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Hierarchical formation of Fe-9eG supramolecular networks *via* flexible coordination bonds[†]

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From the interplay between high-resolution scanning tunneling microscopy imaging/manipulations and density functional theory calculations, we display the hierarchical formation of supramolecular networks by codeposition of 9eG molecules and Fe atoms on Au(111) based on the flexible coordination bonds (the adaptability and versatility in the coordination modes). In the first step, homochiral islands composed of homochiral G_4Fe_2 motifs are formed; and then in the second step, thermal treatment results in the transformation into the porous networks composed of heterochiral G_4Fe_2 motifs with the ratio of the components being constant. *In situ* STM manipulations and the coexistence of some other heterochiral G_4Fe_2 motifs and clusters also show the flexibility of the coordination bonds involved. These studies may provide a fundamental understanding of the regulations of multilevel supramolecular structures and shed light on the formation of designed supramolecular nanostructures.

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Introduction

Hierarchical assembly, as a multilevel assembling process based on elementary components, is ubiquitous in biosystems.¹⁻³ Derived from nature's wisdom, it is also widely applied in the fabrication of functional supramolecular architectures and materials. In addition to complex three-dimensional (3D) architectures, hierarchical assembly has also shown its versatility in tuning the nano-patterns of 2D supramolecular structures,⁴ and transformation, recognition and conservation of chirality in the 2D surface nanostructures.^{5,6} In the 2D framework, techniques allowing real-space observations should be the tools of choice, such as scanning tunneling microscopy (STM), which enables the submolecular resolution of the involved nanostructures⁴ and the detection of multilevel interactions.^{7,8} Recent years have witnessed the great success of hierarchical assembly on a surface and at a liquid-solid interface by regulation of different levels of non-covalent interactions between the elementary components, mainly involving: (i) hydrogen bonds and/or van der Waals interactions^{5–7,9–12} among multiple or single molecular components; (ii) dominant metal-organic coordination bonds or sometimes with secondary hydrogen bonds^{8,13-15} between molecules and metal atoms. Such kinds of assembling processes are usually accompanied by varied factors such as surface coverages or ratios of the components. However, the hierarchical assembly

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without changing the surface coverages or ratios of the components, to the best of our knowledge, has been less investigated. Thus, it is interesting to explore a system to investigate other factors in a hierarchical assembly, for instance, the flexibility of coordination bonds, which may provide a fundamental understanding of the regulations of multilevel supramolecular structures.

In this work, 9-ethylguanine (shortened as 9eG) molecules, with two neighboring coordination binding sites O6 and N7 (*cf.* Scheme 1), are chosen as the molecular component; while transition metal Fe is chosen due to its coordination diversity



Scheme 1 Schematic illustration showing the hierarchical formation of supramolecular networks from 9eG molecules and Fe atoms. The 9eG molecule is depicted by a triangle (the guanine moiety) connected by an ellipse (the ethyl group), where the molecular chiralities are classified as L and R by light red and blue, respectively. The relationships among the corresponding motifs, clusters and networks are displayed by different geometry shapes.

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with both O6 and N7 sites.¹⁶ It may thus allow us to construct a hierarchical supramolecular coordination system depending on the flexible coordination bonds, instead of regulations on surface coverages or ratios of the components. From the interplay between high-resolution STM imaging/manipulations and density functional theory (DFT) calculations, we display the hierarchical formation of supramolecular networks on Au(111) via flexible coordination bonds. In the first level, after codeposition of 9eG and Fe on Au(111) held at room temperature (RT), homochiral islands are formed which are composed of homochiral G₄Fe₂ motifs as the elementary building units. Then, in the second level, further thermal treatment leads to the structural transformation into the novel porous networks composed of heterochiral G₄Fe₂ motifs. Interestingly, different kinds of heterochiral G₄Fe₂ motifs and clusters are found to be involved in such networks, and chirality transfer takes place in such two steps. The key to the hierarchical construction of the supramolecular networks is revealed to be the flexible coordination bonds (*i.e.*, the adaptability and versatility in the coordination modes) involved, which is also further confirmed by reversible STM manipulations. Furthermore, a control experiment also shows one more example of the hierarchical formation of supramolecular networks based on the flexible coordination bonds. These studies provide an interesting model system of hierarchical supramolecular assembly, which may shed light on the formation of designed supramolecular nanostructures in the related areas such as host-guest chemistry.

