

Supporting Information

Site-Selective Effects on Guest-Molecular Adsorption and Fabrication of Four-Component Architecture by Higher Order Networks

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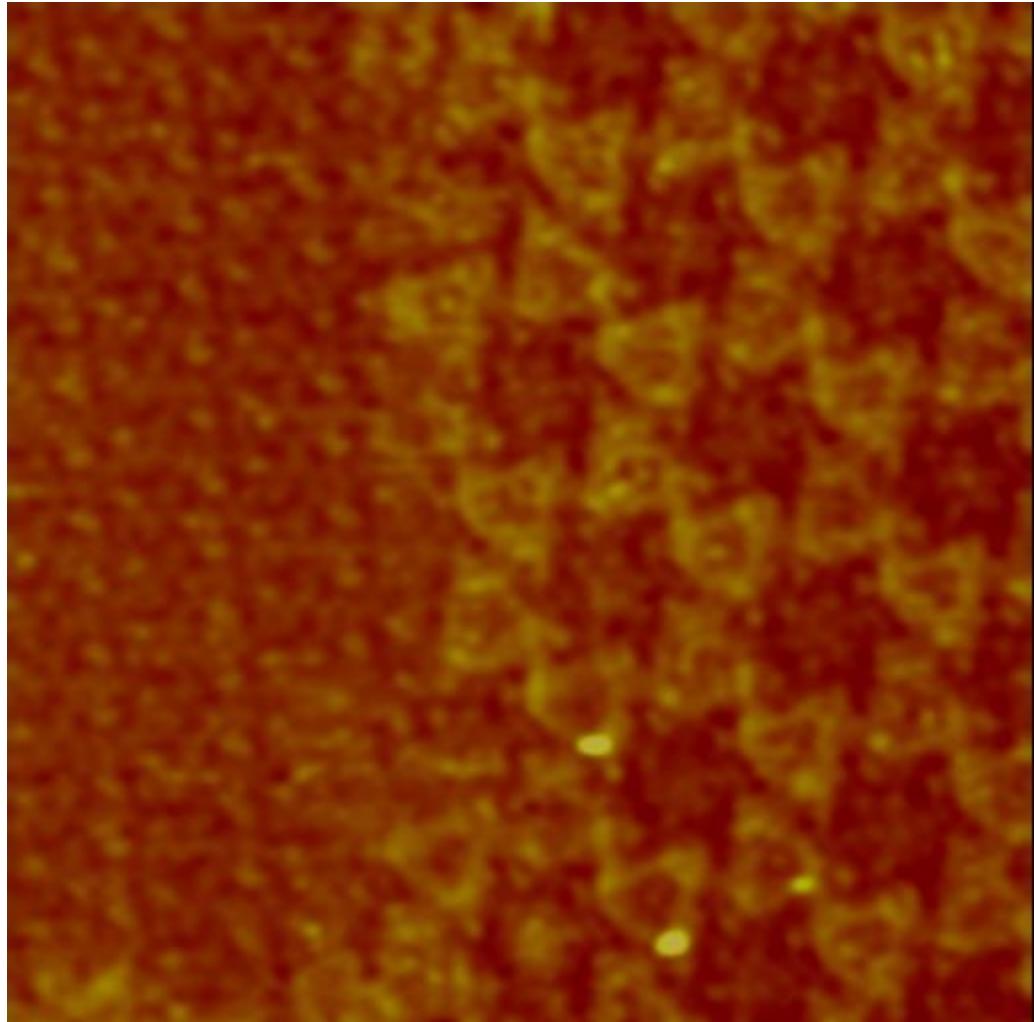


Figure S1. An STM image of hybrid networks and pure TCDB domains (30.9 nm \times 30.9 nm, I = 467 pA, V = 671 mV).

