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Controlled Adsorption Orientation for Double-Decker Complexes

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Control of the molecular orientation of double-decker complexes comprised of rare-earth metals sandwiched with naphthalocyanine and porphyrin/phthalocyanine, at the interface of a graphite surface and 1-phenyloctane solution, has been demonstrated for the future application of molecular rotor assembly. Scanning tunneling microscope images clarified the internal structures of the top ligands. The observed images indicate that naphthalocyanine ligands were selectively adsorbed onto the graphite surface and the counterpart ligands of porphyrin/phthalocyanine were oriented off the surface. Control of the orientation of monolayers of mixed double-decker complexes has also been demonstrated.

Introduction

Design of synthetic molecules makes it possible to form assemblies with predictable structures.¹ Control of the lateral arrangements of molecules in two-dimensional arrays and their exposed chemical functionality is necessary for the development of molecular-scale devices.^{1–3} Elaborate control of porphyrin (Por) and phthalocyanine (Pc) assemblies has been achieved by varying their substituent groups⁴ as well as through coadsorption.⁵ Three-dimensional structures of Por/Pc arrays can be constructed from two-dimensional arrays by attaching ligands to the center metals in the Por/Pc rings.^{1,6,7}

Lanthanide sandwich complexes such as double-decker (DD) molecules, as shown in Chart 1, where parallel naphthalocyanine (Nc) and Por/Pc rings are connected by rare-earth cations,⁸ are promising candidates for controlled functional arrays of molecular switches⁹ and molecular motors^{10,11} as DD molecules have been demonstrated as redox-modulated rotary machines in the solution phase.¹² Recently, well-ordered arrays of homoleptic DD molecules with octakis(octyloxy)phthalocyaninato ligands were observed by scanning tunneling microscopy (STM), and the periodicity was regulated by the surrounding alkyl chains,^{13–15} because molecules substituted with the long alkyl chains made it possible to immobilize them on highly oriented pyrolytic graphite (HOPG) surfaces, allowing their observation by STM.^{16–19} Heteroleptic DD molecules with long alkyl chains surrounding the bottom ligands were also observed, and isolation of the DD molecules was also achieved.^{20,21}

Control of the distances between DD molecules is a key element in building functional arrays of DD-based molecular

rotors. Alkyl chains can act as spacers to produce nearest neighbor distances of 2.5 nm or longer.²¹ In this work, we demonstrate the ability to control the molecular orientation in DD arrays using Nc as bottom ligands on the HOPG substrate, utilizing the difference in adsorption energies between top and bottom ligands. The surface periodicity of the DDs with various top ligands was maintained constant, indicating that the two-dimensional periodicity of the molecular arrays having the bottom ligands larger than the top can be controlled. The smaller lattice constant, 1.7 nm, makes it possible to introduce interactions between rotors for the construction of molecular gears and rotary machines.¹¹

Experimental Section

Heteroleptic double-decker complexes in this study were synthesized according to published procedures.^{22–25} These compounds have been characterized by elemental analysis and a wide range of spectroscopic methods including electronic absorption spectroscopy, infrared absorption spectroscopy, matrix-assisted laser desorption time-of-flight mass spectrometry, and ¹H nuclear magnetic resonance spectroscopy. The double-decker compounds were dissolved in 1-phenyloctane. The concentrations of the solution were kept in the range of 0.1–1 mM. The molar ratio of mixed double-deckers shown in Figure 3 was 1:1. The prepared solution was dropped on an HOPG substrate (SPI Supplies, ZYA-grade, 10 mm × 10 mm) at room temperature. A mechanically cut Pt–Ir (80–20%) wire was used as the STM tip. The STM observations were carried out on a Pico SPM microscope head (Molecular Imaging) controlled by a low-noise controller RHK SPM 1000 (RHK Technology). Scanning speeds slower than 1 line/s made it possible to record images at tunneling currents below 1 pA. All the horizontal scales of the STM images were calibrated using the hexagonal lattice of the HOPG (*a* = 0.246 nm), and all the vertical scales of the STM images were calibrated with monatomic steps of HOPG (*c*/2 = 0.34 nm). The azimuthal orientations

