

# Multilevel Supramolecular Architectures Self-Assembled on Metal Surfaces

Dingyong Zhong,<sup>†</sup> Katrin Wedeking,<sup>‡</sup> Tobias Blömker,<sup>‡</sup> Gerhard Erker,<sup>‡</sup> Harald Fuchs,<sup>†,§</sup> and Lifeng Chi<sup>†,\*</sup>

<sup>†</sup>Physikalisches Institut and Center for Nanotechnology (CeNTech), Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany, <sup>‡</sup>Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, 48149 Münster, Germany, and <sup>§</sup>Institut für Nanotechnologie, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany

Noncovalent interactions play an important role in nature, for example, in protein folding and supramolecular assembly. In the past decades, surface-supported supramolecular assembly based on noncovalent interactions, including hydrogen bonds, dipolar coupling, metal coordination, and van der Waals (vdW) interaction, has been intensively studied.<sup>1–15</sup> By carefully adjusting the intermolecular interactions, diverse supramolecular structures with considerable complexity, such as size-controlled aggregates,<sup>1</sup> nanowires,<sup>2</sup> honeycomb and square networks,<sup>3–6</sup> multilevel or hierarchical structure,<sup>7–10</sup> orientational superstructure,<sup>13</sup> and chiral systems,<sup>14,15</sup> were investigated. Although vdW interaction, which exhibits an indispensable effect on multilevel structures of biomolecules, is weak among noncovalent interactions, collective behavior of this weak interaction may result in unexpected phenomena.<sup>11,13,16</sup>

The assembly of molecules with hydrogen bonds or metal coordination is usually dominated by the relatively strong intermolecular interactions, while the oligoethylene-bridged diferrocenes [Fc-(CH<sub>2</sub>)<sub>n</sub>-Fc, Fc = ferrocenyl, *n* = 12, 14, 18] (diFc-*n*) investigated here exhibit only weak vdW interactions between the molecules, which are also only physisorbed on metal surfaces such as Cu, Ag, and Au.<sup>17–20</sup> The comparable strength of intermolecular and molecule–substrate interactions makes the assembled molecular structure sensitive to the balance of these interactions and may induce certain complicated structures. Here we report the controllability of the complexity of diferrocene supramolecular assembly on metal surfaces by adjusting the mismatch between the molecular packing

**ABSTRACT** We report the controllability of the complexity of surface-supported supramolecular assembly on metal surfaces. By introducing mismatch between the molecular packing and the surface atomic periodicity in the systems with comparable strength of intermolecular and molecule–substrate interactions, a homomolecular assembly exhibiting two-dimensional multilevel structures up to quaternary level was observed. In such a multiperiodicity modulated system, neither the intermolecular nor molecule–substrate interactions solely dominate the assembly, resulting in complicated multilevel structures. We further demonstrated that the multilevel assemblies can serve as templates for site-selective adsorption of guest molecules.

**KEYWORDS:** self-assembly · STM · noncovalent interactions · multilevel · template

and the surface atomic periodicity. By using scanning tunneling microscopy (STM), we observed a homomolecular assembly exhibiting two-dimensional multilevel structures up to quaternary level, which can serve as templates for site-selective adsorption of guest molecules. The formation mechanism of the multilevel structures is discussed.

## RESULTS AND DISCUSSION

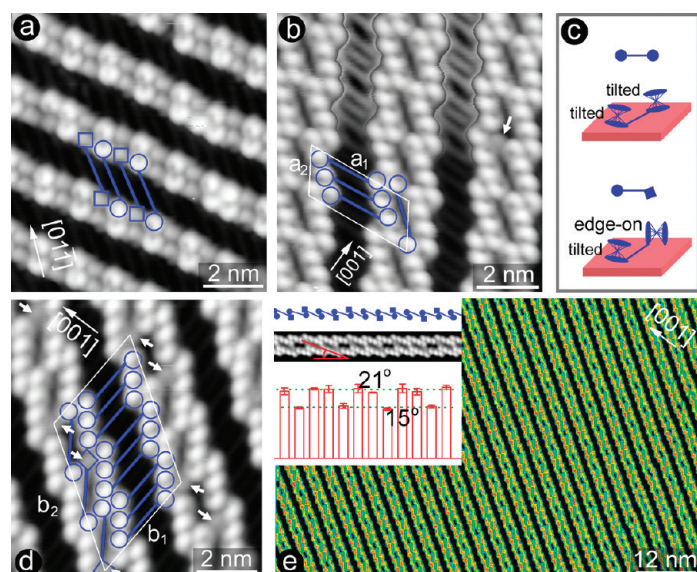
In our experiments, diferrocene molecules were deposited onto single-crystalline metal surfaces at room temperature under ultrahigh vacuum conditions. The as-prepared samples were then analyzed by STM at a temperature of 78 K. The assembly of diferrocene molecules depends sensitively on experimental parameters including the chain length, substrate, growth temperature, and coverage. The complexity of the surface-supported assembly can be well-controlled by adjusting the above parameters. On Cu(111) surfaces, diFc-14 molecules form linearly stacked columns, as shown in Figure 1a. The bright protrusions represent Fc groups, while the oligoethylene chains are located in the dark grooves. There are two types of configurations of Fc groups with respect to the substrate

