Coordination Preference of Pyridine-Based Ligands on Ag(111)

Chanyu Li[1], Jiayi Lu[2], Juan Xiang[2], Fengru Zheng[2,3], Qi Huang[2], Hao Jiang[2], Yizhang Li[2], Liangliang Cai[1,2], Qiang Sun[1,2]*

[1]Qianweichang College, Shanghai University, Shanghai 200444, China

[2]Materials Genome Institute, Shanghai University, Shanghai 200444, China

[3]Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China

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Methods

STM characterization. We used a custom-designed commercial low-temperature STM system (Bosezi (Beijing) Co. Ltd.) for in situ characterization under ultra-high vacuum (UHV) conditions at a base pressure equivalent to 1×10-10 mbar. The Ag(111) single crystal were cleaned by standard ion sputtering and annealing under UHV conditions until large terraces separated by monoatomic steps were achieved. We have carried out the STM measurements at liquid nitrogen temperature (~77.8 K) if not stated otherwise. And STM images were acquired in constant-current mode with the tunneling current setpoint I_t and the sample bias voltage V_b indicated in the manuscript. The bias was applied to the sample, and the STM tip was grounded.

Sample preparation. The molecule precursors A, (4,4'-di(pyridin-4-yl)-1,1'-biphenyl and B, 4,4'-(5'-(4-(pyridin-4-yl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl, were commercially available from Tansoole; C, 3,3',5,5'-Tetra(pyridin-4-yl)-1,1'-biphenyl, was commercially available from Bidepharm. After degassing under UHV conditions, the molecular precursors were thermally evaporated from a 3-fold organic evaporator onto the metal surface in an UHV preparation chamber. The sublimation rates of molecular precursors were monitored by using a quartz crystal microbalance (SQM-160, from INFICON). Following molecular deposition, Cu was evaporated onto the Ag(111) surface under controlled liquid nitrogen flow to maintain the sample stage at around room temperature (monitored via PT1000 resistance thermometer; see Supporting Note 1 for full experimental details). This step serves the critical purpose of preventing the formation of Cu clusters which would be detrimental for the construction of coordination structure, and demonstrated by the control experiments (Figure S5). We therefore selected the non-annealed, RT-deposited samples as our experimental standard for the analyses. All STM data in this work (including Figures 2 and 4) were acquired on samples prepared by co-deposition of molecules A, B, and C on Ag(111). The ligands were deposited in the order of A→C→B using three-fold organic evaporator from CHI-VAC Research & Development Co., Ltd. Specifically, molecule A was deposited at a rate of 0.8-1.0 Å/min, and the estimated coverage of

molecule A is ~0.47 ML (monolayer). Here for simplicity, the full-covered coordinated network resembles that in Figure 4c is defined as 1 ML for molecule A, also equals to 64 molecules per 100 nm^2. Then molecule C was deposited at the deposition rate of 1.7-2.2 Å/min with the estimated coverage of ~0.45 ML. Finally, molecule B was deposited at the rate of 1.2-2.0 Å/min at an estimated coverage of ~0.39 ML. The most compact phases of molecules B and C are defined as 1 ML, equal to 52 molecules of B and 91 molecules of C per 100 nm^2, respectively.

DFT calculations. The calculations were performed in the framework of DFT by using Vienna Ab Initio Simulation Package (VASP)[1]. The projector augmented wave (PAW) method was employed to describe the ion-electron interactions,[2] and the Perdew−Burke−Ernzerh (PEB) generalized gradient approximation (GGA) was used for the exchange−correlation functional.[3] Van der Waals corrections to the PBE density functional were also included using the DFT-D3 method of Grimme.[4] The plane wave was expanded to an energy cutoff of 400 eV for the models. The atomic structures were geometrically relaxed until the forces on all of the unconstrained atoms were <0.03 eV/Å. For molecule A, a 4 by 14 slab model was employed to ensure negligible interactions between the periodic images; For molecule B, an 8 by 14 slab model was constructed; For molecule C, a 6 by 12 slab model was used. Given the relatively large size of the model structures and to maintain a consistent effect of the substrate across all the molecules, the Ag(111) substrate was modeled using two layers, with the bottom layer kept frozen during structural relaxations.

