

Site-Dependent Oxidation State of Single Cobalt Atoms in a Porphyrin-based Monolayer on Graphene

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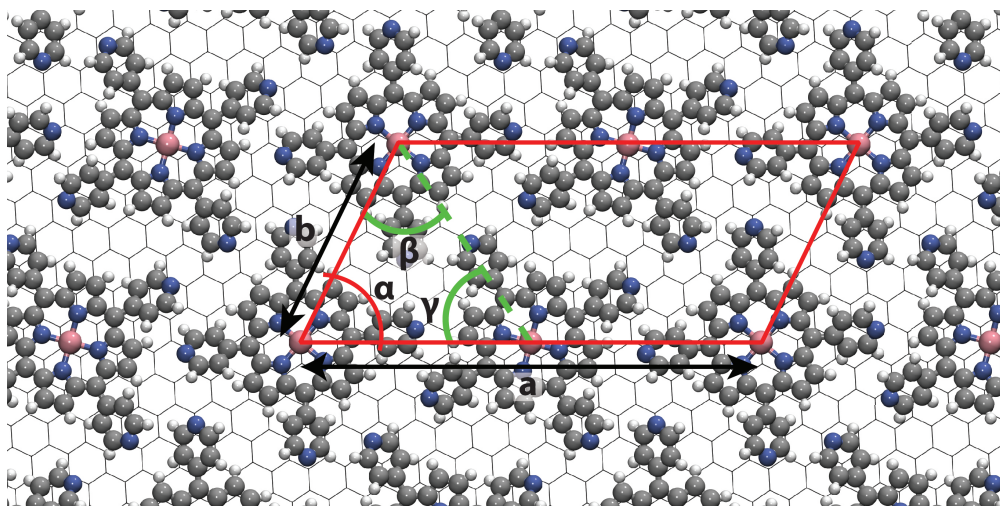


Figure S1: Stick-and-ball model (top view) with DFT optimized coordinates for the monometallic molecular layer: highlighted in red is the unit cell with parameters: $a = 30.97 \text{ \AA}$, $b = 14.84 \text{ \AA}$, $\alpha = 63.8^\circ$. Other angles characterizing the structure are drawn in green: $\beta = 60.0^\circ$, $\gamma = 56.2^\circ$

