

## Supplementary Information

### **Steric matching and concentration induced self-assembled structural variety of 2,7-bis(n-alkoxy)-9-fluorenone at the aliphatic solvent/graphite interface**

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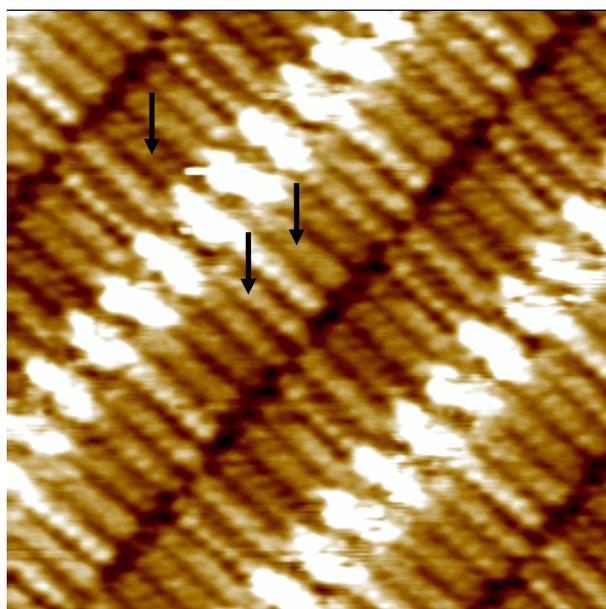
**Corresponding author:** College of Materials Science and Engineering

South China University of Technology,

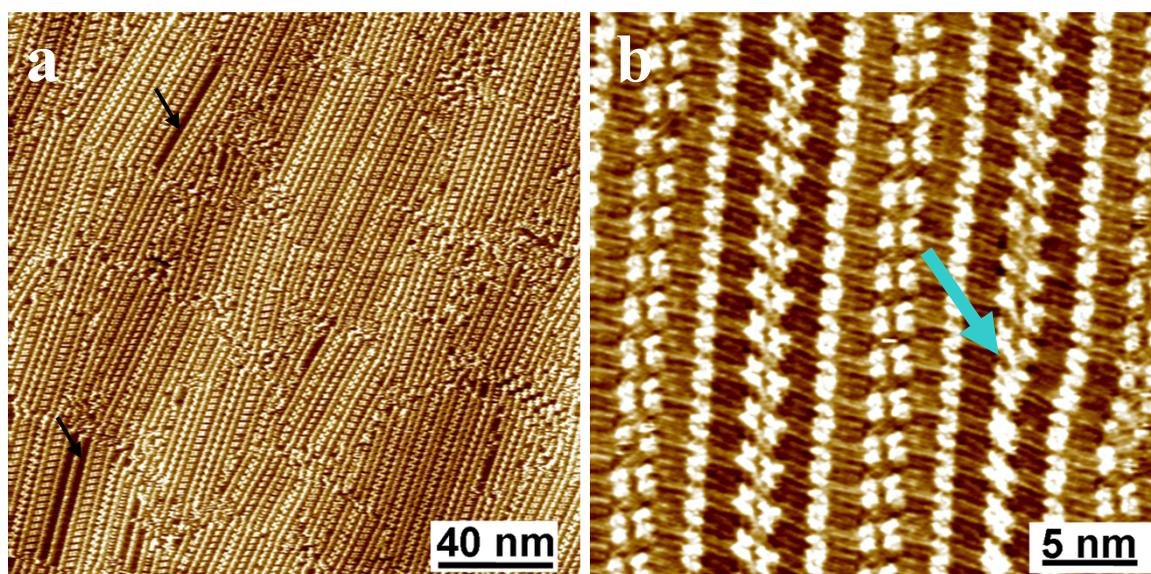
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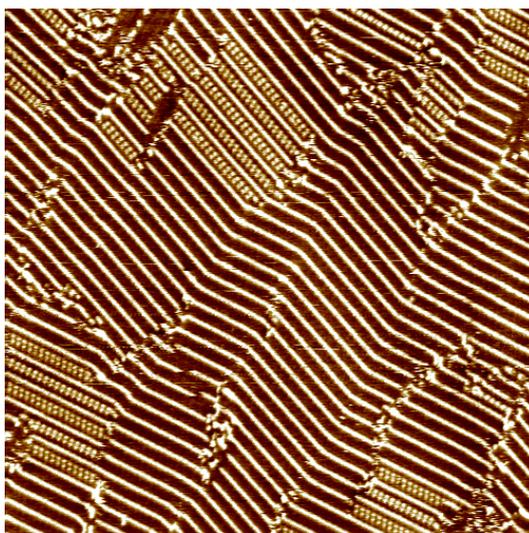
E-mail: msxrmiao@scut.edu.cn, wldeng@scut.edu.cn