\*Address correspondence to chi@uni-muenster.de.

Received for review January 20, 2010 and accepted February 23, 2010.

Published online March 4, 2010. 10.1021/nn100116y

© 2010 American Chemical Society



**Figure 1.** Controlling the complexity of surface-supported diFc-14 assembly. (a) On Cu(111) (1 V, 50 pA). The molecules are stacked in parallel with alternative tilted and edge-on Fc end groups. (b) On Cu(110) with monolayer coverage (−1 V, 100 pA). The unit cell (parallelogram) consists of three stacked molecules and one intercalated molecule. Most of the Fc groups are oriented with the five-fold axis 10–20° tilted with respect to the surface normal, while the arrowed one is edge-on with its axis parallel to the surface. The contrast of the upper part is enhanced in order to show the oligoethylene chains. (c) Schematic diagram of the two possible configurations of diFc-14 adsorbed on Cu(110). Top, both Fc groups tilted; bottom, one tilted and the other edge-on. (d) On Cu(110) with submonolayer coverage (−1 V, 10 pA). The unit cell is three times greater than that of the monolayer coverage structure. (e) Large-scale image of the submonolayer structure on Cu(110). Inset, periodic modulation of the stacking direction and the orientation of intercalated molecules. Top, the intercalated molecular chains (circles denoting tilted Fc groups and squares edge-on Fc groups); middle, a stripe picked up along  $\mathbf{b}_2$  direction; bottom, the stacking angle with respect to  $\mathbf{b}_2$ .

surface: The brighter protrusions are tilted Fc groups with their five-fold axis 10–20° off the surface normal, exhibiting an asymmetric ring-like feature of cyclopentadienyl rings,<sup>22</sup> and the gray protrusions without a ring-like feature showing an apparent height about 0.7 Å lower than the bright ones are the edge-on Fc groups with their main symmetry axis parallel to the surface. The tilted and edge-on Fc groups tend to be arranged alternately.

When diFc-14 molecules were deposited on a Cu(110) surface at room temperature with monolayer coverage, a more complicated structure was observed, as shown in Figure 1b. The unit cell of the ordered structure consists of four molecules, three of them stacked nearly along the  $[1 \ -1 \ \mp 1]$  direction with the long axis almost parallel to the  $[1 \ -1 \ 0]$  direction of the Cu(110) surface, and the fourth is intercalated between two columns of stacked molecules with the long axis in the stacking direction. The orientation of the structure relative to the Cu(110) surface is given by  $(\mathbf{a}_1|\mathbf{a}_2) = (\mp 1, 14^2/3|\pm 4, 3^2/3)$  ( $\mathbf{a}_{\text{Cu}[001]}|\mathbf{a}_{\text{Cu}[1-10]}$ ), which exhibits a point-on-line coincidence to the substrate.<sup>21</sup> The average area occupied per molecule is 1.44 nm<sup>2</sup>, slightly greater than the value of the  $(-2 \ 1 \ 1)$  plane of the crystalline struc-

ture of diFc-14 (1.38 nm<sup>2</sup>).<sup>17,18</sup> The zigzag feature along the direction of the shorter base vector  $\mathbf{a}_2$  is a result of repeated location offsets every three stacked molecules. Similar periodic offset of molecular location has been previously observed on the assembly of alkylcyclobiphenyl molecules on graphite surfaces.<sup>23,24</sup> Most of the Fc groups (bright protrusions) are tilted, while some of the intercalated molecules have one of the two Fc groups edge-on (small arrow). In Figure 1c, two possible configurations of diFc-14 adsorbed on Cu(110) (*i.e.*, with both Fc groups tilted or with one tilted and the other edge-on) are illustrated.