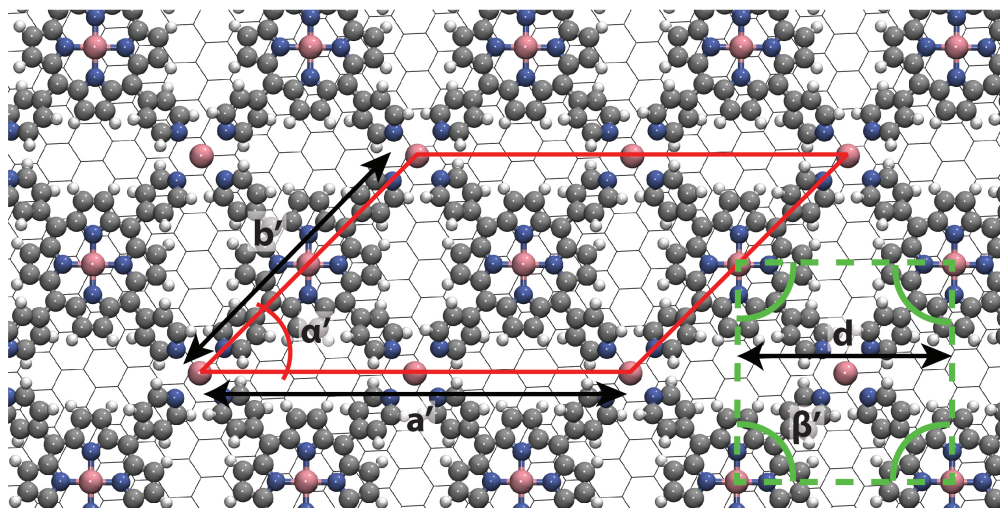


Figure S2: Stick-and-ball model (top view) with DFT optimized coordinates for the bimetallic molecular layer: highlighted in red is the unit cell with two molecules rotated by 90° one respect to the other and characterized by the parameters: $a' = 28.36 \text{ \AA}$, $b' = 20.23 \text{ \AA}$, $\alpha' = 44.9^\circ$. The pattern of the metallic centers, disregarding the orientation of the molecules, is almost a square lattice, whose unit cell is drawn in green and is characterized by the parameters: $d = 14.23 \pm 0.05 \text{ \AA}$ and $\beta = 90 \pm 0.5^\circ$.

