Supporting information for

Minor adjustments in chemical structures of pyridine derivatives induced different co-assemblies by O-H…N hydrogen bond

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Content

S1. Experimental section

1.1 Sample preparation

Three pyridine derivatives PEBP-C4, PEBP-C6 and PEBP-C8 were synthesized according to the previous study[38]. PDE and DPE and two acid compounds H_4BTE and H_4BTY were bought from Jilin Chinese Academy of Sciences-Yanshen Technology Co. Ltd and they were utilized without further purification. Acid compounds were all dissolved into 1-heptanoic acid (HA) with the concentration about 1×10^{-5} mol/L. The pyridine derivatives were dissolved into HA with the concentration about 1×10^{-4} mol/L. After dissociating HOPG (grade ZYB, NTMDT, Russia) with ordinary scotch tape, fresh and clean HOPG was exposed, and corresponding solutions were added onto HOPG surface. After obtaining mono-component self-assembly structures, the pyridine solutions with concentrations less than 1×10^{-4} mol/L were added into the H_4BTE or H_4BTYsystems.

1.2 STM detection

The STM detections were all implemented on Nanoscope IIIa (Bruker, USA) instrument and Pt/Ir (80/20) wire was utilized as tips. The constant-current pattern was applied into instruments under atmospheric conditions and scanning conditions of STM images were depicted in figure captions. All STM images were obtained from more than three results with different tips to avert artifacts and they were polished by NanoScope analysis software.

1.3 DFT simulation

The self-assembled mechanisms were probed by DMol^3 code and the periodic boundary conditions (PBC) were utilized for obtaining periodic molecular structures. Perdew and Wang parameterization was selected to achieve local exchange correlation and its energy was calculated by local spin density approximation when all-electrons adopted a medium grid and the convergence criterion was 10^{-5} au during the field procedure. On the basis of STM images, the parameters and geometries of unit cells were optimized and the interaction energy of nanostructures were acquired till density convergence criterion were obtained. The infinite graphene monolayer was applied to simulate the HOPG and there are only two carbon atoms in the periodic orthorhombic unit cell, and the distance between them were 40 Å. Besides, the Brillouin zone was sampled by a 1 × 1 × 1 k-point mesh and the Gibbs free energy of the adsorbates E_{inter} were depended on the equation: $E_{inter} = E_{tot(adsorbates/graphene)} - E_{ot(isolated/\ adsorbates\ in\ vacuum)} - E_{tot(graphene)}$.

S2 The large scale STM image of H_4BTE and H_4BTY self-assembly structure at 1-heptanoic acid/HOPG interface

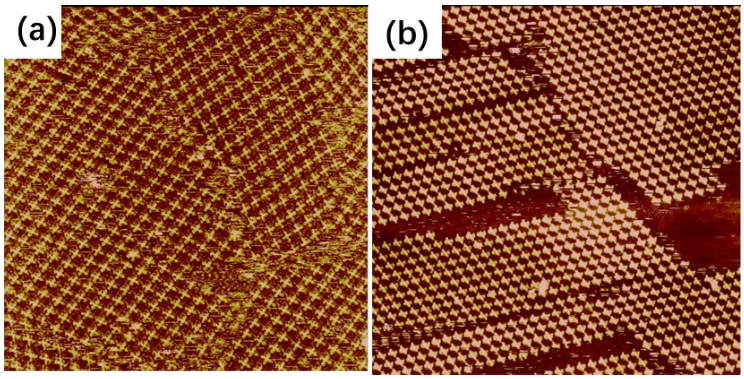

Figure S1. (a) The large scale STM image of H_4BTE at HA/HOPG interface (I_{set} =281 pA, V_{bias}= 692 mV, scan size: 83 nm×83 nm); (b) large-scale STM image of H_4BTY at HA/HOPG interface (I_{set} =183 pA, V_{bias}= 894 mV, scan size: 83 nm×83 nm).

S3 The large scale STM image of H_4BTE/PDE and H_4BTE/PEBP-C8 co-assembly structure at 1-heptanoic acid/HOPG interface

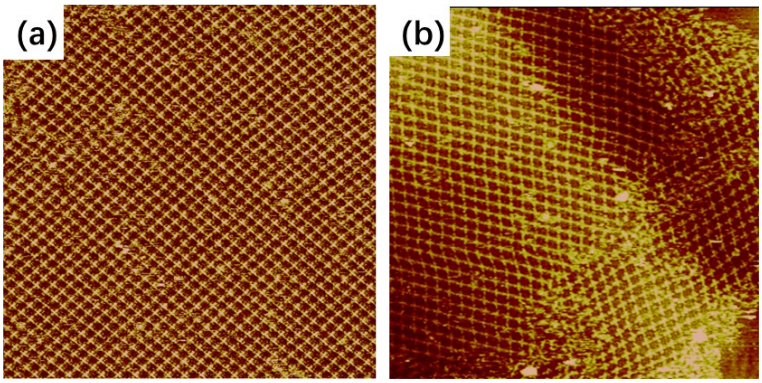

Figure S2. (a) Large-scale STM image of assembly structure when PDE was added into H_4BTE system (I_{set} =327 pA, V_{bias}= 752 mV, scan size: 84 nm×84 nm); (b) Large-scale STM image of assembly structure when PEBP-C8 was added into H_4BTE system (I_{set} =242 pA, V_{bias}= 872 mV, scan size: 76 nm×76 nm).

