

# Supplementary Information

## Tuning the packing density of host molecular self-assemblies at the solid-liquid interface using guest molecule

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### Experimental Section

1,3,5-tris(10-ethoxycarbonyldecyloxy) benzene (TECDB) was home-synthesized. 1,3,5-trihybenzene (THB) was purchased from TCI and used without further purification. 1-phenyloctane was purchased from Aldrich. Highly oriented pyrolytic graphite (HOPG) substrates were obtained from Veeco, Santa Barbara, CA. Sample solution was prepared by dissolving the compounds in phenyloctane. A solution drop (5 $\mu$ L) was deposited on a fresh cleaned HOPG surface with a dimension of 10mm $\times$ 10mm and the tip was immersed into the droplet for STM image. STM measurements were carried out in a constant current mode at ambient conditions with a Nanoscope IIIa Multi-SPM (Veeco, Santa Barbara, CA). The STM tips were mechanically cut from a Pt/Ir (90:10) wire.

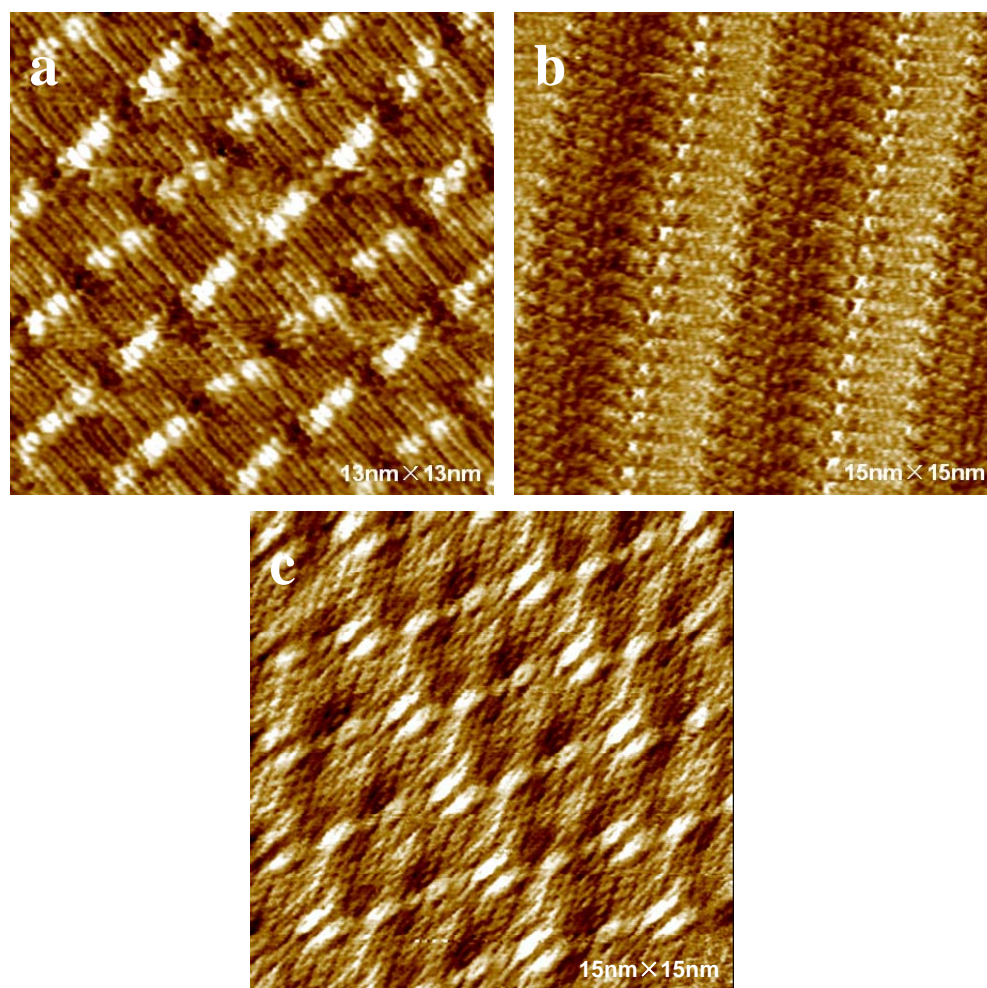


Fig. S1 High-resolution STM images of the self-assembled TECDB molecules on HOPG at different concentrations: (a) porous pattern,  $5.0 \times 10^{-4}$  mol/L ( $V_{\text{bias}} = 620$  mV;  $I_t = 436$  pA) and (b) linear pattern,  $2.1 \times 10^{-6}$  mol/L ( $V_{\text{bias}} = 817$  mV;  $I_t = 436$  pA). These images show the typical transition from a porous pattern to a close-packed linear structure when the TECDB concentration decreases. (c) Self-assembled structure after the solvent evaporated completely.