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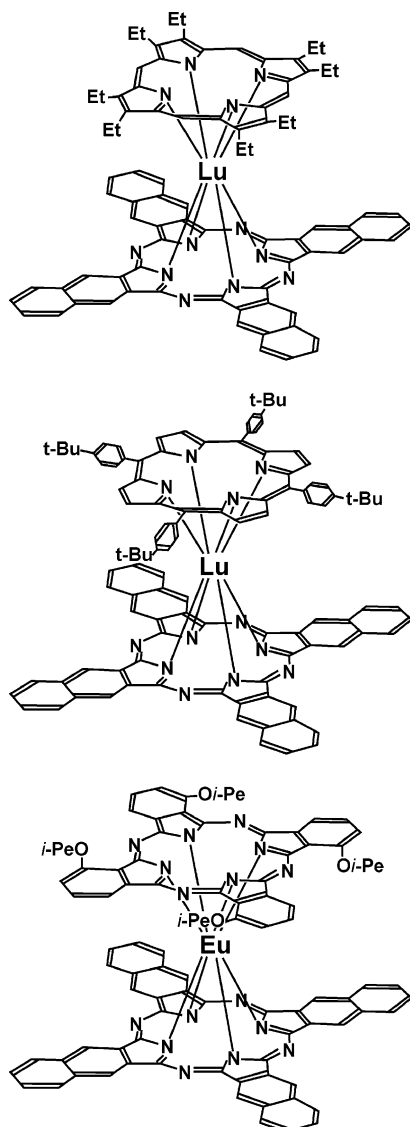
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CHART 1: Molecular Structures of Double-Decker (Nc)Lu(OEP) (Upper), (Nc)Lu(TBPP) (Middle), and (Nc)Eu(α -TPPc) (Lower)^a



^a Nc = naphthalocyanine; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin; TBPP = 5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin; α -TPPc = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine. Et = $-\text{CH}_2\text{CH}_3$, *t*-Bu = $-\text{C}(\text{CH}_3)_3$, *i*-Pe = $-\text{CH}(\text{CH}_2\text{CH}_3)_2$.

of the substrate graphite [100] and [210] directions were determined from the observed steps in STM images.

Results and Discussion

Nearly square unit cells formed on graphite surfaces with each of the three different kinds of DD molecules (Chart 1). Figure 1 shows molecular resolution images of three kinds of DD complexes. The left images show rhombic unit cells with lattice constants of 1.7 ± 0.1 nm and an angle $82 \pm 5^\circ$. The unit cells align along the [100] direction, and the lattice constant of 1.7 nm corresponds to 7 times the periodicity of the graphite substrate (0.246 nm). Although different unit cells, for example, twice (3.4 nm) the periodic unit cells or hexagonal unit cells, were sometimes observed in different areas, the most common close-packed structures are shown. Lackinger et al. observed Nc molecules adsorbed on graphite in ultrahigh vacuum at 50 K.²⁶ The lattice constant of 1.7 nm and the angle 82° of the Nc unit cell in their study are in agreement with our STM study of

DD molecules, and we concluded that the DD unit cells with close-packed structures found here were determined by the bottom Nc ligand.

Even for these close-packed structures, gaps between the DD molecules were observed; the Nc–Lu–OEP (2,3,7,8,12,13,17,18-octaethylporphyrin) image in the upper left frame of Figure 1 showed a gap of ca. 0.5 nm between the DD molecules, and the apparent size of Nc–Lu–OEP from the image was 1.2 nm, which is in good agreement with the size of OEP, as shown in the superimposed molecular schematic in the upper left frame. Therefore, the STM images show the top ligands of DD molecules, and the Nc ligands were underneath the top ligands. Higher resolution images of the DD molecules were consistent with the shapes of respective Por/Pc ligands, each shown in the center column in Figure 1. Models of the molecules in the center column images are shown in the right column of Figure 1. The top ligands, with eight ethyl moieties in OEP, four *tert*-butylphenyl moieties in 5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin (TBPP), and four *iso*-pentyloxy moieties in 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine (TPPc), can be recognized as the corresponding protrusions in the high-resolution images, and the protrusions cannot be explained supposing that the top ligand is Nc because the protrusions are smaller than the size of the protrusions in the Nc ligand alone (2.1 nm, observed previously).²¹ These images are evidence that Nc ligands were placed on the graphite while the counterpart Por and Pc ligands were lifted off and oriented toward the solvent. Moreover, the four protrusions in the single-molecular image of the TBPP ligand shown in the center frame of Figure 1 were not homogeneous; the lower left and upper right protrusions were higher than upper left and lower right protrusions. This is due to the difference of the torsional angles between the phenyl rings and the Por ring in the TBPP top ligand, which is in agreement with measurements of tetraphenylporphyrin.²⁷