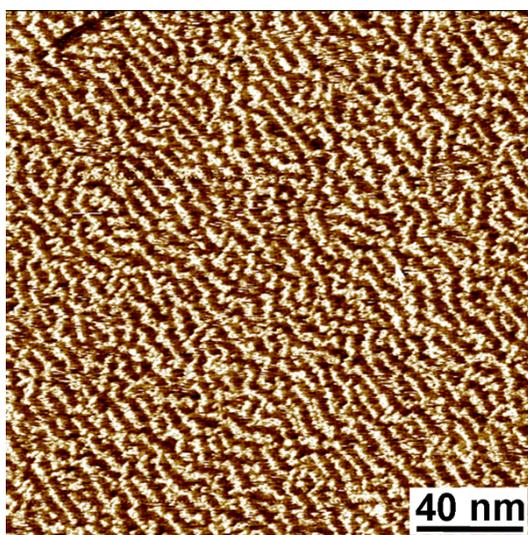
**Figure S1.** Higher-resolution STM image of F-OC<sub>14</sub> self-assembled adlayer in tetradecane ( $1.3 \times 10^{-6}$  mol L<sup>-1</sup>) on HOPG surface showing the coadsorbed solvent as the black arrows indicated.



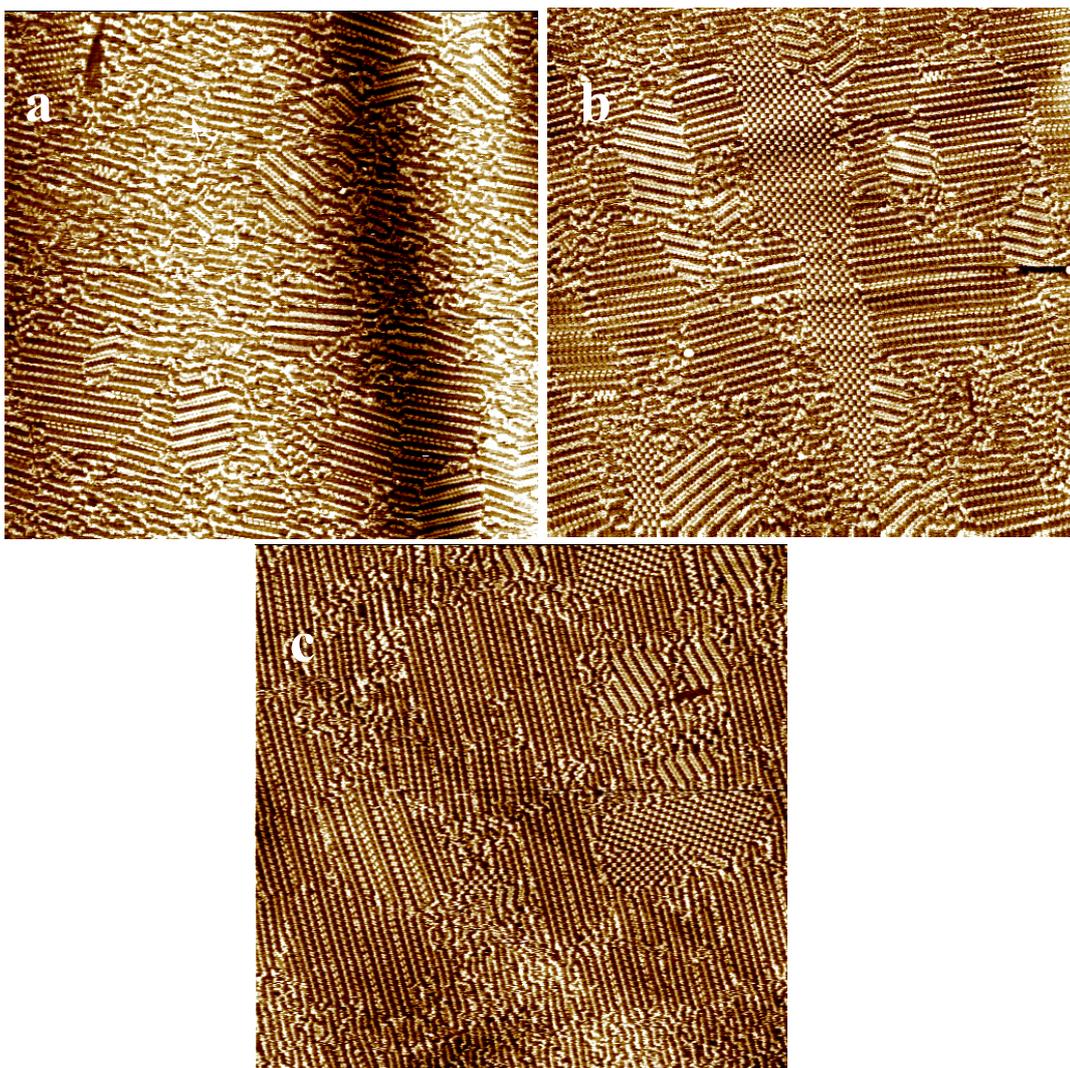
**Figure S2.** (a) Large-scale STM image of F-OC<sub>14</sub> self-assembly in tetradecane ( $2.5 \times 10^{-4}$  mol L<sup>-1</sup>) on HOPG surface showing the whole area is covered by an alternate pattern.  $V_{\text{bias}} = 650$  mV,  $I_t = 500$  pA. (b) High-resolution STM image of F-OC<sub>14</sub> self-assembly in tetradecane ( $1.5 \times 10^{-4}$  mol L<sup>-1</sup>) on HOPG surface showing the coexistence of two kinds of alternated patterns in one lamella indicated by a green arrow.



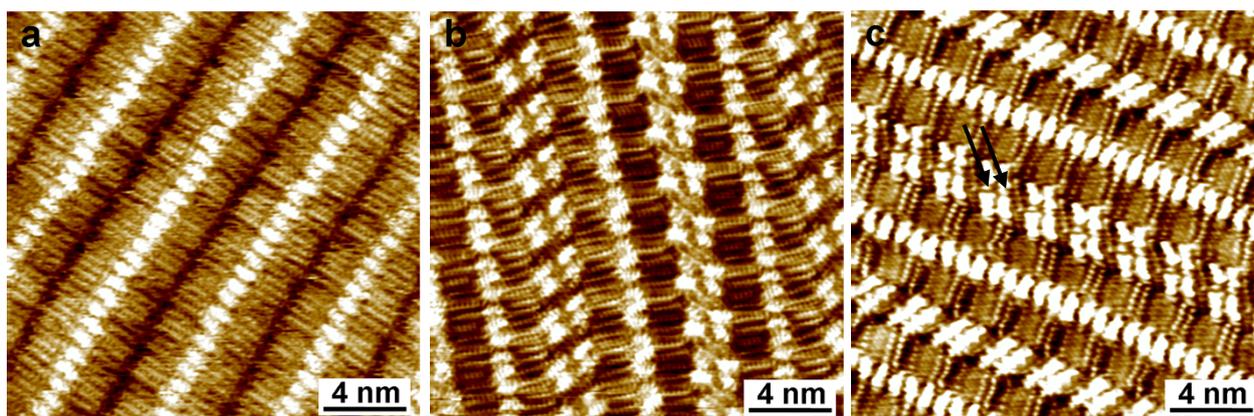
**Figure S3.** Large-scale STM image of F-OC14 self-assembly in tetradecane under a relative low concentration ( $2.5 \times 10^{-6} \text{ mol L}^{-1}$ ) showing the coexistence of alternate pattern and coadsorbed structure.  $V_{\text{bias}} = 620 \text{ mV}$ ,  $I_t = 515 \text{ pA}$ . Scan area:  $197 \text{ nm} \times 197 \text{ nm}$ .



