Electronic Supporting Information (ESI):

Tip-induced C–H activation and oligomerization of thienoanthracenes

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Methods

The STM experiments were carried out in ultra-high vacuum (UHV) chamber with a base pressure of 10^{-10} mbar. The Cu(111) and Ag(111) substrates were cleaned by repeated cycles of sputtering with 1 keV Ar^+ for 10 minutes followed by annealing at 500 °C for 20 minutes. The HOPG substrate (Structure Probe Inc., grade SPI-2) was cleaved in air and subsequently transferred into the vacuum system. The resulting surfaces had large terraces with randomly distributed steps.

2TTA, the synthesis of which was described elsewhere,[1] was purified by vacuum sublimation (10^{-1} mbar; 300 °C). In our UHV experiments, the molecule was sublimated from a pyrolitic boron nitride (PBN) crucible in a Knudsen-type effusion cell at approximately 170 °C. For each surface, we used the same evaporation time (5 minutes). Presumably, due to the lower sticking coefficient there was a lower amount deposited on the Ag(111) and the HOPG than on the Cu(111).

Except for the estimation of surface coverage, when the surface was cooled at -160 °C, during the depositions (for the "patterning" experiments) the substrate was held at RT.

STM characterization was performed at room temperature using a commercial variable-temperature instrument (Aarhus 150, SPECS GmbH) equipped with cut Pt/Ir tips. Bias voltages are reported with respect to the STM tip.

Tunneling current was maintained near 1 nA for all patterning experiments. Systematic tests of different tunneling currents (0.2 ÷ 1.5 nA) did not produce noticeably different results. Scan speeds during patterning were between 3 and 6 ms/nm. There were no noticeable differences in the results using scan speeds in this range.

Because of the lack of substrate resolution near the patterned regions (likely due to diffusing molecules), we calibrated our images based on atomic resolution images of the surface acquired during the same imaging session. This calibration allowed us to measure intermolecular distances with sufficient precision to differentiate between covalent and metal-coordinated molecules.

List of figures:

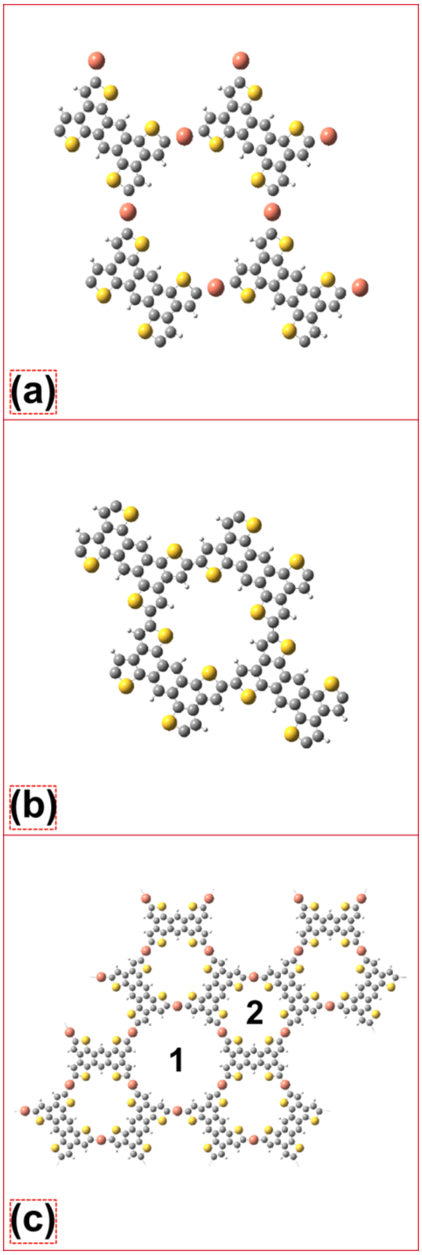

Figure S1. Schematic representation of 2-dimensional motifs of 2TTA: (a) Oblique organometallic. For the copper-coordinated network in this geometry the distance between the center of mass of any two neighboring molecules measures 1.45 nm (as reported by Gutzler *et al.*, from gas-phase DFT).[2] (b) For the oblique covalent structure, the same distance measures only 1.21 nm (gas-phase DFT).[2] (c) Kagome 2D-organometallic structure comprising conformations of six (cage **1**) and three (cage **2**) molecules. The structures were cut out of larger networks generated with periodic boundary conditions; the copper atoms are colored in red, sulfur - in yellow, and carbon - in grey color.