Results and discussion

As reported by our group,¹⁶ various metal–organic nanostructures composed of different elementary building units can be achieved by the deposition of Fe atoms on a 9eG-precovered Au(111) surface at RT in a well-controlled stepwise dosage or by codeposition at the corresponding ratios, where the coordination priority and diversity is revealed. In this study, we try to investigate the hierarchical assembly from 9eG molecules and Fe atoms on the basis of the flexible coordination bonds. After codeposition of 9eG molecules and Fe atoms (at a ratio of $\sim 2:1$) on Au(111) held at RT, as expected, we gain the formation of the homochiral networks constructed by homochiral G₄Fe₂ motifs as the elementary building units¹⁶ (Fig. 1a). From the high-resolution STM image of the individual motif and the superimposed DFT-optimized structural model (inset in Fig. 1a), we can clearly see that each 9eG molecule is resolved as a triangle and a bright ellipse which is assigned to the flat-lying guanine moiety and tilted ethyl group, respectively, as reported.¹⁶⁻¹⁹ Besides, each Fe atom coordinates with two O6 sites and one N7 site, and intra-motif NH···N and NH···O hydrogen bonds are simultaneously formed.¹⁶

Then further annealing the above sample at 400 K for 10 min results in the appearance of porous network structures as typically shown in Fig. 1b. After systematic analysis, we find that such porous network structures usually contain two kinds of cavities, *i.e.*, the bigger ones (highlighted by blue, shaped like the letter f) (Fig. 1b and c) and the remaining smaller ones





Fig. 1 Hierarchical formation of porous network structures on Au(111). (a) Large-scale STM image showing the formation of islands composed of homochiral G₄Fe₂ motifs as the first step. The upper right panel: the magnified elementary homochiral $G_4 \mbox{\rm Fe}_2$ motif superimposed with the DFT-optimized structural model. (b) Large-scale STM image showing the formation of new porous networks containing two kinds of cavities after further annealing. (c and d) Close-up STM images showing the typical network structures with different cavities. The hexagonal contours in (c) and the rhombic contours in (d) highlight the corresponding connecting clusters and motifs for construction of the networks, respectively. (e) High-resolution STM image showing details of each cluster which is made up of three identical heterochiral G4Fe2 motifs as depicted by the rhombuses. (f and g) Submolecularly resolved STM images and the corresponding DFT-optimized structural models of (f) the heterochiral G₄Fe₂ motif and (g) the constructed cluster. The molecular chiralities are indicated by L and R notations. The hydrogen bonds are depicted by dotted lines. Scanning conditions: It = 0.90 nA, Vt = 1200 mV. H: white; C: gray; N: blue; O: red; Fe: light purple.

(Fig. 1b and d). From the close-up STM image (Fig. 1c), we can identify that the f-shaped cavities are surrounded by big clusters as depicted by hexagonal contours. Each cluster is composed of twelve 9eG molecules with different chiralities. While, the other coexisting smaller cavities are usually surrounded by rhombus-like motifs as marked (Fig. 1d), and each motif is constructed by four 9eG molecules. A detailed comparison between the big cluster and the motif enables us to identify that the big cluster is exactly constructed by three such motifs with a three-fold symmetry (Fig. 1e).

From the submolecularly resolved STM image of the individual motif and cluster (left panels of Fig. 1f and g), it can be seen that within the motif there is only one 9eG molecule with different chirality (indicated by L notation) involved and that molecule is only positioned at the edge of the cluster (indicated by L notations). In order to gain atomic insights into such a structure, systematic DFT calculations have been performed and the energetically most favorable structural models for the motif and cluster are shown in the corresponding right panels, respectively. The motif is constructed by four 9eG molecules coordinating with two Fe atoms, in which one Fe atom interacts with three O6 sites and the other one interacts with one O6 site and one N7 site. Simultaneously, intermolecular NH···O and NH···N hydrogen bonds stabilize the motif. Then, three such motifs bind together via inter-motif NH···N hydrogen bonds and van der Waals interactions, forming a big cluster. Such a big cluster usually diffuses as a whole entity (Fig. S1, ESI⁺) indicating the relative stability. Based on the elementary heterochiral G_4Fe_2 motifs, porous networks are further constructed with two kinds of cavities as mentioned above (also see Fig. S2, ESI⁺). From the comparison between the two typical networks (Fig. S3, ESI⁺), we can see the similar connecting motifs and clusters, where the only difference exits in the adsorption directions of one motif leading to the different secondary intermotif interactions and then different patterns, similar to the situation of the reported literature on hierarchical self-assembly.⁶ Such kinds of networks are stable below 520 K until higher temperature destroys them.

