Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Synthesis of corrugated C-based nanostructures by Br-corannulene oligomerization.

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1. Additional experimental and computational details.

Synthesis of Br-corannulene

Br-corannulene was synthesized following a reported procedure(1). Corranulene (Tokyo chemical industries co., ltd.), dichloromethane dry (Acros organics), iron(III) bromide (Fluorochem ltd.) were used as received. Corannulene (30 mg, 0.12 mmol) and ferric bromide (2 mg, 0.012 mmol) were dissolved in dichloromethane (50 mL, dry, deareated) under nitrogen atmosphere. Bromine (21 mg, 0.13 mmol) was slowly added to the solution at -80 °C. When the addition was complete, the reaction mixture was slowly allowed to warm to room temperature over 4 h and quenched with a saturated solution of sodium bisulfite. The organic layer was washed 3 times with water, dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure. The residue was purified by passage through a pad of silica gel with benzene as the eluent to afford Br-corannulene as pale yellow solid (36 mg, 90%). This product, containing a limited quantity of polyhalogenated by-products, was used without further purifications. As already mentioned in the manuscript, the physical and spectroscopic data corresponded to those reported in the literature: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.93 (d, $J = 8$ Hz, 1H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.76-7.79 (m, 5H), 7.70 (d, $J = 8.8$ Hz, 1H).

Scanning Tunnelling Microscopy experiments

Microscopy experiments were carried out at the IMEM-CNR laboratory in Genoa. The apparatus consists of a main UHV chamber, hosting a low-temperature STM (Createc manufacturer), and of a preparation chamber equipped with a homemade evaporator for deposition of organic molecules and with all typical vacuum facilities for sample cleaning and residual gas analysis. STM images were recorded at liquid helium temperature, using a Pt/Ir tip. The tip is a 0.2 mm wire cut in air under strain and then reshaped by controlled crashes into the surface, so that tunneling occurs effectively through an Ag tip. The procedures for image acquisition, calibration and analysis are detailed in the manuscript.

Spectroscopic experiments

High-resolution synchrotron-excited XPS and NEXAFS data were recorded at the BACH beamline of the Elettra synchrotron (Trieste, Italy), in an UHV chamber with the base pressure lower than 1×10^{-9} mbar, by means of a hemispherical electron energy analyser (VG Scienta model R3000).
Br 3d and C 1s photoemission spectra were analysed after subtracting a Shirley type background and referencing all binding energies (E_b) to the Fermi level of the Ag substrate.
The NEXAFS spectra were normalized to the signal from the clean Ag(110) substrate and subsequently to the pre- and post-edge intensity. Polarization-dependent measurements were performed with linearly polarized x-rays varying the beam incidence angle.

DFT calculations

The adsorption of Br-CRN on a Ag(110) surface was modelled by using the Van der Waals density functional vdW-DF2^{C09x}, which gives an accurate description of the adsorption energies and distances of graphene on metal surfaces(2) and has also been successfully applied to describe self-assembly of brominated tetracene (DBT) on different metal surfaces(3–5). Preliminary calculations were performed for hyrogenated and brominated CRN monomer using a 3x4 Ag(110) supercell, while for the calculations of dimers in different configurations the cell is resembling that found in the experimental set-up, with a distance between dimer of 21.9 Å along the dimers row and a distance of

10.0 Å between dimers rows. The angle between the dimers row and the 110 direction is 22°. For the simulation of the trimer the cell has been doubled along the shortest direction. The Ag surface is modeled using a five-layer slab where the top three layers are allowed to fully relax together with the adsorbed molecules, while the bottom two layers are fixed at the Ag optimized lattice (4.10 Å). The Perdew-Burke-Ernzerhof (PBE) standard ultrasoft pseudopotentials, as implemented in the plane-wave based Quantum Espresso package,(6) were used with energy cutoff of 30 and 240 Ryd (for kinetic-energy and charge-density grids, respectively). The calculations were performed with a 2×2×1 sampling of the Brillouin zone for the monomers, while a 2×1×1 grid was used for the dimer and only the Gamma point for the trimer. The STM image simulations were obtained within the Tersoff–Hamann approximation,(7) in which the tunneling current is considered to be proportional to the integrated local density of the states in a given energy window, determined by the bias voltage, as applied in the corresponding experiments.

