Supporting Information for

"Steering on-surface polymerization through coordination with a bidentate ligand"

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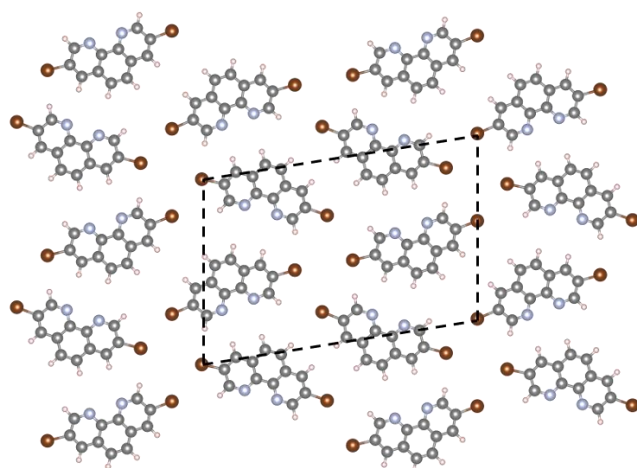
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Fig. S1 DFT optimized self-assembled structure of the room-temperature phase of the DBPA molecules. The black dashed lines indicate the unit cell.
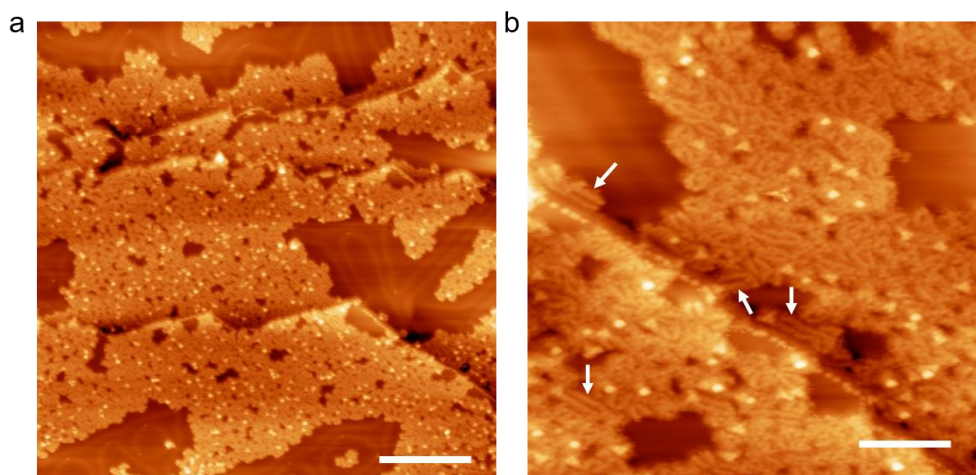

