Supplementary Information

A Cu₂(C₆O₆) metal-organic framework monolayer assembled on silicon carbide grown graphene exhibiting a metallic band structure

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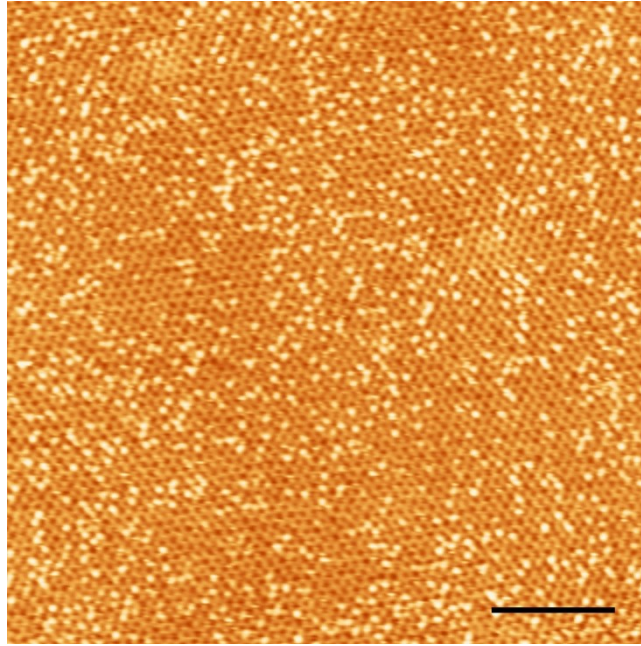1. STM Image of graphene grown epitaxially from 4H-SiC (0001)

Figure S1 Large-Scale STM image of graphene grown epitaxially from 4H-SiC (0001) extending to 100 nm without any boundaries. (Bias voltage: -1.8 V, current: 200 pA, scale bar: 20 nm).

The graphitization takes place when heating SiC above 1150 °C in the UHV chamber with a base pressure of 6×10^{-10} mbar. A well ordered $(6\sqrt{3} \times 6\sqrt{3})R30°$ reconstruction is formed on the SiC substrate around the graphitization temperature, which acts as an interfacial buffer layer between graphene and bulk SiC. The interfacial buffer layer makes the epitaxial graphene intrinsically n-type doped while preserving its intrinsic electronic properties of graphene. The C atoms in the buffer layer strongly bind to the top Si atoms of the SiC (0001) substrate.[1] Figure S1 shows a large-scale STM image of graphene grown epitaxially from 4H-SiC (0001), which extends up to 100 nm without any boundaries. At this bias voltage, the electronic states are primarily attributed to the SiC substrate rather than the graphene layer. It shows a $(6\sqrt{3} \times 6\sqrt{3})R30°$ reconstruction with a periodicity of $6\sqrt{3}$.[2, 3]

2. Sequential deposition of BHO molecules and Cu atoms on graphene substrate
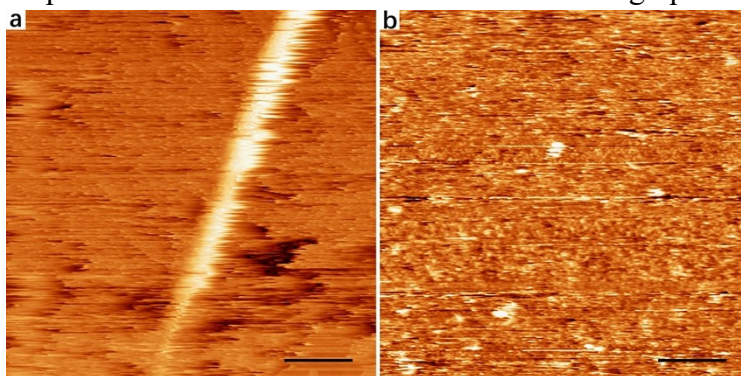

Figure S2 (a) STM image of G/SiC substrate covered with BHO molecules. (Bias voltage: 1.0 V, current: 200 pA, scale bar: 10 nm). **(b)** STM image of BHO molecules and Cu atoms on G/SiC substrate without annealing treatment. (Bias voltage: 0.8 V, current: 155 pA, scale bar: 10 nm).

