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From a Lamellar to Hexagonal Self-Assembly of Bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborin) Molecules: A *trans*-to-*cis*-Isomerization-Induced Structural Transition Studied with STM**

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Self-assembly or self-organization of molecules on solid surfaces is of ever increasing importance in chemistry and material science and plays an important role in the “bottom-up” strategy used in nanofabrication.^[1] With the development in preparing supramolecular assemblies and molecular nanostructures, the precise control of the structure of two-dimensional (2D) molecular assemblies attracts increasing attention.^[2] As a result of these studies, it is known that the common method to change the structure of a self-assembly is to modify the molecular chemical structure.^[3] Furthermore, the molecular ordering can be tuned to a certain extent by using different types of substrates^[4] and by employing different film-growth conditions.^[5] On the other hand, a promising approach to form a 2D adlayer is to exert external stimuli such as light irradiation, heating, chemical treatment, or electric and/or magnetic fields.^[6] Finally, it is possible to manipulate molecules and molecular structures on surfaces with an STM tip.^[7]

The well-established STM technique has been successfully used to study the structure of self-assembled monolayers (SAMs) and their ordering, molecular orientation, intermolecular reaction, and structural transformation.^[2–7] For example, the light-induced *cis/trans* isomerization of azobenzene derivatives has been intensively investigated by STM in the past.^[8] However, as the *trans*-to-*cis* isomerization does not occur in adlayers of azobenzene derivatives, the isomerization is typically initiated in solution, followed by the adsorption of the *cis* molecules on the substrate. Because the molecular assemblies of *cis* isomers of azobenzene adlayers are not stable, the *cis*-isomer domains disappear quickly and only *trans*-isomer domains are observed.^[8a,9] Recently, in situ light-induced *cis*-to-*trans* isomerization of stilbene on Ag/Ge(111)

surfaces was demonstrated.^[10] In this particular case, the *cis*-isomer domains formed spontaneously and simultaneously along with the *trans*-isomer domains from the gas phase. The *cis*-isomer domains are metastable and can be transformed to *trans*-isomer domains by brief exposure to 248-nm UV-light radiation. The attempt to induce the *cis*-to-*trans* isomerization by thermal annealing was unsuccessful.^[10] It is known that the isomerization on surfaces originates from the energetically unstable *cis* isomer and leads to the energetically stable *trans* isomer. To the best of our knowledge, there are no previous STM reports on thermally induced *cis*-to-*trans* isomerization on surface-adsorbed molecules. Although a few papers have described thermally induced changes in the morphology of adlayers of various molecules, no significant changes in the molecular structure were observed.^[6b,11]

Recently, we have synthesized a series of connected two-core dioxaborines (DOBs) that were substituted with dodecyloxy groups. DOBs possess interesting and potentially beneficial properties such as electron transport in electronic devices, for example, organic light emitting diodes.^[12] The molecular structure of bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine, **4** is shown in Figure 1. The

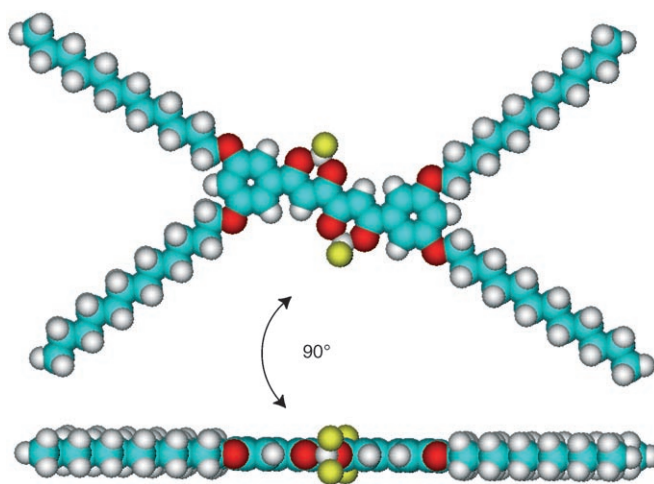


Figure 1. Top and side views of molecule **4** calculated by using the Gaussian program.

