[Article]

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基于全氟酞菁铜和碗烯双分子体系在银和石墨表面自组装行为的低温扫描隧道显微镜研究

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摘要: 由于其独特的分子构型和电子结构, 碗烯被认为是组成有机分子电子器件的一种重要的结构单元。在不同金属表面上单一组分的碗烯或其衍生物进行自组装的行为, 及其所形成自组装薄膜的电子结构已经被广泛研究。这里我们利用低温扫描隧道显微镜(LT-STM), 对全氟酞菁铜和碗烯两种组分在高定向热解石墨和银(111)两种不同衬底上的自组装结构进行了报道。在石墨衬底上, 全氟酞菁铜和碗烯分子间形成的氢键成为双分子网络结构能够形成的关键; 同时, 由于这种分子间氢键的存在, 碗烯分子大多采取“开口朝下”的空间构型, 以保证分子间氢键最大限度的形成。但在银衬底上观察到的碗烯分子则随机采取“开口向上”或“开口向下”两种构型, 并没有一种优势构型的存在。我们认为此时银(111)衬底和有机分子间强烈的相互作用限制了碗烯两种构型之间的翻转, 使得碗烯分子一旦被吸附就只能保持其原本的构型, 从而导致了在结果上两种构型的随机分布。

关键词: 分子自组装; 双分子网络结构; 碗烯; 低温扫描隧道显微镜; 分子间氢键

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LT-STM Investigation of the Self-Assembled F₁₆CuPc-Corannulene Binary System on Ag(111) and Graphite Surfaces

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Abstract: Corannulene (COR) is considered a promising molecular building block for organic electronics owing to its intriguing geometrical and electronic properties. Intensive research efforts have been devoted to understanding the assembly behavior and electronic structure of COR and its derivatives on various metal surfaces *via* low-temperature scanning tunneling microscopy (LT-STM). Here we report the formation of binary molecular networks of copper hexadecafluorophthalocyanine ($F_{16}CuPc$)-COR self-assembled on the highly oriented pyrolytic graphite (HOPG) and Ag(111) substrates. Intermolecular hydrogen bonding between $F_{16}CuPc$ and COR facilitates the formation of binary molecular networks on HOPG and further induces a preference for bowl-down configured COR molecules. This observed configuration preference disappears on Ag(111) substrate, where COR molecules lie on the substrate with their bowl openings pointing up and down randomly. We propose that strong interfacial interactions between the molecule and Ag(111) surface constrain the bowl inversion of the COR molecule, which thus retains its initial configuration upon adsorption.

Key Words: Molecular assembly; Binary molecular networks; Corannulene; Low-temperature scanning tunneling microscopy; Intermolecular hydrogen bonding

1 Introduction

Corannulene (COR) is a bowl-shaped molecule and can be regarded as a fragment of fullerene, as shown in Fig. 1a. Since its first successful synthesis in 1966¹, COR has attracted intensive attention due to several intriguing properties. With fivefold symmetry, COR provides a unique opportunity to study the symmetry mismatching between adsorbate and substrate, given the incompatibility between the fivefold rotational symmetry of molecule and translational order of the underneath crystal lattice². The combination of non-planar shape and aromaticity makes COR an interesting system with unique geometry and electronic properties^{2c}. Specific π - π interactions between curved and planar structures give rise to fascinating photoelectric properties³. Buckybowls also serve as ideal hosts to form the host-guest complexes in supramolecular chemistry⁴. COR has always been regarded as a fragment of C_{60} molecule for its symmetry and conformation. But considering its high solubility in most common solvents^{2c}, COR can be a better choice than fullerenes as a promising candidate for acceptor materials in organic optoelectronic devices^{2c}. It should be mentioned that Kuvychko *et al.*⁵ have recently reported a COR derivative (with electron withdrawing groups) that has a higher electron affinity and thus can be a stronger electron acceptor than the well-studied C_{60} .

