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## Host-Guest Architectures with a Surface Confined Imine Covalent Organic Framework as Two-Dimensional Host Networks

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

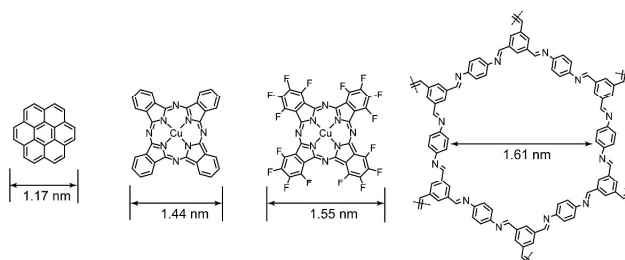
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**Two-dimensional covalent organic framework (2D COF), synthesized on highly oriented pyrolytic graphite (HOPG) surface with benzene-1,3,5-tricarbaldehyde and p-phenylenediamine as the precursors, is used as a host to accommodate three guest molecules, coronene, copper phthalocyanine (CuPc), and fluorin-substituted copper phthalocyanine (F<sub>16</sub>CuPc). The host-guest interaction and dynamic behavior were investigated by scanning tunneling microscopy and density functional theory.**

Two-dimensional nanoporous networks, which are generally surface-confined, are of fundamental importance and great interest due to their application as host network to incorporate functional molecular species in a spatially ordered manner, because of their nanometer-sized cavities of periodic pattern.<sup>1-10</sup> The commonly seen 2D networks employed as host matrix are those in which building units are connected by non-covalent interactions, such as van de Waals forces, metal-organic coordination, hydrogen bonding, etc.<sup>11-15</sup> On the one hand, the size and symmetry of some of the aforementioned flexible networks are adjustable with respect to the size and shape of the guest molecules,<sup>16</sup> which enriches the kaleidoscope of the host-guest composite arrangements on the solid surface; while on the other side of the coin, this kind of adjustability limits, to some extent, the specific recognition between host network and guest species. In order to improve the selectivity between host network and guest species, a more rigid network is in demand. By virtue of studies on surface reaction, an emerging group of 2D networks, known as surface supported covalent organic framework (surface COF), have been fabricated under both ultra-high-vacuum and ambient conditions through a variety of surface reactions, such as Ullmann coupling, boronic acid condensation, Schiff base

reaction, etc.<sup>17-21</sup> The covalent linkage between the building units renders more rigidity to the surface COF, which makes it an ideal host network in terms of selectivity towards guest species, as its size and shape is hardly influenced by the accommodation of guest molecule because of its intrinsic inflexibility.<sup>21,22</sup> Herein, benzene-1,3,5-tricarbaldehyde (BTA) and p-phenylenediamine (PDA) are employed as starting materials to construct, via surface Schiff base reaction, surface COF<sub>BTA-PDA</sub>, which is utilized as host network to investigate the surface COF-guest interactions.

Surface COF<sub>BTA-PDA</sub> was synthesized as previously reported.<sup>17</sup> Chemical structures of the host and guest molecules are shown in Scheme 1.



**Scheme 1** Chemical structures of the coronene, CuPc, F<sub>16</sub>CuPc and surface COF<sub>BTA-PDA</sub>. The sizes of the guests and pore are indicated.

For all three guest species used in this work, the host-guest architectures were readily constructed soon after a saturated solution of the guest molecule was deposited onto the HOPG surface with surface COF<sub>BTA-PDA</sub> pre-fabricated. The detailed structure of the composite architecture is presented in Fig. 1. As shown in Fig. 1a, when a saturated solution ( $\sim 5.5 \times 10^{-4}$  mol/L) of coronene was deposited, almost all the cavities are filled with coronene molecules which appear as fuzzy bright spots. Because the pore size of the surface COF<sub>BTA-PDA</sub> ( $1.6 \pm 0.1$  nm) is larger than that of the coronene (1.2 nm), but not large enough to accommodate two or more coronene molecules, the fuzzy bright spot is attributed to single coronene molecule entrapped in each cavity. Due to the high mobility, no submolecular detail can be revealed. In some rare

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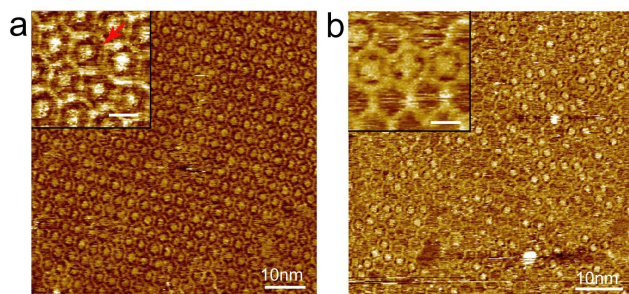
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cases dimmer linear features can be observed to coexist with coronene in the cavity (as highlighted with the red arrow in Fig. 1a, inset), which can be assigned to coadsorbed octanoic acids or imine oligomers.



