

Solvent Effect on Self-Assembled Structures of 3,8-Bis-hexadecyloxy-benzo[*c*]cinnoline on Highly Oriented Pyrolytic Graphite

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3,8-Bis-hexadecyloxy-benzo[*c*]cinnoline (BBC16) self-assembled into two structures at highly oriented pyrolytic graphite (HOPG) surface: one was formed by molecules with a V-like configuration (C_{2v} symmetry) and the other by molecules with a Z-like configuration (C_s symmetry). The self-assembled structures could be tweaked by the solvents used. In the self-assembled monolayers (SAMs) on HOPG, the BBC16 molecule adopted the V-like configuration in polar solvents and the Z-like configuration in nonpolar solvents. Moreover, the solvent viscosity, solvent dissolvability of BBC16, and substrate temperature also played some roles in tuning the two-dimensional self-assembled structures.

1. Introduction

Self-assembling is a promising and efficient approach to building molecular devices that are vital for nanoscience and nanotechnology in the long term. Self-assembled monolayers (SAMs) at surfaces have many potential applications such as lubrication, wetting, catalysis, and molecular detection¹ where design and control of the assembled structures plays a key role. Polymorphism has been identified widely in three-dimensional (3D) crystals and two-dimensional (2D) SAMs as well. Controlling the formation of pure polymorphs has been a very important and fascinating aspect.^{2–5}

Among all of the preparation methods of SAMs, drop-deposition has been proven to be the simplest and the most efficient.^{4–9} In this approach, the solvent used is an important factor determining the resulted assembly structures. Until now, only a few studies discussed the solvent effect on molecular self-assemblies formed at chemically inert highly oriented pyrolytic graphite (HOPG) surfaces despite the many researches that have been carried out for thiols self-assembled on metal substrates.⁶ Flynn et al.⁷ reported that solvents could greatly influence the adsorption and mobility of triacontane and triacontanol on the graphite surfaces. Very recently they reported⁸ the effect of *n*-alkyl acids on the selective chicken-wire and flower self-assembly structures of trimesic acid (TMA) on HOPG. Wan and co-workers⁹ also reported the solvent effect on the assembly chirality of a banana-shaped molecule. Sometimes, the solvents coassembled with solute molecules to form two-component SAMs.^{10–12}

STM has been used extensively to detect single molecules and SAMs because of its powerful atomic resolution in imaging.¹³ Various molecules have been studied on HOPG. They include alkanes and their functional derivatives, liquid crystals, coordination and organometallic compounds, and others.¹⁴ Benzo[*c*]cinnoline (BC) and its derivatives (see Figure 1) are a family of physiologically active molecules. They have mutagenic, antirheumatic, herbicidal, and carcinogenic activities and can also be used as bleach catalysts because of their chromophore

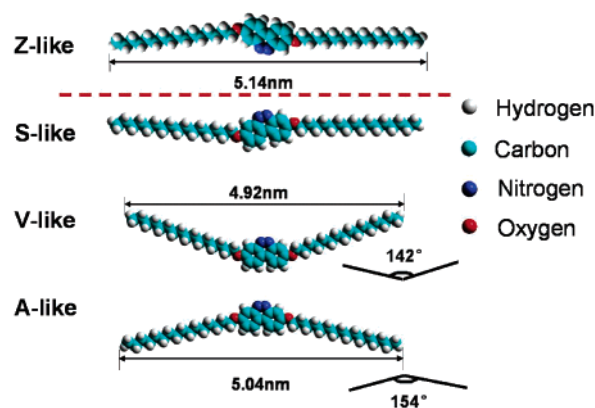


Figure 1. Optimized possible configurations of the BBC16 molecule in the gas phase.

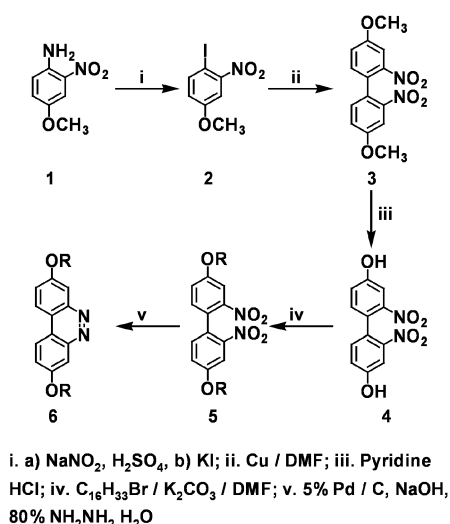
moiety.¹⁵ Similar to phenanthrene, such a molecule has a bent core that possesses a C_{2v} symmetry. The nitrogen atoms at the 5 and 6 positions have a strong electron-attracting effect that may dramatically change the molecular configurations of the molecules with substituted groups. These two nitrogen atoms can also serve as electron donors for metal ions or other Brønsted acids.¹⁶ Alkoxyated BC molecules have a core slightly different from those of alkylated biphenyl and bipyridine derivatives frequently forming various SAMs on HOPG that could be further used as secondary templates for other molecules.¹⁷

