Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

On-surface synthesis of doubly-linked one-dimensional pentacene ladder polymers

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Experimental details

General wet synthesis methods

All chemicals were purchased from commercial suppliers and used as received. Toluene was dried according to standard procedures. NMR spectrum was recorded on a Bruker AV 400 MHz Wide Bore spectrometer at 298 K. FT-IR spectra was recorded on a Bruker Tensor 27 (ATR device) spectrometer. Mass spectrum Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiment (MALDI-TOF) was recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively.

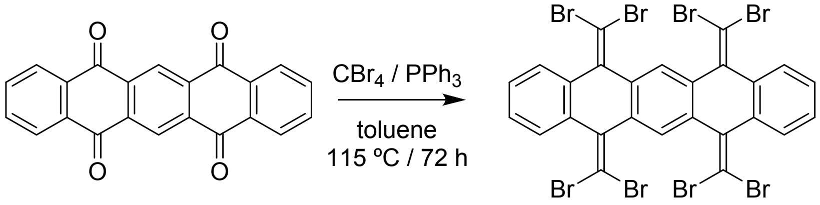
Surface science experimental methods and on-surface synthesis of doubly-linked one-dimensional pentacene ladder polymers

Experiments were performed in a custom-designed ultra-high vacuum system (base pressure below 4 x 10^{-10} mbar) hosting a commercial low-temperature microscope with STM/AFM capabilities from Scienta Omicron and located at IMDEA Nanoscience.

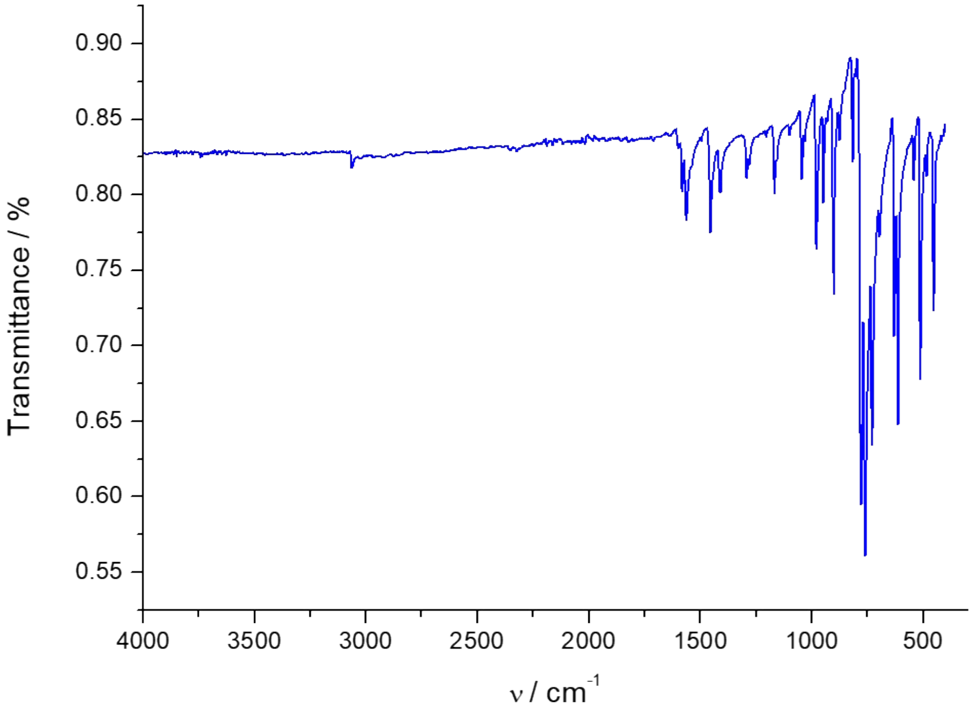
The Au(111) substrate was prepared by repeated cycles of Ar^+ sputtering (E = 1 keV, SPECS IQE 11/35) and subsequent annealing to 740 K for 10 minutes. All STM images shown were taken in constant current mode, unless otherwise noted, with electrochemically etched tungsten tips, at a sample temperature of 4.3 K (LakeShore). Scanning parameters are specified in each figure caption. Molecular precursor **8BrPN** was thermally deposited (Kentax TCE-BSC) onto the clean Au(111) surface held at room temperature with a typical deposition rate of 0.4 Å/min (sublimation temperature of 241 °C), controlled by a quartz micro balance (LewVac). After deposition of 8BrPN, the sample was post-annealed to 360 °C for 10 min to induce the debromination.

