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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 functional[7] and van der Waals interactions were included using the DFT-D2 method of Grimme[8]. We have chosen an energy cut-off value of 400 eV. We chose a 20×40×15 extended supercell that had been checked to be big enough to avoid interactions between the molecules and a 2×1×2 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 $\leqslant$ 0.03 eV/Å.

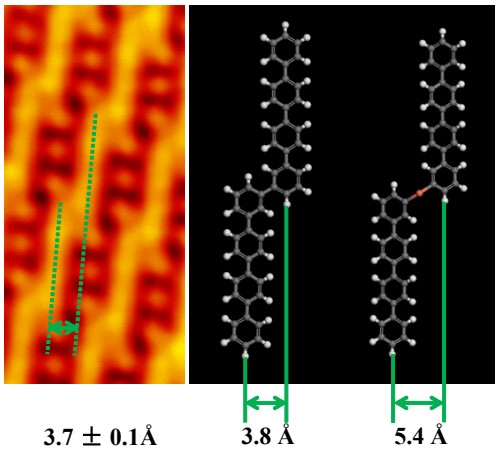

Figure S1. The comparison of the theoretical models of direct C-C coupling and C-Cu-C interlinking indicates a good agreement between the direct C-C coupling and the experimental lateral offset of the polyphenyl chain.

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.

References

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