Electronic Supplementary Information

Manipulation of C-C Coupling Pathways by Different Annealing Procedures

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Experimental and theoretical methods

STM measurements were performed in an ultrahigh vacuum system (SPECS-NAP150, Berlin, Germany) with a base pressure better than 2×10^{-10} mbar. All STM images were acquired at room temperature in the constant-current mode, and processed afterwards by the WSXM software (4.0 Beta) [1]. A clean and structurally well-defined Au(111) surface was obtained through cycles of sputtering with Ar^+ ions and subsequent annealing at 723K, as judged by the presence of the herringbone reconstruction. BBPB molecules was sublimated onto Au(111) via an evaporation source in the preparation chamber with the base pressure of 1×10^{-9} mbar. The sample was thereafter transferred within the preparation chamber to the STM chamber, where measurements were about RT(~295K).

Density functional theory (DFT) calculations were performed by using the Vienna Ab initio Simulation Package (VASP) [2]. The projector augmented wave (PAW) [3] was employed and the Perdew-Burke-Ernzerhof (PBE) was utilized in the framework of generalized gradient approximation (GGA) [4] and the dispersion corrected DFT-D3 method of Grimme [5] was used for the calculations when including the weak interactions. The electronic wave functions were expanded in plane waves with the energy cutoff of 400 eV. During structure relaxation, the bottom one Au layers from substrate were fixed while all the other atoms were free to relax until the atomic force was less than 0.05 eV/Å. Reaction pathways were calculated with a combination of the climbing image-nudged elastic band (CI-NEB).

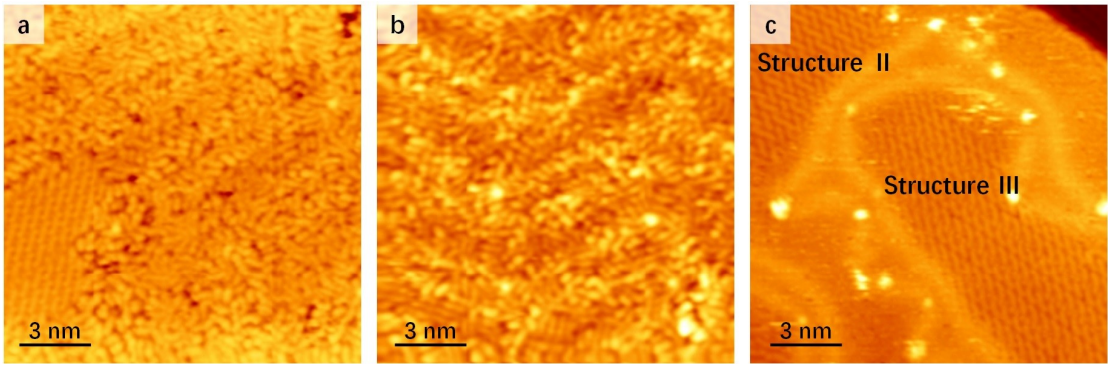

Figure S1. STM images of BBPB molecules on Au(111) surface after stepwise gentle annealing. (a, b) STM image of structure after annealing at 323 K for 10 min. (c) STM image of structure II and structure III after annealing at 353 K. Scanning parameters: (a) U_{bias} = 1.2 V, I_t = 0.9 nA; (b) U_{bias} = 1.0 V, I_t = 0.7 nA; (c) U_{bias} = -1.2 V, I_t = 2.2 nA.

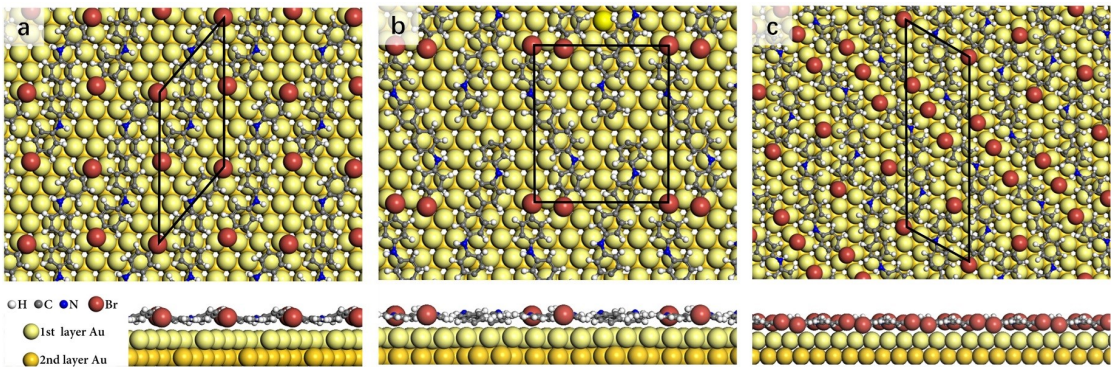

Figure S2. (a) DFT optimized structural model of structure I after annealing at 323 K for 10 min. The DFT optimized structural models of structure II (b) and structure III (c) after annealing at 353 K.

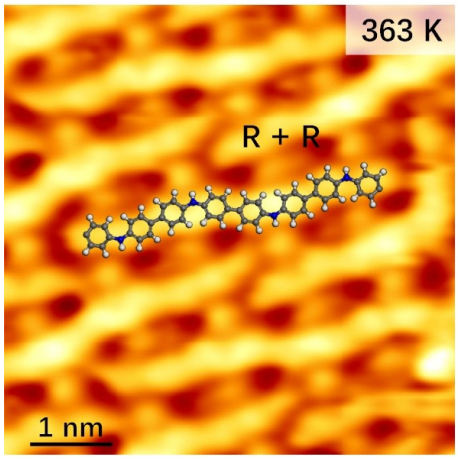

Figure S3. High-resolution STM images of various BBPB dimers formed by Ullmann coupling on Au(111) surfaces after annealing to 363 K for 20 min. Scanning parameters: U_{bias} = -0.9 V, I_t = 0.8 nA.

Notes and references

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