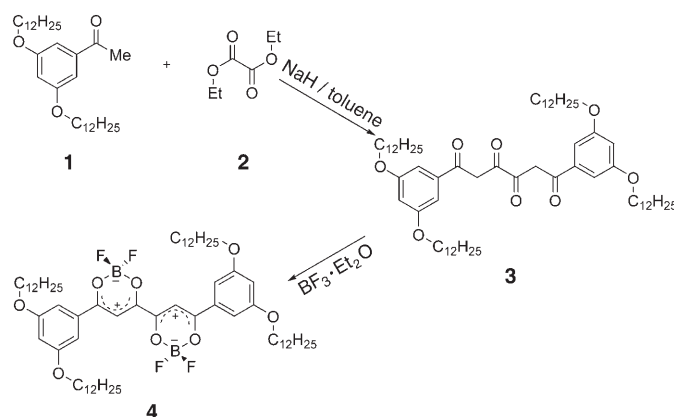
molecule was synthesized by conversion of the corresponding tetraketone **3** with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in acetic acid/toluene. The tetraketone **3** was obtained by a classical Claisen condensation from *m,m'*-di(dodecyloxy)-acetophenone and oxalic acid ethyl esters with sodium hydride in toluene.^[13] Scheme 1 simply describes the synthesis process and shows that the molecule has four dodecyloxy groups. The presence of the dodecyl chains among the molecules may produce unusual and unexpected effects on the assembly structure at HOPG surfaces.

AUSTIN model 1 semiempirical quantum chemical method (AM1) structure optimization of the molecular geometry by using the Gaussian program shows that bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine) is in a planar conformation with an achiral C_{2h} symmetry. The details can be seen in the top side views in

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Scheme 1. Synthesis and chemical structure of bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine).

Figure 1. The two DOB moieties have a dihedral angle of 180° . The molecule exists in a *trans* conformation. The two outer phenyl groups are arranged in the same plane as the DOB moieties and with a dihedral angle of 0° .

A theoretical calculation of the binding energy of a single molecule in the gas phase with different dihedral angles between the DOB moieties, as illustrated in Figure 2,

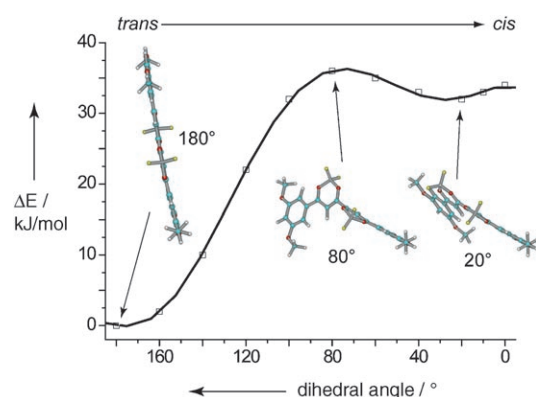


Figure 2. Theoretical calculation of structures and energy variations for the rotation about the central bond of bis(4,4'-(*m,m'*-di(methoxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine) in the gas phase.

confirms that the *cis* isomer of molecule **4** is energetically unstable and has a higher energy than that of the *trans* isomer. However, the energy barrier of the isomerization is much lower than that for azobenzene^[14] or stilbene.^[15] This lower energy barrier may allow the DOB molecules to change their conformation by thermal stimulation. In a differential scan calorimetric (DSC) experiment on solid bulk material of **4**, a *trans*-to-*cis* transition was found at 132°C . The computations also indicated that the most stable conformation is not the planar *cis* isomer but the *gauche cis* isomer with a dihedral angle of about 20° as shown in Figure 2. NMR spectroscopic investigations and absorption measurements in solution gave no indication of a *cis/trans* isomerization (see the Experimental Section). In solution, the *trans* isomer dominates and occupies the global energy minimum of molecule **4**. However,

the most stable isomer of molecule **4** that is adsorbed on a solid surface such as on highly oriented pyrolytic graphite (HOPG) is as of yet unknown.

Herein, we report the results of self-assembly on HOPG surfaces. Molecular-symmetry breaking and chiral assemblies were observed on the SAMs. Self-assembly symmetry can be tuned from lamellar to hexagonal through a thermal-annealing process. This transformation, for the first time, was found to be owing to the *trans*-to-*cis* isomerization of the molecules within the adlayer. Although thermodynamically unstable in solution, the *cis* isomer was stabilized through adsorption onto the HOPG surface.