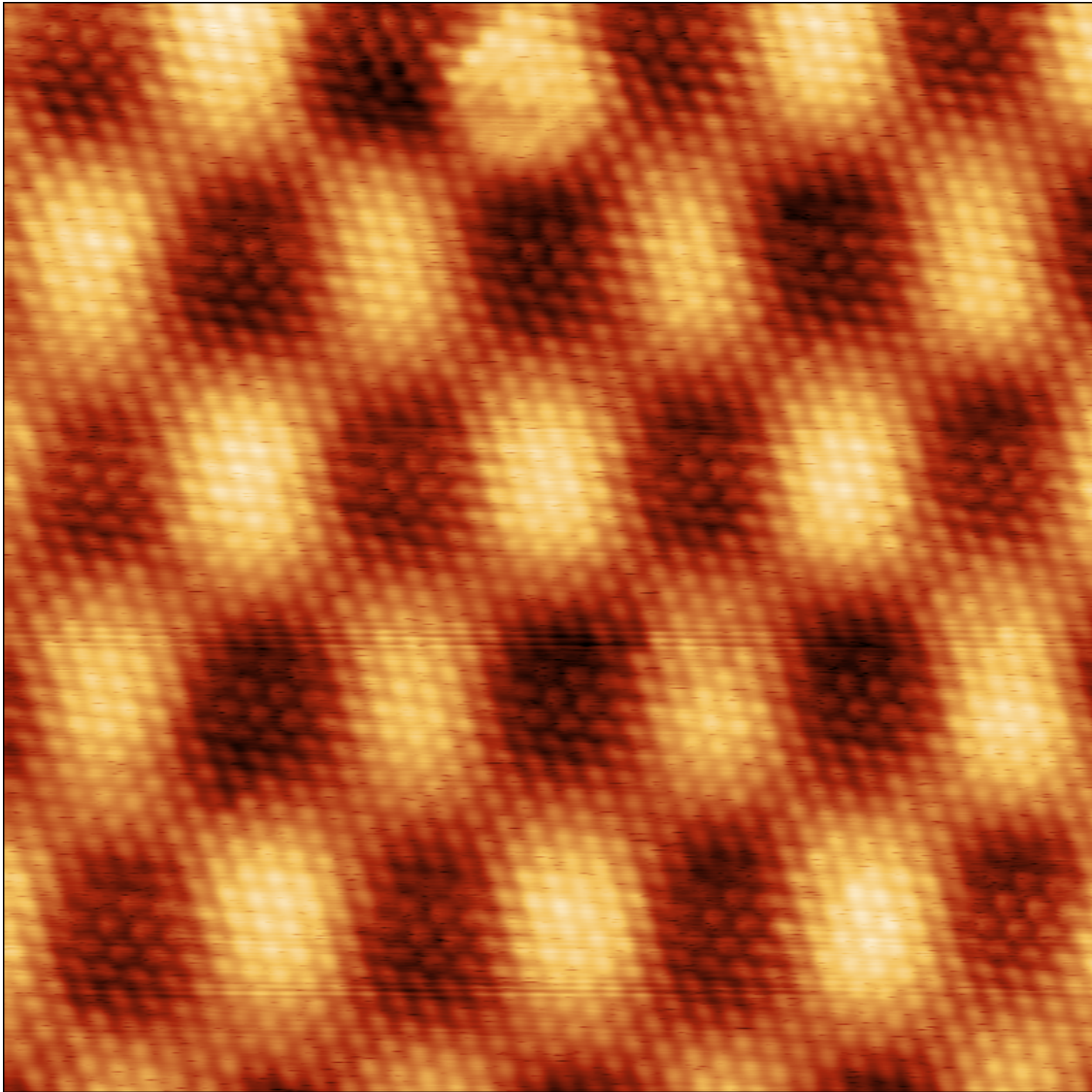


Figure S3: STM image of bare graphene on Ir(111) acquired at -150 mV and 1.2 nA, image size $9 \times 9 \text{ nm}^2$.

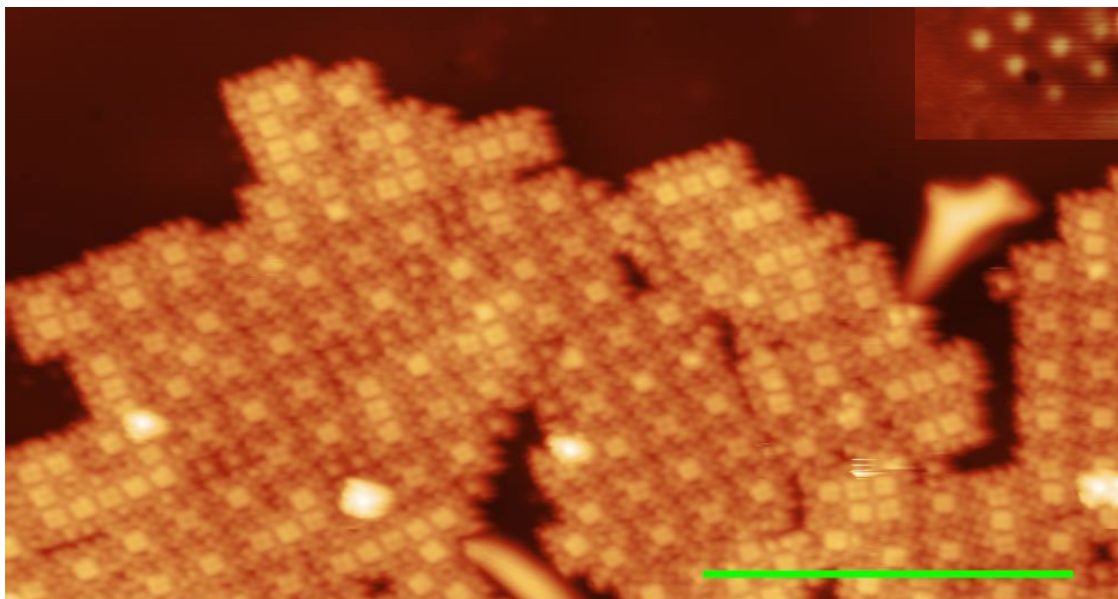


Figure S4: STM image of the CoTPyP/Gr/Ir(111) layer after 3 min of Co deposition. In the top right inset, the contrast is augmented to show cobalt clusters on graphene. Image acquired at +2.2 V and 50 pA, scale bar = 5 nm.

