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

Figure S2. (a) Large-scale STM image of F-OC$_{14}$ self-assembly in tetradecane (2.5 × 10$^{-4}$ mol L$^{-1}$) on HOPG surface showing the whole area is covered by an alternate pattern. $V_{bias}$ = 650 mV, $I_t$ = 500 pA. (b) High-resolution STM image of F-OC$_{14}$ self-assembly in tetradecane (1.5 × 10$^{-4}$ mol L$^{-1}$) 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 ($2.5 \times 10^{-6}$ mol L$^{-1}$) showing the coexistence of alternate pattern and coadsorbed structure. $V_{\text{bias}} = 620$ mV, $I_t = 515$ pA. Scan area: $197$ nm $\times$ $197$ nm.

**Figure S4.** Large–scale STM image of F-OC14 self-assembly in tetradecane under a high concentration ($7.5 \times 10^{-4}$ mol L$^{-1}$). $V_{\text{bias}} = 640$ mV, $I_t = 520$ 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\textsubscript{14} was placed more than 5 hours. Scan area: 200 nm × 200 nm.

**Figure S6.** (a) STM image of F-OC\textsubscript{14} self-assembly in tridecane (1.5 × 10\textsuperscript{-6} mol L\textsuperscript{-1}) on HOPG surface. (b, c) STM images of F-OC\textsubscript{14} self-assembly in tridecane (3.5 × 10\textsuperscript{-4} mol L\textsuperscript{-1}) on HOPG surface. \(V_{\text{bias}} = 640\) mV, \(I_t = 510\) pA.
Figure S7. A typical STM image of the F-OC\textsubscript{14} 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 × 132 nm.

Figure S8. (a) STM image of F-OC\textsubscript{12} self-assembly in tetradecane at a low concentration ($1.5 \times 10^{-6}$ mol L$^{-1}$) on HOPG surface. (b) STM image of F-OC\textsubscript{12} 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$_{15}$ self-assembled monolayer in tridecane (1.5 × 10$^{-6}$ mol L$^{-1}$) on HOPG surface. (b) STM image of F-OC$_{15}$ self-assembled monolayer in tetradecane (1.5× 10$^{-6}$ mol L$^{-1}$) on HOPG surface. (c) STM image of F-OC$_{16}$ self-assembled monolayer in tetradecane (1.5× 10$^{-6}$ mol L$^{-1}$).
Figure S10. (a) STM image of F-OC$_{15}$ self-assembled monolayer in tetradecane ($1.0 \times 10^{-4}$ mol L$^{-1}$) on HOPG surface after the sample was placed more than 3 hours. (b) STM image of F-OC$_{15}$ in tridecane under a high concentration ($2.0 \times 10^{-4}$ mol L$^{-1}$). Scan area: 150 nm × 150 nm. (c) STM image of F-OC$_{15}$ in tetradecane under a high concentration ($2.0 \times 10^{-4}$ mol L$^{-1}$). Scan area: 100 nm × 100 nm.
Figure S11. STM image of F-OC$_{16}$ self-assembled monolayer in tetradecane (1 × 10$^{-6}$ M) on HOPG surface.

Figure S12. (a) Large-scale STM image of F-OC$_{16}$ self-assembled monolayer in tridecane (1.5 × 10$^{-6}$ M) on HOPG surface. (b) High-resolution STM image of F-OC$_{16}$ showing the packing details of alternate pattern. (c) High-resolution STM image of F-OC$_{16}$ showing the packing details of zigzag pattern.
Table S1. Schematic Representation of all Phases Observed in 2D Assembly of F–OC\textsubscript{n} at Tetradecane and Tridecane/HOPG Interfaces under Different Concentrations

<table>
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<th>Self-assembled structures in tridecane/ concentration</th>
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The self-assembled models of F-OC\textsubscript{13} were represented according to reference 21.