Figure 3a shows a large-scale STM image of the 2D molecular assembly on HOPG. Several domains larger than 50 nm are seen in the scanning area. Each domain consists of highly ordered molecular rows. The molecules in the domains form a lamellar structure with aligned bright spots as shown in

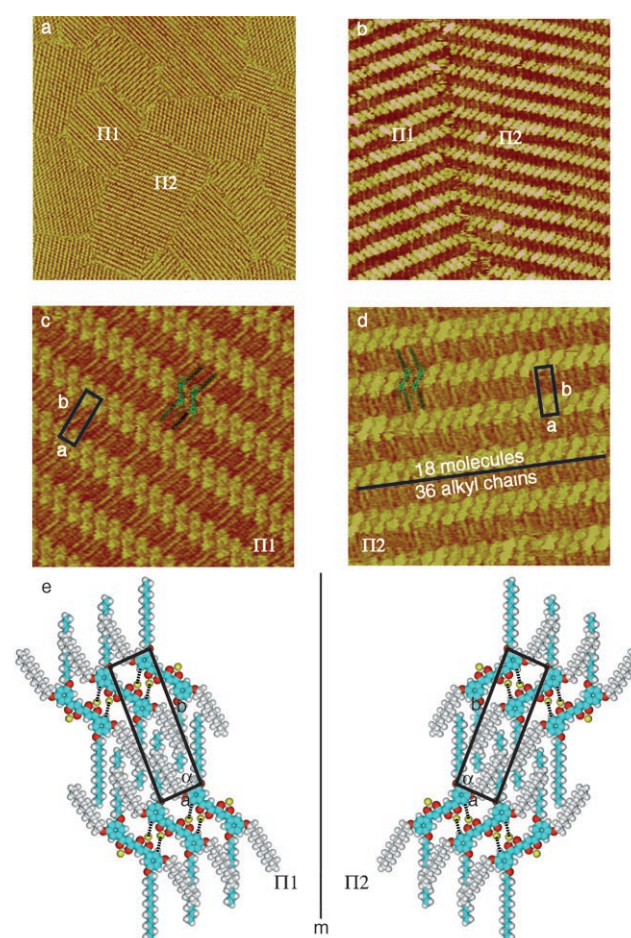


Figure 3. a) A large-scale STM image of molecular assembly with a scanning area of $203 \times 203 \text{ nm}^2$. Tunneling conditions: $I_{\text{set}} = 422 \text{ pA}$, $V_{\text{bias}} = 512 \text{ mV}$. b) STM image with a domain boundary between $\Pi 1$ and $\Pi 2$. The scanning area is $38.2 \times 38.2 \text{ nm}^2$. Tunneling conditions: $I_{\text{set}} = 434 \text{ pA}$, $V_{\text{bias}} = 487 \text{ mV}$. c) High-resolution STM image showing domain $\Pi 1$. The image size is $15.6 \times 15.6 \text{ nm}^2$. Tunneling conditions: $I_{\text{set}} = 511 \text{ pA}$, $V_{\text{bias}} = 671 \text{ mV}$. d) High-resolution STM image showing domain $\Pi 2$. The image size is $19.7 \times 19.7 \text{ nm}^2$. Tunneling conditions: $I_{\text{set}} = 531 \text{ pA}$, $V_{\text{bias}} = 372 \text{ mV}$. e) Structural models for domains $\Pi 1$ and $\Pi 2$. The out-of-plane alkyl chains are illustrated in light gray.