Fig. S2 STM images of the sample after 200 °C annealing **a**, Large area of the molecular island (V_s = -1.5 V, I_t = 100 pA). Scale bar: 20 nm. **b**, White arrows indicate the oligomers observed from the molecular islands (V_s = -1.5 V, I_t = 100 pA). Scale bar: 6 nm.
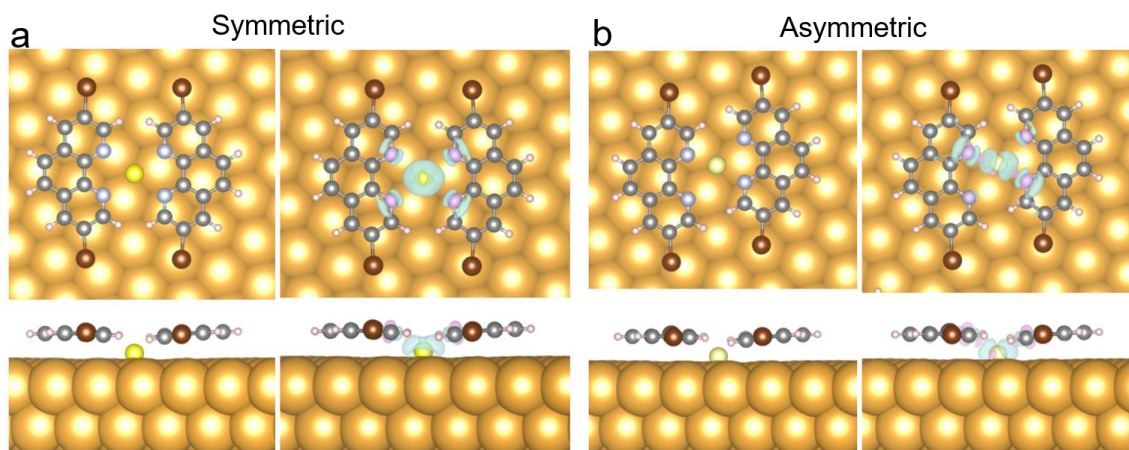
Fig. S3 a,**b** The DFT optimized structures and charge density maps of the two dimer configurations on Au(111). In the left: top and side views of the optimized structure, in the right: the charge density difference map between the Au adatom and two DBPA. The asymmetric configuration is energetically more stable than the symmetric one by -0.1 eV.
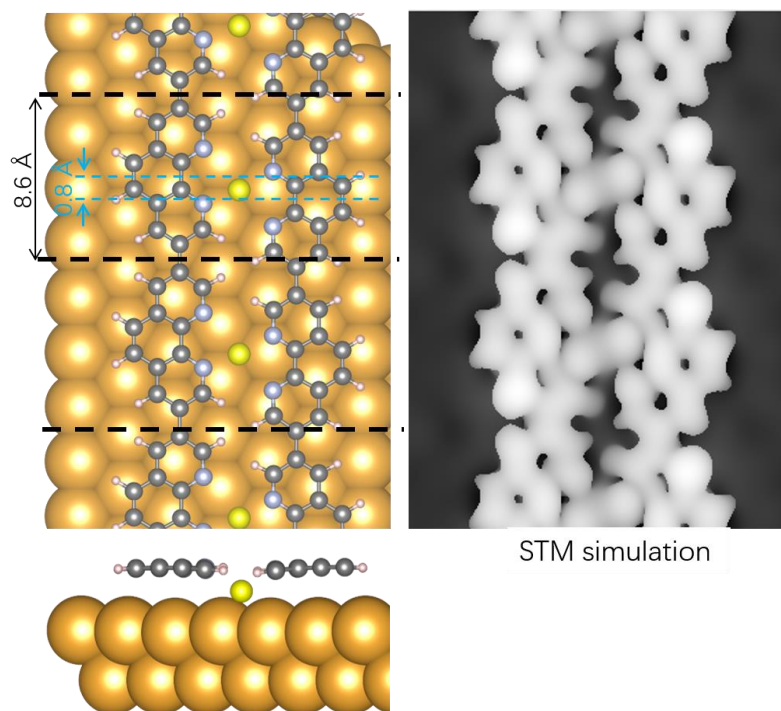

STM simulation

Fig. S4 DFT optimized structure and its corresponding STM simulation of the double-chain structure.