By reducing the coverage to a submonolayer (0.5–0.8 ML), the amount of edge-on Fc groups increases and they tend to be organized in a regular pattern (Figure 1d,e). Although at first glance the arrangement of the molecules is similar to those at monolayer coverage, one can find that there is an additional larger periodicity along  $\mathbf{a}_2$ . The orientation of the structure relative to the Cu(110) surface is given by  $(\mathbf{b}_1|\mathbf{b}_2) = (\mp 1, 15|\pm 12, 11)$  ( $\mathbf{a}_{\text{Cu}[001]}|\mathbf{a}_{\text{Cu}[1-10]}$ ), which is about three times larger than  $(\mathbf{a}_1|\mathbf{a}_2)$ . In a repeated unit, the intercalated molecules have their Fc groups oriented tilted and edge-on, both tilted, edge-on and tilted, in sequence. A difference in stacking direction of *ca.* 6° exists between the molecular columns in the surrounding of both tilted intercalated molecules and those in the surrounding of intercalated molecules with one Fc group tilted (inset of Figure 1e).

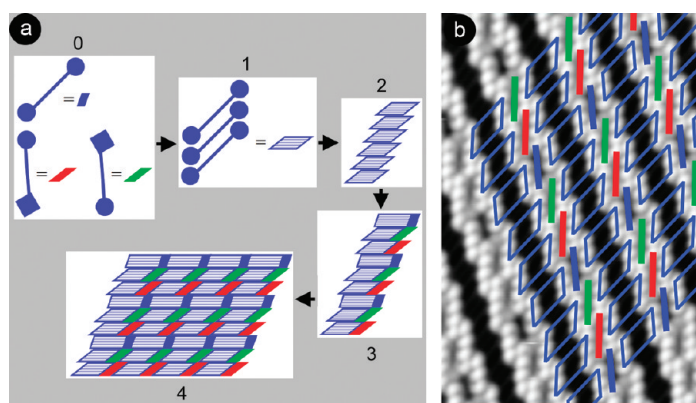
We have systematically investigated the assembly of diferrocene molecules with variable chain lengths ( $n = 12, 14,$  and  $18$ ) on Au(111), Ag(110), and Cu(110), as well as diFc-14 on Cu(110) at elevated temperatures (70–80 °C) (see Supporting Information). Briefly, the assembly on Au(111) is similar to that on Cu(111), while on Ag(110) and Cu(110) surfaces, all surface-supported architectures exhibit stacked molecular columns and intercalated molecular chains similar to diFc-14 assembled on Cu(110), and the molecules are almost stacked nearly along the  $[1 \ -1 \ \mp 1]$  direction of the (110) surfaces with intermolecular distance equivalent to the substrate periodicity in this direction. The general assembly rule is that the intercalated molecules are arranged such that the projection of the molecular chains has an integer multiple of the substrate periodicity in the  $[001]$  direction.

The results presented here indicate the hierarchical structure of the supramolecular assembly with multiple levels, as it is illustrated in Figure 2a. The diFc- $n$  molecules are the only building element of the multi-level architectures. When the molecules are adsorbed on a surface with weak or no surface potential modulation, the molecules are linearly stacked forming the primary structure (1). With the modulation of the substrate, the stacked molecules are repeatedly shifted in order to match the substrate potential, resulting in the secondary structure (2). Due to the interplay between

the intercalated and the stacked molecules, the location and orientation of the molecules are further reorganized and the tertiary structure (3) with a greater periodicity is formed. The molecules with the tertiary structure tile over the whole surface, and a two-dimensional quaternary structure (4) is constructed.

