

## Manipulating Double-Decker Molecules at the Liquid–Solid Interface

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**Abstract:** We have used a scanning tunneling microscope (STM) to manipulate heteroleptic phthalocyaninato, naphthalocyaninato, and porphyrinato double-decker (DD) molecules at the liquid–solid interface between 1-phenyloctane solvent and graphite. We employed nanografting of phthalocyanines with eight octyl chains to place these molecules into a matrix of heteroleptic DD molecules; the overlayer structure is epitaxial on graphite. We have also used nanografting to place DD molecules in matrices of single-layer phthalocyanines with octyl chains. Rectangular scans with a STM at low bias voltage resulted in the removal of the adsorbed DD molecular layer and substituted the DD molecules with bilayer-stacked phthalocyanines from phenyloctane solution. Single heteroleptic DD molecules with lutetium sandwiched between naphthalocyanine and octaethylporphyrin were decomposed with voltage pulses from the probe tip; the top octaethylporphyrin ligand was removed, and the bottom naphthalocyanine ligand remained on the surface. A domain of decomposed molecules was formed within the DD molecular domain, and the boundary of the decomposed molecular domain self-cured to become rectangular. We demonstrated a molecular “sliding block puzzle” with cascades of DD molecules on the graphite surface.

### Introduction

Controlled construction of desired molecular nanostructures on suitable substrates will be required to realize and to test molecular devices such as molecular integrated circuits. Fabrication of such nanostructures is based on the adsorption and properties of functional molecules and assemblies on substrates.<sup>1–9</sup> Porphyrin (Por), phthalocyanine (Pc), and naphthalocyanine (Nc) are particularly interesting compounds because of their char-

acteristic strong light absorption cross sections and photoinduced charge separation at the photosynthesis reaction center; their versatile properties are strongly affected by peripheral substituents and the center metal atom.<sup>10–12</sup> Some center metal atoms can also lead to three-dimensional stacking structures to form double-decker (DD) complexes,<sup>13,14</sup> and the arrangements can be controlled by substitution.<sup>2,3,15–19</sup>

Double-decker phthalocyaninato and porphyrinato metal complexes<sup>13,14</sup> are promising candidates for molecular devices

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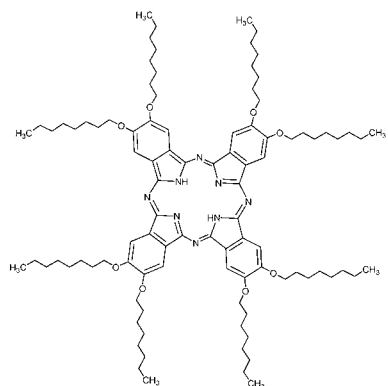
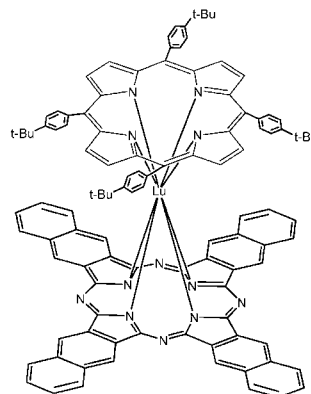
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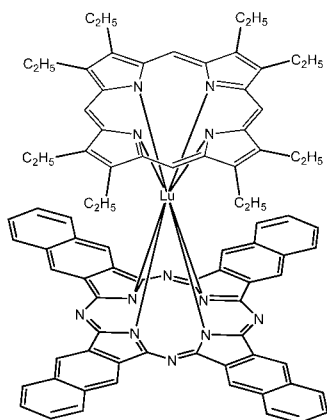
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Scheme 1<sup>a</sup>