3. Large-scale STM images of the sample after annealing treatment at 75 °C and 120 °C
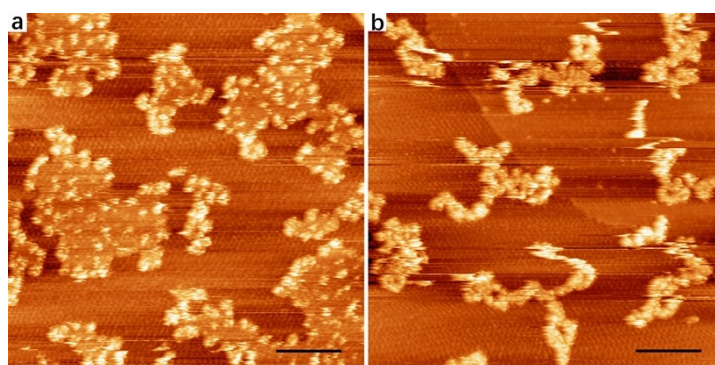

Figure S3 (a) Large-scale STM image of the sample after annealing at 75 °C. (Bias voltage: -0.6 V, current: 150 pA, scale bar: 20 nm). **(b)** Large-scale STM image of the sample after annealing at 120 °C. (Bias voltage: -0.9 V, current: 135 pA, scale bar: 20 nm).

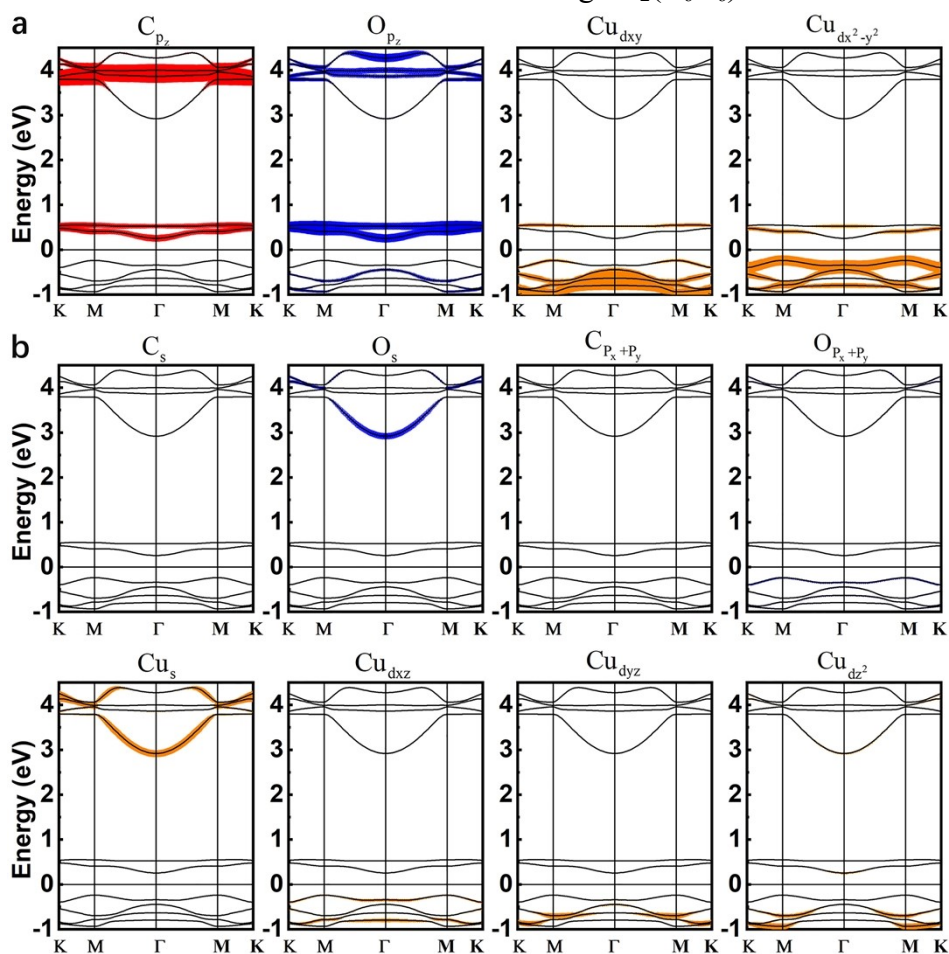4. Orbital-resolved band structure of freestanding $Cu_2(C_6O_6)$ coordination network

Figure S4 The orbital-resolved band structure determined by DFT calculations, with **(a)** and **(b)** showing the major and minor contributors, respectively. Contributions from C, O and Cu orbitals are color-coded as red, blue and orange, respectively. The thickness of the markings indicates the relative weight of each contribution.

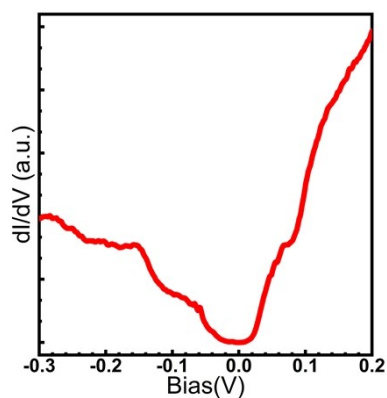5. Scanning tunneling spectroscopy on bare graphene substrate

Figure S5 Scanning tunneling spectroscopy of the bare graphene substrate acquired at 4.8 K.