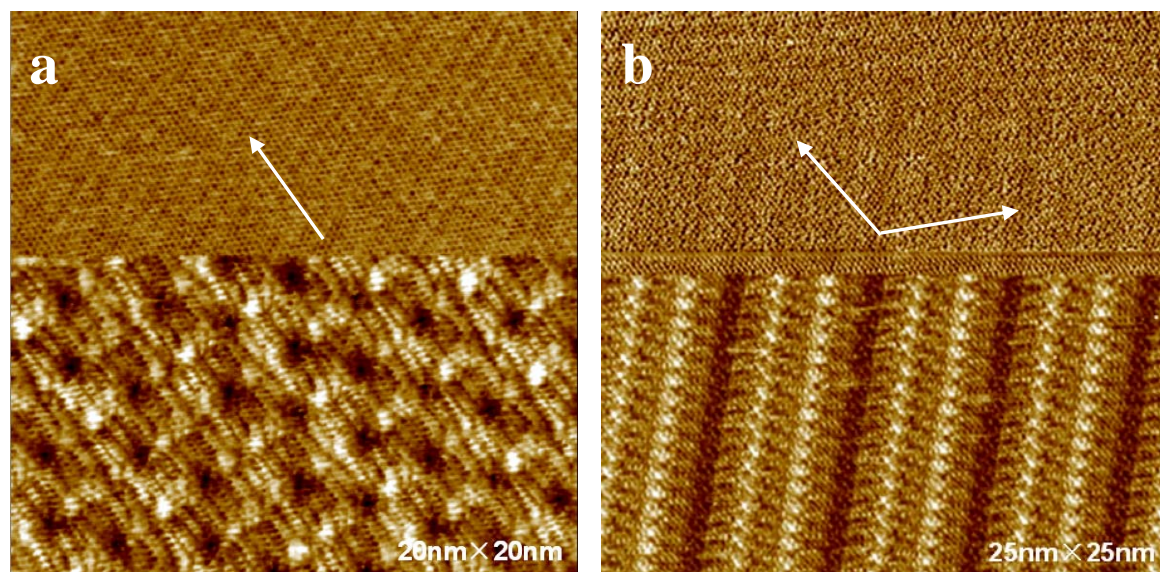


Fig. S2 (a) Composite STM image showing the underlying HOPG lattice and the porous structure. (b) Composite STM image showing the underlying HOPG lattice and the linear structure.  $V_{\text{bias}} = 600 \text{ mV}$ ,  $I_t = 400 \text{ pA}$  for the molecular adlayer (Lower) and  $V_{\text{bias}} = 100 \text{ mV}$ ,  $I_t = 400 \text{ pA}$  for the HOPG lattice (Upper). The images were obtained by switching the bias during the STM scan from the bottom to the upper frame.