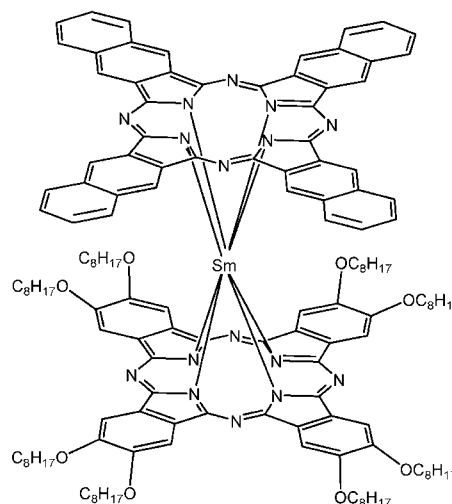
## 1 octakis(octyloxy)-Pc (OctOPc)

3 Nc-lutetium-tetra(*t*-butylphenyl)Por (Nc-Lu-TBPP)

## 2 Nc-lutetium-octaethylPor (Nc-Lu-OEP)



## 4 Nc-samarium-octakis(octyloxy)-Pc (Nc-Sm-OctOPc)



<sup>a</sup> Pc = phthalocyanine, Nc = naphthalocyanine, Por = porphyrin.

such as molecular switches<sup>20–22</sup> and synthetic molecular motors.<sup>23–25</sup> Thermal rotation of DD porphyrinato metal complexes around the metal centers has been observed through studies on optical resolution and racemization behavior of a chiral metal bis(tetraarylporphyrinate), with symmetry group  $D_2$ ,<sup>26–28</sup> supporting the possibility that DD phthalocyaninato or porphyrinato complexes could be utilized as molecular rotors.<sup>23,24</sup>

The scanning tunneling microscope (STM) can identify the conformation of individual molecules adsorbed on solid surfaces,<sup>29–43</sup> and homoleptic DD molecules with octakis(octyl-

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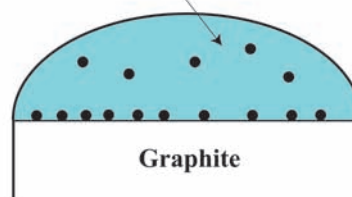
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oxy)phthalocyaninato ligands have previously been observed.<sup>44–46</sup> Moreover, direct observation of single-molecular rotation with the STM<sup>24,47–52</sup> is an exciting method for exploring molecular machines for future applications such as molecular information storage<sup>53</sup> and molecular phase memory.<sup>54</sup> Otsuki et al. tried to observe the rotation of DD molecules with two-fold symmetry of the top ligand.<sup>55</sup> We have recently demonstrated not only the controlled adsorption orientation of DD molecules and mixed DDs<sup>56</sup> but also tuned interactions between ligands in DD arrays.<sup>57</sup>

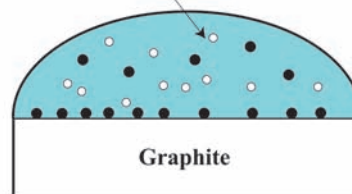
The STM is also a powerful tool to manipulate single atoms and molecules. Eigler and co-workers and then others demonstrated the manipulation and placement of atoms and molecules on surfaces at 4 K.<sup>4,58–63</sup> Large molecules such as copper tetra(3,5-di-*tert*-butylphenyl)porphyrin can physisorb sufficiently strongly that single molecules can be manipulated at room temperature.<sup>64</sup> Chemical reactions can also be induced and run using STM manipulation.<sup>65–67</sup> A catalytic STM tip can induce chemical reaction.<sup>68,69</sup> A voltage pulse from a STM tip can be used to induce polymerization reactions of polydiacetylene<sup>70</sup> to form molecular lines and cloth.<sup>71–73</sup>

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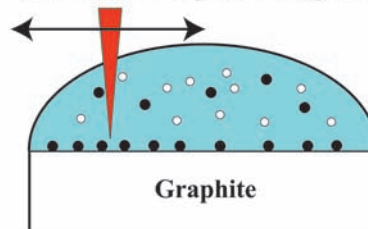
### Deposit monolayer from Nc-Lu-OEP phenyloctane solution



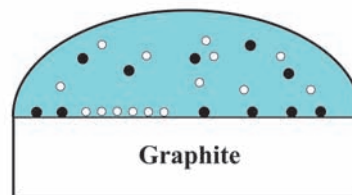
### Immerse in OctOPc phenyloctane solution



