

Template-Induced Inclusion Structures with Copper(II) Phthalocyanine and Coronene as Guests in Two-Dimensional Hydrogen-Bonded Host Networks

Jun Lu,[‡] Sheng-bin Lei,[†] Qing-dao Zeng,[†] Shi-zhao Kang,[†] Chen Wang,^{*,†} Li-jun Wan,^{*,†} and Chun-li Bai^{*,†}

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, People's Republic of China, and Graduate School of Chinese Academy of Sciences, Beijing, China

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Hydrogen-bonded two-dimensional networks of 1,3,5-tris(10-carboxydecyloxy) benzene (TCDB) were formed on the surface of highly oriented pyrolytic graphite (HOPG). With these networks as host networks and copper(II) phthalocyanine (CuPc) and coronene as guest molecules, the host–guest architectures of CuPc/TCDB and coronene/TCDB were achieved when host and guest molecules coadsorb on HOPG. The monolayer structure of the networks of TCDB and the inclusion structures of host–guest systems were investigated by STM.

Advances in techniques for the nanoscale manipulation of molecules are of great importance in the realization of molecule-based miniature devices with new or advanced functions.^{1–4} Atom-by-atom crafting of structures with scanning tunneling microscopes (STM),^{5,6} although essential to fundamental advances, is yet to develop into an effective tool for any practical fabrication process. Molecular self-assembly is the spontaneous association of molecules into stable, structurally well-defined aggregates joined by noncovalent bonds. It provides unique routes to obtain highly organized nanoscale supramolecular structures.^{7–9} Recent STM studies revealed that at well-defined surfaces direct insight into self-assembly phenomena in two dimensions can be gained.^{10–12} Systematic investigations in this field may eventually lead to recipes for deliberate construction of supramolecular geometries at nanoscale. Nevertheless, up to date, two-dimensional self-assembly approaches lack the ability to control growth sites and geometry. Here we report a new approach for fabricating nanoscale organic structures on solid substrates, employing self-assembled two-dimensional networks as hosts to construct nanoarrays of copper(II) phthalocyanine (CuPc) and coronene on highly oriented pyrolytic graphite (HOPG). Control of growth sites and geometry in this self-assembly process was achieved by template networks.

Molecular semiconductors, such as coronene and other aromatics, phthalocyanines, porphyrins and charge-transfer systems, have been widely investigated during the past decades because of their unique electronic and optoelectronic properties. They have been used to set up organic transistors,¹³ solar cells,¹⁴ or information storage systems,¹⁵ etc. Coronene can be considered as the smallest possible flake of a graphite sheet saturated by hydrogen atoms; on the other hand, coronene is one of the most complex molecules encountered in interstellar space and possibly plays a basic role in interstellar extinction.¹⁶ The use of thin films of phthalocyanine compounds has attracted considerable interest in recent years due to their potential

applications as photoconductors, electronic devices, and gas sensors.^{17–19} Therefore, the knowledge of their structural and electronic behavior as molecular adsorbates on well-defined substrates is of genuine interest. But until now, most of these studies have been carried out in a ultrahigh vacuum²⁰ or in solution.²¹ To our knowledge, there is no report on highly ordered molecular monolayers of coronene on HOPG performed in ambient conditions. In the case of CuPc, we have reported the stabilization effect of alkane buffer layer on formation of nanometer-sized metal phthalocyanine domains.²² In addition, we have demonstrated Pc insertions in the domain boundaries of self-assembled monolayer of octa-alkoxyl-substituted phthalocyanine (PcOC₈).²³ Only sporadically distributed Pc molecules were found entrapped inside the PcOC₈ networks.

We have previously reported the hydrogen-bonded two-dimensional hexagonal networks²⁴ formed by adsorption of 1,3,5-tris(carboxymethoxy) benzene (TCMB) on HOPG. To make the networks controllable in cavity size and shape by changing the length of the alkyl chains, we have synthesized another triple-armed amphiphile, 1,3,5-tris(10-carboxydecyloxy) benzene (TCDB) (the molecular structure is shown in Figure 1a). Experiments show that TCDB also forms two-dimensional networks but with tetragonal cavities with inner widths of 2.3 nm × 1.3 nm. Here we use the networks formed by TCDB as the template to achieve inclusion of CuPc and coronene (molecular structures of them are shown in parts b and c of Figure 1, respectively) on the surface of HOPG.

