Electronic Supplementary Material (ESI) for ChemComm.

Efficient Molecular Recognition Based on Nonspecific van der Waals Interaction at the Solid/Liquid Interface

1. **Extra STM images of the binary mixture and pure system.**
2. **Statistic on the recognition efficiency**
3. **Dependence of surface composition on the concentration and solution composition**
4. **Experimental Section**

1. Extra STM images of the binary mixture and pure system.

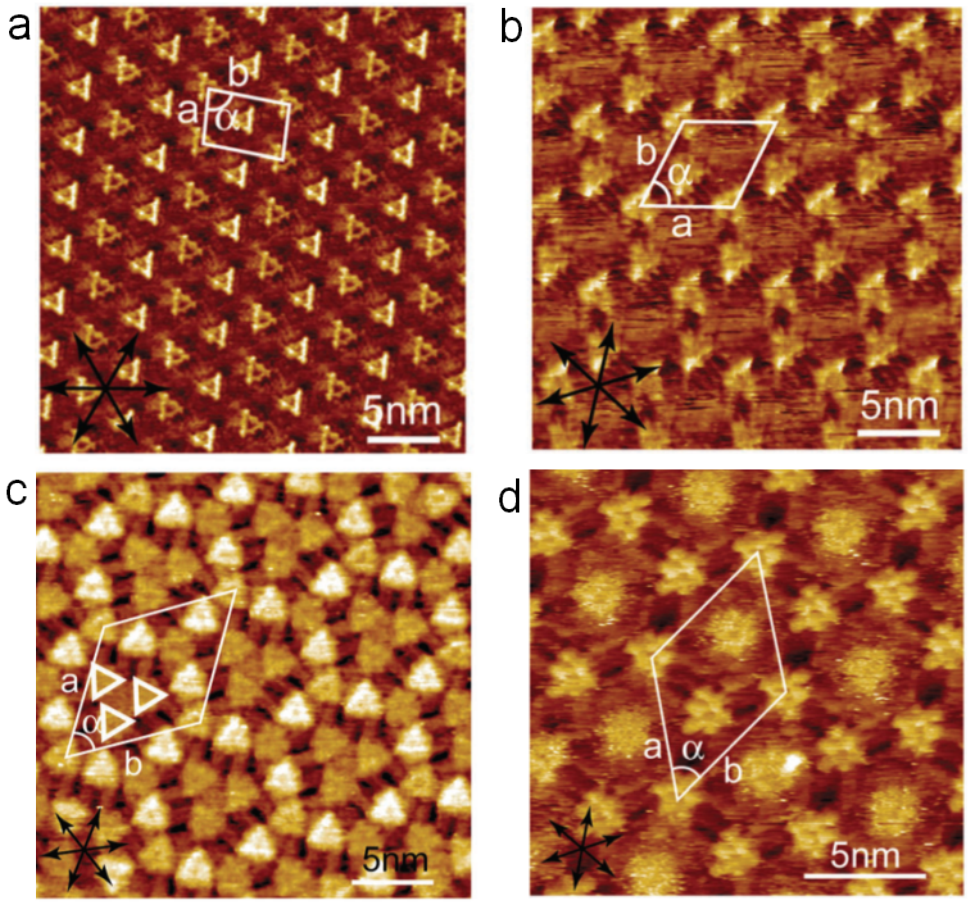

Figure. S1. STM images of linear (a) and honeycomb (b) networks of **2** and flower (c) and filled-honeycomb (d) networks of **3** obtained at the TCB–graphite interface at two different concentrations: (a) 5.33×10^{-5} mol L^{-1} and (b) 5.33×10^{-7} mol L^{-1}, (c) 4.90×10^{-5} mol L^{-1} and (d) 4.90×10^{-6} mol L^{-1}. The linear network of **2** has an oblique unit cell and the symmetry is p2gg, while for honeycomb network of **2**, flower and filled-honeycomb of **3**, they all have rhombic unit cells and the symmetry is p6.

