

Electronic Supplementary Information for

Selective Synthesis of Kagome Nanoporous Graphene on Ag(111) via Organometallic Template

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Table of Contents

| | |
|-------------------------------------|------|
| Additional STM data and Table | page |
| 2 | |
| Experimental methods..... | page |
| 6 | |
| References | page |
| 7 | |

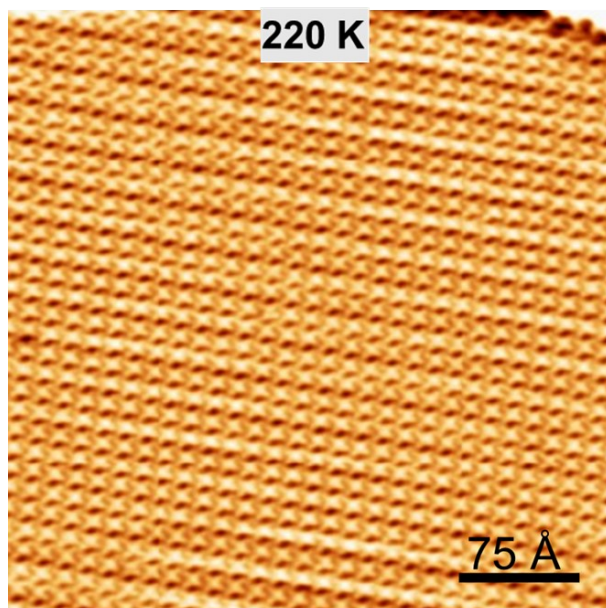


Figure S1. Overview STM image taken after depositing TBBDTP molecules on 220 K Ag(111). Tunneling parameters: $I=0.1$ nA, $U=557.5$ mV.

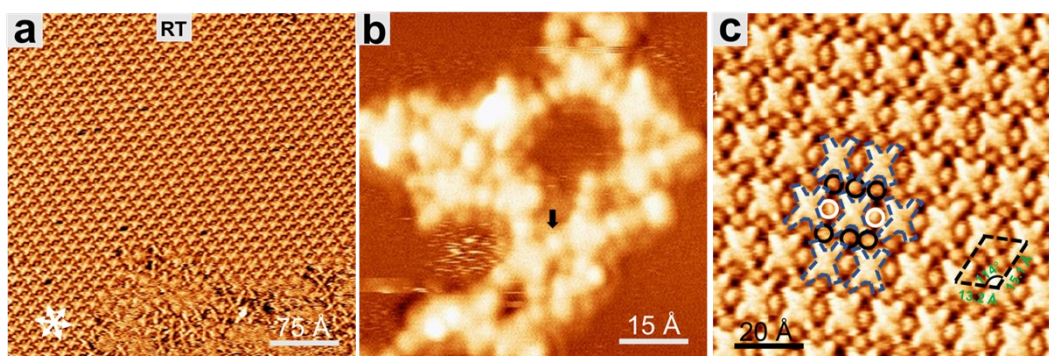


Figure S2. (a) STM images recorded after annealing sample in Figure 1a to RT. Both ordered self-assembly and irregular oligomers at periphery of islands are observed. The cross-like species in close-packed self-assembly feature four bright terminus, and fail to link with each other. Thus, we presume them to be intact monomers. The oligomers at island periphery are attributed to OM chains. (b) Zoom-in STM images of short oligomers. The bright dots marked by black arrows are attributed to interstitial Ag adatoms in OM chains. (c) Zoom-in STM images of self-assembly phase in (a), where cross-like species are surrounded by round protrusions. The round protrusions are ascribed to either Br and Ag adatoms. Tunneling parameters: (a) $I=-0.13$ nA, $U=-939.6$ mV. (b) $I=-0.12$ nA, $U=-691.2$ mV. (c) $I=-0.09$ nA, $U=-508.4$ mV.