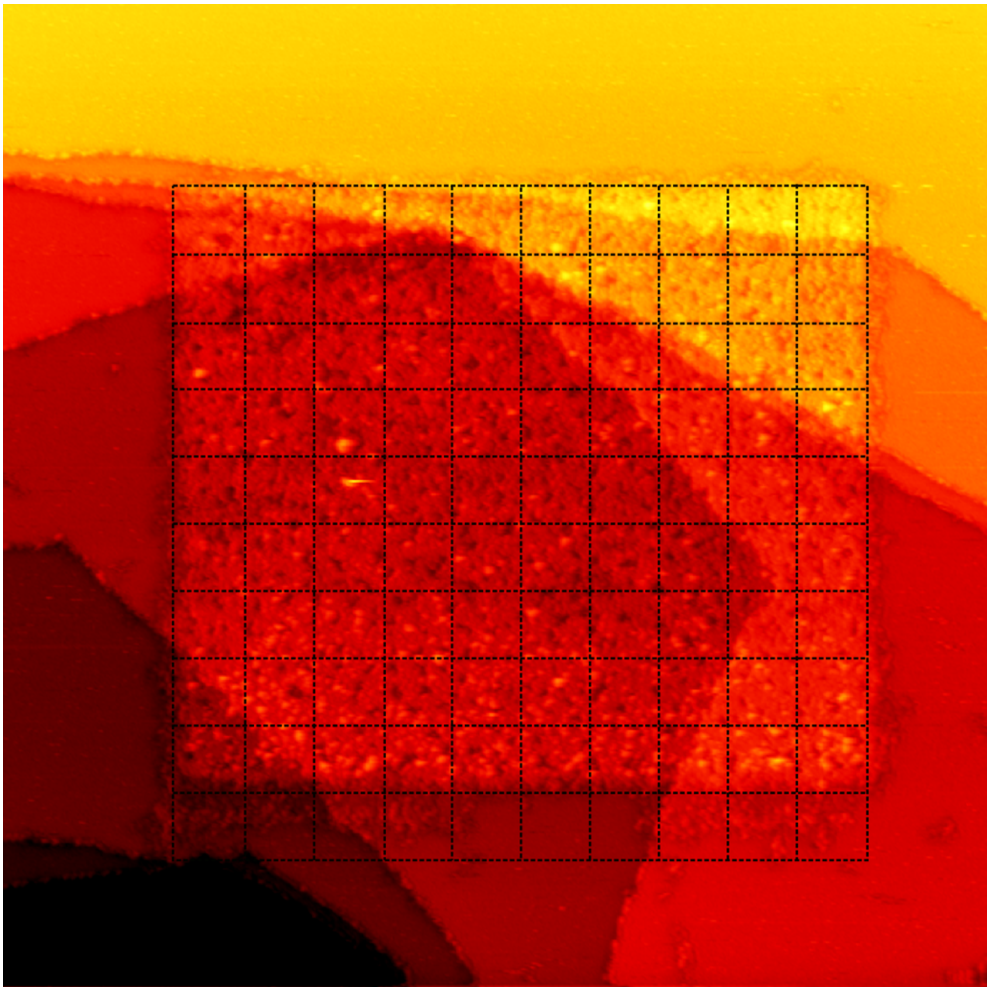

Figure S2. STM images of a rectangular region patterned from 2TTA on Cu(111) using $U_{bias,pattern}$ ~5 V (image duplicated from Figure 1(a), the main document). Image parameters: 150×150 nm^2 with a patterned region of 100×90 nm^2. A grid of 100×100 nm^2 with lattice of 10×10 nm^2 was used inside the patterned region. We estimated (average over 10 points on each side of the patterned region, along the grid lines) the deviations between scanned and patterned distances: 2.6±0.6 nm at the right side, 1.0±0.2 nm at left, 1.4±0.5 nm at the top, and 5.7±1.7 at the bottom.