TCDB was synthesized by a method similar to that of TCMB.²⁴ The details of the synthesis and characterization of the compound can be found in the Supporting Information.

Prior to imaging TCDB networks, TCDB was dissolved in toluene with concentration less than 1 mM. Samples were prepared by depositing a droplet of the above solution on freshly cleaved HOPG. After evaporation of the solvent, experiments were performed with a Nanoscope IIIA system (Digital Instrument, Santa Barbara, CA) operating in ambient conditions. STM tips were mechanically formed Pt/Ir wire (90/10). All the STM images were recorded using the constant current mode of operation. The specific tunneling conditions are given in the

* To whom correspondence may be addressed. E-mail: wangch@iccas.ac.cn (C.W.); wanlijun@iccas.ac.cn (L.-j.W.); clbai@iccas.ac.cn (C.-l.B.).

[†] Chinese Academy of Sciences.

[‡] Graduate School of Chinese Academy of Sciences.

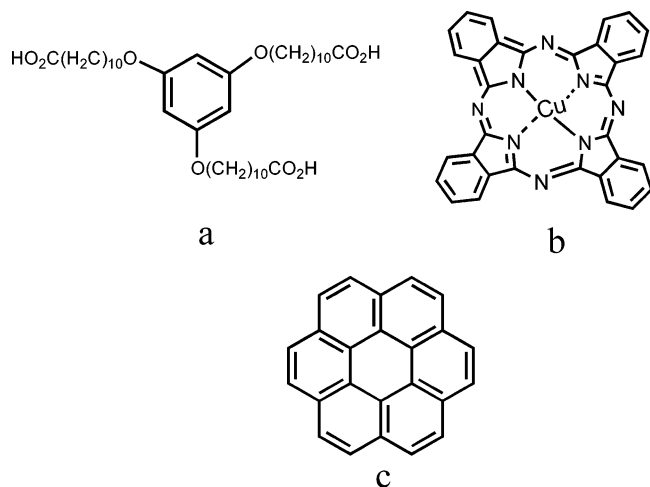


Figure 1. Molecular structures of (a) TCDB, (b) CuPc, and (c) coronene.

figure captions. As to the imaging of the assemblies of CuPc and coronene, the mixture of TCDB and CuPc and the mixture of TCDB and coronene were dissolved in toluene. Other conditions are the same as in the case of TCDB networks.

Figure 2a is a large-scale STM image, in which tetragonal cavities are aligned in well-ordered columns. Except for a very few tetragonal cavities filled by impurities, nearly all the tetragonal cavities are empty. More details of the networks structure are revealed in the high-resolution image Figure 2b. There are bright spots and some chains between the spots in

Figure 2b. The bright spots are the benzene cores of TCDB, while the chains are the alkyl chains (ending with a carboxylic acid) attached to the core. A tetragonal cavity is formed by the alkyl chains connected by hydrogen bonds from two TCDB molecules. That is to say the formation of dimer of TCDB causes the cavity. The inner width of the cavity is $m = 2.3 \pm 0.1$ nm and $n = 1.3 \pm 0.1$ nm. A model of a dimer is superimposed on the image. The image and the model fit well with each other. The dimer formation is demonstrated schematically in Figure 2c. The circle represents the benzene core of TCDB, while the three curves attached to the circle represent the three long alkyl chains. Two carboxylic groups of a TCDB form four hydrogen bonds with the two carboxylic groups of another TCDB molecule. Therefore, these two hydrogen-bonded TCDB molecules form a dimer. A unit cell is also superimposed on the image in Figure 2b with $a = 4.3 \pm 0.2$ nm, $b = 2.2 \pm 0.1$ nm, and $\alpha = 69.8 \pm 2.9^\circ$. A unit cell includes two molecules of TCDB. Figure 2d is an array of molecular models suggested on the basis of STM observation using Hyperchem Pro 6.0 software. It shows TCDB molecules form two-dimensional networks through hydrogen bonding.