### Locally displace Nc-Lu-OEP monolayer with the STM tip for nanografting



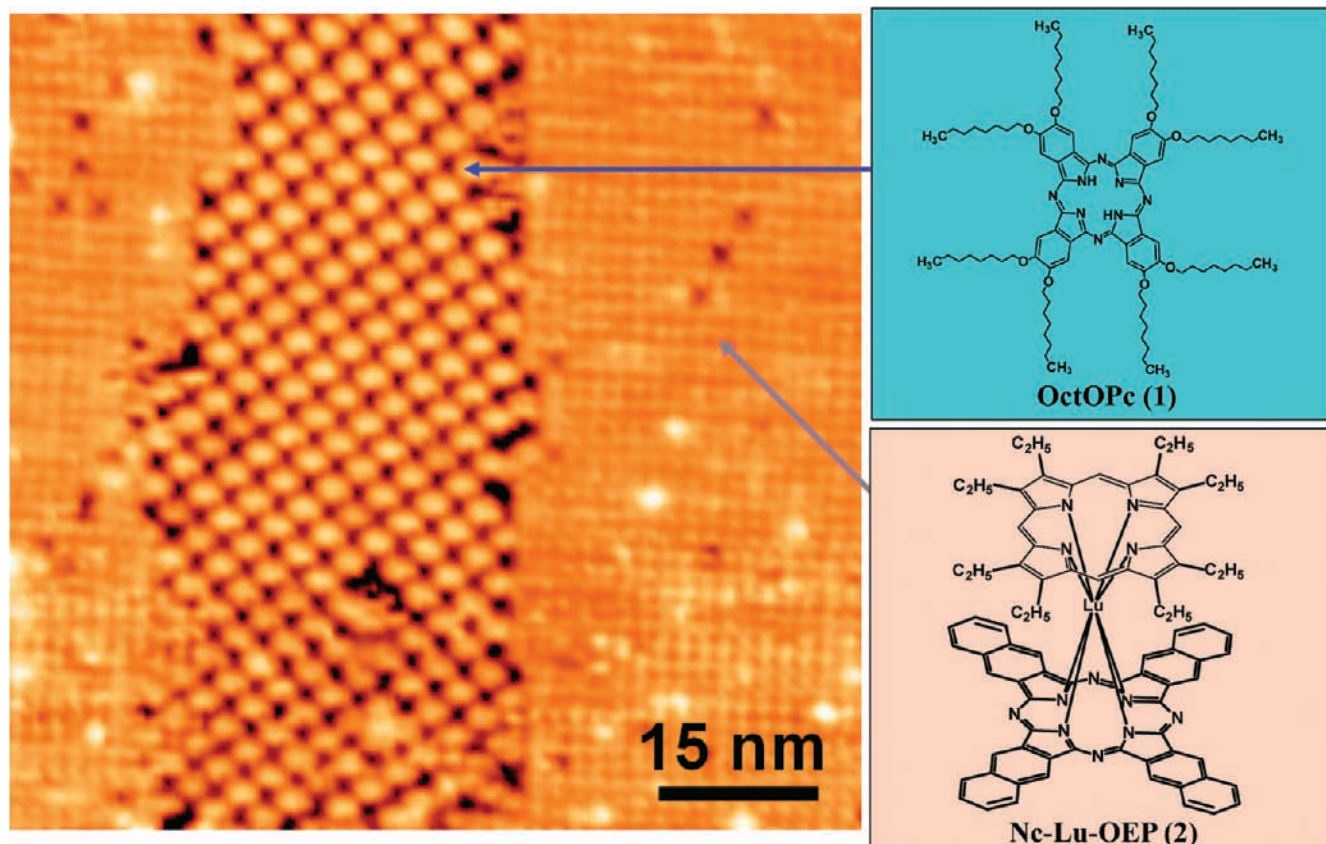
### OctOPC molecules replace Nc-Lu-OEP in the nanografted areas



**Figure 1.** Schematics showing the preparation of mixed layers of octakis(octyloxy)phthalocyanine (1) and Nc-Lu-OEP double-decker (2) on graphite by nanografting.

