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Supplementary information

On-surface synthesis of polyazulene with 2,6-connectivity

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Methods

STM/STS/nc-AFM. A commercial low-temperature STM/nc-AFM (Scienta Omicron) system was used for sample preparation and *in situ* characterization under ultra-high vacuum conditions (base pressure below $1×10^{-10}$ mbar). The Au(111) single crystal was cleaned by argon sputtering ($p = 6 × 10^{-6}$ mbar) and annealing cycles to 750 K for 15 minutes. Deposition of the molecular precursors was done by thermal evaporation from a 6-fold organic evaporator (Mantis GmbH). STM images were recorded in constant-current mode, and the dI/dV spectra were recorded using the lock-in technique (U_{RMS} = 20 mV). nc-AFM images were recorded with a CO-functionalized tip attached to a quartz tuning fork sensor (resonance frequency 23.5 kHz, peak-to-peak oscillation amplitude below 100 pm).

Density functional theory calculations. DFT orbitals of the isolated azulene and the band structures were calculated with the Quantum Espresso software package using the PBE exchange correlation functional. A plane wave basis with an energy cutoff of 400 Ry for the charge density was used together with PAW pseudopotentials (SSSP[1]). For the band structure of the primitive (super) cell calculations a Monkhorst k-mesh of 40 x 1 x 1 (10 x 1 x 1) was used. The models of the gap-phase calculated polyazulenes were constructed in flat geometries. The cell and atomic geometries were relaxed until forces were smaller than $1\ e^{-4}$ a.u. To perform these calculations we used the AiiDA platform.[2]

The equilibrium geometry of the polyazulene polymer on the Au(111) substrate was obtained with the CP2K code.[3] The gold slab consisted of 4 atomic layers of Au along the [111] direction and a layer of hydrogen to suppress one of the two Au(111) surface states. 40 Å of vacuum were included in the cell to decouple the system from its periodic replicas in the direction perpendicular to the surface. We used the TZV2P Gaussian basis set[4] for C and H and the DZVP basis set for Au together with a cutoff of 600 Ry for the plane wave basis set. We used norm conserving Goedecker-Teter-Hutter[5] pseudopotentials, the PBE[6] parametrization for the exchange correlation functional and the Grimme's DFT-D3 dispersion corrections[7]. To obtain the equilibrium geometries we kept the atomic positions of the bottom two layers of the slab and hydrogen layer fixed to the ideal bulk positions, all other atoms were relaxed until forces were lower than 0.005 eV/Å.

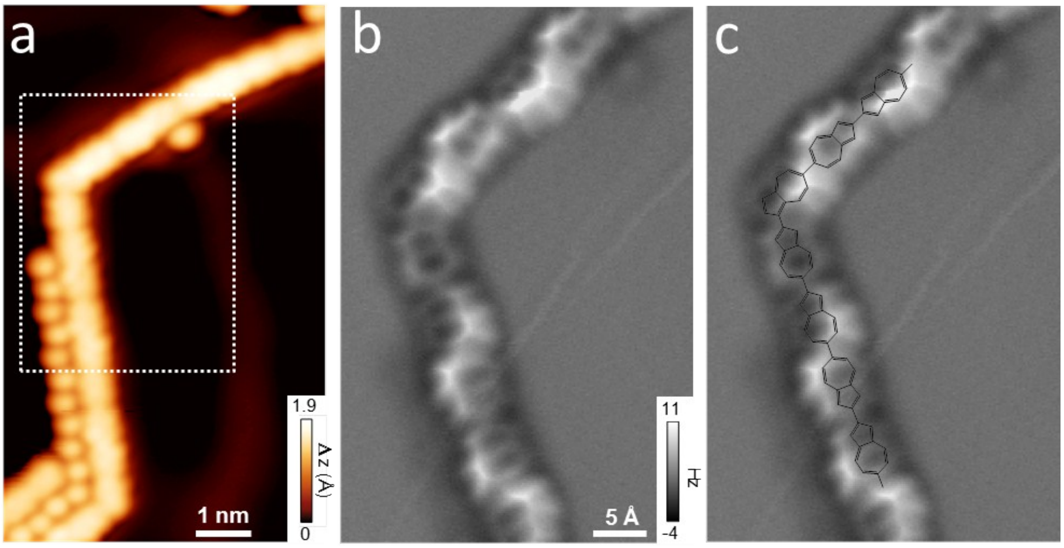

Figure S1. (a) STM image of a kinked polymer. (b) nc-AFM image of the area which is highlighted by a dashed rectangle in (a). (c) The same nc-AFM image as (b) with the chemical structure of the polymer overlaid, where we clearly see that the kink is due to a 1,6-connected azulenylene unit. The protrusions beside the polymer in the STM image are the detached iodine atoms, which are not seen in the nc-AFM image.

