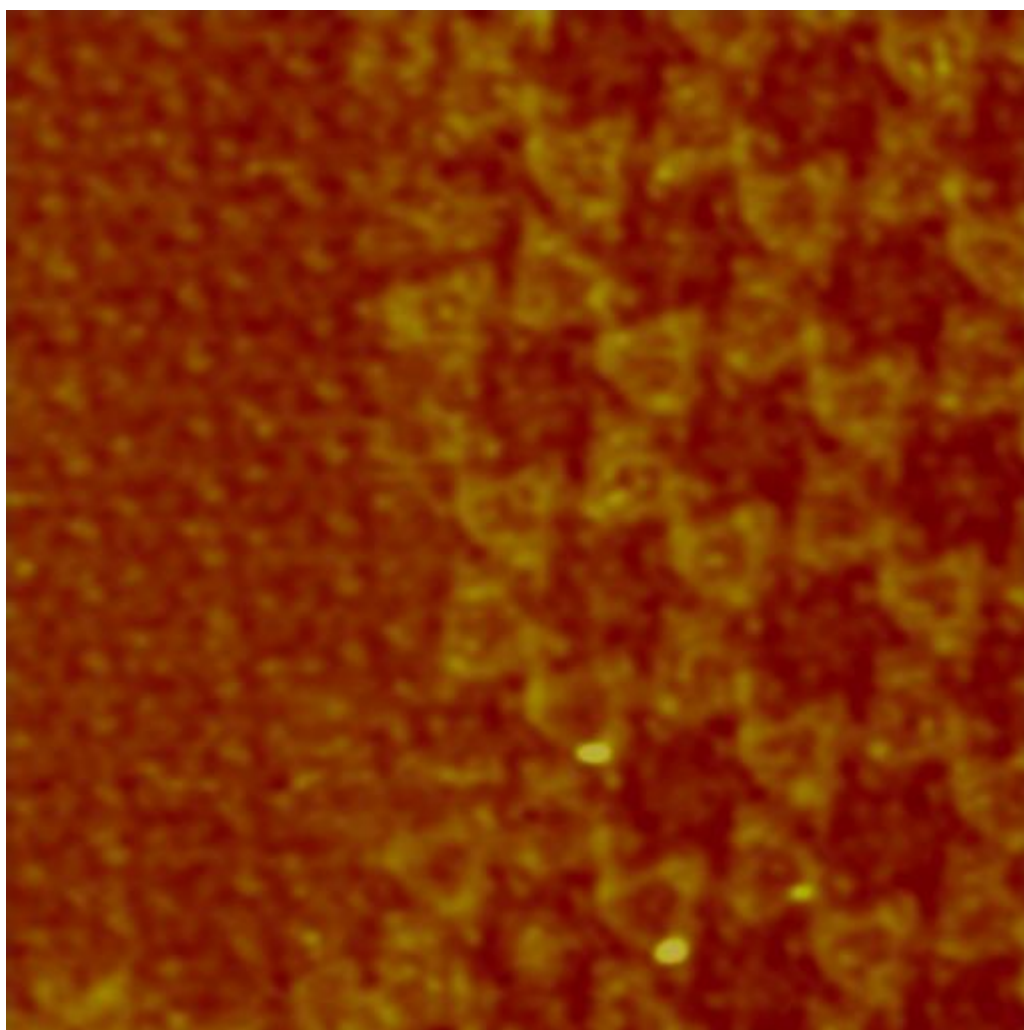


Supporting Information

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

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FigureS1. An STM image of hybrid networks and pure TCDB domains ($30.9 \text{ nm} \times 30.9 \text{ nm}$, $I = 467 \text{ pA}$, $V = 671 \text{ mV}$).

