

Molecular Dipole dot Arrays on Graphite

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Introduction

Organic molecular self-assembly structures are critical components for the construction of nanoscale electronic devices and biosensors. The preparation of such intermixed self-assembled molecular arrays is a main approach to the creation of functional devices and nanotemplates.

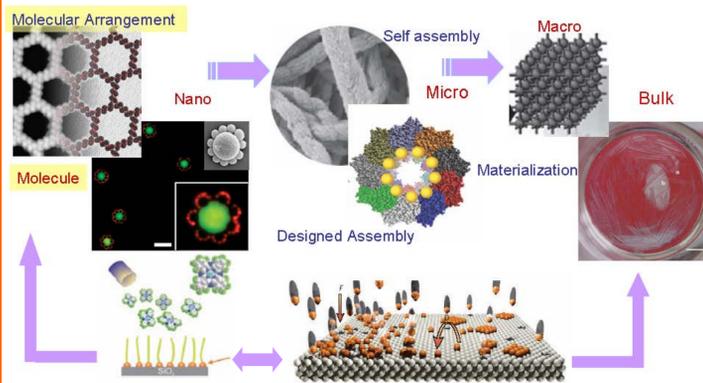


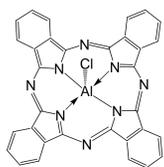
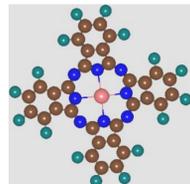
Fig 1. Strategies for material fabrication from molecules

Functional 2D Binary structures

Choice of species with functional groups give path to the fabricating of molecular arrays with novel properties. In this experiment, the supramolecular growth of binary F₁₆CuPc and CIAIPc monolayer with distinct structural ordered dipole arrays of different mixing ratios has been investigated by low-temperature scanning tunneling microscopy (LT-STM) on graphite surface.



Copper hexadecafluorophthalocyanine F₁₆CuPc



Chloroaluminum Phthalocyanine (CIAIPc)
permanent dipole P=1.87 debye

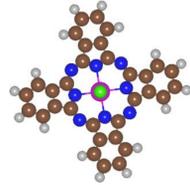


Fig 2. Formulas of F₁₆CuPc and CIAIPc

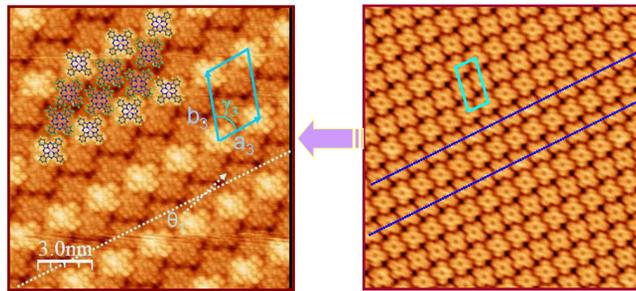
Methodology

LT-STM experiments were carried out in a custom-built multichamber ultrahigh vacuum system with base pressure lower than 6.0×10^{-11} mbar, housing an Omicron LT-STM. STM imaging was carried out in constant current mode with a chemically etched tungsten tip at 77K.

The F₁₆CuPc and CIAIPc are deposited from different knudsen cells at 605K and 560K respectively onto HOPG surface at room temperature in the UHV chamber.

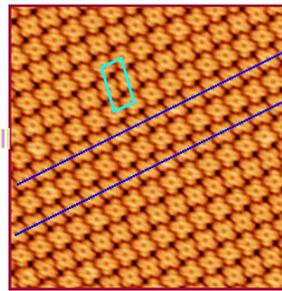
Deposition rates were measured by quartz crystal microbalance and further calibrated

Experimental Results

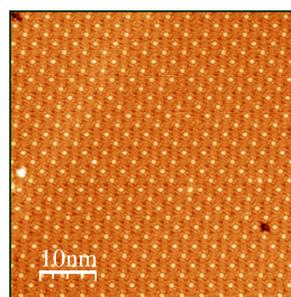


F₁₆CuPc and CIAIPc in a 2:1 ratio

Fig 3. STM image of the binary network of F₁₆CuPc and CIAIPc on HOPG with an intermixing ratio of 2:1; U = 2.4 V, I = 0.08nA, 15nm × 15nm)



Single component of F₁₆CuPc on HOPG



F₁₆CuPc and CIAIPc with intermixed ratio of 1:1

Fig 4. (a) Large scale STM image of the binary networks F₁₆CuPc:CIAIPc on HOPG with an intermixing ratio of 1:1. (b) Magnified STM image of 1:1 binary network. Scanning parameters: (a) U = 2.3 V, I = 0.09nA, 50nm × 50nm. (b) U = 2.1 V, I = 0.09nA, 15 nm × 15 nm.

