Electronic Supplementary Information (ESI)

Dynamic host-guest behavior in halogen-bonded two-dimensional molecular networks investigated by scanning tunneling microscopy at the solid/liquid interface

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Additional STM images and interaction energies of the complex

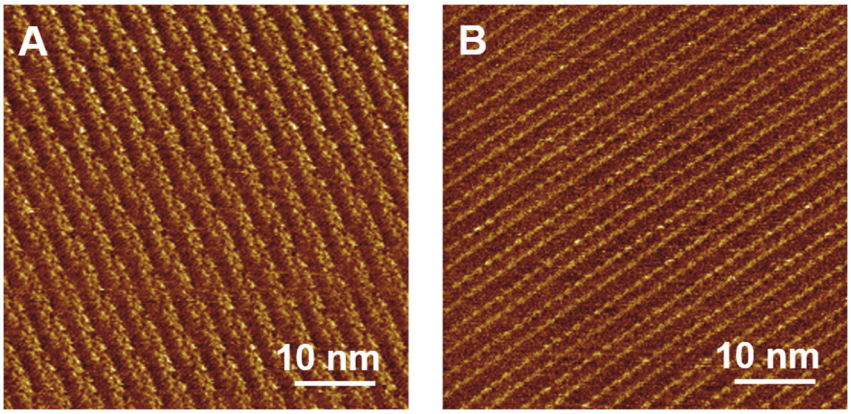


Fig. S1 Large area STM images of **Py-C14** (A) and **FI-C14** (B) physisorbed at the HOPG/1-phenyloctane interface. Tunneling conditions: (A) I = 25 pA, V = -1000 mV, (B) I = 25 pA, V = -676 mV.

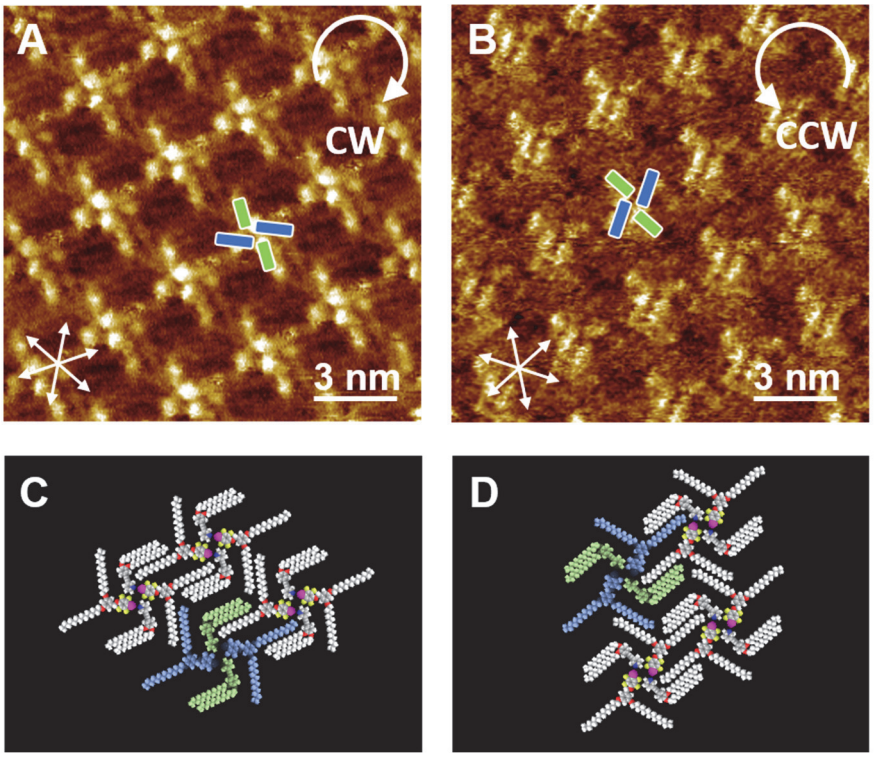
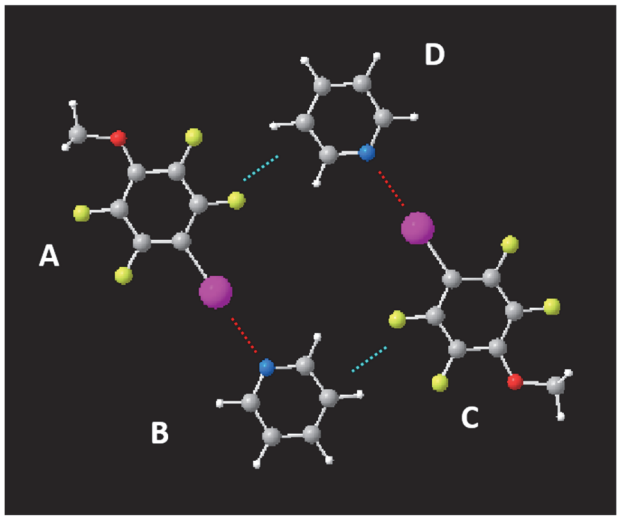


Fig. S2 STM images of the bi-component blends of **Py-C14/FI-C14** (25 mM) showing the chiral assembly. The locations of **Py-C14** and **FI-C14** are highlighted in green and blue, respectively. Tunneling conditions: (A) I = 35 pA, V = -813 mV, (B) I = 25 pA, V = -883 mV.



