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**Fullerenes**

# Site-Selective Fabrication of Two-Dimensional Fullerene Arrays by Using a Supramolecular Template at the Liquid-Solid Interface**

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Fullerenes have attracted a great deal of attention since their discovery[1] because of their unique physical and chemical properties and potential applications.[2] Many applications require the deposition of fullerenes onto a variety of surfaces including metals[3–6] or semiconductors.[7] The fabrication of ordered arrays of fullerenes on solid surfaces is of interest from both scientific and technological viewpoints. It has been demonstrated that fullerenes can form well-ordered arrays on metal or semiconductor surfaces under ultrahigh vacuum (UHV) conditions at low temperatures.[8–12] The arrangement is determined by the size and symmetry of the fullerenes and rigidly maintains its shape. On the other hand, $C_{60}$ is highly mobile at room temperature (RT) even when adsorbed on metal surfaces, and has no preferential orientation unless cooled to low temperatures.[13–20] Therefore, a well-decorated surface, which serves as a molecular template and provides binding sites, is important and necessary for the fabrication of highly ordered arrays of fullerenes at RT. Open porous networks obtained by metal–organic coordination,[21] the formation of hydrogen bonds,[8] or even van der Waals interactions[22–24] have been successfully used to direct the formation of ordered fullerene arrays. In this way the interfullerene distance and symmetry of the arrangement are solely determined by the molecular template and can be changed by adjusting its structure. More importantly, interactions between fullerenes can also be modified with this strategy.

We have designed and synthesized a tetraacidic azobenzene molecule NN4A (Figure 1a) that exclusively forms Kagomé open networks with two types of cavities that have different size and symmetry at the liquid–solid interface. These cavities are capable of accommodating fullerene molecules as guest species. Herein, we examine the site selectivity of the networks for different fullerenes, a feature which has not been observed for other systems at liquid–solid interfaces. Azobenzene derivatives are typical photochromic compounds that have a wide range of potential applications, including for optical switching, holographic storage, light harvesting, long-term energy storage, and nonlinear optical materials.[25,26] The attractive photosensitive properties of azobenzene compounds have resulted in them being utilized as photoswitching units to control the structure and function of supramolecular systems.[27–31] Thus, the use of azobenzene units in the host matrix could allow for further control of the host–guest architectures.

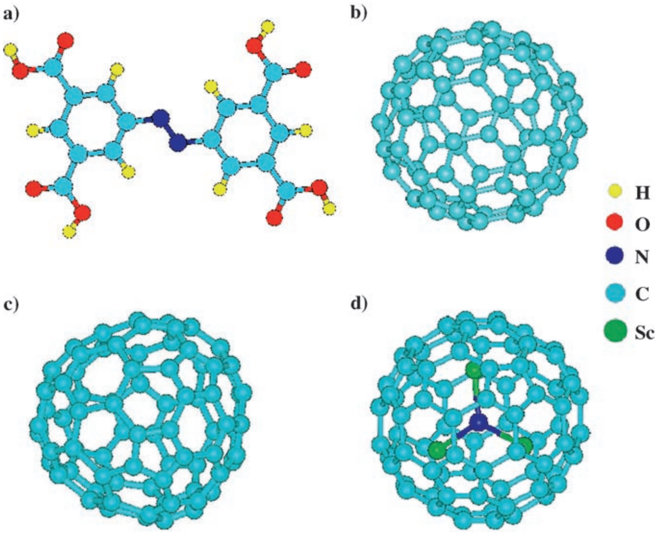

***Figure 1.*** Chemical structures of NN4A and guest molecules: a) NN4A, b) $C_{60}$, c) $C_{80}$, and d) $Sc_3N@C_{80}$

When deposited onto a graphite surface, NN4A forms a well-ordered open network with a Kagomé structure which is correlated to molecular geometry and network symmetry.[32,33] An STM image of the resulting molecular network is shown in Figure 2a. The backbones of the *trans*-NN4A molecules appear as bright rods in the image because of their high electron density, which results in a raised tunneling probability.[34] As observed in the high-resolution STM image (inset in Figure 2a), two different types of cavities are observed in the well-ordered network (marked A and B in Figure 2b). The comparatively larger A-type cavity with sixfold symmetry is composed of six benzene rings that have hydrogen bonds between the carboxylic groups. The van der Waals radii (1.1 Å) of the hydrogen atoms lead to a cavity diameter of 12.0 Å. The B-type cavity, with an inner width of about 8.6 Å,

