

Electronic Supplementary Information

## **The self-assembly and pyridine regulation of a hydrogen-bonded dimeric building block formed by low-symmetric aromatic carboxylic acid**

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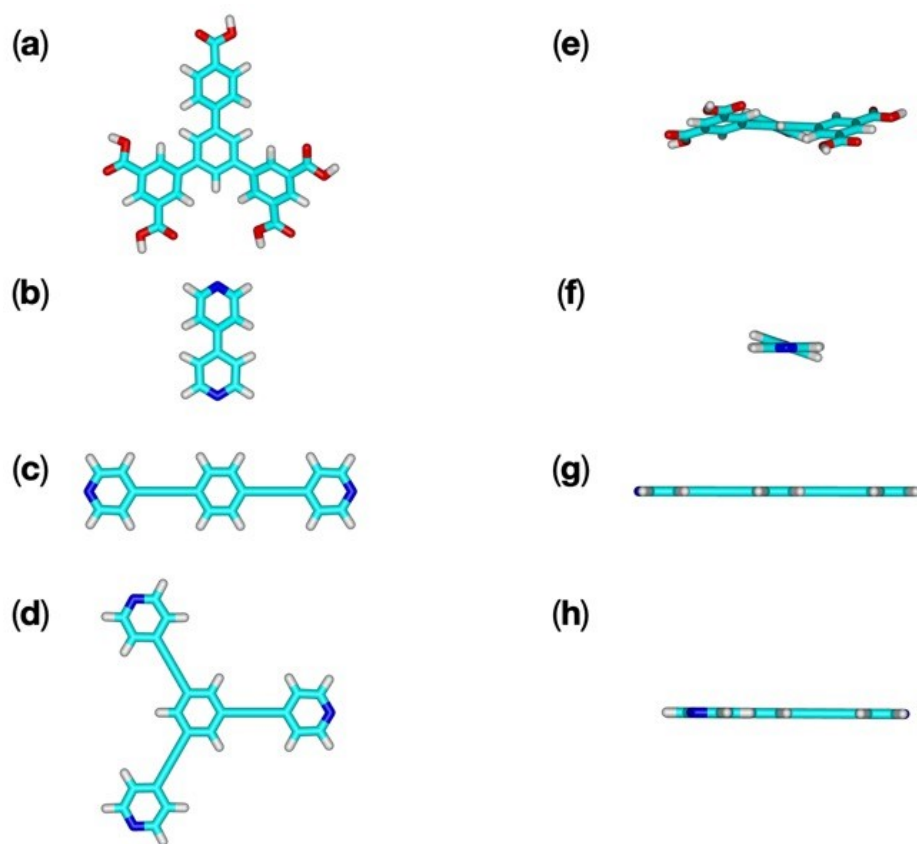
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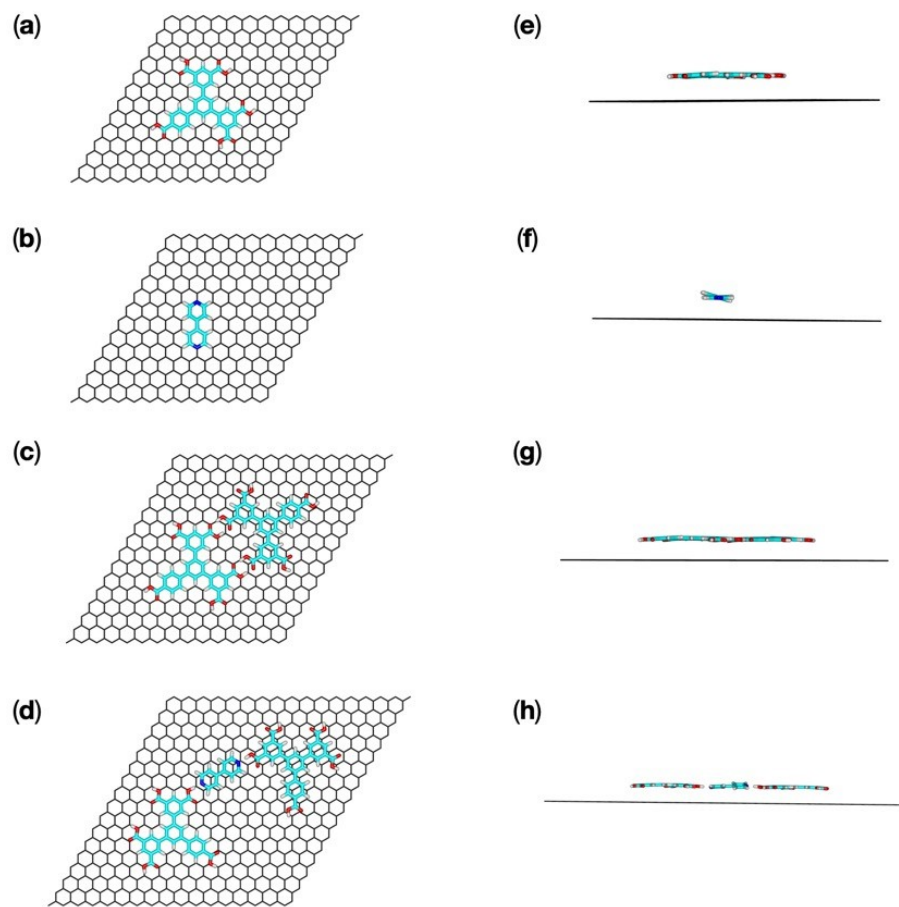
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1 DFT simulated single molecular models.