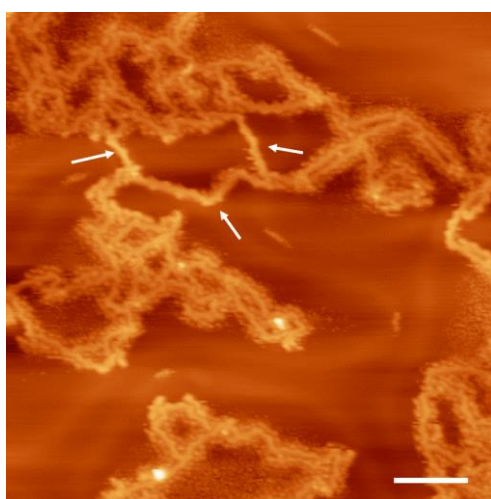**Fig. S5** STM image of the sample after 200 °C annealing (V_s = -1.3 V, I_t = 400 pA). Scale bars: 4.5 nm. The white arrow indicates the single-chain structures.
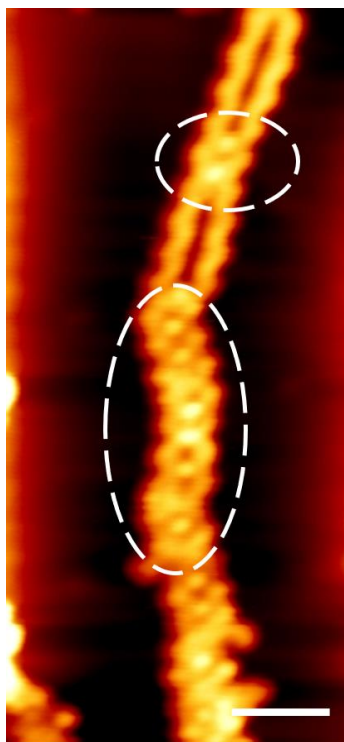
Fig. S6 STM image of the double-chain structure after annealing to above 400 °C (V_s = -1.5 V, I_t = 40 pA). Scale bars: 2 nm. The white circles highlight the increased contrasts inside the double-chain, which are assigned to the gold adatoms.
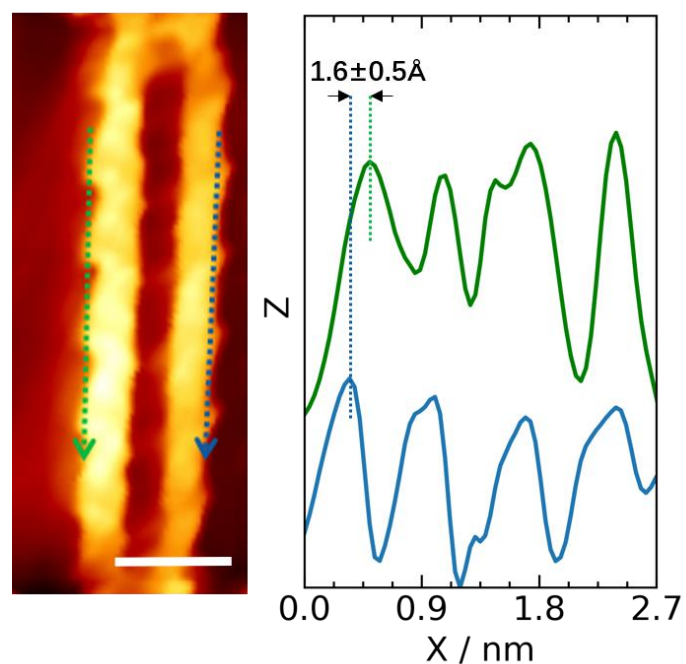
Fig. S7 Line scans on shorter chains. The trajectories where the two line-cuts are acquired are indicated by the arrows with corresponding colours on the STM image (Vs = -1.5 V, It = 100 pA). Scale bar: 1 nm.
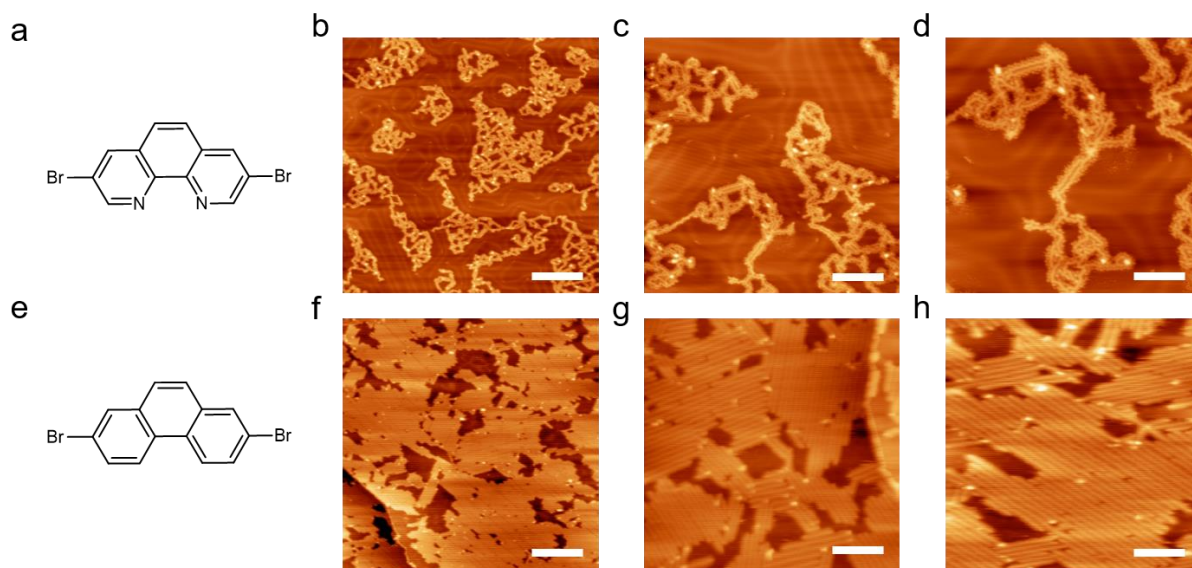
Fig. S8 The effect of metal coordination on C-C coupling. **a, e** Chemical structures of the two molecules (DBPA and dibromophenanthrene) used for comparison. **b-d** STM images of the DBPA covered sample after 250 ℃ annealing. **f-h** STM images of the dibromophenanthrene covered sample after 250 ℃ annealing. The scale bar is 20 nm for **b** and **f**, 10 nm for **c** and **g**, and 6 nm for **d** and **h**. The scan parameters are V_s = -1.5 V, It = 100 pA for all images.