Larger manipulations of monolayers can be performed using nanografting, a technique developed by Liu and co-workers.<sup>74–81</sup>

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**Figure 2.** Scanning tunneling microscope images of the mixed double-layered octakis(octyloxy)phthalocyanine (1) and Nc-Lu-OEP double-decker molecules (2) on graphite, prepared by STM tip manipulation (nanografting), as shown in Figure 1;  $V_{\text{sample}} = -0.60$  V,  $I_{\text{tunnel}} = 1.0$  pA.

With this method, molecules from solution replace those in a monolayer when the former are physically removed using a scanning probe microscope tip. At low tunneling gap impedance, a STM tip penetrates the monomolecular layer<sup>58,82</sup> and can disrupt it to allow access to molecules from solution. We apply nanografting here to create artificially separated domains of different Por, Pc, and Nc molecules.

We demonstrate molecular manipulation of sandwich DD complexes of Por, Pc, and Nc with the STM, both in domains and as single molecules. Such manipulation enables the construction and the elucidation of the properties of supramolecular test structures (as for atomic manipulation<sup>63</sup>) that might later be targeted for direct assembly via parallel methods.

## Experimental Section

2,3,9,10,16,17,23,24-Octakis(octyloxy)-29*H*,31*H*-phthalocyanine (OctOPc, Scheme 1) was obtained from Aldrich (Milwaukee, WI) and used without further purification. The other DD compounds, naphthalocyanine-lutetium-octaethylporphyrin and naphthalocyanine-lutetium-tetra-*tert*-butylphenylporphyrin (Nc-Lu-OEP and Nc-Lu-TBPP, Scheme 1), were prepared according to published procedures.<sup>83–87</sup> Their electrochemical behavior in  $\text{CH}_2\text{Cl}_2$  was also studied by cyclic voltammetry and differential pulse voltammetry using 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte with a BAS CV-50W voltammetric analyzer (BASi, West Lafayette, IN).<sup>84,88</sup>

Each compound was dissolved in 1-phenyloctane from Aldrich (CAS 2189-60-8). The concentrations of the solutions were kept in the range of 0.1–1 mM. The prepared solution was dropped onto a highly oriented pyrolytic graphite (HOPG) substrate (SPI Supplies, West Chester, PA, 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, now Agilent, Santa Clara, CA) controlled by a low-noise controller (RHK SPM1000, RHK Technology, Troy, MI). Scanning speeds slower than 1 line/s made it possible to record images at tunneling currents below 1 pA. All the lateral scales of the STM images were calibrated using the hexagonal lattice of the HOPG ( $a = 0.246$  nm), and all the surface normal scales of the STM images were calibrated with monatomic steps of HOPG ( $c/2 = 0.34$  nm). The orientations of

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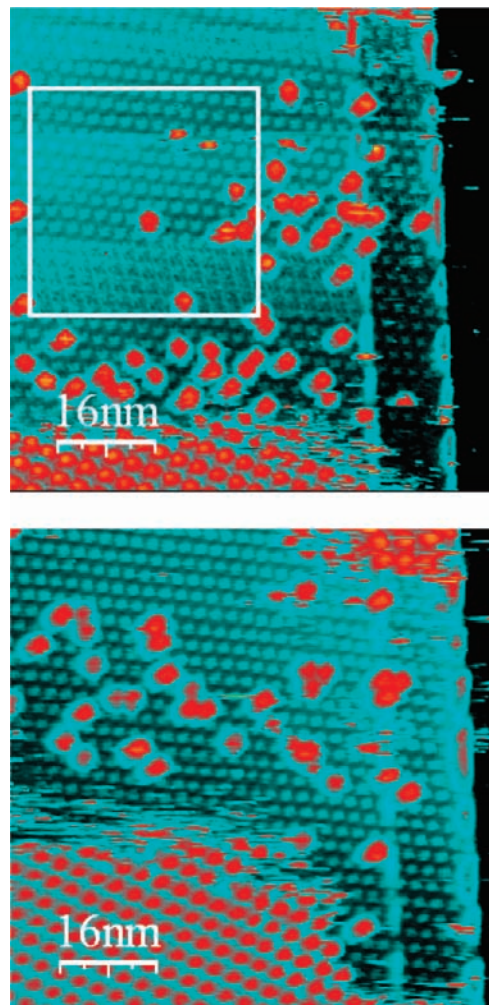
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the substrate graphite [100] and [210] were determined from the observed steps in STM images.