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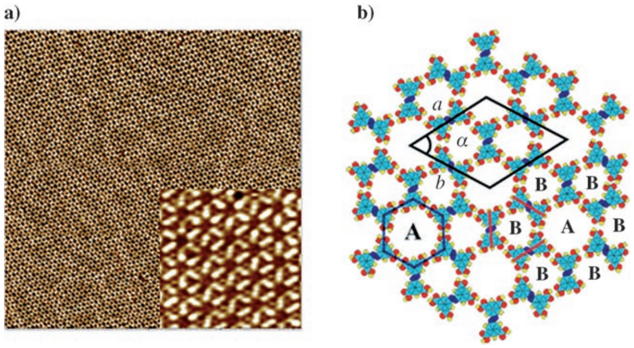

*Figure 2.* a) Constant-current STM image (103 × 103 nm) of a self-assembled monolayer of NN4A networks on highly ordered pyrolytic graphite (HOPG) surface. $I = 549$ pA, $V = 540$ mV. Inset: High-resolution view showing the detailed NN4A network structure. b) Proposed molecular model for the NN4A networks.

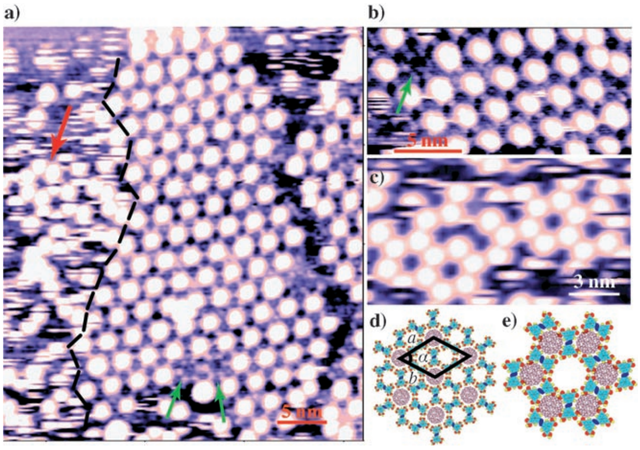

*Figure 3.* a) Constant-current STM image of the $C_{60}$–NN4A host–guest architecture on an HOPG surface. $I = 119$ pA, $V = 900$ mV. The green arrow indicates an empty cavity missing one $C_{60}$ molecule. b) High-resolution view showing the detailed $C_{60}$–NN4A host–guest structure with $C_{60}$ trapped within the A-type network. c) High-resolution view showing the $C_{60}$–NN4A host–guest structure with $C_{60}$ trapped within the B-type network. d), e) Suggested molecular models of the assembly structures for (b) and (c), respectively.

is formed from three NN4A molecules arranged in a triangular shape (Figure 2b). The proposed structural model derived from STM observations is presented in Figure 2b, which indicates that the two-dimensional networks were formed by hydrogen-bonding interactions between carboxylic groups. A unit cell with $a = b = (26.1 \pm 2.0)$ Å and $\alpha = (60.0 \pm 1.5)°$ is also superimposed on the molecular model. Each of the four carboxylic groups of a NN4A molecule forms two hydrogen bonds with its neighbors, which confers great stability to the network. Unlike the tetraacid analogues reported recently, no parallel network or frustration of the 2D crystallization is observed for the NN4A molecule.[33] This finding indicates the Kagomé structure is energetically favored for NN4A, probably because of the difference in the hydrogen-bonding interactions in the two polymorphs.

Both the A- and B-type cavities are large enough in diameter to accommodate guest molecules such as $C_{60}$; therefore, the open Kagomé networks of NN4A could serve as a two-dimensional molecular template, which offers two different types of binding sites to accommodate functional target molecules. It is thus of interest to investigate the selectivity of the molecular network towards the inclusion of guest molecules.