In this paper, we report a detailed study of the solvent effect on tuning the assembled structures of 3,8-bis-hexadecyloxy-benzo[*c*]cinnoline (BBC16), an alkoxyated BC molecule, on HOPG. The solvents used in this study mainly changed the BBC16 molecular configurations in solution that further determined the assembled structures of BBC16 on HOPG. These solvents did not form coassembled structures with the BBC16 molecule. This provides a new case study on successful control of the polymorphism of two-dimensional assemblies, and may promote our understanding and controlling of polymorphism in 3D crystals and help design useful molecular assemblies for future molecular device applications.

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SCHEME 1: Synthesis Procedure for 3,8-Bis-hexadecyloxy-benzo[*c*]cinnoline (BBC16)

2. Experimental Section

A. Synthesis of 3,8-Bis-hexadecyloxy-benzo[*c*]cinnoline (BBC16). The BBC16 synthesis is described in Scheme 1. From commercially available 2-nitro-4-methoxyaniline (**1**), 2,2'-dinitro-4,4'-dimethoxybiphenyl (**3**) can be obtained via diazotization, iodination, and Ullmann coupling with a high yield.¹⁸ Compound **4** is produced by demethylation of compound **3** in refluxed pyridine and HCl . Thus 4,4'-disubstituted analogues of compound **3** can be synthesized conveniently by compound **4** and alkyl bromide in $\text{K}_2\text{CO}_3/\text{DMF}$. Here, hexadecyl bromide is used, and thus compound **5** is prepared. Compound **5** can be further reductively cyclized in Pd/C and 80% hydrazine hydrate to form BBC16.¹⁹ The final product was further purified and recrystallized. It had a color of light grass green. ^1H NMR (CDCl_3): 0.856–0.897 (s, 6H), 1.260–1.360 (m, 52H), 1.516–1.537 (d, 2H), 1.888–1.936 (m, 2H), 4.201–4.245 (t, 4H), 7.515–7.540 (d, 2H), 8.028 (s, 2H), 8.378–8.409 (d, 2H). The melting point was measured to be 104.7°C – 106.2°C .

B. STM Experiments. All of the STM experiments were performed in ambient with a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) microscope. The tips were prepared by mechanically cutting a platinum iridium wire ($\text{Pt/Ir} = 90/10$, Alfa Inc.) of 0.25 mm in diameter. Solutions containing BBC16 were prepared with various solvents including 1-phenyloctane (98%, Aldrich), 1-octanol (99%, Acros), toluene (HPLC grade, Acros), chloroform (HPLC grade, Acros), 1,2-dichloroethane, and carbon tetrachloride (A. R. grade, Beijing Chemicals). The latter two solvents were further purified by distillation and all of the other solvents from Acros and Aldrich were used without further purification. Because BBC16 was not very soluble in 1-phenyloctane and 1-octanol, saturated BBC16 solutions in these solvents were used to prepare the SAMs by dropping $\sim 1\ \mu\text{L}$ solution on to a freshly cleaved HOPG (ZYB grade, Mikromasch) surface. For this kind of sample, the STM tip was dipped into the solutions to image the assembled structures. For other solvents, the solution concentrations were controlled to be $0.1 \sim 1.0\ \text{mg/mL}$ and $\sim 4\ \mu\text{L}$ solutions were deposited on to the HOPG surface to prepare the samples for STM. These four solvents are volatile and vaporize quickly. Hence, in the experiments the STM tip scanned on the dried solid/air interfaces of these samples prepared with the volatile solvents. For thermal treatments, the samples were heated to about 100°C in a vacuum oven and kept for about 1 h before they were cooled down to room temperature in air.