The binding energy E_b is determined from the energy difference between most stable structures with N-Cu-N bonding and the corresponding one without the N-Cu-N bonding. Both structures are fully relaxed for calculating the binding energy. A representative pair of structures used to determine E_b is shown below. We believe that this method for calculating E_b offers a relatively simple but straightforward and reliable way to evaluate molecular interactions.

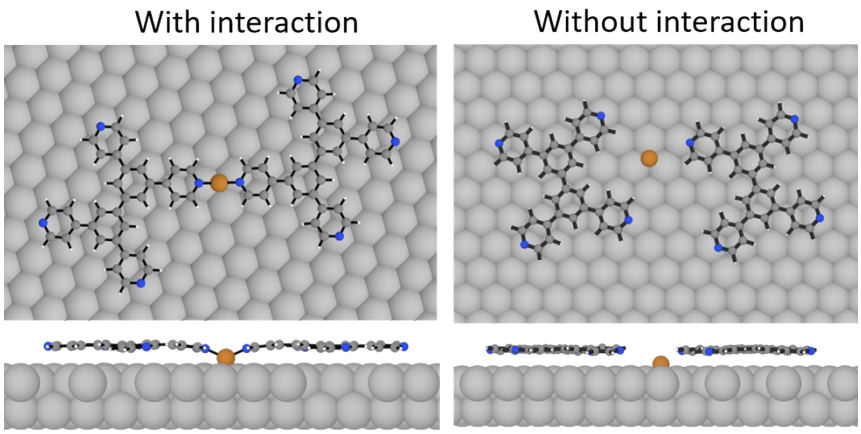

Figure S1. The most stable structures with N-Cu-N bonding (left panel) and the corresponding one without the N-Cu-N bonding (right panel).

Supporting figures

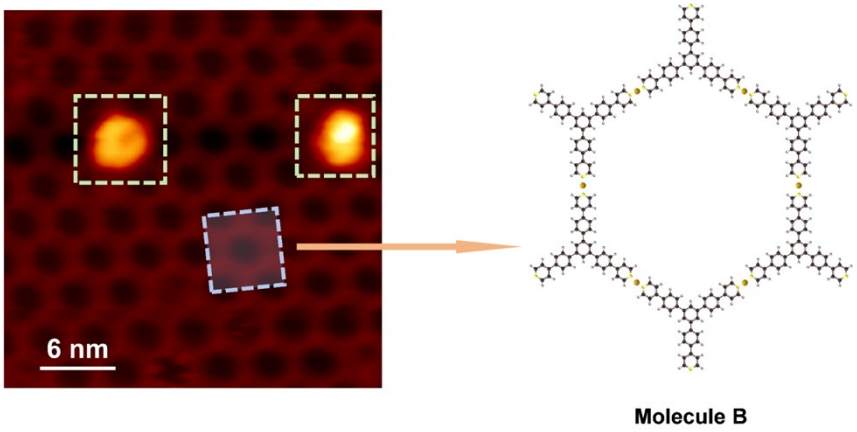

Figure S2. STM image of the metal clusters formed by excessive Cu on Ag(111). The Cu clusters are framed in green boxes, which indicate excessive Cu. The blue square points to the hexagonal ring formed by two-fold coordination between six molecules B and six Cu atoms. The fully coordination also demonstrate that the Cu adatoms are abundant. Yellow, light gray, brown, and dark yellow balls represent N, H, C and Cu atoms, respectively. Scanning parameters: It = 100 pA, Vb = -2.0 V.

