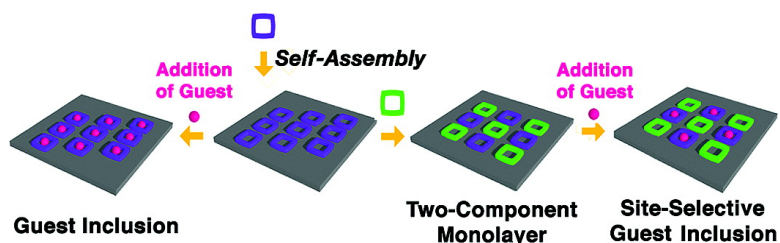## Communication

Site-Selective Guest Inclusion in Molecular Networks of Butadiyne-Bridged Pyridino and Benzeno Square Macrocycles on a Surface

Kazukuni Tahara, Shengbin Lei, Wael Mamdouh, Yui Yamaguchi, Tomoyuki Ichikawa, Hiroshi Uji-i, Motohiro Sonoda, Keiji Hirose, Frans C. De Schryver, Steven De Feyter, and Yoshito Tobe

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Site-Selective Guest Inclusion in Molecular Networks of Butadiyne-Bridged Pyridino and Benzeno Square Macrocycles on a Surface

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Alignment of functional molecules on two-dimensional (2D) molecular networks on solid surfaces is of current interest owing to potential nanotechnological applications, such as the fabrication of molecular scale devices and machines.[1] Recently, multi-component networks formed by directional intermolecular interactions[2] or by 2D host–guest chemistry involving a molecular network[3] have received considerable attention. These multicomponent monolayers are typically investigated by means of scanning tunneling microscopy (STM), revealing submolecular resolution under ultrahigh vacuum conditions or at the liquid–solid interface.[4] In this contribution, we present the first observation of modular molecular networks formed by two different types of square-shaped "host" molecules and site-selective "guest" inclusion.

Among numerous molecular building blocks, butadiyne-bridged planar macrocycles **1**–**3** (Chart 1) were chosen because of the anticipated formation of a regular porous network (pore diameter ~1 nm).[5] Moreover, pyridinophane **1** shows a high binding affinity to tropylium (Tr) cation via ion−dipole interactions, at least in solution.[5a] We expected, therefore, that the molecular network of macrocycle **1** would serve as an appropriate template layer for guest adsorption. With these components in hand, we examined the formation of modular networks formed by a mixture of macrocycles—**1/2**, **1/3**, or **2/3**—having different side chains and site-selective guest binding properties.
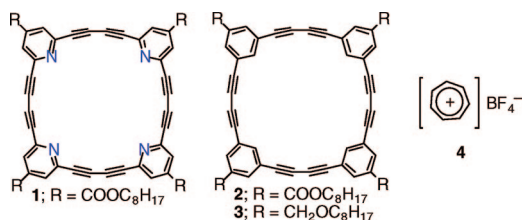
Chart 1

Figure 1a shows an STM image of a so-called linear pattern (linear A) of octyl ester substituted pyridinophane **1** at the 1,2,4-trichlorobenzene (TCB)/graphite interface with a tentative packing model superimposed on the image. The square bright features correspond to the conjugated macrocycle rim. Adjacent molecules most probably interact via hydrogen bonding interactions between
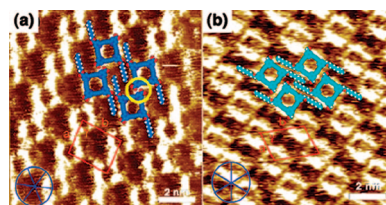