Non-contact AFM measurements were performed with a tungsten tip attached to a Qplus tuning fork sensor (Omicron).[1] The tip was a posteriori functionalized by a controlled adsorption of a single CO molecule at the tip apex from a previously CO-dosed surface.[2] The functionalized tip enables the imaging of the intramolecular structure of organic molecules.[3] The sensor was driven at its resonance frequency (26 kHz for Qplus) with a constant amplitude of ~60 pm. The shift in the resonance frequency of the sensor (with the attached CO-functionalized tip) was recorded in a constant-height mode (Omicron Matrix electronics and MFLi PLL by Zurich Instruments for Omicron). The STM and nc-AFM images were analyzed using WSxM.[4]

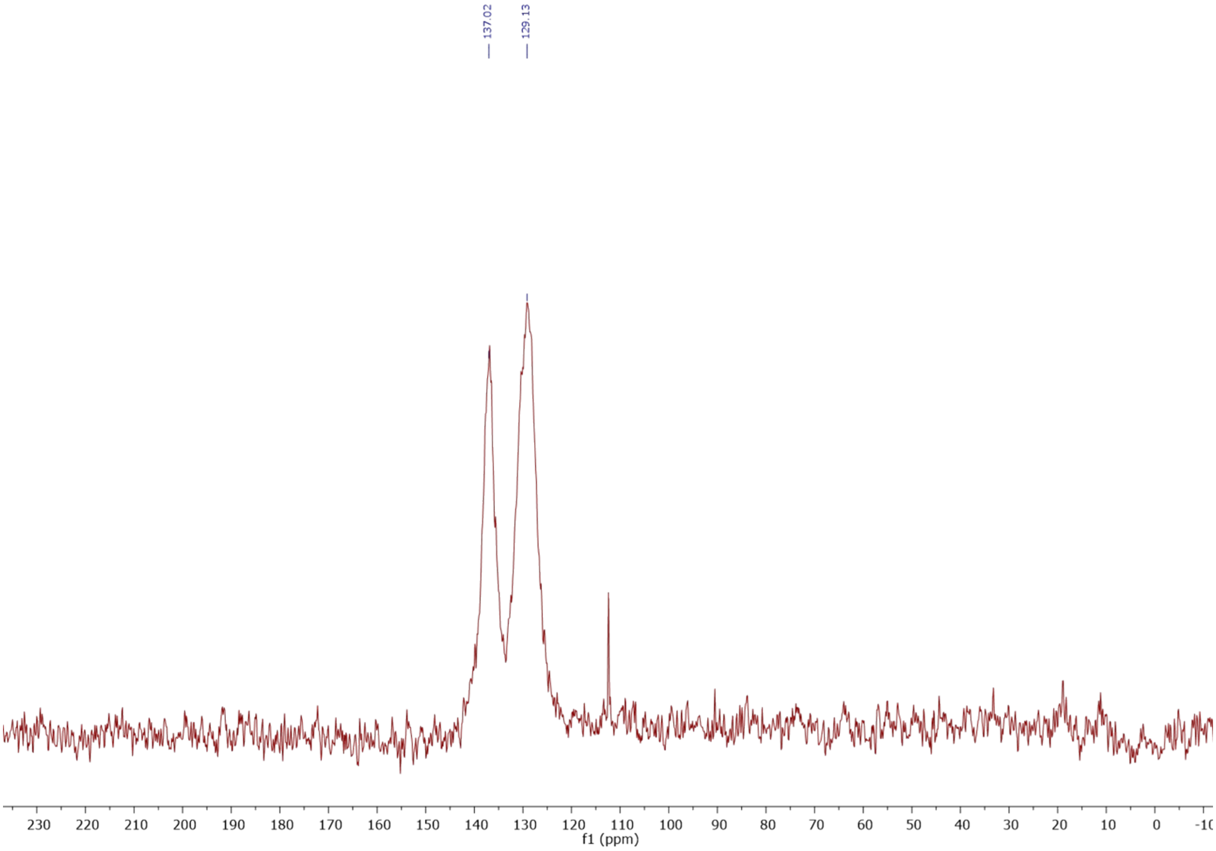
Synthesis of 8BrPN



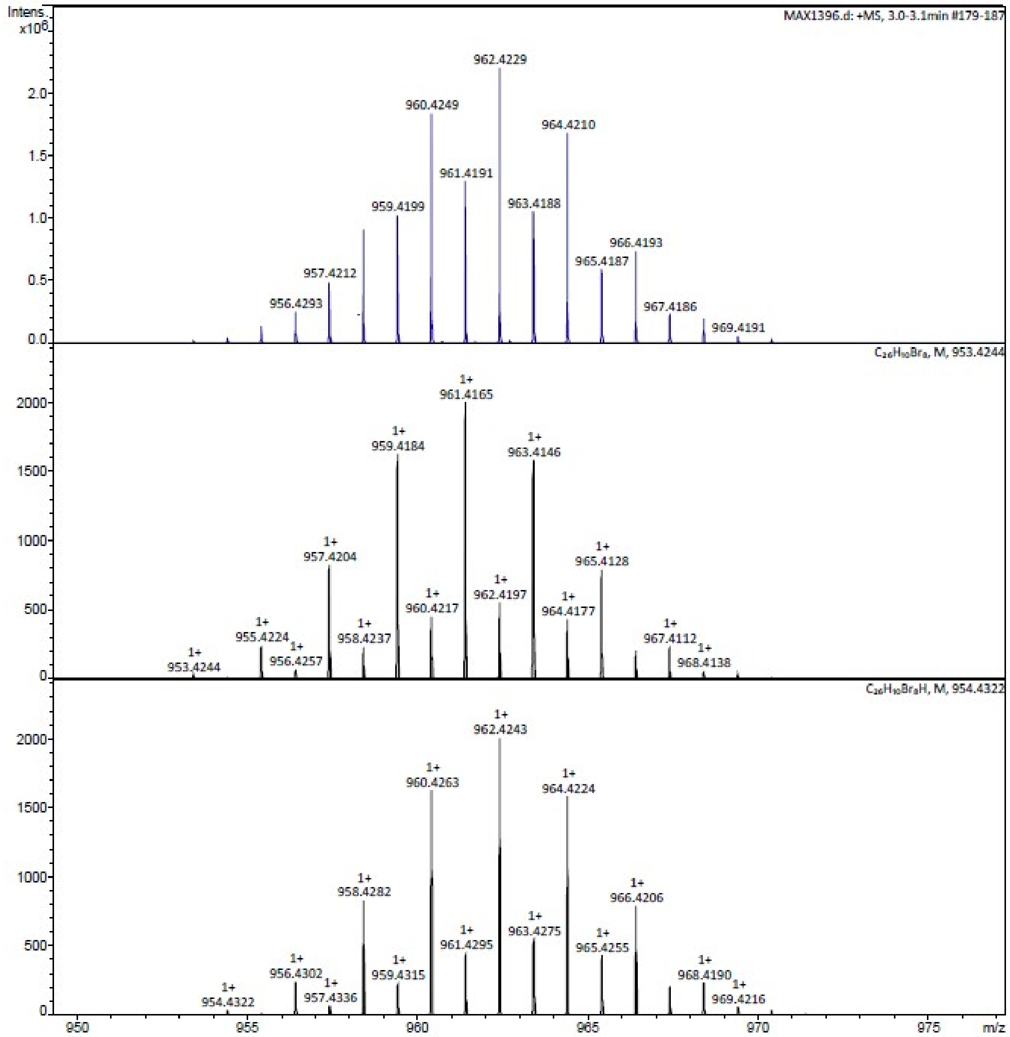
Into a two-neck round flask filled with argon, carbon tetrabromide (3.92 g, 11.823 mmol, 8 eq) and triphenylphosphine (6.20 g, 23,648 mmol, 16 eq) are dissolved in dry toluene (100 mL) at room temperature. After stirring for 30 min, pentacene-5,7,12,14-tetraone (500 mg, 1.478 mmol, 1 eq) is added in one portion and the resulting suspension is stirred at 115 °C for 72 h. Upon cooling to room temperature an off-white insoluble precipitate is isolated. Resulting solid is purified by suspending and sonicating it in methanol, after filtering it off the same washing procedure is followed with dichloromethane and hexane, yielding an off-white solid (481 mg, 0.500 mmol, 34%). The lack of solubility in common organic solvents prevents from running conventional solution NMR experiments, instead solid state ^{13}C-NMR and FTIR measurements are performed to confirm the absence of carbonyl signals from the starting tetraquinone. ^{13}C-NMR (101 MHz) *δ*: 137.0 (br), 129.1 (br) ppm. HRMS (MALDI-TOF): *m/z* calculated for $C_{26}H_{10}Br_8$: 962.4197, found: 962.4229.



