

## *Supporting Information*

### **Selective aryl C–H activation governed by molecular nonplanar conformation on Au(111)**

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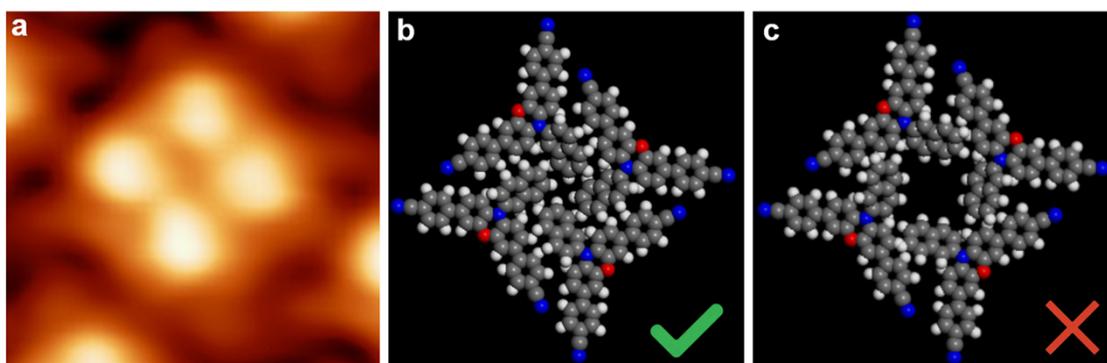
## Experimental and theoretical methods

### STM experiment

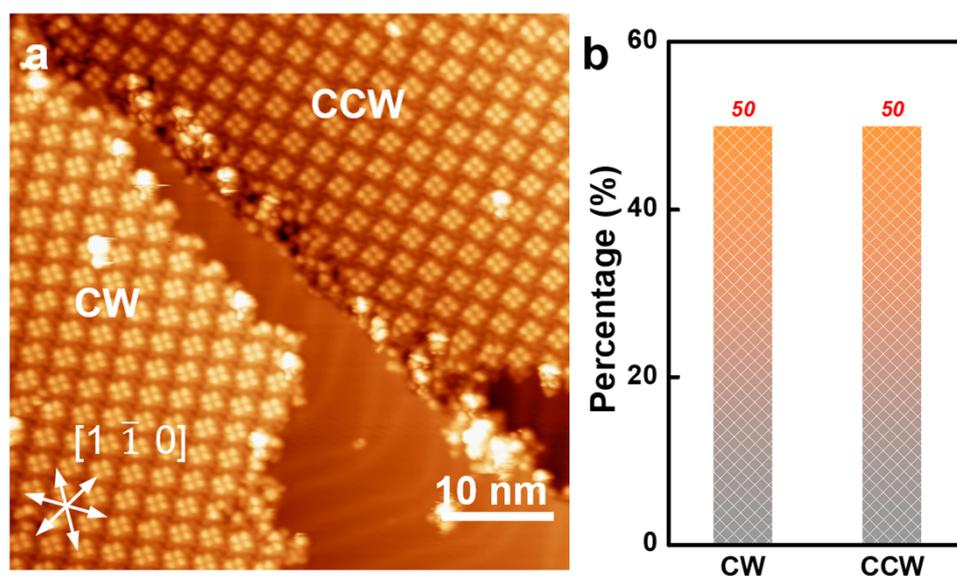
All the STM experiments were performed at 78 K with commercial Createc LT-STM. The base pressure was better than  $1.0 \times 10^{-10}$  mbar. The tip used in the experiment was a tungsten tip, which was corroded using a 3 mol/L NaOH solution. STM images were taken in the constant-current mode and all scanning probe images were edited using WSxM software.<sup>1</sup> Atomically clean Au(111) (from MaTeck GmbH) were prepared through repeated cycles of argon ion ( $\text{Ar}^+$ ) bombardment (0.8 kV for 20 min) and annealing (750 K for 20 min). The 3,7-di(4-cyanophenyl)-2-naphthalene-10-phenoxazine (CNP) molecule, provided by Dr. Yaju Chen, was synthesized using the methods described in the literature<sup>2</sup> and thermally sublimated onto the metal surface at approximately 500 K under a vacuum of  $\sim 2 \times 10^{-9}$  mbar using a commercial molecular evaporator.

