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Supporting Information

The Br···π halogen bond assisted self-assembly of asymmetric molecule regulated by concentration

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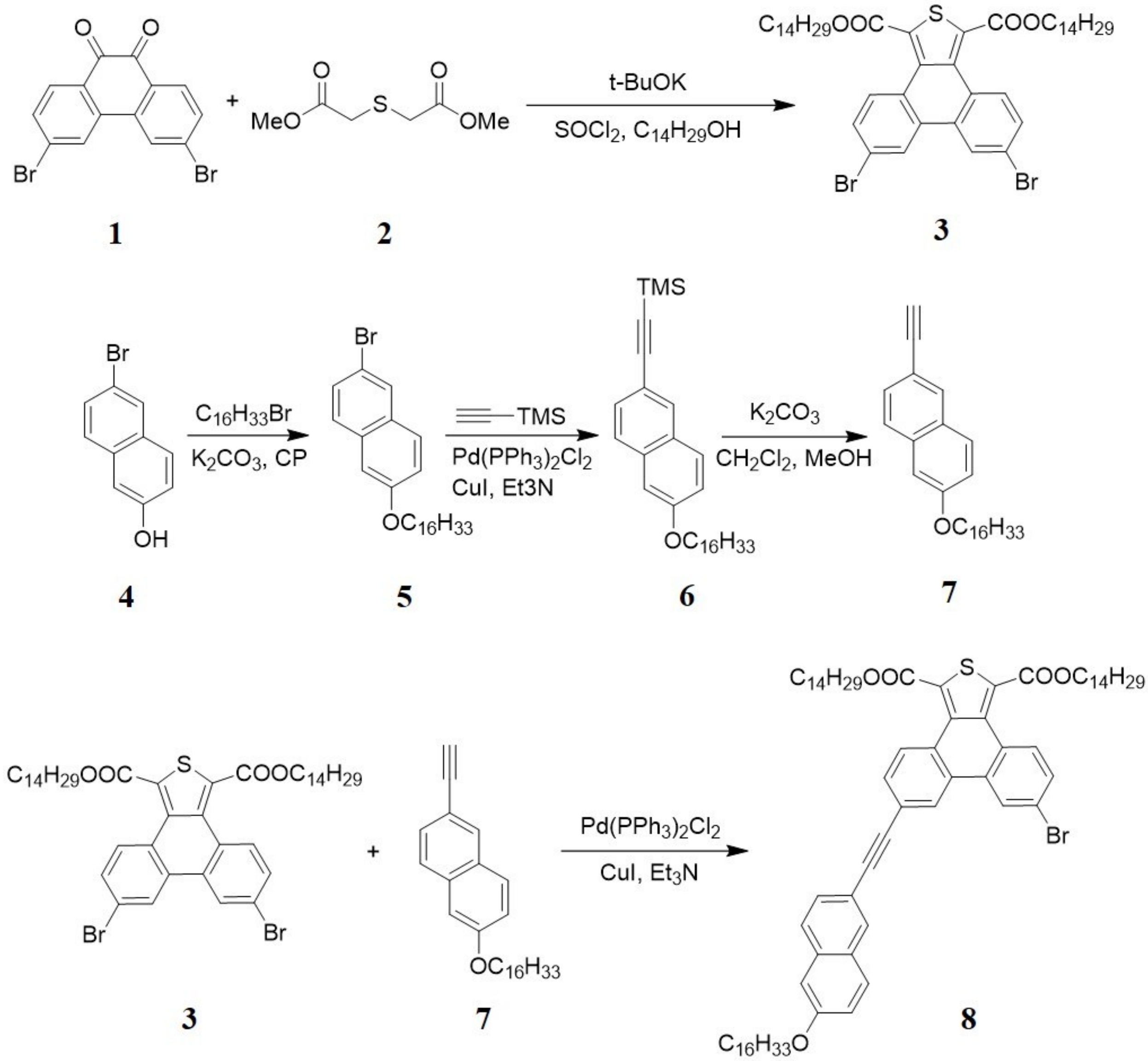
Synthesis of ditetradecyl 6-bromo-9-((6-(hexadecyloxy)naphthalen-2-yl)ethynyl)phenanthro[9,10-c]thiophene-1,3-dicarboxylate (M1)

General. The synthetic procedure of **M1** is described in the Scheme S1. All reactants were purchased from TCI and used without further purification. All commercially available solvents were used as received. ^{1}H (600 MHz) NMR spectra were measured on a Bruker AVANCE III HD 600 spectrometer. For NMR measurements, chloroform-d was used as solvent and the spectra were referenced to residual solvent proton signals in the ^{1}H NMR spectra (7.26 ppm).

