Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Halogen bonding versus hydrogen bonding induced 2D self-assembled nanostructures at the liquid-solid interface revealed by STM

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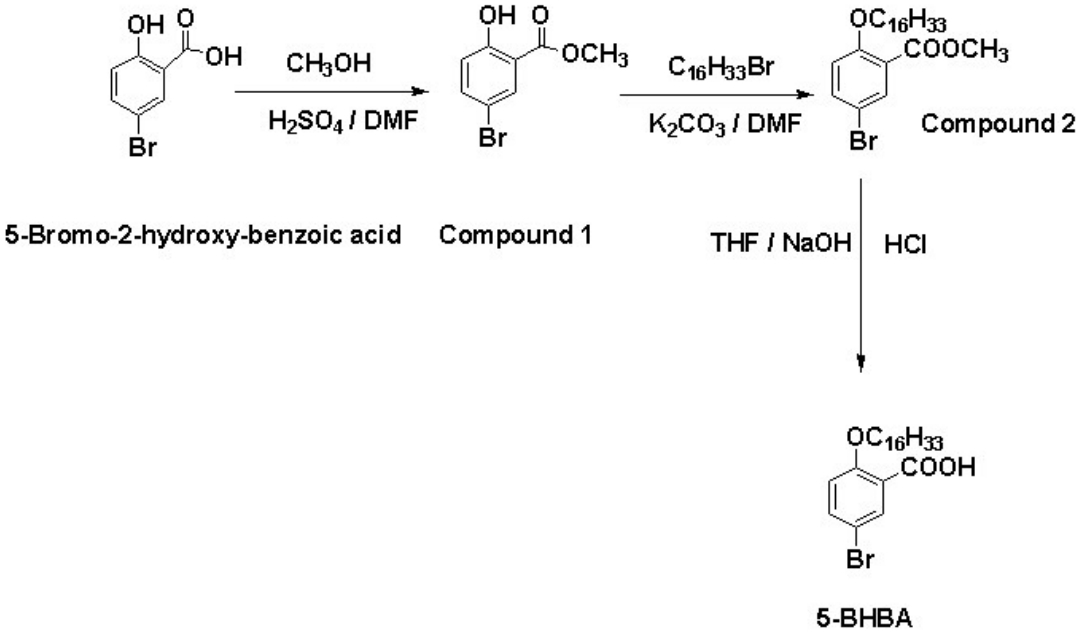
Synthesis

Compound 1 was synthesized from the commercially available 5-Bromo-2-hydroxy-benzoic acid (4.0 g, 18.4 mmol) with methanol (100 mL) in several droplets of DMF and concentrated sulphuric acid (8 mL). After stirring and refluxing at 98 °C for 24 h. Then the reaction mixture was diluted with sodium bicarbonate (40 mL) and dichloromethane (50 mL) before the organic phase was separated. The solvent was monitored by TLC (PE: EA = 4:1). The organic phase was extracted 3 times with dichloromethane by suction filtration, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The product was isolated as a yellow oil.

Compound 2 A mixture of **Compound 1** (2.5 g, 10.8 mmol), potassium carbonate (20.0 g, 145mmol) in DMF (50 mL) was stirred at room temperature for 3 min. Then 1-bromohexadecane (6.6 g, 21.6 mmol) was added. After stirring and refluxing at 98 °C for 48 h, the reaction mixture was extracted with saturated salt water (20 mL) and dichloromethane (20 mL). The organic phase was evaporated in vacuo. The crude residue was dissolved in hot dichloromethane and ethanol, recrystallized as a white powder.

5-BHBA A mixture of **Compound 2** (2.87 g, 6.3 mmol), sodium hydroxide (5 g, 125 mmol) in H_2O (50 mL) and THF (50 mL) was stirred and refluxed at 88 °C for 24 h. The mixture was evaporated, then the aqueous phase was diluted with H_2O and acidified to pH 3 with HCl (30 mL). The aqueous phase was filtered and the precipitate was dried to give a white product.

Data for 5-BHBA: 1HNMR (600 MHz, CDCl3, ppm): δ 8.33 (1H, m), 7.65 (1H, m), 6.96 (1H, m), 4.25 (2H, m), 1.93 (2H, m), 1.51 (2H, m), 1.29 (24H, m), 0.91 (3H, m)



Scheme S1 Synthesis of 5-BHBA molecule.

