

**Formation of polyphenyl chains through hierarchical
reactions: Ullmann coupling followed by
cross-dehydrogenative coupling**
Supporting information

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Experimental and computational methods:

The STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature “Aarhus-type” STM using electrochemically etched W tips purchased from SPECS^{1,2}, a molecular evaporator and standard facilities for sample preparation. After the system was thoroughly degassed, the 4-bromobiphenyl molecules (purchased from TCI, purity >95%) were deposited by thermal sublimation (at 300 K with cooling water) onto the Cu(110) and Ag(110) substrates, respectively. The sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at ~ 150 K. All the calculations were carried out 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}. We employed the PBE-GGA as the exchange correlation functional⁷ and van der Waals interactions were included using the DFT-D2 method of Grimme⁸. We have chosen an energy cut-off value of 400 eV. We chose a $20 \times 40 \times 15$ extended supercell that had been checked to be big enough to avoid interactions between the molecules and a $2 \times 1 \times 2$ k-point grid determined by the Monkhorst-Pack method was used. The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were ≤ 0.03 eV/Å.

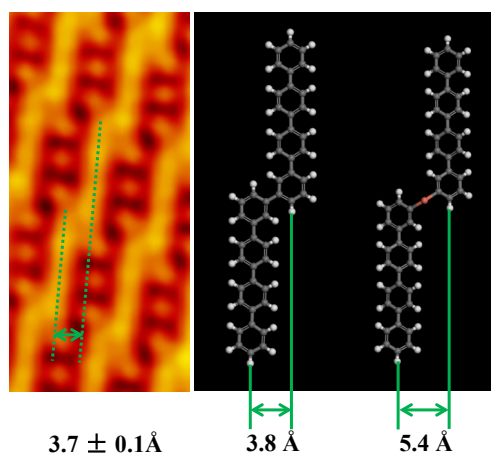


Figure S1. The comparison of the theoretical models of direct C-C coupling and C-Cu-C interlinking indicates a good agreement between the direct C-C coupling and the experimental lateral offset of the polyphenyl chain.

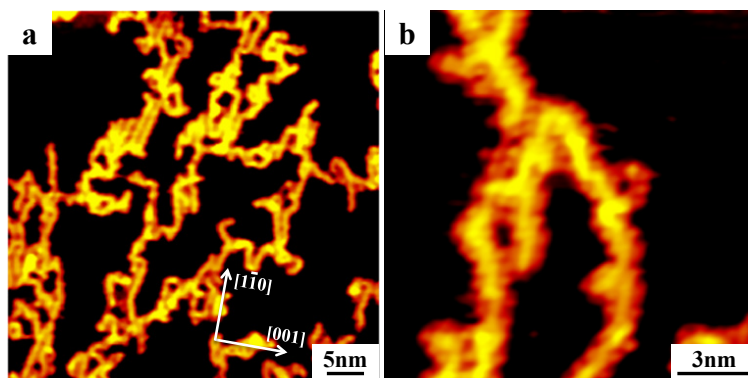


Figure S2. (a) The large-scale STM image and (b) the close-up STM image showing the formation of disordered chains after further annealing the Cu(110) sample to 525 K. Scanning conditions: $I_t = 0.90$ nA, $V_t = -1200$ mV.

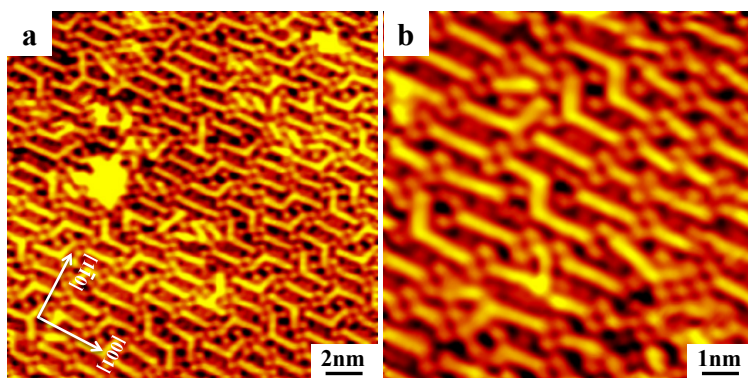


Figure S3. (a) The large-scale STM image and (b) the close-up STM image showing the formation of disordered short chains after further annealing the Ag(110) sample to the temperature window ranging from 500 K to 525 K. Scanning conditions: $I_t = 0.70$ nA, $V_t = -1200$ mV.

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