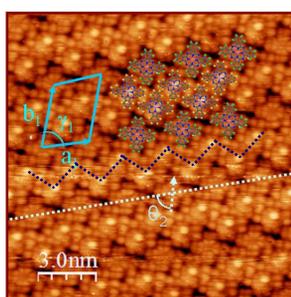
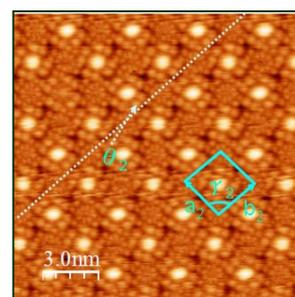
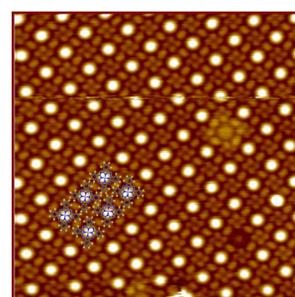


Fig 5. (a) High-resolution STM image of 1:2 binary network. Scanning parameters: U = 2.3V, I = 0.09nA, 15 nm × 15 nm. (b) STM image of CIAIPc monolayer on HOPG.



Molecular Dynamics

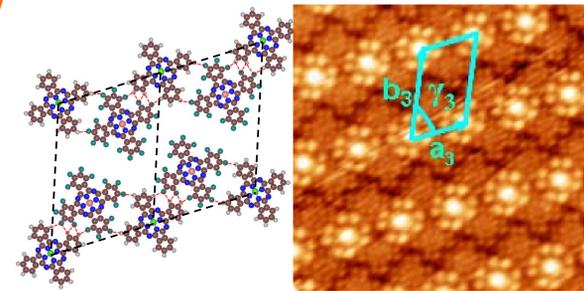


Fig 6. The MD snapshot of the binary network with 2:1 intermixing ratio. The optimized supercell is $a_3 = 23.28 \pm 0.2 \text{ \AA}$, $b_3 = 32.97 \pm 0.1 \text{ \AA}$, and $\gamma_3 = 70.17 \pm 0.5^\circ$. The red dashed lines indicate the possible intermolecular hydrogen bond.

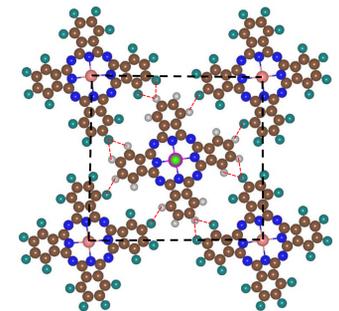


Fig 7. The snapshot of MD simulation of F₁₆CuPc and CIAIPc with intermixed ratio of 1:1. The optimized supercell indicated by black dashed lines is $a_2 = 21.09 \pm 0.3 \text{ \AA}$, $b_2 = 20.0 \pm 0.2 \text{ \AA}$, and $\gamma_2 = 89.5 \pm 0.8^\circ$. The red dashed lines indicate the possible intermolecular hydrogen bond.

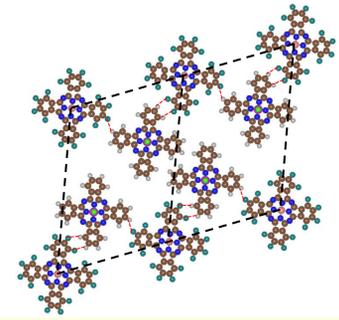


Fig 8. MD snapshot of 1:2 binary network. The optimized supercell as indicated by black dashed lines is $a_1 = 23.57 \pm 0.3 \text{ \AA}$, $b_1 = 33.68 \pm 0.01 \text{ \AA}$, and $\gamma_1 = 69 \pm 3^\circ$, in good agreement with experiments. The red dashed lines indicate the possible intermolecular hydrogen bond.

Conclusion

- ❖ Selectivity and directionality provided by hydrogen bonding in favourable situations, the molecular tectons are adsorbed in configurations promoting molecular recognition and formation of ordered nanostructures.
- ❖ The dipole-dipole interaction between neighbouring CIAIPc molecules can be engaged in H-bridges which may mediate the self-assembly nanosystems, forming well-aligned dipole dot arrays.
- ❖ The numbers of possible hydrogen bonds for each molecule in the superstructure of 1:1 and 2:1 dipole array network are 6 and 14/3. The 1:1 dipole array network is most energetically favorable due to the maximum intermolecular hydrogen bonds.

References

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