J|A|C|S ARTICLES

Published on Web 11/16/2009

Molecular Motion of Surface-Immobilized Double-Decker Phthalocyanine Complexes

Koji Miyake,*[†] Megumi Fukuta,[†] Masumi Asakawa,*[‡] Yukari Hori,[§] Taichi Ikeda,[||]
and Toshimi Shimizu[‡]

Advanced Manufacturing Research Institute (AMRI), National Institute of Advanced Industrial Science and Technology (AIST), 1-2-1 Namiki, Tsukuba, Ibaraki 305-8564, Japan, Nanotube Research Center (NTRC), AIST, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, Oita Industrial Research Institute, 1-4361-10 Takaenishi, Oita 870-1117, Japan, and Organic Nanomaterials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received June 8, 2009; E-mail: koji-miyake@aist.go.jp; masumi-asakawa@aist.go.jp

Abstract: The molecular motion of surface-immobilized double-decker phthalocyanine complexes was examined using STM. $(C_8OPc)_2Ce$ (**1**), $(C_{12}OPc)_2Ce$ (**2**), and $(C_8OPc)Ce(Pc)$ (**3**) double-decker complexes, of which two ligands contained *Pc* nuclei, formed well-ordered self-organized structures on their own. Square-shaped top *Pc* ligands were clearly observed for complexes **1**, **2**, and **3** even though free space presented around the top ligands caused by mixing the complexes with template molecules. However, the details of the shapes of the top ligands of complexes **1**, **2**, and **3** were changed by the surrounding environment. The surrounding environment was considered to have influenced the mobility of the top ligands. Another complex, $(C_8OPc)Ce(TPP)$ (**4**), had difficulty forming a self-organized structure by itself. Complex **4** could have been immobilized by coadsorbing on the substrate with the C_8OPc template, but the intramolecular structure of the top ligands of complex **4** was difficult to observe. The results strongly suggested that combinations of molecules composed of double-decker complexes as well as the free space presented around a top ligand are important factors that control the molecular motion of immobilized double-decker complexes on solid surfaces.

Introduction

The molecular motors that have been reported previously[1,2] to convert chemical or light energy into directional rotary or linear motion all operated in solution. To overcome Brownian motion and perform useful work, anchoring and subsequently addressing molecular machines on surfaces is critical to the successful interfacing of nanomechanical systems with the macroscopic world. However, for nanomachines to be able to operate in devices, it is essential that the motors do not lose their functionality if immobilized.

Double-decker phthalocyanines are one of the promising candidates for molecular mechanical devices because of their molecular motion, such as trampoline-like movement and rotation.[3] In addition, several research groups have reported on the unique properties of the molecular rotation of double-decker complexes.[4,5] This rotation can be controlled by cooperative binding of guest molecules to specific functional groups within the complex[4] or by the redox properties of rare-earth central metals.[5] Effectively using their high potential and controlling the rotational motion of molecules requires effective techniques to immobilize these molecules and form ordered structures of them on substrates.

It is well-known that the alkyl-substituted phthalocyanines (C_nOPc) were arranged in lines or discrete states with regular spacing on highly oriented pyrolytic graphite (HOPG)[6,7] and metal[8] surfaces under ambient conditions. Therefore, we considered that double-decker phthalocyanines composed of alkyl-substituted phthalocyanine would be useful to form the ordered structure of double-decker complexes. Recently, ordered structures of double-deckers composed of alkyl-substituted phthalocyanines[9−15] and triple-decker complexes[16] have been observed using scanning tunneling microscopy (STM).

First, De Feyter and colleagues observed the ordered structure of bis[octakis(dodecyloxy) phthalocyaninato] erbium(III) complexes [$(C_{12}OPc)_2Er$], but they could not obtain any fine structure of phthalocyanine molecules.[9,12] They concluded that the lack of the fine structure was due to three possible reasons: (1) the

---

[†] AMRI, AIST.

[‡] NTRC, AIST.

[§] Oita Industrial Research Institute.

[||] National Institute for Materials Science.

(1) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25.

(2) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72.

(3) Maeda, F.; Hatsusaka, K.; Ohta, K.; Kimura, M. *J. Mater. Chem.* **2003**, *13*, 243.

(4) (a) Takeuchi, M.; Imada, T.; Shinkai, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 2096. (b) Sugasaki, A.; Ikeda, M.; Takeuchi, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3839.

(5) Tashiro, K.; Konishi, K.; Aida, T. *J. Am. Chem. Soc.* **2000**, *122*, 7921.

(6) (a) Qiu, X. C.; Wang, C.; Zeng, Q.; Xu, B.; Yin, S.; Wang, H.; Xu, S.; Bai, C. *J. Am. Chem. Soc.* **2000**, *122*, 5550. (b) Qiu, X.; Wang, C.; Yin, S.; Zeng, Q.; Xu, B.; Bai, C. *J. Phys. Chem. B* **2000**, *104*, 3570.