FTIR (neat) spectrum of **8BrPN** evincing the absence of carbonyl groups.



Solid 13C-NMR spectrum of **8BrPN**.



HRMS (MALDI-TOF) spectrum of **8BrPN**.

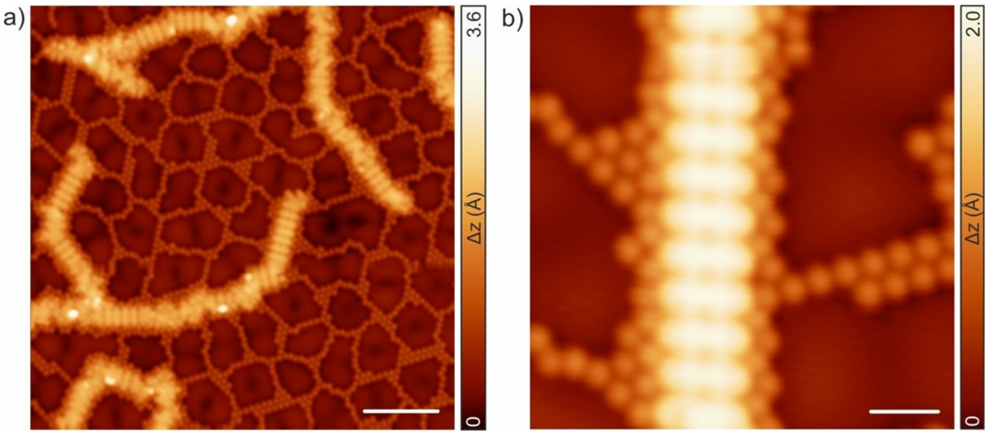


Figure S1. Initial reaction step of the formation of ethynylene linked polymer on Au (111) with coexistence of bromine atoms on the surface. a) Overview STM image showing the formation ethynylene-like connected pentacene ladder polymers on Au (111) after deposition of **8BrPN** molecules at room temperature and subsequent annealing at 493 K. Scanning parameters: V_b = 100 mV, I_t = 300 pA, scale bar = 5 nm. b) Magnified high-resolution STM images of the polymer chain on a selected area. Scanning parameters: V_b = 100 mV, I_t =300 pA, scale bar = 0.5 nm.