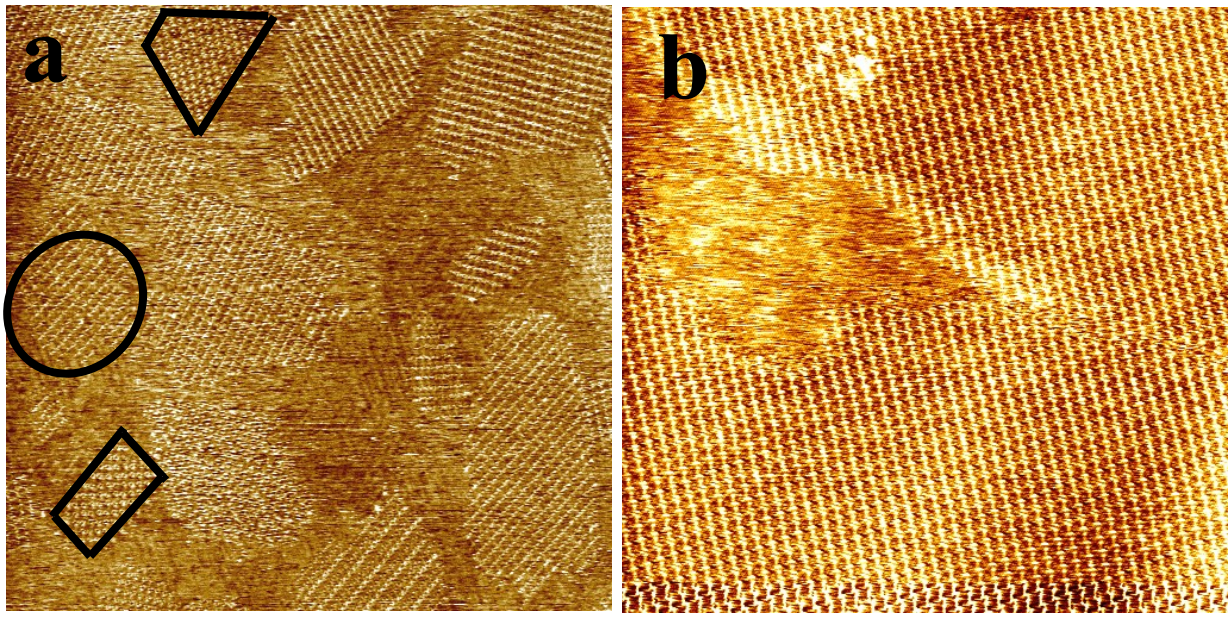


Fig. S1 Large-scale STM images for 5-BHBA, depicting the instantaneous phase transition from lip-like to T-like patterns in 1-octanoic acid under a saturated concentration. (a) 200 × 200 nm^2; (b)135 × 135 nm^2; V_{bias} = 630 mV, I_t = 450 pA.