### DFT Calculations

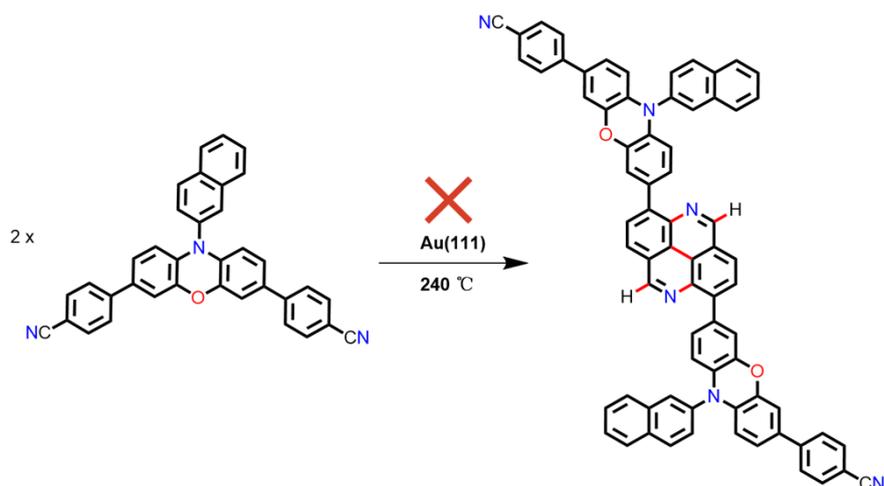
The calculations were carried out in the framework of DFT by using the Vienna ab initio Simulation Package (VASP).<sup>3-4</sup> The projector augmented-wave (PAW) method described the interaction between ions and electrons.<sup>5-6</sup> We used the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) formalism to treat exchange-correlation interaction,<sup>7</sup> and van der Waals (vdW) interactions were considered by using the DFT-D3 developed by Grimme.<sup>8</sup> The energy cutoff for the plane wave basis sets is 400 eV, and the energy and force convergence value between two consecutive self-consistent steps were set as  $10^{-5}$  eV and 0.05 eV/Å, respectively. Calculated lattice constants of 4.14 Å for Au were used. The Au(111) surface was modeled by two or three-layered slabs separated by at least 20 Å of vacuum. For all adsorption configurations, we performed calculations with a  $\Gamma$ -point only k-point sampling. The simulations of the reaction barriers in the manuscript are performed with the climbing image nudged elastic band (CI-NEB) method for finding saddle points and minimum energy paths (<http://theory.cm.utexas.edu/vtsttools/neb.html>), which is at  $T = 0$  without including entropy and vibrations.<sup>9</sup> The dehydrogenation process (Fig. 3c, d) along the  $[11\bar{2}]$  direction were both performed on Au(111) surface ( $5 \times 7$ ). Two distinct adsorption conformations (type I and type II) of the CNP molecule were both performed on a rectangular ( $3\sqrt{3} \times 7$ ) supercell. The STM simulation was performed with the Tersoff-Hamman method.<sup>10-12</sup>



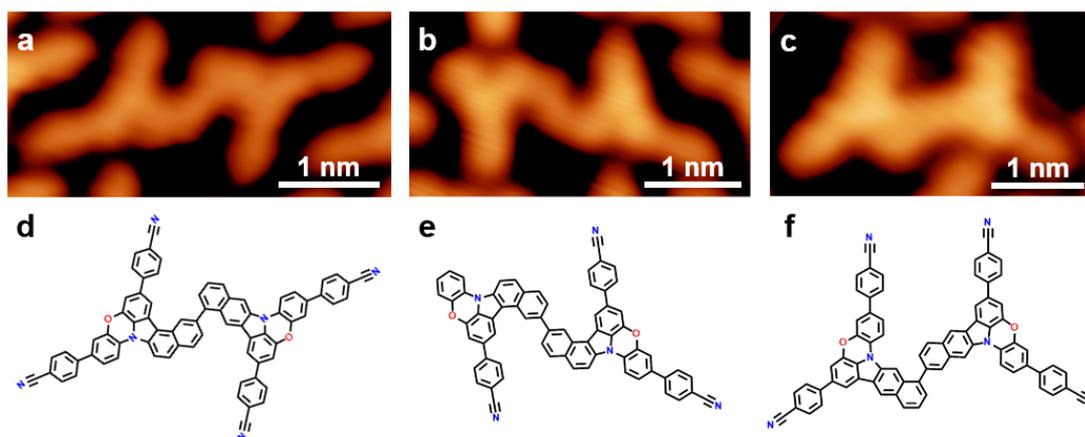
**Figure S1** (a) Close-up STM image of a CNP tetramer on the Au(111) surface. (b) Structural model of the CNP tetramer with a plausible orientation of the naphthyl substituents, consistent with the experimental STM contrast. (c) Structural model of the CNP tetramer with unfavorable naphthyl orientations, which can be excluded based on comparison with the STM observations.



