# On-surface synthesis of $\pi$ -conjugated ladder-type polymers

# comprising nonbenzenoid moieties

José I. Urgel,<sup>\*a,</sup> Julian Bock,<sup>b,c</sup> Marco Di Giovannantonio,<sup>a, $\phi$ </sup> Pascal Ruffieux,<sup>a</sup> Carlo A. Pignedoli,<sup>a</sup> Milan Kivala<sup>\*b,c</sup> and Roman Fasel<sup>\*a,d</sup>

## **Supporting Information**

## **1** General and materials

#### **1.1** General procedures, materials and instruments

#### **General procedures**

All reactions including oxygen or moisture sensitive substances were conducted under N<sub>2</sub> atmosphere, using anhydrous solvents and standard Schlenk techniques. All sensitive compounds were transferred via syringes. Reaction controls were done with silica gel TLC. All procedures in this section were inspired by the work of *Plunkett* and his coworkers.<sup>1</sup>

### Reagents

The reagents were purchased at reagent grade from commercial suppliers (*Fisher Scientific, SIGMA-ALDRICH* and *abcr*) and were used without further purification. Toluene and THF were used from a Braun solvent drying system. For aqueous workup MgSO<sub>4</sub> was used as a drying agent.

#### Instrumentals

NMR spectra data were measured on the Bruker Avance III 300 and the Bruker Avance III 600. Chemical shifts ( $\delta$ ) are reported in ppm and were referenced to the residual solvent signal as an internal reference (CDCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H, 77.0 for <sup>13</sup>C). Melting points were measured on a Buchi M-560. Mass measurements were all conducted with a Bruker ApexQe hybrid 9.4 T FT-ICR.

#### **1.2** Synthetic protocols

#### 2,7-Bis(trimethylsilyl)cyclopenta[*hi*]aceanthrylene (S1)<sup>1</sup>



9,10-Dibromoanthracene (4.02 g, 12.0 mmol) was dissolved in dry and degassed toluene (20 mL) and triethylamine (12mL, 8.76 g, 86.6 mmol) was added under N<sub>2</sub> atmosphere. Triphenylphosphine (741 mg, 2.83 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>)Cl<sub>2</sub>] (423 mg, 603 µmol) were added. The mixture was heated to 110 °C under reflux before trimethylsilylacetylene (7 mL, 4.83 g, 49.2 mmol) was added dropwise over 10 min. Additionally toluene (5 mL) was added to the reaction mixture. After stirring overnight the brown mixture was filtered and washed with petroleum ether (PE). The filtrate was concentrated under reduced pressure and passed through a plug (SiO<sub>2</sub>, PE). The solvent was removed and the residual was crystalized from ethanol. Compound **S1** was isolated as dark needles (1.22 g, 3.28 mmol, 27%).

Mp: 247–249°C.

R<sub>f</sub>: 0.34 (SiO<sub>2</sub>, PE) <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 6.5 Hz, 2H), 7.74 (s, 2H), 7.68–7.63 (m, 2H), 0.46 (s, 18H) ppm. MALDI-MS: m/z 370.1571

#### 2,7-Dibromocyclopenta[hi]aceanthrylene (1)<sup>1</sup>



2,7-Bis(trimethylsilyl)cyclopenta[*hi*]aceanthrylene (**S1**) (1.06 g, 2.86 mmol) was dissolved in dry THF (100 mL) and cooled to 0°C. NBS (1.09 g, 6.10mmol) was added to the mixture and stirred for 20 min before being allowed to reach RT. After 2.5 h TLC analysis showed the reaction was still incomplete and further NBS (61.4 mg, 345  $\mu$ mol) was added. After 1 h the solvent was removed under reduced pressure and the residue dispersed in ethanol (100 mL) and heated to 100 °C and filtered while still hot. The crude product was recrystallized from chloroform to yield the title compound **1** as green powder (1.03 g, 2.73 mmol, 95%).

Mp: >400°C

R<sub>f</sub>: 0.73 (SiO<sub>2</sub>, PE/DCM 20:1)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 6.7 Hz, 2H), 7.74–to 7.70 (m, 2H), 7.58 (s, 2H) ppm.

<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>): δ139.5, 136.4, 129.5, 127.6, 127.2, 127.0, 126.1, 123.5, 119.5 ppm.

MALDI-MS: 381.8991 m/z

### 2 **Experimental details**

#### 2.1 On-surface experimental methods and on-surface synthesis of 2 and 3

Experiments were performed under ultrahigh vacuum conditions (base pressure below 5 x  $10^{-10}$  mbar) with a commercial low-temperature STM/AFM from Scienta Omicron.

The Au(111) substrate was prepared by repeated cycles of Ar<sup>+</sup> sputtering (E = 1 keV) and subsequent annealing to 750 K for 15 minutes. All STM images shown were taken acquired in constant current mode, unless otherwise noted, with electrochemically etched tungsten tips at a sample temperature of 4.8 K. Scanning parameters are specified in each figure caption. Monomer **1** was thermally deposited onto the clean Au(111) surface held at room temperature with a typical deposition rate of 0.6 Åmin<sup>-1</sup> (sublimation temperatures of 110 °C). After deposition of **1**, the sample was post-annealed to 330 °C to induce the polymerization (**2**) and to 420 °C to afford cyclodehydrogenation and the subsequent formation of nonbenzenoid CLPs (**3**).