(7) Miyake, K.; Hori, Y.; Ikeda, T.; Asakawa, M.; Shimizu, T.; Sasaki, S. *Langmuir* **2008**, *24*, 4708.

(8) Suto, K.; Yoshimoto, S.; Itaya, K. *J. Am. Chem. Soc.* **2003**, *125*, 14976.

10.1021/ja904629d

relative orientation of both ligands, the two ligands are rotated 45° with respect of each other,[12] (2) some mobility of the phthalocyanine, or (3) electronic effects caused by the presence of the lanthanide ion. However, Yang and colleagues showed the fine intramolecular structure of bis[oktakis(octyloxy) phthalocyaninato] praseodymium(III) complexes [$(C_8OPc)_2Pr$].[10] In addition, STM images of lutetium(III) [$(C_8OPc)_2Lu$] observed at the solid−liquid interface also revealed the fine intramolecular structure.[11] These results indicate that top ligands do not move in contrast with the result of $(C_{12}OPc)_2Er$.[9,12] To control the molecular motion, it is important to clarify what causes the difference between the results of $(C_{12}OPc)_2Er$[9,12] and $(C_8OPc)_2Pr$[10] or $(C_8OPc)_2Lu$.[11] The origin of two conflicting data [$(C_{12}OPc)_2Er$[9,12] and $(C_8OPc)_2Pr$[10] or $(C_8OPc)_2Lu$[11]] is expected to be the difference in the length of the substituted alkyl chains or rare earth metal.

Recently, Otsuki et al. showed heterolepic cerium double-decker complexes of 5,15-bis[4-(phenylethynyl)phenyl]porphyrin and 5,10,15,20-tetrakis(4-decosyloxyphenyl)porphyrin [(BPEPP)(C_{22}OPP)Ce] flanked by free base molecules, where $H_2(C_{22}OPP)$ showed only isotropic STM images.[13] They concluded that the isotropic images might have been caused by the rotation of the top ligand. Therefore, the free space around the top ligands is also one of the important factors in determining molecular motion. Furthermore, we considered that the combination of two ligands would also be one possible cause for suppressing or inducing the molecular motion. However, recent reports about heterolepic double-deckers have indicated that the fine molecular structures of the top ligands were observed, although they had free space around the top ligands.[14,15] To successfully construct molecular machine devices, such as surface-mounted molecular motors, it is necessary to clarify the factors governing the motion of molecules peculiar to surface-immobilized double-decker complexes.

To clarify the factors governing the motion of molecules adsorbed on solid surfaces, we used STM to examine the ordered structures of molecular machine elements and the relationships between the ordered structures and molecular motion. Four double-decker complexes composed of combinations of octa-alkoxyl-substituted phthalocyanines (C_nOPc; n is the number of carbon atoms), phthalocyanine (*Pc*), and 5,10,15,20-tetra(phenyl)porphyrins (TPP) with cerium were synthesized. The molecular structures of the double-decker complexes, (C_nOPc)CeX (X = C_nOPc, *Pc*, TPP), are shown in Figure 1. Using STM, we examined varied combinations of the two ligands of double-decker complexes, the ordered structures of molecular machine elements, and the relationships between the ordered structures and molecular motion. To clarify the effect of the substituted alkyl chains on their molecular motion, we used $(C_8OPc)_2Ce$ and $(C_8OPc)Ce$(*Pc*), and to clarify the effect of the combination of molecules composed of double-decker complexes, we used $(C_8OPc)Ce$(TPP).

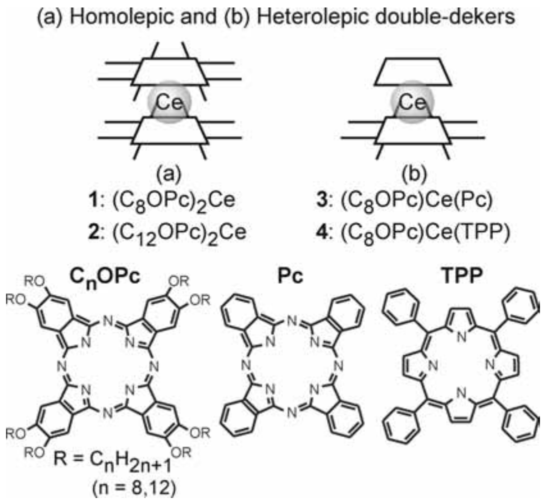

Figure 1. Molecular structures.

Experimental Section

Molecules. We synthesized two homolepic and two heterolepic cerium double-decker complexes (Figure 1). The two homolepic complexes were bis[octakis(octyloxy) phthalocyaninate] cerium complex [$(C_8OPc)_2Ce$] (**1**) and bis[octakis(dodecyloxy) phthalocyaninate] cerium complex [$(C_{12}OPc)_2Ce$] (**2**). The heterolepic double-decker complexes were $(C_8OPc)Ce$(*Pc*) (**3**) and $(C_8OPc)Ce$(TPP) (**4**). Column chromatography was performed using a Wakogel C-400HG (Wako Pure Chemical Industries). ^1H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 400 spectrometer (400 and 100 MHz for ^1H and ^{13}C NMR, respectively), using residual solvent as an internal standard. These materials produced satisfactory ^1H NMR and MALDI-TOFMS data.