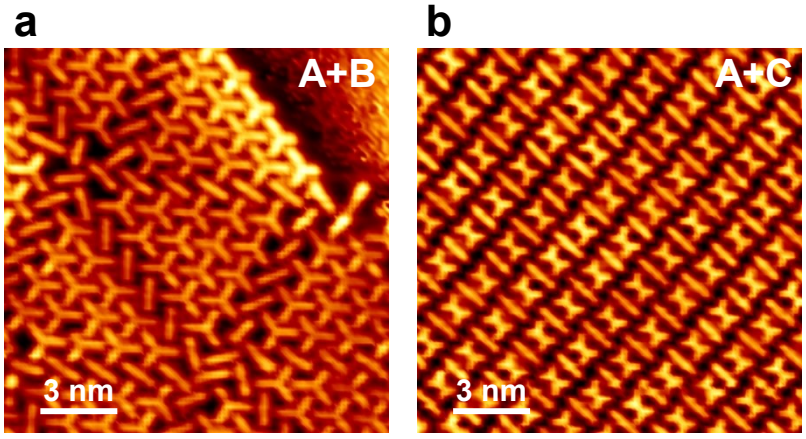

Figure S3. STM images of co-assembly phases formed by molecule A with other ligands on Ag(111) in the absence of Cu. (a) mixed A + B hydrogen-bonded assembly. (b) mixed A + C hydrogen-bonded assembly. Scanning parameters: (a, b) I_t = 100 pA, V_b = -1.50 V.

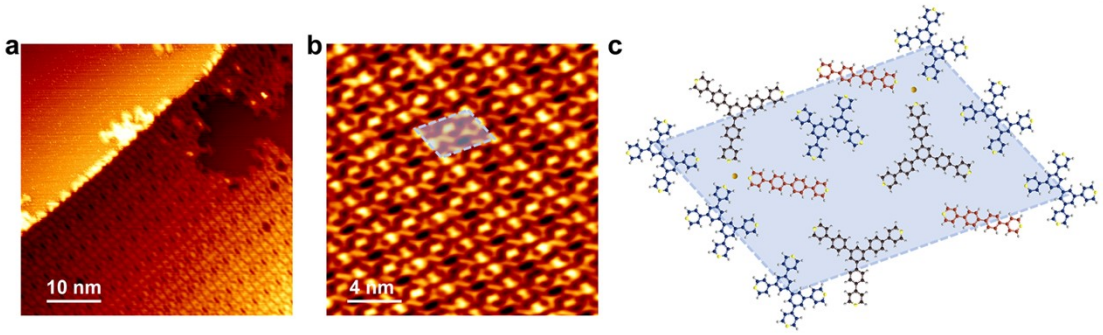

Figure S4. STM images and model of the phase formed by molecules A, B and C under reduced limited Cu condition. (a) Large-scale and (b) zoomed-in STM image of the ternary structure formed by molecules A, B, and C, and partially coordinated with Cu. The unit cell is indicated by light blue rhomboid. (c) The tentative molecular model corresponding to the structure framed in the light blue rhomboid. Yellow, light gray, and dark yellow balls represent N, H and Cu atoms, respectively. Red, brown and blue balls represent the aromatic frameworks of C atoms in molecules A, B and C, respectively. Scanning parameters: (a) I_t = 60 pA, V_b = -1.5 V; (b) I_t = 100 pA, V_b = -1.5V.