Figure 3a shows the STM image of the $C_{60}$–NN4A complex, which was acquired after depositing $C_{60}$ molecules onto the NN4A template, with ordered hexagonal molecular arrays evident. Each bright spot corresponds to an individual molecule of $C_{60}$. Two kinds of assembly structures were formed when $C_{60}$ became trapped in the A- and B-type cavities, which are separated by the phase boundary marked by the dotted lines in Figure 3a. More details of the two complex structures are shown in Figure 3b and c. The corresponding molecular models of the hybrid assembly structures are presented in Figure 3d and e. The internal structure of a single $C_{60}$ molecule could not be observed during the experiment; this result might be attributed to the thermally induced instabilities of the encapsulated $C_{60}$ molecules at room temperature.[35,36] For the domain shown on the right in Figure 3a (or in Figure 3b), the green arrow indicates the defect in the ordered $C_{60}$ array, where one $C_{60}$ molecule is missing, leaving an open individual cavity. The cavity of the NN4A molecules underneath the $C_{60}$ molecules can be directly observed at the vacant sites, and shows that $C_{60}$ molecules occupy the A-type cavities in this inclusion structure. A unit cell with $a = b = (26.3 \pm 2.0)$ Å and $\alpha = (60.0 \pm 1.5)°$ is superimposed on the molecular model (Figure 3d). The distance between the neighboring $C_{60}$ molecules is similar to that of the NN4A network unit cell ((26.1 ± 2.0) Å, see Figure 2b) and such spacing is large enough to avoid steric $C_{60}$–$C_{60}$ repulsion.[20,37] As indicated by the green arrows in Figure 3a and b, the six benzene moieties of the empty cavity could be clearly seen. Apparently, the cavities formed by NN4A introduce a grid of stable adsorption sites for the fullerenes, rather than for the NN4A backbone through electronic donor–acceptor interactions.[38,39]

According to theoretical computations, the average interaction energy for the $C_{60}$–NN4A–graphite system is 36.21 kJ mol$^{-1}$ in the case of a $C_{60}$ molecule trapped within an A-type cavity. This value indicates that, as mentioned above, the binding sites in the molecular cavity could interact with the $C_{60}$ molecules and play an important role in their immobilization. In addition, the interaction of $C_{60}$ with the graphite substrate may be dominated by van der Waals interactions,[40] which are also essential to stabilize the $C_{60}$ molecule. When trapped in a B-type cavity (indicated by the red arrow in Figure 3a) the interaction energy for the $C_{60}$–NN4A–graphite system is 31.83 kJ mol$^{-1}$. Furthermore, the distance between the neighboring $C_{60}$ molecules is about 16 Å, which suggests that the van der Waals attraction[41] between $C_{60}$ molecules (1.86 kJ mol$^{-1}$ according to the calculated results) also plays a role in their stabilization in the B-type cavity. It should be noted that the interaction energies of a $C_{60}$ molecule with the A- and B-type cavities are nearly equal, which is consistent with our experimental observation that $C_{60}$ is trapped nearly nonpreferentially in the two types of cavities. The corresponding STM images are presented in Figures S1–S3 in the Supporting Information. This result indicates that $C_{60}$ molecules show no site selectivity for the two types of cavities formed by NN4A on graphite. However, $C_{60}$ could not be observed in both A- and B-type cavities in the same domain, possibly because of repulsive interactions. Theoretical results show that if $C_{60}$ molecules are deposited in such a configuration, a strong repulsion will occur between the molecules (within a unit cell, the repulsion is about 355.7 kJ mol$^{-1}$).

$C_{80}$ molecules[42] (Figure 1) were introduced as an example of a guest species with a larger diameter to examine the selectivity of the molecular network for guest inclusion (the theoretical diameter of $C_{80}$ is 8.22 Å, while that of $C_{60}$ is 6.80 Å). Figure 4a shows highly uniform arrays of $C_{80}$–NN4A architectures over a large area. Each bright spot corresponds to an individual molecule of $C_{80}$, and well-ordered hexagonal $C_{80}$ molecular arrays can be observed. Figure 4b shows the high-resolution STM image of the $C_{80}$–NN4A assembled structure. The corresponding molecular models of the structures are shown in Figure 4c, with a unit cell, with $a = b = (27.0 \pm 1.5)$ Å and $\alpha = (60.0 \pm 1.5)°$, superimposed on the molecular model. It could be deduced from the unit cell parameters that $C_{80}$ filled the A-type cavity. On the basis of theoretical computations (Table 1), the average interaction energy for the $C_{80}$–NN4A–graphite system is 49.45 kJ mol$^{-1}$ in the case of a $C_{80}$ molecule trapped within the A-type cavity. This energy is much larger than that for a $C_{80}$ molecule trapped within the B-type cavity (34.56 kJ mol$^{-1}$).

