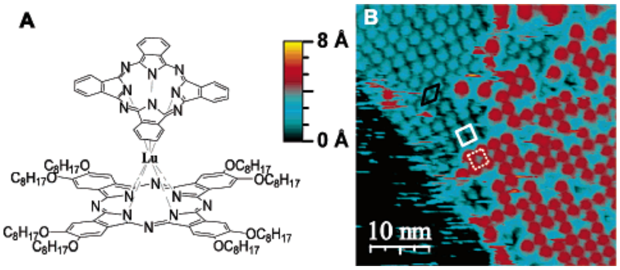


Figure 1. (A) Molecular structure of $(Pc)Lu[Pc(OC_8H_{17})_8]$ and (B) STM image of mixed adlayers of $(Pc)Lu[Pc(OC_8H_{17})_8]$ and $H_2Pc(OC_8H_{17})_8$ under phenyloctane on HOPG: sample bias, −0.5 V; tunneling current, 2 pA. The blue area corresponds to the $H_2Pc(OC_8H_{17})_8$ adlayer. The black parallelogram indicates a quasi-hexagonal lattice with a nearest neighbor distance of 2.5 ± 0.1 nm. The solid white square indicates a square lattice with a nearest neighbor distance of 2.5 ± 0.1 nm. The red protrusions correspond to the $(Pc)Lu[Pc(OC_8H_{17})_8]$ adlayer.

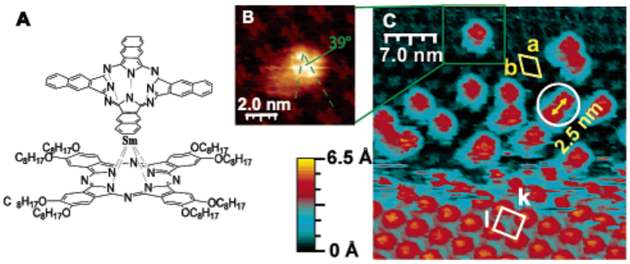
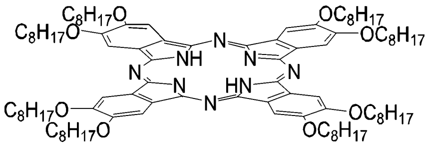


Figure 2. (A) Molecular structure of $(Nc)Sm[Pc(OC_8H_{17})_8]$. STM images of coadsorbed DD $(Nc)Sm[Pc(OC_8H_{17})_8]$ and $H_2Pc(OC_8H_{17})_8$ on HOPG: sample bias, −0.5 V; tunneling current, 1 pA. Panel B shows an area of an isolated DD molecule. Panel C is an area showing aggregated DD molecules. Red dots correspond to DD, lattice constants: $k = 3.0 \pm 0.1$ nm; $l = 3.0 \pm 0.1$ nm; angle = 91 ± 5°. Blue features correspond to metal-free $H_2Pc(OC_8H_{17})_8$, lattice constants: $a = 2.5 \pm 0.1$ nm; $b = 2.4 \pm 0.1$ nm; angle = 70 ± 5°.

Chart 1. Molecular Structure of a Metal-Free Phthalocyanine $H_2Pc(OC_8H_{17})_8$. $Pc(OC_8H_{17})_8$ = 2,3,9,10,16,17,23,24-Octakis-(octyloxy)-phthalocyanine



To understand the role of the bottom ligand in the surface arrangement of DDs, we coadsorbed $(Pc)Lu[Pc(OC_8H_{17})_8]$ with metal-free $H_2Pc(OC_8H_{17})_8$ on highly oriented pyrolytic graphite (HOPG). Two types of areas with apparent heights differing by 0.3−0.4 nm were observed (Figure 1B). At the lower area, both quasi-hexagonal and square lattices with lattice constants of 2.5 ± 0.1 nm were observed, consistent with results for adlayers of metallized $Pc(OC_8H_{17})_8$.[19] To maintain such short distances, the alkyl chains must interdigitate.[19] A square lattice with the same lattice constant of 2.5 ± 0.1 nm was again observed in the more protruding domains (white dotted square in Figure 1B), along with some defects 0.3−0.4 nm deep. We assign the lower area to $H_2Pc(OC_8H_{17})_8$ and the more protruding area to DD. The DD molecules appear in registry with the $H_2Pc(OC_8H_{17})_8$ adlayer; that

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10.1021/ja060029o CCC: $33.50 © 2006 American Chemical Society

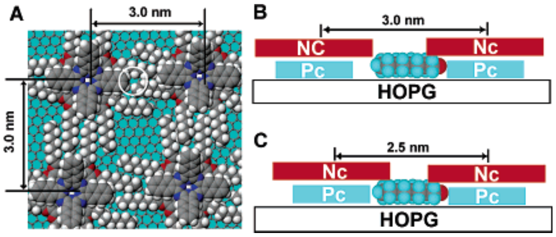

Figure 3. Proposed model for packing of (Nc)Sm[$Pc(OC_8H_{17})_8$] on HOPG. (A) Top view: The white circle indicates that an alkyl chain terminal is aligned at the outer edge of a naphthalene group to form a distance of 3.0 nm; (B) side view; (C) side view, the alkyl chain is forced to occupy the cavity between Nc and HOPG.