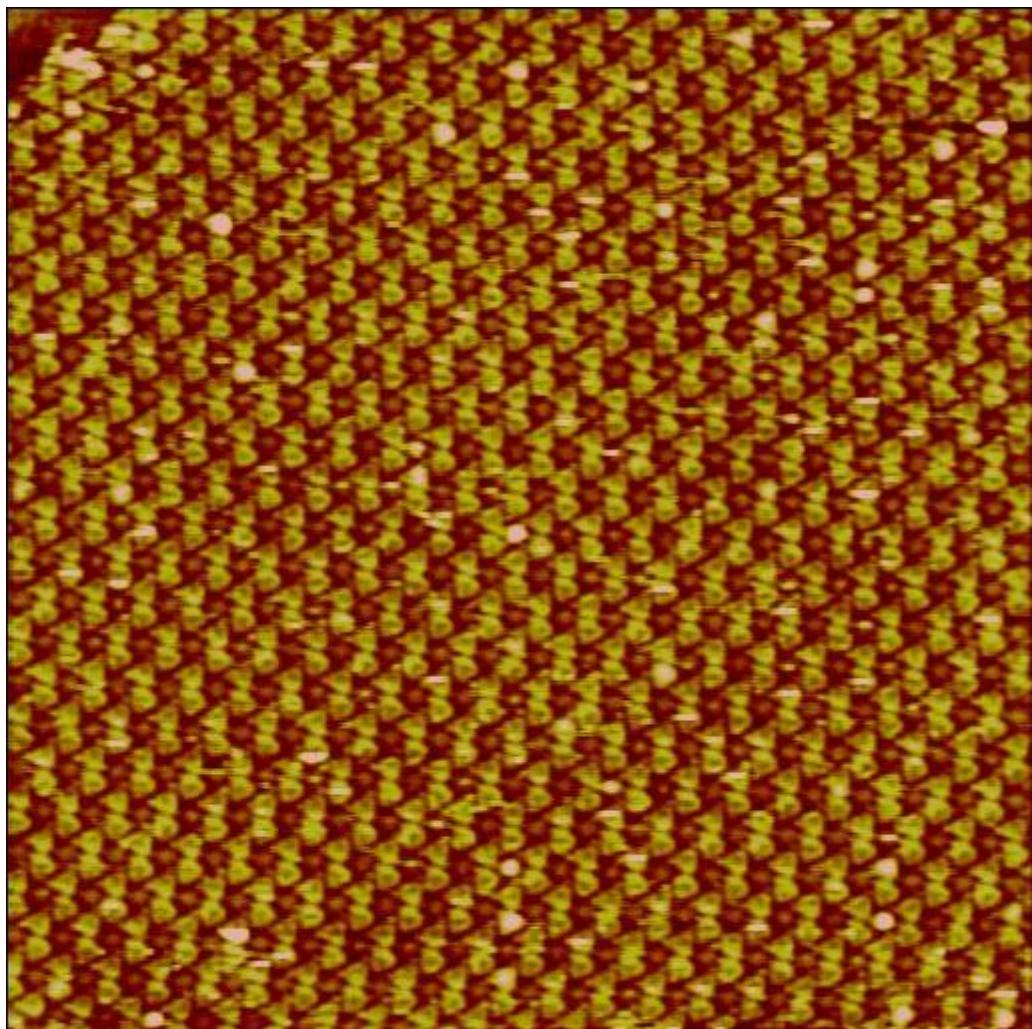


Figure S2 A large-scale STM image ($121\text{ nm} \times 121\text{ nm}$) of the $\text{C}_{60}/\text{TCDB}/\text{3NN-Macrocycle}$ three-component network on HOPG surface, in which the C_{60} molecules are trapped in the empty pores of two-component network. The imaging conditions: $I = 180\text{ pA}$, $V = 1024\text{ mV}$.