One can argue that Nc ligands may be transparent in STM images because of the electron density of states of DD molecules, and the top ligands may not be observed by STM. However, this possibility can be discounted by the following evidence. We reported STM images of homoleptic DD and triple-decker molecules, and the images showed the slipped stacking of the molecules; both the top and bottom ligands in DD molecules and the top, middle, and bottom ligands in triple-decker molecules were observed,¹⁴ which is evidence that top ligands are not transparent. We also reported STM images of isolated DD molecules in a Pc matrix, and apparent height differences of DD molecules of 0.3–0.4 nm from the Pc monomer matrix were observed.²¹ Moreover, theoretical studies indicate that both top and bottom ligands have local density of states for the highest occupied molecular orbitals and the lowest occupied molecular orbitals, and the electronic structure indicated that DD molecules were semiconducting (i.e., exhibited a gap).⁸

Since Nc is a larger π -conjugated system than Pc and Por, the Nc ligands in the DD molecules were selectively adsorbed on graphite and the counterpart ligands of the Por/Pc were oriented up, as indicated by the aforementioned STM results. Theoretical calculations supported the STM results. We have performed classical mechanics (MM3) calculations using CAChe (Fujitsu) software to obtain energy-minimized conformations with a graphite monolayer sheet of 984 carbon atoms with the edges terminated with hydrogen atoms and single-adsorbed molecules of Nc, OEP, TBPP, or α -TPPc attached onto the graphite sheets. The calculated results showed that adsorption energy of Nc is the largest among the calculated molecules, which is consistent with the STM results. Moreover, we have