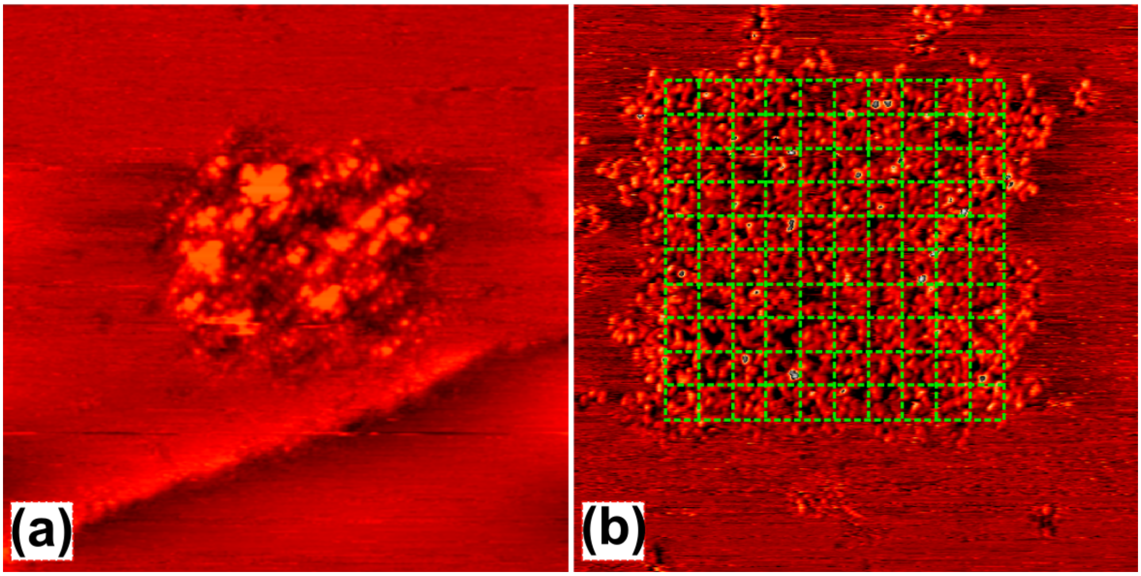

Figure S3. STM images of a square patterned from 2TTA on Cu(111) using $U_{bias,pattern}$ ~ 5 V. Image parameters: 50×50 nm^2 in (a) with a patterned region of 20×20 nm^2; 50×50 nm^2 in (b) with a patterned region of 30×30 nm^2. Scanning parameters: I_t = 0.40 nA, U_b = 1903.69 mV for (a) and I_t = -0.37 nA, U_b = -493.16 mV for (b). A grid of 30×30 nm^2, with the lattice of 3×3 nm^2, was used in (b). We estimated (average over 10 points on each side of the patterned region, along the grid lines) the deviations between scanned and patterned distances: 2.2±0.8 nm at the right side, 2.5±0.7 nm at left, 0.7±0.4 nm at the top, and 1.2±0.5 at the bottom.