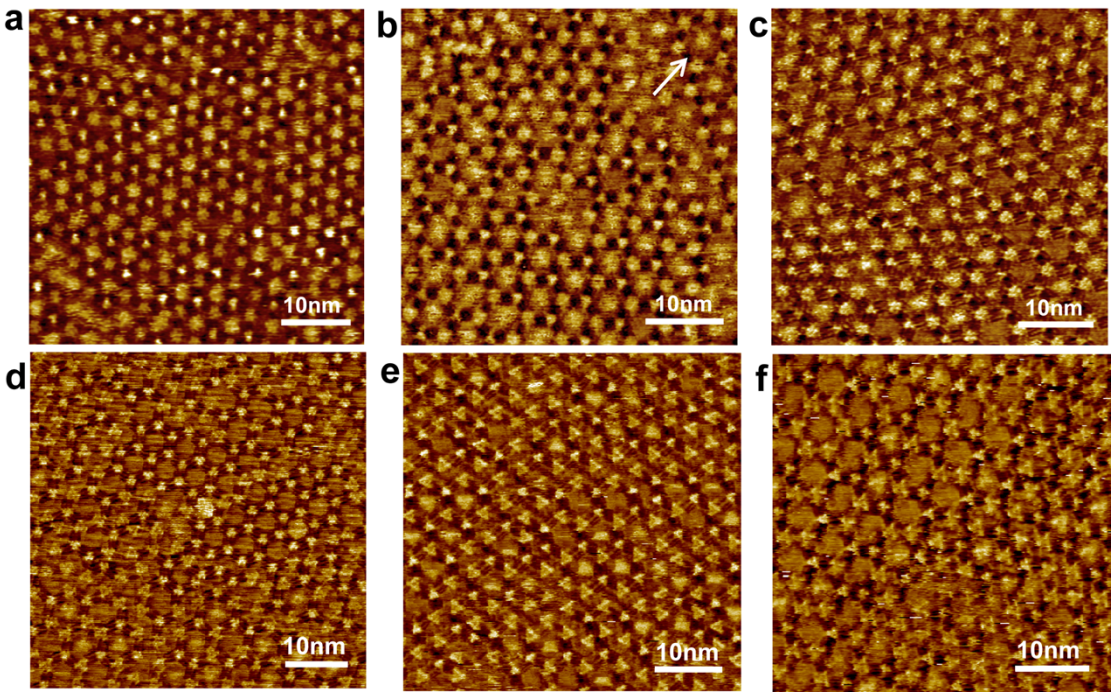

Figure. S2. STM images of the self-assembled monolayer structures from binary mixtures of (a, b, c) **1** and **3** (**1**: **3**=1.32:1 in solution before deposition). The white arrow in (b) points to a small pure **3** domain. (d, e, f) **1** and **2** (**1**: **2**=1.22:1 in solution before deposition).

(a) Concentration of **1** : 5.16×10^{-5} mol L^{-1}, V_{bias} =1.00 V, I_{set} = 0.035 nA, (b) Concentration of **1** : 5.16×10^{-6} mol L^{-1}, V_{bias} = 1.00 V, I_{set} = 0.060 nA, (c) Concentration of **1** : 2.58×10^{-6} mol L^{-1}, V_{bias} =1.10 V, I_{set} =0.050 nA

(d) Concentration of **1**: 5.16×10^{-5} mol L^{-1}, V_{bias} = 0.80 V, I_{set} =0.039 nA, (e) Concentration of **1** : 5.16×10^{-6} mol L^{-1}, V_{bias} = 0.60 V, I_{set} = 0.040 nA, (f) Concentration of **1** : 2.58×10^{-6} mol L^{-1}, V_{bias} = 0.80 V, I_{set} = 0.10 nA.