## Results and Discussion

**a. Nanografting Double-Decker Monolayers with Phthalocyanines.** First, we demonstrated selectively controlled mixed layers: partial manipulation and substitution of DD monolayers with double layers of phthalocyanines using the STM tip.<sup>74</sup> Since the sticking probability of OctOPc is higher than that of Nc-Lu-OEP, the mixed layer cannot be formed simply by depositing a mixed solution on graphite. The mixed layer was prepared as shown schematically in Figure 1. First, the monolayer of Nc-Lu-OEP was prepared on a graphite surface from phenyloctane solution. Second, a solution of OctOPc in phenyloctane was dropped on the surface, and we scratched the monolayer of Nc-Lu-OEP with the STM probe tip by reducing the sample bias voltage to below 0.2 V, thereby lowering the gap impedance and the tip–sample separation. This results in a sufficiently low tunneling gap impedance to lead to displacement and thus nanografting of OctOPc.<sup>74–80</sup> Figure 2 shows a STM image as described in Figure 1 that shows that the apparent height of the OctOPc layer in STM images is almost the same as that of the Nc-Lu-OEP monolayer. We attribute this to the OctOPc layer being a bilayer. The depths of the apparent depressions in the domains of Nc-Lu-OEP were typically 0.4 nm, but several appeared to be 0.2 nm. We attribute the 0.4 nm depressions to the vacancies of single Nc-Lu-OEP molecules, and the 0.2 nm depressions to the Nc bottom ligand following the decomposition of Nc-Lu-OEP, discussed below. On the other hand, we attribute the apparent heights of the 0.2 nm protrusions in the STM image to the Nc-Lu-OEP molecules adsorbed onto the Nc bases. The lateral sizes of the protrusions assigned to Nc-Lu-OEP on Nc are larger than those of Nc-Lu-OEP, due to the convolution of the surface feature with the STM tip.<sup>89</sup> The boundaries between OctOPc and NcLuOEP domains tend to form lines, due to energy minimization of the two-domain system, a key factor in the self-curing system, described below.

**b. Nanografting Phthalocyanine Monolayers with Double-Decker Molecules.** We have also been able to perform nanografting of Nc-Sm-OctOPc molecules on the OctOPc matrix on graphite (Figure 3). Co-adsorbing OctOPc with Nc-Sm-OctOPc on HOPG results in an array of four-lobed features with a diagonal size of 1.6 nm, OctOPc. In addition, a four-lobed protrusion 0.3–0.4 nm high was also observed. 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; the OctOPc ligand is adsorbed onto the surface due to its stronger interaction with HOPG. Most of the isolated DD molecules were in registry with the surrounding OctOPc lattice, suggesting that the DD molecules and OctOPc can mix at the molecular scale. This is in sharp contrast to Figure 2, which displays almost complete phase separation, indicating that by changing the similarity between the ligands, the degree of mixing can be controlled. Figure 3 shows STM images of a mixed layer of Nc-Sm-OctOPc and OctOPc, before and after nanografting with a STM probe tip set at the bias voltage of 0.2 V. This bias voltage is usually used to image the graphite lattice, and hence bared the graphite surface, which was then



