

Supplementary Materials for
**On-surface Aryl-aryl Coupling via Selective C-H
Activation**

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The experimental and computational methods

All the STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature “Aarhus-type” STM,^{1,2} a molecular evaporator and standard facilities for sample preparation. After the system was thoroughly degassed, the 4Ph molecules were deposited by thermal sublimation onto the substrate held at RT with submonolayer coverage. The STM measurements were carried out in a typical temperature range of 100 K–150 K.

All of the calculations were performed in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP)^{3,4}. The projector augmented wave method was used to describe the interaction between ions and electrons^{5,6}, and the Perdew–Burke–Ernzerhof generalized gradient approximation exchange–correlation functional was employed⁷, and van der Waals (vdW) interactions were included using the dispersion corrected DFT-D2 method of Grimme⁸. The simulated STM image was obtained using the Tersoff–Hamann method⁹. The climbing-image nudged elastic band was applied to locate the transition state¹⁰. The atomic structures were relaxed until the forces on all unconstrained atoms were ≤ 0.03 eV/Å for both geometry optimization and transition state search.

The slab model for the adsorption of 4Ph molecules on Cu(110) and the NEB calculation includes two layers of copper atoms and a 15 Å vacuum along the surface normal, and the bottom layer was fixed at their bulk positions. We chose a 4×10 extended supercell that had been checked to be big enough to avoid interactions between the molecules across the surface for modeling the 4Ph molecule on the substrate, and a 4×15 supercell for modeling the 4Ph dimer molecule on the substrate. A $2 \times 1 \times 1$ k-point grid determined by the Monkhorst-Pack method was used in both adsorption and NEB calculations.

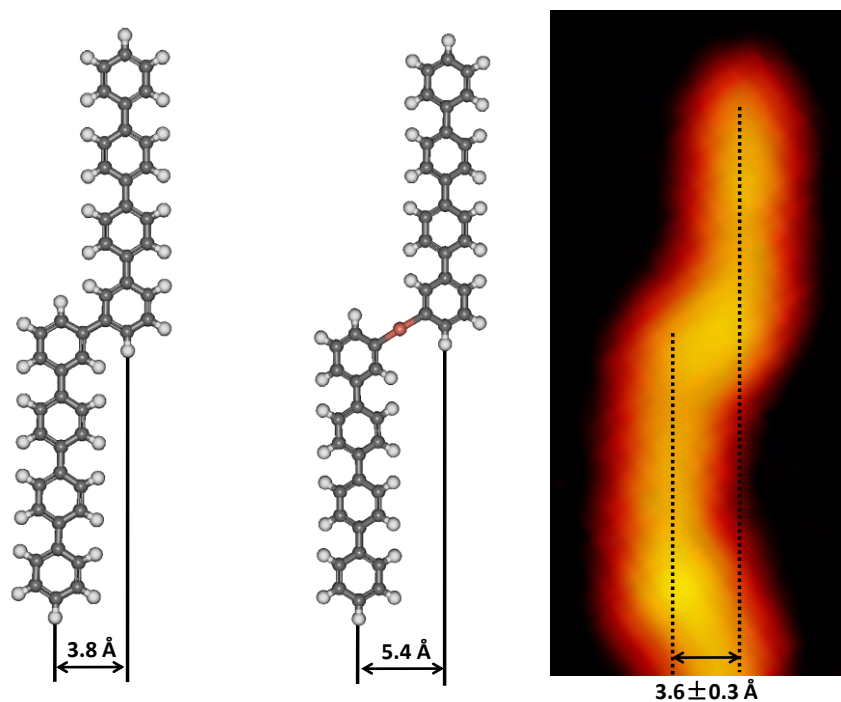


Fig. S1. The comparison of the theoretical models of direct C-C coupling and C-Cu-C interlinking indicates a good agreement between the direct C-C coupling and the experimental result.