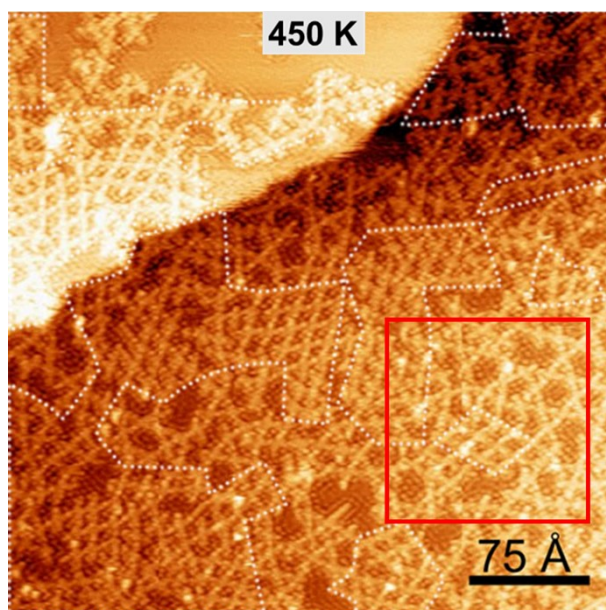


Figure S3. Overall STM image recorded by annealing sample in Figure S2a sample to 450 K. Tunneling parameters: $I=-0.14$ nA, $U=-301.8$ mV.

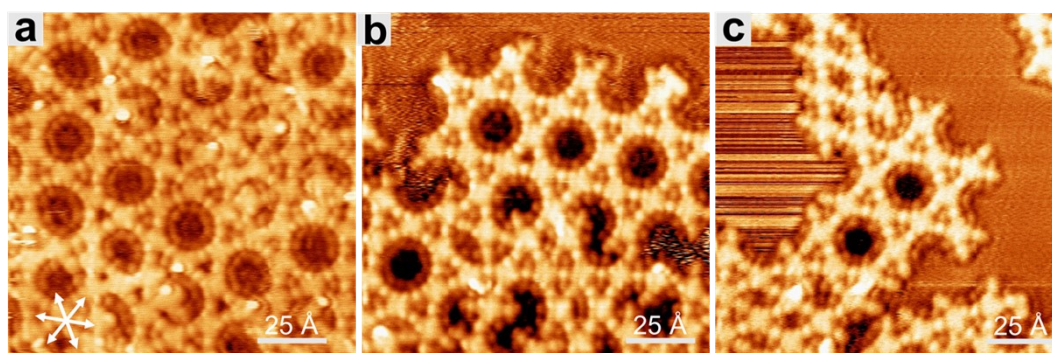


Figure S4. (a-c) High-resolution STM image of organometallic Kagome structure attained by sublimating TBDTP molecules onto Ag(111) preheated at 450 K (a), 430 K (b), and 410 K (c), respectively. Each organometallic Kagome are composed of 12 monomers linked by Ag adatoms (appear as bright dots in STM image). The detached Br adatoms are either trapped in Kagome pores or besides the oligomers. In the Kagome pores, even some monomers are trapped. The yield of complete organometallic Kagome are found to increase with surface temperature. Tunneling parameters: (a) $I=-0.12$ nA, $U=-734.9$ mV; (b) $I=-0.11$ nA, $U=-611.3$ mV; (c) $I=-0.12$ nA, $U=-712.9$ mV.

Table S1. The OM and covalent Kagome yields (with uncertainty) of samples prepared at different experimental conditions.

| Experimental condition | OM Kagome yield (%) | Covalent Kagome yield (%) |
|--|---------------------|---------------------------|
| T_surf=410 K T_evap=503 K | 20±4 | 15±3 |
| T_surf=430 K T_evap=503 K | 29±6 | 24±3 |
| T_surf=450 K T_evap=503 K | 50±4 | 36±5 |
| T_surf=300 K T_evap=503 K T_anne=450 K | 30±4 | 32±2 |
| T_surf=450 K T_evap=493 K | 56±3 | 71±8 |
| T_surf=450 K T_evap=483 K | 60±3 | 82±6 |

- ◆ T_surf denotes the temperature of surface onto which precursor molecules are deposited.
 - ◆ T_evap denotes the temperature used to evaporate precursor molecules.
 - ◆ T_anne denotes the temperature to which the sample is annealed for OM Kagome.
- Note all covalent Kagomes are attained by annealing OM Kagome to 520 K.

