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COMMUNICATION

Site-selection and adaptive reconstruction in a two-dimensional nanoporous network in response to guest inclusion

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In the present investigation, we report the fabrication of flexible binary network formed by tetraacidic azobenzene (NN4A) and *trans*-1,2-bis(4-pyridyl)ethylene (DPE) at the liquid-solid interface. When coronene (COR) molecule is added into these systems, the binary networks break and the reconstruction structures of NN4A/COR host-guest systems are subsequently formed. Scanning tunneling microscopy (STM) measurements, as well as density function theory (DFT) calculations, reveal that the NN4A/COR host-guest system is the energetically favourable structure and with the most thermodynamic stability. These studies give us insight into a better comprehension of competitive adsorption for the fabrication of functional molecular assemblies.

The self-assembly of molecular building blocks on solid surfaces has become a subject of interest owing to their potential applications in surface template and nanopatterning.¹⁻³ Especially two-dimensional (2D) networks with vacant spaces, known as “2D porous networks”, have gained significant attention due to the possibility to immobilize functional targets in a repetitive and spatially ordered organization.⁴⁻⁶ Such 2D porous networks formed by physisorption on atomically flat conductive substrates can act as an ideal template to investigate the chemical reactions and the dynamic behaviour of guest inclusion, and their structures have been studied under ultrahigh

vacuum conditions (UHV) as well as at the liquid–solid interface by scanning tunneling microscopy (STM).⁷⁻¹⁰

In most cases, the incorporation of the guest molecules into multicomponent 2D network could further inspire the category of molecular architectures.¹¹⁻¹³ In addition, the flexible networks are of great significance in site-selection “guest” inclusion recently.¹⁴⁻¹⁵ A potential advantage of flexible networks is that they undergo slight structural change to host a large set of different guest molecules, which provides the reasonably high guest selectivity in order to achieve targeted multicomponent surface confined patterns.¹⁶⁻¹⁸ However, some examples that the binding properties of host-guest system are focused on the rigid molecular networks with permanent porosities have been reported.¹⁹⁻²⁰ In contrast, less work has been done on the reconstruction phenomenon of flexible binary networks which arises from competition adsorption by including the guest molecule.

In the present work, we construct flexible binary networks based on the molecular arrays of *trans*-1,2-bis(4-pyridyl)ethylene (DPE) and tetraacidic azobenzene (NN4A) (Figure 1) on the highly oriented pyrolytic graphite (HOPG) surface. To investigate the properties of these binary networks, coronene (COR) as a guest molecule was added into this system. Scanning tunneling microscopy (STM) measurements and density function theory (DFT) calculations are utilized to reveal the reconstruction phenomenon of two-dimensional nanoporous network induced by coadsorbed guest molecule.

NN4A was synthesized as previously reported procedures.²¹ DPE was purchased from Aldrich company. COR was purchased from Acros. All these materials were used without further purification. All the studied samples were dissolved in heptanoic acid, and the concentration of all solutions for STM investigation was less than 1.0×10^{-4} M. The sample was prepared in a two-step procedure. First, after depositing a droplet of mixture solution containing the NN4A and DPE (1:2) in heptanoic acid, the nanoporous networks were formed on the freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, grade ZYB, NTMDT, Russia). Second, a droplet of guest molecule (COR molecule) in heptanoic acid was added onto the networks. The self-assembly of host-guest systems was monitored by STM.

The STM measurements were performed using a Nanoscope IIIa scanning probe microscope system (Bruker, USA) under ambient conditions. Tips were mechanically cut from Pt/Ir wires (80/20). All STM images were recorded in the constant-current mode.

The theoretical calculation was carried out using density functional theory (DFT) provided by the DMol3 code.²²⁻²³ We use the periodic boundary conditions (PBC) to describe the 2D periodic structure on the graphite in this work. The Perdew and Wang parameterization of the local exchange correlation energy was applied in the local spin density approximation (LSDA) to describe exchange and correlation.²⁴ We expanded the all-electron spin-unrestricted Kohn-Sham wave functions in a local atomic orbital basis. In such a double numerical basis set, the polarization was depicted. All calculations were all-electron ones and performed with the Extra-Fine mesh. Self-consistent field procedure was carried out with a convergence criterion of 10^{-5} a.u. on the energy and electron density.