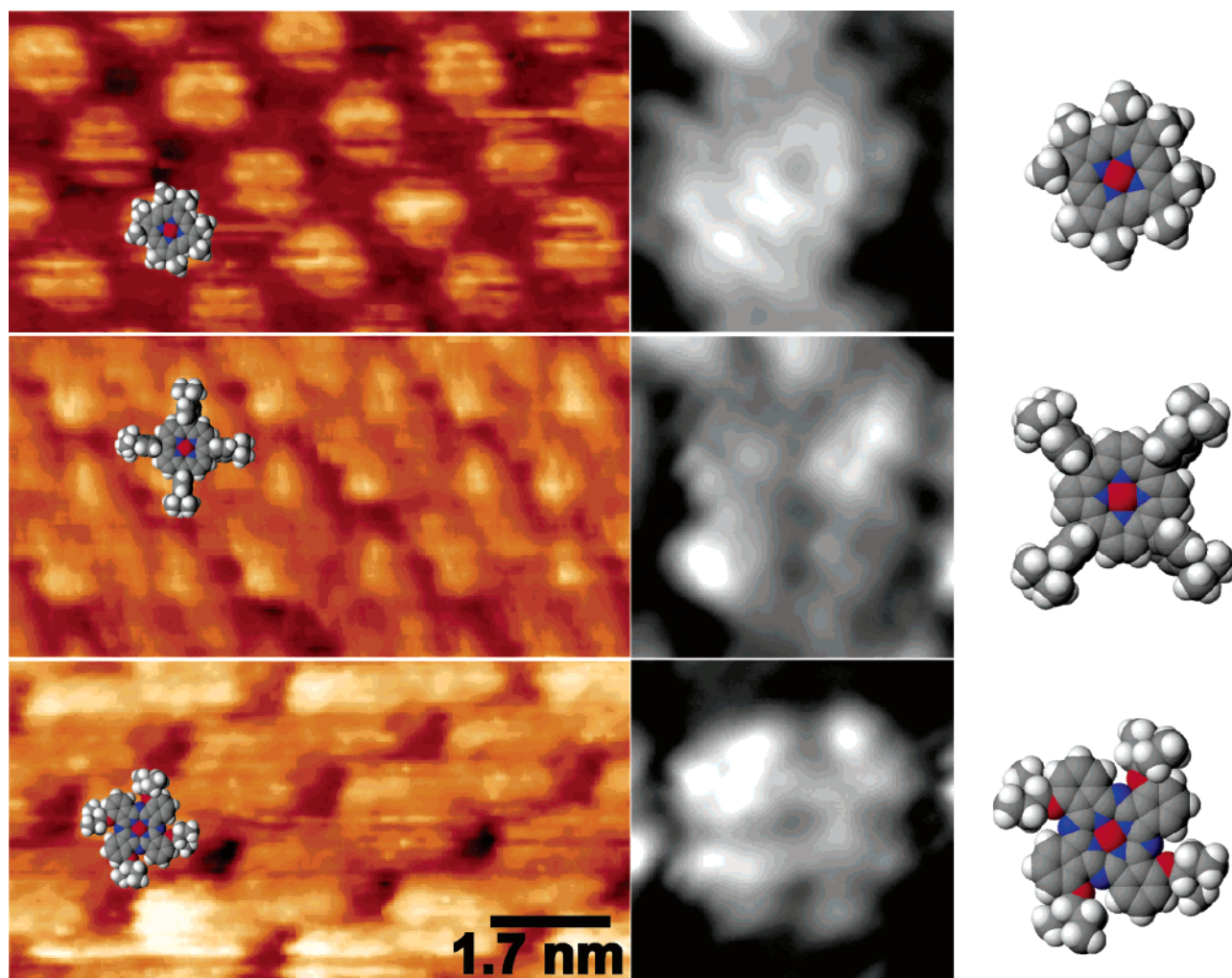


Figure 1. Scanning tunneling microscope images of double-decker complexes of rare-earth metals sandwiched with naphthalocyanine (Nc) and porphyrin/phthalocyanine under 1-phenyloctane. Upper, Nc-Lu-OEP; middle, Nc-Lu-TBPP; lower, Nc-Eu- α TPPc. Left: two-dimensional arrays with the unit cell of 1.7 nm; middle, single-molecular images; right, schematic molecular structures of the corresponding top layers in the double-deckers. The corresponding schematic molecular structures are also superimposed in the left images. Sample bias voltage: -0.6 V; tunneling current: 1 pA.

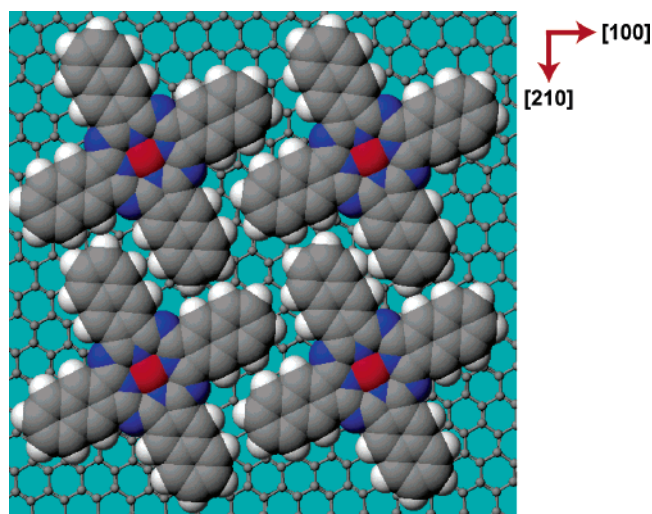


Figure 2. Proposed structure of naphthalocyanines on graphite with a nearly square unit cell of 1.7 nm. The gray, white, blue, and red spheres indicate carbon, hydrogen, nitrogen, and center metal atoms, respectively.

also performed the same calculations for the DD molecules of Nc-Lu-X ($X = \text{OEP, TBPP, } \alpha\text{TPPc}$) by comparing the adsorption energies with the Nc ligands attached on the graphite

sheet and with the counterpart ligands of Por/Pc attached on the sheet (upside down). The results indicated that the adsorption energies of the DD molecules with the Nc ligands onto the graphite sheet were larger than those with the counterpart ligands onto the sheet, also consistent with the STM results. Figure 2 shows a proposed structure of four Nc molecules on graphite. The nearest neighbor distance is 1.7 nm, which is in agreement with the STM images in this study. This value is approximately the same distance of $7a_0$ along the $[100]$ direction and $4\sqrt{3}a_0$ along the $[210]$ direction, where a_0 is the lattice constant of graphite (0.246 nm) though the square lattice of DD monolayers is incommensurate with the substrate graphite and has 3-fold symmetry.