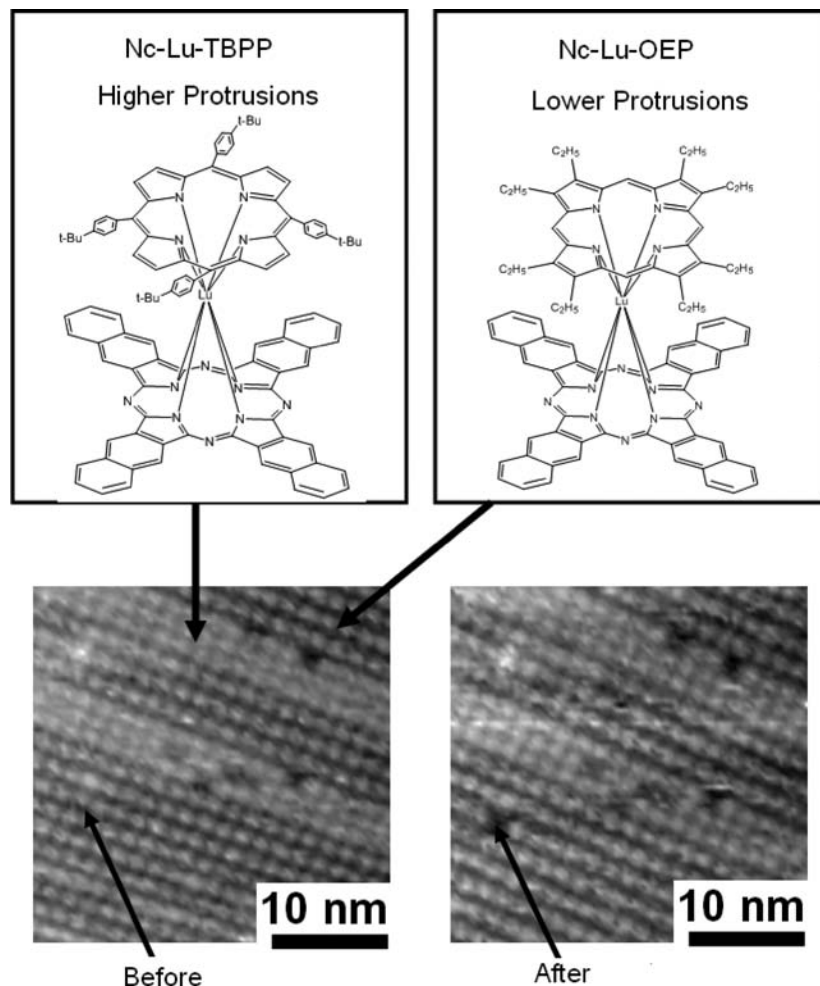
**Figure 3.** Increasing the number of adsorbed double-decker (4) molecules in a monolayer matrix of phthalocyanine on graphite. Scanning tunneling microscope images of these matrices: (top) before manipulation by scratching the area shown as a white square and (bottom) after the manipulation.  $V_{\text{sample}} = -0.6$  V,  $I_{\text{tunnel}} = 0.7$  pA.

covered predominantly with Nc-Sm-OctOPc DD molecules; the solution at the interface consists of a mixture of Nc-Sm-OctOPc and OctOPc. Nanografting with the opposite result, replacing Nc-Sm-OctOPc DD molecules with OctOPc, is also possible on this system, as described above.

**c. Single-Molecule Manipulation of Double-Decker Molecules.** Next, we demonstrated single-molecule extraction with the STM probe tip. Figure 4 shows STM images of the mixed monolayer of Nc-Lu-OEP and Nc-Lu-TBPP.<sup>56</sup> A sample bias voltage pulse of 3 V was applied to a Nc-Lu-OEP complex for 1 s to create a single-molecule defect. The apparent height measurement showed that the created depression's apparent depth was 0.2 nm, corresponding to top-ligand extraction. We note that Nc-Lu-OEP DD complexes are less stable than Nc-Lu-TBPP DD molecules because the ring-to-ring separation is slightly larger, resulting in insufficient interactions between the macrocycles of the molecular sandwich.<sup>86</sup> We attribute our ability to induce dissociation here to this.

**d. Self-Curing Naphthalocyanine Rectangular Domains in Double-Decker Matrices.** Self-curing is a simple means to create organized systems. Self-curing of induced defects in monolayers and substrates has previously been observed in

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**Figure 4.** Scanning tunneling microscope images of single-molecular manipulation of Nc-Lu-OEP (2) in the mixed layer of 2 and Nc-Lu-TBPP (3).