**Fig. 1** Large-scale STM images showing the host-guest architectures formed between surface COF<sub>BTA-PDA</sub> and a) coronene, b) F<sub>16</sub>CuPc, respectively. High resolution images are shown in the inset in the upper-left corner of each image. The scale bars in the insets equal 2 nm. Tunneling conditions: V<sub>bias</sub> = 0.50 V, I<sub>set</sub> = 0.05 nA for all the images.

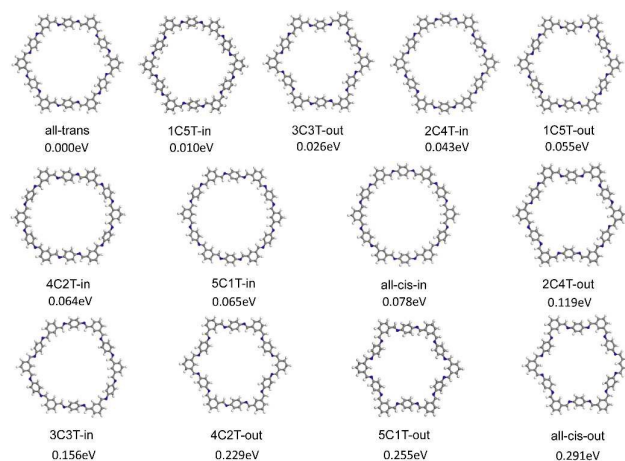
As to CuPc molecules (Fig. S1), similar to coronene, the surface COF<sub>BTA-PDA</sub> cavities are also filled with fuzzy bright spots which are denoted as CuPc molecules. Compared with the case of coronene, only a fraction (~13%) of host cavities are filled with CuPc molecules, and the CuPc molecules can fully occupy the space within the pores (Fig. S1, inset). The interaction between host lattice and guest species is mainly attributed to van der Waals forces. Given the fuzzy appearance of the CuPc molecules in the cavities, it can be concluded that van der Waals forces between the host network and CuPc molecules are not strong enough to stabilize the CuPc molecules, hence the mobility of the CuPc molecules in the cavities.

Different from coronene and CuPc, F<sub>16</sub>CuPc molecules can be better immobilized in the surface COF<sub>BTA-PDA</sub> as demonstrated in Fig. 1b. Identical to CuPc, F<sub>16</sub>CuPc molecules are entrapped in part of the surface COF<sub>BTA-PDA</sub> cavities. But instead of being fuzzy within the pores, F<sub>16</sub>CuPc molecules appear as a cross-shaped feature attributed to their skeleton structure, which means that F<sub>16</sub>CuPc molecules are well immobilized in the cavities, indicating stronger interactions between the host cavities and the guest species. Considering the peripheral fluorin-substitution of F<sub>16</sub>CuPc species, hydrogen bonds of F...H-C might be formed between the host lattice and F<sub>16</sub>CuPc molecules which serves to stabilize it within the host pores.

As discussed in our previous report<sup>17</sup>, the surface COF<sub>BTA-PDA</sub> consists mainly of hexagons, and also partly of pentagons and heptagons. In view of distinct degrees of filling and the size of guest molecules, it is plausible that the coronene molecules have no selectivity in terms of entrapment in the cavities. In other words, coronene molecules are readily accommodated in all the host cavities, regardless of the size and symmetry of the host pores (>99% of the cavities are filled). While when it comes to CuPc and F<sub>16</sub>CuPc, it is a totally different scenario in which CuPc or F<sub>16</sub>CuPc molecules are selectively entrapped in a portion of cavities, suggesting the influence of size and symmetry of the host pores on the selective entrapment of those guest molecules. A statistic on

the filling ratio of F<sub>16</sub>CuPc indicates that about 48% and 39% of the hexagon and heptagon cavities, while no pentagon cavities are filled. It should be noted that the higher filling ratio of coronene is due to its much higher concentration in comparison with F<sub>16</sub>CuPc in the saturated solution ( $5.5 \times 10^{-4}$  mol/L vs  $2.9 \times 10^{-8}$  mol/L). While when both guests present with equal concentration ( $1.2 \times 10^{-8}$  mol/L), only F<sub>16</sub>CuPc were observed in the surface COF<sub>BTA-PDA</sub> network (Fig. S2).