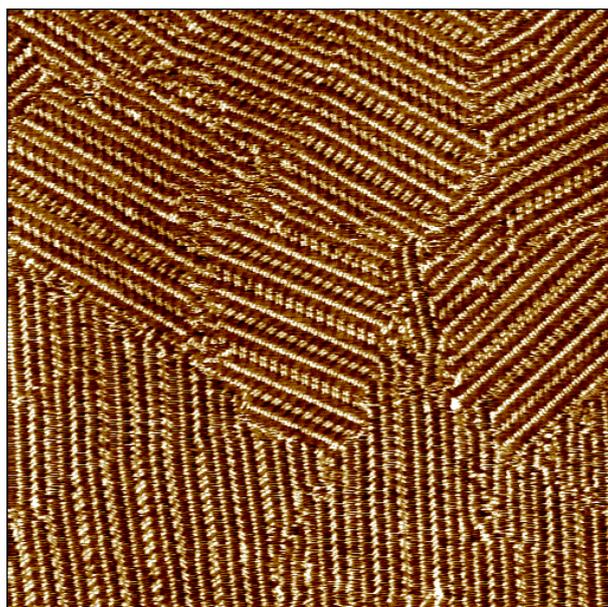
**Figure S4.** Large-scale STM image of F-OC14 self-assembly in tetradecane under a high concentration ( $7.5 \times 10^{-4} \text{ mol L}^{-1}$ ).  $V_{\text{bias}} = 640 \text{ mV}$ ,  $I_t = 520 \text{ pA}$ .



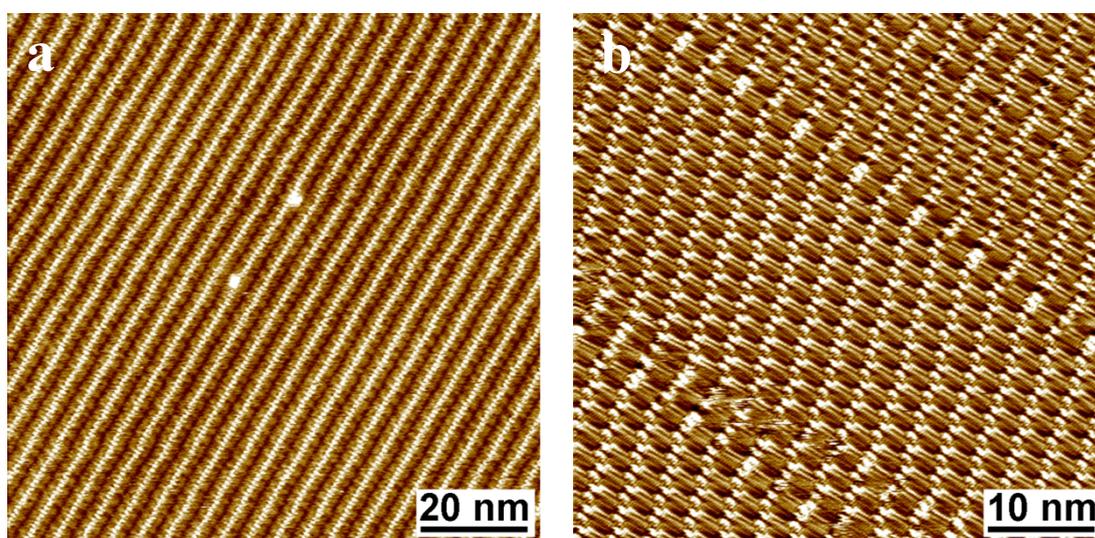
**Figure S5.** (a-c) Large-scale STM images obtained in different regions with the extension of the scanning time after the sample of F-OC<sub>14</sub> was placed more than 5 hours. Scan area: 200 nm × 200 nm.