The tetragonal cavity of the networks of TCDB reminds us that it could be used as two-dimensional hosts to construct two-dimensional molecular host–guest architectures. The tetragonal cavity size of the TCDB networks is large enough for the purpose of templates to trap some functional molecules of appropriate size. At first we have tried to introduce CuPc and coronene into the networks because of their significance in surface science.

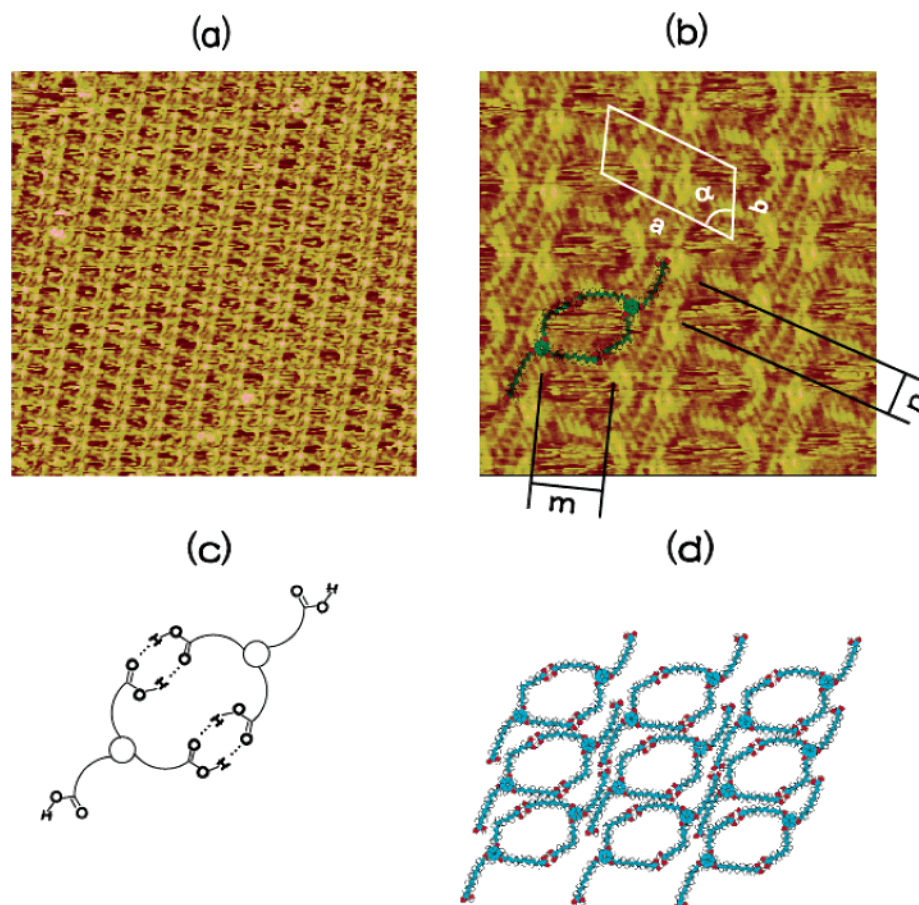


Figure 2. (a) STM image ($46.4 \text{ nm} \times 46.4 \text{ nm}$) of a self-assembled monolayer of TCDB networks on HOPG surface. The imaging conditions are $I = 758 \text{ pA}$ and $V = 606 \text{ mV}$. The z axis is 0.4 nm . (b) A higher-resolution STM image ($12.4 \text{ nm} \times 12.4 \text{ nm}$) of TCDB networks. The imaging conditions are $I = 614 \text{ pA}$ and $V = 666 \text{ mV}$. The z axis is 0.4 nm . (c) A schematic picture to show the formation of a dimer. (d) Formation of tetragonal networks by the hydrogen bonding of dimers.