STM measurements.<sup>90</sup> Here, we show a self-curing system of a rectangular Nc domain fabricated in a Nc-Lu-OEP matrix. Figure 5 shows STM images of a Nc domain in a DD matrix. A hole with an apparent depth of 0.4 nm in the Nc domain indicates the single-molecular vacancy. In the upper image, there are two vertical vacancy lines corresponding to five and eight missing molecules. The image also has several scan noise lines; the lines are due to the molecules diffusing on the surface while the area was scanned.<sup>91,92</sup> Some molecules at the bottom of the image are observed as partial features because they are moving about during imaging, prior to locating a stable position. The lower image was collected 20 min after the upper image was recorded. The number of noise lines was found to decrease. The initial irregular shape of the middle vacancy changed to a  $2 \times 8$  rectangular molecular vacancy. We attribute this rectangular steady state of the vacancy islands to the large Gibbs–Thomson effect and the small Mullins–Sekerka instability at the nanoscale.<sup>93</sup> It is also noted that DD molecules are aligned within the  $2 \times 8$  vacancy sites, as is evident from a missing molecule

(circled for clarity). The DD molecules formed a multilayer in the image, and the molecules *on* the DD layer are straightforward to move and to remove from the surface. We observed that DD molecules are available to move into vacancies with small perturbing forces, as described in the next section.

**e. Sliding Block Puzzle with Double-Decker Molecules.** Finally, the manipulation of single molecules in a Nc-Lu-OEP monolayer is shown. Figure 6 shows STM images of a Nc-Lu-OEP monolayer with several depressions. The images were sequentially recorded, one every 5 min. After the first image was recorded (top), two DD molecules slid to the adjacent vacancies, as indicated by blue arrows in the upper image. Moreover, after the second image was recorded (middle), a DD molecule was extracted from the layer and another DD molecule filled in a vacancy, as indicated by blue arrows in the middle image. With this system, we were able to demonstrate room-temperature manipulation of single molecules with the STM tip at the liquid–solid interface. Previously, Griessl et al. succeeded in manipulating  $C_{60}$  on a hydrogen-bound two-dimensional host network of trimesic acid at the liquid–solid interface.<sup>94</sup> In this work, we demonstrated that the manipulation

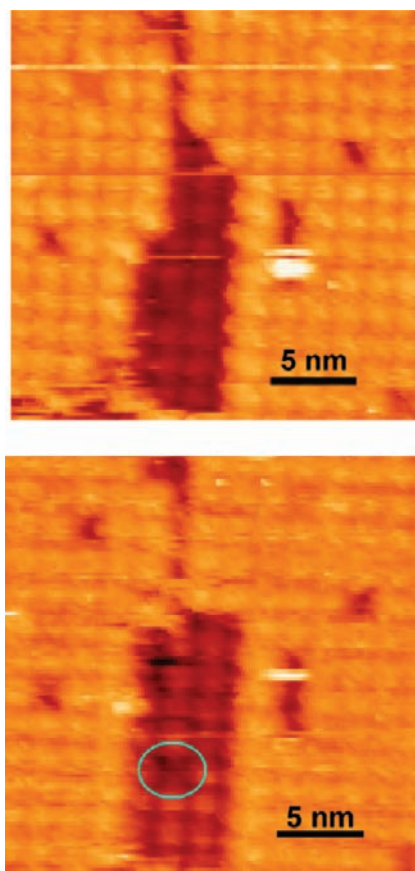
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**Figure 5.** Scanning tunneling microscope images of self-curing of a naphthalocyanine square vacancy in a matrix of Nc-Lu-OEP double-decker molecules: (top) before self-curing and (bottom) 20 min after the top image was recorded.  $V_{\text{sample}} = -0.6$  V,  $I_{\text{tunnel}} = 0.7$  pA.