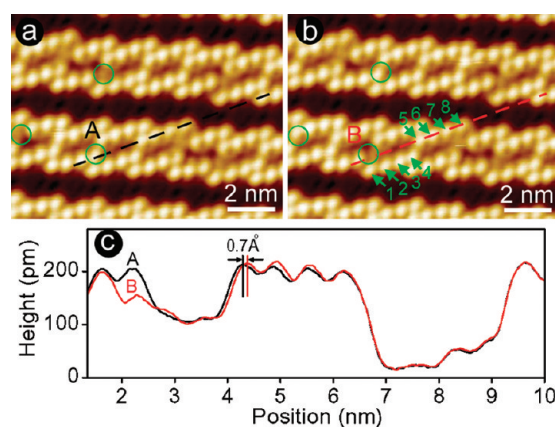
The multilevel supramolecular assembly is attributed to the interplay between the molecules and the surface potential of the substrate. The diFc-*n* molecules adsorbed on metal surfaces prefer the orientation with their oligoethylene chains parallel to the surface to strengthen the molecule–substrate interaction. On a substrate with a “flat” surface potential, such as Au(111) and Cu(111),<sup>25</sup> the molecules adopt the simple stacking configuration (primary structure). The ideal Fc–Fc stacking distance without modulation from the substrate is 6.8 Å, as in the (−2 1 1) plane of the molecular crystal.<sup>17</sup> On a substrate with large local variation of the surface potential, the stacking of the molecules will be modulated in order to match the surface lattice. The diFc-*n* molecules are preferentially stacked along the [1 −1  $\bar{1}$ ] direction of the Cu(110) and Ag(110) surfaces, and the oligoethylene chains are constrained roughly along the [1 −1 0] direction, owing to the preferential orientation of oligoethylene chains in the [1 −1 0] direction of the Cu(110) surface.<sup>26</sup> Our molecular mechanics simulations also indicate that for diFc-14 molecules the orientation with the long axis in the [1 −1 0] direction is energetically favorable (see Supporting Information). The periodicity of the Cu(110) surface in the [1 −1  $\bar{1}$ ] direction, 6.3 Å, is slightly smaller than the periodicity of the ideally stacked molecules. As a result, considerable strain exists in the linearly stacked molecules if the periodicity of the substrate is strictly followed. As a consequence, the stacked molecules will perform repeated offset in order to release the mismatch-induced strain. The offset takes place per three molecules in the case of diFc-14 adsorbed on a Cu(110) surface, while it is four molecules on a Ag(110) surface,<sup>18</sup> which has a periodicity along the [1 −1  $\bar{1}$ ] direction of 7.1 Å.

Similar to our previous work,<sup>27</sup> the supramolecular structure of diFc-14 on Cu(110) at submonolayer coverage is an extended phase with its base vector  $\mathbf{b}_1$  2% longer than the compressed phase at monolayer coverage. The relatively larger spacing between two columns of stacked molecules makes the intercalated molecules free to some extent to take a more energetically favorable configuration with the environment. Owing to the flexibility of oligoethylene chains,<sup>28</sup> the Fc groups are free to rotate around the axis of the chains to adopt an optimal orientation. As evidence of the flexibility of the intercalated molecules, we have observed that in the less regular regions some of the Fc groups of the intercalated molecules stochastically switch between the tilted and edge-on configurations. Nevertheless, the Fc groups in the ordered quaternary structure are rather

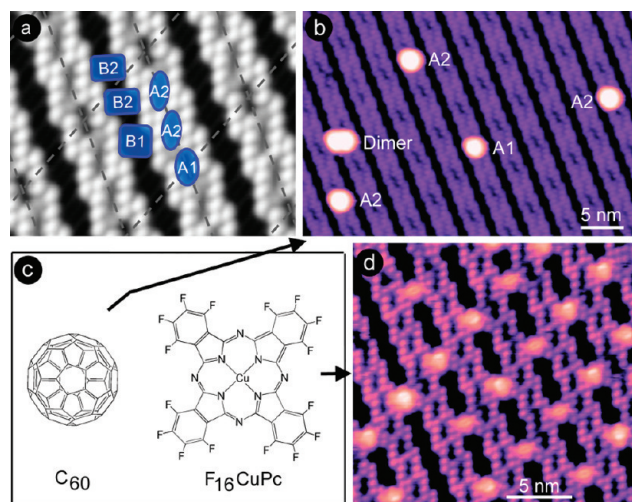


**Figure 2.** Two-dimensional multilevel supramolecular structures. (a) Schematic diagrams showing the levels of the supramolecular structure. Primary structure: linearly stacked molecular columns. Secondary structure: repeated offsets of stacked molecules. Tertiary structure: modulation of the orientation of intercalated molecules and the stacking direction of stacked molecules with a larger periodicity. Quaternary structure: tiling of stacked molecular columns and intercalated molecular chains over the surface. (b) Schematic drawing of the multilevel structures overlaid on the STM image of diFc-14 assembled on Cu(110) at submonolayer coverage.