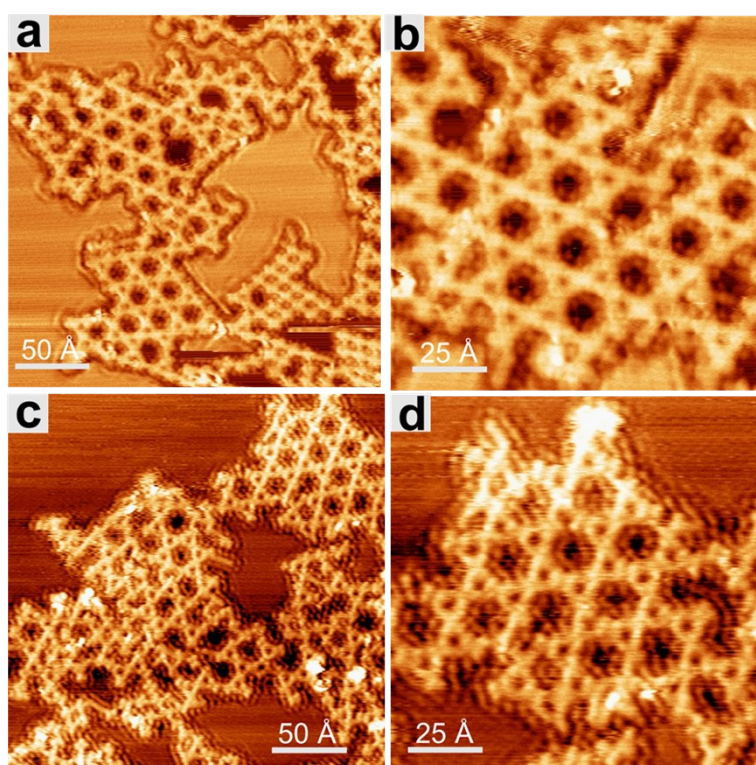


Figure S5. (a, b) Magnified STM images of sample in Figure 4e. (c, d) High-resolution STM images of sample in Figure 4f. Both two samples exhibit well-defined covalent Kagome network patches. Various Br adatoms are found in the Kagome pores. Tunneling parameters: (a) $I=-0.12$ nA, $U=-734.8$ mV; (b) $I=-0.14$ nA, $U=-734.8$ mV; (c) $I=-0.11$ nA, $U=-691.2$ mV; (d) $I=-0.12$ nA, $U=-734.8$ mV.

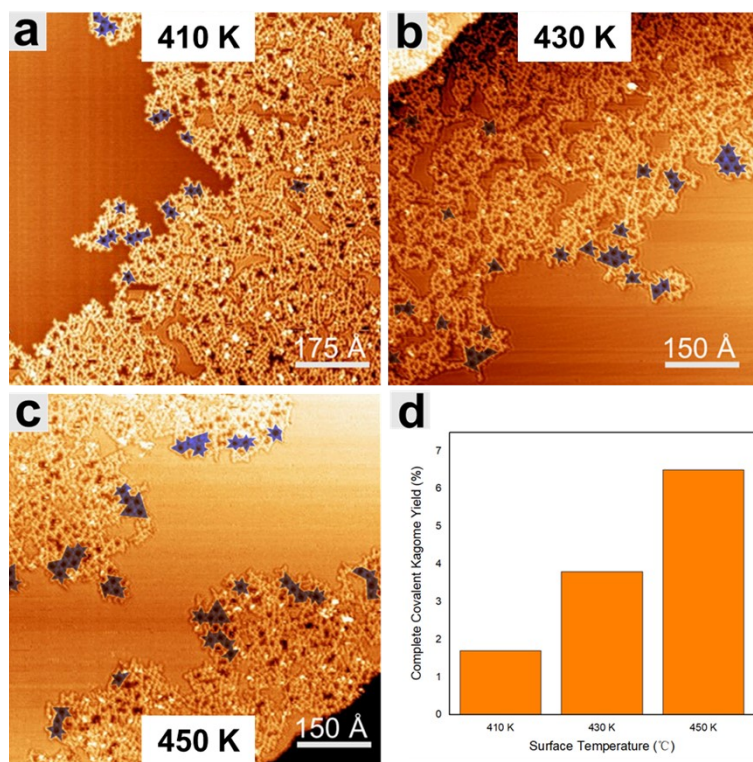
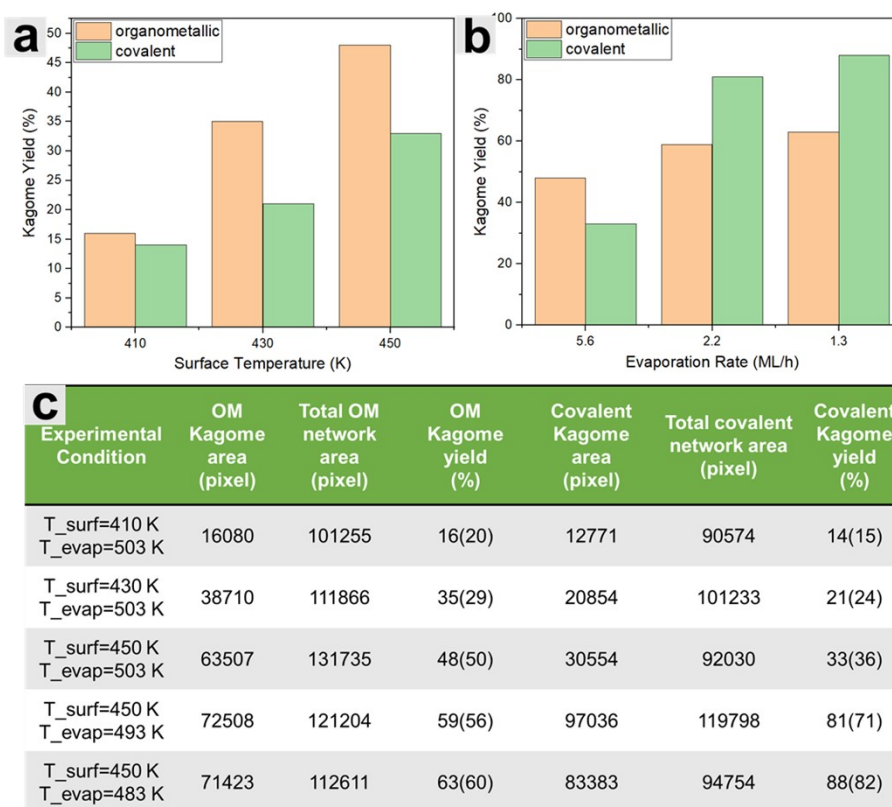


