SUPPORTING INFORMATION

Molecules-Oligomers-Nanowires-Graphene Nanoribbons: A Bottom-Up Stepwise On-Surface Covalent Synthesis Preserving Long Range Order

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Figure S1: Low energy electron diffraction (LEED) patterns of the self-assembled structure acquired from (a) as-deposited DBTP molecules and (b-c) after annealing at different temperatures, as indicated for each figure. The simulated patterns are partially superimposed to experimental images and the corresponding matrix notation is written below.



Figure S2: Simulated STM images of DBTP, left panel, and of the debrominated bi-radical species attached to Au adatoms, central panel, on Au(111) at ± 0.8 V with respect to the Fermi level. Side views of space filling models are shown in the bottom part of each panel. The color code is gray for carbon, white for hydrogen, brown for bromine, magenta for surface gold atoms and cyan for gold adatoms. In the right panel: STM experimental image acquired at 0.8 V. The line profile shows that the molecule bears a bright feature at each apex.

To confirm the nature of DBTP molecules after annealing at 320 K, we have simulated the STM images of the [4 2, 2 6] structure by assuming three different molecular networks on Au(111): debrominated DBTP molecules directly bonded to the substrate, intact DBTP adsorbed on the substrate and debrominated DBTP bonded to Au adatoms (one Au replacing each Br).

The equilibrium geometry for debrominated DBTP molecules on Au(111) reveals that the molecules considerably bend to form metal organic bonds and the surface Au atoms bonded to the molecules pop out from the surface plane. The resulting considerable distortion of the molecules allows us to exclude this geometry.

Also debrominated DBTP attached to Au adatoms have a geometry that appear more bent compared to the experimental STM image. In particular the brighter part of the STM image in the simulation appears at the center (and the extremes of the molecules are less bright), contrary to the experimental evidence. The best matching is obtained for the DBTP intact molecules where also the ends appear bright.



Figure S3: (a) STM image of an overlayer obtained after short annealing at 360 K and (b) after annealing at 520 K. The line profiles report the length of monomers (1), dimers (2) and trimers (3), whereas the line profile (4) reports the length of 6 consecutive phenyl rings.

In the case of DBTP molecules deposited on Cu(111) and Ag(111)¹ the formation of organometallic wires is reported: in these cases regular bumps, assigned to metal atoms, are visible along the wires and the distance between two bumps is an integer multiple of the length of a single DBTP molecule. As far as DBTP on Au(111) is concerned, the comparison of the single molecule length with the length of different oligomers indicates that the latter are slightly shorter than an integer multiple of the former. For example, a dimer is 0.28 ± 0.04 nm shorter than two monomers and the trimer 0.64 ± 0.04 nm shorter than three monomers. These evidences are compatible with the formation of *p*-phenylene oligomers and incompatible with the formation of metal-organic wires.² Moreover, in high resolution STM images of PPP wires, the individual phenyl rings can be distinguished and the periodicity of 0.45 ± 0.02 nm measured along the wires is in excellent agreement with the gas-phase calculated value of 0.433 nm between adjacent rings in poly(*p*-phenylene) (PPP)³ or measured in crystalline para-septiphenyl.⁴



Figure S4: Statistical analysis of the oligomer size distribution as a function of the final annealing temperature. $N_{\overline{X}}$ corresponds to the number of molecules with lengths \overline{X} times that of DBTP and the probability for each oligomer is normalized with respect to the total number of counted molecules $(\sum N_{\overline{X}})$.

We have investigated whether a further conversion of the dimers to tetramers and other longer oligomers can be promoted by a slightly higher annealing temperature. Our idea is based on the different mobility of the oligomers: indeed a gradual increase of the temperature should selectively promote the diffusion of molecules with smallest size. Statistical analysis of the size dispersion of the molecules as a function of temperature (Figure S4) shows that the control of the oligomers polydispersion is viable by fine-tuning the time and the temperature of the annealing step. Indeed, at about 360 K *ter*-phenyl radicals form mainly dimeric and trimeric species, as expected for single unit diffusion along the $[11\overline{2}]$ direction, while at 390 K unreacted monomers are not found any more on the surface and oligomers longer than trimers start to become prevalent.



Figure S5: Raman spectra measured with a 50x objective at 532 nm of PPP wires organized in the [4 2, 0 3] superstructure (blue line), GNRs obtained after a thermal treatment of the PPP wires at 650 K (black line) and 800 K (green line). The Raman shift of the major peaks is also reported.

Raman spectroscopy is a powerful tool to characterize carbonaceous materials and in particular it has been widely applied to characterize graphene-based materials, ranging from the determination of the number of graphene layers in a sample, through the doping level and the chemical functionalization, to the distance between zero-dimensional point-like defects.^{5,6} Here we have used Raman spectroscopy to characterize the main steps of the synthesis.

In the literature, the Raman spectrum of oligophenyl crystals is mainly characterized by three intense peaks between 1200 and 1700 cm⁻¹, associated with the C-H in-plane bending mode (1220 cm⁻¹), the inter-ring C-C stretching mode (1280 cm⁻¹) and the ring C-C stretching mode (1600 cm⁻¹).⁷ It has been observed that the Raman intensity ratio of the inter-ring C-C stretching and the C-H in plane bending modes (I_{1280}/I_{1220}) is a good indication for the planarity of the oligomers. In particular, the I_{1280}/I_{1220} ratio decreases from 0.8 to 0.3 between 0 and 15 kbar, beyond which the ratio remains almost constant. Since lower I_{1280}/I_{1220} corresponds to higher planarity, it has been concluded that at 15 kbar all the molecules are completely planarized.^{8,9}

The spectrum acquired on PPP wires arranged in the [4 2,0 3] superstructure (blue line) is dominated by the expected three peaks: 1218, 1275 and 1583 cm⁻¹. The experimental value of $I_{1280}/I_{1220}=0.29$ suggests a planar conformation of the PPP wires, in agreement with the uniform height profile observed by STM. In this case, the necessary conformational adaptation due to the adsorbate–substrate interactions is the driving force for the planarization of the molecules.

The Raman spectrum acquired after thermal treatments at 650 K shows a larger number of peaks, as reported in Figure S5 (black line). In particular, new modes appear at 1245 and 1315 cm⁻¹, while the most intense transition is at 1590 cm⁻¹ with a shoulder at 1612 cm⁻¹. All these transitions are in good agreement with what is usually observed for the bottom-up fabrication of graphene nanoribbons (N=7) from 10,10'-dibromo-9,9'-bianthryl.¹⁰ In particular, the modes at 1325 and 1612 cm⁻¹ are related to the disorder-induced D and D' bands, while the peak at 1590 cm⁻¹ is due to C-C stretching in graphitic materials (the G-band).^{11–13} Moreover, additional signals are clearly resolved at higher Raman shift values and are related to the two-phonon band G' (2D) at 2630 cm⁻¹, the D+D' band at 2915 cm⁻¹ and the 2G band at 3177 cm⁻¹. Together with the G band, the presence of the G' band is an unambiguous Raman signature of graphitic sp² materials.¹¹ The second-order region shows additional bands at 2490 and 2890 cm⁻¹ attributed to overtone scattering of the 1245 cm⁻¹ mode and tentatively to the C-H stretching of partially hydrogenated amorphous carbon, respectively.^{14,15}

After the annealing treatment at 800 K (green line in Figure S5), we observe an increase of the intensity of the D band, while the G', the D+D' and the 2G bands are still discernible, in agreement with the highly defective graphene layer observed by STM.^{6,11}

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