

Host-Guest Architectures with an Imine Covalent Organic Framework as Two-Dimensional Host Networks

Jiang Sun,^a Xin Zhou*^a and Shengbin Lei*^{ab}

MATERIAL AND METHODS

Benzene-1, 3, 5-tricarbaldehyde; *p*-Phenylenediamine; octanoic acid; dimethylsulfoxide (DMSO) were purchased from J&K and used without further purification. For preparation of surface COF_{BTA-PDA} at gas/HOPG interface, the monomers were first dissolved in DMSO with a mass concentration of 1 mg/g respectively. Then mixed the aromatic amine and aromatic aldehyde with the mol ratio about 3:1. Then the solutions were diluted 100 times. An amount of ~5 μL of the mixing solution was drop-cast on the freshly cleaved surface of HOPG. The drop-cast samples were positioned in a preheated vacuum oven at 140°C for ~30 min. Undergone this thermal treatment, the solvent, water, and other impurities were evaporated. The samples were taken out of the vacuum oven and cooled to room temperature, then characterized by scanning tunneling microscopy (STM).

The guest molecules were first dissolved in *n*-octanoic acid at room temperature (about 25°C), and directly used as a saturated solution, or diluted accordingly. The actual concentration of these solution were determined by UV-Vis spectrum. The sample was prepared by casting a droplet of the solution containing the guest species onto the HOPG surface on which the surface COF_{BTA-PDA} has already grown. The STM observations were carried out under ambient conditions by using an Agilent 5100 Scanning Probe Microscopy, and the tips were mechanically cut Pt/Ir (80/20) wires. All the STM images were recorded using constant current mode, and the specific tunneling conditions were illustrated in the corresponding figure captions. The calibration of STM images were carried out by using atomic resolution of HOPG lattice.

Details of Theoretical Calculations

Details of Theoretical Calculations

Spin-polarized DFT calculations have been performed within the generalized gradient approximation (GGA) and the periodic plane-wave approach, using the PBE exchange-correlation functional as implemented in Vienna ab initio simulation package.^{1,2} Periodic boundary condition (PBC) model was used for all calculations. For the host-guest calculations, the host and guest molecules are put in the centre of a relatively big super cell (60×60×20 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 F₁₆CuPc on graphene (HOPG is replaced with graphene in the calculation), 3×3×1 k-mesh was used in optimization. The unit cell of graphene is hexagonal with dimensions of $a = b = 24.6$ Å. For these two cases, uniform calculation parameters (cutoff, force and energy convergence) were used. The cutoff energy for the plane-wave basis was set as 500 eV, the energetic convergence threshold for self-consistent field was set at 1×10^{-5} eV/atom, and the atomic relaxation was carried out until all components of the residual forces were less than 0.01

eV/Å. As the important role of van der Waals (vdw) forces and hydrogen bond to the binding energy and adsorption energy for the host-guest and adsorption simulations, DFT-D2 approach consisting of a semi-empirical dispersion potential was added to the PBE functional to describe such weak interactions.³

The binding energies (E_{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 $\text{COF}_{\text{BTA-PDA}}$ with various configurations and the molecules of coronene, CuPc, and F_{16}CuPc , respectively.

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.

1. Host-guest architecture formed between surface $\text{COF}_{\text{BTA-PDA}}$ and CuPc

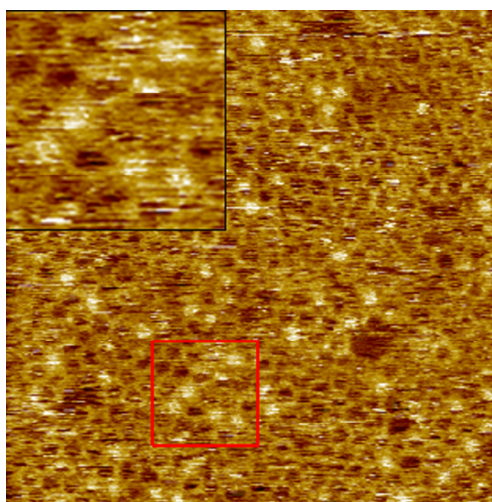


Fig. S1 Large-scale STM image showing the host-guest architecture formed between surface $\text{COF}_{\text{BTA-PDA}}$ and CuPc. Magnified view of the area marked by the red square is overlaid in the upper-left corner of the image. Image scale: $60 \times 60 \text{ nm}^2$. Tunneling conditions: $V_{\text{bias}} = 0.50 \text{ V}$, $I = 0.05 \text{ nA}$.