Though the high symmetric hexagonal cavities of the host lattice provide appropriate size for F<sub>16</sub>CuPc molecules to be entrapped in (Scheme 1), the diverse configurations of the surface COF<sub>BTA-PDA</sub> skeleton structures caused by the conformation of the imine moiety may influence the host-guest interaction, leading to selective filling of the network.<sup>23</sup> In order to prove this deduction, density functional theory (DFT) calculations were carried out. Periodic boundary condition (PBC) model was used for all calculations. For the optimization of host and host-guest calculations, the host and guest molecules are put in the centre of a relatively big super cell ( $60 \times 60 \times 20$  Å) to avoid interactions of the system with its images, and only gamma point was sampled in the Brillion zone, *i.e.* the PBC model was used to simulate isolate systems in this case. While for the adsorption of coronene, CuPc and F<sub>16</sub>CuPc, HOPG is replaced with graphene and  $3 \times 3 \times 1$  k-mesh was used in the optimization (For details see ESI).



**Fig. 2** Optimized structures of thirteen configurations and the relative energies of the hexagonal pore of surface COF<sub>BTA-PDA</sub> (top view).

A hexagon molecule consists of six p-phenylenediamine units are selected. When two hydrogen atoms in the imine moieties connected to one p-phenylenediamine are on different sides of the phenyl ring the unit conformation is defined as "trans", otherwise is named "cis". In view of two possible directions of hydrogen atoms of imine moiety to the COF pores, the cis unit can be further divided into cis-in or cis-out. Therefore, given the diverse conformation and orientation adopted by the imine moiety, a total of thirteen configurations were taken into account in this work, *i.e.*, all-trans(T), all-cis(C)-in, all-cis-out, 1C5T-in, 1C5T-out, 2C4T-in, 2C4T-out, 3C3T-in, 3C3T-out, 4C2T-in, 4C2T-out, 5C1T-in, and 5C1T-out. The structures and the relative energy of these thirteen

configurations (top view) were shown in Fig. 2, in which the planarity of all molecules is retained. The most stable conformation is all-trans and the most unstable one is all-cis-out. The overall trend is that the cis-imine units destabilize the COF, and with the same trans-cis combination, the "in-mode" is always more stable than the "out-mode". One obvious exception is 3C3T, and the main reason is that the alternative cis and trans units lower the energy of the COF. As presented in Fig. 2, with the increase of the cis units, the tension of the "out-mode" configuration is larger in energy than that of "in-mode", which results in the instability of the molecules. However, 3C3T-out and 1C5T-out are more stable than most of the "in-mode" COF conformations. It is not surprising because the 3C3T-out has higher symmetry (which makes the ring tension evenly distributed) while 1C5T-out and 1C5T-in bear much similarity in structure, which lowers their energy and makes them more stable than most "in-mode" COF.

The guest-substrate and host-guest interactions were also explored. Four high symmetric configurations including the most stable all-trans configuration were chosen as host to explore the host-guest interactions. The optimized structures of the host-guest architectures for the three guest molecules in the all-trans host cycle were displayed in Fig. 3 and the interaction energies are summarized in Table 1. After the introduction of those guest molecules, the pore expansion of the surface COF is small (less than 0.5%), especially for the coronene, suggesting high stability of the host matrix. Hydrogen bond and van der Waals forces contribute to the binding energy between the host and guest molecules. For the four configurations except the all-cis-in, most F-H distances in  $F_{16}CuPc$  (Fig. 3c and Fig. S4) fall in the range of hydrogen bonds, indicating the stronger interaction between the host and guest molecules than the other two cases. For all the configurations, the binding energy of the host-guest composite are in the order of  $F_{16}CuPc > CuPc > coronene$ . In addition, the guest-substrate interaction also follows the same order (Table 1). This order is in good accordance with the STM observation.

Table 1. Adsorption and host-guest interaction of coronene, CuPc and  $F_{16}CuPc$ . The unit of all the energies is eV.

	$F_{16}CuPc$	CuPc	coronene
$E_{\text{adsorption}}^a$	-3.03	-2.68	-1.41
$E_{\text{binding-All-trans}}^b$	-0.48	-0.22	-0.18
$E_{\text{binding-2C4T-out}}$	-0.57	-0.25	-0.17
$E_{\text{binding-4C2T-out}}$	-0.59	-0.23	-0.18
$E_{\text{binding-All-cis-in}}$	-0.32	-0.21	-0.17