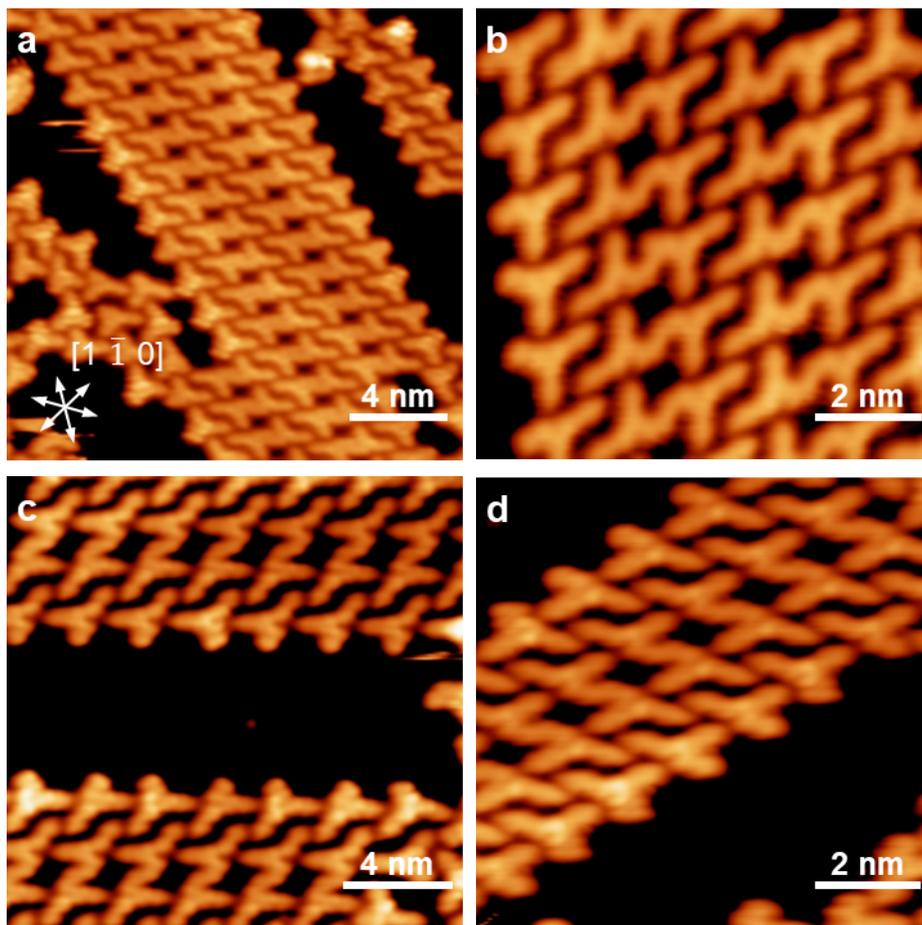
**Figure S2** (a) Large-area STM image showing the coexistence of clockwise (CW) and counterclockwise (CCW) chiral domains on the Au(111) surface. (b) Statistical analysis of the surface area fractions of the CW and CCW domains, indicating their relative abundance.



**Figure S3** No evidence of cyano–cyano coupling of CNP molecules was observed experimentally in the present system, in contrast to previous reported cyano-coupling reactions on metal surfaces.



**Figure S4** Close-up STM images of different minor dimeric byproducts observed on the Au(111) surface, together with the corresponding proposed structural models. Tunneling parameters: (a)  $V_s = -2.0$  V,  $I_t = 100$  pA. (b, c)  $V_s = -0.9$  V,  $I_t = 100$  pA.