Two-dimensional (2D) self-assembly of functional organic molecules into ordered arrays represents one of the most promising strategies to fabricate functional molecular nanostructures over macroscopic areas⁶. Modification of metal surfaces with COR and its derivatives has been studied for symmetry mismatch between substrate and adsorbate^{2a,7}, multi-component packing^{4,8}, templated assembly^{8a,9}, interface dipole formation¹⁰, as well as 2D phase transitions^{6c,11}. The assembly behaviors of the single-component molecules with fivefold symmetry on surface are of fundamental interest¹². The structure of self-assembled COR monolayer on Cu(111) and Cu(110) has been reported. On Cu(111), each COR molecule adsorbs on either fcc or hcp threefold hollow site with its bowl opening pointing up^{11b}. One of the five hexagonal rings orients parallel to the surface plane and therefore a tilt between molecular bowl with respect to the surface exists. A tem-

perature-controlled reversible phase transition was also observed in this system. It is explained that low temperature constrains the vibration of COR molecules, thus leads to a more effective intermolecular attraction, and finally results in the transition to the phase with higher packing density^{11b}. On Cu(110), a similar quasi-hexagonal lattice with slightly tilted COR molecules was observed^{2a}. In addition to monolayer, a bilayer bowl-in-bowl stacking structure of COR was also reported on Cu(111) at low temperature¹³. Each second-layer molecule locates directly above one first-layer molecule, leading to the formation of a bowl-in-bowl dimer.

In contrast to the intensive studies on single component self-assembly of COR and its derivatives, investigation on multi-component molecular assembled system consisting of COR is rarely reported. Multicomponent 2D assemblies provide more functionality and tunability for the molecular nanostructures¹⁴. Calmettes *et al.*^{8a} reported binary molecular networks comprising 2,3,9,10,16,17,23,24-octachlorozinc phthalocyanine ($ZnPcCl_8$) and the COR derivative of 1,3,5,7,9-penta-tert butylcorannulene (PTBC). In this case, the metastable phase of $ZnPcCl_8$ can be used as a flexible template to realize the controllable insertion of PTBC molecule. By selecting different phases formed by $ZnPcCl_8$, the final bimolecular 2D structure, which resembles the original packing of template, can be regulated. Xiao *et al.*⁴ reported a COR- C_{60} buckybowl-buckyball host-guest complexes by depositing C_{60} onto the ordered monolayer of COR on Cu(110). The concave structure of COR is optimal to realize a "face-to-face" contact with the convex surface of C_{60} and their complementary electron environments are favorable for binding. *Via* thermal activation, a strongly bound COR- C_{60} host-guest system is formed. Delicate balance between various intermolecular and interfacial interactions plays essential role in tailoring these supramolecular structures^{6b,8a,14a,15}.

Herein we report the formation of self-assembled binary molecular networks of COR and copper hexadecafluorophthalocyanine ($F_{16}CuPc$) on the highly oriented pyrolytic graphite (HOPG) and Ag(111). The geometrical arrangements of the binary system on different substrates were systematically investigated by low-temperature scanning tunneling microscopy/spectroscopy (LT-

STM/STS).

2 Experimental methods

The Ag(111) and HOPG single crystal substrates are purchased from MaTeck Material-Technologie & Kristalle GmbH. The F₁₆CuPc molecules are twice sublimed and purchased from CREAPHYS. Both sample preparation and investigation were performed in an ultrahigh vacuum system at a base pressure around 10^{-10} mbar (1 mbar = 101 Pa). The Ag(111) surface was prepared *via* repeated cycles of sputtering by Ar⁺ and then annealing to 750 K. Freshly cleaved HOPG was thoroughly degassed in UHV at 800 K overnight. COR and F₁₆CuPc were thermally evaporated from separate Knudsen cells at 380 and 670 K, respectively, onto the substrate (kept at room temperature).

In-situ STM investigation was carried out in a custom-designed Omicron LT-STM with an electrochemically etched tungsten tip scanning at 77 K. All STM images were obtained under constant current mode with bias voltages applied to the tip. To collect the differential conductance dI/dV (local density of states), a lock-in technique was adopted together with a modulation voltage of 50 mV and a frequency of 625 Hz. When ramping the voltage, the feedback loop was opened¹⁶.