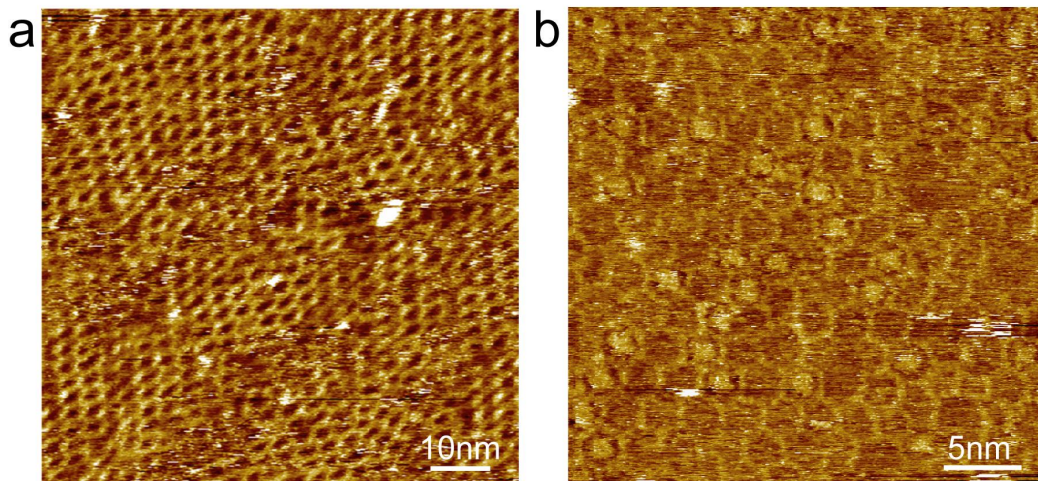


Fig. S2 (a) STM image show the empty surface $\text{COF}_{\text{BTA-PDA}}$ obtained with presence of 2.3×10^{-8} mol/L coronene, no coronene was observed in the pores of the network. (b) Host-guest architecture obtained with presence of 1.2×10^{-8} mol/L coronene and F_{16}CuPc . Tunneling conditions: $V_{\text{bias}} = 0.50$ V, $I = 0.05$ nA.

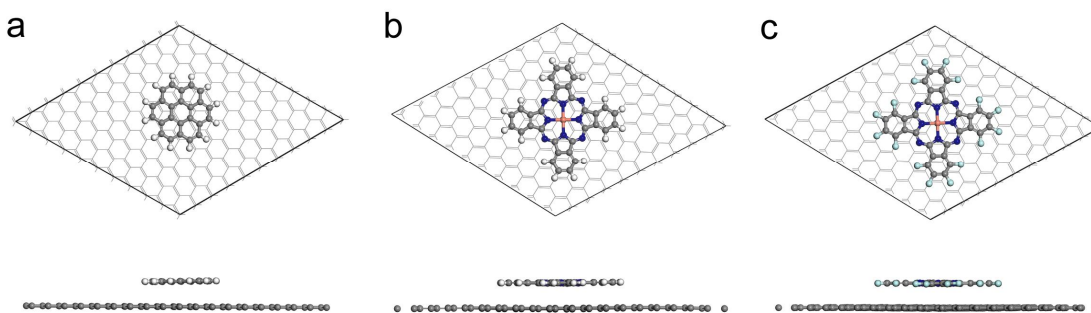


Fig. S3. Top and side view of the optimized conformation of coronene (a), CuPc (b) and F_{16}CuPc (c) on graphene.

