Supporting Information

Same building block, diverse surface-confined self-assemblies: solvent and concentration effects induced structural diversity towards chirality and achirality

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1. STM data



Fig. S1 Large-scale STM images for HPF at the 1-phenyloctane/HOPG interface, showing the phase transition from Tetramer-S (No. 1) and Irregular-linear (No. 2) nanostructures to Tetramer-linear (No. 3) structure. Time interval between (a, b) and (c, d), (c, d) and (e, f) is about fifteen minutes. Scanning parameters: $I_t = 200 \text{ pA}$, $V_{\text{bias}} = -210 \text{ mV}$.



Fig. S2 Large-scale STM images for HPF at the 1-octanoic acid/HOPG interface, showing the stable monolayer obtained more than thirty minutes after the solution was deposited onto the substrate. Corresponding to Fig. 4 in the main text, No. 2 to 5 represent the left-handed Hexamer-S, right-handed Hexamer-S, left-handed Tetramer-S-II and right-handed Tetramer-S-II structures, respectively. Scanning parameters: $I_t = 220$ pA, $V_{\text{bias}} = -220$ mV.



Fig. S3 (a) High-resolution STM image for the Tetramer-S-II structure at the 1-octanoic acid/HOPG interface. (b) Topography image which shows the distance between the two points in panel (a). The distance is about 2.2 nm, which is longer than the heptyloxy chain and 1-octanoic acid, thus the long chain observed in the STM image is speculated to be the adjacent heptyloxy chain and two 1-octanoic acid molecules.



Fig. S4 Large-scale STM images for HPF on the dry HOPG interface, showing the co-existent Tetramer-S and Irregular-linear structures. Concentration: $1/10 \text{ C}_0 (2.1 \times 10^{-4} \text{ M})$. The image in (a) was obtained spontaneously after the sample was applied to the HOPG surface. The images in (b–d) were obtained six hours later. No. 1 and 2 represent the Tetramer-S and Irregular-linear structures, respectively. Scanning parameters: $I_t = 180 \text{ pA}$, $V_{\text{bias}} = -190 \text{ mV}$ for (a); $I_t = 200 \text{ pA}$, $V_{\text{bias}} = -190 \text{ mV}$ for (b–d).



Fig. S5 Large-scale STM images for HPF at the 1-octanoic acid/HOPG interface, at the concentration of C₀ (2.1×10^{-3} M). Scanning parameters: $I_t = 200$ pA, $V_{\text{bias}} = -200$ mV.



Fig. S6 Large-scale STM images for HPF at the 1-octanoic acid/HOPG interface, at the concentration of $1/100C_0$ (2.1×10^{-5} M). Under this concentration, only Tetramer-S-II structure was observed. Scanning parameters: $I_t = 210$ pA, $V_{\text{bias}} = -200$ mV.



Fig. S7 Large-scale STM images for HPF in (a) n-tetradecane and (b) 1-phenyloctane, at the concentration of C₀ (2.1×10^{-3} M). Scanning parameters: $I_t = 200$ pA, $V_{\text{bias}} = -200$ mV for (a); $I_t = 210$ pA, $V_{\text{bias}} = -210$ mV for (b).



Fig. S8 Large-scale STM images for HPF in n-tetradecane, at low concentration of 2.1×10^{-5} M. Scanning parameters: $I_t = 200$ pA, $V_{\text{bias}} = -300$ mV. Only Tetramer-S-I structure was observed on the HOPG surface.



Fig. S9 Large-scale STM images for HPF in 1-phenyloctane, at low concentration of 2.1×10^{-5} M. Scanning parameters: $I_t = 220$ pA, $V_{\text{bias}} = -200$ mV. Only Tetramer-linear structure was observed on the HOPG surface.



Fig. S10 (a–c) Large-scale STM images for HPF on the dry HOPG surface, which were obtained spontaneously after the sample was applied onto the substrate, showing the co-existed phases. Concentration: $1/100 C_0 (2.1 \times 10^{-5} \text{ M})$. The blue, yellow, green and red circles labeled as No. 1 to 4 represent the Alternate, Tetramer-S, Hexamer-S and Octamer-S structures. The green arrows in (a) and (c) are used to indicate the Octamer-S structure. (d–f) Large-scale STM images for HPF on the dry HOPG surface, which were obtained about two hours after the sample was applied onto the substrate. As the sample was scanned for more than two hours, we found that the Alternate structure was not the dominant phase in the monolayer. Instead, chiral Octamer-S structure covered almost all of the HOPG surface. Scanning parameters: I_t = 200 to 230 pA, V_{bias} = -300 to -200 mV.

2. Characterization data

¹**H NMR** (400 MHz CDCl₃) δ 7.29 (s, 2H), 7.17 (d, 2H), 6.94 (m, 2H), 4.00 (t, 4H), 1.80 (m, 4H), 1.47 (m, 4H), 1.28 (m, 28H), 0.90 (m, 6H)



Fig. S11 ¹H NMR (400 MHz CDCl₃) image for HPF.