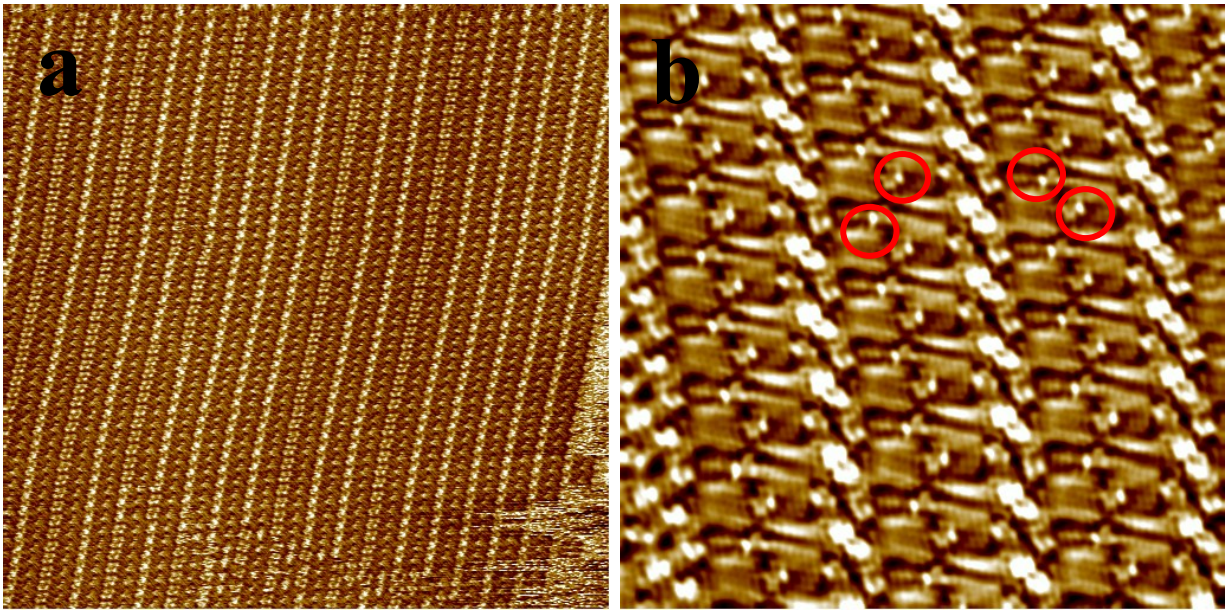


Fig. S2 STM images of 5-BHBA molecules self-assembly at the 1-octanoic acid /HOPG interface under a low concentration (3.5×10^{-5} M). The bright dots in red circles are Br atoms. (a) 100×100 nm^2; (b) 25×25 nm^2; $V_{bias} = 640$ mV, $I_t = 470$ pA.

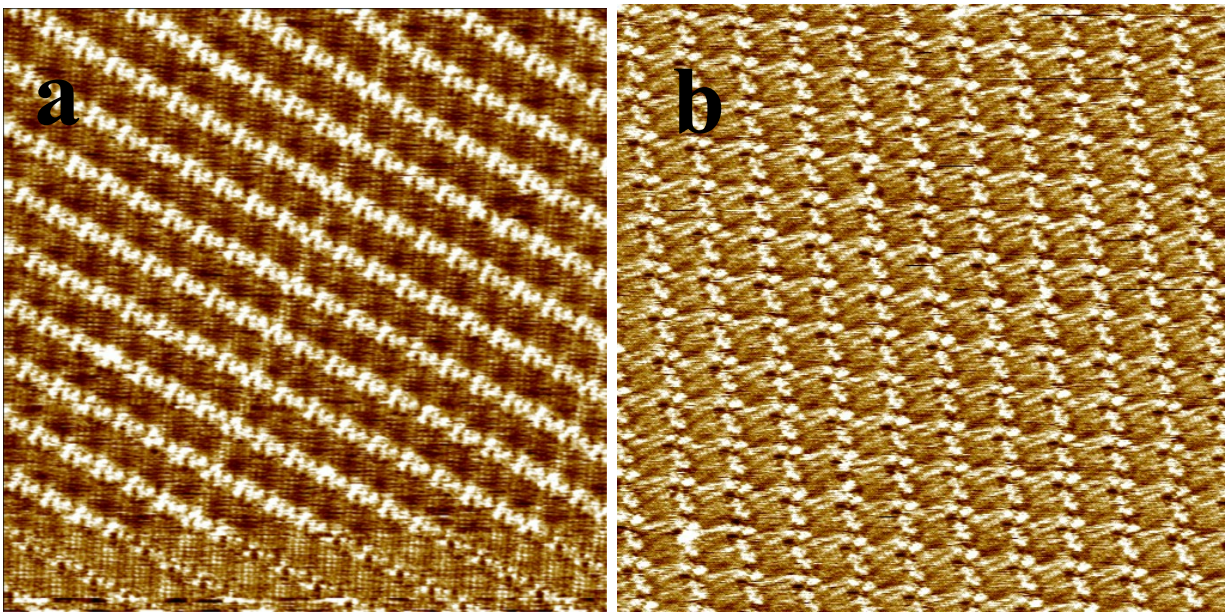
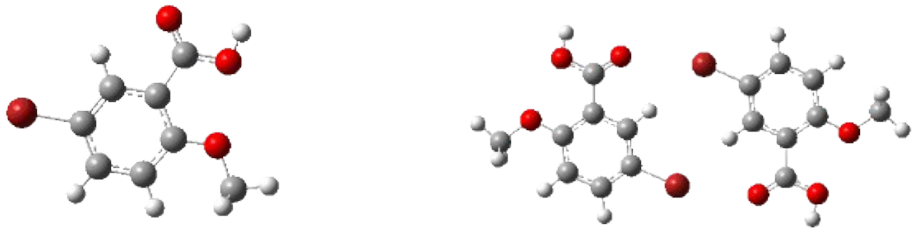


