## SUPPORTING INFORMATION

## On-surface photo-dissociation of C-Br bonds: towards room temperature Ullmann coupling

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**Figure SI1:** Representation of the physisorbed monolayer of DBT on Au(111) with corresponding partial charge distribution on the left (colour code: yellow gold, red bromine, grey carbon, white hydrogen). Difference in the electronic densities (isosurface 0.001) between the physisorbed monolayer and the isolated monolayer and the gold surface on the right (colour code: red represents a depletion of electronic density and blue an increase of electronic density).

Figure SI1 shows a representation of the partial charges, estimated with the Bader charge analysis, for the physisorbed DBT molecules organized according to the experimental supercell. Due to the electronegativity difference between Br and C, there is an anisotropic charge distribution resulting in a partial negative charge around the halogen atom, while the outermost hydrogens are opposite in sign. The lateral interaction between physisorbed DBT molecules is estimated to be about -0.14 eV/molecule. The interaction between the monolayer and the gold surface is driven by dispersion forces, as confirmed by the typical physisorption distance of about 3.2 Å, and a tiny charge transfer from the DBT to the metal (see right plot of Figure SI1).



**Figure SI2**: Distribution of the partial charges computed for the Br and Au adatoms for different configurations of DBT on the Au (111) surface: (a) as an intact physisorbed species on the Au (111) surface with Au adatoms; (b) partially debrominated and (c) completely debrominated in the monomeric phase (colour code: yellow gold, red bromine, grey carbon, white hydrogen). Adsorption energies are reported in eV and calculated with respect to the DBT molecule in the gas phase and the Au surface with adsorbed Au adatoms.

In the physisorbed state, the bromine atoms of DBT are slightly negatively charged, while the isolated gold adatoms on the surface hold a more significant negative charge of -0.1e (Figure SI2a). As the C-Br bond dissociation is activated, bromines are replaced by gold adatoms, which leads to the formation of the organometallic species. These metallic substituents still show a negative charge when they are free on the surface, but become positive as they bind the tetracene core, see Figure SI2b. As a result, the whole outermost part of the organic molecule is positively charged and one would expect a bigger unit cell, as commonly observed for repulsive molecular units.<sup>1,2</sup> However, the bromine atoms consistently decrease their charge by chemisorption and so they attenuate the electrostatic repulsion among the tetracene units once a close packed structure is formed. Full debromination is shown in Figure SI2c, where the second Br atom has been replaced by a gold adatom, which is now positively charged.



**Figure SI3**: Simulated unit cells of the experimentally observed monomeric phase (a) with and (b) without chemisorbed bromine among the molecules.

This dampening effect of the Br atoms has been estimated for the experimental cell [3 3.5; 0 5] by comparing the calculated binding energy for the observed structure, Figure SI3a, and for the same self-assembled motif but with the bromine atoms chemisorbed on a separate slab, Figure SI3b, (the chemisorption sites have been kept the same).

In detail:

$$E_{binding}^{SI3a} = E^{SI3a} - \left[E_{Au\,slab} + E_{DBT}^{\circ}\right] = -2.98 \ eV$$
$$E_{binding}^{SI3b} = E^{SI3b} + E_{2Br\,chem} - \left[E_{Au\,slab} + E_{DBT}^{\circ}\right] = -2.61$$

where  $E^{SI3a}$ ,  $E^{SI3b}$  are the total energy for the shown structures,  $E_{2Br chem}$  the energy for the bromine atoms chemisorbed on a separate slab and  $E_{DBT}$ ,  $E_{Au slab}$  the energy for a dibromo-tetracene molecule in vacuum and for an isolated Au slab with two adsorbed adatoms, respectively.

The results show that the inclusion of the bromine atoms contributes to stabilize the self-assembled network by as much as -0.38 eV; we therefore conclude that the halogen atoms are a critical stabilizing element of the structure.



**Figure SI4**: Simulated unit cells of the experimentally observed <u>dimeric</u> phase (**a**) with and (**b**) without chemisorbed bromine among the molecules.

The same result (-0.41 eV) is obtained even for the structure of the dimeric species, see Figure SI4. Similarly to before the binding energies have been computed according to:

$$E_{binding}^{SI4a} = E^{SI4a} + E_{2Br \ chem} - \left[E_{Au \ slab} + 2 \times E_{DBT}^{\circ}\right] = -6.03 \ eV$$
$$E_{binding}^{SI4b} = E^{SI4b} + 2 \times E_{2Br \ chem} - \left[E_{Au \ slab} + 2 \times E_{DBT}^{\circ}\right] = -5.62 \ eV$$

Since the unit cell contains two DBT molecules, the total energy of two additional bromine atoms has to be added in order to keep the stoichiometry with respect to the reference.



Figure SI5: Collection of STM images from a monolayer of DBT molecules acquired after a thermal treatment at 470 K for 30 minutes. a) 105 × 105 nm<sup>2</sup>, b) 50 × 50 nm<sup>2</sup> and c) 40 × 40 nm<sup>2</sup> (V<sub>bias</sub>=0.57 V, I=2.3 nA)



Figure SI6: Comparison of the Br 3d XPS signals (hv=150 eV) acquired before (red line) and after (black line) the heating treatment at 340 K within the illuminated area of a DBT monolayer on Au (111).