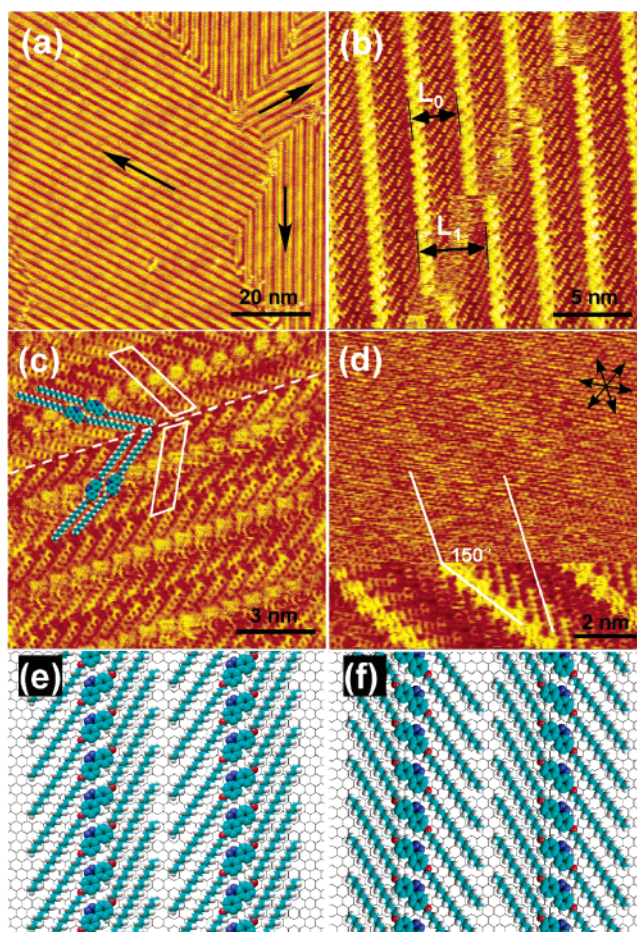


Figure 2. Self-assembled structures of BBC16 from saturated solution prepared with 1-phenyloctane and proposed models of the assemblies. (a) Low magnification image showing various domains and the domain orientations (image size: $100 \times 100\ \text{nm}^2$, sample bias voltage: 650 mV, feedback current: 250 pA). (b) High-resolution image showing the frequently observed dislocation of the domain ($20 \times 20\ \text{nm}^2$, -600 mV, 300 pA). (c) Chiral assembly structures ($12 \times 12\ \text{nm}^2$, -450 mV, 300 pA). The superposed modeled molecules are used to enhance visual identification. The dashed line marks the boundary of the chiral structures, and the two solid frames indicate the unit cells in both domain. (d) Simultaneous imaging of the assembling structure and the HOPG lattice structure achieved by changing the sample bias voltage from -400 mV to -30 mV during scanning ($12 \times 12\ \text{nm}^2$, 300 pA). e and f are proposed molecular models for the self-assembled CW and CCW structures.

STM images were recorded under various tunneling conditions in constant current mode (sample at a negative potential). All of the reported data were calibrated with the underlying HOPG honeycomb lattice structure measured in situ by changing the bias voltage. To determine the 2D lattice parameters of the assemblies, we averaged tens to hundreds of up and down scanning images to reduce the measuring errors. All of the images presented in this paper were flattened to remove the tilting effect of the substrate plane, and some were low-pass filtered to remove the high-frequency noise as indicated in the corresponding figures. Different tips and samples were used in the experiments in order to eliminate any uncertain artificial and random effects.

3. Results and Discussions

A. Assembled Structure in 1-Phenyloctane. Figure 2 shows the STM results of the BBC16 molecule assembled from the saturated solution prepared with 1-phenyloctane on to the HOPG surface. Repeated scans with different tips reached the same 2D assembled structures, as shown in Figure 2a–d. It is

frequently observed that a particular domain could be dislocated and interrupted and the dislocation gap could be any number from zero to one inter-row distance ($L_0 < L_1 < 2L_0$, as depicted in Figure 2b). Its high-resolution image indicated that the molecules in the SAM adopted a Z-like configuration, consistent with one of its most stable configurations in the gas phase according to semiempirical quantum mechanics calculations²⁰ (Figure 1).