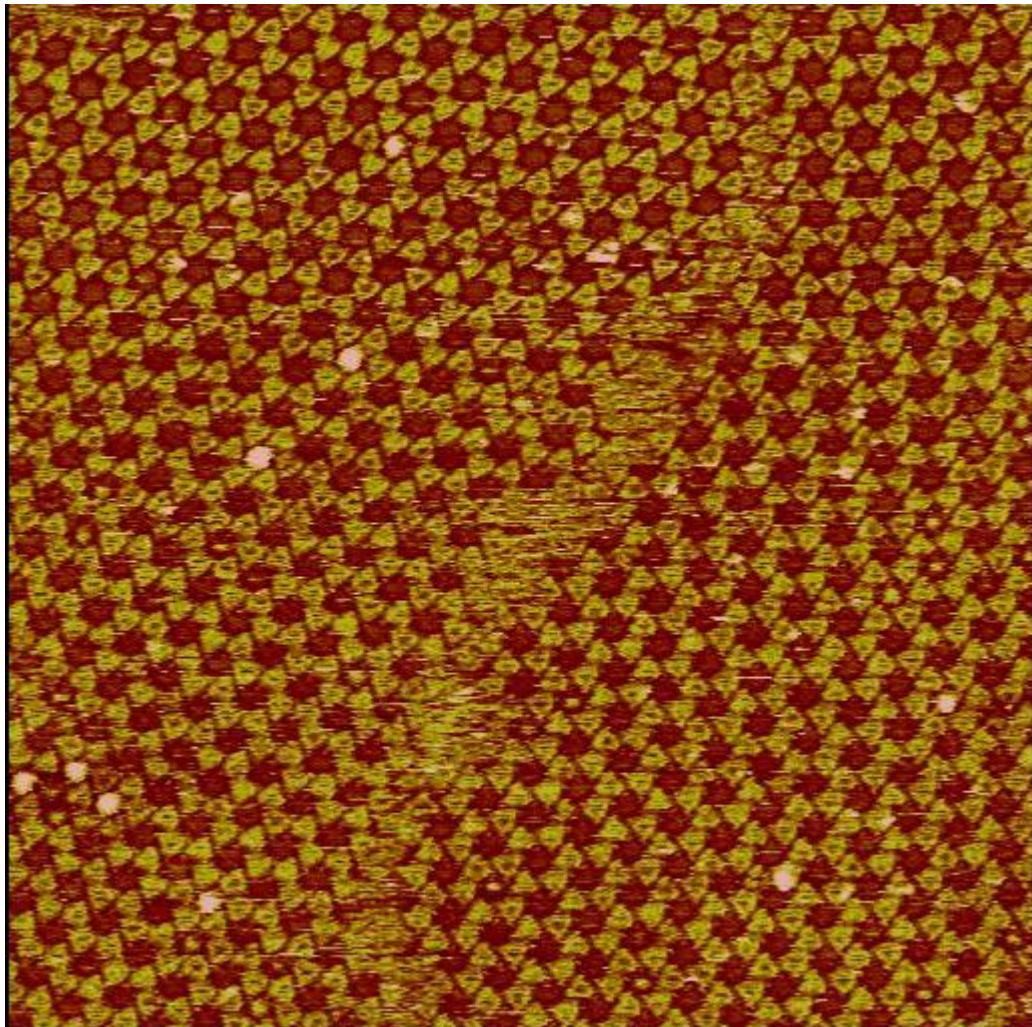


Figure S3. A Large-scale STM image (120 nm × 120 nm) of the C₇₀/TCDB/3NN-Macrocycle three-component network on HOPG surface, in which the C₇₀ molecules are trapped in the empty pores of two-component network. The imaging conditions: $I = 220$ pA, $V = 1161$ mV.