Figure 3b. Because π -conjugated systems are well known to give a high contrast in STM images,^[16] the bright rows were identified as the π -conjugated backbones of the molecules. The distance between the bright rows is about 3.3 nm. A careful analysis of the image in Figure 3b reveals that there are two types of domains, labeled Π 1 and Π 2, that appear like mirror images. The high-resolution STM images in Figure 3c,d show that the dodecyl chains are arranged in a comblike fashion between the neighboring bright π -conjugated backbones. Because of the large packing density, not all dodecyl chains can find room to adsorb on the surface. This large packing density is thought to be owing to the intermolecular reaction through hydrogen bonding between adjacent molecules (shown as black dashed lines in Figure 3e). When we count the alkyl chains and the π -conjugated groups in a lamella, as an example, we find only half as many alkyl chains as expected in Figure 3d. This finding suggests a packing model in which every other alkyl chain is not adsorbed on the HOPG surface. On the basis of the adlayer symmetry and intermolecular distances, a unit cell for the self-assembly in domains Π 1 and Π 2 is outlined in Figure 3c,d, respectively. Figure 3e is a structural model for the molecular arrangements of domain Π 1 and Π 2 in Figures 3c,d. In the packing model shown in the left column of Figure 3e and corresponding to the domain Π 1, the out-of-plane alkyl chains are illustrated in light grey. These alkyl chains are positioned out of the plane of the molecule and can not be detected by STM.^[17] The alkyl chains may not exist as illustrated in the model (oriented in a certain direction) owing to significant thermally induced motion and disorder. From STM results, a unit cell of the assembly on HOPG is defined with the parameters of $a = 0.98 \pm 0.2$ nm, $b = 3.34 \pm 0.2$ nm, and $\alpha = 95 \pm 2^\circ$. The molecular arrangement in domain Π 2 is the same as that in domain Π 1. The model is shown in the right column of Figure 3e. After careful observation, it is found that the adsorption of the molecules on the HOPG surface causes breaking of the molecular symmetry. Compared with the two molecular domains Π 1 and Π 2, the molecules exist in an axial chirality. It is well known that adsorption can cause a chiral discrimination^[2,18] and that achiral molecules can form enantiomerically pure, chiral, 2D assemblies on solid surfaces.^[11b,19] For the particular molecule discussed here, the driving force for the symmetry breaking is the hydrogen bonding between the molecules, that is, between the fluorine atoms of the BF_2 group and the hydrogen in the *ortho* position of the phenyl ring. The chirality of the two domains is illustrated with a mirror plane, *m*, in Figure 3e.

When the HOPG substrate is heated to 100 °C, an increase in domain size is observed. After annealing for 10 minutes, the domains grew larger than the STM scanning area of 600×600 nm². Figure 4a is a typical large scale STM image showing the feature of the adlayer. The adlayer consists of ordered molecular rows. The results indicate that a stable and uniform molecular assembly exists after an annealing process. This therefore provides a simple method for surface modification and molecular manipulation.

After heating the HOPG substrate at 130 °C, small regions like domain Θ in Figure 4b with a different ordering feature appear in the assembly. The new domain Θ shows a hexagonal