As shown in Figure 1, the Z-like configuration has a C_s symmetry and the two chains extend in opposite directions at the two sides of the benzo[c]cinnoline core. These two chains are actually not parallel to each other, and the angle between them was measured to be about 6° in high-resolution STM images (not shown here), in good accordance with the calculated results. This molecular configuration with C_s symmetry makes it chiral when adsorbed on to the HOPG surface because of the loss of the mirror symmetry, just as many other molecules that have a characteristic plane parallel to the surface would induce self-assembled chiral structures when adsorbed on surfaces.^{5,9,21–23} Because both faces of the same molecule have an equal probability to attach to the surface, there must be domains constructed by molecules of opposite chirality. This was observed in our experiments. In Figure 2c, a clear mirror (dashed line) exists between two chiral domains. Tens of measurements of these chiral domains resulted in same 2D unit cell parameters. For the clockwise (CW) chiral structure (upper part in Figure 2c), the unit cell is $a = 0.84 \pm 0.04$ nm, $b = 3.61 \pm 0.06$ nm, and $\gamma = 117 \pm 2^\circ$; and for the counterclockwise (CCW) one (lower part in Figure 2c) the parameters are $a = 0.85 \pm 0.05$ nm, $b = 3.51 \pm 0.10$ nm, and $\gamma = 116 \pm 2^\circ$. Both unit cells contain one BBC16 molecule and have an area of about 2.70 nm² per molecule.

The bright bands in the molecular rows in Figure 2 are attributed to the benzo[c]cinnoline cores in terms of the p- π conjugation between BBC16 and HOPG. The width of the bright band is about 0.9 nm, in consistence with the width of the aromatic core. The distance from the bright band edge to the center of two adjacent rows along the alkyl chain direction is about 5.1 nm and coincides well with the length of the Z-like molecule configuration given in Figure 1. With the change of the bias voltage during STM imaging, both the HOPG lattice structure and the BBC16 assembled structure can be recorded in the same image (Figure 2d). In Figure 2d, one can find that one alkyl chain of the BBC16 molecule is roughly parallel to the HOPG lattice direction and the molecular rows bisect the angle between the nearest two HOPG lattice vectors. This result agrees very well with the observations that the row directions in adjacent domains form an angle of 120° , without any exceptions. The spacing between two neighboring alkyl chains in the same row is 0.4–0.5 nm, a value normally reported for molecules with alkyl chains self-assembled on the HOPG surface.^{3–5,7,10–12} The other alkyl chain of the BBC16 molecule forms an angle of $\sim 145^\circ$, and the benzo[c]cinnoline core longitude axis adopts an angle of $\sim 128^\circ$, both with respect to molecular row. Using all of the measured data, we proposed molecular self-assembly models shown in Figure 2e and f for the CW structure and CCW structure formed in 1-phenyloctane, respectively.

In Figure 3, a detailed explanation is presented for the molecular configurations in the CW structure we observed experimentally (similar explanation can be applied to the CCW structure). To build the models, the molecular rows are restrained along the solid arrow, 30° with respect to the HOPG cell vector (dash arrows). In the four possible arrangements, model b seems

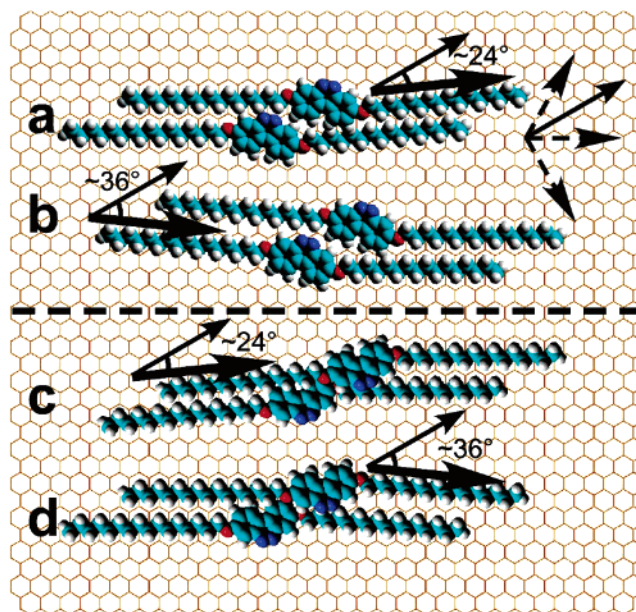


Figure 3. Proposed models for describing the molecular configuration in the assembled structure. A. a and b are built with the Z-like configuration and only b shows the right chain-row angle; c and d are built with the S-like configuration but obviously they are less stable because of the spatial congestion of the adjacent aromatic cores. Solid and dashed arrows point out the molecular row and the HOPG lattice directions. Bold arrows point out the alkyl chain direction that does not match any zigzag carbon chains of the HOPG lattice.