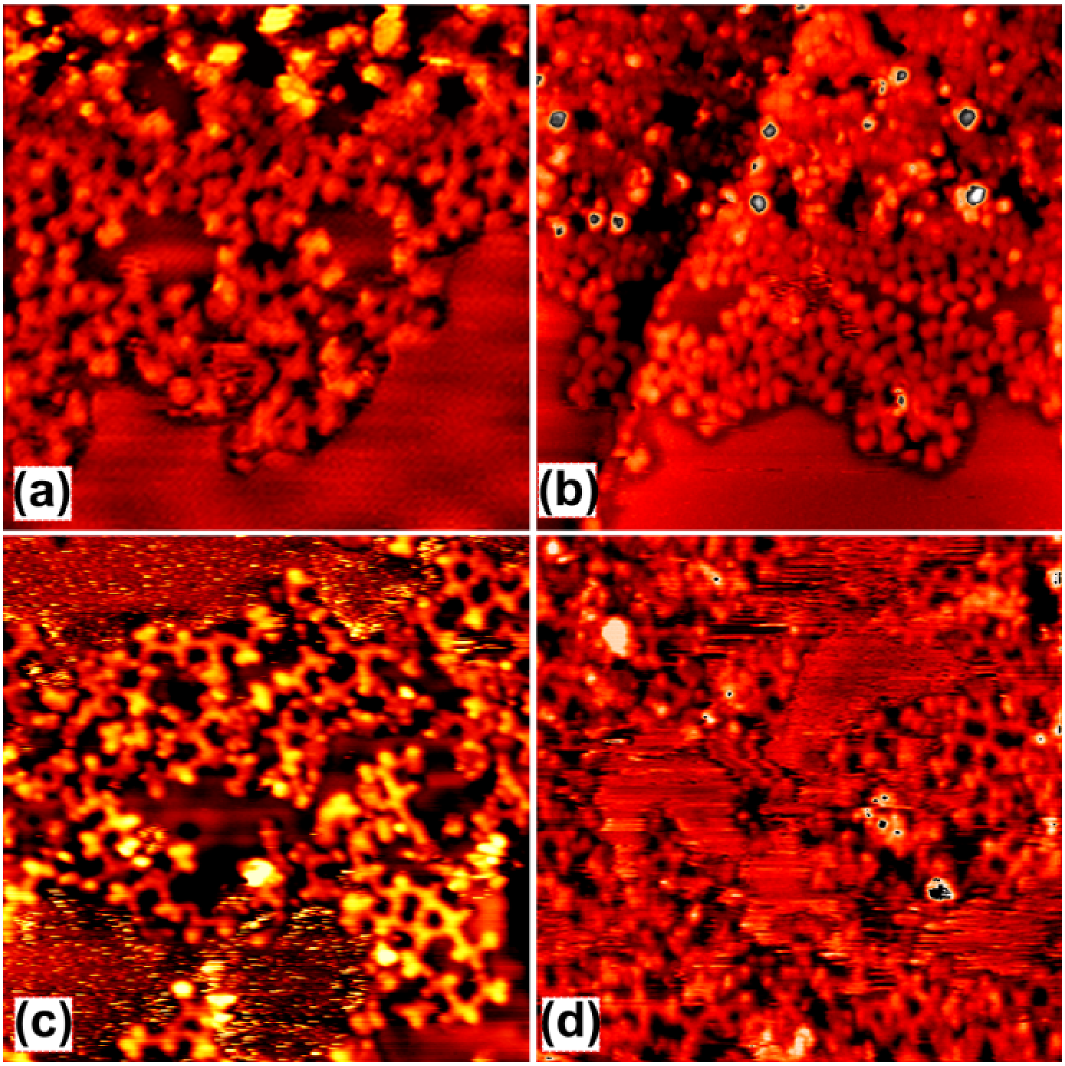

Figure S4. STM imaging of regions patterned from 2TTA on Cu(111) using $U_{bias,pattern}$ ~ 5 V for (a), (b) and (d), and ~ 3.5 V for (c). Image sizes: 20×20 nm^2 in (a); 30×30 nm^2 in (b), 15×15 nm^2 in (c), and 20×20 nm^2 in (d). Scanning parameters: (a) I_t = -0.50 nA, U_b = -691.33 mV; (b) I_t = -0.42 nA, U_b = -691.22 mV; (c) I_t = 0.11 nA, U_b = 116.58 mV; (d) I_t = -0.34 nA, U_b = -670.47 mV.

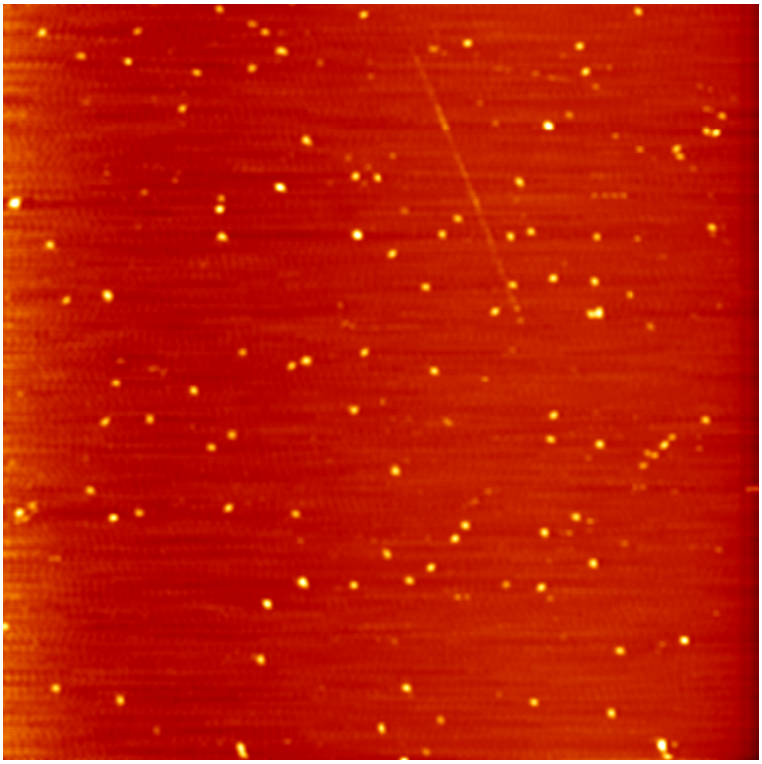

Figure S5. 150×150 nm^2 STM image for coverage estimation of Cu(111) by 2TTA molecule. The molecule was sublimated onto Cu(111) at RT, and imaging was performed at -160 °C. Each bright spot represents a single molecule. The molecular coverage on the surface was estimated to ~1% of a monolayer, after performing the patterning experiments, on the same surface at low temperature.