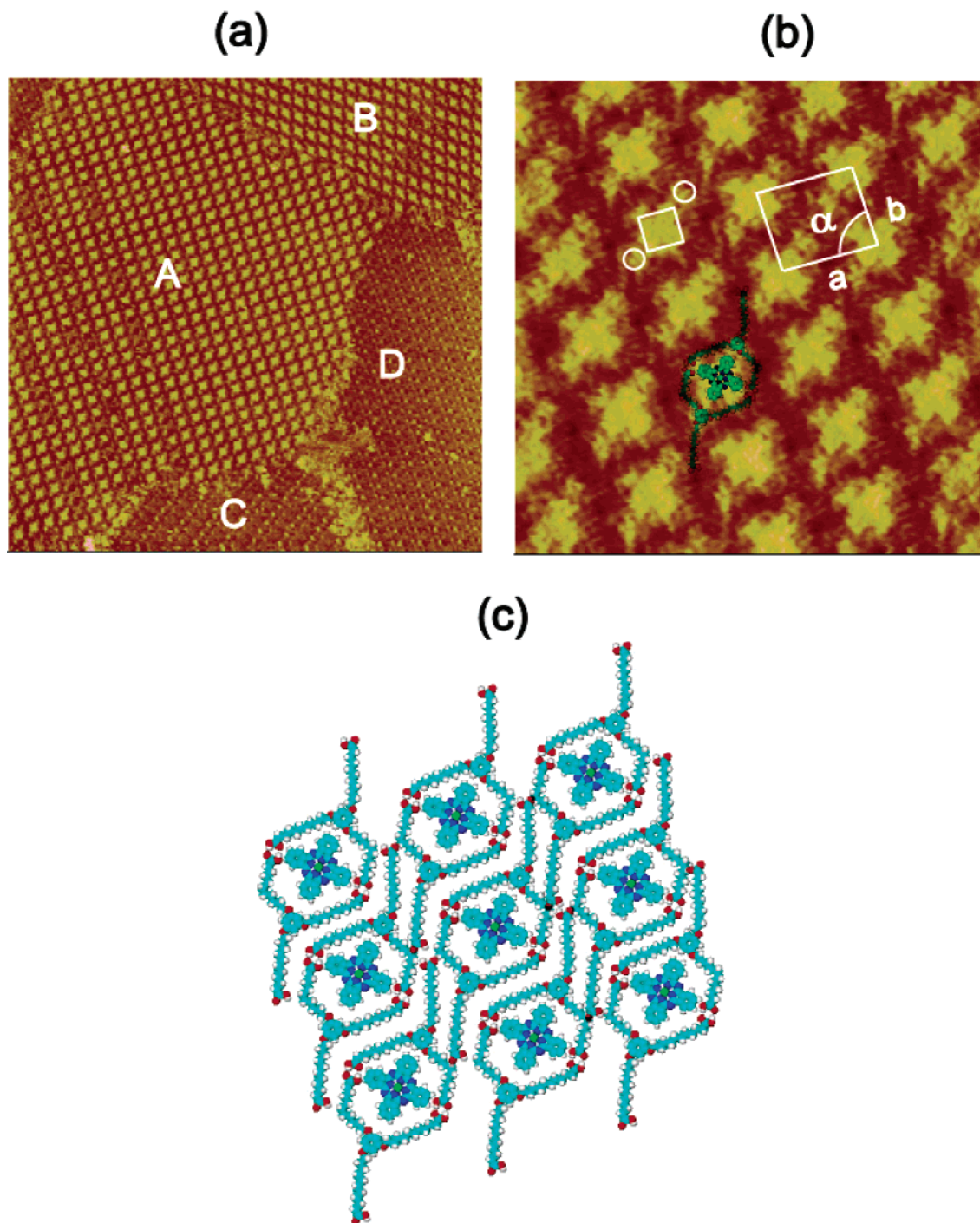


Figure 3. (a) STM image ($86.4 \text{ nm} \times 86.4 \text{ nm}$) of TCDB networks and CuPc/TCDB host-guest architecture. The imaging conditions are $I = 853 \text{ pA}$ and $V = 700 \text{ mV}$. The z axis is 0.5 nm . (b) A higher-resolution STM image ($13.2 \text{ nm} \times 13.2 \text{ nm}$) of CuPc/TCDB host-guest architecture. The imaging conditions are $I = 853 \text{ pA}$ and $V = 700 \text{ mV}$. The z axis is 0.5 nm . (c) Suggested molecular model for the formation of CuPc/TCDB host-guest architecture.