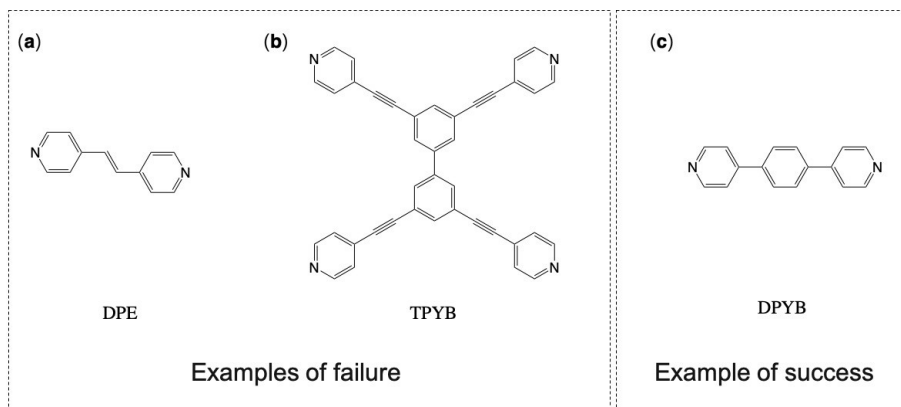


**Fig. S1** DFT simulated molecular models in the gas phase. (a-d) Top view of H<sub>5</sub>BHB, BPD, BPDYB, TPDYB respectively. (e-h) Side view of H<sub>5</sub>BHB, BPD, BPDYB, TPDYB, respectively.

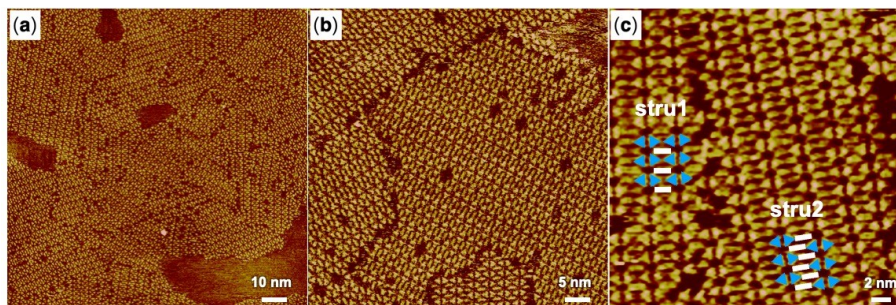


**Fig. S2** DFT simulated molecular models on the graphite surface. (a-d) Top view of H<sub>5</sub>BHB, BPD, H<sub>5</sub>BHB dimer, H<sub>5</sub>BHB-BPD unit cell, respectively. (e-h) Side view of H<sub>5</sub>BHB, BPD, H<sub>5</sub>BHB dimer, H<sub>5</sub>BHB-BPD unit cell, respectively.