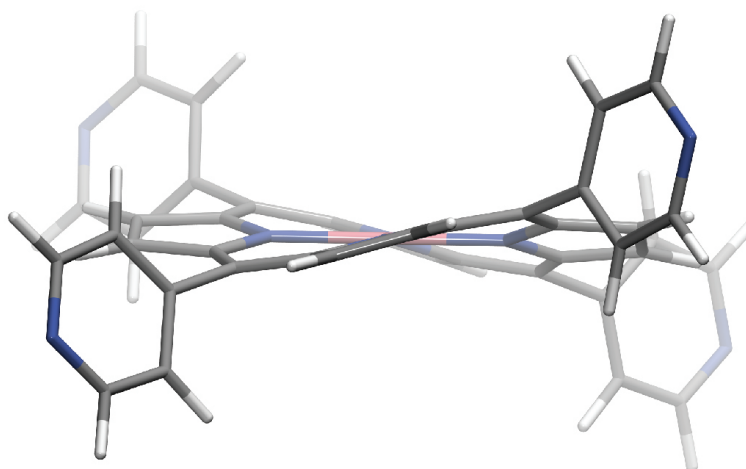


Figure S5: Configuration of a single CoTPyP molecule relaxed in the gas phase.

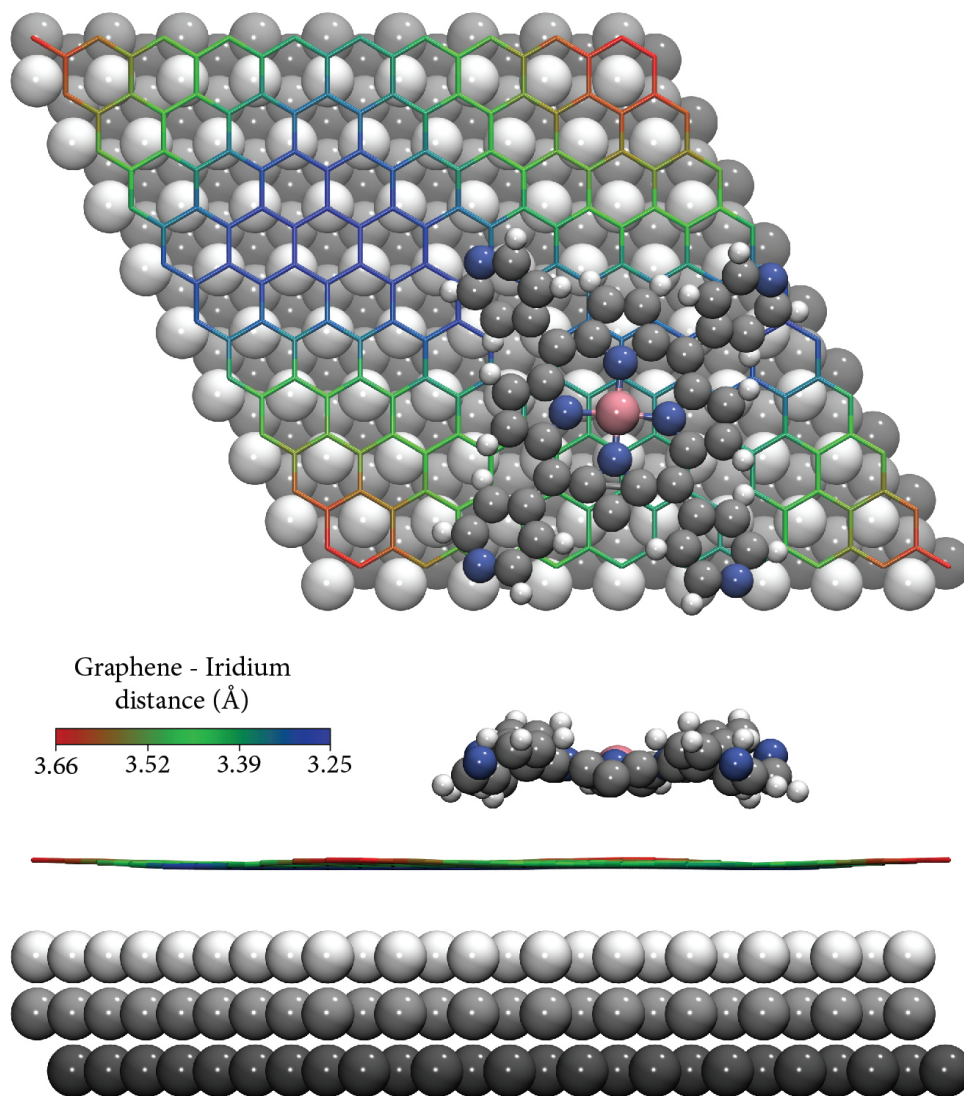


Figure S6: Top and side view of the relaxed configuration of a single CoTPyP molecule adsorbed on graphene on Iridium (111). The color variation of graphene corresponds to the