3 Results and discussion

F₁₆CuPc, as shown in Fig.1b was first deposited onto HOPG to form a self-assembled monolayer. STM image (Fig.1c) clearly

reveals a typical close packing structure where F₁₆CuPc molecules lie flat on substrate with their molecular planes parallel to the substrate, arising from the interfacial π - π interaction¹⁷. A unit cell with $a = 1.66$ nm, $b = 3.5$ nm, $\theta_1 = 108^\circ$ is outlined in Fig.1c and schematic packing model of one unit cell is shown in Fig.1d. Two different molecular orientations exist in F₁₆CuPc monolayer on HOPG, which has been concretely analyzed in previous report¹⁷. In one unit cell, the orientation of four F₁₆CuPc molecules on the corner is deviated from that of two F₁₆CuPc molecules centered at the b edge. Then COR molecules were evaporated onto the F₁₆CuPc covered HOPG. Co-assembly of F₁₆CuPc and COR, as shown in Fig.1e and 1f, forms a long range-ordered structure with an intermixing ratio of 1 : 2. A unit cell with $c = 2.87$ nm, $d = 2.17$ nm, $\theta_2 = 114^\circ$ is highlighted in Fig.1f and the schematic packing model of one unit cell is shown in Fig.1g. It is noteworthy that in the supramolecular structure, only one orientation of F₁₆CuPc molecule is observed and each F₁₆CuPc molecule is surrounded by 6 COR molecules.

Here we observe two kinds of dots around F₁₆CuPc, including the dots that are brighter and the dots that are slightly darker. We propose both kinds of dots are COR molecules but with different configurations: bowl opening pointing up and pointing down. STS measurements (Fig.2b) confirm this assumption and reveals the highest occupied molecular orbital (HOMO)- the lowest unoccupied molecular orbital (LUMO) gap of around 3.10 eV, which agrees with the theoretically calculated HOMO-LUMO gap of COR molecule¹⁸. The simulated topographic STM images of COR,

Fig.1 Molecular structures for (a) COR and (b) F₁₆CuPc; (c) STM image of F₁₆CuPc monolayer deposited on HOPG; (d) schematic packing structure for F₁₆CuPc molecule on HOPG; (e, f) STM images of long range-ordered binary molecular networks formed by F₁₆CuPc and COR with a molecular ratio of 1 : 2 on HOPG; (g) schematic packing model for the F₁₆CuPc-COR binary structure on HOPG

In figure c: The unit cell is highlighted with $a = 1.66$ nm, $b = 3.5$ nm, $\theta_1 = 108^\circ$. $V_{\text{tip}} = 1.654$ V, $20 \text{ nm} \times 20 \text{ nm}$. In figures e, f: The COR molecules adopting the bowl up and bowl down configurations are indicated by the arrows. The unit cell is highlighted in the image with $c = 2.87$ nm, $d = 2.17$ nm, $\theta_2 = 114^\circ$.

$V_{\text{tip}} = 1.496$ V, $20 \text{ nm} \times 20 \text{ nm}$; $V_{\text{tip}} = 1.496$ V, $10 \text{ nm} \times 10 \text{ nm}$

Fig.2 (a) High resolution STM image of the $F_{16}CuPc$ -COR binary molecular networks on HOPG; (b) dI/dV spectra recorded on the bowl-up and bowl-down COR molecules

based on semi empirical extended Hückel calculation, have been used to determine the configuration of adsorbed COR by Parschau *et al.*^{2a}. For bowl up configuration, both the HOMO and LUMO topographic simulated images show a density minimum at the center of the molecule together with a distinct fivefold doughnut shape. On the contrary, for bowl down configuration, both the HOMO and LUMO topographic simulated images show a density maximum at the center of the molecule and the outline of COR molecule is rather vague^{2a}. Hence by comparing the simulated STM image with our high resolution STM results in Fig.2a, we assign these brighter dots to COR with bowl opening down and darker dots to COR with bowl opening up.

It is noticed that in the $F_{16}CuPc$ -COR binary molecular networks on HOPG, COR molecules that adopt bowl-down configuration hold majority. We propose that this configuration preference may arise from the formation of multiple intermolecular hydrogen bonding. As $F_{16}CuPc$ molecules lie flat on the plane, peripheral hydrogen atoms of COR molecule with bowl-down configuration can stand closer to the neighboring $F_{16}CuPc$, which facilitates the formation of multiple intermolecular hydrogen bonding between neighboring $F_{16}CuPc$ and COR. In this way, the binary supramolecular structure is effectively stabilized and bowl-down configuration of COR thus is energetically favorable.

