Tunable 2D Binary Networks on Graphite

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Abstract: *Here we present a novel approach to construct tunable and robust 2D binary molecular nanostructures on an inert graphite surface. The guest molecules are embedded into a host molecular matrix and constrained via the formation of multiple intermolecular hydrogen bonds to ensure the structural stability. By varying the binary molecular ratio as well as the molecular geometry of the host molecules, we have fabricated various molecular arrays with tunable intermolecular distances.*

Sketch (a) Molecular structures of **1** F_{16}CuPc, **2** pentacene, **3** 6P and **4** DIP. The short pink lines between F_{16}CuPc and pentacene represent the possible C-F···H-C intermolecular hydrogen bonds. (b) The proposed arrangements of F_{16}CuPc dot arrays with pentacene (**1+2**), 6P (**1+3**) and DIP (**1+4**). The intermolecular seperations indicated by black dashed lines are tunable by varying geometrical parameters of embedded molecules.

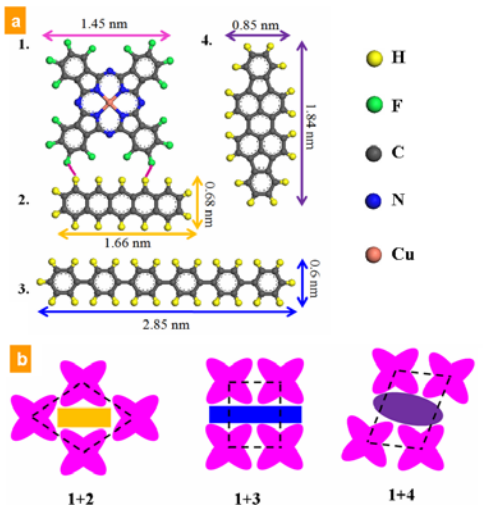
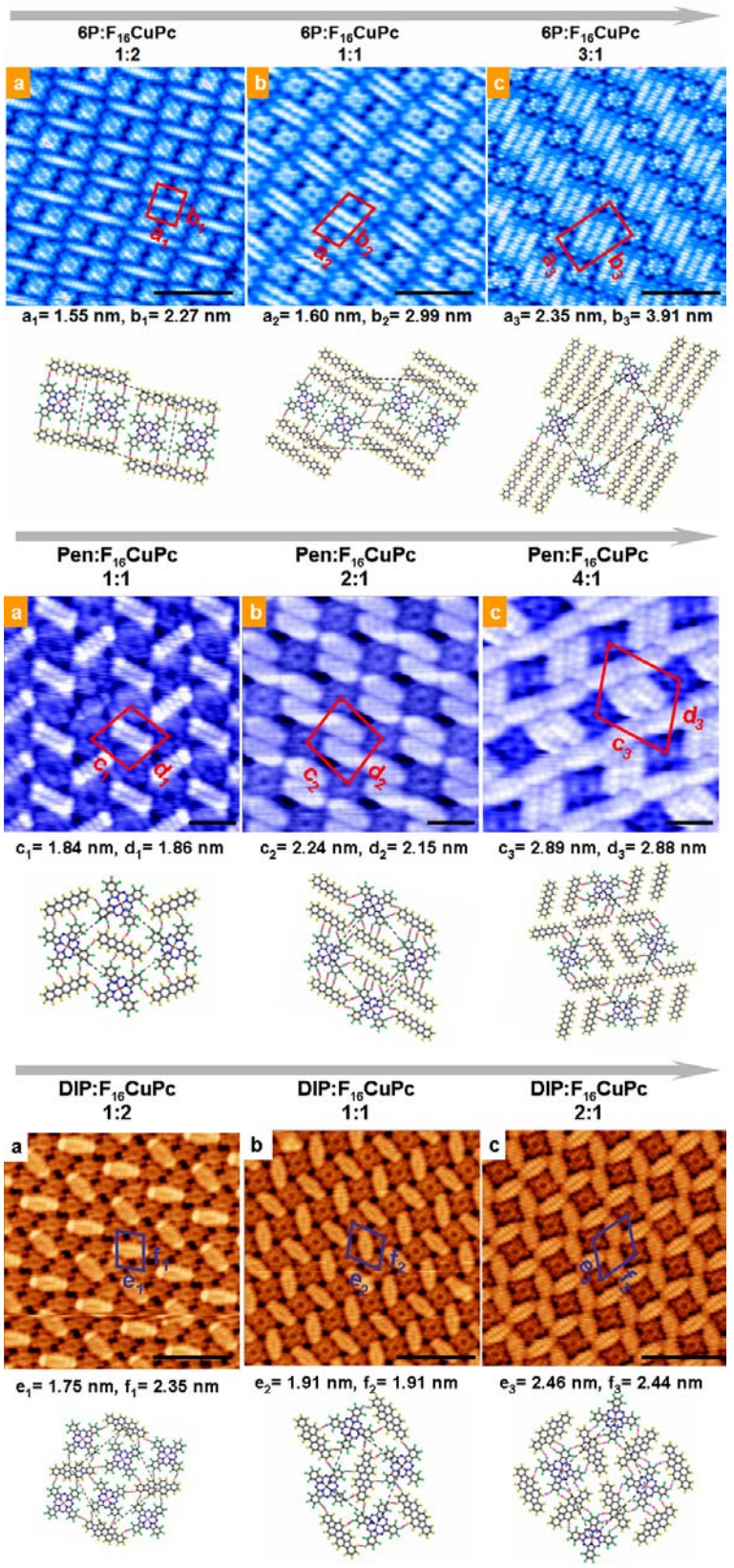