is, if a grid is drawn on the lattice of $H_2Pc(OC_8H_{17})_8$, the centers of all the protruding DD molecules align to the grid. This provides evidence that (1) the DD molecules are embedded in rather than being adsorbed on top of the $H_2Pc(OC_8H_{17})_8$ adlayer, and (2) the $Pc(OC_8H_{17})_8$ ligands of the more protruding DD are adsorbed onto the surface to assume identical packing to the neighboring $H_2Pc(OC_8H_{17})_8$ adlayer. In this case, the top ligand, unsubstituted Pc, does not change the surface packing. This is understandable since the diagonal size of Pc is only about 1.6 nm. Therefore, the interactions between the bottom ligands of DD molecules and $H_2Pc(OC_8H_{17})_8$ produced a square lattice similar to that of pure $H_2Pc(OC_8H_{17})_8$.[19]

To gain more insight into the effect of the top ligand, we chose a DD with a bulkier ligand, naphthalocyanine (Nc). Coadsorbing $H_2Pc(OC_8H_{17})_8$ with (Nc)Sm[$Pc(OC_8H_{17})_8$] (Figure 2A) results in an array of four-lobed features with a diagonal size of 1.6 nm, consistent with $H_2Pc(OC_8H_{17})_8$[19] (Figure 2B). In addition, a four-lobed protrusion 0.3−0.4 nm high was also observed in Figure 2B. The diagonal size of 2.1 nm is slightly larger than that of Pc and consistent with the molecular size of Nc. Therefore, we attribute the protrusions to DD with the Nc ligand facing up to be resolved by STM and $Pc(OC_8H_{17})_8$ ligand adsorbed onto the surface because of its higher interaction with the surface.[19] Most of the isolated DD molecules were in registry with the surrounding $H_2Pc(OC_8H_{17})_8$ lattice (Figure 2C). Therefore, we assume that the bottom $Pc(OC_8H_{17})_8$ ligand of the double-decker is parallel to the $H_2Pc(OC_8H_{17})_8$ matrix. Through measuring the angles between Nc of the DD molecules and neighboring $H_2Pc(OC_8H_{17})_8$, the angles between the two ligands of the DD molecule were found to be 39 ± 5°, close to 41°, the value from X-ray crystallography.[12]

The protrusions were either isolated or segregated into domains (Figure 2C). The aggregated molecules, also appearing 0.3−0.4 nm high under these conditions, assumed a nearly square surface arrangement with lattice constants of 3.0 ± 0.1 nm, in contrast to the 2.5 nm observed on the $H_2Pc(OC_8H_{17})_8$ lattice. It appears that, unlike Pc, the top Nc ligands are large enough to have significant repulsion, leading to an expanded lattice. However, with a distance of 2.5−3.0 nm and an Nc diagonal size of 2.1 nm, the smallest possible distance between the naphthalene units is 0.4−0.9 nm, where van der Waals repulsion with each other should be small. To explain the expanded lattice, we juxtaposed molecular models of DD (optimized by MM3 in CAChe, Fujitsu) in a square lattice similar to that of $Pc(OC_8H_{17})_8$,[19] where the alkyl chains are known to interdigitate (Figure 3).[19] When the distance is 2.5 nm (Figure 3C), steric repulsion between the naphthalene units and alkyl chains is present because the size of the cavities between the naphthalene units and graphite surface, 0.3−0.4 nm,[12] is slightly smaller than the van der Waals diameter of the alkyl chain, 0.4−0.5 nm.[5] However, when the DD molecules are far away enough to eliminate such repulsion, that is, the methyl termini of the alkyl chains are placed at the outer edges of the naphthalene, the distance becomes 3.0 nm, in agreement with the experimental value (Figure 3A,B). Therefore, we suggest that steric repulsion between the naphthalene units and alkyl chains is responsible for the expanded lattice.

It is also worth noting that when two DD molecules are next to each other and surrounded by $H_2Pc(OC_8H_{17})_8$, the nearest neighbor distance, 2.5 nm, is almost identical to that of $H_2Pc(OC_8H_{17})_8$ (circle in Figure 2C). In this case, the alkyl chains may be forced to occupy the cavities between the naphthalene groups and the HOPG surface (Figure 3C) or to bend to accommodate the smaller intermolecular distance. If the distance between the two neighboring DD molecules were to expand because of the repulsion between the alkyl chains and naphthalene groups, the distance DD and its neighboring $H_2Pc(OC_8H_{17})_8$ must decrease. However, the fully interdigitated alkyl spacers between a DD and its neighboring $H_2Pc(OC_8H_{17})_8$ are more difficult to compress because of the lack of free space. Therefore, the two DD molecules are confined in the lattice of the neighboring $H_2Pc(OC_8H_{17})_8$ with identical lattice constants.

In conclusion, DD molecules represent an interesting system to engineer intermolecular interactions systematically at different distances from the surface. Increased size of the top ligand in DD eventually expanded the lattice in the adlayer. Such atomic-level understanding and control are crucial for molecular devices such as field effect transistors and surface-mounted rotors.[7,14]

Acknowledgment. This work was supported by Visionarts, NSF (T.Y., T.T., and P.S.W.), NSFC, and MOST (R.W. and J.J.). We thank Prof. Vin Crespi for helpful discussions.

Supporting Information Available: Experimental and modeling procedures; high-resolution STM images of DD molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA060029O