Scheme S1. Synthesis of M1



Compound 3: To a suspension of **compound 1** (1.09g, 2.98mmol) in Toluene (60mL), **compound 2** (0.618g, 3.00mmol) was injected under the protection of N_2 atmosphere. The mixture was stirred at 70 °C for 30 min

and cooled to 40 °C. After the injection of the methanol solution of *t*-BuOK, the mixture was stirred at room temperature for five days. 100mL deionized water was added to the reaction mixture and the organic phase was removed under reduced pressure. HCl solution was added to the mixture to adjust the pH = 1, thereafter, the mixture was heated at 60 °C for 2 hours. It gives yellow solid after the suspension was filtered. Then, the yellow product was dissolved in 10mL thionyl chloride. After the addition of 1mL DMF, the mixture was heated at 80 °C for 12 hours. Tetradecyl alcohol (1.37g, 5.65mmol) and 25mL THF were added after the removal of redundant thionyl chloride under reduced pressure. The mixture continually heated at 80 °C for 12 hours. The organic solvent was evaporated in vacuum. The crude product was extracted by CH_2Cl_2 and H_2O for three times and dried by anhydrous $MgSO_4$. After purified by silica chromatography, it yielded cyan solid **compound 3**.

^{1}H NMR (600MHz, $CDCl_3$, ppm) δ: 8.79 (m, 2H), 8.43 (m, 2H), 7.62 (m, 2H), 4.43 (m, 4H), 1.83 (m, 4H), 1.48 (m, 4H), 1.25 (m, 40H), 0.88 (m, 6H).

Compound 5: **Compound 4** (1.0g, 4.48mmol), anhydrous K_2CO_3 (1.1g, 8mmol) and 1-bromohexadecane (1.31g, 8mmol) were added in 10mL acetone. The suspension was stirred at 85 °C for 20 hours. After the mixture was cooled to room temperature, the organic solvent was evaporated under reduced pressure. The solid product was extracted by CH_2Cl_2 and H_2O and the organic phase was dried by anhydrous $MgSO_4$. The crude product was purified by silica chromatography after the removal of CH_2Cl_2. It yielded white solid **compound 5**.

^{1}H-NMR (600MHz, $CDCl_3$, ppm) δ: 7.90 (m, 1H), 7.66 (m, 1H), 7.60 (m, 1H), 7.50 (m, 1H), 7.15 (m, 1H), 7.07 (m, 1H), 4.03 (m, 2H), 1.86 (m, 2H), 1.51 (m, 2H), 1.26 (m, 24H), 0.88 (m, 3H).

Compound 6: **Compound 5** (1.0g, 3.25mmol), CuI (22.8mg, 0.12mmol), and $Pd(PPh_3)_2Cl_2$ (0.14g, 0.12mmol) were added into a round bottom flask. TMSA (0.55mL, 4mmol) and 35mL Et_3N were injected under the protection of N_2. The suspension was stirred at 80 °C for 16 hours. The organic solvent was removed under reduced pressure after the mixture was cooled to room temperature. The solid product was extracted by PE and HCl solution, and dried by anhydrous $MgSO_4$. The crude product was purified by silica chromatography. It yielded white solid **compound 6.**

^{1}H-NMR (600MHz, $CDCl_3$, ppm) δ: 7.80 (m, 1H), 7.56 (m, 1H), 7.48 (m, 1H), 7.25 (m, 1H), 6.94 (m, 1H), 6.90 (m, 1H), 3.88 (m, 2H), 1.66 (m, 2H), 1.32 (m, 2H), 1.08 (m, 24H), 0.77 (m, 3H), 0.08 (m, 9H).

Compound 7: To a solution of **compound 6** (0.5g, 1.83mmol) in a mixture of methanol (20mL) and THF

(20mL) was added anhydrous K_2CO_3 (1.3g, 9.33mmol). The suspension was stirred at room temperature for 2 hours. The mixture was extracted by diethyl ether and H_2O after the removal of organic solvents. The organic phase was dried by anhydrous $MgSO_4$ and evaporated under reduced pressure. It yielded white solid **compound 7**.

^{1}H-NMR (600MHz, $CDCl_3$, ppm) δ: 7.80 (m, 1H), 7.56 (m, 1H), 7.48 (m, 1H), 7.25 (m, 1H), 6.94 (m, 1H), 6.90 (m, 1H), 3.88 (m, 2H), 2.99 (m, 1H), 1.66 (m, 2H), 1.32 (m, 2H), 1.08 (m, 24H), 0.77 (m, 3H).

M1 (compound 8): **Compound 3** (1.0g, 1.15mmol), **compound 7** (0.45g, 1.14mmol), CuI (11mg, 0.06mmol) and $Pd(PPh_3)_2Cl_2$ (65.5mg, 0.06mmol) were added in a round bottom flask. 30mL Et_3N was injected in a N_2 atmosphere. The mixture was stirred at 80 °C for 16 hours. After the mixture was cooled to room temperature, the organic solvent was removed under reduced pressure. The product was extracted by diethyl ether and H_2O, and dried by anhydrous $MgSO_4$. The crude product was purified by silica chromatography and yielded yellow solid **M1**.

^{1}H-NMR (600MHz, $CDCl_3$, ppm) δ: 7.99 (m, 2H), 7.70 (m, 2H), 7.66 (m, 2H), 7.51 (m, 1H), 7.49 (m, 1H), 7.17(m, 1H), 7.15 (m, 1H), 7.09 (m, 2H), 5.35 (m, 2H), 4.07 (m, 4H), 1.75 (m, 6H), 1.42 (m, 6H), 1.22 (m, 64H), 0.82 (m, 9H).