	Two body interactions (kcal/mol)	
A – B	-6.7	I···N Halogen bonding
C – D	-6.7	
A – D	-2.1	Ar-F···H-Py interaction
B – C	-2.1	
A – C	-0.2	
B – D	-0.2	
Total	-20.2*	

* Total interaction energy is greater than the sum of the two body interaction energies, since it includes the contributions of many body interactions.

Fig. S3 Optimized structures of the 4 head groups in **Py-C14** (pyridine) and **FI-C14** (2,3,5,6-tetrafluoro-1-iodo-4-methoxybenzene), and interaction energies of the complex (two body interaction and total interaction energies), obtained by DFT calculation.

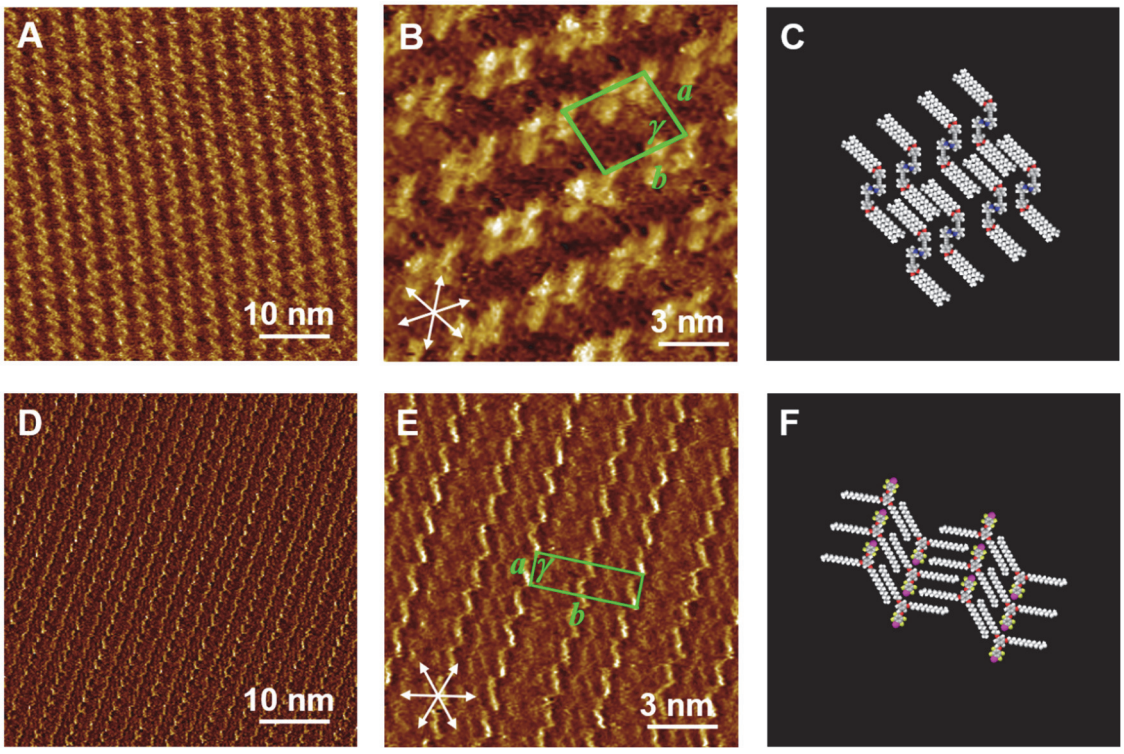


Fig. S4 STM images of **Py-C15** (A, B) and **FI-C15** (D, E) physisorbed at the HOPG/1-phenyloctane interface. A set of arrows indicates the HOPG lattice directions. Proposed molecular models in (C and F) are drawn based on the STM images in (B and E), respectively. The lattice constants of **Py-C15** are

a = 3.18 ± 0.03 nm, b = 3.78 ± 0.05 nm, γ = 84 ± 3 °, whereas those of **FI-C15** are a = 1.44 ± 0.06 nm, b = 4.53 ± 0.03 nm, γ = 87 ± 1 °. The 2D structure of the **Py-C15** was different from that of **Py-Cn** (n = 14 and 18), possibly due to the alkyl chain length effect. The **FI-C15** formed a single columnar structure, which was also found in the monolayers of **FI-Cn** (n = 14 and 18). Tunneling conditions: (A) I = 35 pA, V = -900 mV, (B) I = 25 pA, V = -1000 mV; (D) I = 25 pA, V = -566 mV, (E) I = 25 pA, V = -701 mV.