to be the most reasonable because once one alkyl chain matches with the zigzag carbon chain of the HOPG honeycomb lattice, the other chain can only adopt an angle of $\sim 36^\circ$ with respect to the molecular row. The experimentally measured angle of the other alkyl chain is 145° with respect to the molecular row (a supplementary angle of 35°). Model a is built in a way similar to model b except the other chain extends along the zigzag carbon chain direction of the HOPG lattice while keeping the same molecular face attached to the HOPG surface. This leads to a structure in which the left alkyl chain of the BBC16 molecule forms an angle of $\sim 24^\circ$ with respect to the molecule row direction, in discrepancy with the experimental observation. Therefore, model a is not likely possible. In models c and d, the BBC16 molecule is flipped (the S-like molecular configuration in Figure 1, an enantiomer of the Z-like configuration at the surface) when attached to the HOPG surface. The alkyl chains are arranged in similar ways as for models a and b: c is similar to b and d to a. In consideration of the intermolecular distance in the same row observed experimentally, both models c and d are less likely possible because of the spatial hindrance between the phenyl cores. With these in mind, one can immediately judge that only the Z-like molecular configuration (model b) can form the CW chiral structure (Figure 2e). Hence, the CCW pattern (Figure 2f) can be built simply by flipping the BBC16 molecules in model b along another zigzag carbon direction of the HOPG lattice with the CCW row formed an angle of 120° with respect to that in the CW pattern. Therefore, the CCW pattern consists of only the S-like molecular configuration shown in Figure 1.

B. Assembled Structures in 1-Octanol. Although it has a higher polarity than 1-phenyloctane, 1-octanol is not a good solvent for BBC16. To prepare the BBC16 SAMs on HOPG, we used a saturated solution made of BBC16 and 1-octanol in the experiments. The solution concentration was estimated to be less than 0.3 mg/mL. Two assembled structures in 1-octanol are observed, as shown in Figure 4a. They are termed as

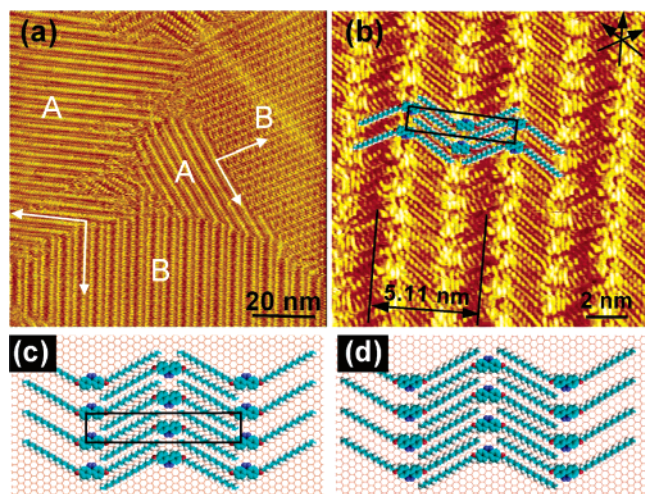


Figure 4. Assembled structures of the BBC16 molecules in 1-octanol. (a) Coexistence of structures A and B and their domain orientations ($100 \times 100 \text{ nm}^2$, 300 mV, 350 pA). (b) High-resolution image showing the V-like molecular configuration superposed with modeled molecules that enhance visibility ($15 \times 15 \text{ nm}^2$, 300 mV, 350 pA). The arrows represent the HOPG lattice vector directions. The solid frame indicates the unit cell. c and d are two tentative molecular models for assembled structure B. In c the molecules adopt a V-like configuration like that shown in Figure 1 where the N atoms are embraced by the two alkyl chains, whereas in d the molecules adopt an A-like configuration like that shown in Figure 1 where the N atoms and the two alkyl chains stay at opposite sides of the BBC16 molecule.

structures A and B. Experimentally, the surface area occupied by structure A was about twice as large as that occupied by structure B. The molecular configuration in structure A is identical to that observed in 1-phenyloctane. However, structure B shows a larger unit cell, consisting of the V-like molecular configuration shown in Figure 1. The row periodicity of structure B was $5.05 \pm 0.10 \text{ nm}$, and the intermolecular distance in the same molecular row was measured to be $1.09 \pm 0.10 \text{ nm}$, yielding a unit cell: $a = 1.09 \pm 0.10 \text{ nm}$, $b = 5.05 \pm 0.10 \text{ nm}$, and $\gamma = 88 \pm 3^\circ$ (Figure 4b). There are two molecules in one unit cell, so each molecule occupies an area of $\sim 2.75 \text{ nm}^2$, a little bit bigger than that in structure A.