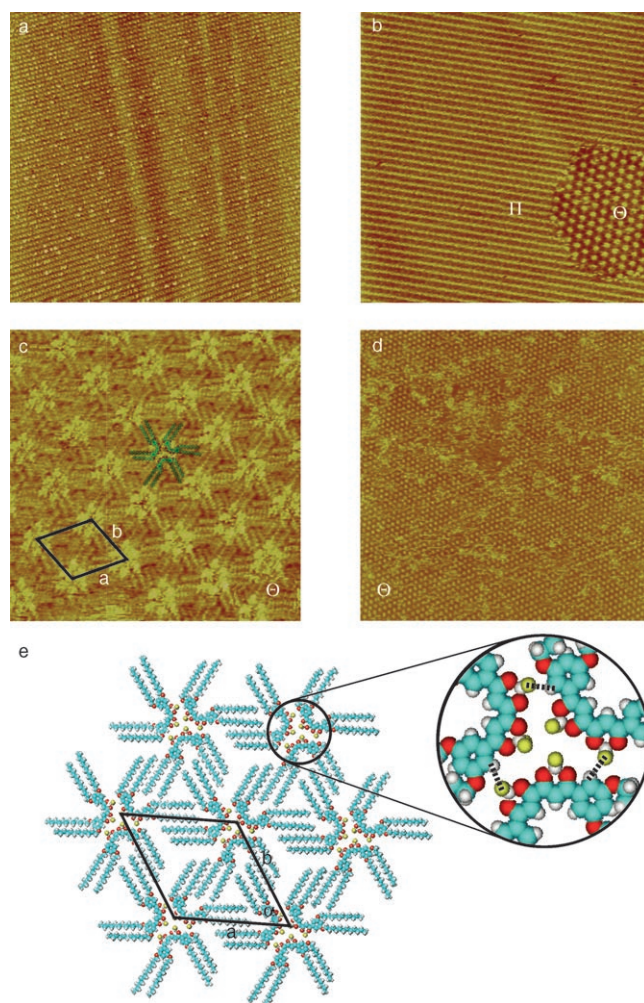


Figure 4. a) A large-scale STM image of the molecular assembly after thermal annealing at 100 °C for 10 min. The scanning area is 200×200 nm². Tunneling conditions: $I_{\text{set}} = 363$ pA, $V_{\text{bias}} = 567$ mV. b) A large-scale STM image after thermal annealing at 130 °C. The scanning area is 100×100 nm². Tunneling conditions: $I_{\text{set}} = 422$ pA, $V_{\text{bias}} = 539$ mV. c) High-resolution STM image showing domain Θ . The image size is 19.6×19.6 nm². Tunneling conditions: $I_{\text{set}} = 376$ pA, $V_{\text{bias}} = 529$ mV. d) A large-scale STM image of the adlayer after thermal annealing at 150 °C. The image size is 200×200 nm². Tunneling conditions: $I_{\text{set}} = 433$ pA, $V_{\text{bias}} = 644$ mV. e) Structural model for domain Θ determined from the STM images.

symmetry with bright spots rather than the previous lamellar structure in the domain Π in Figure 3 and Figure 4b. The domains Θ can be as large as 50 nm. The high-resolution STM image in Figure 4c reveals the details of the hexagonal structure. Although a thermal drift in recording the image can be seen in Figure 4c, it is clear that each of the bright spots in the domain Θ consists of three molecules. However, the geometry of the molecular structure with *trans*-connected DOB moieties, as shown in Figure 1, does not allow for such a molecular arrangement. Instead, domain Θ is composed of the *cis* isomer of the molecules. The hydrogen bonding between the molecules is responsible for the formation of the trimers. An enlarged inset in Figure 4e shows the details of the trimers. The possible hydrogen bonding in the trimer is

indicated by black dashed lines. The hydrogen bonding is considered to exist between the fluorine atoms of the BF_2 group and the hydrogen in the *ortho* position of the phenyl ring. From the adlayer symmetry and intermolecular distances, a unit cell for the assembly is outlined in Figure 4c. Figure 4e shows a structural model for the molecular assembly shown in Figure 4c. The unit cell dimensions are $a = 3.92 \pm 0.2$ nm, $b = 3.92 \pm 0.2$ nm, $\alpha = 60 \pm 5^\circ$. The model is in good agreement with the observed results from STM images.

A size increase in these hexagonal domains was observed when the adlayer was heated to 150°C . Finally, the hexagonal structure covers the entire substrate surface. Figure 4d is a typical STM image of the new phase. Some molecular clusters can be seen in the image indicating the starting of the molecular desorption from the HOPG surface. However, until this temperature, the retransformation from *cis* isomers to *trans* isomers was not observed. The in-solution unstable *cis* isomers can stably exist on HOPG surface owing to the molecule–molecule and molecule–substrate interactions. The hexagonal arrangement of the *cis* isomers in domain Θ allows all dodecyl chains to adsorb on the HOPG surface resulting in a more stable assembly and stronger adsorption. The adsorption of those dodecyl chains which were previously not adsorbed on the surface releases sufficient energy to thermodynamically favor domain Θ . Therefore, the hexagonal assembly is stabilized by the adsorption and is remarkably stable and still clearly observable without noticeable changes after several months.

The self-assembly of *cis/trans*-conformation molecules was well reported. The conformational change does not occur in all assemblies as can be seen from the differences between azobenzene/stilbene^[8a,9,10] and DOB molecules. There are several important factors that influence the *cis/trans* transformation; First, the substrate is very important, on Au and Ag surfaces, the interaction between the molecule and the substrate would be usually stronger than that on HOPG surfaces. Second, the difference in molecular structure is also important to the transformation as it is not possible that just one DOB changes its conformation in close-packed assemblies. All DOB molecules in the assembly changed their conformation from *trans* to *cis*, however, the details on the transformation are not clear. For example, it is not clear whether all molecules change in uniform steps or the transformation is translated by a process of disorder to order. As thermal drift is so heavy, no STM imaging can be carried out during thermal annealing. As a guess, we propose that the transformation is through a process of disorder to order and results in the adsorption of all molecules on the HOPG surface in a *cis* conformation.