STM Observations. The double-decker complexes were dissolved in phenyloctane with a concentration of less than 1 μM. Mixed self-organized structures were prepared using the mixture containing complexes **1**−**4** and template molecules. The total concentrations of the mixed systems were less than 1 μM. Next, the solution was dropped onto a freshly cleaved HOPG surface. The STM tip was immersed into the solution to observe the self-organized structures of these complexes formed at the solid−liquid interface. All STM (Nanoscope IIIa multimode SPM) observations were performed at room temperature using mechanically cut Pt/Ir tips (80:20). All STM images reported in this Article were collected with a constant current mode, and we used only flattened processing. The tunneling current (I_t) and the sample bias voltage (V_s) were set between 1 and 50 pA and between −2.0 and +2.0 V, respectively.

CPK Model Calculation. The models shown in this Article were based on the self-organized structures of the template molecules (C_nOPc). Our STM results indicated that double-deckers had assembly behaviors similar to those of C_nOPc (n = 8, 12) due to the similar molecular structures between the ligands of the (C_nOPc)CeX (X = C_nOPc, *Pc*, TPP) and C_nOPc molecules. Therefore, we optimized the self-organized structures of C_nOPc by calculation, and then superimposed top ligands on the optimized self-organized structure. The CPK models were optimized by molecular mechanics calculation (MM2 method). In this calculation, the optimized structures strongly depend on the initial structures. Therefore, the structure we show may not be a global minimum energy structure but a local minimum energy structure. However, in an actual system, the surface exists under the molecules, and we considered that the effect of the surface on the stability of the

---

(9) Binnemans, K.; Sleven, J.; De Feyter, S.; De Schryver, F. C.; Donnio, B.; Guillon, D. *Chem. Mater.* **2003**, *15*, 3930.

(10) Yang, Z. Y.; Gan, L. H.; Lei, S. B.; Wan, L. J.; Wang, C.; Jiang, J. Z. *J. Phys. Chem. B* **2005**, *109*, 19859.

(11) Takami, T.; Arnold, D. P.; Fuchs, A. V.; Will, G. D.; Goh, R.; Waclawik, E. R.; Bell, J. M.; Weiss, P. S.; Sugiura, K.-i.; Liu, W.; Jiang, J. *J. Phys. Chem. B* **2006**, *110*, 1661.

(12) Klymchenko, A. S.; Sleven, J.; Binnemans, K.; De Feyter, S. *Langmuir* **2006**, *22*, 723.

(13) Otsuki, J.; Kawaguchi, S.; Yamakawa, T.; Asakawa, M.; Miyake, K. *Langmuir* **2006**, *22*, 5708.

(14) Ye, T.; Takami, T.; Wang, R.; Jiang, J.; Weiss, P. S. *J. Am. Chem. Soc.* **2006**, *128*, 10984.

(15) Takami, T.; Ye, T.; Arnold, D. P.; Sugiura, K.; Wang, R.; Jiang, J.; Weiss, P. S. *J. Phys. Chem. C* **2007**, *111*, 2077.

(16) (a) Yoshimoto, S.; Sawaguchi, T.; Su, W.; Jiang, J.; Kobayashi, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 1071. (b) Lei, S.; Deng, K.; Yang, Y.; Zeng, Q.; Wang, C.; Jiang, J. *Nano Lett.* **2008**, *8*, 1836.

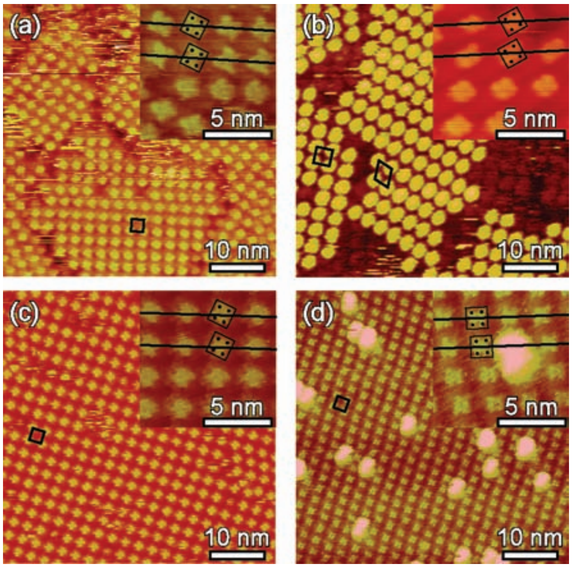

Figure 2. STM images of (a) $(C_8OPc)_2Ce$, (b) $(C_{12}OPc)_2Ce$, (c) $(C_8OPc)Ce(\mathit{Pc})$, and (d) mixture of $(C_8OPc)Ce(TPP)$ and C_8OPc. The unit cells of each structure are indicated by squares in each image. Scanning conditions: (a) sample bias (V_s) = −1100 mV, tunneling current (I_t) = 2 pA, (b) $V_s = -1000$ mV, $I_t = 2$ pA, (c) $V_s = -900$ mV, $I_t = 5$ pA, (d) $V_s = -600$ mV, $I_t = 3.5$ pA.

molecular structure was large in our system. The initial structures were decided on the basis of our STM results of the template molecules, C_nOPc ($n = 8$, 12).