According to the simultaneous imaging of both BBC16 assembly and the underlying HOPG lattice structures (not shown here), we observed that both the alkyl chains of the BBC16 molecules and the molecular rows oriented along the zigzag carbon lattice direction of HOPG, that is, both the angles between the alkyl chains of a single BBC16 molecule and between the row directions in neighboring assembly domains were 120° . The actually measured data of the two angles are $120.4 \pm 2.4^\circ$ and $120.5 \pm 2.7^\circ$, respectively. The measured angle between the two chains in a single BBC16 molecule is 120° , seriously deviating from 142° or 154° for the gas-phase V-like or A-like configuration (Figure 1). This angle change leads to an energy increase that could be compensated by the energy decreases upon assembling of the molecules on surface and a better match between the deformed molecule backbone and the substrate HOPG lattice. The alkyl chains of BBC16 molecules in neighboring molecular rows interdigitate alternately so that the distance between two adjacent alkyl chains in a row becomes $\sim 0.47 \text{ nm}$ in order to match the bottom HOPG lattice.

In Figures 4c and d, two models are proposed according to the experimentally measured data, composing of the V-like and A-like molecular configurations shown in Figure 1. Both the V-like and A-like molecular configurations are possible. However, semiempirical optimization²⁰ showed that the A-like

configuration has a larger chain–chain angle (154° in gas phase) than the V-like configuration (142°) and needs more energy than the V-like configuration does to change the COC bond angle into 120° . Furthermore, A-like molecules are about 1.6 kcal/mol higher in energy than the V-like ones, so the appearance probability of the A-like molecules should be lower. On the basis of these considerations, the V-like configuration is more likely to be the one in the assembled structure.

It should be pointed out that 1-octanol is somewhat more volatile than 1-phenyloctane and, hence, imaging cannot be taken for a long time in 1-octanol. But control experiments showed that the assembled structure of BBC16 in 1-octanol did not change even after the solvent completely vaporized, which means that the BBC16 SAM is quite stable on HOPG at room temperature.

C. Assembled Structures in Other Solvents. To further check the solvent effect on the BBC16 self-assembly structure, we used four more solvents. They can be catalogued into two groups: two polar solvents, chloroform and 1,2-dichloroethane, and two nonpolar ones, toluene and carbon tetrachloride.

In nonpolar volatile solvents such as toluene and carbon tetrachloride, only assembled structure A was observed experimentally, similar to the case in 1-phenyloctane. One demonstrating example is given in Figure 5a for BBC16 in toluene. Figure 5b is the high-resolution image sampled in the square area marked in Figure 5a, clearly showing the assembled structure, A. This assembled structure is quite stable on HOPG at room temperature and could not be disrupted by after-treatments in polar solvents such as 1,2-dichloroethane and chloroform.

In polar solvents such as chloroform, however, both assembled structures A and B were observed. The latter showed up more frequently than the former, which is somewhat different from the case in 1-octanol. In 1,2-dichloroethane (more polar than chloroform), both structures A and B were also detected. But the situation changed again, namely, structure B took up most of the HOPG surface to form quite large domains as wide as $\sim 100 \text{ nm}$ while structure A was just occasionally detected in smaller domains as narrow as 30 nm . A representative STM image is shown in Figure 5c. It is noted that in many other images (not shown here) structure A hardly appeared. Statistically averaged from tens of independent scans in different area, the appearing structural probability ratio of these two structures (A:B) was roughly 5:95.

D. Thermal Stability of the BBC16 SAMs. As aforementioned, both assembled structures A and B are stable on HOPG at room temperature. However, their appearance probabilities vary in different solvents, implying that they are different energetically and thus may have different stabilities. To determine which structure is more stable, we treated the BBC16 SAMs thermally on HOPG after the used solvents evaporated. This was done by heating the BBC16 SAMs formed in polar solvents to $\sim 100^\circ \text{C}$ in a vacuum oven for 1 h. After thermal treatment, phase transition indeed occurred. Only assembled structure A survived the thermal treatment regardless of whether the solvent used was chloroform or 1,2-dichloroethane. This means that structure B transforms into structure A after the thermal treatment and, hence, structure A is superior in stability to structure B. Therefore, structure A is thermodynamically more stable, and structure B is more kinetically controlled.