When CuPc molecules are entrapped in the cavities of TCDB networks, highly uniform arrays of host-guest architecture form in large areas covering whole domains. Figure 3a can be divided into four domains (A, B, C, and D). In domains A and B, the cavities are nearly fully occupied by CuPc molecules, while the cavities in domains C and D remain empty. The structure of these unoccupied domains is similar to the empty networks in parts a and b of Figure 2. This phenomenon suggests that spontaneous aggregation of CuPc molecules occurs in order to form host-guest architecture in the coadsorption process. The coincidence of the site and geometry of CuPc arrays with the TCDB networks cavities confirms the entrapment of CuPc

molecules into the TCDB networks. The more detailed inclusion structure is shown in Figure 3b. A unit cell is superimposed on the image with $a = 2.8 \pm 0.1 \text{ nm}$, $b = 2.2 \pm 0.1 \text{ nm}$, and $\alpha = 86.6 \pm 1.0^\circ$. Besides the unit cell, we have drawn two small white circles and one white square on the STM image of one CuPc entrapped in one cavity. The small circles are the benzene core of TCDB, while the white square represents CuPc. The long alkyl chains cannot be seen clearly because of large image contrast between the alkyl chains and the π electron enriched CuPc and benzene core of TCDB. A model of a CuPc molecule entrapped in a tetragonal cavity of TCDB is also superimposed on the STM image of Figure 3b. A suggested molecular model