2. Additional STM results.

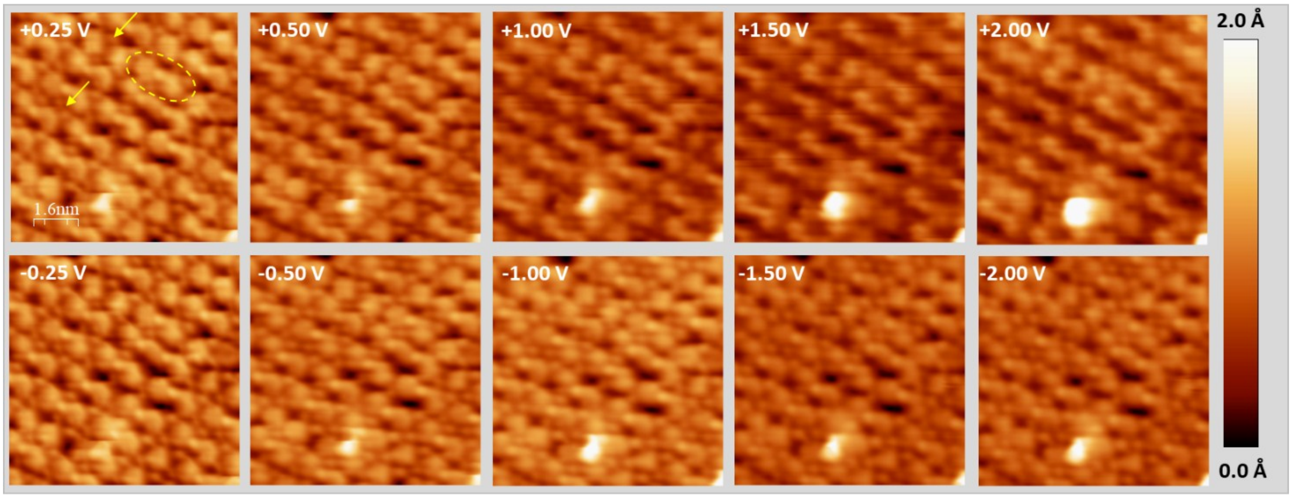

Figure S1. Sequence ofSTM images showing an enlargement of the Br-CRN island reported in Figure 1 of the manuscript and recorded at different bias voltage (image size: 8.0 x 8.0 nm^2, I=0.26 nA). For an easier comparison, the same Z-scale (reported on the right) is used for all images after global plane subtraction. The different bias dependence of the Br adatoms (small protrusions as those marked by the arrows) with respect to the CRN-Ag-CRN dimers (see, e.g., the one in the dashed oval) is evidenced by their different relative contrast. In particular, Br adatoms are poorly visible for V≥1.00V.