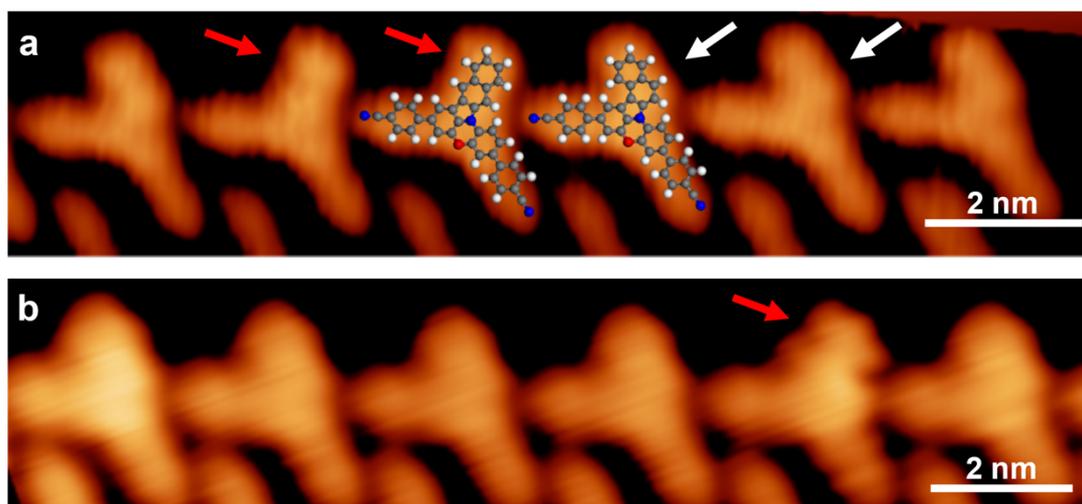


**Figure S5** STM images of the *d*-dimers domains. Tunneling parameters: (a, c, d)  $V_s = -1.0$  V,  $I_t = 100$  pA. (b)  $V_s = -2.0$  V,  $I_t = 100$  pA.

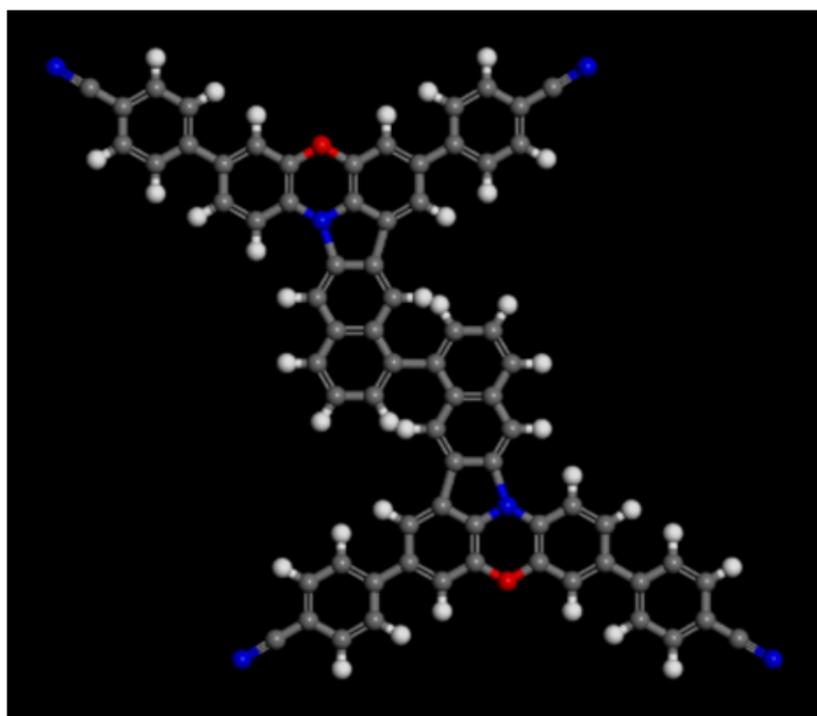
	Type I	Type II
$E_{Scf}/\text{eV}$	-798.26626	-798.24119
$E_{Au}/\text{eV}$	-362.54845	-362.54845
$E_{mole}/\text{eV}$	-432.05259	-432.03952
$E_{ad}/\text{eV}$	-3.66522	-3.65322

**Table S1** Calculated adsorption energies for two adsorption configurations (Type I and Type II) on the Au(111) surface. The total energy of the adsorbed system ( $E_{Scf}$ ), the energy of the clean Au surface ( $E_{Au}$ ), and the energy of the isolated molecule ( $E_{mole}$ ) are listed. The adsorption energy ( $E_{ad}$ , in eV) is defined as:

$$E_{ad} = E_{Scf} - E_{Au} - E_{mole}$$



**Figure S6** STM images of CNP monomers on Au(111) exhibiting different naphthyl orientations after intramolecular dehydrogenative cyclization. White arrow: Product of intramolecular cyclization of Type I CNP molecule. Red arrow: Product of intramolecular cyclization of Type II CNP molecule. Tunneling parameters: (a)  $V_s = -2.0$  V,  $I_t = 100$  pA. (b)  $V_s = -1.0$  V,  $I_t = 100$  pA.



**Figure S7** Dimeric product that was not observed experimentally.

## References

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