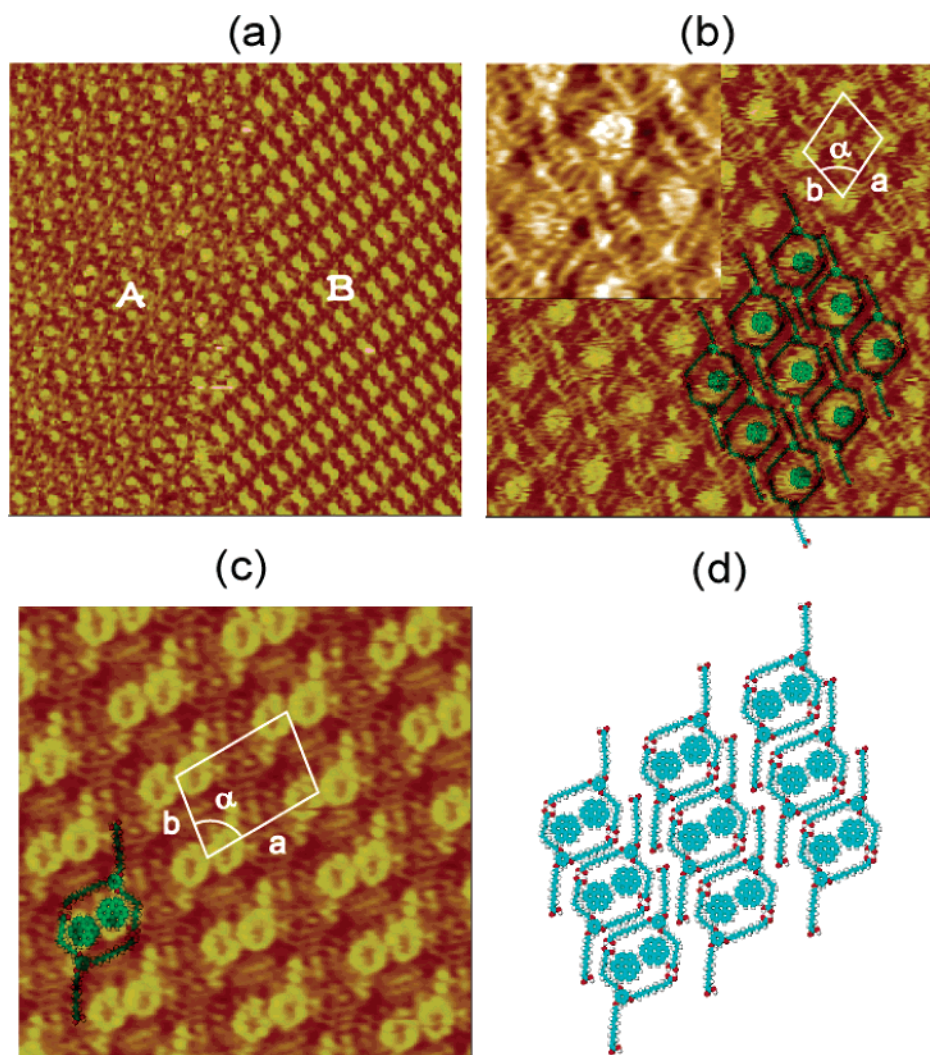


Figure 4. (a) Large-scale STM image ($45.5 \text{ nm} \times 45.5 \text{ nm}$) of coexistence of two kinds of coronene/TCDB host-guest architectures. The imaging conditions are $I = 963 \text{ pA}$ and $V = 600 \text{ mV}$. The z axis is 0.5 nm . (b) An STM image ($18.7 \text{ nm} \times 18.7 \text{ nm}$) of coronene/TCDB host-guest architecture (I). The imaging conditions are $I = 796 \text{ pA}$ and $V = 658 \text{ mV}$. The z axis is 0.4 nm . The area of the inset is $6.1 \text{ nm} \times 6.1 \text{ nm}$. (c) A high-resolution image ($11.8 \text{ nm} \times 11.8 \text{ nm}$) of coronene/TCDB host-guest architecture (II). The imaging conditions are $I = 671 \text{ pA}$ and $V = 700 \text{ mV}$. The z axis is 1.0 nm . (d) Suggested molecular model of coronene/TCDB host-guest architecture (II).

to illustrate the coadsorption structure is given in Figure 3c. The structure of the TCDB network changes slightly due to the inclusion of CuPc.

Presented in Figure 4 is the inclusion of coronene molecules in TCDB networks. Figure 4a covers an area of $45.5 \text{ nm} \times 45.5 \text{ nm}$. It is made up of two domains, A and B. In both domains, nearly all the cavities of TCDB networks are filled by coronene molecules. In domain A, one coronene molecule is entrapped in one cavity. While in domain B, each cavity of TCDB network is filled by two coronene molecules. Figure 4b is an image of host-guest architecture of one coronene per cavity, designated as coronene/TCDB host-guest architecture (I). The bright round spots are coronene molecules. Around the bright round spots are the less bright linear structures which can be attributed to alkyl chains of TCDB. A unit cell is placed upon the images with $a = 3.0 \pm 0.1 \text{ nm}$, $b = 2.4 \pm 0.1 \text{ nm}$, and $\alpha = 75.4 \pm 1.6^\circ$. At the top left of Figure 4b, an inset is given to show the details of this inclusion structure. It has been observed that the entrapped coronene molecule is not in the center of the cavity but rather positioned relatively randomly within the cavity. A molecular model is superimposed on the image. Because the cavity of TCDB networks (inner width is $2.3 \text{ nm} \times 1.3 \text{ nm}$) is not fully occupied by a single coronene

molecule (diameter is 0.9 nm), the coronene molecules cannot be totally stabilized within the cavity, thus having some free space to move in the cavities of the networks. The detailed structure of coronene cannot be imaged in high resolution by STM as it will be discussed in Figure 4c.