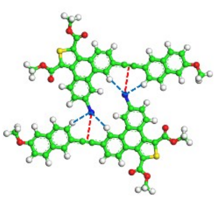
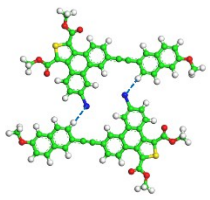
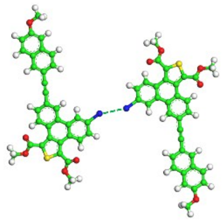
Experimental details: Scanning Tunneling Microscope (STM)

Commercially available 1-octanoic acid (TCI) and *n*-hexadecane (TCI) were used as received. The highly oriented pyrolytic graphite (HOPG, grade ZYB, Bruker, USA) substrate was freshly cleaved using adhesive tape to obtain an atomically flat surface. STM tips were prepared by mechanically cutting a Pt/Ir wire (80/20). The STM samples were obtained by dissolving **M1** molecules in *n*-hexadecane solvent. The mother liquor was the saturated solution (concentration: $C_0 \approx 10^{-3}$ mol L^{-1}) and it was diluted further to make a series of solution with diluted concentration. A droplet of solution (~2μL) containing **M1** molecules was deposited onto the HOPG surface to obtain the self-assembly structures. All STM experiments were performed by using a Nanoscope IIIa Multimode SPM (Bruker, USA) operating in constant-current mode at ambient conditions with the tip immersed in the supernatant liquid. All the STM measurements were repeated at least three times using different tips to check for reproducibility and to avoid experimental artifacts. Detailed imaging parameters are indicated in the figure caption: sample bias (V_{bias}) and tunneling current (I_{set}). STM images were corrected via FabViewer software.[1]

Experimental details: computational simulation

The structural models were built by using Materials Studio 7.0. The models of physisorbed monolayers were constructed by placing the molecules according to the intermolecular distance and angles obtained from the analysis of the high-resolution STM images. Theoretical calculations were performed using DFT provided by the Gaussian 09 software package. The geometry optimization and single point energy of dimers were calculated through the hybrid M06-2X functional and the split-valence polarized 6-31+g(d) basis set.[2–4] The surface electrostatic analysis and QTAIM analysis were carried out by using Multiwfn software[5] and visualized with the VMD program.[6]

Tab. S1 Calculated Building Blocks, Geometry Parameters, Interaction Energies and Electron Densities of Possible Dimers

	Dimer Ⅰ		Dimer Ⅲ	Dimer Ⅳ
Building Blocks				
Bonds	C−H···Br	C−Br···π	C−H···Br	C−Br···Br
Distance (Å)	2.69 2.74	3.78	2.71	3.44
Angle (°)	154.7 155.9	157.9	166.8	154.4
ΔE/(kJ mol^{-1})	−9.49		−1.89	−0.61
ρ_{CP} (e Å^{-3})	0.0795 0.0601	0.0321	0.0744	0.0581

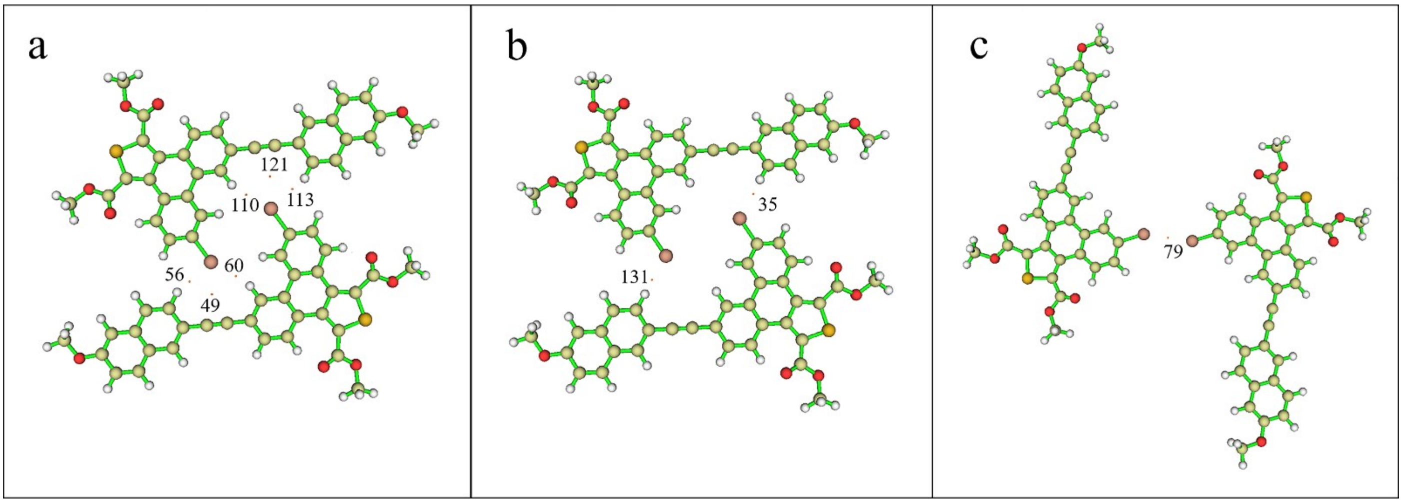


Fig. S1 (a, b, c) Bond critical point (BCP) distribution map of dimer Ⅰ, Ⅲ and Ⅳ, respectively. Orange dots and numbers indicate the existence of noncovalent interactions.