stable and hardly perform a switching process at 78 K. Figure 3a,b shows two STM images sequentially scanned at the same region with irregular quaternary structure. The circles mark the Fc groups, which change their orientation during the scanning process (a video of STM images indicating the switching is available in Supporting Information). The switching process takes place more likely on the Fc groups of the intercalated molecules that have different orientation compared with their neighbors intercalated in the adjacent columns. Then, the molecules in the surrounding of the orientation-switched Fc groups change their location accordingly. For example, the Fc groups arrowed as



**Figure 3.** Stochastic orientation switching of the Fc groups of intercalated diFc-14 molecules in a region with irregular tertiary structure. (a,b) STM images sequentially scanned at the same region (−1 V, 10 pA). The Fc groups that switch their orientations are marked by circles. The Fc groups labeled by 1–8 show slight displacement due to the switch of the nearby circled Fc group. (c) Height profiles across the dashed lines in panels a and b, showing a 0.7 Å displacement of the Fc group 5, which belongs to the same molecule of the switched Fc group.



**Figure 4.** Site-selective adsorption of guest molecules on the multilevel structure of diFc-14 on Cu(110) at submonolayer coverage. (a) Possible adsorption sites. (b) Adsorption of  $C_{60}$  on the multilevel structure, preferring A-type cavities with the adsorption probability at A2-type cavities about 2–4 times greater than that at A1-type cavities (2 V, 2 pA). (c) Molecular structures of  $C_{60}$  and  $F_{16}CuPc$ . (d) Adsorption of  $F_{16}CuPc$  on the multilevel structure (–1.5 V, 5 pA).  $F_{16}CuPc$  molecules prefer adsorbing at B-type sites and form ordered structures following the tertiary periodicity of the underneath template.

1–8 have a tiny change on their locations due to the tilted to edge-on switch of the Fc group denoted by A in Figure 3b. Figure 3c shows the height profile along the long axis of the intercalated molecule. It is clearly seen that there is a 0.7 Å displacement of the Fc group marked by 5, which is part of the same diFc-14 molecule as the switched Fc group. Thus, the location and orientation of intercalated molecules and stacked molecules are correlated.

According to the above observation, the molecules with one Fc group tilted and the other edge-on occupy a relatively larger space and are closer to the neighboring stacked molecules. As a result, the edge-on and the tilted Fc groups have a face-to-edge configuration. Such configuration is also adopted in the molecular crystals of ferrocene and its derivatives, and it was also found to be an energetically favorable configuration by density functional theory calculations.<sup>17,29,30</sup> The stacked molecules are further relaxed in order to fit the orientation of the intercalated molecules. As for the compressed structure, no tertiary structure is found because the intercalated molecules in the monolayer coverage assembly are confined in a limited space between two columns of stacked molecules and have no additional freedom to adopt a face-to-edge configuration.

The surface-supported multilevel supramolecular assembly can serve as a template for site-specific physical and chemical reactions. Here we demonstrated the site-selective adsorption of guest molecules on the multilevel architecture of diFc-14 on Cu(110). Here we refer to the molecules in the template as host molecules

and the latter adsorbed molecules as guest molecules without taking chemical sense into consideration. Due to the periodic arrangement of the tilted and edge-on Fc groups of the intercalated molecules and the modulation of the stacking angles, there are four possible adsorption sites: the cavities of intercalated molecules with both Fc groups tilted (A1-type) or with one Fc group tilted (A2-type), and the oligoethylene chain grooves (B1-type and B2-type) (Figure 4a). Fullerene ( $C_{60}$ ) molecules were deposited at a temperature of 150–250 K with low coverage (0.005–0.01 molecules/nm<sup>2</sup>). Higher  $C_{60}$  coverage or deposition temperature will result in the aggregation of  $C_{60}$  molecules and disordering of the underneath diferrocene template. At low coverage, the spherical fullerene molecules prefer adsorbing at the A-type cavities. More importantly, we found that the adsorption probability at A2-type cavities is about 2–4 times higher than that at A1-type cavities. The result implies that the tiny difference between A1-type and A2-type cavities owing to the tertiary structure does affect the adsorption behavior of guest molecules. We attribute the above site-selective adsorption phenomena to the geometrical effect, analogous to a previous report on the site-selective fabrication of two-dimensional fullerene arrays by using a supramolecular template.<sup>31</sup> Due to the stacking direction difference, the A1-type cavities with diFc-14 having both Fc groups tilted is slightly larger than the A2-type cavities, which may benefit the contact and enhance the vdW interactions between fullerene and underlying Fc groups.