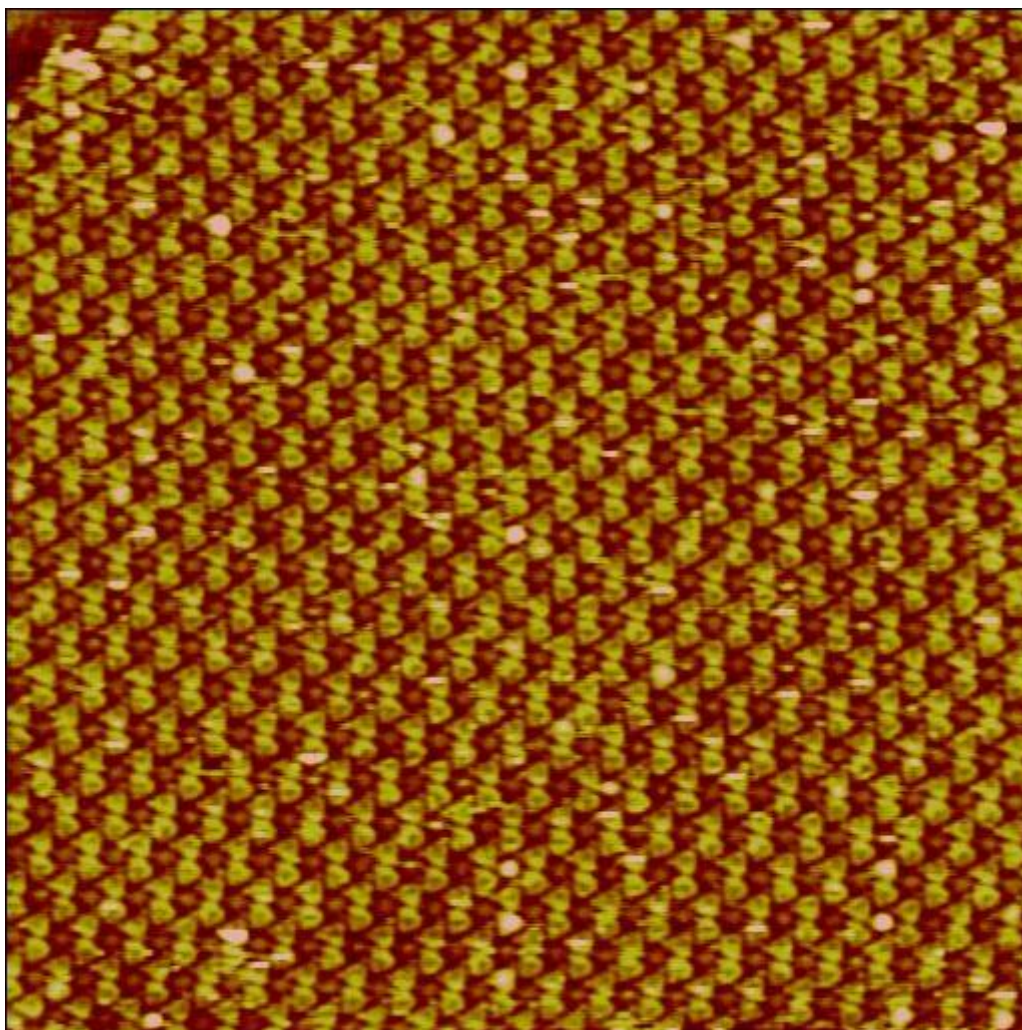


Figure S2 A large-scale STM image ($121\text{ nm} \times 121\text{ nm}$) of the C_{60} /TCDB/3NN-Macrocyclic three-component network on HOPG surface, in which the C_{60} molecules are trapped in the empty pores of two-component network. The imaging conditions: $I = 180\text{ pA}$, $V = 1024\text{ mV}$.