distance variation from the Ir substrate. The typical graphene corrugation on Ir(111) is preserved even in presence of an adsorbed CoTPyP molecule.

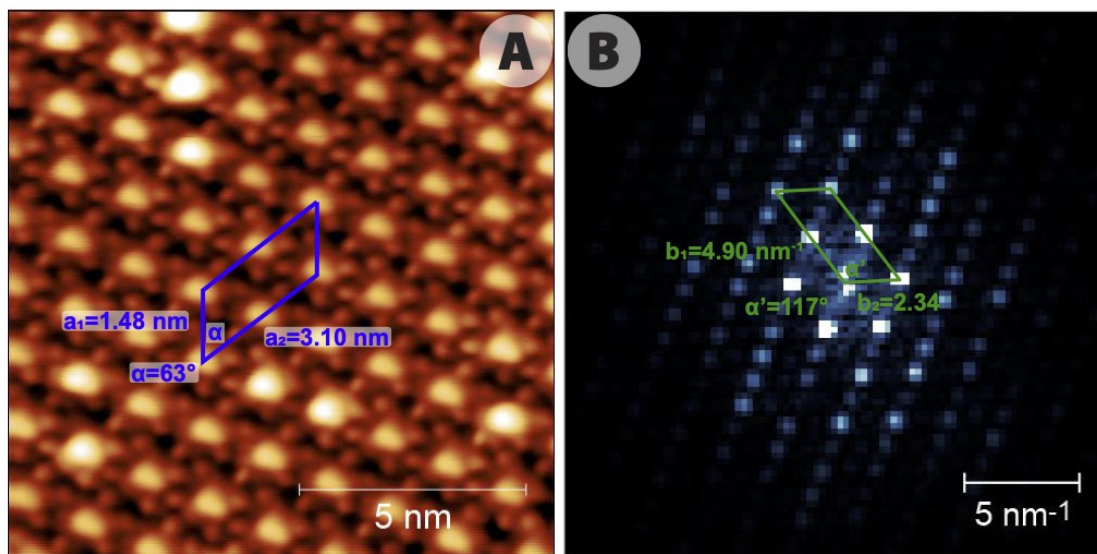


Figure S7: A) STM image of the monometallic CoTPyP/Gr/Ir(111) layer (200 pA/+2.0 V) and in B) the corresponding FFT. Unit cells and parameters are indicated.