We also grew the same $F_{16}CuPc$ -COR binary system on Ag(111) to compare the co-assembly structures on different substrates. Ag (111) has shown much stronger molecule–substrate interactions for various organic adsorbates¹⁹, compared with HOPG. Hence we were able to grow a monolayer of COR onto Ag(111). A large scale and the corresponding close up STM images of COR on Ag (111) are shown in Fig.3(a, b) with a unit cell outlined ($e = 1.02$ nm, $f = 1.17$ nm, $\theta_3 = 73^\circ$). Each COR molecule is shared by four unit cells (Fig.3c). Likewise, we observe brighter and slightly darker dots in the STM image of COR monolayer. Careful inspection of high-resolution STM (Fig.3d) confirms the co-existence of COR molecules with different configurations. Herein the brighter dot obviously has an intensity minimum in the center. Hence by using the aforementioned comparison of high-resolution STM images with simulated results, these brighter dots should be assigned to COR molecules with bowls opening up and the darker and vague dots should be COR molecules with bowls opening down.

To further confirm our assignment, a comparison of the brighter dots on HOPG and Ag(111) under high-resolution STM is shown in Fig.4. It is obvious that in Fig.4a, the COR molecule with bowl-up configuration possesses a hollow center with a rough pentagonal doughnut shape, which is consistent with features of the

Fig.3 (a) Large scale STM image of COR monolayer deposited on Ag(111); (b) close up STM image of COR on Ag(111); (c) proposed schematic packing model for COR on Ag(111); (d) high resolution STM image of COR on Ag(111) with the bowl-up and bowl-down configurations indicated by red arrows

In figure a: $V_{tip} = 1.0$ V; 60 nm $\times$ 60 nm. In figure b: The unit cell is highlighted by the red rhombus with $e = 1.02$ nm, $f = 1.17$ nm, $\theta_3 = 73^\circ$; $V_{tip} = 1.0$ V, 10 nm $\times$ 10 nm. In figure d: $V_{tip} = -1.5$ V; 6 nm $\times$ 6 nm

Fig.4 Comparison of the brighter dots under high-resolution STM

- (a) COR molecule with bowl-up configuration on Ag(111);
(b) COR molecule with bowl-down configuration on HOPG

Fig.5 (a) High resolution STM image of $F_{16}CuPc$ -COR binary molecular networks on Ag(111) with a molecular ratio of 1 : 4; (b) schematic packing model for the $F_{16}CuPc$ -COR binary structure on Ag(111)

In figure a: The unit cell is highlighted by the red rhombus with $g = h = 2.73$ nm, $\theta_4 = 100^\circ$. $V_{tip} = 1.26$ V, $10 \text{ nm} \times 10 \text{ nm}$

simulated bowl-up COR. While in Fig.4b, the COR molecule accounted as bowl-down configuration is more protruding in the center and the molecule shape is obscure, which also resembles simulated bowl-down topography. We noted that on Ag(111) substrate, the configuration preference of COR disappears: both bowl-up and bowl-down COR exist in almost equal amount. In other words, the adoption of bowl-up or bowl-down configuration is random. We suggest that the strong COR-Ag(111) interfacial interaction constrains the movement and bowl inversion of COR molecules. Once adsorbed on Ag(111), COR molecule could only retain its initial configuration and therefore both configurations have equal chance to appear.

Co-assembly monolayer of $F_{16}CuPc$ and COR on Ag(111) was also prepared by further evaporating $F_{16}CuPc$ molecules onto the COR covered substrate. STM image reveals the long range-ordered binary molecular networks with a molecular ratio of 1 : 4. The unit cell is outlined in Fig.5a with features including $g = h = 2.73$ nm and $\theta_4 = 100^\circ$. Corresponding schematic packing model for the binary structure is shown in Fig.5b. All the $F_{16}CuPc$ molecules lie in the same orientation and each $F_{16}CuPc$ molecule is surrounded by 8 COR molecules.

4 Conclusions

In summary, we have investigated the binary supramolecular structure of $F_{16}CuPc$ -COR monolayer assembled on HOPG and Ag(111) substrates. The formation of multiple intermolecular hydrogen bonding between $F_{16}CuPc$ and COR could result in a preferred bowl-down configuration for COR molecules on the weakly interacting HOPG. In contrast, this configuration preference disappears on Ag(111) substrate where the adoption of bowl-up or bowl-down configuration is random, resulting from the strong molecule-substrate interactions. Our work would further reinforce the modification of surface with binary molecular networks consisting of COR and its derivatives.

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