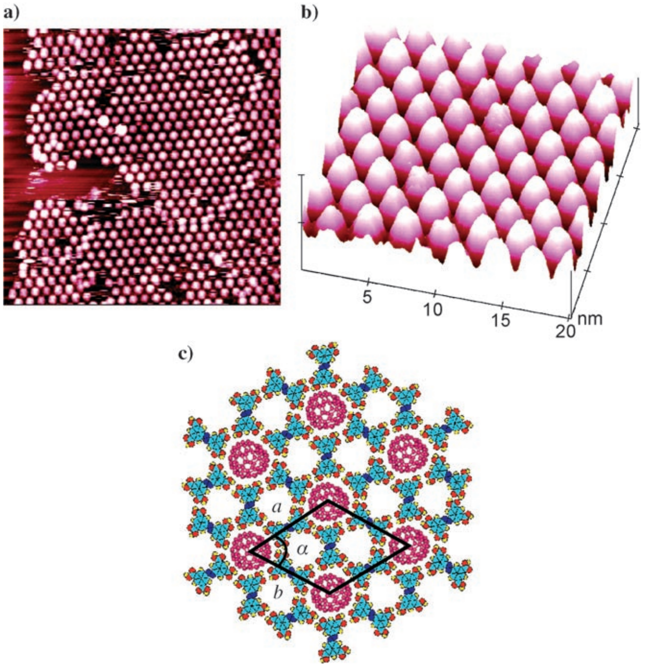

***Figure 4.*** a) STM image (67.4×67.4 nm) of the $C_{80}$–NN4A host–guest architecture on an HOPG surface. $I = 169.5$ pA, $V = 918.5$ mV. b) High-resolution STM image (20.1×20.1 nm) of $C_{80}$–NN4A assembled structure. $I = 169.5$ pA, $V = 918.5$ mV. c) Plan view of the proposed structural model.

***Table 1:*** Total interaction energy (kJ mol$^{-1}$) for the fullerene within different cavities.[a]

| | $C_{60}$ | $C_{80}$ | $Sc_3N@C_{80}$ |
|---|---|---|---|
| NN4A-A | 36.21 | 49.45 | 50.37 |
| NN4A-B | 31.83 | 34.56 | 35.50 |

[a] The total energy includes the interaction energy of fullerene–NN4A, fullerene–graphite, and fullerene–fullerene.

To further analyze the inclusion selectivity of the molecular network, $Sc_3N@C_{80}$ molecules were introduced. These fullerenes, which have metal atoms encapsulated within the carbon cage, have novel electronic and structural properties.[43,44] The electronic effect of the metal atoms results in an increased electronegativity of the carbon cage, which enhances the electronic interaction between $Sc_3N@C_{80}$ molecules and the template. Highly uniform arrays of architectures over large areas can be obtained (Figure 5a). The bright spots correspond to individual $Sc_3N@C_{80}$ molecules in the cavities, and the characteristics of the images are essentially the same as those of $C_{60}$ trapped in the A-type cavities (see Figure 3). Theoretical calculations (Table 1) indicate an interaction of 50.37 kJ mol$^{-1}$ for the $Sc_3N@C_{80}$–NN4A–graphite system when trapped in an A-type cavity, which is larger than that of $C_{60}$ (36.21 kJ mol$^{-1}$). In comparison with that of $C_{60}$, the host–guest architecture formed by $Sc_3N@C_{80}$ and NN4A shows a higher degree of stability and ordering (see Figure 5a), which is indicative of stronger interactions between $Sc_3N@C_{80}$ and the NN4A host network. Furthermore, the high-resolution STM image (Figure 5b) suggests that only A-type cavities are occupied by the $Sc_3N@C_{80}$ guest molecules. The coincidence of the size and geometry of $Sc_3N@C_{80}$ with the A-type cavity must play a substantial role