This template effect of the tertiary structure is even more pronounced in the case of a planar molecule  $F_{16}CuPc$  (fluorinated copper phthalocyanine).  $F_{16}CuPc$  molecules, which were deposited at about 150–250 K onto the multilevel diferrocene assembly followed annealing to room temperature, prefer adsorbing at B-type sites. Ordered arrangement of  $F_{16}CuPc$  molecules following the tertiary periodicity of the underneath template was observed (Figure 4d). From the distance of the equivalent positions, we can deduce that B1 is the preferred position. It is interesting to note that no difference between B1 and B2 can be observed after the absorption of  $F_{16}CuPc$ , which hints at the reorientation of the Fc groups. Our above results imply that the template effect and the preferential adsorption sites are dependent on the choice of guest molecules, partially owing to the tininess of difference within the tertiary structure. In principle, it is possible to obtain ordered arrays of guest molecules over large scales by carefully choosing appropriate guest molecules and adjusting the kinetic parameters such as deposition temperature, which should be high enough to activate the surface diffusion of guest molecules and low enough to keep the supramolecular template stable.

## CONCLUSION

Complicated structural and phase behaviors are commonly observed in multiperiodicity modulated systems with more than one set of noncovalent interactions that have comparable strength. The relation of the stacked and intercalated molecules in our system is analogous to the host–guest system of inclusion compounds.<sup>32</sup> Because the periodicities of the columns of stacked molecules and the chains of intercalated molecules as well as the periodicity of the substrate surface in the stacking direction are mismatched, without a predominant interaction in the system, the assembly of the molecules that follow any simple periodicity is not energetically favorable. The deformability of the organic molecules

and the nonrigid feature of the vdW interactions make it possible to choose a more complicated arrangement of the molecules in order to reduce the total energy of the system. We believe the study of the two-dimensional multilevel architecture reported here will help to understand the effects of collective or cooperative behavior of noncovalent interactions in nature. The use of the supramolecular structure as a template to direct the adsorption/reaction of other molecules opens the possibility to arrange the molecules in an ordered but not densely packed manner. The concept of multilevel structures based on noncovalent interactions may be extended to three dimensions to build hierarchical structures with novel physical and chemical properties.<sup>33</sup>

## METHODS

Diferrocenes were synthesized as reported in ref 17, and F<sub>16</sub>CuPc and C<sub>60</sub> were purchased from Sigma-Aldrich. The surfaces of single-crystalline metallic substrates were treated by repeated sputtering–annealing processes for several times under ultrahigh vacuum conditions (base vacuum, ~10<sup>-8</sup> Pa). Organic materials loaded in quartz crucibles were thermally deposited on the substrates. The as-prepared samples were then transferred to the Omicron LT-STM stage, which was precooled to 78 K, for STM measurements. The substrates were kept at room temperature or elevated temperatures (substrates were heated by a tungsten filament) for diferrocene deposition, while F<sub>16</sub>CuPc and C<sub>60</sub> were deposited on diferrocene prepatterned surfaces at a temperature lower than room temperature (the deposition process was conducted immediately after the substrates were transferred from the STM stage) followed by annealing to a temperature close to room temperature.

**Acknowledgment.** This work was financially supported by the Deutsche Forschungsgemeinschaft through SFB 424 and TRR 61.