E. Solvent Effects. The experimental results can be summarized as follows: (1) Both structure A and B are composed of pure solute molecules (BBC16) without any solvent molecules involved or mixed in the BBC16 SAMs because both structures can be achieved in different solvents. (2) Structure

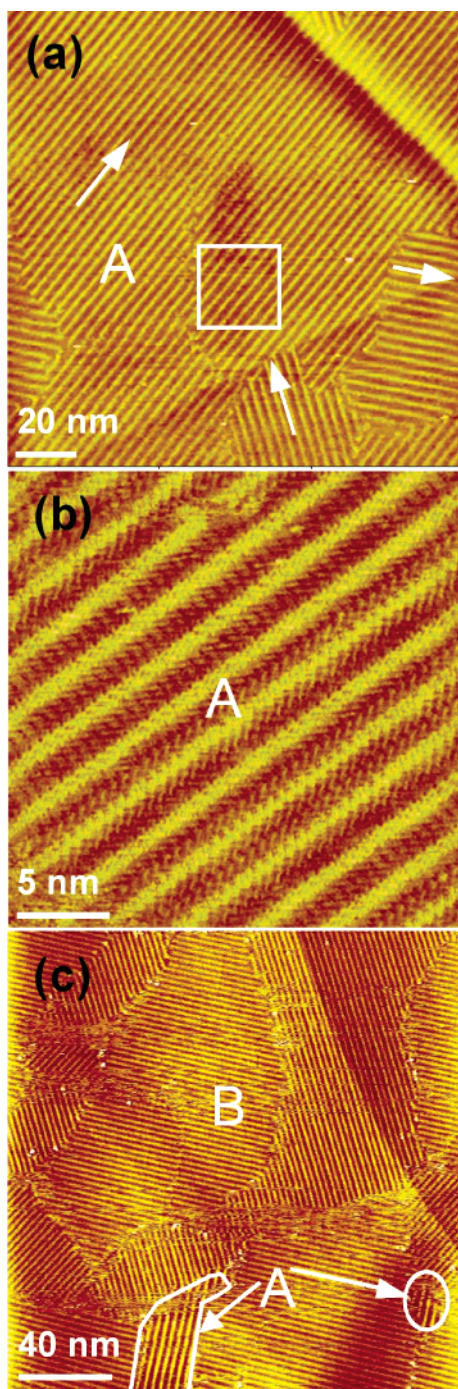


Figure 5. Self-assembled structures of BBC16 in toluene (a and b) and 1,2-dichloroethane (c). (a) Various domains of assembled structure A. The arrows indicate the domain orientations ($150 \times 150 \text{ nm}^2$, -1000 mV , 98 pA , low-pass filtered). (b) High-resolution image of structure A sampled in the square area marked in a ($25 \times 25 \text{ nm}^2$, 500 mV , 100 pA , low-pass filtered). (c) STM image of the coexisted structures A and B in 1,2-dichloroethane ($200 \times 200 \text{ nm}^2$, 880 mV , 65 pA). Normally, structure A would be hardly observed in this solvent.

A is more stable than B according to the thermal transformation from B to A when heated, but the energy difference between these two structures should not be very large because their appearance probabilities vary with the solvents used and no phase transition is observed experimentally in solutions. This is reinforced by the fact that both structures have a similar unit cell area, and both the Z-like and V-like configurations have a close energy in gas-phase according to semiempirical calcula-

TABLE 1: Physical Properties of the Used Solvents and the Statistical Probability Ratio of Structure A to B in These Solvents^a

chemicals	boiling point (°C)	viscosity (mN s m ⁻²)	dielectric constant (ϵ/ϵ_0)	dipole moment (Debye)	structure probability ratio (A:B) ^e
1-phenyloctane	261–263 ^b	2.61 (20) ^c	2.26 (20) ^c	0	100:0
carbon tetrachloride	76.7	0.908 (25)	2.23 (25)	0	100:0
toluene	110.6	0.623 (15) 0.523 (30)	2.36 (30)	0.375	100:0
chloroform	61	0.596 (15) 0.514 (30)	4.81 (25)	1.04	30:70
1-octanol	195	10.6 (15) 6.13 (30)	10.3 (20)	1.72 (20, B) ^d	70:30
1,2-dichloroethane	83.5	0.779 (25)	10.4 (20)	1.48	5:95