To evaluate the interaction between the adsorbates and HOPG, we design the model system. In our work, adsorbates are consisted with benzene-ring π -conjugated structures. Since adsorption of benzene on graphite and graphene should be very similar, we have performed our calculations on infinite graphene monolayers using PBC. In the superlattice, graphene layers were separated by 35 Å in the normal direction and represented by orthorhombic unit cells containing two carbon atoms. When modeling the adsorbates on graphene, we used 6×6 graphene supercells with 216 Carbon atoms and sampled the Brillouin zone by a $1 \times 1 \times 1$ k-point mesh. The interaction energy E_{inter} of adsorbates with graphite is given by $E_{\text{inter}} = E_{\text{tot}}(\text{adsorbates/graphene}) - E_{\text{tot}}(\text{isolated adsorbates in vacuum}) - E_{\text{tot}}(\text{graphene})$.

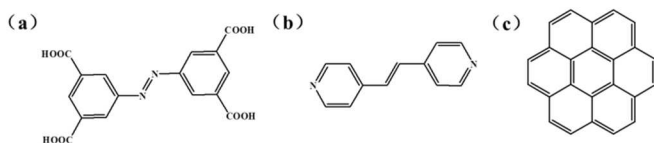


Figure 1. The chemical structures of (a) NN4A; (b) DPE; (c) COR.

After depositing a droplet of NN4A solution on HOPG, the well-ordered open networks with Kagomé structure were formed on the HOPG surface.²⁵ A large scale STM image of the self-assembled structure of NN4A is shown in Figure S1. Figure 2a presents a higher resolution image. Obviously, two different type of cavities (marked A and B in Figure 2b) are found in the well-ordered NN4A network. The comparatively larger A-type cavity, with a cavity diameter of 1.2 nm, is composed of six NN4A molecules constructed between carboxylic groups with intermolecular hydrogen bonds. However, with an inner width of about 0.9 nm, the triangular B-type is formed from three NN4A molecules which act as the edges of cavity. Six B-type cavities surround each A-type cavity. Figure 2b is the corresponding molecular model calculated by DFT method on the basis of STM observations. The measured unit cell is also superimposed on the molecular model with $a = b = 2.5 \pm 0.1$ nm, $\alpha = 120^\circ$.

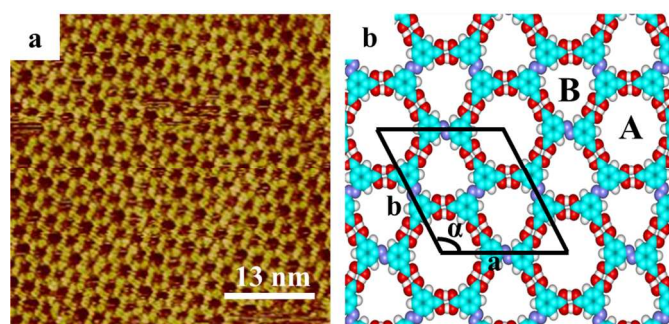


Figure 2. (a) A higher resolution STM image of the self-assembled structure of NN4A networks on the HOPG surface. $I_{\text{set}} = 343.6$ pA; $V_{\text{bias}} = 685.1$ mV. (b) The proposed molecular model for NN4A.

Furthermore, DPE as bipyridine derivative was chosen to mediate the network properties of NN4A. When a droplet of heptanoic acid containing DPE was deposited on the networks of NN4A, the original Kagomé structure was broken and completely replaced by the ordered rectangular network.²⁶ Figure S2 presents a large scale STM image of the self-assembled structure of the NN4A/DPE networks. A higher resolution STM image is shown in Figure 3a. An inset clearly shows the detailed co-assembled structure in Figure 3a. The NN4A molecules appear as two separated spots (indicated by the red arrow) in this image, while the DPE molecules appear as a line (indicated by the green arrow). NN4A molecules act as the bridge to connect DPE molecules through $\text{N} \cdots \text{H} - \text{O}$ hydrogen bonds, forming a rectangular network rather than pure NN4A itself. Careful analysis of this rectangular network structure reveals that four HO- in carboxyl groups of two NN4A molecules are linked with four N atoms of two DPE molecules. In the co-assembled structure, the adsorbed heptanoic acid molecules (marked by the yellow arrows in an inset) which can form the dimer through carboxyl groups interactions are observed in the dark bands. Owing to the lower tunneling efficiency, the assembled structures between the dark

bands seemed to be blurred compared with the rectangular network. According to the STM image, a corresponding molecular model was proposed in Figure 3b. The measured unit cell is also presented with: $a' = 2.1 \pm 0.1$ nm, $b' = 2.0 \pm 0.1$ nm, $\alpha' = 114^\circ \pm 1^\circ$.