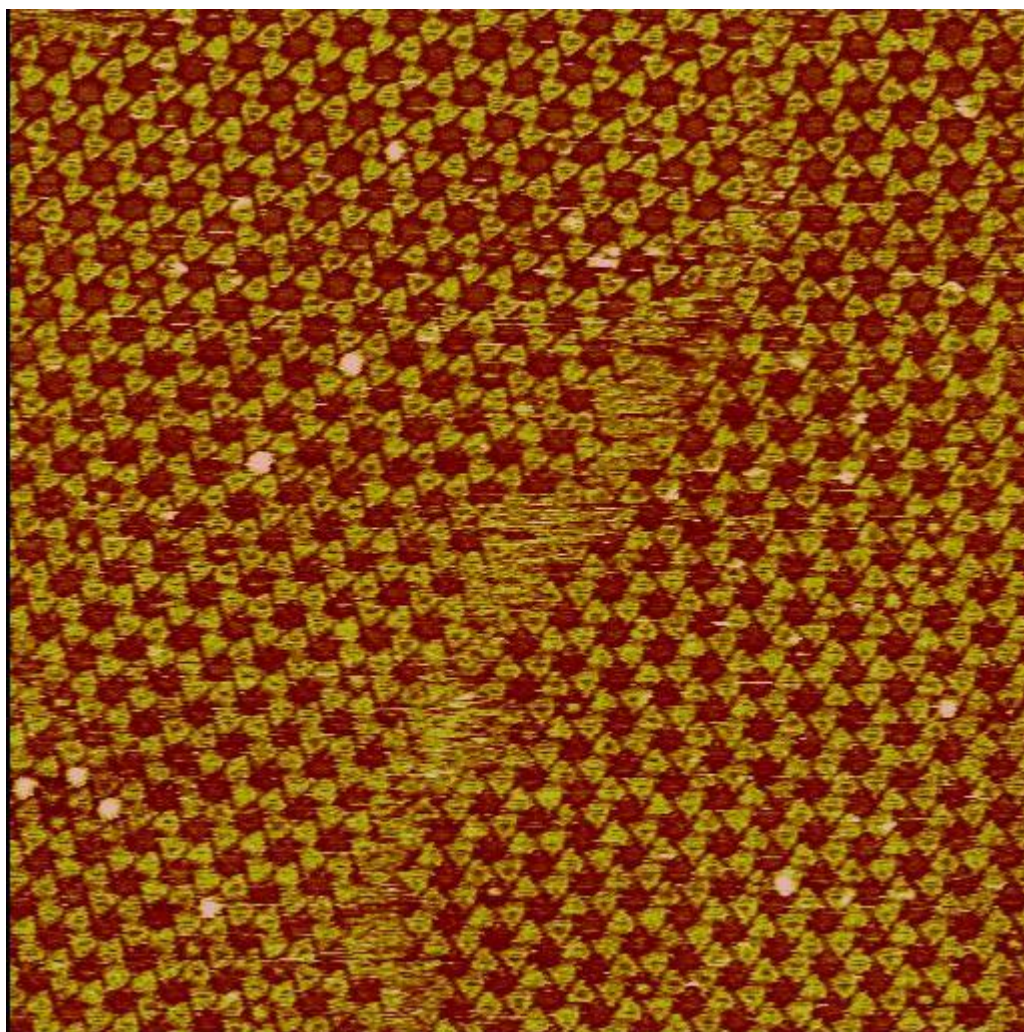


Figure S3. A Large-scale STM image ($120\text{ nm} \times 120\text{ nm}$) of the C_{70} /TCDB/3NN-Macrocycle three-component network on HOPG surface, in which the C_{70} molecules are trapped in the empty pores of two-component network. The imaging conditions: $I = 220\text{ pA}$, $V = 1161\text{ mV}$.