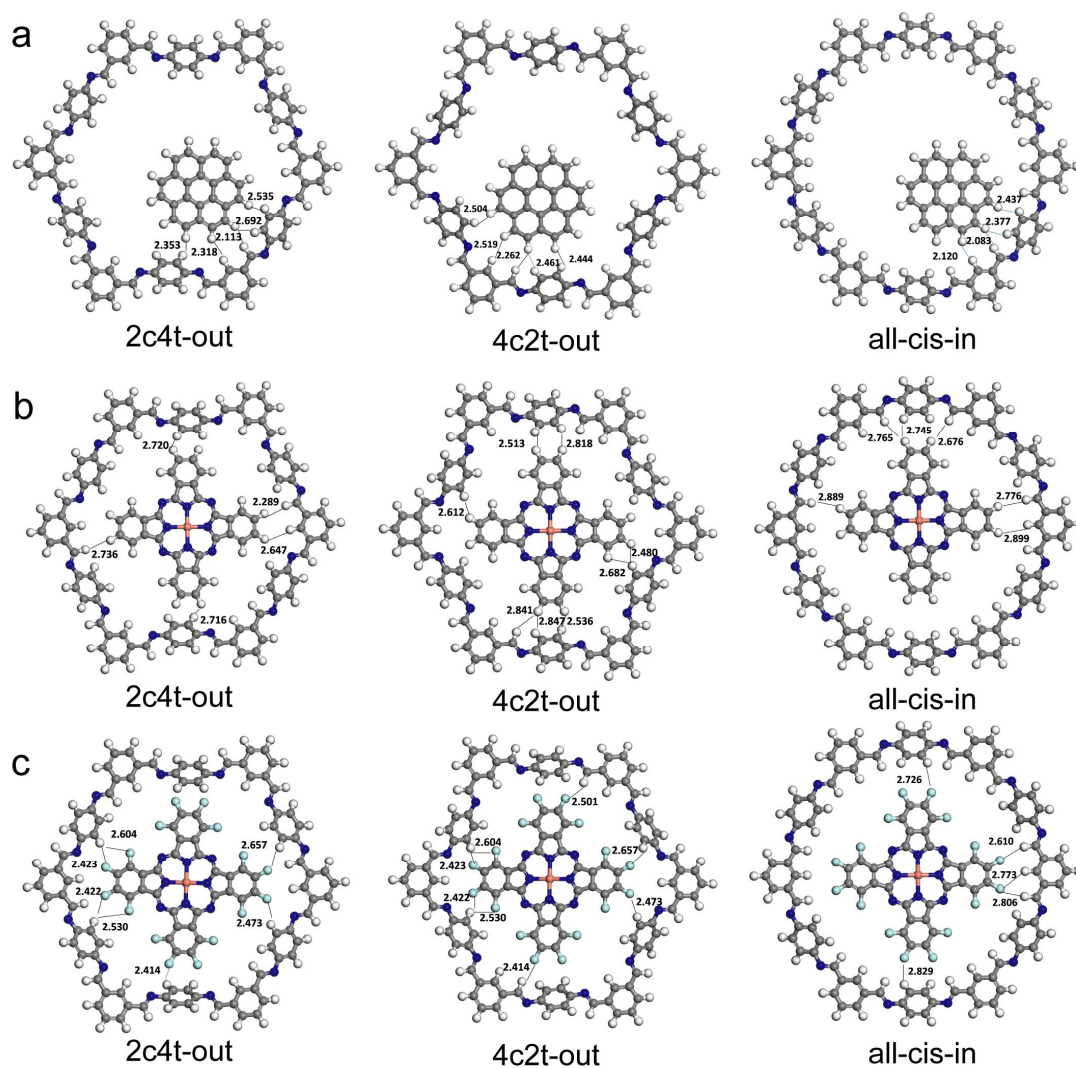


Fig. S4. Simulated host-guest architectures with other conformations of the host network. All the interaction energies are summarized in Table 1.

Notes and references

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
2. G. Kresse and Furthmuller, *J. Phys. Rev. B*, 1996, **54**, 11169.
3. X. Wu, M. C. Vargas, S. Nayak, V. Lotrich and G. Scoles, *J. Chem. Phys.* 2001, **115**, 8748.