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Supporting Information

for

Pathway regulation of an on-surface stepwise reaction through a metal

coordination template

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1. Methods

STM Experiments. All sample preparation and STM measurements were performed in a commercial ultra-high vacuum system from Physcryo (Suzhou) with a base pressure below 5×10^{-10} mbar. The single crystalline Cu(111) substrate (Mateck, 99.9999%) was cleaned through cycles of Ar⁺ ion sputtering, followed by annealing to 700 K. The molecular precursor, 2-bromo-1,8-naphthyridine (Bide Pharmatech Ltd., 95%), was evaporated by organic molecular beam epitaxy (OMBE) from a quartz crucible at 300 K. All STM images were collected in constant current mode with a chemically etched tungsten tip when the sample was held at 78 K. The STM images were processed using WSxM software.¹

DFT Calculations. Density functional theory calculations were performed using the Vienna Ab initio Simulation Package (VASP)² within the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.³ The electron–ion interaction was described by the projector augmented wave (PAW) method.⁴ The DFT-D3 was used to evaluate the van der Waals (vdW) effect.⁵ To simulate the molecules on the surface, a two-layer Cu(111) slab was built with the bottom layer fixed. A vacuum layer along the z-axis, perpendicular to the cleaved surfaces, was larger than 15 Å to prevent the interactions between systems in the neighboring cells. To simulate the molecules in the gas phase, a $40 \times 40 \times 25$ Å³ unit cell was utilized to avoid the interactions between neighboring molecules. The energy cutoff for plane-wave functions was set as 450 eV. The systems were fully relaxed until the force acting on each atom was less than 0.02 eV/Å. The VASPKIT was used for postprocessing of the VASP calculated data to obtain the molecular orbitals of the U unit and O unit.⁶

2. Supplementary results

2.1 Self-assembled chains from intact BNs.

The deposition of BN molecules on a cold Cu(111) substrate (approximately 200 K) results in the formation of individual dots (marked by the red arrows) and short-chains composed of two or three dots (marked by the blue and green arrows, respectively) (Fig. S1a). We attribute these dots to intact BN molecules. A close-up STM image (Fig. S1b) shows fuzzy dots (marked by the red circles), indicating the monomers are mobile at 78 K. The periodicity of the chain measures 7.2 Å, which approximately equals three times the lattice constant of Cu(111) along the <1-10> directions. Compared to the sample after annealing at 330 K (Fig. 1), we propose that these chains are formed through intermolecular π - π bonds between neighboring intact BNs in a standing configuration. Fig. S1c presents the self-assembly of intact BNs adsorbed on the Cu(111) in the standing configuration via DFT calculations.



Fig. S1 (a) STM image ($40 \times 40 \text{ nm}^2$) of BN molecules deposited on Cu (111) surface held at approximately 200 K. (b) Close-up STM image ($10 \times 10 \text{ nm}^2$) of the short chains. Scanning parameters of (a) and (b): U=-1.0 V, I=0.1 nA, $T_{\text{STM}}=78$ K. (c) The energetically favored adsorption geometry of the self-assembly of intact BNs and the corresponding simulated STM images (U=-1.0 V).

2.2 Self-assembled networks of [2+2] units.

As the coverage increases, the [2+2] units self-assemble into a close-packed island, likely assisted by the cleaved Br atoms through Br-H bonding.^{7, 8} The periodicity of the packing measures a = 2.12 nm, b = 1.73 nm, $\gamma = 65^{\circ}$.



Fig. S2 STM image $(32 \times 32 \text{ nm}^2)$ of a self-assembled island formed by [2+2] units at a high coverage. Scanning parameters: U=-1.0 V, I=0.1 nA, $T_{\text{STM}}=78 \text{ K}$.

2.3 Tentative models of [2+2] units with different numbers of Cu nuclei.



Fig. S3 The energetically favored adsorption geometries of [2+2] units with 1, 2, 3, 4, 6, and 8 Cu nuclei obtained from DFT calculations, respectively.

2.4 Tentative models of O-units with different numbers of Cu nuclei.

The simulated STM image of the O-unit containing 1 nucleus differ from the other two, since the molecular orbitals can be manipulated by the Cu-atom contact.⁹ To gain some insight of the relationship between the brightness and the number of Cu atoms, we standardized the contrast of the simulated STM images by setting the substrate as zero in these greyscale images. This approach allows for the comparison of dot brightness by referencing the maximum grey value at the center of the Cu clusters. The centers exhibit the brightness values of 0.62, 0.67, and 1.00 for the models containing 1, 5, and 6 Cu nuclei, respectively. Note that the grey value at the center is normalized relative to the model featuring 6 Cu nuclei. The heights of the Cu layer above the first layer of the substrate are 1.88 Å, 2.13 Å, and 2.11 Å, respectively. This height difference leads that the brightness of the model with 1 nucleus is relatively lower than those of the other two. Additionally, the absence of a Cu atom at the center results in that the brightness of the model with 5 nuclei is lower than that of the model with 6 nuclei.