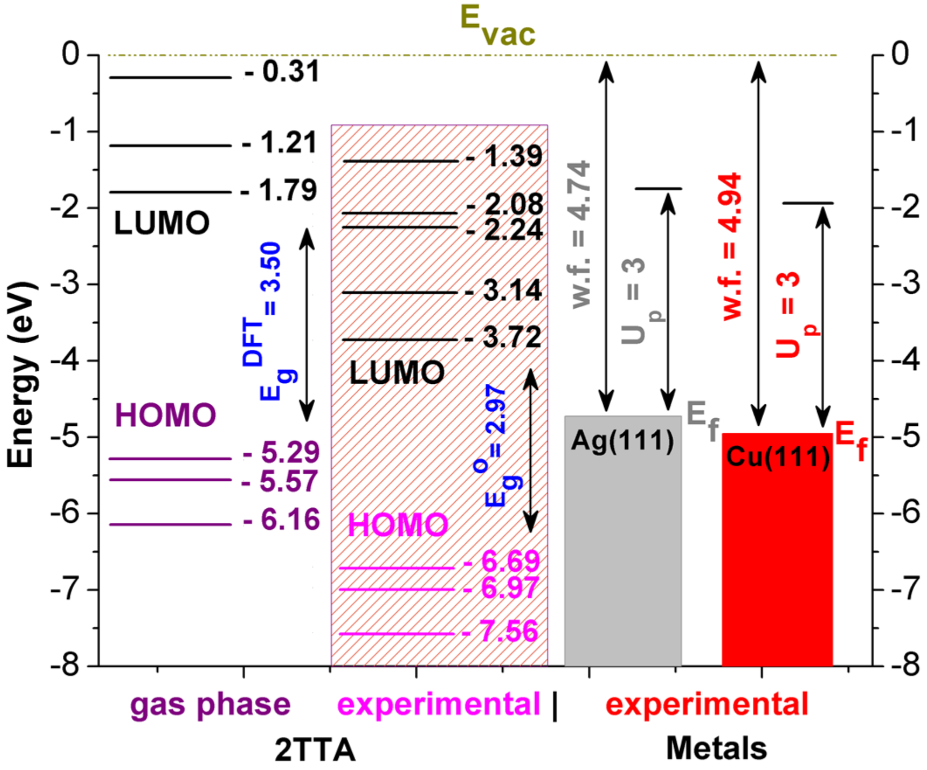

Figure S6. Schematic representation of energetics in the 2TTA, Cu(111) and Ag(111) systems. The eigenvalues of a single 2TTA molecule were obtained from the gas-phase DFT calculations of the molecular orbitals (at the B3LYP/6-31G(d,p) level). The work functions (w.f.) of Cu(111),[3] and Ag(111),[4] are published experimental values. The dashed rectangle contains the energy levels of 2TTA based on the reported experimental values of the HOMO (-6.69 eV) and the optical bandgap (E_g^o = 2.97 eV);[1] the remaining energy levels are the DFT-derived values, and are referenced to the LUMO (unfilled states) and HOMO (filled states). In the diagram, E_{vac} = energy of the vacuum level, E_g^{DFT} = calculated value for the bandgap of 2TTA (3.5 eV), E_g^o = optical band-gap of 2TTA measured experimentally; E_f = energy of the Fermi level, HOMO – highest occupied molecular orbital, LUMO – lowest unoccupied molecular orbital; U_p = bias voltage at which patterning occurs (~3 V).

This diagram represents a first order approximation, where: (1) the molecules are physisorbed, and (2) the molecule-metal vacuum levels are aligned. The presence of metallic surface will introduce perturbations to the positioning of these molecular energy levels obtained from gas-phase calculations; metallic surfaces are acknowledged as lowering, and broadening the molecular orbitals, by direct coupling of the surface electronic states with the molecular states.[5]

However, with these in mind, the diagram provides a visual representation of the possible levels involved in the charge injection scheme at U_p = 3 V bias associated with molecular patterning on Cu(111).

Supporting References:

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