After depositing a droplet of solution containing COR on the rectangular network structure, the structural transformation of binary network is shown in Figure 4a. A higher resolution image is revealed in Figure 4b. It should be noted that the COR

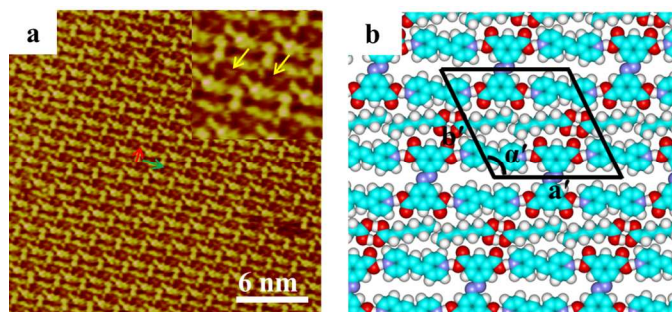


Figure 3. (a) A higher resolution STM image of the NN4A/DPE networks. $I_{\text{set}} = 299.6$ pA; $V_{\text{bias}} = 530$ mV. (b) A suggested molecular model for NN4A/DPE.

molecule was not entrapped into the rectangular network but in the re-constructed NN4A network. COR, as planar guest molecule of large π -conjugated cores with C_6 symmetry, can be stabilized and entrapped in the A-type cavity of the NN4A network in domain I. The white round spot superimposed in the image corresponds to the COR molecule which was surrounded by six unfilled triangular B-type cavities. The suggested molecular model together with the measured unit cell: $a'' = b'' = 2.5 \pm 0.1$ nm, $\alpha'' = 60^\circ \pm 1^\circ$ is presented in Figure 4c. In domain II, there are some empty rectangular networks formed by the co-assembled structure of

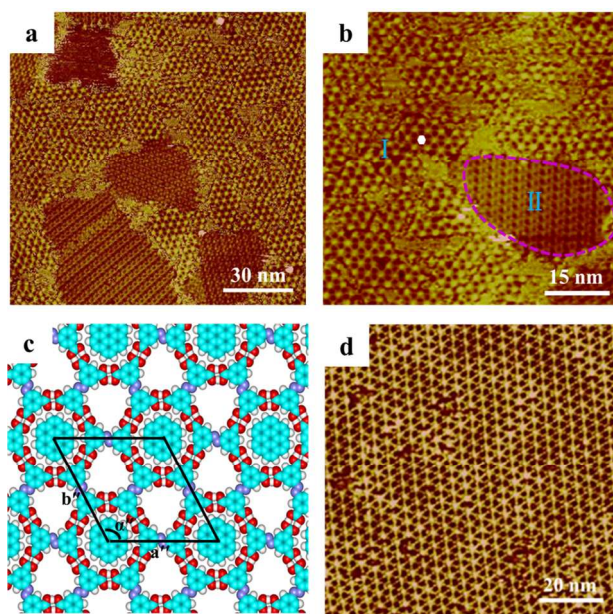


Figure 4. (a) A large scale STM image of the self-assembled structure of NN4A/DPE/COR host-guest construction on the HOPG surface. $I_{\text{set}} = 315.6$ pA; $V_{\text{bias}} = 636.4$ mV. (b) An STM image of self-assembled structure of the NN4A/DPE/COR host-guest construction on the HOPG surface. $I_{\text{set}} = 299.9$ pA; $V_{\text{bias}} = 568.3$ mV. (c) A suggested molecular model of the NN4A/COR. (d) An STM image of the self-assembled structure of NN4A/COR host-guest system on the HOPG surface. $I_{\text{set}} = 420.3$ pA; $V_{\text{bias}} = 669.3$ mV.

NN4A/DPE, in which the COR molecule was not observed. In addition, after adding a droplet of solution containing COR on the NN4A networks alone, the self-assembled structures of NN4A/COR host-guest systems are shown in Figure 4d.²⁷ It should be noted that one hexagonal COR molecule is entrapped into the A-type cavity of the NN4A network, which is different from the reconstruction phenomenon of flexible binary networks by including the COR guest molecule. Therefore, it is notable that size and geometry selectivity play a significant role in the structural transformation of rectangular network after introducing COR guest molecule.

To further investigate both the stability of network structure and the effect of introducing guest molecules into these systems, we performed the density functional theory (DFT) calculations based on the above observed phenomena.