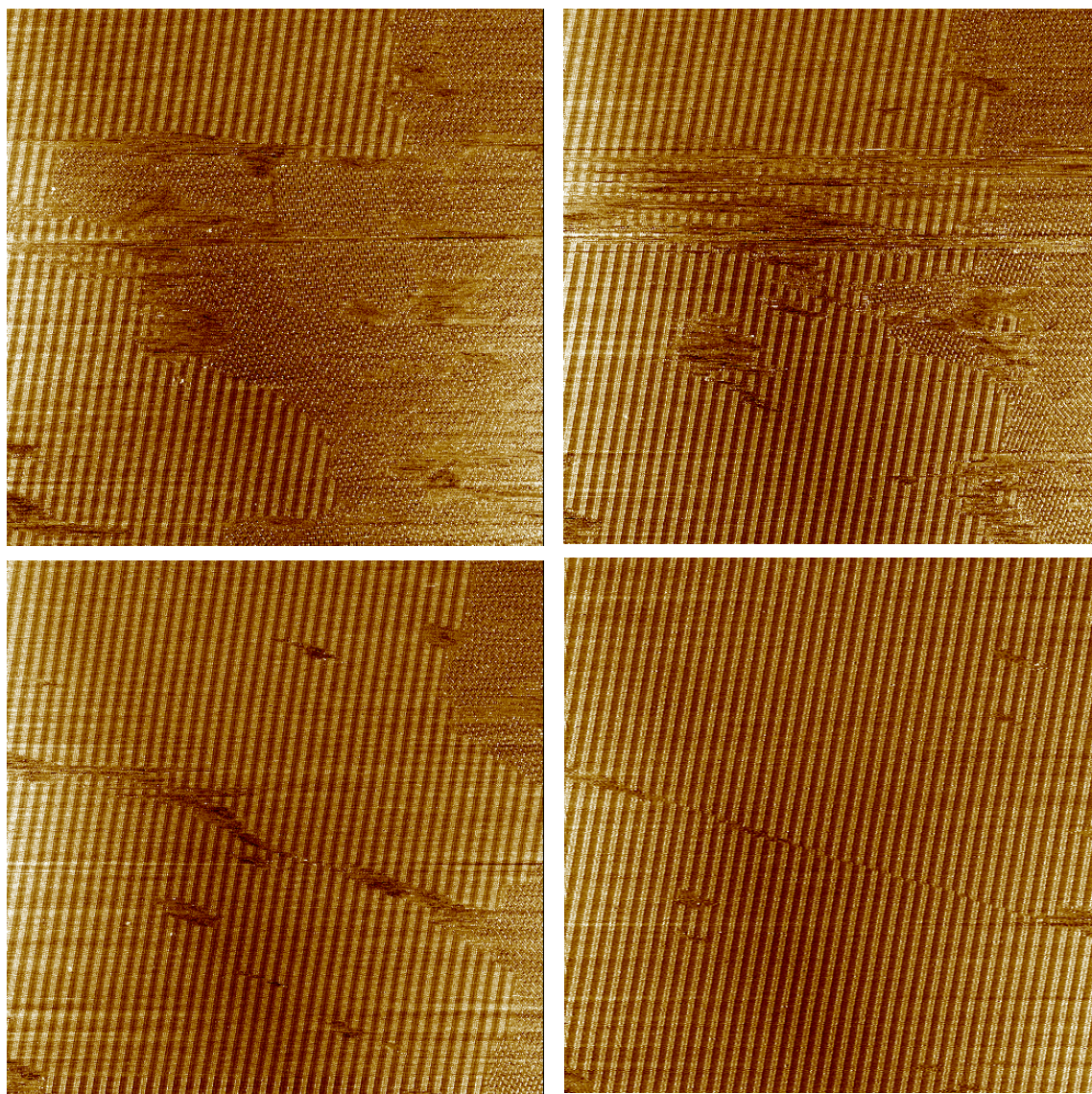


Fig. S3 Consecutive STM images showing the surface pattern changes from a porous motif to a linear polymorph within a certain concentration range. Scan area:  $250 \text{ nm} \times 250 \text{ nm}$ .  $V_{\text{bias}} = 478 \text{ mV}$ ;  $I_t = 410 \text{ pA}$ .

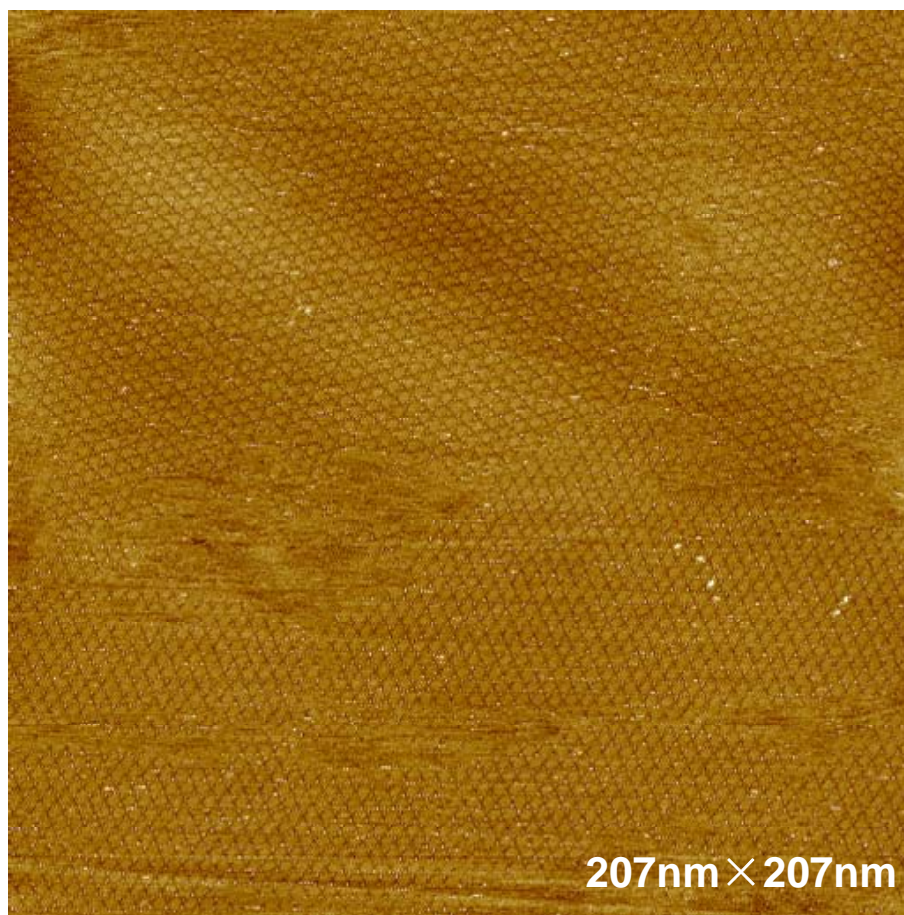


Fig. S4 Large-scale STM image of honeycomb structure formed from a mixture of TECDB and THB at the phenyloctane-HOPG interface.  $V_{\text{bias}} = 818 \text{ mV}$ ;  $I_t = 400 \text{ pA}$ .