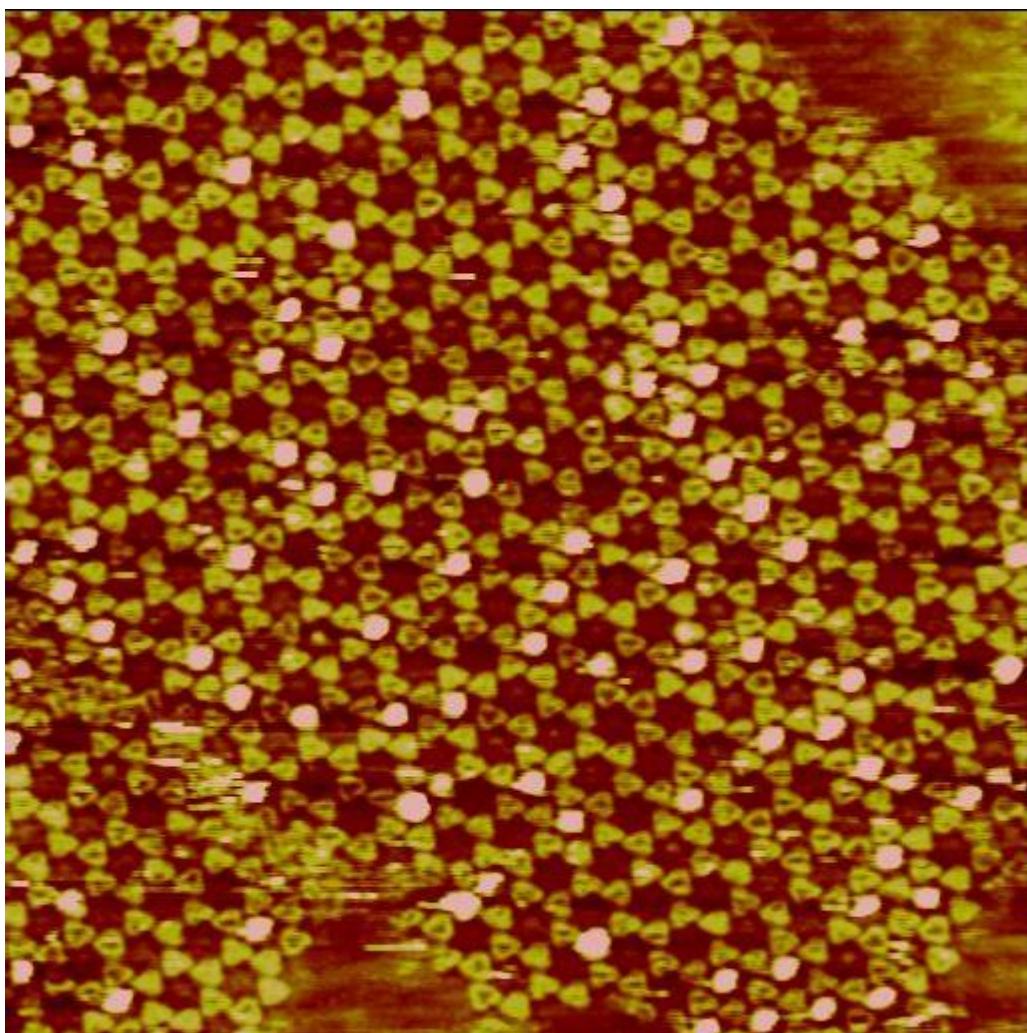


Figure S4. A large-scale STM image ($104 \text{ nm} \times 104 \text{ nm}$) of the $\text{C}_{80}/\text{TCDB}/\text{3NN-Macrocycle}$ three-component network on HOPG surface, in which the C_{80} molecules are trapped in the empty pores of two-component network. The imaging conditions: $I = 117 \text{ pA}$, $V = 1172 \text{ mV}$.

The tetradecane phenyloctane and heptanoic acid are the good solvents for STM experiments. However, in the tetradecane solvent the TCDB does not self-assemble on the HOPG surface as shown in Figure S5a. After dropping a phenyloctane solution including 3NN-Macrocyle and TCDB in the fabrication process of 3NN-Macrocyle/TCDB molecular template on HOPG, we found that the majority of TCDB domains are “empty”. It is slightly different from that of the pure TCDB adlayer. We could identify that two phenyloctane molecules could be entrapped in the cavity of the TCDB as shown in the insert of Figure S5b. In the heptanoic acid solution the 3NN-Macrocyle and TCDB self-assemble very well. The solvent molecules are not co-adsorbed on the surface and competitively absorbed in the cavities of TCDB. So we have to choose the heptanoic acid as the solvent.