**Supporting Information Available:** Assembly of diFc-14 on Au(111); assembly of diFc-14 on Cu(110) at elevated temperature; assembly of diFc-*n* (*n* = 12, 18) on Cu(110); assembly of diFc-*n* (*n* = 12, 14, 18) on Ag(110); molecular mechanics simulation of diFc-14 adsorbed on Cu(110); and stochastic switching of Fc orientation in less regular region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. Selective Assembly on a Surface of Supramolecular Aggregates with Controlled Size and Shape. *Nature* **2001**, *413*, 619–621.
- Barth, J. V.; Weckesser, J.; Cai, C.; Günter, P.; Bürgi, L.; Jeandupeux, O.; Kern, K. Building Supramolecular Nanostructures at Surfaces by Hydrogen Bonding. *Angew. Chem., Int. Ed.* **2000**, *39*, 1230–1234.
- Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. Controlling Molecular Deposition and Layer Structure with Supramolecular Surface Assemblies. *Nature* **2003**, *424*, 1029–1031.
- Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. Steering Molecular Organization and Host–Guest Interactions Using Two-Dimensional Nanoporous Coordination Systems. *Nat. Mater.* **2004**, *3*, 229–233.
- Schlickum, U.; Decker, R.; Klappenberger, F.; Zoppellaro, G.; Klyatskaya, S.; Ruben, M.; Silanes, I.; Arnau, A.; Kern, K.; Brune, H.; Barth, J. V. Metal–Organic Honeycomb Nanomeshes with Tunable Cavity Size. *Nano. Lett.* **2007**, *7*, 3813–3817.
- Pawin, G.; Wong, K. L.; Kwon, K.-Y.; Bartels, L. A. Homomolecular Porous Network at a Cu(111) Surface. *Science* **2006**, *313*, 961–962.
- Vonau, F.; Suhr, D.; Aubel, D.; Bouteiller, L.; Reiter, G.; Simon, L. Evolution of Multilevel Order in Supramolecular Assemblies. *Phys. Rev. Lett.* **2005**, *94*, 066103.
- Spillmann, H.; Dmitriev, A.; Lin, N.; Messina, P.; Barth, J. V.; Kern, K. Hierarchical Assembly of Two-Dimensional Homochiral Nanocavity Arrays. *J. Am. Chem. Soc.* **2003**, *125*, 10725–10728.
- Yang, Y.; Wang, C. Hierarchical Construction of Self-Assembled Low-Dimensional Molecular Architectures Observed by Using Scanning Tunneling Microscopy. *Chem. Soc. Rev.* **2009**, *38*, 2576–2589.
- Lei, S.; Surin, M.; Tahara, K.; Adisojoso, J.; Lazzaroni, R.; Tobe, Y.; De Feyter, S. Programmable Hierarchical Three-Component 2D Assembly at a Liquid–Solid Interface: Recognition, Selection, and Transformation. *Nano Lett.* **2008**, *8*, 2541–2546.
- Pivetta, M.; Blüm, M.-C.; Patthey, F.; Schneider, W.-D. Two-Dimensional Tiling by Rubrene Molecules Self-Assembled in Supramolecular Pentagons, Hexagons, and Heptagons on a Au(111) Surface. *Angew. Chem., Int. Ed.* **2008**, *47*, 1076–1079.
- Ye, Y.; Sun, W.; Wang, Y.; Shao, X.; Xu, X.; Cheng, F.; Li, J.; Wu, K. A Unified Model: Self-Assembly of Trimesic Acid on Gold. *J. Phys. Chem. C* **2007**, *111*, 10138–10141.
- Schull, G.; Berndt, R. Orientationally Ordered (7 × 7) Superstructure of C<sub>60</sub> on Au(111). *Phys. Rev. Lett.* **2007**, *99*, 226105.
- Fasel, R.; Parschau, M.; Ernst, K.-H. Chirality Transfer from Single Molecules into Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2003**, *42*, 5178–5181.
- Fasel, R.; Parschau, M.; Ernst, K.-H. Amplification of Chirality in Two-Dimensional Enantiomorphous Lattices. *Nature* **2006**, *439*, 449–452.
- Sheiko, S. S.; Sun, F. C.; Randall, A.; Shirvanyants, D.; Rubinstein, M.; Lee, H.; Matyjaszewski, K. Adsorption-Induced Scission of Carbon–Carbon Bonds. *Nature* **2006**, *440*, 191–194.
- Wedeking, K.; Mu, Z.; Kehr, G.; Sierra, J. C.; Lichtenfeld, C. M.; Grimme, S.; Erker, G.; Fröhlich, R.; Chi, L.; Wang, W.; Zhong, D.; Fuchs, H. Oligoethylene Chains Terminated by Ferrocenyl End Groups: Synthesis, Structural Properties, and Two-Dimensional Self-Assembly on Surfaces. *Chem.—Eur. J.* **2006**, *12*, 1618–1628.
- Zhong, D. Y.; Wang, W. C.; Dou, R. F.; Wedeking, K.; Erker,