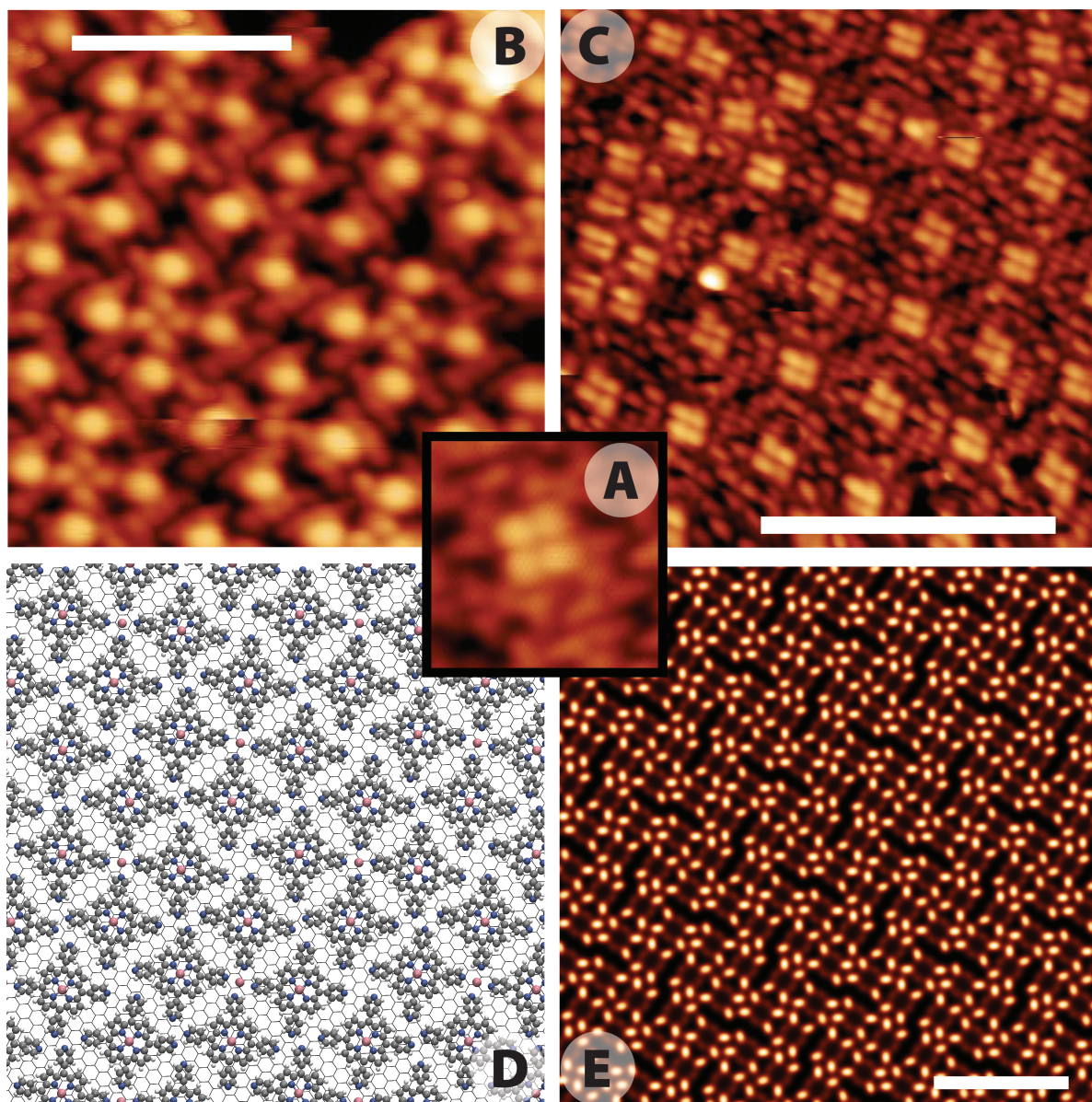


Figure S8: Experimental STM images and models for an unsaturated molecular layer: A) STM image of a single $(\text{CoTPyP})_4\text{Co}$ block acquired at $I = 60$ pA and $U_{\text{bias}} = +2.0$ V; B) STM image of a domain with a regular periodicity and a peripheral Co coverage $\theta_{\text{Co}}/\theta_{\text{CoTPyP}} = 0.25$ acquired at $I = 100$ pA and $U_{\text{bias}} = +2.0$ V; C) STM image of a different domain with the same periodicity and Co coverage of panel B) acquired at $I = 100$ pA and $U_{\text{bias}} = +1.4$ V; D) Model of the periodic layer of panels B) and C); E) Topographic map at 3.0 Å above Co atoms for the model in D) obtained by considering a superposition of 3D gaussians with $\sigma = 0.5$ Å centered on the atomic sites of the model (scale bar 5 nm).