In order to further confirm the constitution of the heterochiral G_4Fe_2 motif, precise STM manipulations have been performed on the individual motif in the network (Fig. 2). After disturbing the circled 9eG molecule (with L chirality) within the motif by the STM tip, we can observe that it can be converted to the one with the opposite chirality (R), resulting in the transformation into the homochiral G_4Fe_2 motif (Fig. 2a and b). Then the molecule can also be converted back after another manipulation (Fig. 2b and c). Thus, the reversible structural transformation between heterochiral and homochiral G_4Fe_2



Fig. 2 Continuous STM images showing the reversible structural transformations from (a) the heterochiral G_4Fe_2 motif to (b) the homochiral G_4Fe_2 one and then back to (c) the heterochiral one by STM manipulations. Scanning conditions: $I_t = 1.00$ nA, $V_t = 1200$ mV. (d) The corresponding DFT-optimized structural models in the structural transformation process.

motifs can be successfully achieved, which undoubtedly verifies the composition of the heterochiral G₄Fe₂ motif (the same as the homochiral one). That means there is no change in the ratios of the components (9eG molecules and Fe atoms). From the corresponding DFT-optimized structural models (Fig. 2d), it can also be seen that at first the target 9eG molecule only coordinates with the left Fe atom by the O6 site; and then after chirality transfer the N7 and O6 sites are involved in the coordination with the two Fe atoms, respectively; additional hydrogen bonds are formed at the same time. Thus, the coordination modes vary with the engagement of different interacting atoms and angles, from three-fold (with three O6 sites) and two-fold (with one O6 and one N7 site) to both three-fold (with one N7 and two O6 sites), respectively. Then the reversed process is also feasible. Such a reversible process demonstrates the flexibility of the coordination bonds, which is the adaptability and versatility in the coordination modes (such as different interacting atoms, angles, and coordination folds involved with the reversed chirality of the 9eG molecules).

Also, it deserves noting that a large number of literature studies concerning the coordinative flexibility have been reported hitherto, mainly focusing on the lanthanide-directed coordination.^{20–24} While, other transition metal induced coordinative flexibility is usually expressed with the influence of conformational freedom of the organic molecules.^{25–28} For this system, the guanine moiety remains rigid. Thus, the flexibility of the coordination bonds should be the main reason for the hierarchical formation of the porous networks (constructed by heterochiral G_4Fe_2 motifs) from the first-step islands (constructed by homochiral G_4Fe_2 ones).

Despite the well-known intrinsic reversibility of coordination bonds, systematic studies demonstrating the adaptability and versatility in the coordination modes (*i.e.*, the flexibility of the coordination bonds we mentioned) at the constant ratio of the components are still limited. That is one point that, from our perspective, is different from other coordination systems.

Interestingly, we can also see some other motifs involved in the porous networks, which are a little bit different from the above mentioned heterochiral G_4Fe_2 one, for instance, the ones marked by blue and green rhombuses (Fig. 3a). From the highresolution STM images of these motifs (top row of Fig. 3b), we can observe the difference between the dominant heterochiral G_4Fe_2 one (left panel) and the other two (middle and right panels). In the middle motif marked in blue, there are two 9eG molecules with L chiralities positioned on the one side; while, in the right one marked in green, there are also two 9eG molecules with L chiralities yet diagonally positioned.

From the corresponding DFT-optimized structural models (bottom row of Fig. 3b), it can be seen that the binding mode of the blue one is similar to the dominantly existing one, in which one Fe atom coordinates with three O6 sites and the other Fe atom coordinates with one O6 and one N7 site, and NH···O and NH···N hydrogen bonds stabilize the motif as well. The green one, however, is distinct from these two, in which each Fe atom only coordinates with two N7 sites and four-fold NH···O hydrogen bonds are formed at the center of the motif. Note that the