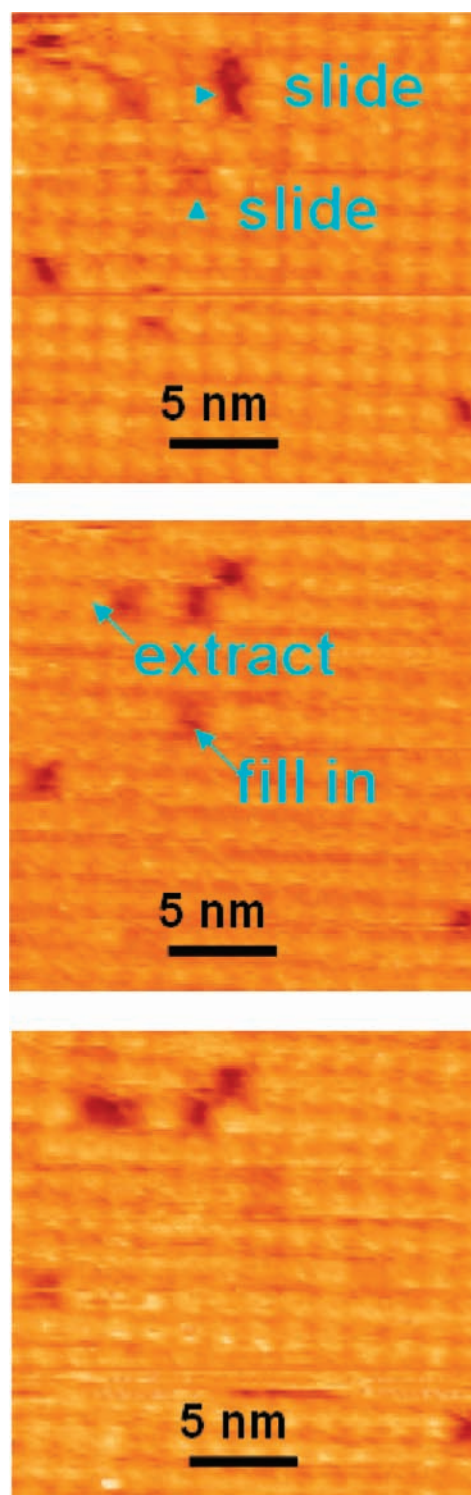
of a vacancy in a monolayer is also possible at room temperature at the liquid–solid interface.

### Conclusions and Prospects

We have controlled and manipulated Pc and DD molecules with STM. Partial substitution of DD monolayers with OctOPc was accomplished by nanografting, and the substituted domains formed bilayer stacks epitaxially on graphite. We have demonstrated nanografting of DD molecules in matrices of single-layer OctOPc. Rectangular scans with a STM tip at low bias voltage resulted in the removal of the adsorbed DD molecular layer and substituted bilayer-stacked OctOPc from phenyloctane solution. These results demonstrate compositional control through scanning probe lithography at the liquid–solid interface at room temperature.

Single-molecular decomposition of heteroleptic DD molecules of a lutetium complex sandwiched with Nc and octaethylporphyrin with voltage pulses applied by the STM tip was demonstrated: the top octaethylporphyrin ligand was removed, and the bottom Nc ligand remained on the surface. A domain of the decomposed molecules was formed in the DD molecular domains, and the boundary of the decomposed molecular domain re-formed to be rectangular via self-curing. We also demonstrated a molecular “sliding block puzzle” with the cascades of DD molecules.

**Acknowledgment.** This work was supported by VRI, the National Science Foundation through the Center for Nanoscale



**Figure 6.** Scanning tunneling microscope images of sliding blocks of Nc-Lu-OEP double-decker molecules: (top) before sliding (sliding molecules are indicated by arrows), (middle) after sliding but before extracting and filling the double-decker molecule (indicated by arrows), and (bottom) after extracting and filling.  $V_{\text{sample}} = -0.6$  V,  $I_{\text{tunnel}} = 0.7$  pA.

Science (a Materials Research Science and Engineering Center) at Penn State and UCLA (T.T., T.Y., B.K.P., and P.S.W.), NSFC (Y.B. and J.J.), MOST (Y.B. and J.J.), and the Kavli Foundation (P.S.W.). We thank Prof. Vincent Crespi of The Pennsylvania State University for helpful discussions.

JA105421K