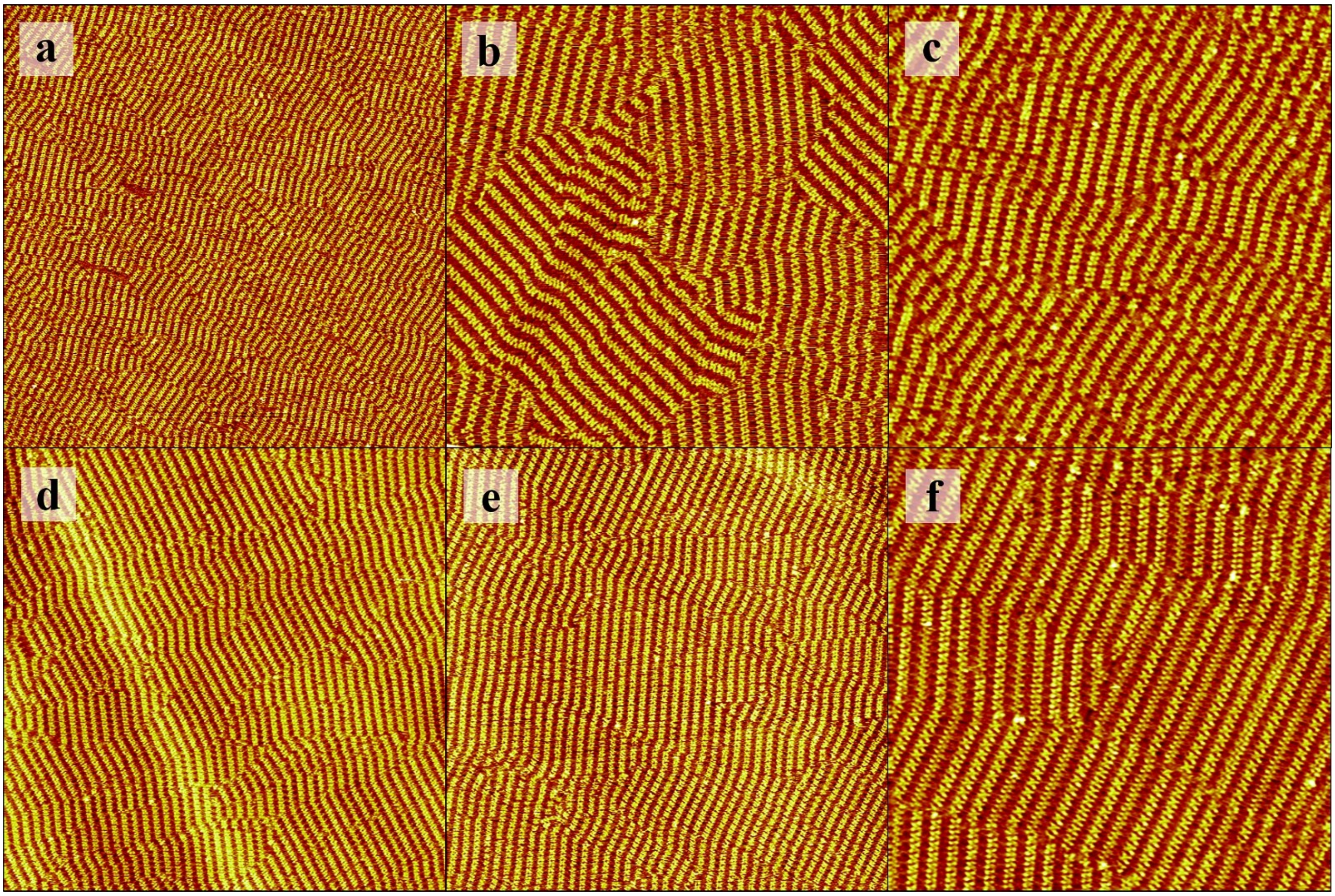


Fig. S2 Large-scale STM images of the self-assembly patterns of **M1** molecule at 1-octanoic acid/HOPG interface (a, b, c) and *n*-hexadecane/HOPG interface (d, e, f) under high concentration ($C \approx 1 \times 10^{-3}$ **M** $\times 10^{-4}$ **M**). Image size: (a) 200 × 200 nm^2 (b) 100 × 100 nm^2 (c) 90 × 90 nm^2 (d) 150 × 150 nm^2 (e) 150 × 150 nm^2 (f) 80 × 80 nm^2. Tunneling parameters: V_{bias} = 590−610 mV and I_t = 500−510 pA.