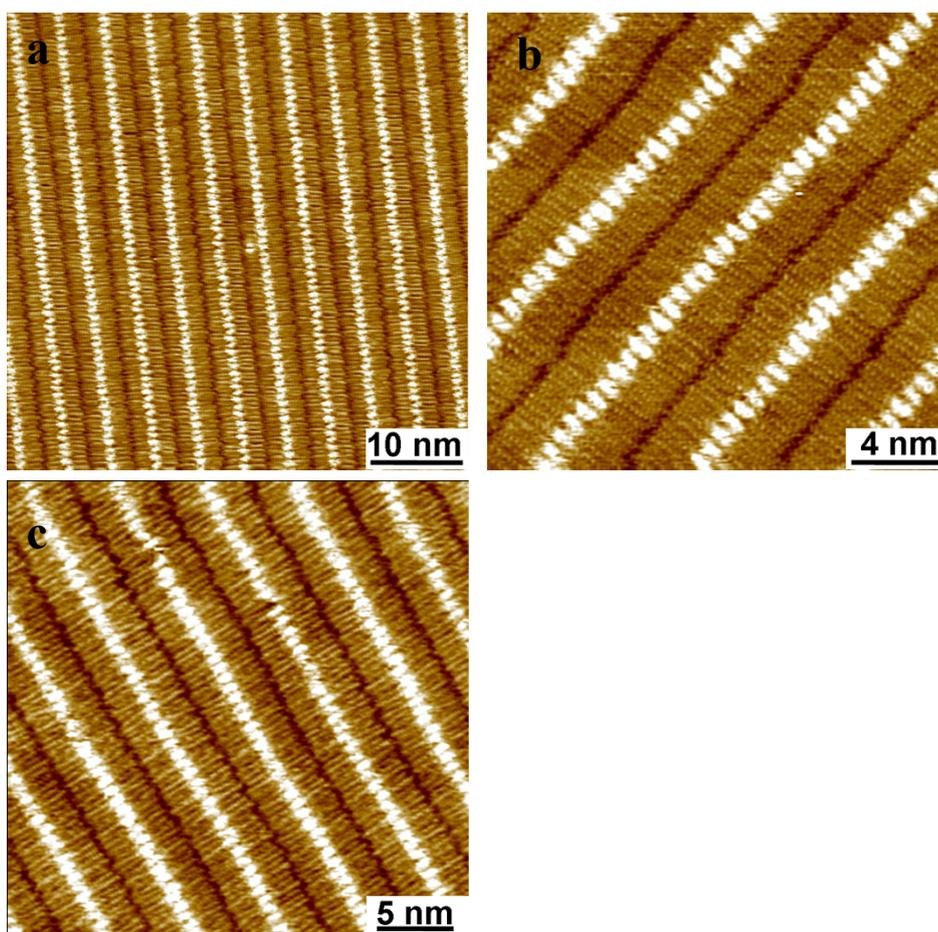
**Figure S6.** (a) STM image of F-OC<sub>14</sub> self-assembly in tridecane ( $1.5 \times 10^{-6}$  mol L<sup>-1</sup>) on HOPG surface. (b, c) STM images of F-OC<sub>14</sub> self-assembly in tridecane ( $3.5 \times 10^{-4}$  mol L<sup>-1</sup>) on HOPG surface.  $V_{\text{bias}} = 640$  mV,  $I_t = 510$  pA.