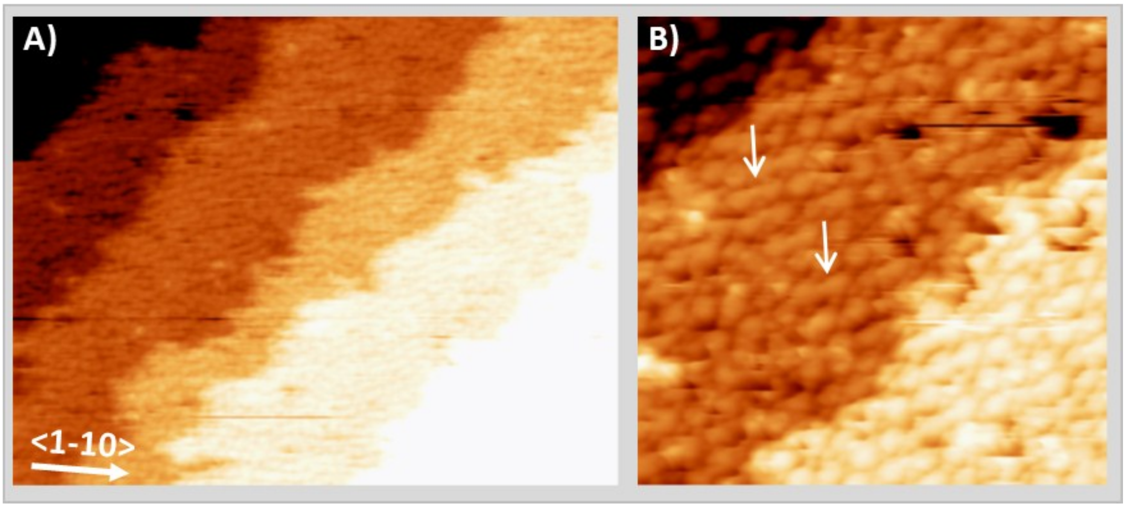

Figure S2.A) STM image of the Ag(110) surface after deposition of a full monolayer of Br-CRN molecules at room temperature. Image size: 55x43 nm^2, V=0.15 V, I=0.11 nA. B) Enlarged image of the same preparation as in A). Image size: 15x15 nm^2, V=0.15 V, I=0.11 nA.

It is evident that after 30 minutes of exposure the surface is fully covered by the adsorbate. The Br-CRN units tend to arrange in dimeric structures as those evidenced by the arrows in panel B, which are very similar to those described in the manuscript for the sub-monolayer coverage preparation. However, the high density of molecules on the surface reduces the mobility and therefore inhibits the formation of ordered islands of CNR dimers, so that long range order cannot be achieved.

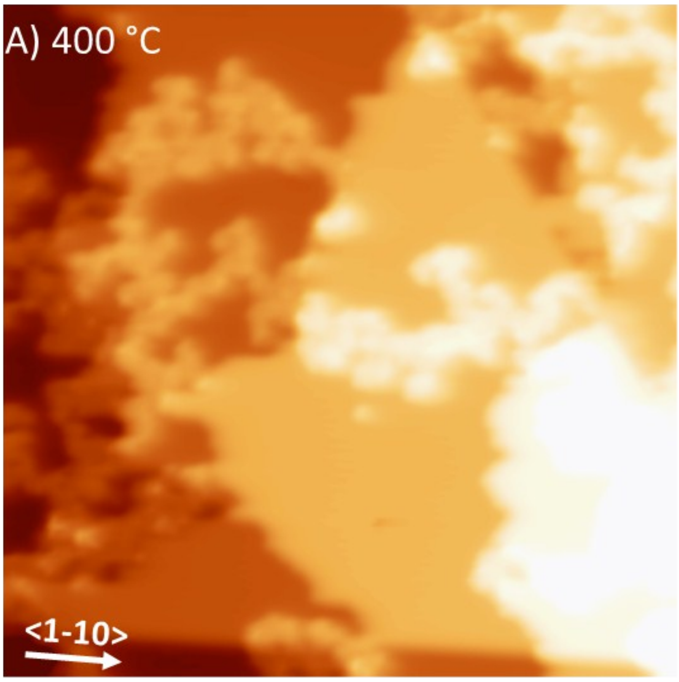

Figure S3. *STM image showing the Ag(110) surface covered by the polymer network, obtained after deposition of Br -CRN at RT, annealing to 150 °C for 15 minutes and then to 400 °C for 3 minutes. Image size: 25 x 25 nm*^{2}*, V=-1.0 V, I=0.09 nA.*