Figure S6. (a-c) Overview STM images recorded upon deposition of TBDDTP molecules onto Ag(111) preheated at 410 K (a), 430 K (b), and 450 K (c), followed by annealing to 520 K. The complete covalent Kagome phase is highlighted by blue shadow. (d) Histogram showing complete covalent Kagome yield as a function of surface temperatures during hot deposition. Tunneling parameters: (a) $I=-0.11$ nA, $U=-734.8$ mV; (b) $I=-0.14$ nA, $U=-$



- ◆ T_surf denotes the temperature of surface onto which precursor molecules are deposited.
- ◆ T_evap denotes the temperature used to evaporate precursor molecules.
- ◆ The values in bracket are results for statistic analysis in Fig. 5.

Figure S7. (a, b) Histograms illustrating both organometallic and covalent Kagome structure yields as a function of surface temperatures during hot deposition (a) and molecular evaporation rate (b). The covalent products stem from the annealing of corresponding organometallic structure to 520 K. (c) Table summarizing the details of statistic analysis. Note that the values in brackets are derived from Fig. 5, which are used as for comparison.

Methods

The whole experiments were conducted in the three-chamber UHV system with a base pressure better than 6×10^{-10} mbar, as described previously.¹ The used single crystal Ag(111) was purchased from MaTeck, Germany, with an alignment better than 0.1° with respect to surface normal. The Ag(111) was cleaned with several cycles of Ar⁺ sputtering and annealing to 750 K. For sample preparation, the TBDTP monomers were evaporated from a Kentax cell at 230 °C. 220 and 210 °C were used for varying evaporation rate. Note that the Kentax evaporator was located in a chamber separated from preparation chamber by a gate valve. The gate valve was only open when sublimating molecules. The STM measurement was performed on a STM Aarhus 150 with SPECS 260 electronics, where bias refer to the sample.

All STM images were recorded at constant-current mode at RT if not indicated. Molecular coverages of samples were estimated from STM images. For the quantification of Kagome species (OM/covalent) yields of samples, Software Photoshop was used by counting the pixel numbers of Kagome species area with respect to that of surface structure area. SRPES experiments were conducted at Catalysis and Surface Science Endstation of National Synchrotron Radiation Lab, Hefei, China. The SRPE spectra were acquired at an emission angle of 50° with respect to surface normal. Br 3d and C 1s spectra were collected with photon energies of 180 and 380 eV, respectively. The chosen emission angle and photon energy aim to render SRPES surface-sensitive.

Notes and references

1. M. Chen, J. Xiao, H.-P. Steinrück, S. Wang, W. Wang, N. Lin, W. Hieringer and J. M. Gottfried, *The Journal of Physical Chemistry C*, 2014, **118**, 6820-6830.