Fig. 3 Diversity of the motifs and clusters. (a) STM image showing the coexistence of the other two motifs in the networks. (b) High-resolution STM images and the corresponding DFT-optimized structural models showing the comparisons among the three coexisting motifs. The left panel: heterochiral G_4Fe_2 one as mentioned above; middle and right panels: the ones marked by blue and green rhombuses in (a), respectively. The molecular chiralities are indicated by L and R notations. (c) STM image showing the coexistence of the dominant big cluster (labelled as A cluster) and another kind of cluster (labelled as the B cluster, in which one motif with different chiralities is involved as marked by blue rhombuses). (d) High-resolution STM images of the two big clusters (A and B) superimposed with the DFT-optimized structural models. Scanning conditions: $I_t = 1.00$ nA, $V_t = 1200$ mV.

energies of these three motifs are similar, which results in their coexistence in the networks and may explain the origin of the flexible coordination bonds. Similar to the situation of these motifs, another kind of big cluster with the involvement of one blue motif has also been found (labelled as B cluster) coexisting with the dominant A cluster (Fig. 3c). In comparison with the A cluster (Fig. 3d), the B cluster has one 9eG molecule flipped at the edge, which does not influence the remaining part. Note that a big cluster with the involvement of the green motif has

not been found, as the centrally located flipped 9eG molecule (with L chirality) may result in the steric hindrance. Thus, the diversity of such coexisting motifs and clusters also demonstrates the flexibility of the coordination bonds involved.

A control experiment has also been performed to demonstrate the versatility of the flexible coordination bonds in the hierarchical formation of another supramolecular structure. After codeposition of 9eG molecules and Fe atoms on Au(111) (held at RT) at a ratio of a little bit less than 2:1, we gain the



Fig. 4 Control experiment showing the hierarchical formation of another supramolecular network at a different 9eG/Fe ratio. (a) STM image showing the coexistence of islands and chains composed of heterochiral G_3Fe_1 motifs and homochiral G_4Fe_2 motifs, respectively, as the first step. The upper right panel: the STM image of the individual heterochiral G_3Fe_1 motif superimposed with the DFT-optimized structural model. (b) The STM image showing the appearance of parallelogram-shaped networks after thermal treatment. (c) The close-up STM image showing the composition of such a network in which heterochiral G_4Fe_2 motifs and heterochiral G_3Fe_1 ones are involved as depicted by white rhombuses and trapezoids (red and blue represents two chiralities), respectively. Scanning conditions: $I_t = 1.00$ nA, $V_t = 1200$ mV.

coexistence of islands (composed of heterochiral G₃Fe₁ motifs) and chains (composed of homochiral G4Fe2 motifs) (Fig. 4a) as reported.16 The high-resolution STM image of the individual heterochiral G₃Fe₁ motif is superimposed with the DFT-optimized structural model¹⁶ as shown in the upper right panel. Interestingly, annealing such a sample at ~ 400 K for 10 minutes results in the appearance of parallelogram-shaped networks as typically shown in Fig. 4b. The high-resolution STM image (Fig. 4c) shows the details that such a network is constructed by the initial heterochiral G₃Fe₁ motifs (depicted by the trapezoid-like contours with different chiralities) and heterochiral G_4Fe_2 motifs (depicted by white rhombuses). Note that after annealing the initial homochiral G₄Fe₂ motifs disappear and instead they convert to the heterochiral ones, in good accordance with the case shown in Fig. 1. The tentative structural model for such a complex structure can be seen in Fig. S4 (ESI⁺). In this way, the control experiment also presents another example of hierarchical assembly by the use of the flexible coordination bonds involved.

Conclusions

In conclusion, by combination of STM imaging/manipulation and DFT calculations we have investigated the hierarchical formation of porous supramolecular networks based on the flexible coordination bonds involved. In the first step, homochiral islands composed of homochiral G_4Fe_2 motifs are formed, and then in the second step, thermal treatment results in the transformation into the porous networks composed of heterochiral G4Fe2 motifs with the ratio of the components being constant. STM manipulations demonstrate the reversibility of the structural transformation between homochiral and heterochiral G₄Fe₂ motifs. Besides, the coexistence of some other heterochiral G₄Fe₂ motifs and clusters also shows the flexibility of the coordination bonds. What is more, another example of hierarchical supramolecular assembly has been achieved as well. Our findings may provide a fundamental understanding of the design and regulation of multilevel metal-organic supramolecular structures.

Conflicts of interest

There are no conflicts to declare.

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