To understand the role of the Nc bottom ligand in the surface arrangement of DD molecules, we coadsorbed DD Nc-Lu-OEP and Nc-Lu-TBPP complexes on graphite. Figure 3 shows STM images of the coadsorbed area. The apparent height of Nc-Lu-OEP is 0.1 nm lower in the images than that of Nc-Lu-TBPP, which is comparable to the physical height difference between Nc-Lu-OEP and Nc-Lu-TBPP. The DD complex phase segregates and the domains form stripes aligned along the $[100]$ direction of the substrate graphite. The periodicities along the $[100]$ direction for Nc-Lu-OEP and Nc-Lu-TBPP complexes are the same, with 7 times the spacing

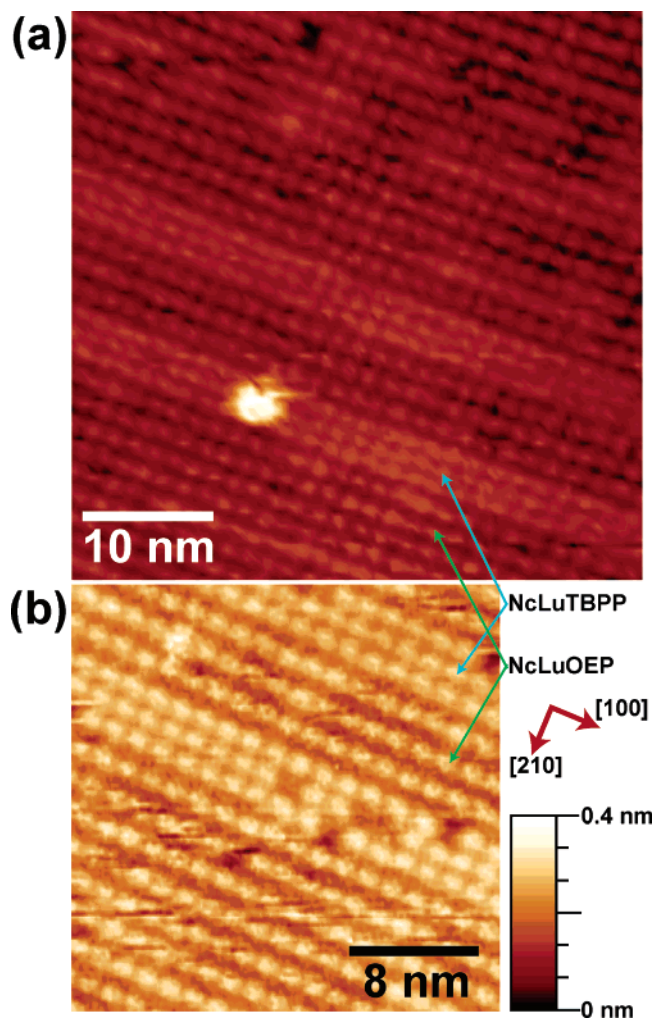


Figure 3. Scanning tunneling microscope images of the mixed layer of Nc-Lu-OEP and Nc-Lu-TBPP. Lower protrusions are assigned to Nc-Lu-OEP, indicated by green arrows, and higher protrusions to Nc-Lu-TBPP, indicated by blue arrows. Red arrows indicate the orientation of the graphite substrate lattice. Sample bias voltage: -0.6 V; tunneling current: 0.7 pA.

of the graphite lattice. In this way, we can control the orientation of the mixed DD layer and keep the same periodicity determined by the bottom ligands. The segregated Nc-Lu-OEP and Nc-Lu-TBPP domains share identical lattice constants, reinforcing the conclusion that the bottom Nc ligands, instead of the smaller top Por or Pc ligand, determine the surface periodicity. However, the segregation suggests a subtle role of the interactions of the top ligands, in the absence of which there would be random mixing of the two DD molecules.

Conclusion

Two-dimensional adlayers of rare-earth double-decker sandwich complexes with Nc and Por/Pc ligands on HOPG have been studied. The Nc ligands were always found to be attached to the graphite surface in this study. The nearly square surface unit cells of the double-decker monolayers studied were determined to have 1.7 ± 0.1 nm spacings and angles between the unit vectors of $82 \pm 5^\circ$, indicating that the Nc ligands dominate the periodicity. The ordered arrangements of the double-decker thin films provide opportunities for future applications in coupled molecular gear systems,¹⁵ molecular information storage,²⁸ and molecular phase memory.²⁹

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