- G.; Chi, L. F.; Fuchs, H. Oligoethylene-Bridged Diferrocene on Ag(110): Monolayer Structures and Adsorbate-Induced Faceting. *Phys. Rev. B* **2007**, *76*, 205428.
19. Dou, R. F.; Zhong, D. Y.; Wang, W. C.; Wedeking, K.; Erker, G.; Chi, L.; Fuchs, H. Structures and Stability of Ferrocene Derivative Monolayers on Ag(110): Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **2007**, *111*, 12139–12144.
20. Zhong, D. Y.; Franke, J.; Blömker, T.; Erker, G.; Chi, L. F.; Fuchs, H. Manipulating Surface Diffusion Ability of Single Molecules by Scanning Tunneling Microscopy. *Nano Lett.* **2009**, *9*, 132–136.
21. Braun, K.-F.; Iancu, V.; Pertaya, N.; Rieder, K.-H.; Hla, S.-W. Decompositional Incommensurate Growth of Ferrocene Molecules on a Au(111) Surface. *Phys. Rev. Lett.* **2006**, *96*, 246102.
22. Hooks, D. E.; Fritz, T.; Ward, M. D. Epitaxy and Molecular Organization on Solid Substrates. *Adv. Mater.* **2001**, *13*, 227–241.
23. Foster, J. S.; Frommer, J. E. Imaging of Liquid Crystals Using a Tunnelling Microscope. *Nature* **1988**, *333*, 542–545.
24. Smith, D. P. E.; Hörber, J. K. H.; Binnig, G.; Nejjoh, H. Structure, Registry and Imaging Mechanism of Alkylcyanobiphenyl Molecules by Tunnelling Microscopy. *Nature* **1990**, *344*, 641–644.
25. Hansen, L.; Stoltze, P.; Jacobsen, K. W.; Nørskov, J. K. Self-Diffusion on Copper Surfaces. *Phys. Rev. B* **1991**, *44*, 6523–6526.
26. Öström, H.; Triguero, L.; Nyberg, M.; Ogasawara, H.; Pettersson, L. G. M.; Nilsson, A. Bonding of Saturated Hydrocarbons to Metal Surfaces. *Phys. Rev. Lett.* **2003**, *91*, 046102.
27. Seidel, C.; Kopf, H.; Fuchs, H. Growth Process and Compressed Phase of DMe-DCNQI on Ag(110) in the Monolayer Regime Observed by LEED, XPS, and STM. *Phys. Rev. B* **1999**, *60*, 14341–14347.
28. Iancu, V.; Hla, S.-W. Realization of a Four-Step Molecular Switch in Scanning Tunneling Microscope Manipulation of Single Chlorophyll-a Molecules. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 13718–13721.
29. Braga, D.; Grepioni, F. Crystal Construction and Molecular Interplay in Solid Ferrocene, Nickelocene, and Ruthenocene. *Organometallics* **1992**, *11*, 711–718.
30. Maharaj, F.; McDonagh, A.; Scudder, M.; Craig, D.; Dance, I. Crystal Packing Principles for Ferrocenyl Groups Linked by Polyene Chains: Dimorphism of Fc-C<sub>4</sub>-Fc. *CrystEngComm* **2003**, *5*, 305–309.
31. Li, M.; Deng, K.; Lei, S.-B.; Yang, Y.-L.; Wang, T.-S.; Shen, Y.-T.; Wang, C.-R.; Zeng, Q.-D.; Wang, C. Site-Selective Fabrication of Two-Dimensional Fullerene Arrays by Using a Supramolecular Template at the Liquid–Solid Interface. *Angew. Chem., Int. Ed.* **2008**, *47*, 6717–6721.
32. Toudic, B.; Garcia, P.; Odin, C.; Rabiller, P.; Ecolivet, C.; Collet, E.; Bourges, P.; McIntyre, G. J.; Hollingsworth, M. D.; Breczewski, T. Hidden Degrees of Freedom in Aperiodic Materials. *Science* **2008**, *319*, 69–71.
33. Lakes, R. Materials with Structural Hierarchy. *Nature* **1993**, *361*, 511–515.