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Figure 1. STM images of molecular networks of the macrocycles at the TCB/graphite interface. (a) Linear A network of **1** (I_{set} = 0.70 nA, V_{bias} = –0.39 V). Unit cell parameters are a = 1.9 ± 0.1 nm, b = 2.4 ± 0.2 nm, and γ = 81 ± 1°. (b) Linear B network of **3** (I_{set} = 0.40 nA, V_{bias} = –1.78 V). Unit cell parameters are a = 1.8 ± 0.1 nm, b = 2.4 ± 0.1 nm, and γ = 70 ± 1°. Molecular models of **1** and **3**, unit cells (red), and main symmetry directions of graphite (blue) are superimposed on the respective images.

the carbonyl group and the hydrogen atom on the pyridine ring (indicated by a yellow circle in Figure 1a).[6] Though the alkyl chains are not visible, we assume that two of them are adsorbed on graphite preferentially along one of the three equivalent directions (the <1,−2,1,0> directions) and that the other two chains are free to move in solution. Similary, octyl ester substituted cyclophane **2** forms the same linear A structure, indicating little effect of the aromatic units (pyridine vs benzene) on the network structure (see Figure S1). On the other hand, (octyloxy)methyl substituted cyclophane **3** forms a more densely packed linear pattern (linear B; Figure 1b) and also a minor polymorph (see Figure S2), presumably because of the absence of hydrogen bonding interactions between adsorbed macrocycles.

Complexation experiments were performed on the molecular host network of **1** with tropylium tetrafluoroborate (**4**) as a guest.[5a] Figure 2a shows a typical STM image obtained by the "ex situ" method; **1** and **4** are mixed (1:13 molar ratio) in TCB/CH₃CN/CHCl₃ (10/9/1) before applying a drop of this mixture onto the surface. The brighter spots within the macrocycle cavity of **1** are trapped Tr ions (Figure 2b). The unit cell parameters match those of the linear A network of **1**. In situ experiments where a drop of a solution of **4** in CH₃CN/CHCl₃ (7/1) was applied onto the graphite surface after imaging a stable physisorbed adlayer of **1** in TCB gave rise to the same results (see Figure S4). Similar experiments on the molecular network of **2** or **3** did not reveal any host–guest complexation, in line with results obtained in solution[5a] and the lack of ion−dipole interactions.

In a next step, the formation of modular molecular networks was investigated. A 1:1 mixture of **1** and **2** did not reveal any difference compared to the networks of pure macrocycle **1** or **2** (see Figure S5). As **1** and **2** are indistinguishable in the STM images, the composition of the mixed networks remains unknown. However,
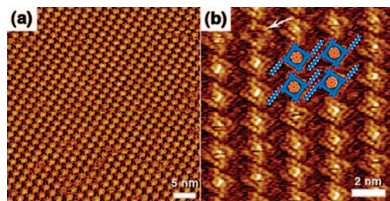
Figure 2. STM images of the monolayer of the **1** + **4** complex (I_{set} = 0.79 nA, V_{bias} = −0.45 V for (a) and I_{set} = 0.85 nA, V_{bias} = −0.45 V for (b)). The white arrow indicates an empty macrocycle **1**. Molecular models are superimposed on the image: **1** (blue) and Tr cation (orange). Enlargement of Figure 2 is given in Supporting Information Figure S3.
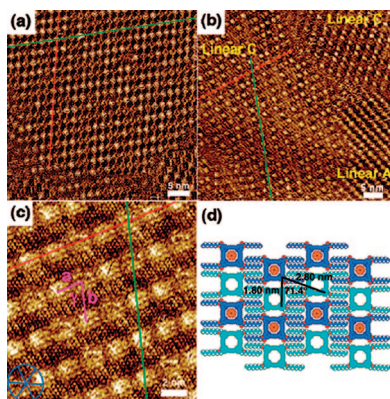