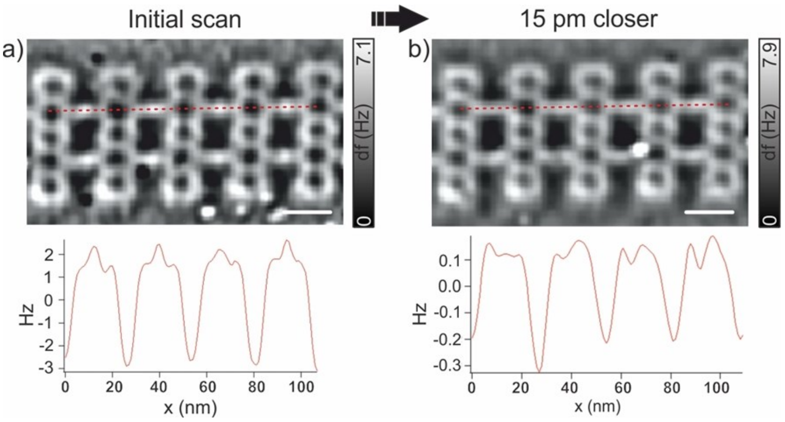


Figure S2. Close-up high resolution nc-AFM image with CO tip allowing the identification of ethynylene-like C-C bond. a) nc-AFM image on the polymer chain at an adequate distance between tip and sample, the triple bond can be identified as a bright protrusion. b) nc-AFM image of the polymer chain recorded on approaching the tip further closer to sample by an amount 15 pm, the bright protrusions disappear. A horizontal cut (marked as dotted line) along the lateral direction of bonds is made to represent the variation of consecutive bond configuration and to distinguish triple bond as shown in the bottom of each images. Scale bars of both the nc-AFM images (a,b) = 5 nm.

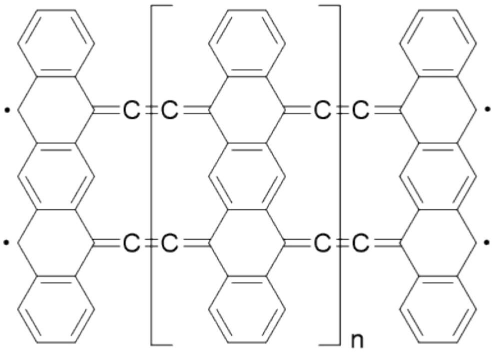


Figure S3. Alternative and not experimentally observed resonant form of doubly-linked pentacene polymers.

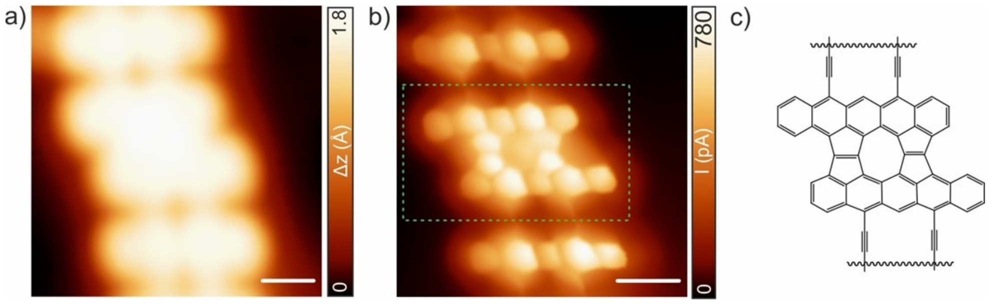


Figure S4. On-surface synthesis of pentalene-bridged 8BrPN polymers. a) High resolution STM topographic image of **8BrPN** precursor after being deposited on Au (111), annealed to 360 °C, produce an irregular defective polymers. Scanning parameters V_b=100 mV, I_t =300 pA, scale bar = 0.5 nm. b) Constant-height STM image with functionalized CO tip with open feedback loop. Open feedback parameters: V_b = 100 mV, I_t = 150 pA, scale bar = 0.5 nm. c) Schematic drawing of chemical structure pentalene-bridged **8BrPN** defective polymer.

Computational details

Total energy DFT and SPM calculations

Density functional theory (DFT) calculations were performed using the FHI-AIMS code[5] within hybrid exchange-correlation functional B3LYP.[6] In all the calculations, we employed the tight settings for the atomic basic sets. The atomic structures were thoroughly relaxed until the *Hellman*-Feynman forces were smaller than 10^{-3} eVÅ^{-1}. An infinite chain has been calculated using periodic boundary conditions and the atomic structure and the unit cell was optimized using 18 k-points. The band structure shown on Figure 2c was calculated using 50 k-points. We employed the PP-STM code[7] to simulate constant-height dI/dV maps, shown on Figure 2d and S8. CO-tip was represented by linear combination of s-like (15%) and p_x,p_y-like (85%) orbitals without tip relaxation at tip-sample distance 4.5 Å. High-resolution AFM image shown in Figure 1e was calculated using PP-AFM[8] with default Lennard-Jones parameters for both molecule and CO-tip. The parameters of the tip were chosen to mimic a CO-tip, using a quadrupole charge distribution[9] with a lateral stiffness of the CO molecule of 0.25 Nm^{-1} and a charge of -0.1 e. The electrostatic interaction was described in the AFM calculations using the potential calculated by DFT.

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