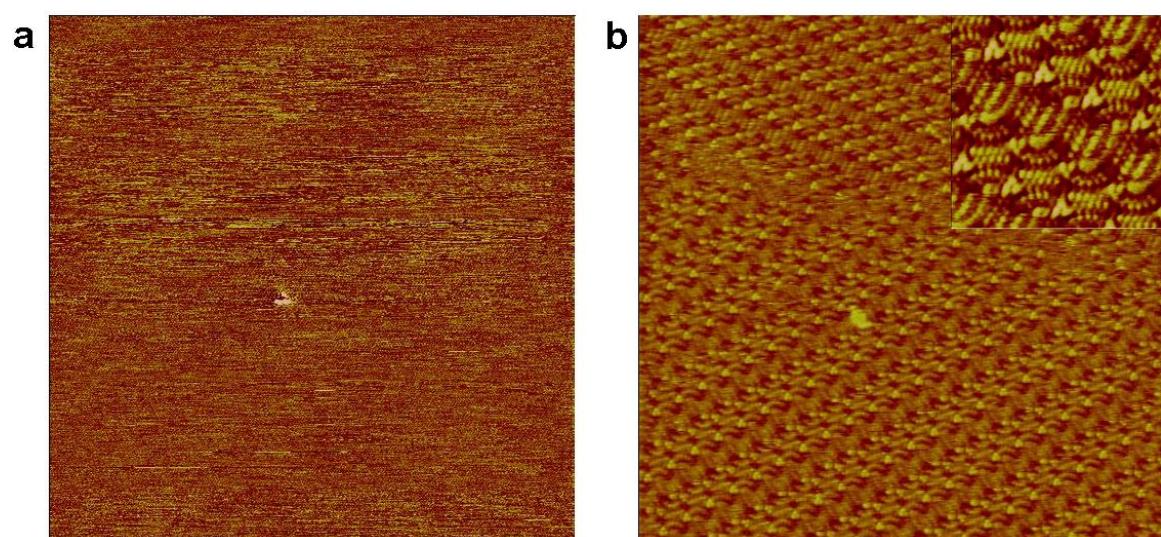


Figure S5. a) A STM image ($90\text{ nm} \times 90\text{ nm}$, $I = 247\text{ pA}$, $V = 600\text{ mV}$) of the TCDB/3NN-Macrocyle/tetradecane mixed solution on HOPG surface. b) A STM image of the TCDB/3NN-Macrocyle/phenyloctane adlayer on HOPG. ($40\text{ nm} \times 40\text{ nm}$, $I = 230\text{ pA}$, $V = 700\text{ mV}$). The insert of the figure is a STM image of two phenyloctane molecules entrapped in the cavity of the TCDB.

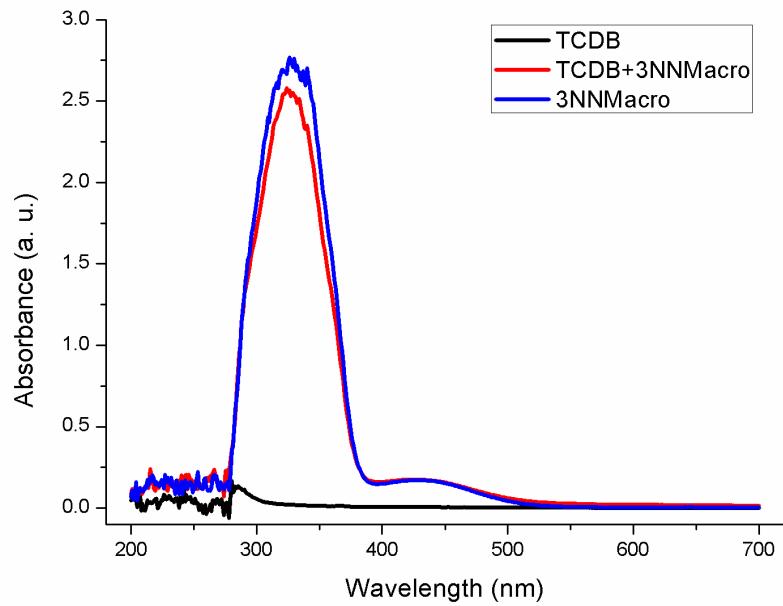


Figure S6. The UV-Vis spectra of TCDB (black), TCDB+3NNMacro (red) and 3NN Macro (green) in heptanoic acid.