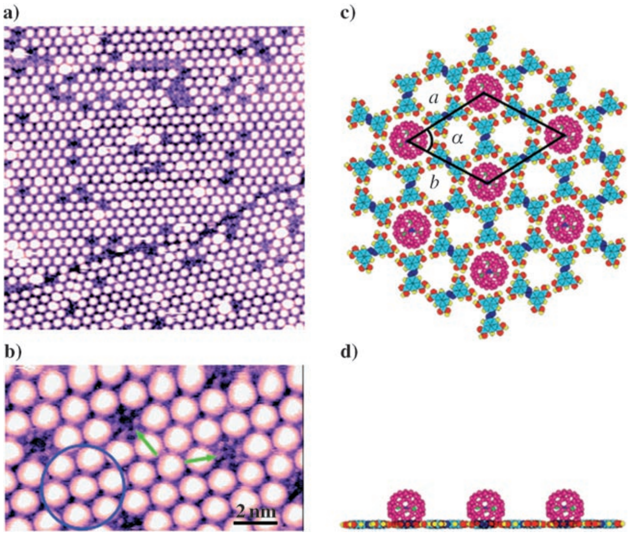

***Figure 5.*** a) STM image (68×68 nm) of the $Sc_3N@C_{80}$–NN4A host–guest architecture on an HOPG surface. $I = 165$ pA, $V = 1008$ mV. b) High-resolution STM image of the $Sc_3N@C_{80}$–NN4A structure. $I = 218$ pA, $V = 916$ mV. The green arrows indicate individual cavities missing one $Sc_3N@C_{80}$ molecule. c) Plan view of the proposed structural model. d) Side view of the model.

in this observed site selectivity. Therefore, $Sc_3N@C_{80}$ molecules could only fill A-type cavities, which means a higher site selectivity for $Sc_3N@C_{80}$ than $C_{60}$. The suggested molecular model that corresponds to the host–guest architecture marked by the blue circle in Figure 5 b is given in Figure 5 c. A unit cell, with $\alpha = (60.0 \pm 1.5)°$ and $a = b = (25.7 \pm 2.0)$ Å, is also marked on the model. The unit cell constants are slightly smaller than that of the NN4A network determined in Figure 2 b because of the van der Waals attractions between the $Sc_3N@C_{80}$ and NN4A molecules, as mentioned above. It should be noted that fullerenes always appear with a broadened apparent diameter in the STM image[8] compared with planar aromatic molecules such as phthalocyanine and porphyrins. Therefore, the distance between the Sc3N@$C_{80}$ molecules in the STM image in Figure 4 b appears to be smaller than that in the proposed models.

Theoretical calculations were carried out to rationalize the site selectivity effect for $C_{60}$, $C_{80}$, and $Sc_3N@C_{80}$ (Table 1). The simulation indicates a strong interaction in the $C_{60}$–NN4A–graphite system (36.21 kJ mol$^{-1}$ in the A-type cavity and 31.83 kJ mol$^{-1}$ in the B-type cavity). Thus, $C_{60}$ molecules have nearly equal stability in these two types of cavities. The interactions of $C_{80}$ or $Sc_3N@C_{80}$ with the sixfold A-type cavity are more favorable (49.45 kJ mol$^{-1}$ and 50.37 kJ mol$^{-1}$, respectively; see Table 1).

In summary, we have shown that NN4A molecules can exclusively form 2D porous Kagomé networks with two types of cavities of different size and symmetry through hydrogen-bonding interactions between carboxyl groups at the liquid–solid interface. The open Kagomé network can serve as an organic template for the accommodation of fullerene molecules. The experimental and theoretical results indicate that $C_{60}$ molecules have no apparent site selectivity for the two types of cavities formed by NN4A. However, the larger $C_{80}$ and $Sc_3N@C_{80}$ molecules are trapped exclusively in the A-type cavities, which implies appreciable site selectivity. In addition, as the metal atoms increase the electronegativity of the carbon cage, $Sc_3N@C_{80}$ shows enhanced interaction with the NN4A–graphite template compared with $C_{60}$. The observation of site selectivity for fullerene molecules has not been observed for other systems at liquid–solid interfaces. These results could benefit studies on the interactions between fullerenes and the template and substrate, and could lead to a better comprehension of template-directed fabrication of functional molecular arrays.

## Experimental Section

$C_{60}$ was purchased from Acros and used without further purification. $Sc_3N@C_{80}$ and NN4A were synthesized by following previously reported methods.[25,45] Heptanoic acid (AR) and phenyloctane (>98 %) were purchased from Acros.

The samples were prepared in two steps. First, the organic template layer was prepared by depositing a droplet of the solution of NN4A molecules in heptanoic acid on a freshly cleaved HOPG surface. The concentration of the solution was less than 1 mM. Heptanoic acid is electrically nonconductive and its vapor pressure at room temperature is low enough to allow stable tunneling experiments over extended time after deposition. A droplet of the solution of $C_{60}$ (or $Sc_3N@C_{80}$) in phenyloctane was then added to the predeposited NN4A solution on the surface for the host–guest complexation. STM experiments were carried out at room temperature (21–22 °C) with a Nano IIIa scanning probe microscope system (Veeco Metrology, USA) at the liquid–solid interface. Tips were mechanically formed from Pt/Ir wires (80/20). All STM images were recorded in the constant-current mode.

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