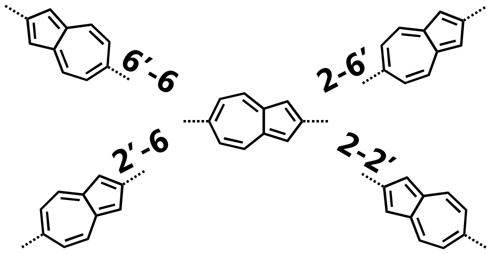

Figure S2. The possible linkages between the 2,6-azulenylene units in non-biased situations. If we take the middle azulenylene as the starting point, it can connect to a second azulenylene in four different ways, that is, 6',6, 2,6', 2',6, and 2,2', where 2,6' and 2',6 lead to the same connectivity (2,6-connectivity) in the polymer chain. Thus, a non-biased statistic ratio of 2,6 (p-h), 2,2 (p-p) and 6,6 (h-h) linkages in the polymer chain would be 2 : 1 : 1.

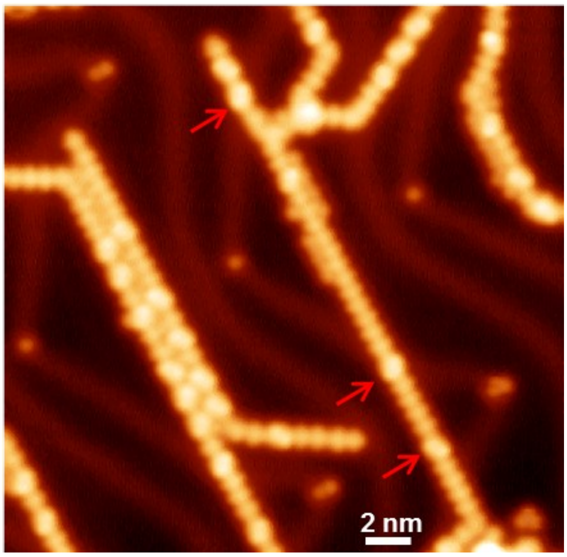

Figure S3. A typical STM image of polyazulene product on Au(111) at a bias voltage of 0.6 V. The h-h-linkage is clearly seen as a bump in the chains, three of them being indicated by red arrows.