S4 The large scale STM image of H_4BTY/DPE and H_4BTY/PEBP-C4 co-assembly structures at 1-heptanoic acid/HOPG interface

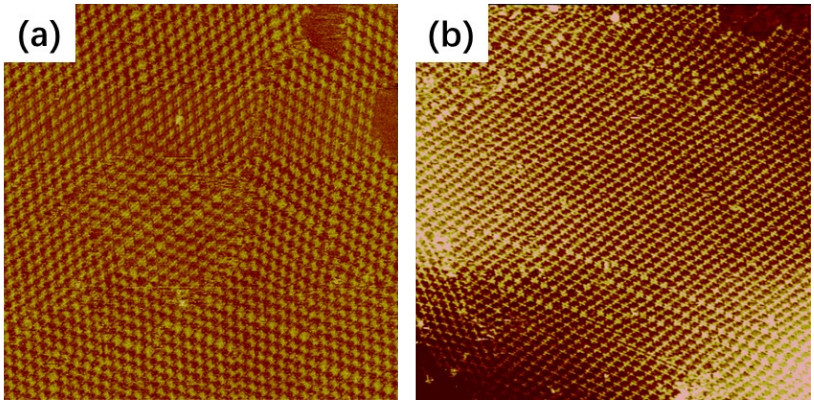

Figure S3. (a) Large-scale STM image of H_4BTY/DPE co-assembly structure at HA/HOPG interface (I_{set}= 418 pA, Vbias= 607 mV, scan size: 82 nm×82 nm); (b) large-scale STM image of H_4BTY/PEBP-C4 co-assembly structure at HA/HOPG interface (I_{set}= 195 pA, V_{bias}= 866 mV, scan size: 102 nm×102 nm).

S5 The large scale STM image of H_4BTY/PDE and H_4BTY/PEBP-C8 co-assembly structures at 1-heptanoic acid/HOPG interface

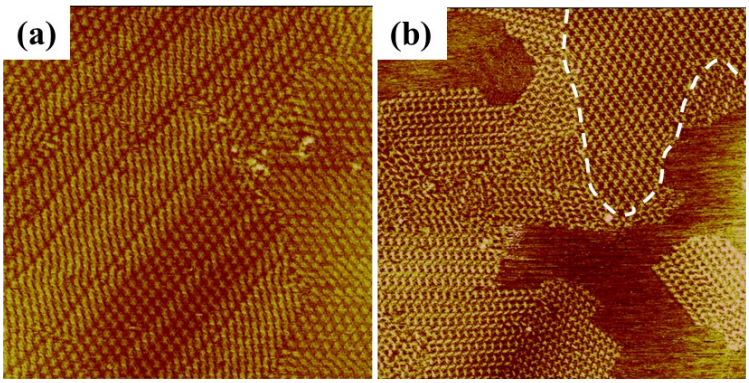

Figure S4. (a) Large-scale STM image of H_4BTY/PDE co-assembly structure at HA/HOPG interface (I_{set}= 383 pA,Vbias= 711 mV, scan size: 79 nm×79 nm); (b) large-scale STM image of H_4BTY/PEBP-C8 co-assembly structure at HA/HOPG interface (I_{set}= 195 pA, V_{bias}= 866 mV, scan size: 96 nm×96 nm).

S6 the summary of unit cell parameters and molecular densities of assembly structures.

Table S1. Summary of experimental (Expt.) and calculated (Cal.) parameters and molecular density (MD) of acid or pyridine in assembly structures H_4BTE, H_4BTY, H_4BTY/PDE, H_4BTY/PEBP-C6@1, H_4BTY/PEBP-C6@2, H_4BTY/PEBP-C8.

		a (nm)	b(nm)	α (°)	MD of acids (nm^{-2})	MD of pyridine (nm^{-2})
H_4BTE	Expt.	2.0±0.1	2.5±0.1	102±1	0.20	/
	Cal.	2.10	2.40	102.0	0.20	/
H_4BTY	Expt.	2.5±0.1	2.5±0.1	120±1	0.19	/
	Cal.	2.40	2.40	120.0	0.20	/
H_4BTY/PDE	Expt.	2.0±0.1	2.5±0.1	63±1	0.23	0.23
	Cal.	2.00	2.40	63.0	0.23	0.23
H_4BTY/PEBP-C6@1	Expt.	1.9±0.1	3.8±0.1	80±1	0.14	0.14
	Cal.	1.90	3.80	80.0	0.14	0.14
H_4BTY/PEBP-C6@2	Expt.	2.7±0.1	2.9±0.1	100±1	0.26	0.13
	Cal.	2.80	3.00	100.0	0.24	0.12
H_4BTY/PEBP-C8	Expt.	1.8±0.1	4.0±0.1	80±1	0.14	0.14
	Cal.	1.80	4.00	80.0	0.14	0.14

S7 the interaction between the adsorbates, the interaction between adsorbates and substrates, total energy and energy per unit area of assembly structures.

Table S2. The total energies and energies per unit cell of assembly structures H_4BTE, H_4BTY, H_4BTY/PDE, H_4BTY/PEBP-C6@1, H_4BTY/PEBP-C6@2, H_4BTY/PEBP-C8.

	Interactions between adsorbates (kcal mol^{-1})	Interactions between adsorbates and substrate (kcal mol^{-1})	total energy (kcal mol^{-1})	total energy per unit area (kcal mol^{-1} $Å^{-2}$)
H_4BTE	-32.913	-34.881	-67.794	-0.138
H_4BTY	-23.977	-48.632	-72.610	-0.146
H_4BTY/PDE	-61.018	-63.437	-124.455	-0.269
H_4BTY/PEBP-C6@1	-90.365	-70.168	-160.533	-0.237
H_4BTY/PEBP-C6@2	-128.800	-128.548	-257.348	-0.311
H_4BTY/PEBP-C8	-80.971	-74.809	-155.781	-0.220