Results and Discussion

STM Observation of Double-Decker Phthalocyanine Complexes. Figure 2 shows STM images of (a) $(C_8OPc)_2Ce$ (**1**), (b) $(C_{12}OPc)_2Ce$ (**2**), (c) $(C_8OPc)Ce(\mathit{Pc})$ (**3**), and (d) mixture of $(C_8OPc)Ce(TPP)$ (**4**) with C_8OPc. The unit cells of each structure are shown in each respective image. The insets in the upper right corner of each image are magnifications of each molecule. We observed well-ordered structures of all of the double-decker complexes, except that complex **4** had difficulty forming a well-ordered structure by itself.

In complex **1**, both 4-fold and 3-fold symmetrical structures were observed, but the 4-fold symmetrical structure was dominant. The lattice parameters in the unit cell were $a = 2.7 \pm 0.3$ nm, $b = 2.7 \pm 0.3$ nm, and $\beta = 92° \pm 4°$. The self-organized structures of the homolepic cerium double-deckers were the same as those of $(C_8OPc)_2Pr$[10] and C_8OPc.[6,7] A 3-fold symmetrical structure was dominant in complex **2**. The lattice parameters in the unit cell were $a = 3.5 \pm 0.3$ nm, $b = 3.5 \pm 0.3$ nm, and $\beta = 124° \pm 10°$. This result was the same as the ordered structure of the $C_{12}OPc$ monolayer,[7] except that the 4-fold symmetrical structure ($a = 3.2 \pm 0.2$ nm, $b = 3.2 \pm 0.2$ nm, and $\beta = 93° \pm 4°$) was partly observed for complex **2** as shown in Figure 2b. These results indicated that the homolepic double-deckers had an assembly behavior similar to C_nOPc ($n = 8$, 12) due to the similar molecular structures between the ligands of the $(C_nOPc)_2Ce$ and C_nOPc molecules. The height of complex **1** and complex **2** was approximately 0.4 ± 0.1 nm, which was obviously higher than that of C_8OPc (0.15 ± 0.1 nm) (see Figures S1 and S2 in the Supporting Information). Our results for the self-organized structures of C_nOPc suggested that the molecules preferred to form densely packed structures.[7] The area of the unit cell of the 3-fold symmetrical structure of C_nOPc was smaller than that of the 4-fold symmetrical structure of C_nOPc for the common n value. C_8OPc formed both quasi-3-fold and 4-fold symmetrical structures. On the other hand, a 3-fold symmetrical structure was dominant in the $C_{12}OPc$. This result would lead us to expect that complex **1** and complex **2** may tend to form both 4- and 3-fold and 3-fold symmetrical structures, respectively. However, the 4-fold symmetrical structure was dominant for complex **1** and partly observed for complex **2**. From this result, we expected that the self-organized structures of the homolepic double-deckers would tend to maintain adequate intermolecular distance between the neighboring molecules. The intermolecular interaction between the neighboring double-deckers induced by the top ligand was expected to be the reason for this result.

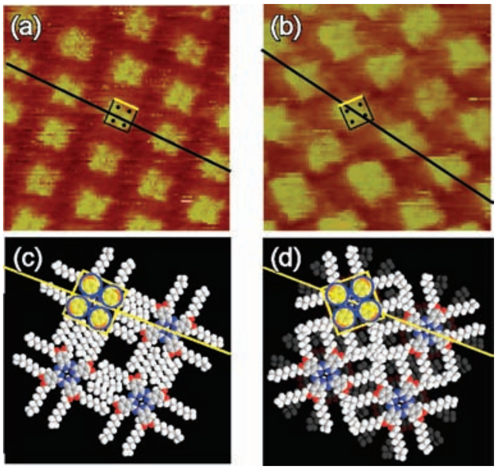

Figure 3. High-resolution STM images of (a) C_8OPc and (b) $(C_8OPc)_2Ce$. CPK models of the self-organized structure of (c) C_8OPc and (d) $(C_8OPc)_2Ce$.