^a Unless otherwise stated, all data come from *Lange's Handbook of Chemistry*, 15th Ed; Dean, J. A., Ed.; McGraw-Hill: New York, 1999. Numbers in parentheses indicate the temperatures at which the data were reported. ^b Schweinitz, V. *Chem. Ber.* **1886**, *19*, 641. ^c Tschamler *Monatsh. Chem.* **1948**, *79*, 162. ^d This was measured in benzene for which B in the parentheses stands. ^e These data were averaged statistically from tens of images in various areas at the same sample surface used in this study.

tions. (3) Solvent plays a critical role in determining the assembled structure.

Table 1 lists the polarities of the solvents used in this study, the statistical structure appearance probability ratio (A:B), and other physical properties of the solvents as well. On the basis of their polarities, the solvents can be catalogued into two groups: polar and nonpolar solvents. In nonpolar solvents such as 1-phenyloctane, carbon tetrachloride, and toluene, only assembled structure A appears that solely consists of the Z-like molecular configuration (or the S-like configuration because it is identical to the Z-like configuration in free space). In polar solvents such as 1-octanol, structures A and B coexist, but the former dominates. In chloroform, both structures appear, but structure B becomes dominant. In 1,2-dichloroethane, structure B becomes even more dominant. Apparently, the solvent polarity greatly affects the assembled structures of BBC16 SAMs. Semiempirical calculations²⁰ point out that the V-like configuration has a dipole moment of $\sim 1.46 \text{ D}$ and the Z-like one, $\sim 3.59 \text{ D}$, so the Z-like configuration is more polar than the V-like one and prefers staying in polar solvents than assembling on the HOPG surface. This can explain why structure B (consisting of the V-like configuration) appears in polar solvents. In nonpolar solvents, the BBC16 molecules prefer attaching to themselves via van der Waals forces (dipole–dipole interaction) and hence would deposit on the HOPG surface to form SAMs. Because the Z-like configuration has a larger dipole moment and forms a larger van der Waals force than the V-like configuration does, assembled structure A dominates in nonpolar solvents. This can explain why only structure A exists in nonpolar solvents. Generally, the less polar the solvent is, the more favorably structure A (containing Z-like configuration) self-assembles on the surface, provided that all of the other properties of the solvents are identical or similar.

On the basis of their boiling points and dissolvability of BBC16, the solvents also fall into two groups: nonvolatile 1-phenyloctane and 1-octanol have a higher boiling point, and their dissolvability of BBC16 is quite limited; the other four solvents are volatile, and their dissolvability of BBC16 is quite high. In experiments, the detected structural ratio A:B is $\sim 70:30$ in 1-octanol and $\sim 5:95$ in 1,2-dichloroethane. One can find in Table 1 that these two solvents have very similar dielectric constants and similar dipole moments, but 1-octanol has a

boiling point of 195 °C, much higher than that of 1,2-dichloroethane (84 °C). Hence, 1-octanol is more viscous (see the viscosity values given in Table 1) and lower in its solubility of BBC16 than 1,2-dichloroethane. Because structure B tends to be more kinetically controlled, it is much easier to form in 1,2-dichloroethane than in 1-octanol. This can explain the structural ratio difference in 1-octanol and 1,2-dichloroethane. Therefore, the solvent viscosity also comes into play in determining the assembled structure of BBC16 on HOPG.

4. Conclusions

Two self-assembled structures of 3,8-bis-hexadecyloxybenzo[c]cinnoline (BBC16) formed on the HOPG surface at room temperature. Each assembled structure contained a particular BBC16 molecular configuration. The solvents that were used to prepare the assembling solutions played an important role in determining the final assembled structures of the BBC16 molecules. The solvent effect could function via either its polarity or other properties such as viscosity and the solubility of the assembled molecules. In this study, only assembled structure A (consisting of the Z-like molecular configuration) existed in nonpolar solvents such as 1-phenyloctane, carbon tetrachloride, and toluene, whereas it coexisted with assembled structure B (comprising the V-like molecular configuration) in polar solvents such as 1-octanol, chloroform and 1,2-dichloroethane. The solvent viscosity and dissolvability of BBC16 also have obvious effects on the assembled structures of BBC16 on HOPG. This typical case study would deepen our understanding of the solvent effect on SAM structures and may help us to better control and design new SAMs for future applications of molecular devices.

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