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\textsuperscript{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)\textsuperscript{3,4}. The projector augmented wave method was used to describe the interaction between ions and electrons\textsuperscript{5,6}. We employed the PBE-GGA as the exchange correlation functional\textsuperscript{7} and van der Waals interactions were included using the DFT-D2 method of Grimme\textsuperscript{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 \( \leq 0.03 \) eV/Å.

![Figure S1](image1.png)

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