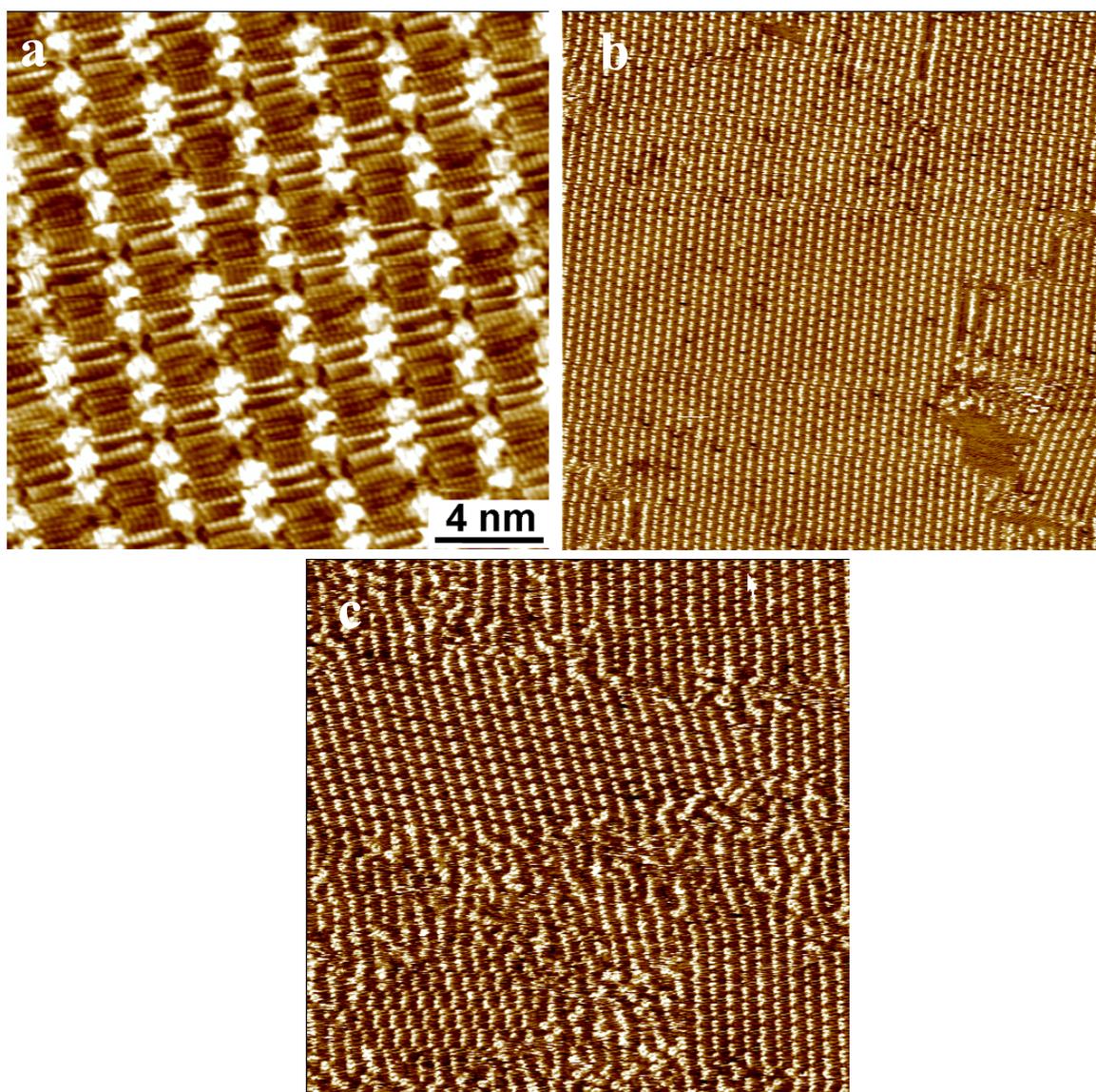
**Figure S7.** A typical STM image of the F-OC<sub>14</sub> self-assembled monolayer in tridecane on HOPG surface after the sample was placed more than 12 hours.  $V_{\text{bias}} = 600$  mV,  $I_t = 530$  pA. Scan area: 132 nm  $\times$  132 nm.