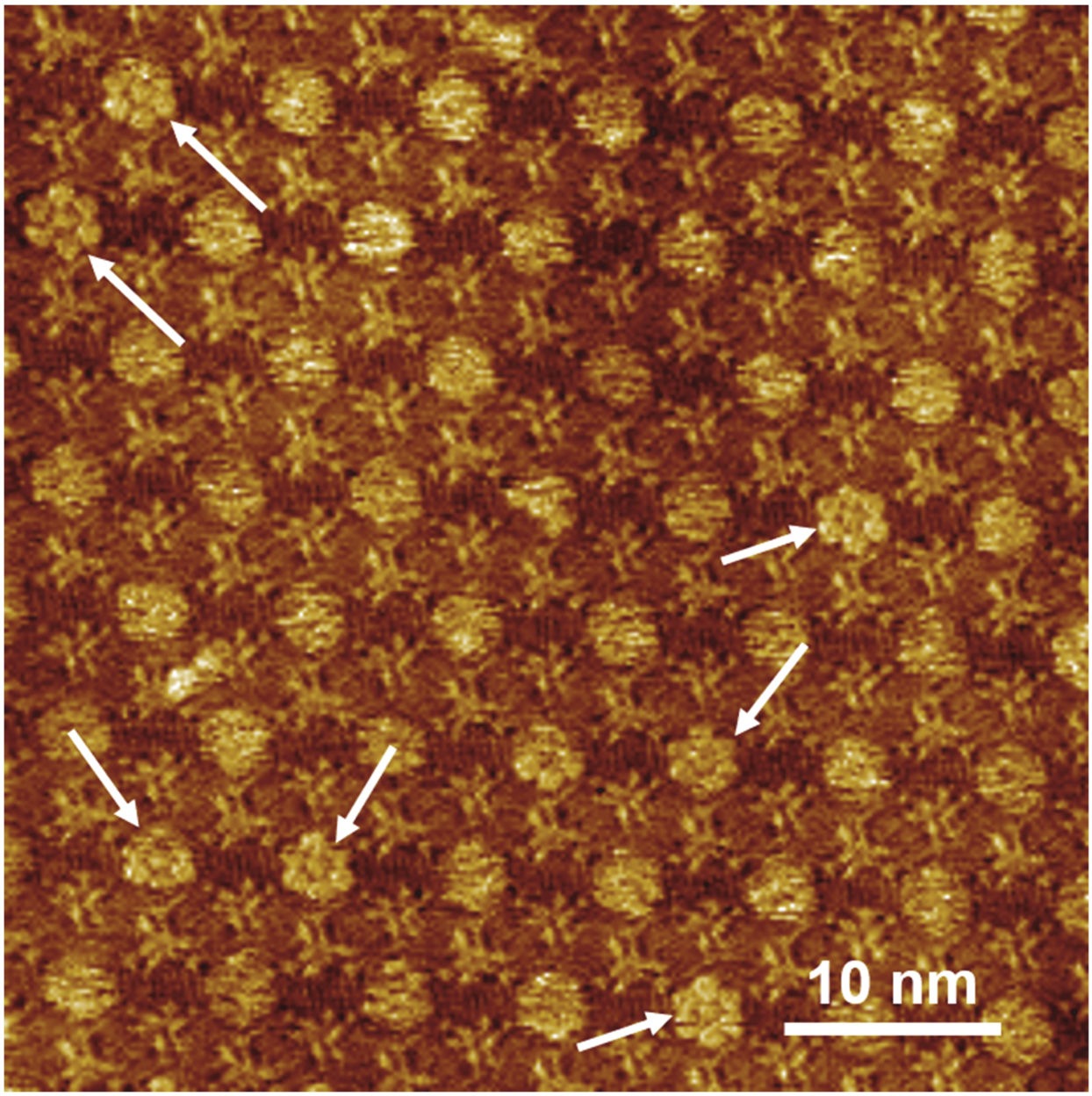


Fig. S5 Enlarged STM image of Fig. 4A.