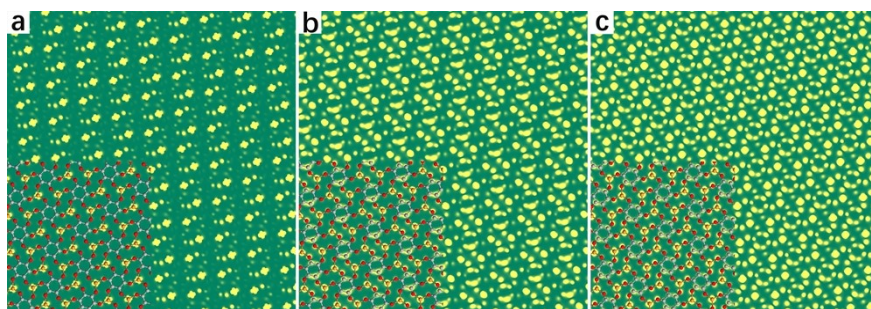6. DFT-simulated images at -50mV with various Fermi levels

Figure S6 DFT-simulated images of $Cu_2(C_6O_6)$ on graphene at a bias voltage of -50 mV with: **(a)** the unshifted Fermi level, **(b)** the Fermi level is upshifted by 0.13 eV, and **(c)** the Fermi level is upshifted by 0.25 eV. The color coding for the structural model is as follows: gray for carbon, red for oxygen, and yellow for copper.

7. STM and DFT-simulated images of $Cu_2(C_6O_6)$ coordination network at different bias voltages

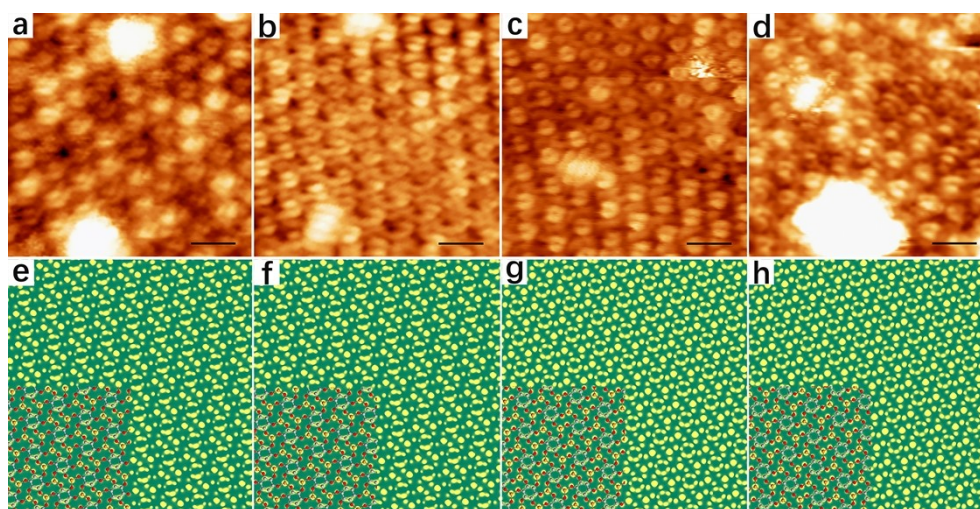**Figure S7 (a)-(d)** STM images of $Cu_2(C_6O_6)$ coordination networks taken at bias voltages of -500 mV (current: 155 pA), -100 mV (current: 200 pA), 150 mV (current: 180 pA), and 500 mV (current: 200 pA), respectively. Scale bar: 1 nm. **(e)-(h)** DFT-simulated images of $Cu_2(C_6O_6)$ on graphene at bias voltages of -500 mV, -100 mV, 150 mV, and 500 mV, respectively. The Fermi Level is upshifted by 0.18 eV. The color coding for the structural model is as follows: gray for carbon, red for oxygen, and yellow for copper.

References

1. M. Ruan, Y. Hu, Z. Guo, R. Dong, J. Palmer, J. Hankinson, C. Berger and W. A. De Heer, *MRS Bulletin*, 2012, **37**, 1138-1147.
2. F. Hiebel, P. Mallet, L. Magaud and J.-Y. Veuillen, *Phys. Rev. B*, 2009, **80**, 235429.
3. P. Lauffer, K. Emtsev, R. Graupner, T. Seyller, L. Ley, S. Reshanov and H. Weber, *Phys. Rev. B*, 2008, **77**, 155426.