2 Supplementary examples of pyridine molecules co-assembled with H<sub>5</sub>BHB.

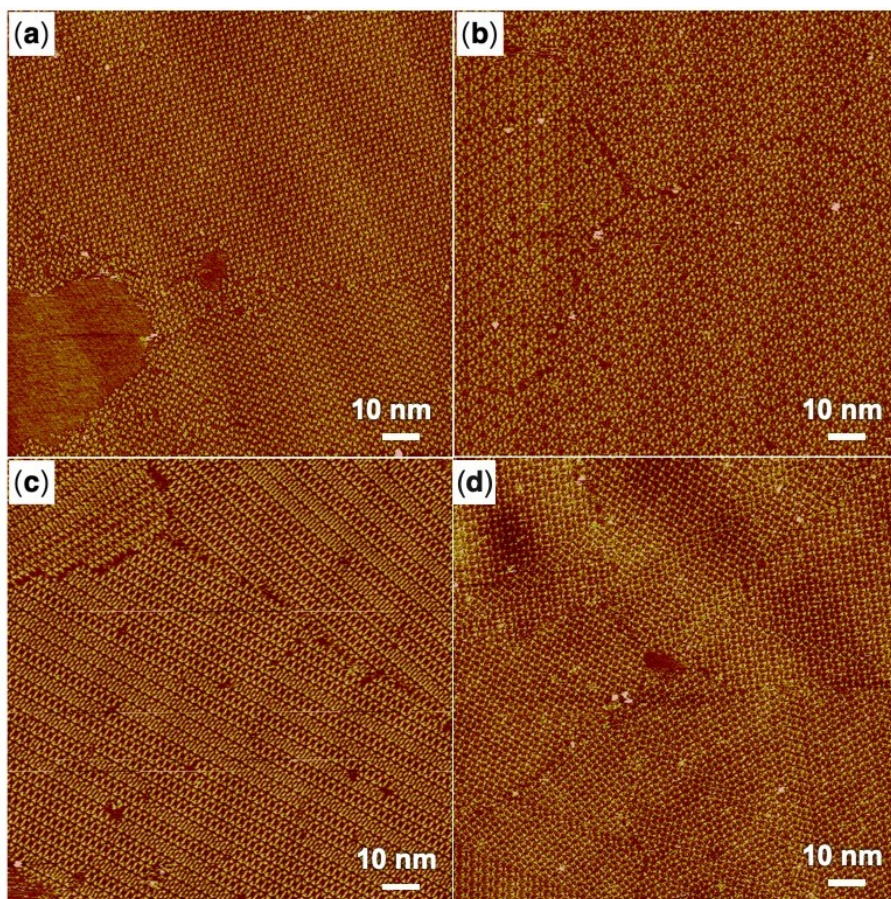


**Fig. S3** Supplementary failure and success examples of pyridine molecules that can form stable ordered co-assembled structure with H<sub>5</sub>BHB molecule. Failure examples: (a) 1,2-Di(4-pyridyl)ethylene (DPE). (b) 3,3',5,5'-Tetrakis(pyridin-4-ylethynyl)-1,1'-biphenyl (TPYB). Success example: (c) 1,4-Di(pyridin-4-yl)benzene (DPYB).



**Fig. S4** STM images of supplementary experiment: H<sub>5</sub>BHB co-assembled with DPYB at heptanoic acid–HOPG liquid–solid interface. (a) Large scale (120 nm × 120 nm) STM image,  $I_{set} = 311.3$  pA,  $V_{bias} = 686.6$  mV. (b) Large scale (60 nm × 60 nm) STM image,  $I_{set} = 152.6$  pA,  $V_{bias} = 1024$  mV. (c) High-resolution STM image (30 nm × 30 nm),  $I_{set} = 158.7$  pA,  $V_{bias} = 904.8$  mV. Two different co-assembled structures were observed, labeled with stru1 and stru2, respectively. The blue triangle shape represents for a H<sub>5</sub>BHB molecule, while the white rod shape represents for a DPYB molecule. The co-assembly behavior of H<sub>5</sub>BHB and DPYB was similar to that of H<sub>5</sub>BHB and BPDYB.

3 Supplementary large scale (120 nm × 120 nm) STM images.



**Fig. S5** Supplementary large scale (120 nm × 120 nm) STM images at the heptanoic acid–HOPG liquid–solid interface of (a) H<sub>5</sub>BHB\_self-assembled,  $I_{\text{set}} = 231.9$  pA,  $V_{\text{bias}} = 815.4$  mV. (b) H<sub>5</sub>BHB–BPD co-assembled structure,  $I_{\text{set}} = 146.5$  pA,  $V_{\text{bias}} = 932.0$  mV. (c) H<sub>5</sub>BHB–BPDYB co-assembled structure,  $I_{\text{set}} = 177.9$  pA,  $V_{\text{bias}} = 932.3$  mV. (d) H<sub>5</sub>BHB–TPDYB co-assembled structure,  $I_{\text{set}} = 164.8$  pA,  $V_{\text{bias}} = 941.8$  mV.