Electronic Supplementary Information:

Reversible intercalation of iodine monolayers between on-surface synthesised covalent polyphenylene networks and Au(111)

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1. Additional STM results



Fig. S1 STM image of BIB-derived covalent polyphenylene networks on Au(111) acquired after room temperature iodine exposure (5×10^{-7} mbar, ~15 min, U_T = +858 mV, I_T = 25 pA). Same image as Fig. 1 a) of the manuscript depicted with alternative color scale.



Fig. S2 STM images acquired after a) room temperature iodination $(2 \times 10^{-6} \text{ mbar}, ~20 \text{ min}, U_T = +114 \text{ mV}, I_T = 200 \text{ pA})$. vs. b) "hot iodination" $(1 \times 10^{-6} \text{ mbar}, ~6 \text{ min}, U_T = -561 \text{ mV}, I_T = 20 \text{ pA})$. The black lines serve as guide to the eye. After room temperature exposure the iodine atoms on either side of the covalent networks or within the pores are not adsorbed on the same lattice, but form incoherent domains. This is a strong indication for a non-closed layer. In contrast, after "hot iodination" all iodine atoms including those within the pores occupy sites of a coherent lattice. This provides evidence for a closed iodine layer underneath the covalent networks.



Fig. S3 Upper row: STM images of BIB-derived covalent polyphenylene networks on Au(111) acquired after a) room temperature iodination (5×10^{-7} mbar, ~ 15 min, U_T = +858 mV, I_T = 25 pA) vs. b) "hot iodination" (1×10^{-6} mbar, ~ 6 min, U_T = -561 mV, I_T = 20 pA) Lower row: corresponding line-profiles along the black lines. The apparent height of the networks after "hot iodination" is almost 200 pm larger than after room temperature iodination. The green circles in a) highlight examples for dangling phenyl groups at the periphery of the covalent networks that showed bright protrusions after iodine exposure. These new contrast features are attributed to reiodination of previously surface-stabilized radical sites.



Fig. S4 Left side: STM image of polyphenylene networks on Ag(111) acquired after room temperature iodination $(5 \times 10^{-7} \text{ mbar}, \sim 5 \text{ min}, U_T = +800 \text{ mV}, I_T = 20 \text{ pA})$. Right side: Corresponding line-profile along the black line. This image facilitates a direct comparison of the apparent heights, because the darker appearing parts of the network (black arrow) remained directly adsorbed on the metal surface, whereas the bright appearing majority of the networks were detached and adsorbed on top of a closed iodine monolayer. The apparent heights in STM of ~236 pm of detached vs. ~66 pm of networks directly on Ag(111) are vastly different.



Fig. S5 STM images of BIB-derived covalent polyphenylene networks on Au(111) acquired after iodine exposure $(1 \times 10^{-6} \text{ mbar}, \sim 6 \text{ min})$ at elevated sample temperatures, i.e. "hot iodination". a) $(U_T = +825 \text{ mV}, I_T = 20 \text{ pA})$. b) $(U_T = -561 \text{ mV}, I_T = 20 \text{ pA})$. These images show a fully closed iodine layer (hexagonal structure in the background). Moreover, the covalent networks appear with internal contrast, resembling frontier molecular orbitals of free-standing networks.

2. Additional XPS and NEXAFS data analysis



Fig. S6 XP spectra of a) I 3d and b) C 1s core levels acquired from BIB-derived covalent polyphenylene networks on Au(111) before (lower spectra, blue line) and after (middle spectra, red line) iodine exposure (2×10^{-6} mbar, ~20 min) at room temperature. Additional spectra were acquired after annealing the sample at 350 °C for ~20 min (upper spectra, green line). All spectra are offset for clarity. After annealing the sample at 350 °C the majority of iodine is desorbed from the surface. I 3d shows a significant decrease of surface-bound iodine almost back to the level before deliberate iodination. The ~0.35 eV shift of C 1s to lower binding energies is entirely restored after iodine desorption.



Fig. S7 Normalized intensities (peak maxima) of the C 1s $\rightarrow \pi^*$ resonance vs. X-ray incidence angles before (blue crosses) and after (red crosses) iodination (2×10⁻⁶ mbar, ~20 min) at room temperature. Incidence angles are referred to the surface plane, i.e. 90° corresponds to normal incidence. The solid line represents the theoretical curve for an average phenyl tilt angle with respect to the surface of 15° (evaluated for the known degree of linear polarization of P=0.92). The dashed curves delineate uncertainty intervals of ±5° to 15°. On Au(111) room temperature iodination does not lead to a measurable change of the phenyl tilt angle.



Fig. S8 Normalized C 1s NEXAFS spectra acquired at an X-ray incidence angle of 45° (a) before and (b) after iodine exposure at room temperature (2×10⁻⁶ mbar, ~20 min) and (c) after thermal desorption of iodine by sample annealing at 350 °C. In all cases the C 1s $\rightarrow \pi^*$ resonances were fitted with Gaussians, resulting in FWHM of a) 1.00 eV (σ =0.42 eV), b) 0.75 eV (σ =0.32 eV) and c) 0.99 eV (σ =0.42 eV). Sharpening of the C 1s $\rightarrow \pi^*$ resonance is commonly associated with a longer lifetime of the excited state. Since this sharpening is reversible, i.e. disappears again after iodine desorption, it most likely already results from co-adsorption of iodine, and does not require decoupling of the covalent networks from the surface.