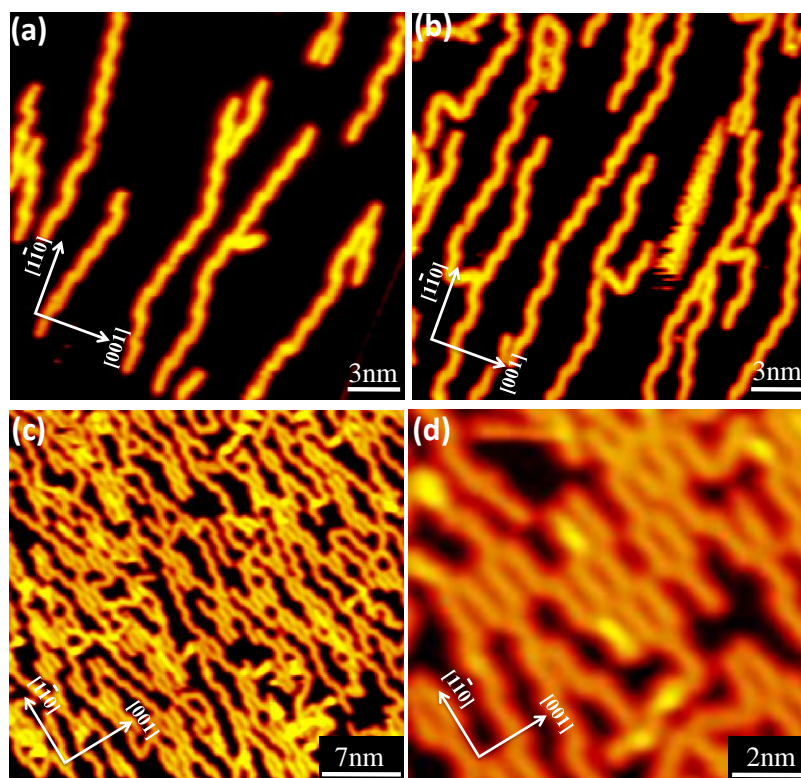


Fig. S2. STM images of 4Ph molecules after anneal at 500K with (a) low, (b) medium and (c)-(d) high molecular coverage.

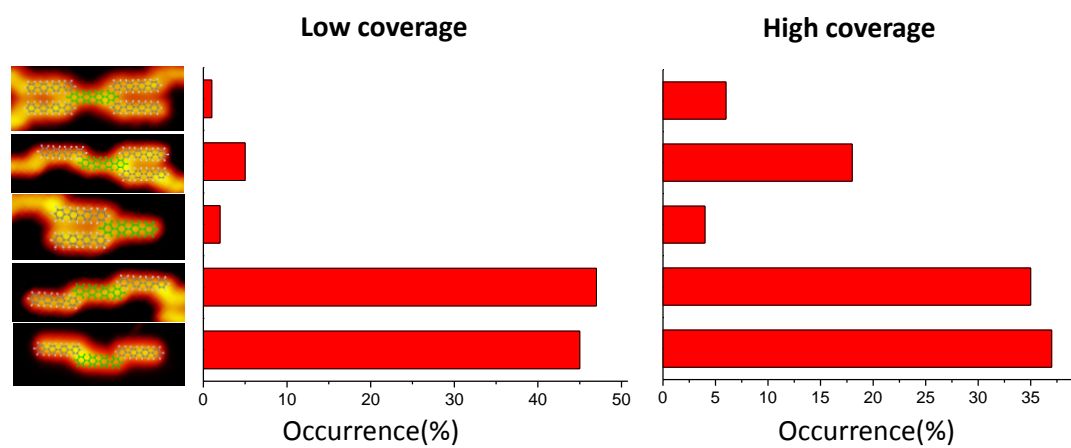


Fig. S3. The relative occurrence of the different structural motifs at low and high coverage.