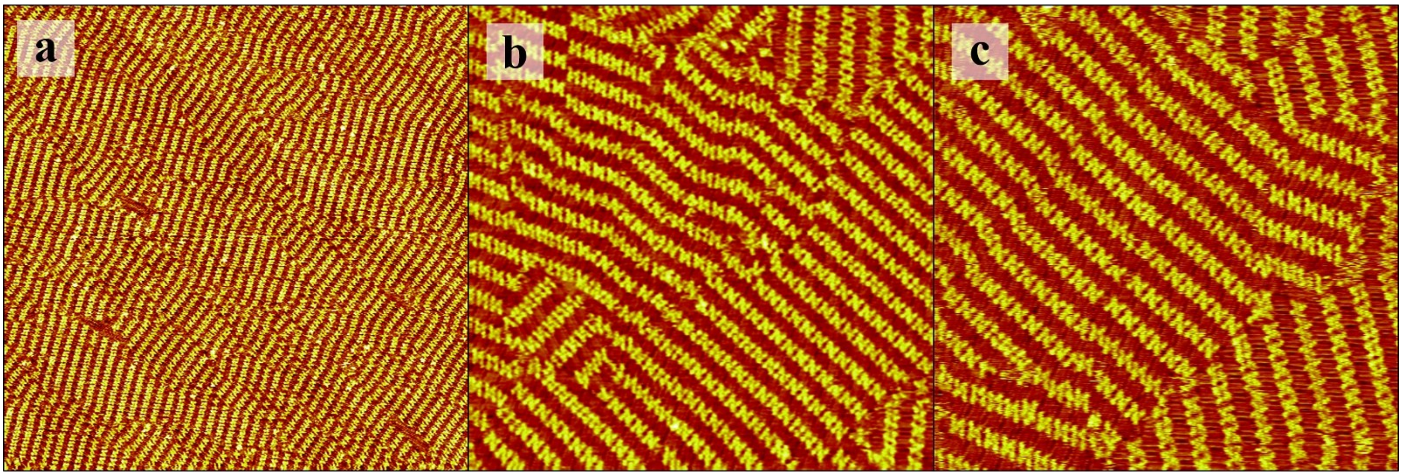


Fig. S3 Large-scale (a), medium-scale (b) and high-resolution (c) STM images of the self-assembly patterns of **M1** molecule at 1-octanic acid/HOPG interface under low concentration ($C < 1 \times 10^{-4}$ **M**). Image size: (a) $150 \times 150\ \mathrm{nm}^2$, (b) $60 \times 60\ \mathrm{nm}^2$ and (c) $50 \times 50\ \mathrm{nm}^2$. Tunneling parameters: $V_{\mathrm{bias}} = 590{-}610$ mV and $I_{\mathrm{t}} = 500{-}510$ pA.