S9. Materials and 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 base pressures below 1×10^{-10} mbar. The Au(111) single crystal (MaTeck GmbH) was cleaned by several cycles of argon sputtering and annealing under UHV conditions until large terraces separated by monoatomic steps were achieved. The measurements were performed at liquid nitrogen temperature (~ 78 K) if not stated otherwise.

Sample preparation. The molecule precursors 3,8-dibromo-1,10-phenanthroline is commercially available from Tansoole. After degassing under UHV condition, the molecular precursors were thermal evaporated from an organic evaporator onto the metal surfaces. The sublimation rates of molecular precursors were monitored by a quartz crystal microbalance (SQM-160, INFICON), and a LabVIEW based program was developed to ensure a stable molecular evaporation rate. The temperatures of the samples were measured by a remote pyrometer.

DFT calculations. The density functional theory calculations are performed with the Vienna Ab Initio Simulation Package (VASP).[1-2] Projector-augmented-wave pseudopotentials and the Perdew–Burke–Ernzerhof exchange-correlation functional were employed.[3-4] Van der Waals (vdW) interactions were taken into account using the dispersion corrected DFT-D3 method of Grimme.[5] The structure was relaxed in DFT until residual forces on all unconstrained atoms were less than 0.03 eV/Å for geometry optimizations. Computations were carried out using the high-performance cluster at Shanghai University.

S10. References

(1) Kresse, G.; Hafner, J., Ab initio molecular dynamics for open-shell transition metals. *Physical Review B* **1993,** *48* (17), 13115-13118.
(2) Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **1996,** *54* (16), 11169-11186.
(3) Blöchl, P. E., Projector augmented-wave method. *Physical Review B* **1994,** *50* (24), 17953-17979.
(4) Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996,** *77* (18), 3865-3868.
(5) Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry* **2011,** *32* (7), 1456-1465.