Figure 3. (a) STM image of the monolayer formed by a mixture of **2** and the **1** + **4** complex (I_{set} = 1.0 nA, V_{bias} = −0.49 V). (b) STM image of monolayer formed by a mixture of **3** and the **1**+**4** complex (I_{set} = 0.80 nA, V_{bias} = −0.45 V). In the linear C domain, **1** and **3** appear with equal probability. (c) High resolution image of the linear C structure (I_{set} = 0.74 nA, V_{bias} = −0.45 V). Unit cell parameters are a = 1.8 ± 0.1 nm, b = 2.8 ± 0.1 nm, and γ = 73 ± 1°. (d) Tentative model of the ideal alternating linear C structure consisting of **1** (blue), **3** (turquoise), and Tr cation (orange). Enlargement of Figure 3 is given in Supporting Information Figure S6.

upon mixing **1**, **2**, and **4** in a 1:1:13 molar ratio in TCB/CH$_3$CN/CHCl$_3$ (20/9/1), squares filled with a bright spot and darker square features appear randomly in the domains (Figure 3a). The appearance of bright spots only for some macrocyles strongly suggests that these are **1** + **4** complexes, while the darker squares are empty macrocycles **2**.[7] Moreover, the ratio between adsorbed **1** + **4** complexes and empty macrocycles **2** is roughly 1:1, though there is no positional relationship between both.[8]

The most important observation though is that a mixture of **1**, **3**, and **4** in a 1:1:13 molar ratio in TCB/CH$_3$CN/CHCl$_3$ (20/9/1) shows, in addition to pure linear A domains of the complex, a new modular network (linear C), not observed for the macrocycles before, *with a nonrandom positional relationship between both macrocycles.* The brighter and darker cores correspond to the **1** + **4** complex and guest-free **3**, respectively, and they appear in the mixed domains in a 1:1 ratio (Figure 3b,c). In contrast to monocomponent monolayers formed by the macrocycles, and the macrocycle mixtures discussed before, a high resolution image of the linear C pattern shows the adsorption of *all* alkyl chains, which is also reflected in the unit cell parameters. Careful analysis of positional relationships between macrocycles reveals a clear tendency of the **1** + **4** complex and **3** to appear in an alternating fashion along unit cell vector a (the red line in Figure 3b,c; Figure 3d for the model). In fact, independent analysis of 268 macrocycle rows along unit cell vector a gives a correlation factor (CF) of 0.79 (CF is 1.0 for strict alternation, 0.5 for random sequence, and 0.0 for phase

separation).[9] A similar treatment along unit cell vector b (the green line in Figure 3b,c) affords a correlation factor of only 0.48, indicating that there is no preferred sequence of macrocycles along that direction. In situ experiments led to identical results (see Figure S7). The linear C pattern was also observed for a 1:1 mixture of **1** and **3** (without **4**) and also **2** and **3** (see Figures S8 and S9 in Supporting Information). Furthermore, the linear A structure of the mixture of **1**, **2**, and **4** shows a random arrangement (CFs are 0.48 and 0.44 along unit cell vector a and b in Figure 3a, respectively). The driving force for this preferred alternation along only one direction in the linear C pattern is attributed to attractive dipolar interactions between adjacent ester and ether groups along the macrocycle rows (unit cell vector a) (see Figures S19–S21).[10] This is supported by the fact that the linear C pattern is not observed for the pure components where these dipolar interactions would be repulsive.

In summary, we observed the formation of modular molecular networks with a favored alternating alignment of two different types of square macrocycles and site-selective guest inclusion. We believe the modular network approach presented here can lead to a general strategy for the construction of multicomponent 2D molecular networks in which different kinds of molecules are aligned on the surface in a site- and space-defined manner.

Supporting Information Available: Experimental details, STM images, and alternative analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) In line with the experiments on the **1** + **4** mixtures using the same excess of **4**, we assume that every macrocycle **1** is complexed.
(8) For a random alignment of free porpyrins and their Rh complexes at the solid−liquid interface, see: Ikeda, T.; Asakawa, M.; Goto, M.; Miyake, K.; Ishida, T.; Shimizu, T. *Langmuir* **2004**, *20*, 5454.
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JA711422H