Since at room temperature the molecule adsorbs intact, initially all the XPS bromine signal comes from those atoms bonded to the molecular scaffold (AreaBr<sub>ini</sub>). After illumination, the Br 3d XPS peak shows both the formation of chemisorbed atoms (AreaBr<sub>chem</sub>) and a decrease of the total subtended area (AreaBr<sub>after</sub>). The reaction yield takes in consideration both these observations and has been calculated according to:

 $Reaction yield \% = \frac{AreaBr_{chem} + (AreaBr_{ini} - AreaBr_{after})}{AreaBr_{ini}} \times 100$ 

In addition, after deconvolution of the C 1s XPS peak measured on the illuminated sample (Figure 2c in the main text) the carbon linked to gold adatoms (C-Au) account for 44% of the as-deposited C-Br related peak. This observation independently corroborates the estimation based on the Br 3d signal.



**Figure SI7:** Spectroscopic and STM data of the sample preparation procedure, the Au(111) was held at RT while the molecular source was at 360 K. a) C 1s and b) Br3d XPS signal (hv=400 eV) as a function of the deposition time, the same colour code has been applied. After 90 minutes of deposition the C 1s and Br 3d saturate and further sublimation does not result in an increase of the signals. c)  $130 \times 130$  nm<sup>2</sup> of a freshly prepared sample at RT and d)  $130 \times 130$  nm<sup>2</sup> the same surface after treatments at 340 K for 30 minutes. The heating causes the desorption of the partially formed second layer (bright stripes in c) without affecting the first layer.

## **Experimental section**

The STM experiments were performed in a multi-characterization chamber under UHV (base pressure 2×10<sup>-</sup> <sup>10</sup> mbar) equipped with an Omicron Scanning Tunneling Microscope (VT-STM), a PBN crucible, a LEED instrument (LPS075D) and standard facilities for sample preparation. After the system was thoroughly degassed, the DBT molecules were sublimated at 360 K onto the Au (111) substrate held at RT. All the investigated samples were prepared by thermal desorption of partially formed multilayer at 340 K, see Figure SI7. The continuous wave laser source at 405 nm (Roithner Laser Technik, GmbH; model X40LM-10, Vienna, Austria) provided a surface power density of 75 mW/cm<sup>2</sup> and the sample was illuminated at RT for ≈12 h. In order to exclude any influence of the laser irradiation in the non-illuminated area, i.e. spurious reflexes, the observed thermal behaviour was compared with two ex-novo prepared samples, which were never illuminated. The STM reproducibility of the optimized illuminating protocol was tested in 5 different samples: all treated samples showed the described reactivity. The temperature of the sample during the irradiation has been monitored by a k-type thermocouple directly connected to the manipulator (1 cm away from the sample holder) and no variation has been observed. In addition, localized thermal effect can be excluded since no variation of the piezoelectric extension occurred during STM imaging at constant current for a period of 8 hours. The sample-laser distance has been kept constant at 24 cm during all the sample preparations and a Torr Scientific VPZ38QAR viewport ensured high transmission efficiency at 405 nm. The beam diameter was set to 4 mm by means of a diaphragm, ensuring a sharp edge profile of the photon flux and then directly pointed toward one edge of the sample. Considering the size of the crystal (1 cm) and the molybdenum stripes used to keep it in position, the working length across the sample was  $\approx 8$ mm.

XPS measurements were performed at the I311 beamline at the MAX-IV laboratory (Lund, Sweden). The spectra were obtained in normal incidence geometry, the photoelectron detection angle being 55° off the surface normal, with a kinetic energy resolution of 50 meV. The Au  $4f_{7/2}$  core level was used as reference for the energy calibration (BE = 84.00 eV). The fitting procedure for the C 1s and Br 3d PE spectra was performed with the XPSpeak software. The XP C 1s core level spectrum has been de-convolved assuming the presence of three different inequivalent carbons within the molecular structure, i.e. C-Br (C<sub>Br</sub>), C-H (C<sub>H</sub>), C-C(C<sub>C</sub>), and keeping constant the ratio between the areas according to the theoretical stoichiometric ratio account that some carbon atoms are then bonded to Au adatoms (C<sub>Au</sub>), therefore the C<sub>Br</sub> area was replaced by C<sup>tot</sup><sub>Br</sub> = C<sub>Au</sub> + C<sub>Br</sub>. Some authors introduced several additional components in the multi-peak analysis, since not all the C<sub>c</sub> are symmetrically equivalent<sup>3</sup> and after adsorption different sites of the single C atoms influence the extent of molecule-metal hybridization. Since a detailed discussion of the molecule/substrate interactions is out of the scope of the present work, we have used as few components as possible; minor discrepancies between the experimental data and the deconvolution analysis might be related to the approximate nature of our choice.

All calculations are based on density functional theory (DFT). The adsorption of DBT molecules on a Au(111) surface was modelled by using the recent Van der Waals density functional vdW-DF2<sup>C09x 4</sup> which has been proven to give the best performance for the adsorption distances of graphene on metal surfaces. Different simulation cells were used, according to the experimental data, with a vacuum of about 20 Å perpendicular to the surface to avoid interaction between the images. The Au surface was modeled by four-layer slabs, in which the top three layers and the adsorbate were allowed to fully relax, and the bottom one was kept fixed at the optimized lattice for vdW-DF2<sup>C09x</sup>, 4.10 Å. The Perdew-Burke-Ernzerhof (PBE) standard ultrasoft pseudopotentials, as implemented in the plane-wave based Quantum Espresso package<sup>5</sup>, are used with energy cutoff of 30 and 240 Ryd (for kinetic-energy and charge-density grids, respectively). The binding

energies are computed at the Gamma point and reported in eV. The STM image simulations were obtained within the Tersoff–Hamann approximation, 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 applied bias, as carried out in the corresponding experiments. The STM images were plotted at a height above the surface of about 3 Å.

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