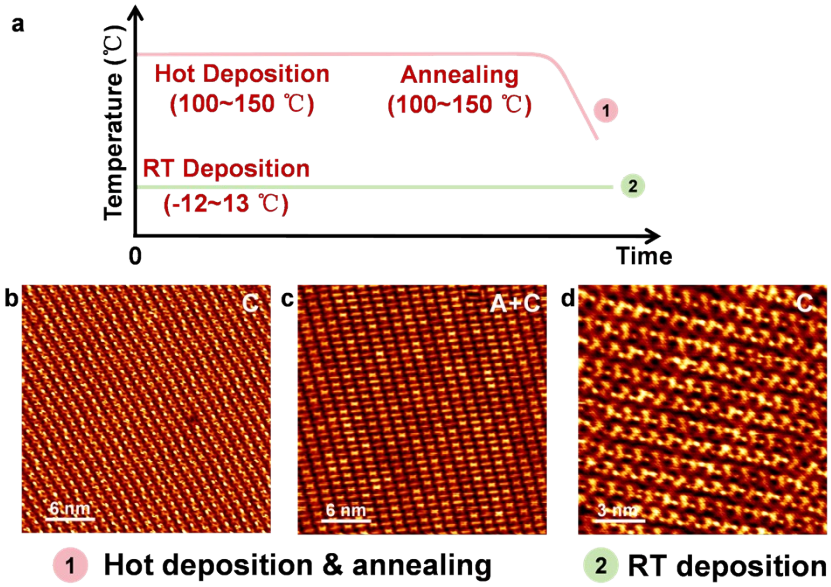

Figure S5. STM images of molecule C on Ag(111) under the different temperature conditions. No ordered Cu-coordinated phase of molecule C is observed under these thermal treatments. (a) Schematic temperature–time diagram illustrating three procedures. Hot deposition & annealing procedure for the Sample **1** means deposition of the copper on the molecule-covered substrate at 100~150 °C, and then heating the sample at the defined temperature under UHV conditions, holding for a certain time. Finally cooling it down for scanning. RT deposition for the Sample **2** means introducing liquid nitrogen to the sample stage to keep it around room

temperature (RT, -12~13 ℃) during metal deposition. (b) Self-assembled phase of molecule C and (c) co-assembled phase of molecules C and A after annealing at 100-150 °C. (d) Self-assembled phase of molecule C after Cu deposition at room temperature. Scan parameters: (b) I_t = 200 pA, V_b = -1.50 V; (c) I_t = 100 pA, V_b = -1.50 V; (d) I_t = 100 pA, V_b = -2.0 V.