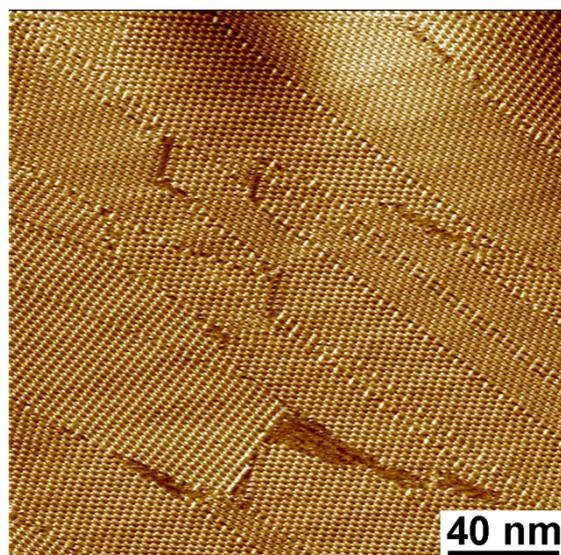
**Figure S8.** (a) STM image of F-OC<sub>12</sub> self-assembly in tetradecane at a low concentration ( $1.5 \times 10^{-6}$  mol L<sup>-1</sup>) on HOPG surface. (b) STM image of F-OC<sub>12</sub> self-assembly in tetradecane on HOPG surface after the sample was placed more than 5 hours.  $V_{\text{bias}} = 640$  mV,  $I_t = 550$  pA.



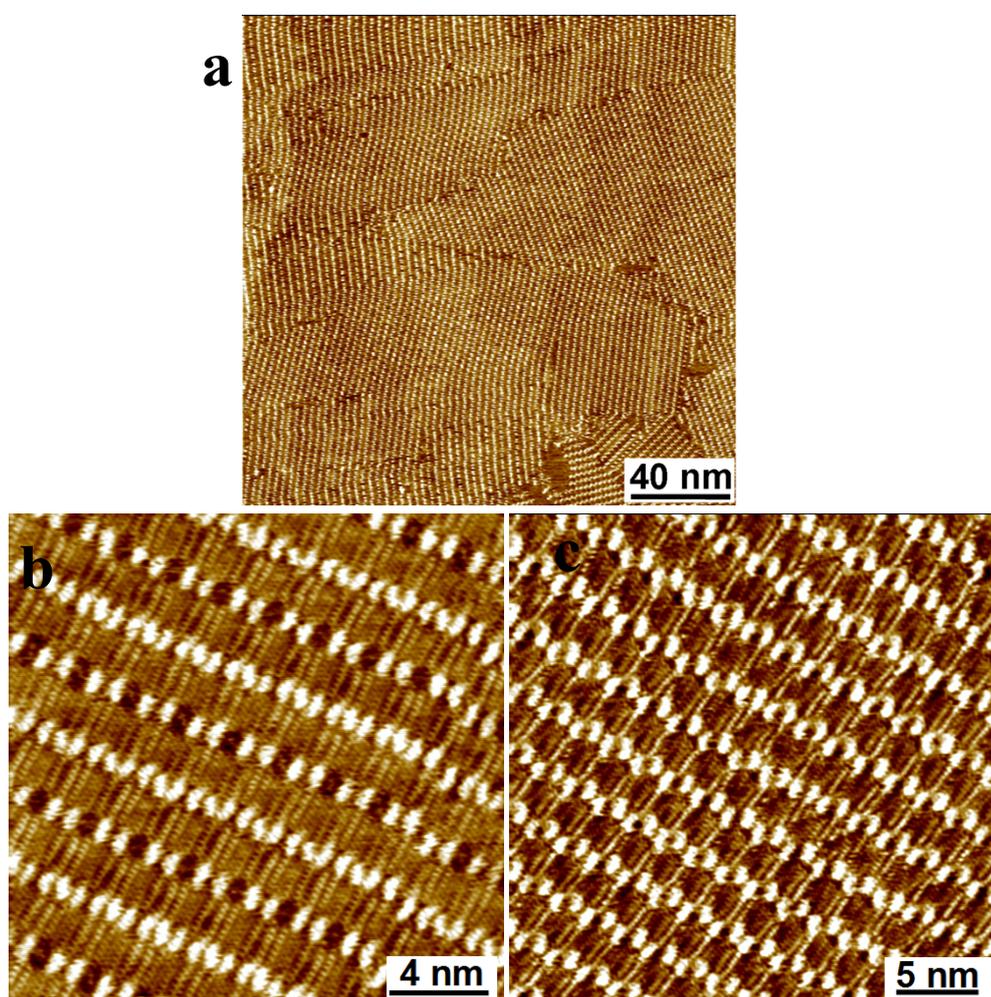
**Figure S9.** (a) STM image of F-OC<sub>15</sub> self-assembled monolayer in tridecane ( $1.5 \times 10^{-6}$  mol L<sup>-1</sup>) on HOPG surface. (b) STM image of F-OC<sub>15</sub> self-assembled monolayer in tetradecane ( $1.5 \times 10^{-6}$  mol L<sup>-1</sup>) on HOPG surface. (c) STM image of F-OC<sub>16</sub> self-assembled monolayer in tetradecane ( $1.5 \times 10^{-6}$  mol L<sup>-1</sup>).