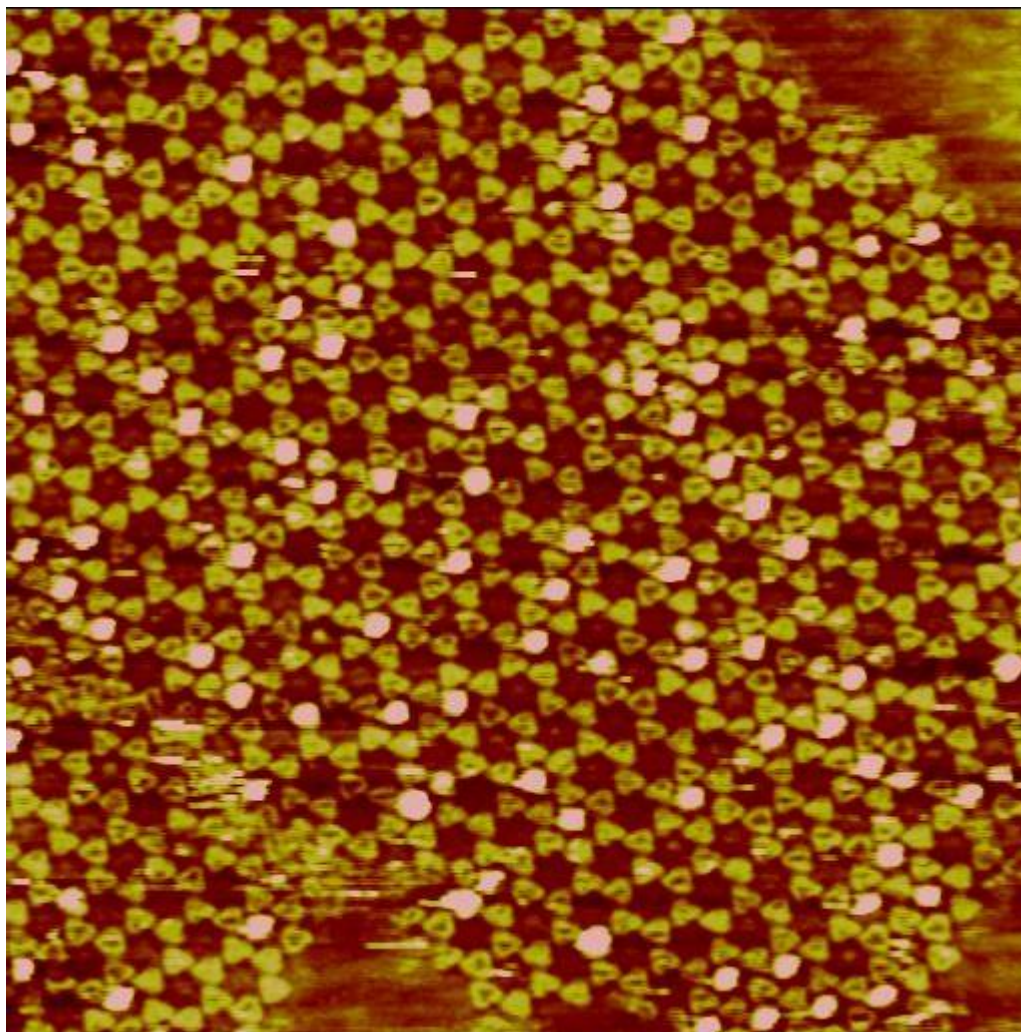


Figure S4. A large-scale STM image (104 nm × 104 nm) of the C₈₀/TCDB/3NN-Macrocyclic three-component network on HOPG surface, in which the C₈₀ molecules are trapped in the empty pores of two-component network. The imaging conditions: $I = 117$ pA, $V = 1172$ mV.

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-Macrocycle and TCDB in the fabrication process of 3NN-Macrocycle/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-Macrocycle 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.