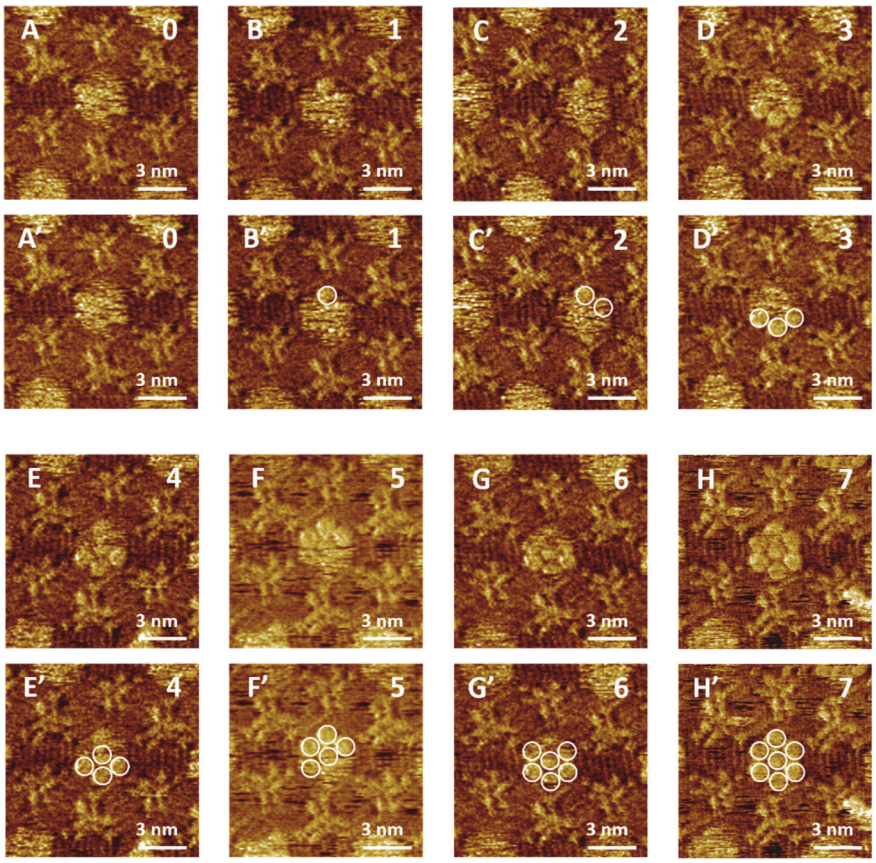


Fig. S6 STM images of **Py-C14/FI-C14/COR** assembly physisorbed at the HOPG/1-phenyloctane interface. Different numbers of **COR** were observed in the central hexagonal pore. (A-H) shows the original STM images, whereas the existence of the **COR** was highlighted with white circle in (A'-H').

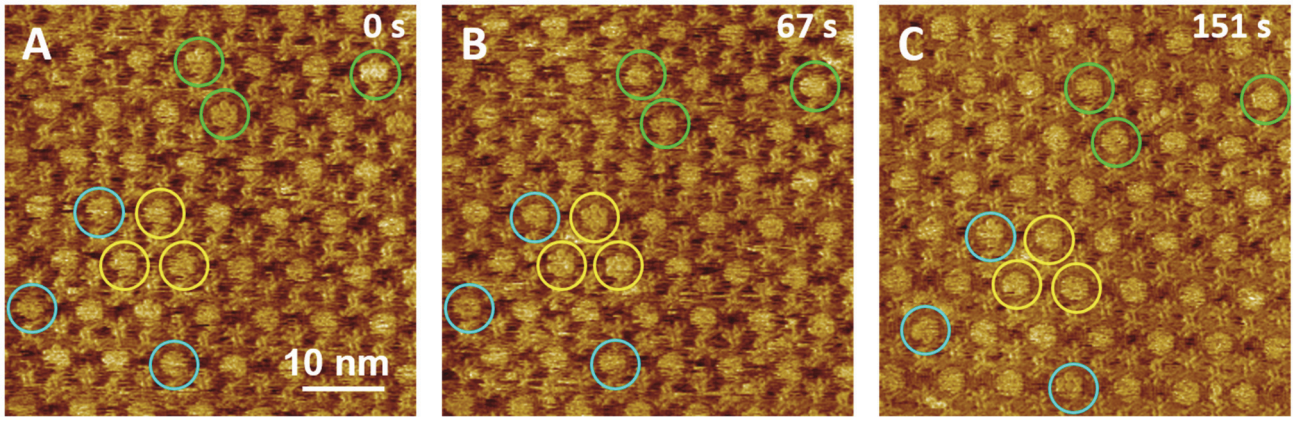


Fig. S7 Consecutive STM images of **Py-C14/FI-C14/COR** assembly taken at the given time (shown at the right corner of each image). The colored circles indicate the examples of pores where the number of the **COR** alters during the STM imaging.