We observed the fine intramolecular structure of the homolepic cerium double-deckers. Figure 3 shows high-resolution STM images of (a) C_8OPc and (b) complex **1**. Four lobes forming the square shape molecules were arranged in the 4-fold symmetrical structures. These corresponded to four six-member rings in a phthalocyanine molecule. However, the orientation of the molecules differed in each. The angle between one unit cell axis (straight line in Figure 3) and one side of the square, which is indicated by a yellow line in Figure 3, was approximately 0° for C_8OPc (Figure 3a) and approximately 45° for the complex **1** (Figure 3b). Because the adsorbed bottom ligands formed the same structure as the C_8OPc monolayer, the top ligands were rotated approximately 45° with respect to the bottom ligands. This value was consistent with the result about the molecular structure of the cerium double-deckers that had been determined by X-ray diffraction analyses.[17] The orientation of molecule of complex **2** was the same as that of complex **1**. These results suggested that the molecules maintained a sandwich-type structure and the top ligands did not move (rotate) during STM scans when the homolepic double-deckers formed well-ordered structures on the solid surface. One possible reason for the deactivation of the molecular motion is the steric hindrance of the top ligands. Figure 3c and d shows CPK models of the self-organized structure of the C_8OPc and complex **1**, respectively. In Figure 3d, the bottom ligands were drawn translucently to make them more visible. Although the alkyl

---

(17) Bian, Y. Z.; Jiang, J. Z.; Tao, Y.; Choi, M. T. M.; Li, R.; Ng, A. C. H.; Zhu, P.; Pan, N.; Sun, X.; Arnold, D. P.; Zhou, Z. Y.; Li, H. W.; Mak, T. C. W.; Ng, D. K. P. *J. Am. Chem. Soc.* **2003**, *125*, 12257.

chains in the top ligands had flexibility in the liquid, intermolecular interaction between the neighboring top and bottom ligands would be expected. The intermolecular interaction between the homolepic double-deckers was considered to be larger than that between the C$_n$OPc. Therefore, the intermolecular interaction between the neighboring top ligands was considered to inhibit the molecular motion. In addition, it was difficult for the homolepic double-deckers to form the large domain of ordered structure, and 4-fold symmetrical structures were observed more frequently for homolepic double-deckers than for C$_n$OPc as shown in Figure 2a and b. Therefore, the two-dimensional ordered structure of the homolepic double-deckers was affected not only by the bottom ligand but also by the top ligands. To clarify the effect of the substituted alkyl chains of the top ligands, we will next discuss the heterolepic double-deckers.

In complex **3**, the 4-fold symmetrical structure was dominant, although both 4-fold and 3-fold symmetrical structures were observed in the C$_8$OPc monolayer.[6,7] The unit cell data of the self-organized structure of complex **3** were almost identical to those obtained for C$_8$OPc. The height of complex **3** was estimated to be approximately 0.4 ± 0.1 nm (see Figure S3 in the Supporting Information). This strongly indicated that complex **3** was directly adsorbed with its C$_8$OPc ligands oriented parallel to the substrate. As a result, the top ligand corresponds to *Pc*. The effect of the alkyl chains on molecular motion could be clarified by observing the intramolecular structure of complex **3**. The inset in Figure 2c shows a magnified STM image of complex **3**. We clearly observed the fine intramolecular structure of the top *Pc* ligands. This result strongly suggested that the effect of the alkyl chains on the molecular motion was not very large. There must be another factor governing the molecular motion. To clarify this other factor governing the molecular motion, we studied the other heterolepic double-decker complex **4**.

The results for complex **4** were drastically different. The self-organized structure of complex **4** was difficult to observe. On the other hand, deposition from the mixture containing complex **4** and C$_8$OPc led to well-ordered areas that were enriched with C$_8$OPc, which acted as a template to induce the formation of the self-organized structure. Both compounds could be distinguished from each other by the difference of their STM contrast. The complex **4** molecules appeared as bright round features. The height of complex **4** was estimated to be approximately 0.4 ± 0.1 nm (see Figure S4 in the Supporting Information). We confirmed this experimentally by changing the ratio of the two compounds. The ordered structure of the mixed system was governed by the C$_8$OPc matrix. Therefore, complex **4** was considered to be directly adsorbed with its C$_8$OPc ligands. Consequently, the top ligand corresponds to TPP.

The intramolecular structure of the top ligands of complex **4** was difficult to observe, even though the fine intramolecular structure of the C$_8$OPc matrix was observed. The difference between complex **4** and the other double-deckers in the STM images was considered to be attributed to (1) the trampoline-like movement or rotation of the top TPP ligands and/or (2) the difference of the top ligands between complex **4** and the other double-deckers.

At first, we considered the effect of the top ligands on the STM images. The electronic effects caused by the presence of the lanthanide ion should have no small effect on the STM images of the top ligands of the double-deckers. However, the fine intramolecular structure of the top ligands could be observed for complexes **1**, **2**, and **3**. This result indicated that the effect of the lanthanide ion on the STM image of the top ligands was small in our experiment. Therefore, we should be able to observe the fine intramolecular structure of the top ligands if the top ligands do not move during STM scans. Alkyl-substituted porphyrin derivatives are also known to form well-ordered structures on HOPG surfaces.[6,18−21] Figure 4 shows an STM image of the self-organized structure of 5,10,15,20-tetra(4-octadecyloxyphenyl)porphyrins. Fine intramolecular structures were observed. The STM image consisted of four lobes forming the square shape. These lobes correspond to the meso-phenyl groups. On the other hand, the STM image of the top ligands of complex **4** had no feature as shown in Figure 2d. These results led us to conclude that complex **4** could have some degree of mobility, such as trampoline-like movement or rotation of the top TPP ligands. The size of the top ligands of complex **4** was larger than that of the C$_8$OPc template as shown in Figure 2d. This indicates that the top ligands moved about freely. The movement of the top ligands may prevent the adsorption of complex **4** adjacent to the initially adsorbed complex. This is a possible reason why the self-organized structure of complex **4** was difficult to observe.