Presented in Figure 4c is a high-resolution image ($20.6 \text{ nm} \times 20.6 \text{ nm}$) of the host-guest architecture structure with two coronene molecules per cavity, designated as coronene/TCDB host-guest architecture (II). A unit cell is placed upon the image with $a = 3.4 \pm 0.1 \text{ nm}$, $b = 2.3 \pm 0.1 \text{ nm}$ and $\alpha = 84.3 \pm 2.6^\circ$. It can be seen that two coronene molecules lie side by side closely forming a dimer. The expected size of the dimer is about $0.9 \text{ nm} \times 1.8 \text{ nm}$, which is commensurate with the cavity size of TCDB networks. Therefore it can be stabilized firmly on HOPG by the networks. Thus, the detailed structure of coronene can be revealed by STM. Each coronene corresponds to a bright ringlike structure which has been reported earlier.^{21a} The distance of the coronene molecules in the dimer is $1.1 \pm 0.1 \text{ nm}$, which is in agreement with the lattice constant of closely packed coronene monolayer adsorbed on Ag(111) (lattice constant is 1.15 nm) in ref 20b and on HOPG (lattice constant is $1.1 \pm 0.1 \text{ nm}$) in ref 25b. Though the adsorption behavior of coronene on solid substrate has been widely investigated,^{20b,21b,25}

TABLE 1: Unit-Cell Parameters of TCDB Networks, CuPc/TCDB Host–Guest Architecture (Side Width of CuPc is 1.2 nm) and Coronene/TCDB Host–Guest Architectures (I and II) (Diameter of Coronene is 0.9 nm)

	TCDB	TCDB/ CuPc	TCDB/ Coronene(I) ^a	TCDB/ Coronene(II) ^b
<i>a</i> (nm)	4.3 ± 0.2	2.8 ± 0.1	3.0 ± 0.1	3.4 ± 0.1
<i>b</i> (nm)	2.2 ± 0.1	2.2 ± 0.1	2.4 ± 0.1	2.3 ± 0.1
α (deg)	69.8 ± 2.9	86.6 ± 1.0	75.4 ± 1.6	84.3 ± 2.6

^a One coronene molecule per tetragonal cavity of TCDB. ^b Two coronene molecules per tetragonal cavity of TCDB.

there is only one report^{20b} on the formation of dimer of coronene on Ag(111). In that work,^{20b} due to the substrate-mediated interaction, the average distance of molecular dimers is 2.4 nm, which is more than twice the next nearest-neighbor distance (1.15 nm) of close-packed monolayers because of the substrate-mediated interaction. The pair distance of the coronene dimer in our work is 1.1 nm, which is similar to lattice constant of closely packed coronene monolayer.^{20b,25b} A model of the two-dimensional host–guest unit is superimposed on the image. To show the adsorption structure more vividly, a model for the array structure is presented in Figure 4d.

One can find that the unit cell parameters of TCDB networks, CuPc/TCDB and two kinds of coronene/TCDB host–guest architectures, which are listed in Table 1, are rather different. It can be seen from the table that their unit cell parameters differ significantly in the *a* direction and in the angle, while the parameters in the *b* direction remain nearly the same. The tetragonal cavity inner size is 1.3 ± 0.1 nm in the *b* direction and 2.3 ± 0.1 nm in the *a* direction. When CuPc (side width is 1.2 nm) and coronene (diameter is 0.9 nm) are entrapped in the networks, the cavity size could be reduced due to van der Waals attraction between CuPc or coronene and the alkyl chains of TCDB networks along the *a* direction because 2.3 nm is much greater than 1.2 nm. But it is impossible for the cavity size to shrink in the *b* direction because 1.3 nm is nearly equal to the side width of CuPc. The variations in sides on the unit cell lead to the change in angle of the unit cell.

In summary, in this work, we have constructed hydrogen-bonded two-dimensional networks of TCDB on a solid substrate. With these networks as hosts, uniform arrays of CuPc/TCDB and coronene/TCDB host–guest architecture were successfully fabricated by using CuPc and coronene molecules as guests. The formed two-dimensional host networks and the inclusion structures could be reproducibly observed in large areas, indicating the high stability of these two-dimensional host–guest architectures.

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Supporting Information Available: Synthesis details of TCDB and more STM images of CuPc and TCDB and coronene and TCDB. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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