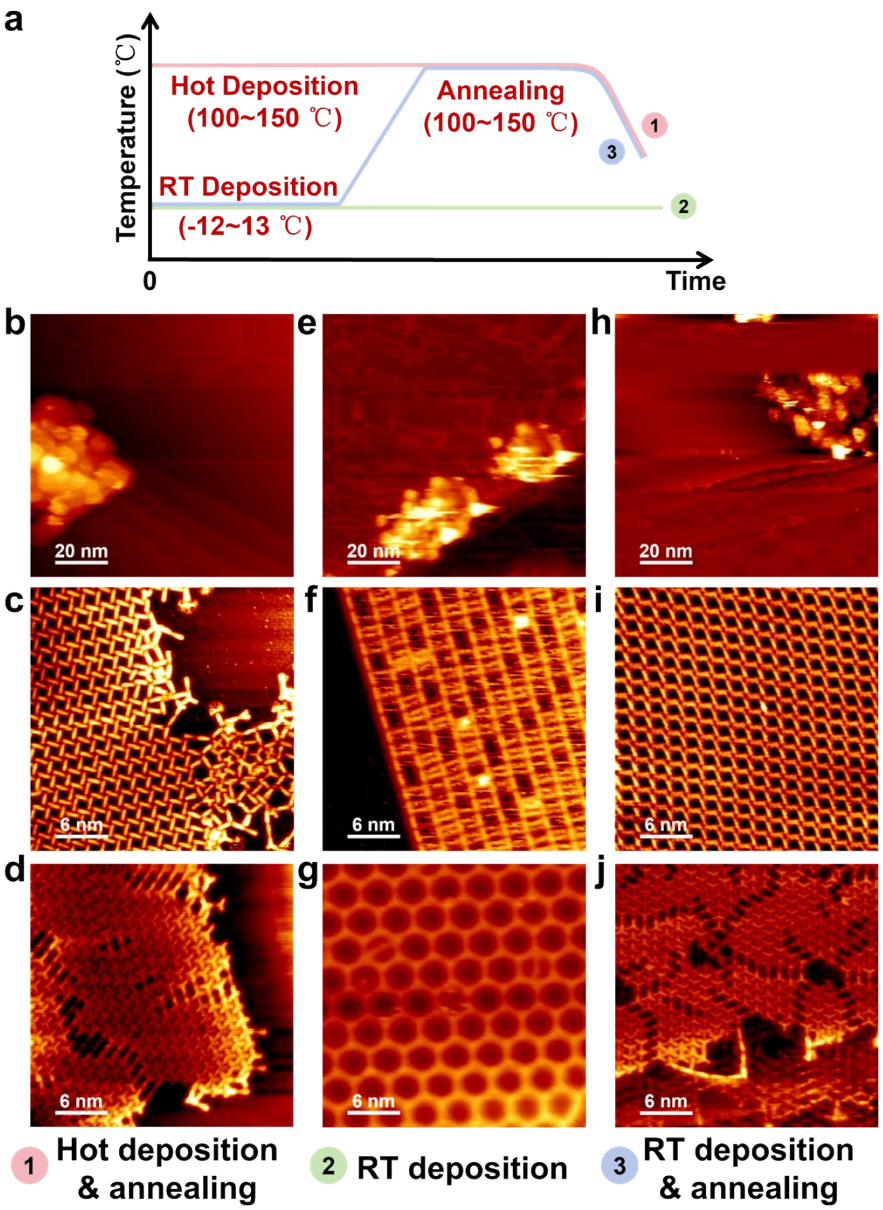

Figure S6. STM images of molecules A and B with excessive Cu on Ag(111) under different conditions. (a) Schematic temperature–time diagram illustrating three procedures. Hot deposition & annealing procedure for the Sample **1** and RT deposition for the Sample **2** is the same to the treatments indicated in the above Figure S5a. RT deposition & annealing for the Sample **3** means deposition of copper at RT, and then annealing the sample at a certain high temperature (100~150 ℃), as shown in (a). (b-d), (e-g), (h-j) are the self-assembled phases of

molecules A and B under three distinct experimental treatments, respectively: (b-d) hot deposition and annealing, (e-g) RT deposition only, and (h-j) RT deposition followed by annealing. (b, e, h) show the Cu clusters, which represents excessive Cu. Scanning parameters: (b-f, h-j) I_t = 100 pA, V_b = -1.5 V; (g) I_t = 100 pA, V_b = -2.0 V.

Supporting note 1: The temperature of sample during Cu evaporation

During Cu evaporation, liquid nitrogen was circulated through the manipulator to maintain the sample at low temperatures. One PT1000 resistance wire is attached to the manipulator for temperature measurement. The PT1000 is a platinum resistance thermometer, in which resistance increases linearly with temperature, and the relationship is standardized in the International Electrotechnical Commission(IEC).[5]

$$R_t = \begin{cases} R_0(1 + At + Bt^2 + C(t-100)t^3) & -200°C \le t \le 0°C \\ R_0(1 + At + Bt^2) & 0°C < t \le 850°C \end{cases}$$

Where, $R_t(\Omega)$ is the resistance at the temperature t (℃) and R_0 is the resistance at t = 0 ℃. For PT1000, R_0 is 1000 Ω. The constants are, A=3.9083×10^{-3} ℃$^{-1}$, B= -5.775×10^{-7} ℃$^{-2}$, C= -4.183×10^{-12} ℃$^{-3}$. In our experiments, the measured resistance during sample preparation ranged from 950 Ω to 1050 Ω, corresponding to the temperature range of approximately -12 ℃ to 13 ℃.

References

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5 IEC, IEC 60751, International Electrotechnical Commission, Geneva, 2022.