Fig. S3 Large-scale STM images of 5-BHBA adlayer in (a) CH_2Cl_2 after the solvent evaporation and (b) 1-octanoic acid at the graphite interface. (a) 45×45 nm^2; (b) 30×30 nm^2; $V_{bias} = 640$ mV, $I_t = 470$ pA. The self-assembly of 5-BHBA in CH_2Cl_2 are the same as T-like structure in 1-octanoic acid.

Table 1 The intermolecular bond distance for dimer 1 calculated by DFT method.

Intermolecular Bond	Bond Distance (nm)	Sum of van der Waals Radii (nm)
Br···H	2.65	3.05
Br···O	3.07	3.37

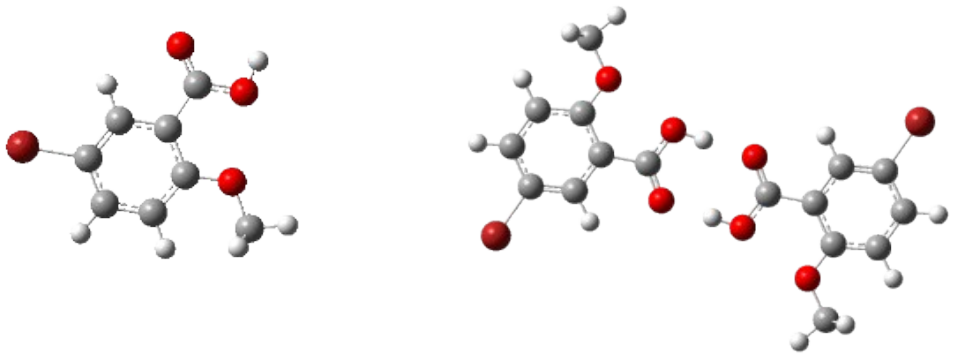


$E_0 = -3106.3414$ a. u. $E_1 = -6212.6960$ a. u.

Fig. S4 DFT optimized atomic structure of 5-BHBA. (a) Single molecule, (b) Structure of Dimer 1. The calculated energy was indicated in each figure.

The binding energy was calculated as below.

$\Delta E_1 = E_1 - 2E_0 = -0.0132$ a. u. $= -8.28$ kcal mol^{-1}

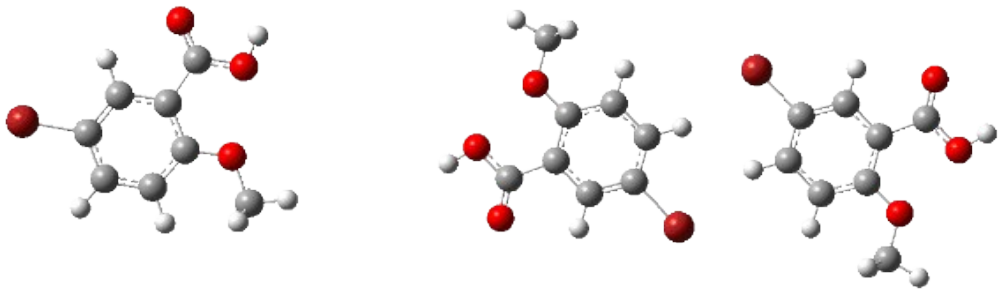


$E_0 = -3106.3414$ a. u. $E_2 = -6212.7119$ a. u.

Fig. S5 DFT optimized atomic structure of 5-BHBA. (a) Single molecule, (b) Structure of Dimer 2. The calculated energy was indicated in each figure.

The binding energy was calculated as below.

$\Delta E_2 = E_2 - 2E_0 = -0.0291$ a. u. $= -18.26$ kcal mol^{-1}



$E_0 = -3106.3414$ a. u. $E_3 = -6212.6916$ a. u.

Fig. S6 DFT optimized atomic structure of 5-BHBA. (a) Single molecule, (b) Structure of Dimer 3. The calculated energy was indicated in each figure.

The binding energy was calculated as below.

$\Delta E_3 = E_3 - 2E_0 = -0.0088$ a. u. $= -5.52$ kcal mol^{-1}