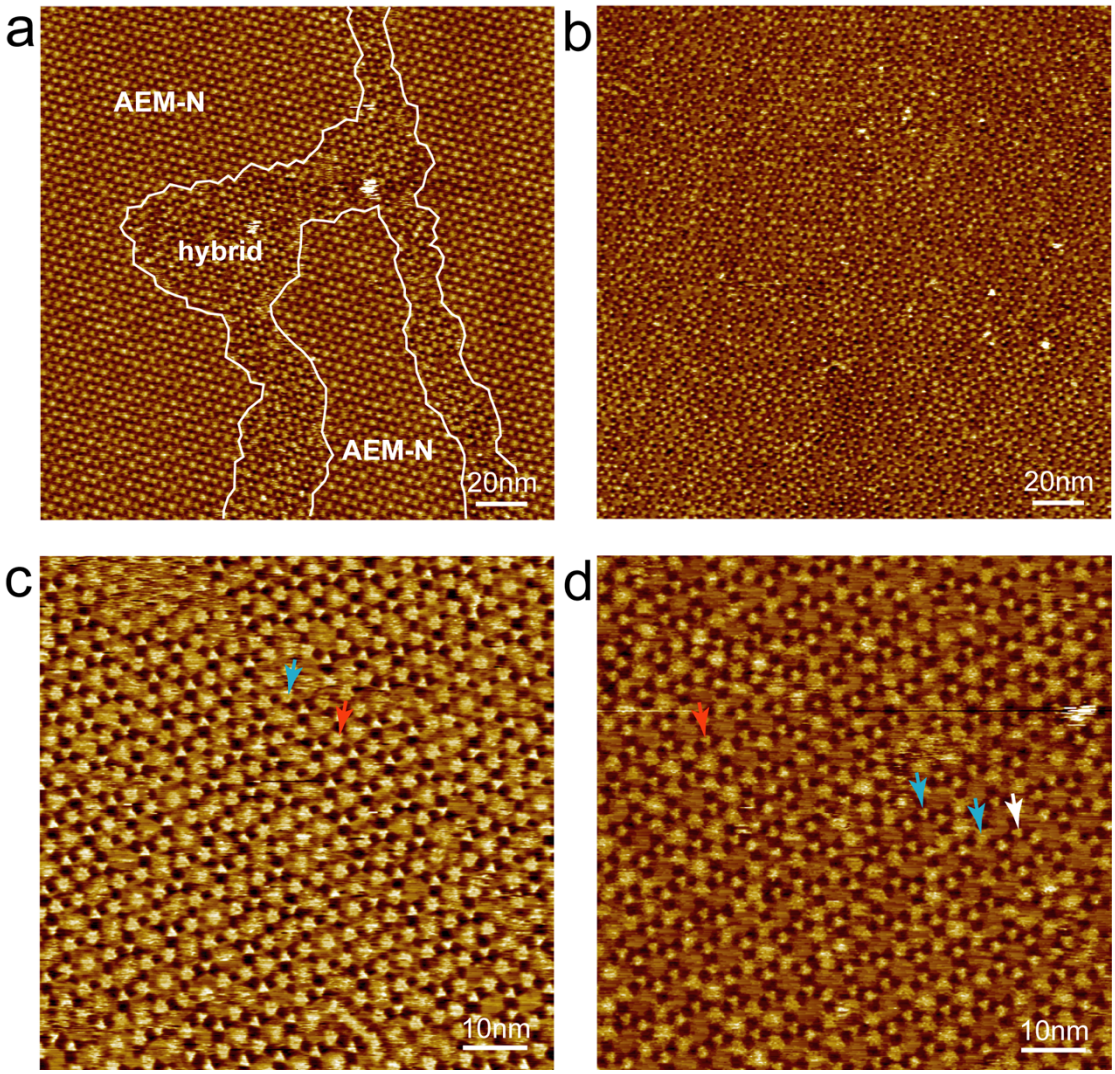

Figure S3. Large scale (a, b) and high resolution (c, d) STM images of the supramolecular structure formed by **1** and **3** with different solution mole ratio. (a and c). The mole ratio of **1** : **3** = 0.33:1, in this case phase separation is significant, 71.78％ and 27.04％ of the surface was covered by pure **3** and hybrid networks, respectively. (b and d). The mole ratio of **1** : **3** = 5.29:1, now most of the surface is covered by the hybrid networks, pure **1** honeycombs are only very rarely observed (the coverage of pure**1** is only 0.26%), as indicated by the white arrows in (d). The red and blue arrows in the high resolution images mark the regular and irregular hybrid honeycombs, respectively.