Table **Energy profile of the binary molecular networks on HOPG**

6P:F_{16}	$E_{F16\text{-}F16}$	$E_{6P\text{-}6P}$	$E_{F16\text{-}6P}$	E_{bind}	No. of H-bonds (<2.6 Å)
1:2	-0.73	-	-14.78	-15.51	8
1:1	-1.17	2.10	-18.70	-17.77	12
3:1	-	6.29	-13.84	-7.55	6
Pen:F_{16}	**$E_{F16\text{-}F16}$**	**$E_{Pen\text{-}Pen}$**	**$E_{F16\text{-}Pen}$**	**E_{bind}**	**No. of H-bonds (<2.6 Å)**
1:1	-	-	-12.12	-12.12	6
2:1	-	0.65	-19.48	-18.83	12
4:1	-	2.97	-13.92	-10.95	8
DIP:F_{16}	**$E_{F16\text{-}F16}$**	**$E_{DIP\text{-}DIP}$**	**$E_{F16\text{-}DIP}$**	**E_{bind}**	**No. of H-bonds (<2.6 Å)**
1:2	0.25	-	-13.74	-13.49	8
1:1	-	-	-13.86	-13.86	6
2:1	-	0.64	-19.26	-18.83	10

$E_{A\text{-}B}$ presents the intermolecular binding energy of the neighboring A and B molecules. E_{bind} is the total intermolecular binding energy of each primitive cell as indicated in the simulated supramolecular packing structures. All the energies are counted in **kcal/mol**. The number of possible C-F···H-C intermolecular hydrogen bonds for each primitive cell with maximum length of 2.6 Å is also given in the Table.

STM images and Simulated Modes



Conclusion: **Our DFT calculations confirm that the intermolecular hydrogen bonding drives the formation of these molecular nanostructure arrays to reach their energy minima. Using this approach, we show the fabrication of ordered and robust molecular nanostructure arrays with a high degree of tunability. Such molecular nanostructures have potential applications in molecular sensors and nanodevices. In particular, the great versatility of the metal phthalocyanines allows the ease of the modification of central metal atoms to feature desired functionalities, such as electronic spins for the construction of molecular spintronic devices.**

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