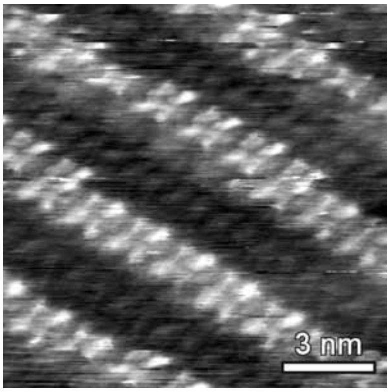

Figure 4. STM image of the self-organized structure of TPP derivatives ($V_s = -1200$ mV, $I_t = 25$ pA).

Mixed solutions containing complex **4** and C$_8$OPc led to well-ordered self-organized structures that were enriched with C$_8$OPc. Therefore, free space presented around the top ligands. On the other hand, complexes **1**, **2**, and **3** formed well-ordered self-organized structures on their own. Therefore, they did not have enough space to produce the molecular motion. The free space around the top ligands is also an important factor that determines the molecular motion. To clarify this effect, we attempted to observe the mixed self-organized structure that formed from mixtures containing complex (**1**, **2**, or **3**) and template molecule.

Effect of the Arrangement of Double-Decker Complexes on Their Molecular Motion. Figure 5 shows STM images of (a) complex **1** and C$_8$OPc and (b) complex **2** and C$_{12}$OPc. In both cases, deposition from a mixture containing double-decker compounds and template molecules led to well-ordered areas that were enriched with double-decker complexes. From the cross-sectional profile, we concluded that C$_n$OPc interspersed with the double-decker complexes for mixed monolayers of

---

(18) Ikeda, T.; Asakawa, M.; Goto, M.; Miyake, K.; Ishida, T.; Shimizu, T. *Langmuir* **2004**, *20*, 5454.

(19) Ikeda, T.; Asakawa, M.; Miyake, K.; Shimizu, T. *Chem. Lett.* **2004**, *33*, 1418.

(20) Otsuki, J.; Nagamine, E.; Kondo, T.; Iwasaki, K.; Asakawa, M.; Miyake, K. *J. Am. Chem. Soc.* **2005**, *127*, 10400.

(21) Ikeda, T.; Asakawa, M.; Miyake, K.; Goto, M.; Shimizu, T. *Langmuir* **2008**, *24*, 12877.

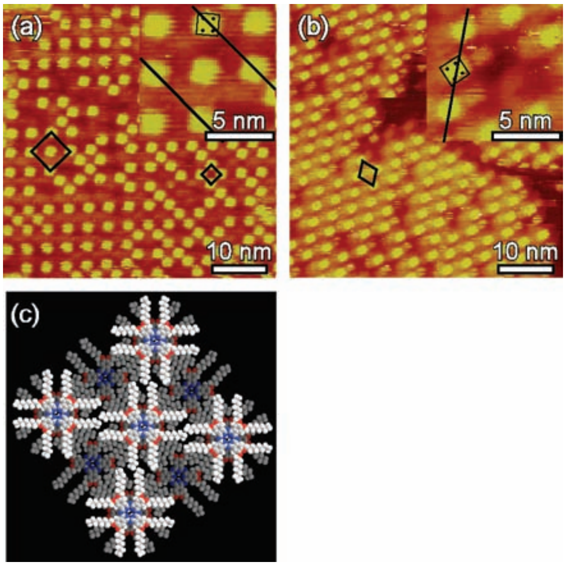

Figure 5. STM images of (a) $\mathrm{(C_8OPc)_2Ce}$ and $\mathrm{C_8OPc}$ ($V_\mathrm{s} = -850$ mV, $I_\mathrm{t} = 4$ pA), and (b) $\mathrm{(C_{12}OPc)_2Ce}$ and $\mathrm{C_{12}OPc}$ ($V_\mathrm{s} = -850$ mV, $I_\mathrm{t} = 3$ pA). The unit cells of each structure are indicated by squares in each image.

