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Supplementary Information

Designing 2D Stripe Random Network Through Crown-Ether Intermediate Ullmann Coupling on Cu(111) Surface

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Figure S1. (a) STM topographic image obtained at 77.8 K on the Cu(111) surface after BrCR island growth without annealing ($100 \times 100 \text{ nm}^2$, -2.5 V, 10 pA). (b) STM topographic image obtained on the BrCR/Cu(111) surface after the thermal annealing at 453 K for 10 min ($200 \times 200 \text{ nm}^2$, -2.5 V, 10 pA).



Figure S2. STM topographic images obtained on the BrCR/Cu(111) surface after the thermal annealing at 433 K for 18 min ($100 \times 100 \text{ nm}^2$, -2.5 V, 10 pA).



Figure S3. STM topographic image ($50 \times 50 \text{ nm}^2$, -1.6 V, 100 pA). of the chains. Height profiles along the lines were used to evaluated numbers of the bright spots in each chain.



Figure S4. FDMS of Ullmann coupling products. The reaction was conducted using 1 mg Br-CR and 2 mg Cu powder at 260 °C for 3h. The main peak at m/z = 1192 corresponds to $[C_{40}H_{40}Br_6O_{12} + H]^+ = 1192$. Plausible chemical structure is shown in the figure.



Figure S5. FDMS of Ullmann coupling products. The reaction was conducted using 1 mg Br-CR and 2 mg Cu powder at 260 °C for 5h. The peaks at m/z = 1034, 1114, and 1192 suggest the presence of $[C_{40}H_{40}Br_4O_{12} + H]^+ = 1033$ or $[C_{40}H_{42}Br_4O_{12}]^+ = 1034$, $[C_{40}H_{41}Br_5O_{12} + H]^+ = 1113$, and $[C_{40}H_{40}Br_6O_{12} + H]_+ = 1192$, respectively. Simulated isotope patterns and plausible chemical structures are shown in the figure.



Figure S6. FDMS of Ullmann coupling products. The reaction was conducted using 1 mg Br-CR and 5 mg Cu powder at 260 °C for 3h. The peaks at m/z = 1034, 1114, 1192, and 1550 suggest the presence of $[C_{40}H_{40}Br_{4}O_{12} + H]^{+} = 1033$ or $[C_{40}H_{42}Br_{4}O_{12}]^{+} = 1034$, $[C_{40}H_{41}Br_{5}O_{12} + H]_{+} = 1113$, $[C_{40}H_{40}Br_{6}O_{12} + H]_{+} = 1192$, and $[C_{60}H_{60}Br_{6}O_{18} + H]_{+} = 1549$, respectively. Simulated isotope patterns and plausible chemical structures are shown in the figure.



Figure S7. Expected chemical reactions using the BrCR precursor molecules on the Cu(111) using thermal annealing before performing the experiments.



Figure S8. Histogram of connection angles between precursors in the STM topographic c image of Fig .3a in the main text.



Figure S9. DFT calculated density of states (DOS) plots of all configurations in Fig. 2.