The calculated lattice parameters for 2D networks are summarized in the Table 1. The calculated parameters agree well with the experimental values. In the surface assembly system, the interaction between adsorbates and substrate plays an important role. Therefore, we present the total energy (including the interaction energy between adsorbates and the interaction energy between adsorbates and substrate) in Table 2. Furthermore, a reasonable way to compare the thermodynamic stability of the different arrays should be the total energy per

unit area. Then we also present the total energy per unit area of the system in Table 2.

Table 1. Experimental (Expt.) and calculated (Cal.) lattice parameters for the 2D networks.

		Unit cell parameters		
		a (nm)	b (nm)	α (°)
NN4A	Expt.	2.5 ± 0.1	2.5 ± 0.1	120 ± 1
	Cal.	2.49	2.49	120
NN4A/DPE	Expt.	2.1 ± 0.1	2.0 ± 0.1	114 ± 1
	Cal.	2.05	1.95	114
NN4A/COR	Expt.	2.5 ± 0.1	2.5 ± 0.1	60 ± 1°
	Cal.	2.49	2.49	60

From Table 2, we notice that the total energy per unit area of the NN4A/DPE system is $-0.556 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-2}$, and is slightly lower than that of the pure network NN4A ($-0.543 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-2}$). Here, it is noteworthy that the rectangular network formed by the two components is more stable compared with the original NN4A network, since the solvent molecules (heptanoic acid) further facilitate the stability of the co-assembled structure. According to the calculation results, the total energy per unit area of NN4A/COR assembled structure is $-0.649 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-2}$ which is with the most thermodynamic stability. The calculation results agree well with our STM observations. Therefore, when COR molecules were introduced into these systems, the formation of molecular self-assembled behaviour undergoes dramatic changes containing the collapse of rectangular network and subsequent the host-guest system reconstruction. COR molecule, as a planar guest molecule with large π -conjugated cores, geometrically matches well with the cavity of NN4A for the adsorption energy and size selectivity.

Table 2. The total energy (including the interaction energy between adsorbates and the interaction energy between adsorbates and substrate) and the energy per unit area for adsorbates on the HOPG surface. Here, the more negative energy means the system is more stable.

	The interaction energy between adsorbates (kcal/mol)	The interaction energy between adsorbates and substrate (kcal/mol)	Total energy (E_{total} , kcal mol ⁻¹)	Total energy per unit area (E_{total} , kcal · mol ⁻¹ · \AA ⁻²)
NN4A	-176.867	-114.77	-291.637	-0.543
NN4A/DPE ^a	-94.032	-108.897	-202.929	-0.556
NN4A/COR	-196.204	-152.222	-348.426	-0.649

^a The total energy and total energy per unit area are associated with the rectangular network structure of NN4A/DPE and the adsorbed heptanoic acid molecules

The density functional theory (DFT) calculation was performed to investigate the reconstruction phenomenon studied in our work. It is significant that stability of co-assembled structure is the key to fabricate multi-component supramolecular assemblies. The method for exploring the

formation of functional molecular structure gives rise to a better comprehension of the concept of competitive adsorption.

Conclusions

In summary, a new approach has been explored to investigate the host-guest systems with highly selectively molecular recognition on the HOPG surface. We have shown that the NN4A/DPE molecules can exclusively form the binary networks via intermolecular hydrogen bonds between carboxyl and pyridine groups. The binary network can break and the new reconstruction structures of NN4A/COR host-guest systems are subsequently formed as a response to the addition of COR guest molecules. The STM images, as well as DFT calculations, reveal that the NN4A/COR host-guest system is the energetically favourable structure and with the most thermodynamic stability. The results presented here give us insight into a better comprehension of competitive adsorption for the fabrication of multicomponent molecular assemblies, which are favorable for the construction of functional nanostructures.

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Notes and references

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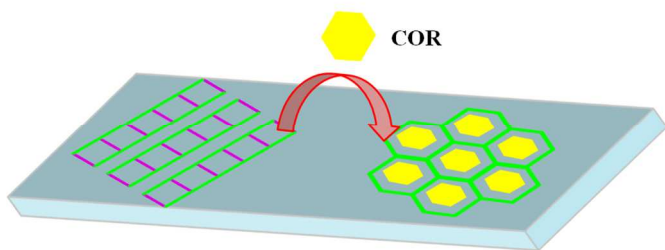
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Supplementary Information (SI) available: additional STM images

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TOC FIGURE



In the present investigation, we report when coronene (COR) molecule is added into the flexible binary network formed by tetraacidic azobenzene (NN4A) and *trans*-1,2-bis(4-pyridyl)ethylene (DPE), the binary network breaks and the reconstruction structures of NN4A/COR host-guest systems are subsequently formed.