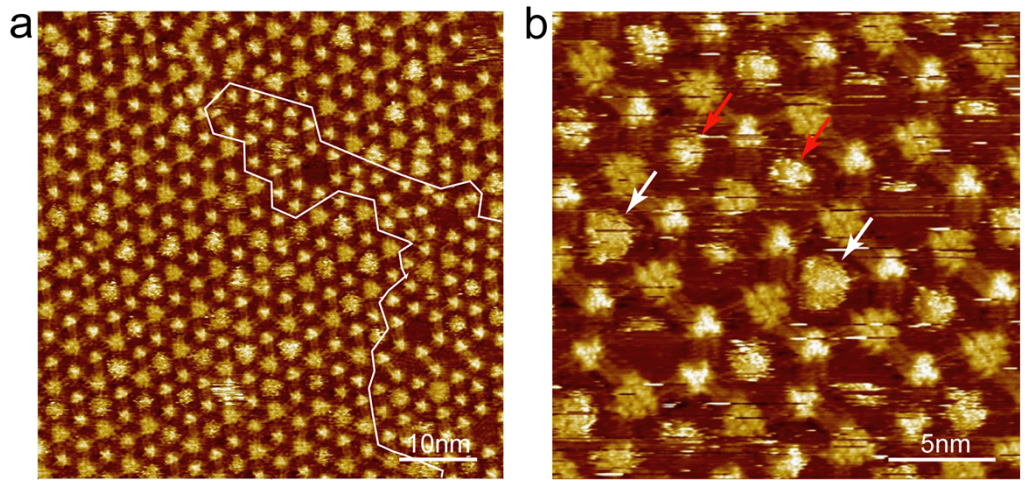

Figure S4. Large scale (a) and high resolution (b) STM images of the supramolecular structure formed by **1** and **3** at the octanoic acid/graphite interface with mole ratio **1**: **3** = 1.32:1. The white line in (a) marked out the domain boundaries of hybrid and pure **1** domains. The red and white arrows in (b) point to the **1** and **3** molecules trapped in the hybrid network. Comparing with that in Figure 3e, these trapped molecules appear more mobile at the current tunneling condition. This proves that the alkoxy chain interdigitation between trapped **1** and **3** in the hybrid network is more dynamic comparing with those between molecules composing the hybrid network.

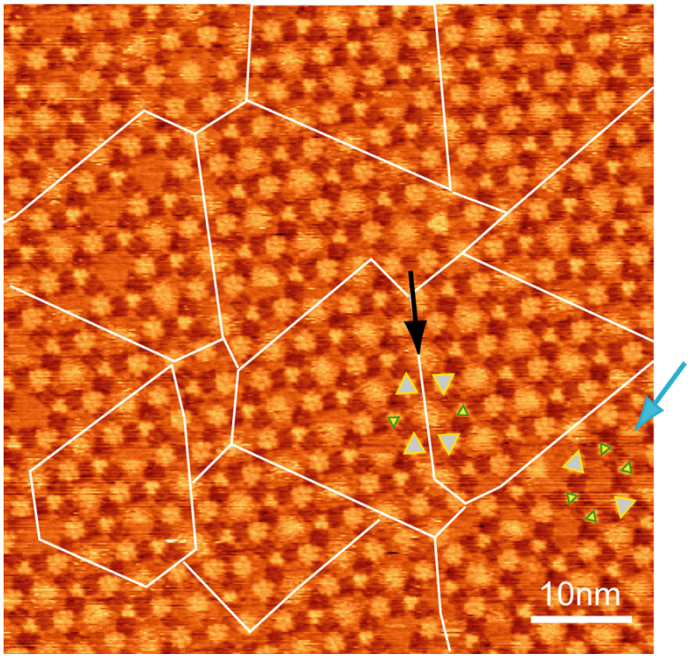

Figure S5. An enlarged image of Figure 3a. The superimposed small and large triangles represent **1** and **3** cores respectively. The black and blue arrows indicate two types of domain boundaries.

2. Statistic on the recognition efficiency

Table S1. Statistical results of the number of **1** and **3** in the hybrid system at different concentrations.

concentration（mg /g）	**1**	**3**	0	1	2	3	**1**:**3** On surface	Recognition efficiency（%）
0.005(annealed at 40℃)	914	1917(f1378+c539）	804	98	12	0	0.477	87.96
0.005	1035	1775	949	82	4	0	0.583	91.69
0.01	1225	1994	1091	110	23	1	0.614	89.06
0.1	1361	1637	1133	188	40	0	0.831	83.25

The numbers “0” “1” “2” and “3” indicate the number of **1** in direct contact with a **1** molecule in the network. “c” and “f” indicate the pure and the hybrid honeycomb network respectively. Here “direct contact” means contact with interdigitated alkyl chains.

Table S2. Statistical results of the number of **1** and **3** in the hybrid system at different mass ratio at the total concentration of 0.01mg/g.

1:**3** In solution	**1**	**3**	0	1	2	3	**1**:**3** On surface	Recognition efficiency（%）
0.33:1	1468	2126	1343	115	9	1	0.154	91.48
1.32:1	1225	1994 (f1825+c169)	1091	110	23	1	0.614	89.06
2.63:1	1543 (f1474+c69)	1403	831	548	91	4	1.10	56.38
5.29:1	2631 (f2203+c428)	1741	764	1093	330	16	1.51	34.68

Table S3. Statistical results of the number of **1** and **2** in the hybrid system at different concentrations.