**Figure S10.** (a) STM image of F-OC<sub>15</sub> self-assembled monolayer in tetradecane ( $1.0 \times 10^{-4}$  mol L<sup>-1</sup>) on HOPG surface after the sample was placed more than 3 hours. (b) STM image of F-OC<sub>15</sub> in tridecane under a high concentration ( $2.0 \times 10^{-4}$  mol L<sup>-1</sup>). Scan area: 150 nm  $\times$  150 nm. (c) STM image of F-OC<sub>15</sub> in tetradecane under a high concentration ( $2.0 \times 10^{-4}$  mol L<sup>-1</sup>). Scan area: 100 nm  $\times$  100 nm.



**Figure S11.** STM image of F-OC<sub>16</sub> self-assembled monolayer in tetradecane ( $1 \times 10^{-6}$  M) on HOPG surface.



**Figure S12.** (a) Large-scale STM image of F-OC<sub>16</sub> self-assembled monolayer in tridecane ( $1.5 \times 10^{-6}$  M) on HOPG surface. (b) High-resolution STM image of F-OC<sub>16</sub> showing the packing details of alternate pattern. (c) High-resolution STM image of F-OC<sub>16</sub> showing the packing details of zigzag pattern.

Table S1. Schematic Representation of all Phases Observed in 2D Assembly of F-OC<sub>n</sub> at Tetradecane and Tridecane/HOPG Interfaces under Different Concentrations

n	Self-assembled structures in tetradecane/concentration			Self-assembled structures in tridecane/ concentration		
	<10 <sup>-6</sup> mol L <sup>-1</sup>	10 <sup>-5</sup> mol L <sup>-1</sup>	>10 <sup>-4</sup> mol L <sup>-1</sup> ~saturated	<10 <sup>-6</sup> mol L <sup>-1</sup>	10 <sup>-5</sup> mol L <sup>-1</sup>	>10 <sup>-4</sup> mol L <sup>-1</sup> ~saturated
12		—			—	—
13			—			—
14			—			
15		—				—
16			—			
17	—	—	—	—	—	—
18	—	—		—	—	—

The self-assembled models of F-OC<sub>13</sub> were represented according to reference 21.