<sup>a</sup> The adsorption energies between graphene and the molecules of coronene, CuPc, and  $F_{16}CuPc$  were evaluated by the following equation:  $E_{\text{adsorption}} = E_{(\text{G+molecules})} - E_{(\text{G})} - E_{(\text{molecules})}$ , where  $E_{(\text{G+molecules})}$  is the total energy of graphene with the molecules of coronene, CuPc, and  $F_{16}CuPc$  adsorbed, and  $E_{(\text{G})}$  and  $E_{(\text{molecules})}$  are the energies of isolated graphene and the molecules, respectively. <sup>b</sup> The binding energies ( $E_{\text{binding}}$ ) between host and guest molecules were defined as:  $E_{\text{binding}} = E_{(\text{host+guest})} - E_{(\text{host})} - E_{(\text{guest})}$ , where  $E_{(\text{host+guest})}$  is the total energy of the compound of the host and guest, and  $E_{(\text{host})}$  and  $E_{(\text{guest})}$  are the energies of the isolated COF<sub>BTA-PDA</sub> with various configurations and the molecules of coronene, CuPc, and  $F_{16}CuPc$ , respectively.

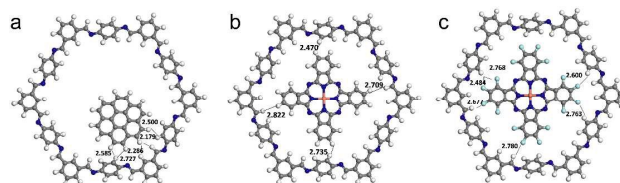


Fig. 3 Structure of the optimized molecular models for the host-guest architectures. a) COF-coronene, b) COF-CuPc, c) COF- $F_{16}CuPc$ .

Meanwhile, although the  $F_{16}CuPc$  molecules are well immobilized in the pores, the host-guest architecture does not maintain the status quo as illustrated in Fig. 4. Fig. 4a and 4b are two sequential STM images acquired on the same area, with the overlaid light cyan pentagon as the marker. It is clearly observable that the filled cavities marked by the white arrow heads in Fig. 4a, become empty in Fig. 4b, suggesting the desorption of the  $F_{16}CuPc$  molecules from within the host cavities. At the same time, filling of empty cavities can also be observed as indicated by the black arrow heads. All those phenomena lead to the conclusion that there exists a dynamic adsorption-desorption process between the host lattice and the  $F_{16}CuPc$  molecules, in spite of the hydrogen bonds formed between the two species.

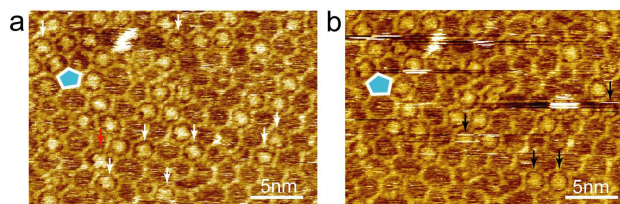


Fig. 4 Sequential high-resolution STM images illustrating the adsorption-desorption equilibrium between the host lattice and the  $F_{16}CuPc$  molecules. Tunneling conditions:  $V_{\text{bias}} = 0.50$  V,  $I_{\text{set}} = 0.05$  nA for both images. In (a) the red arrow indicates a  $F_{16}CuPc$  molecule immobilized in a open pore together with an imine oligomer.

Unlike the 2D networks interlinked by van der Waals forces or hydrogen bonds, whose structures and pore sizes are prone to be altered by the inclusion of guest molecules, the structures and pore sizes of the covalently linked surface COF can hardly be impacted by the accommodation of guest species, showing the stability and robustness of surface COFs to serve as host networks.

In summary, host-guest architectures are readily fabricated and observed on the HOPG surface between an imine surface COF and three guest species, namely, coronene, CuPc, and  $F_{16}CuPc$ . Coronene shows no selectivity in terms of entrapment in the host pores and, at high concentration, fills all the cavities with fuzzy appearance in the STM image, indicating the mobility of the coronene molecules within the pores. With good match of size and symmetry CuPc and  $F_{16}CuPc$  molecules are more stably entrapped in the hexagonal cavities. And due to the hydrogen bonds formed between the  $F_{16}CuPc$  molecules and the host pores,  $F_{16}CuPc$  shows strongest interaction with the host network and can be selectively entrapped when coexist with coronene. This study provide valuable information for the understanding of interaction between the surface confined 2D polymers and

guest species, and because of the well-known optoelectronic properties of metallophthalocyanine and the semi-conductive properties of the surface COF used here, the knowledge obtained in this work is beneficial for the design of nanosensors or nanoscale heterojunctions based on COF materials.

This work is supported by the National Science Foundation of China (21373070, 21572157), the Open Project of State Key Laboratory of Robotics and System (HIT) (SKLRS-2015-MS-11).

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<sup>†</sup>Electronic Supplementary Information (ESI) available: [Experimental and theoretical calculation details, extra STM images]. See

DOI: 10.1039/b000000x/

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