In summary, we have studied the adsorption behavior of bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine) on HOPG surfaces. It was found that the structure of the adlayer can be converted from lamellar to hexagonal through a thermal-annealing process. The hydrogen bonding between the molecules causes a break in molecular symmetry upon adsorption onto the surface and results in chiral assemblies from achiral molecules that were previously clearly observed by STM. For the first time, a

thermally induced *trans*-to-*cis* isomerization of adsorbed molecules was observed and the thermodynamically stable *cis*-isomer adlayers were created. Although thermodynamically unstable in solution, the *cis* isomers become remarkably stable when adsorbed on the HOPG surface. By using only thermal stimulation at different temperatures, we have obtained pure *trans*- and *cis*-isomer adlayers. The results of this research are significant in the study of self-assembly and molecular architecture on solid surfaces.

Experimental Section

A solution of *m,m'*-di(dodecyloxy)acetophenone (0.02 mol), diethyl oxalic acid ester (0.01 mol), and sodium hydride (0.6 g) in toluene (300 mL) was stirred and heated for 10 h. After cooling down to room temperature, the solution was added to a mixture of water/ice/acetic acid (1:1:1). The organic layer was separated, washed with water, dried over Mg_2SO_4 , and then concentrated. The precipitated product was then isolated by filtration. For purification, the product was recrystallized from toluene/hexane (1:1).

1,6-Bis(*m,m'*-di(dodecyloxy)phenyl)hexane-1,3,4,6-tetraone (**3**): yellow crystalline product, yield: 81%; mp. $62\text{--}67^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.26$ (m, 76H; CH_3 , CH_2), 1.46 (quin, 8H; CH_2), 1.79 (quin, 8H; CH_2), 3.94 (t, 8H; CH_2), 6.66 (s, 2H; CH), 7.06 (s, 2H; CH), 7.12 (s, 4H; CH), 15.54 ppm (s, 2H; OH); elemental analysis (%) calcd for $\text{C}_{66}\text{H}_{110}\text{O}_8$: C 76.9, H 10.6; found: C 76.7, H 10.7.

To a boiled solution of **3** in acetic acid, the $\text{BF}_3\cdot\text{Et}_2\text{O}$ adduct was added as the limiting reagent. After addition, the solution was boiled for two minutes. The product crystallized from the cooling solution and was isolated by filtration. The product was then recrystallized several times from dry toluene to purify.

Bis(4,4'-(*m,m'*-di(dodecyloxy)phenyl)-2,2'-difluoro-1,3,2-dioxaborine) (**4**): orange crystalline product, yield: 95%; mp. 122°C (DSC); UV/Vis (toluene): $\lambda_{\text{max}} = 435$ nm; Fluorescence (toluene): $\lambda_{\text{fluoro}} = 500$ nm; ^1H NMR (400 MHz, CDCl_3): $\delta = 1.27$ (m, 76H; CH_3 , CH_2), 1.47 (m, 8H; CH_2), 1.82 (quin, 8H; CH_2), 4.03 (t, 8H; CH_2), 6.88 (s, 2H; CH), 7.32 (s, 4H; CH), 7.55 ppm (s, 2H; CH); elemental analysis (%) calcd for $\text{C}_{66}\text{H}_{108}\text{O}_8\text{B}_2\text{F}_4$: C 70.3, H 9.5; found: C 70.2, H 9.5.

Molecule **4** was dissolved in toluene (HPLC grade, Aldrich) with a concentration of less than 10^{-4} M. A drop of the solution was then deposited on a freshly cleaved surface of HOPG (quality ZYB, Digital Instruments) and dried in air prior to STM imaging. The samples were imaged by STM in ambient conditions. The experiments were performed on a Nanoscope III SPM (Digital Instruments, Santa Barbara, USA). STM tips were made from mechanically cut Pt/Ir wire (90/10). All STM images were recorded in the constant current mode. The specific-tunneling conditions are given in the legends of Figure 3 and 4. All images are shown without further processing such as low-pass and Fourier transformation.

The theoretical calculations were performed for molecules in the gas phase by using GAUSSIAN03 (Gaussian Inc., Pittsburgh, USA) and MATERIALS STUDIO 3.1 (Accelrys, San Diego, USA). The packing models for the various self-assemblies were built by HYPERCHEM (Hypercube Inc., Florida, USA) program packages.

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