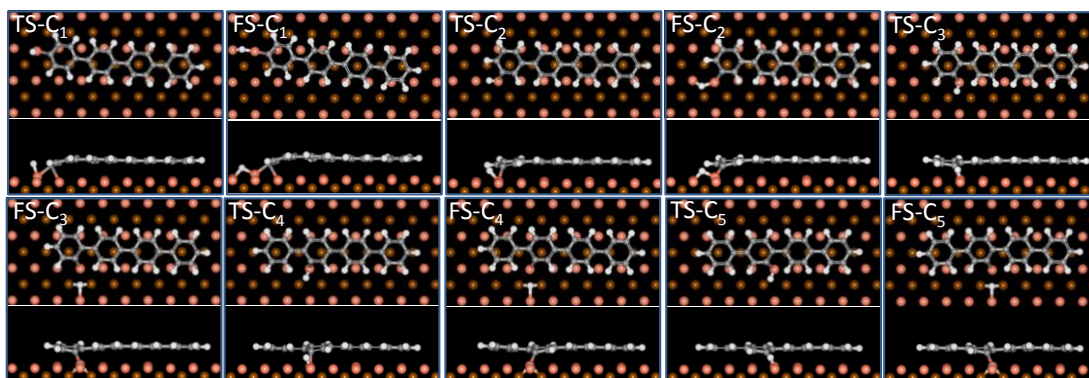


Fig. S4. The structural models of the transition states and final states of the five different C-H activation sites.

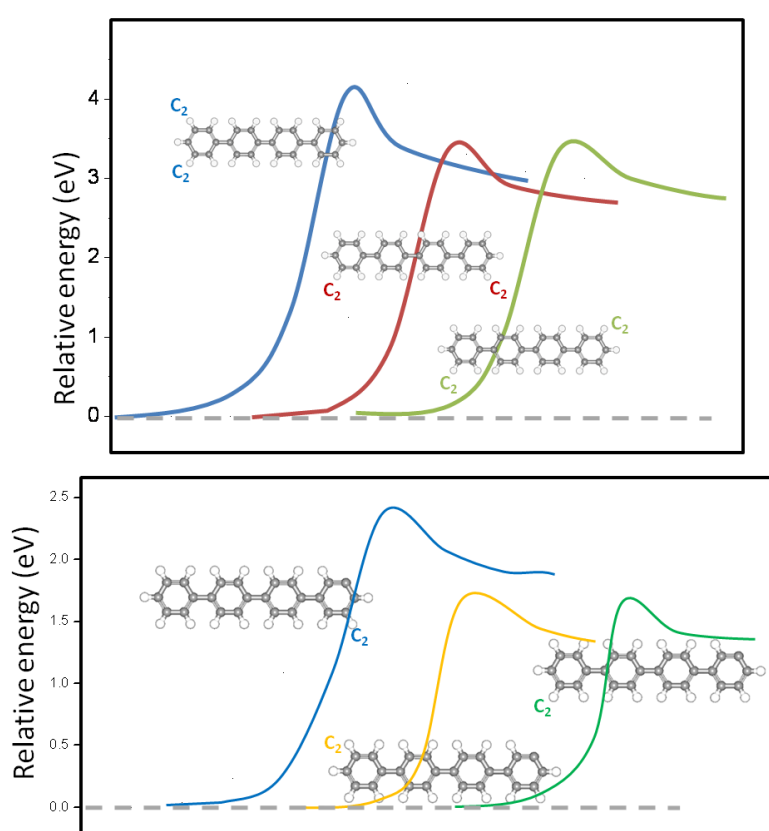


Fig. S5. Upper panel: DFT-calculated energy diagrams for simultaneously activating two identical C_2 sites of 4Ph monomer on Cu(110). Three schematic models showing the C-H activation sites are overlaid on the corresponding energy barrier curves, respectively. Lower panel: DFT-calculated energy diagrams for splitting-off one second hydrogen from an already dehydrogenated molecule at different C_2 sites.

References

1. Besenbacher, F. Scanning Tunnelling Microscopy Studies of Metal Surfaces. *Rep. Prog. Phys.* **1996**, *59*, 1737-1802.

2. Lægsgaard, E.; Osterlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A High-Pressure Scanning Tunneling Microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537-3542.
3. Kresse, G.; Hafner, J. *Ab Initio* Molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B* **1993**, *48*, 13115-13118.
4. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169-11186.
5. Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953-17979.
6. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758-1775.
7. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
8. Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787-1799.
9. Tersoff, J.; Hamann, D. R. Theory of the Scanning Tunneling Microscope. *Phys. Rev. B* **1985**, *31*, 805-813.
10. Henkelman, G.; Uberuaga, B. P.; Jonsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901-9904.