3. Additional XPS results

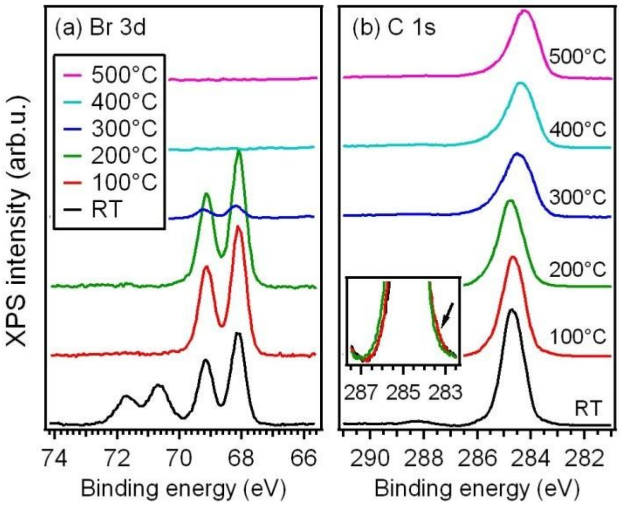

Figure S4. (a) Br 3d and (b) C 1s XPS spectra of (1.1±0.2) ML of Br-CRN deposited on the Ag(110) substrate at room temperature and after subsequent stepwise heating to the indicated temperature (from bottom to top). The spectra are recorded with a photon energy of 383 eV. The enlarged area in the inset of panel (b) shows the presence of the C–Ag component on the as-deposited sample (black line). This component is present also after heating at 100 °C for 10 minutes (red curve) but disappears after heating to 200 °C (green line).

4. Additional DFT results

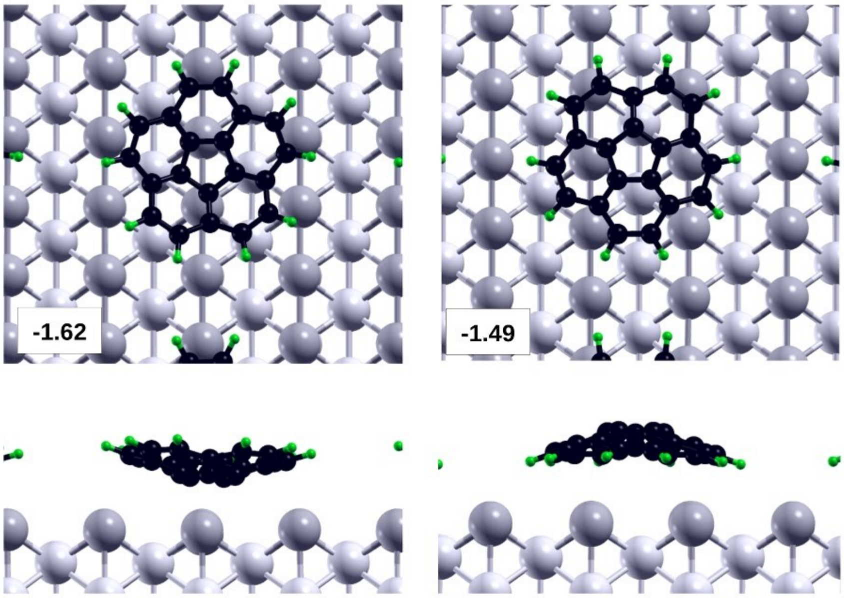

Figure S5. Isolated hydrogenated CRN molecule with bowl-up or bowl-down configuration and corresponding adsorption energies in eV. Color code: C in black, H in green, Ag atom in grey and top Ag atom in dark grey.

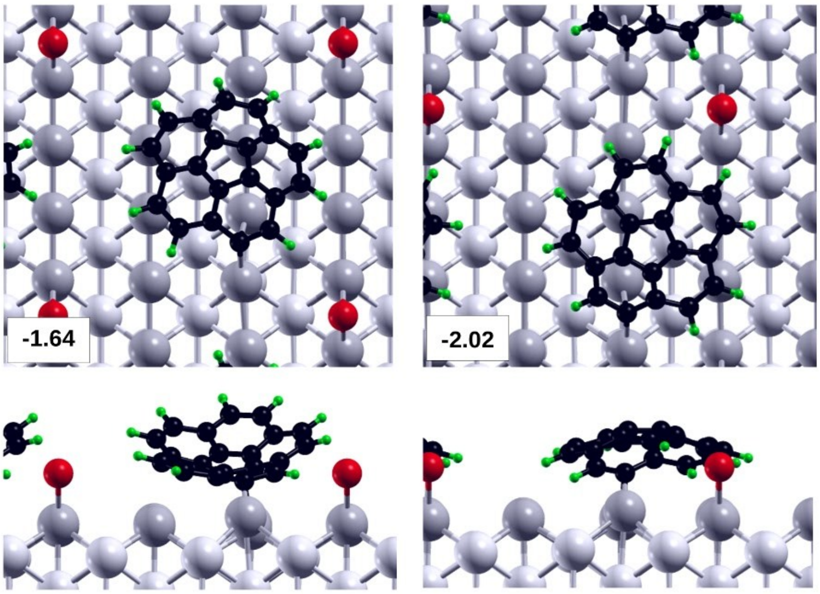

Figure S6. Isolated debrominated Br-CRN molecule with bowl-up or bowl-down configuration and corresponding adsorption energies in eV. Color code: C in black, H in green, Ag atom in grey, top Ag atom in dark grey and Br in red.