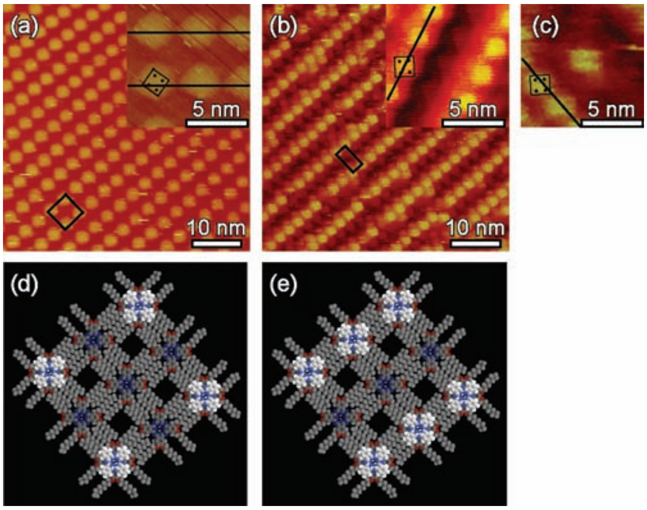

Figure 6. Mixed self-organized structures containing $\mathrm{(C_8OPc)Ce(\mathit{Pc})}$ and $\mathrm{C_8OPc}$. (a) p(2 × 2) structure ($V_\mathrm{s} = -350$ mV, $I_\mathrm{t} = 3.0$ pA), (b) (2 × 1) structure ($V_\mathrm{s} = -650$ mV, $I_\mathrm{t} = 3.5$ pA), and (c) magnified image of isolated $\mathrm{(C_8OPc)Ce(\mathit{Pc})}$ ($V_\mathrm{s} = -900$ mV, $I_\mathrm{t} = 2.5$ pA). The unit cells of p(2 × 2) and (2 × 1) structures are indicated by squares in (a) and (b).

double-decker complexes with $\mathrm{C}_n\mathrm{OPc}$ (see Figure S5 in the Supporting Information). Ordered structures with template-rich regions have never been observed, even when the ratio of the two compounds was varied. One possible reason for the formation of the ordered structures with double-decker-rich regions is that the intermolecular interaction between the homolepic double-deckers was larger than that between the $\mathrm{C}_n\mathrm{OPcs}$. Phase separation is also considered to be a possible reason for the formation of such ordered structures, but we could not observe ordered structures with template-rich regions. The precise mechanism of the formation of the ordered structure of mixed monolayers is still unclear.

In Figure 5a, the small and large squares indicate unit cells consisting of complex **1** and a mixture containing $\mathrm{C_8OPc}$ and complex **1**, respectively. For the mixture containing complex **1** and $\mathrm{C_8OPc}$, a c(2 × 2) structure was preferably formed. The distance between the nearest neighbor molecules of c(2 × 2) was about 3.6 nm, which is $\sqrt{2}$ times larger than that of the (1 × 1) lattice (about 2.6 nm). Therefore, the top ligands of complex **1** in the c(2 × 2) structure had a larger space around them than those in the (1 × 1) structure. A magnified STM image of the c(2 × 2) structure is shown in the inset of Figure 5a. Despite the fact that the top ligands of complex **1** in the c(2 × 2) structure had free space around them, square shape molecules could be observed. Consequently, the top ligands of complex **1** did not move during the STM scans even though free space presented around the top ligands. Contrary to the result of the mixture containing complex **1** and $\mathrm{C_8OPc}$, the mixture containing complex **2** and $\mathrm{C_{12}OPc}$ did not form superstructures like c(2 × 2). However, some defects were formed in the ordered structure for complex **2**. A magnified STM image around the defects is shown in the inset of Figure 5b. Although free space was successfully introduced around the top ligands, square shape molecules could be observed.

For the mixture containing complex **3** and $\mathrm{C_8OPc}$, two kinds of superstructures were observed. Figure 6 shows the observed superstructures of the (a) p(2 × 2) and (b) (2 × 1) structures. The distance between the nearest neighbor molecules of p(2 × 2) was about 5.0 nm, which was twice of the (1 × 1) lattice. From the cross-sectional profile, we concluded that $\mathrm{C_8OPc}$ interspersed with complex **3** for mixed monolayers of complex **3** with $\mathrm{C_8OPc}$ (see Figures S6 and S7 in the Supporting Information). Magnified STM images of each structure are shown in the insets of Figure 6a and b. Despite the fact that the top ligands of complex **3** in the p(2 × 2) and (2 × 1) structures had free space around them, square shape molecules could be observed. These results suggested that the top ligands of complexes **1**, **2**, and **3** did not move (rotate) during STM scans even though free space presented around them. However, the shapes of the STM images of complex **3** in the p(2 × 2) structure were less pronounced than those in the (2 × 1) structure. The difference between them is the distance between the nearest neighbors and the number of molecules within the distance of the (1 × 1) lattice (about 2.6 nm). Two molecules existed within 2.6 nm for the molecules forming the (2 × 1) structure, but the molecules forming p(2 × 2) had adequate space around them.