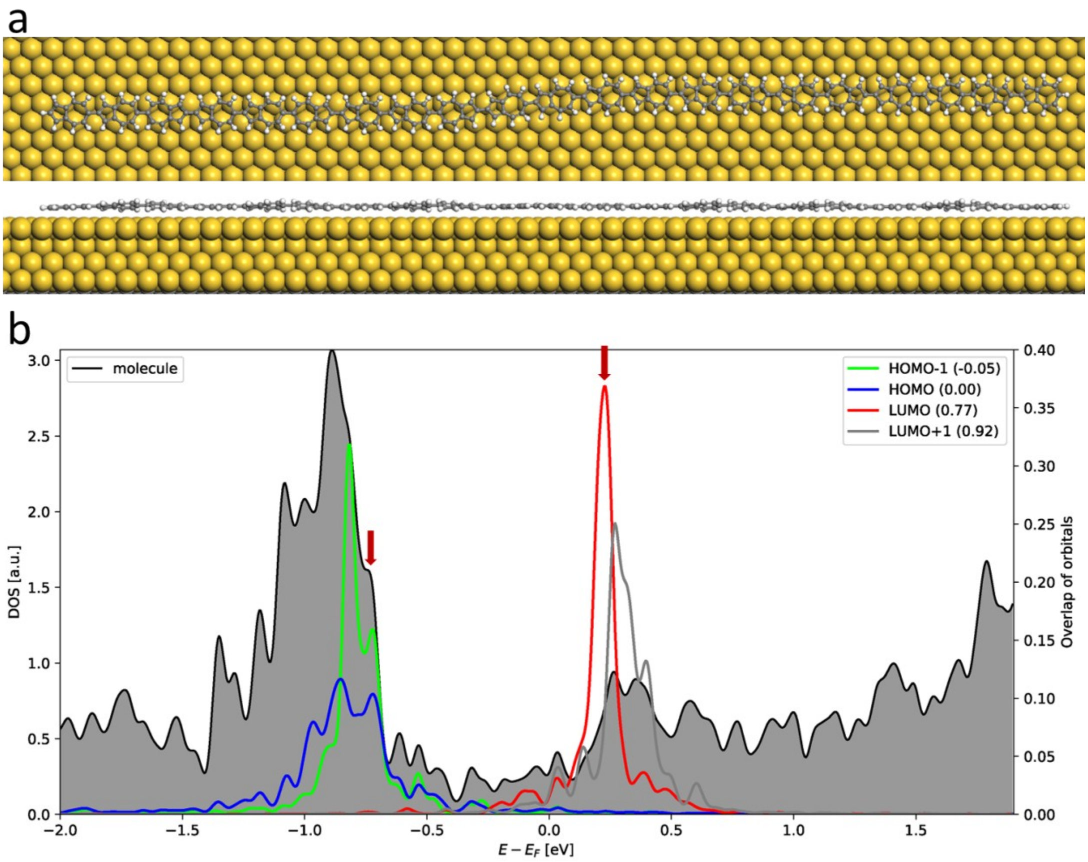

Figure S4. (a) Top and side views of a DFT optimized structure of a finite polyazulene chain on Au(111). (b) Gray filled area shows the DFT calculated density of states (DOS) of the polymer on the surface scaled by a factor of 0.1. Projections of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals from the gas-phase polymer onto the orbitals of the molecule/substrate system are shown in colored lines. The energy positions used for the LDOS map simulations are indicated by red arrows.

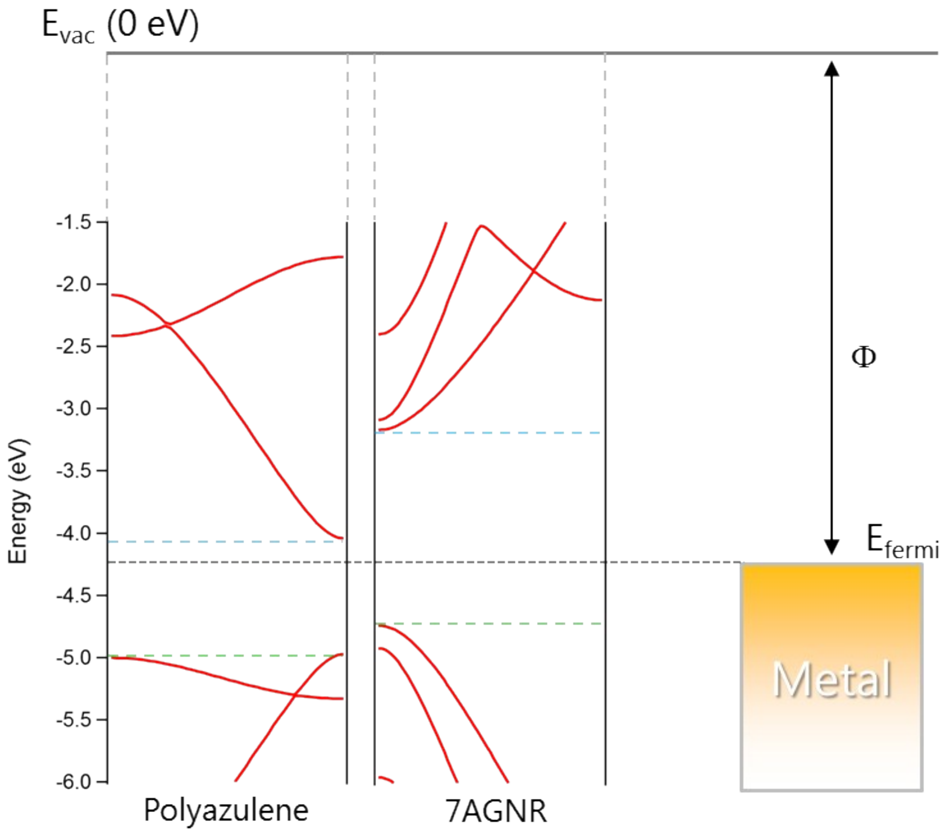

Figure S5. A schematic illustration of the energy level alignment of polyazulene, 7AGNR and the metal substrate. The band structures of polyazulene and 7AGNR are shown with energies taken with respect to the vacuum level. We use blue(green) dashed lines to indicate the onsets of their VB(CB). A metal surface is schematically shown on the right, whose Fermi level position is determined by the work function Φ and a arbitraty value is chosen here.

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