concentration（mg/g）	**1**	**2**	0	1	2	3	**1**:**2** On surface	Recognition efficiency（%）
0.005(annealed at 40℃)	1121 (f947+c174）	2555 (f1624+c931)	819	126	2	0	0.439	86.48
0.005	806	1175	614	186	6	0	0.686	76.18
0.01	1301	1732	1111	184	6	0	0.751	85.40
0.1	1478 (f1471+c7）	1119 (f1051+c68）	439	543	399	90	1.32	29.84

3. **Dependence of surface composition on the concentration and solution composition**

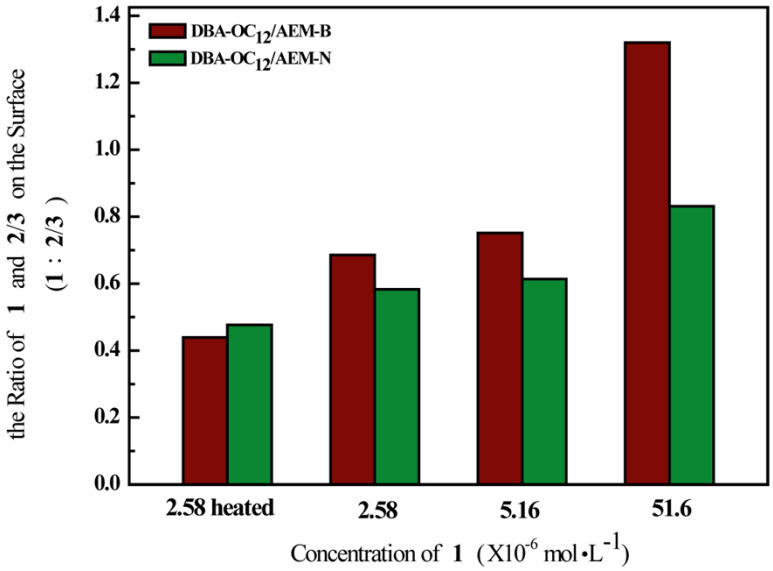

Figure S6. The concentration dependence of mole ratio of **1** against **2** and **3** in the adlayer under the solution mole ratio of **1** : **3** =1.32:1 and **1** : **2** =1.22:1, respectively.

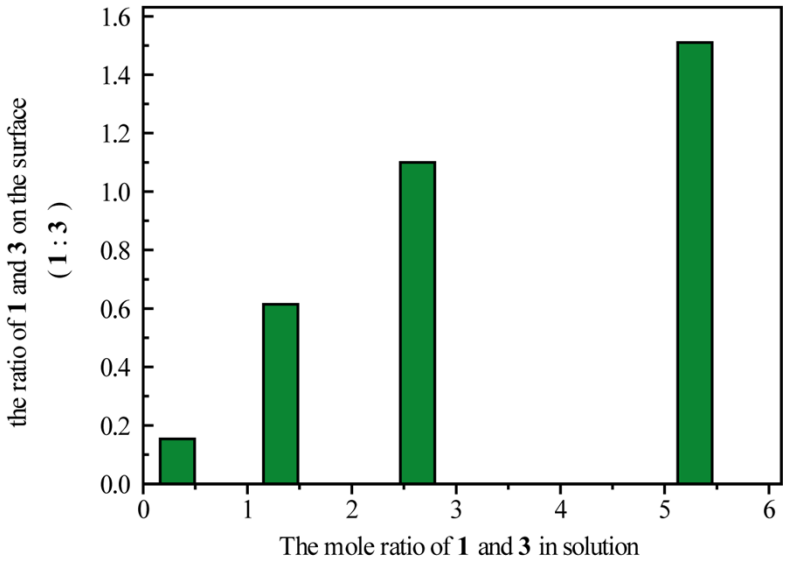

Figure S7. The dependence of mole ratio of **1** against **3** in the adlayer on the mole ratio in solution.

4. Experimental Section

The solvent, 1,2,4-trichlorobenzene (TCB), octanoic acid was purchased from Aldrich, and used without further treatment. The highly-oriented pyrolytic graphite (HOPG) was purchased from Bruker. Samples for STM investigation were prepared by depositing a droplet (~1.5μL) of the solution on freshly cleaved HOPG. STM measurements were performed at room temperature at the liquid-solid interface with a constant current mode (Agilent 5100, USA). Detailed imaging conditions are given in the figure captions. Mechanically cut Pt/Ir (80/20) tips were used. The STM images of the adlayers were corrected for XY drift against HOPG lattice. The statistics on recognition efficiency and surface composition were done on tens of high resolution images with 60nm×60nm scanning area.