The rotation of phthalocyanines composed of double-deckers may be not smooth. The most stable conformation was when the top ligand was oriented about 45° with respect to the bottom ligand. Considering the symmetry of phthalocyanines, there are four energetically equivalent stable sites, and the potential energy barrier existed between the stable sites. For the phthalocyanines composed of double-deckers to be able to rotate, they must overcome the potential barrier. Therefore, we considered that when the Pcs crossed the potential barrier, they moved too fast for their motion to be observed by STM and they basically occupied the stable site. In this case, the fine intramolecular structure might be observed. However, our STM results indicated that the shapes of the STM images of the top ligands varied depending on the distance between the nearest neighbors and the number of molecules within the distance of the (1 × 1) lattice. This means that the probability of overcoming the potential barrier to the rotation of the top ligands may be affected by the surrounding environment, but a distance twice as large as the primitive lattice was not enough to freely rotate the top ligand for double-decker complexes **1**, **2**, and **3** as compared to complex **4**. Furthermore, an isolated single molecule of complex **3** could be also observed as the square shape shown in Figure 6c. Therefore, we considered that the combination of two ligands

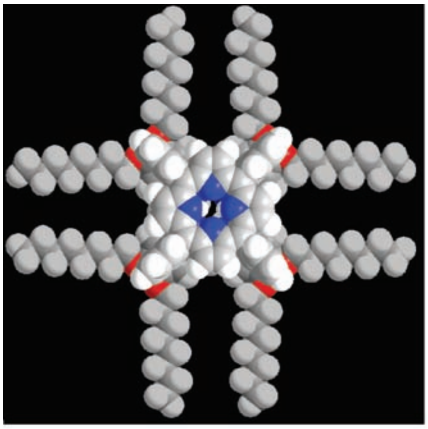

Figure 7. CPK model of complex **4**.

also had an effect on the mobility of surface-immobilized double-decker complexes.

Effect of the Combination of Molecules Composed of Double-Decker Complexes on Their Molecular Motion. Complexes **1**, **2**, and **3** consist of two *Pc* nuclei, respectively. The intermolecular interaction potential between the *Pc* nuclei may have better matching than that between *Pc* and TPP. Therefore, the potential barrier to the molecular motion of complexes **1**, **2**, and **3** is considered to be higher than that of complex **4**. Our STM results suggested that the top ligands were rotated approximately 45° with respect to the bottom ligands. In this conformation, the meso-phenyl group of TPP was located above the benzene rings of the indole units of phthalocyanine as shown in Figure 7. According to a previous report about the calculations of benzene dimer interaction,[22] the calculated interaction energy had a strong orientation dependence. In the reported calculation, one benzene of dimer was rotated by changing the angle from 0° to 90° with respect to the other benzene. The calculated interaction energy values showed that the dimer was most stable when the angle was 90°, which was an arrangement similar to the double-decker complex shown in Figure 7. The difference between the lowest and highest interaction energy values was approximately 2 kcal/mol, which is comparable to room temperature. The estimated value was not directly compared to the energy barrier for the rotational motion of the meso-phenyl groups of a top ligand; however, it is reasonable to assume that the dihedral angles of the meso-phenyl groups with respect to the plane of the porphyrins changed in the liquid condition. This result suggested that interaction energy between TPP and C_8OPc, which consist of complex **4**, could also change and the fluctuation of the meso-phenyl groups would lower the energy barrier to the molecular motion of complex **4** as compared to that of complexes **1**, **2**, and **3**. In addition, it was difficult for complex **4** to form an ordered structure by itself. This means that the interaction between complex **4** and the substrate was likely to be weaker than that between complexes **1**, **2**, and **3** and the substrate. Therefore, interaction between the double-decker complex and substrate, which was decided by the combination of molecules composed of double-decker complex, is also considered to be important. Consequently, the combination of molecules composed of the double-decker complexes is an important issue in controlling the motion of the top ligands of surface-immobilized double-decker complexes, that is, the speed of rotation of the top ligand can be modified by varying the combination of the molecules. Further experiments, such as varying the temperature and varying the combination of the molecules, should be conducted to clarify the details of the mechanism of molecular motion and to control the motion. Such findings would be applicable to bottom-up nanofabrication of the surface by controlling the molecular orientation and the rotation of the ligands.

Conclusion

We examined the molecular motion of double-decker phthalocyanine complexes physisorbed on a graphite surface using STM. STM images of complexes **1**, **2**, and **3**, of which two ligands contained *Pc* nuclei, clearly showed that they formed well-ordered self-organized structures on their own. Furthermore, we observed the fine intramolecular structure of the top *Pc* ligands. However, complex **4**, which was composed of C_8OPc and TPP, did not form the self-organized structure by itself, but by adsorbing from a mixture containing complex **4** and C_8OPc could immobilize complex **4** on the substrate. The intramolecular structures of the top ligands of complex **4**, which correspond to TPP, were difficult to observe. Furthermore, square shape STM images of top ligands were observed even though free space presented around the top ligands by the mixing of complexes **1**, **2**, and **3** with template molecules (C_8OPc or C_{12}OPc). Double-decker complexes containing C_8OPc (complexes **1** and **3**) tended to form reconstructed structures when the complexes were mixed with template molecules of C_8OPc. The results led us to conclude that the combination of molecules composed of the double-deckers as well as the free space presented around a top ligand were important issues in controlling the molecular motion of immobilized double-decker complexes on solid surfaces.

Supporting Information Available: Cross-sectional profiles of double-decker phthalocyanine complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

JA904629D

---

[22] Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104.