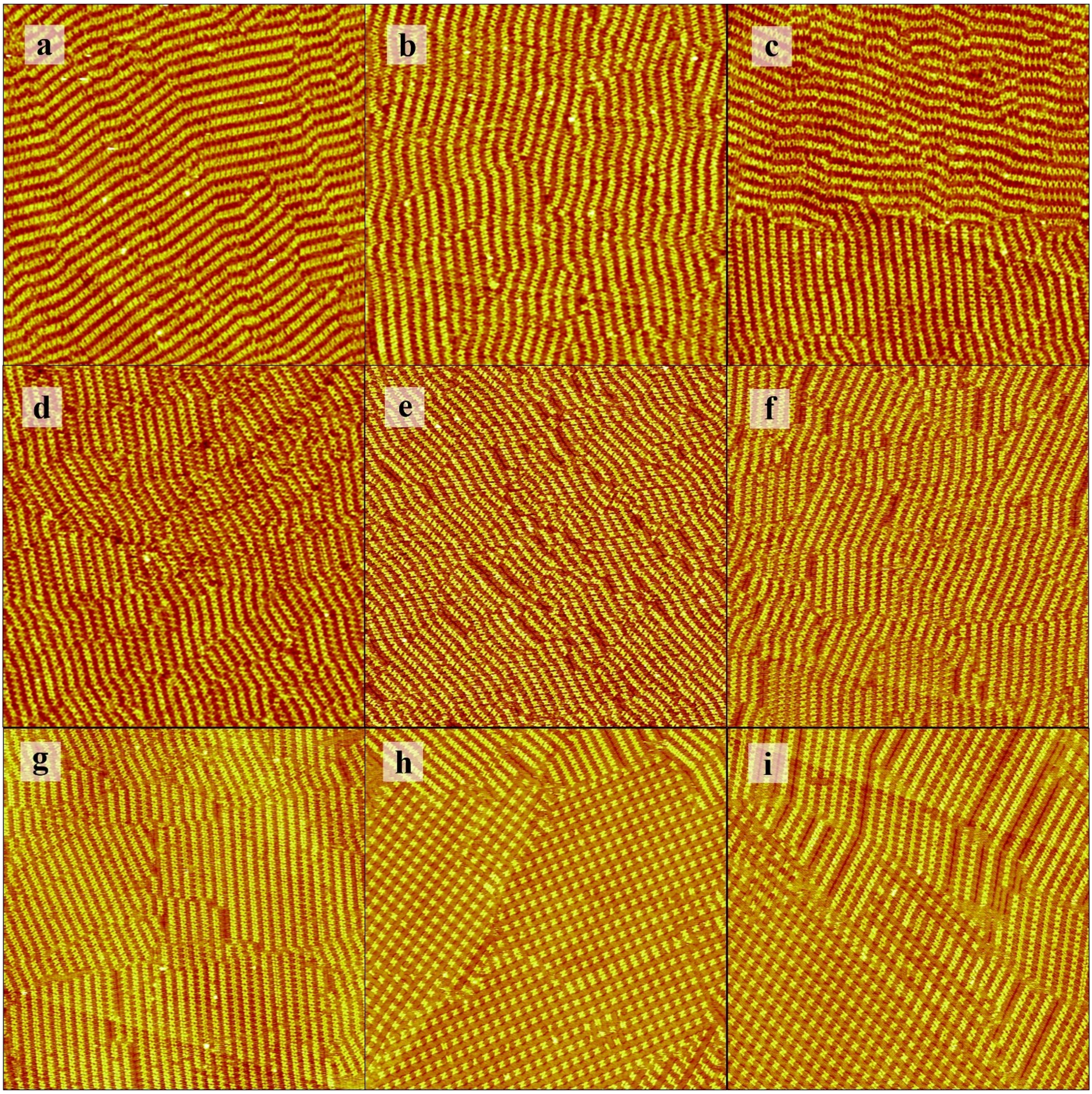


Fig. S4 (a-i) Large-scale STM images of self-assembly monolayers of **M1** molecules on the *n*-hexadecane/HOPG interface. Domain Ⅱ is observed when the concentration is lower than 2×10^{-6} **M**. Concentration: (a) C ≈ 1×10^{-3} **M** ; (b, c) C ≈ 2×10^{-4} **M** ; (d) C ≈ 1×10^{-4} **M** ; (e) C ≈ 1×10^{-5} **M** ; (f) C ≈ 5×10^{-6} **M** ; (g) C ≈ 3×10^{-6} **M** ; (h) C ≈ 2×10^{-6} **M** ; (i) C ≈ 1.2×10^{-6} **M**. Image sizes: (a, b) 100 × 100 nm^2, (c - i) 120 × 120 nm^2. Tunneling parameters: V_{bias} = 580−610 mV and I_{t} = 490−510 pA.

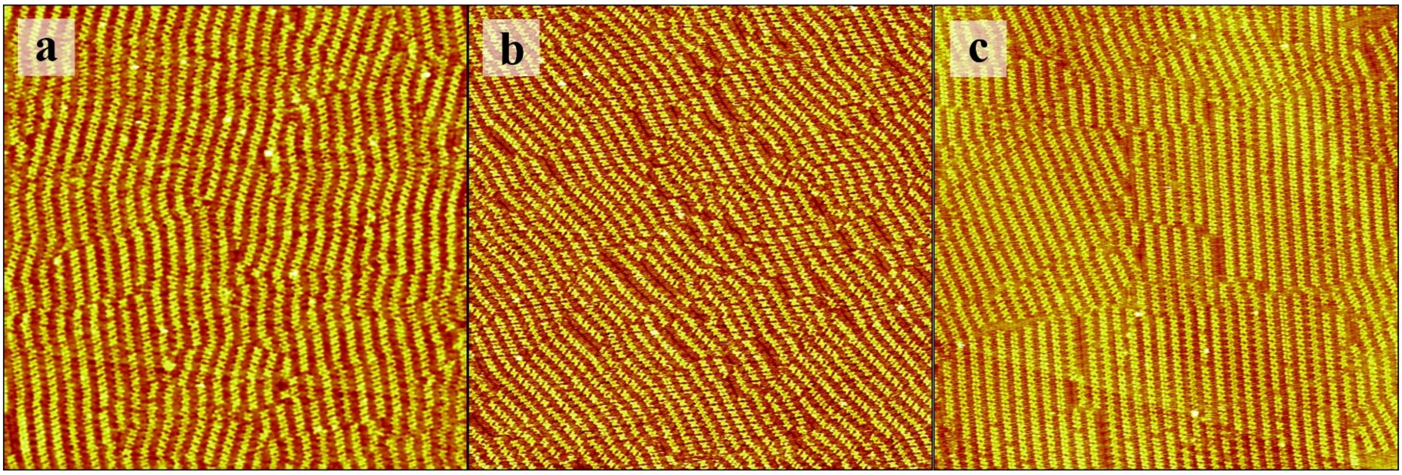


Fig. S5 Large-scale STM images of self-assembled patterns of **M1** molecules on the *n*-hexadecane/HOPG interface with a wide-range of concentration (C ≈ 2 × 10^{-4} **M** − 3 × 10^{-6} **M**). From the images, there are always lots of defects in domain Ⅰ. Image size: (a) 100 × 100 nm^2, (b, c) 120 × 120 nm^2. Tunneling parameters: V_{bias} = 595−610 mV and I_t = 490−510 pA.