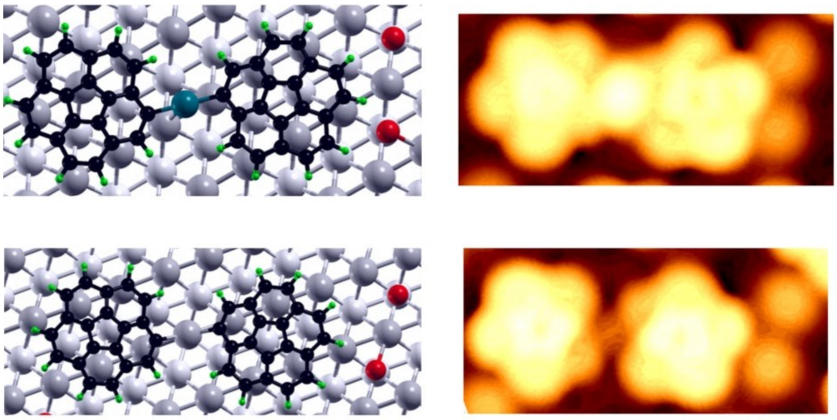

Figure S7. Example of bowl-up dimer with (top) and without (bottom) central Ag adatom and corresponding STM images. The lack of the central adatomdoes not lead to a bright protrusion between monomers as seen in the experimental images.

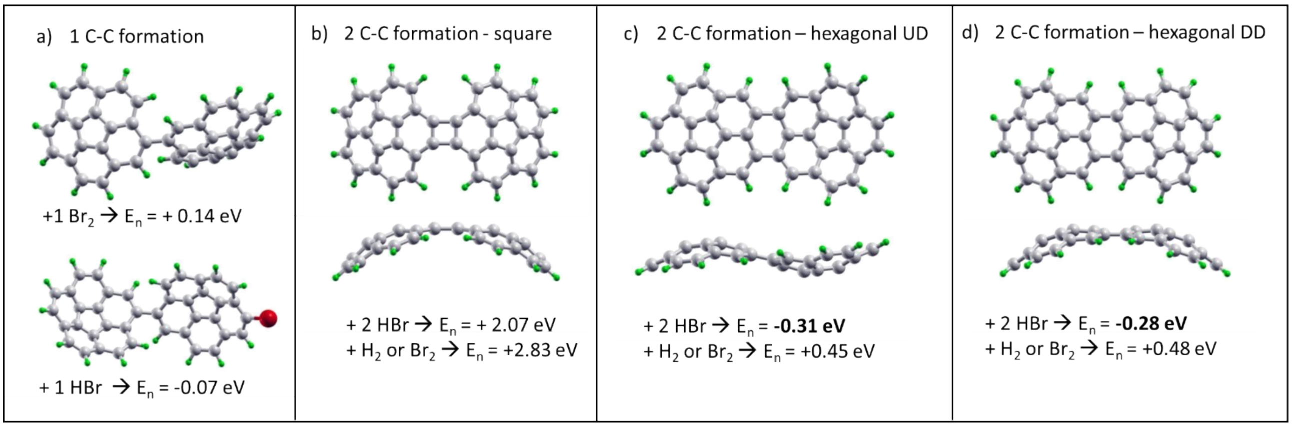

Figure S8. Gas-phase dimer formation and formation energy (starting from two Br-CRN). The different possibilities of C-C bond have been explored, together with the formation of H_2, Br_2 or HBr. Formation of an additional hexagonal ring (panels c and d) with production of 2 HBr molecule is the only endothermic configuration. The configuration is almost iso-energetic for molecules with same or opposite concavity.

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