Fig. S4 The energetically favored adsorption geometries and the corresponding simulated STM images (U= -1.0 V) of O-units with 1, 5, and 6 Cu nuclei obtained from DFT calculations, respectively.

2.5 DFT-optimized geometries of O-units with 6 Cu nuclei.

In the left model, the Cu atoms form coordination bonds with two N atoms from two neighbouring naphthyridines, while in the right model, the Cu atoms form coordination bonds with two N atoms within a single naphthyridine. The energy of the left model is 3.40 eV lower than that of the right one. Therefore, the Cu atoms form coordination bonds with the two N atoms from the neighbouring naphthyridines rather than those within a single naphthyridine.



Fig. S5 The DFT-optimized geometries of O-units with 6 Cu nuclei in the gas phase.

2.6 The plot of the energy difference among different polygons.

In these models, the central Cu clusters are not included in the DFT calculations in the gas phase, since the number of atoms varies in the O-units according to the experimental observations. Note that except the dimer and trimer, all other polygons are in flat configurations.



Fig. S6 The energy per number of naphthyridines in the gas phase plotted against the number of naphthyridines from the dimer to the octamer, using the energy of the pentamer as a reference.

2.7 High-coverage sample.

We carried out a statistical analysis of the sample at approximately 0.18 BN/nm², resulting in that the yields of the U-units, the O-units, and the COS-units are 57.6%, 26.5%, and 15.9%, respectively (1202 units counted in total). Fig. S7a presents a STM image of a high-coverage sample (approximately 0.85 BN/nm²) after annealing at 400 K. The blue, white, and green arrows mark the typical reaction products: a U-unit, an O-unit, and a COS-unit, respectively. The yields of the U-units, the O-units, and the COS-units are 66.9%, 5.1%, and 28.0%, respectively (1051 units counted in total). After further annealing the sample at 440 K, the central Cu atoms remain within these units (Fig. S7b).



Fig. S7 (a) and (b) STM images $(30 \times 30 \text{ nm}^2)$ of the high coverage sample of BNs on Cu(111) after annealing at 400 K and 440 K, respectively. The blue, white, and green arrows indicate a U-unit, an O-unit, and a COS-unit, respectively. Scanning parameters of (a) and (b): U=-1.0 V, I=0.1 nA, $T_{\text{STM}}=78$ K.

2.8 Tentative models of organometallic U-units with different numbers of Cu nuclei.



Fig. S8 The energetically favored adsorption geometries and the corresponding simulated STM images (U= -1.0 V) of organometallic U-units with 6, 7, and 8 Cu nuclei obtained from DFT calculations, respectively.

2.9 Frontier molecular orbitals of the U-unit and the O-unit.

The HOMO-LUMO gaps of the U-unit and the O-unit are 1.92 eV and 1.89 eV, respectively. Furthermore, while the U-unit exhibits no degeneracy in its frontier molecular orbitals, the O-unit displays four doubly degenerate molecular orbitals: HOMO-3 and HOMO-2, HOMO-1 and HOMO, LUMO and LUMO+1, LUMO+2 and LUMO+3. The degeneracy of the frontier molecular orbitals typically plays a vital role in the molecular photophysical properties.¹⁰⁻¹²



Fig. S9 The frontier molecular orbitals of the U-unit and the O-unit obtained from DFT calculations in the gas phase.

2.10 Reaction of BNs on Ag(111).

As shown in Fig. S10a, after annealing at 340 K, BN molecules on Ag(111) form transoid organometallic dimers (superimposed by the structural models). Such organometallic structures are commonly observed in Ullmann coupling on Ag(111) after annealing treatment at around this temperature.¹³⁻¹⁵ The cleaved Br atoms (marked by the white circles) are clearly observed between neighbouring chains, indicating the chains interact through Br-H bonding. The DFT-optimized organometallic dimers in the gas phase are presented in Fig. S10b. The energy difference between the transoid and cisoid organometallic dimers is relatively small, approximately 0.026 eV, as indicated by DFT calculations in the gas phase.



Fig. S10 (a) STM image ($10 \times 10 \text{ nm}^2$) of the sample of BNs on Ag(111) after annealing at 340 K. Scanning parameters: U=-1.0 V, I=0.1 nA, $T_{\text{STM}}=78 \text{ K}$. (b) The transoid and cisoid organometallic dimers in the gas phase optimized through DFT calculations. Color code: gray, carbon; blue, nitrogen; white, hydrogen; purple, silver.

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