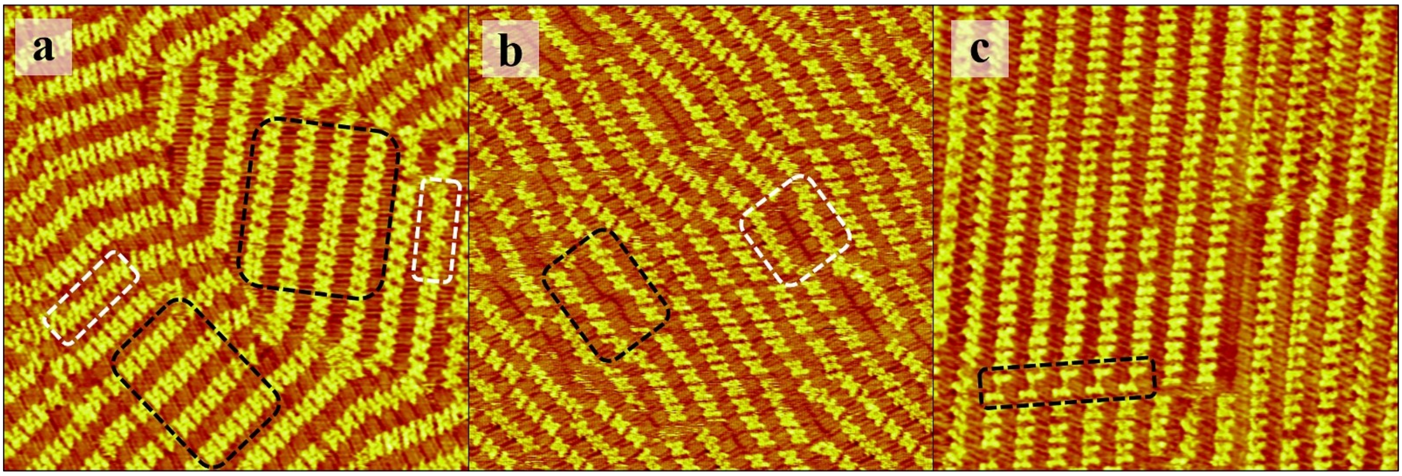


Fig. S6 High-resolution STM images of the self-assembly patterns of **M1** under different concentration. The images show four kinds of structures in domain Ⅰ. (a) The black dotted rectangle and the white dotted rectangle represent for the "N" type structure and single-row linear structure, respectively. (b) The black and white dashed rectangle encircled the "tail-to-tail" structures which are comprised of dimer Ⅰ and dimer Ⅲ, respectively. (c) The black dashed rectangle highlights the barely observed "Z" type structure. Solution concentration: (a) 1 × 10^{-4} **M**, (b) 1 × 10^{-5} **M**, (c) 3 × 10^{-6} **M**. Image size: (a) 47 × 47 nm^2, (b, c) 50 × 50 nm^2. Tunneling parameters: V_{bias} = 595−610 mV and I_t = 490−510 pA.

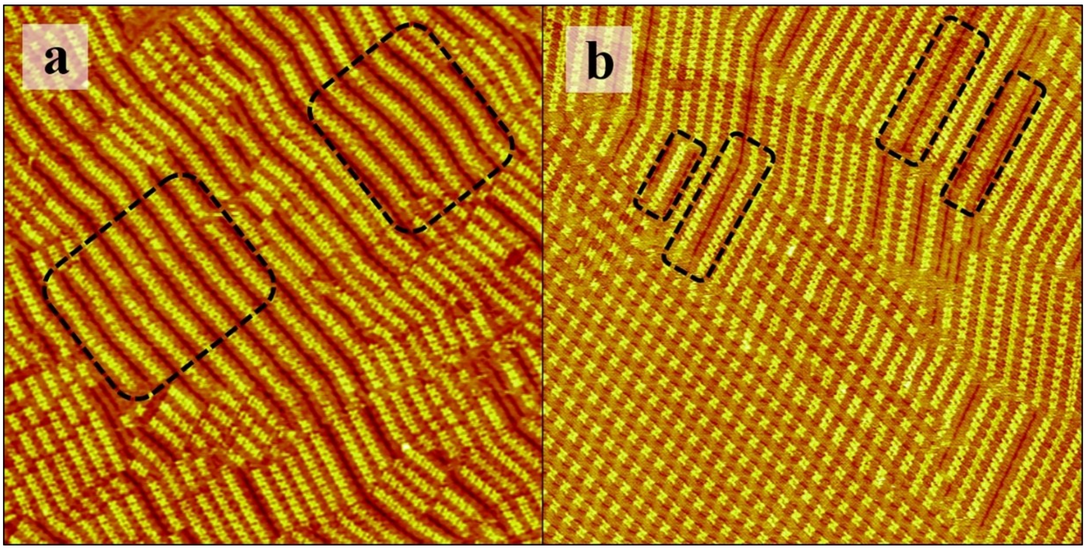


Fig. S7 (a, b) Large-scale STM images of the self-assembly patterns of **M1** under low concentrations showing the increasing of "tail-to-tail" structure. A part of "tail-to-tail" structures are encircled by the black dotted rectangles. Concentration: (a) 2 × 10^{-6} **M**, (b) 1 × 10^{-6} **M**. Image size: (a, b) 120 × 120 nm^2. Tunneling parameters: (a) $V_{\text{bias}} = 595$ mV and $I_t = 495$ pA, (b) $V_{\text{bias}} = 610$ mV and $I_t = 510$ pA.