For the UHR-STM images, the tip was functionalized by the controlled adsorption of a single CO molecule at the tip apex from the previously CO-dosed surface.<sup>2</sup> The functionalized tip enables the imaging of the intramolecular structure of organic molecules.<sup>3</sup> The STM images were analyzed using WSxM.<sup>4</sup>



**Scheme S1.** On-surface synthesis of nonbenzenoid CLPs. The reaction pathway between s-trans and s-cis isomers is depicted.



**Figure S1.** Electronic structure of **2** adsorbed on Au(111). a) High-resolution STM image of **2** consisting of eight cyclopenta[*hi*]aceanthrylene constitutional units. The positions at which the d//dV spectra shown in panel b were acquired are highlighted with blue and pink markers in panel a.  $V_b = -0.3$  V,  $I_t = 200$  pA. Scale bar: 0.5 nm. b) Constant-height differential conductance spectrum of **2**; the blue curve acquired at the polymer shows two resonance peaks assigned to the valence band maximum (VBM) and the conduction band minimum (CBM) of **2**. The onsets of both bands reveal an electronic bandgap of ~1.85 eV. The pink curve is a spectrum taken on the bare Au(111) surface, as indicated by the pink dot in the constant-current STM image. c,d) Constant-current d//dV maps at the VB and CB peak maxima, respectively. c)  $V_b = -0.7$  V,  $I_t = 200$  pA; d)  $V_b = 1.2$  V,  $I_t = 200$  pA. Scale bars: 0.5 nm.



**Figure S2.** HR-STM and UHR-STM images of **2** after annealing at 400° C on Au(111). a,b) Long-range and high-resolution STM images of **2** after annealing of the sample at 400 °C. Relatively long polymeric chains coexisting with several fused and already cyclodehydrogenated segments are observed. The blue-dashed rectangle indicates the region shown in c. a)  $V_b = 0.02$  V,  $I_t = 80$  pA. Scale bar: 10 nm. b)  $V_b = -0.5$  V,  $I_t = 50$  pA. Scale bar: 2 nm. c) CO-functionalized UHR-STM image of **2** where the intramolecular features of the nonbenzenoid molecular backbone in the polymers are discerned.  $V_b = 5$  mV,  $I_t = 100$  pA, scale bar: 1 nm.



**Figure S3.** Constant-current and constant-height dI/dV maps of **3**. a,b) Constant-height dI/dV maps at the VB and CB peak maxima, respectively. c,d) Constant-current dI/dV maps evaluated at the same energy positions as for panels a and b. e,f) DFT-calculated LDOS maps at VB and CB peak maxima, calculated at a height of 3.3 Å above the molecular plane. a-d) All images were acquire with a CO-functionalized tip. Tunneling parameters for the constant-current dI/dV maps: (a), (b)  $V_b = -1.1$  V,  $I_t = 300$  pA; (e), (f)  $V_b = 0.7$  V,  $I_t = 550$  pA. c,d) Open feedback parameters for the constant-height dI/dV maps: c)  $V_b = -1.1$  V,  $I_t = 300$  pA; d)  $V_b = 0.7$  V,  $I_t = 300$  pA. All Scale bars: 0.5 nm.



**Figure S4.** Electronic structure of a **3b** segment adsorbed on Au(111). a) STM image of **3b** consisting of a kinked segment where two five-membered rings are formed. The positions at which the d//dV spectra shown in panel b were acquired are highlighted with blue and pink markers in panel a.  $V_b = -0.1 \text{ V}$ ,  $I_t = 150 \text{ pA}$ . Scale bar: 0.5 nm. b) Constant-height differential conductance spectrum of **3b**; the blue curve acquired at **3b** shows two resonance peaks assigned to the valence band maximum (VBM) and the conduction band minimum (CBM). The onsets of both bands reveal an electronic bandgap of ~1.45 eV. The pink curve is a spectrum taken on the bare Au(111) surface, as indicated by the pink dot in the constant-current STM image. c,d) Constant-current d//dV maps at the VB and CB peak maxima, respectively. c)  $V_b = -1.1 \text{ V}$ ,  $I_t = 300 \text{ pA}$ ; d)  $V_b = 0.5 \text{ V}$ ,  $I_t = 300 \text{ pA}$ . Scale bars: 0.5 nm.

### 3 Computational details

To obtain the equilibrium geometries of the molecules adsorbed on the Au(111) substrate we used the CP2K code<sup>5,6</sup> implementing DFT within a mixed Gaussian plane waves approach.<sup>7</sup> The surface/adsorbate systems where modeled within the repeated slab scheme,<sup>8</sup> i.e., a simulation cell containing 4 atomic layers of Au along the [111] direction and a layer of hydrogen atoms to passivate one side of the slab in order so suppress one of the two Au(111) surface states. 40 Å of vacuum were included in the simulation cell to decouple the system from its periodic replicas in the direction perpendicular to the surface. The electronic states were expanded with a TZV2P Gaussian basis set<sup>9</sup> for C and H species and a DZVP basis set for Au species. A cutoff of 600 Ry was used for the plane wave basis set. Norm Conserving Goedecker-TeterHutter<sup>10</sup> pseudopotentials were used to represent the frozen core electrons of the atoms. We used the PBE parameterization for the general gradient approximation of the exchange correlation functional.<sup>11</sup> To account for van der Waals interactions we used the scheme proposed by Grimme.<sup>12</sup> We considered supercells of 41.27 x 40.85 Å corresponding to 224 surface units. To obtain the equilibrium geometries we kept the atomic positions of the bottom two layers of the slab fixed to the ideal bulk positions, all other atoms were relaxed until forces were lower than 0.005 eV/Å.

### 4 References

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