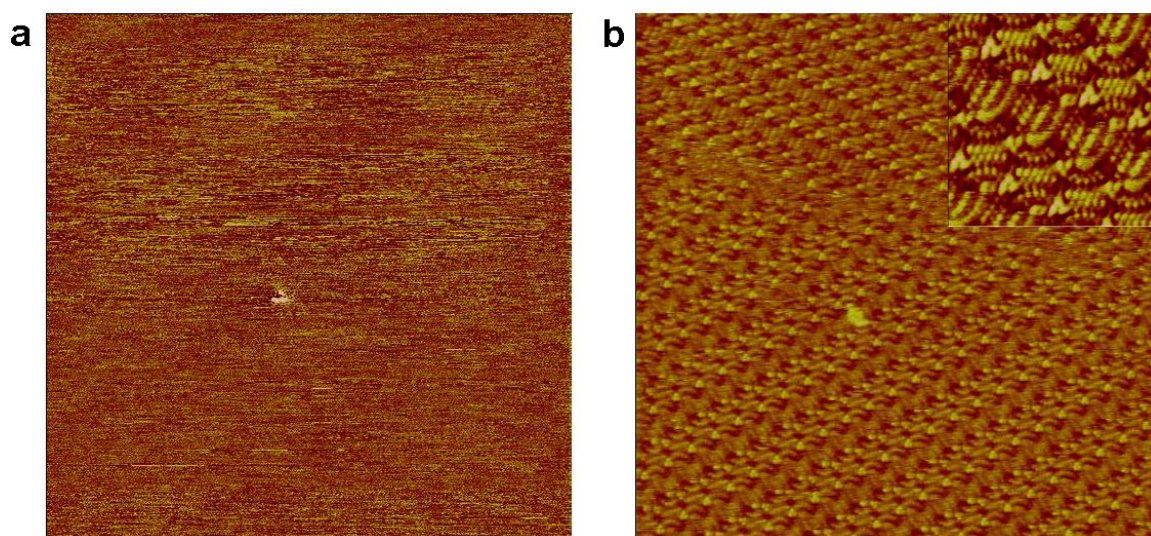


Figure S5. a) A STM image (90 nm \times 90 nm, $I = 247$ pA, $V = 600$ mV) of the TCDB/3NN-Macrocycle/tetradecane mixed solution on HOPG surface. b) A STM image of the TCDB/3NN-Macrocycle/phenyloctane adlayer on HOPG. (40 nm \times 40 nm, $I = 230$ pA, $V = 700$ mV). The insert of the figure is a STM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

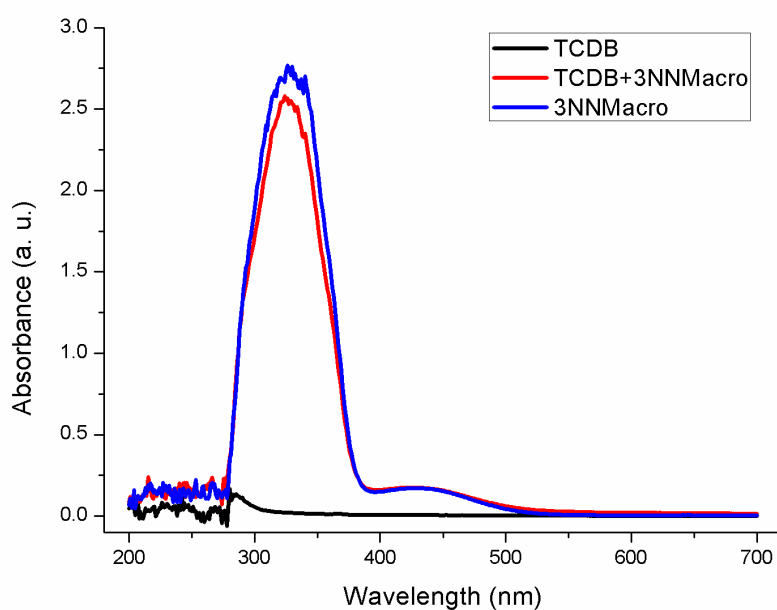


Figure S6. The UV-Vis spectra of TCDB (black), TCDB+3NNMacro (red) and 3NN Macro (green) in heptanoic acid.