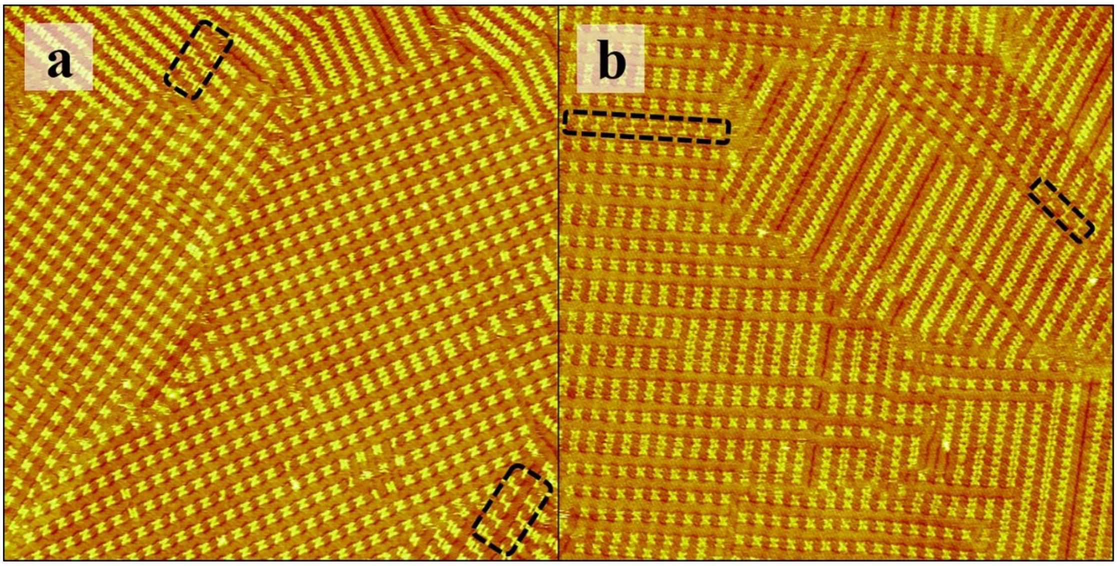


Fig. S8 (a, b) Large-scale STM images of the self-assembly patterns of **M1** under low concentrations showing the mere appearance of the "Z" type structure. All the "Z" type structures are highlighted by black dotted rectangles. Concentration: (a) 2 × 10^{-6} **M**, (b) 1 × 10^{-6} **M**. Image size: (a, b) 120 × 120 nm^2. Tunneling parameters: (a) $V_{\text{bias}} = 601$ mV and $I_t = 495$ pA, (b) $V_{\text{bias}} = 599$ mV and $I_t = 500$ pA.

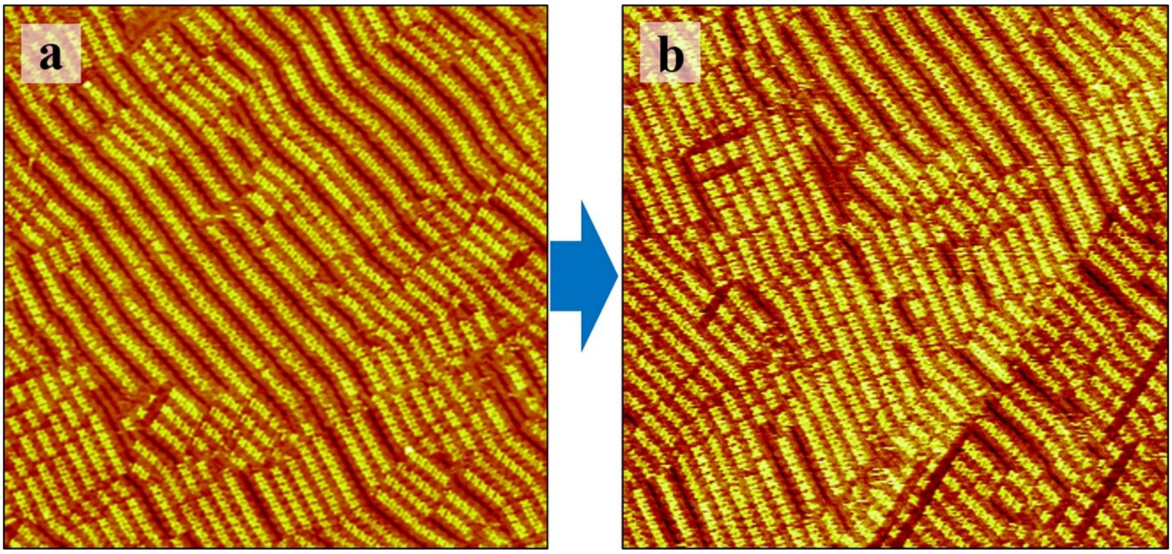


Fig. S9 (a, b) Large-scale STM images of self-assembly structures of **M1** on the *n*-hexadecane/HOPG interface (C ≈ 2 × 10^{-6} **M**). With the continuously scanning, no clear structural transformation was found. Image size: 120 × 120 nm^2. Tunneling parameters: $V_{\text{bias}} = 620$ mV and $I_t = 510$ pA.

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