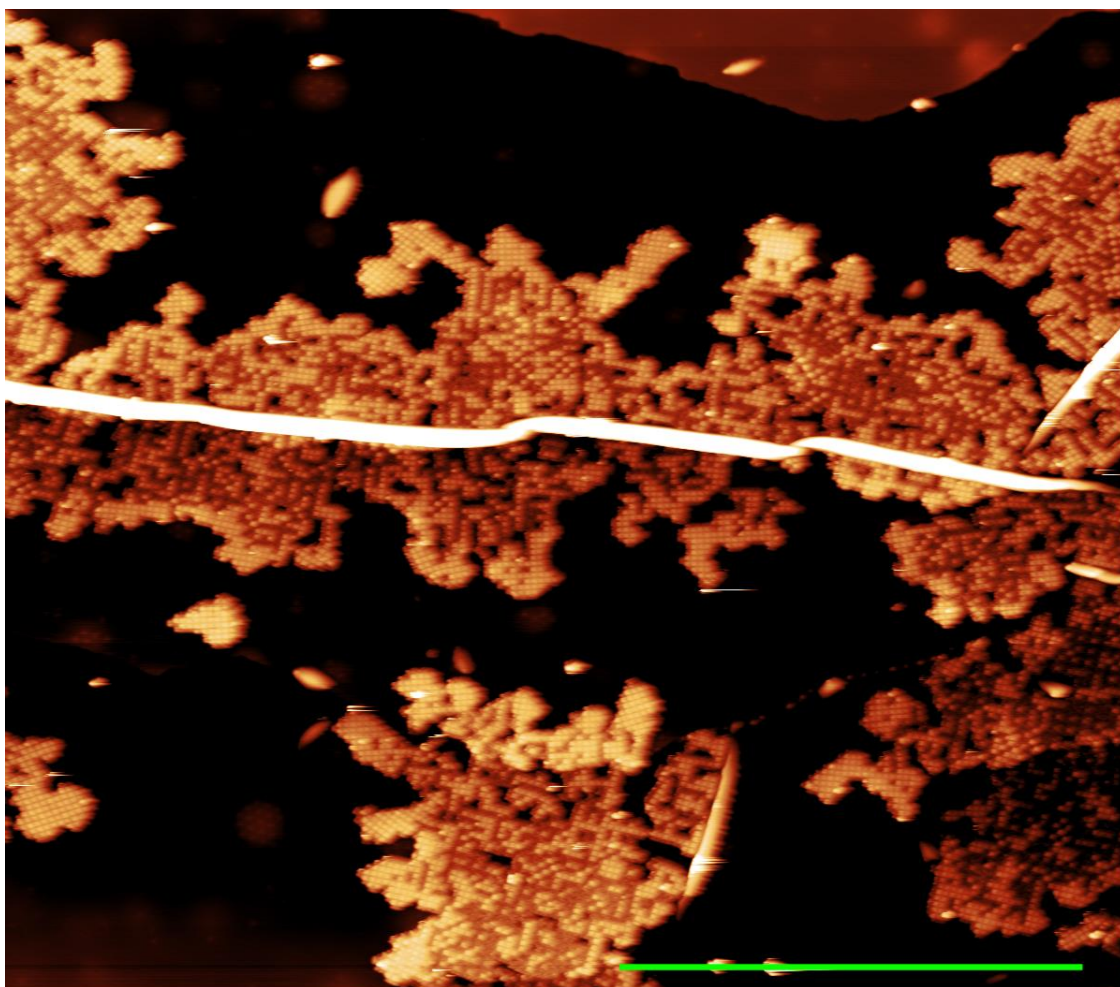


Figure S9: STM image of CoTPyPCo/Gr/Ir(111) at 1.2 ML of Co (with respect to CoTPyP unit cell). It can be observed that the molecular layer reaches saturation first at the borders of the islands. Image acquired at +2.2 V and 50 pA, scale bar = 100 nm.

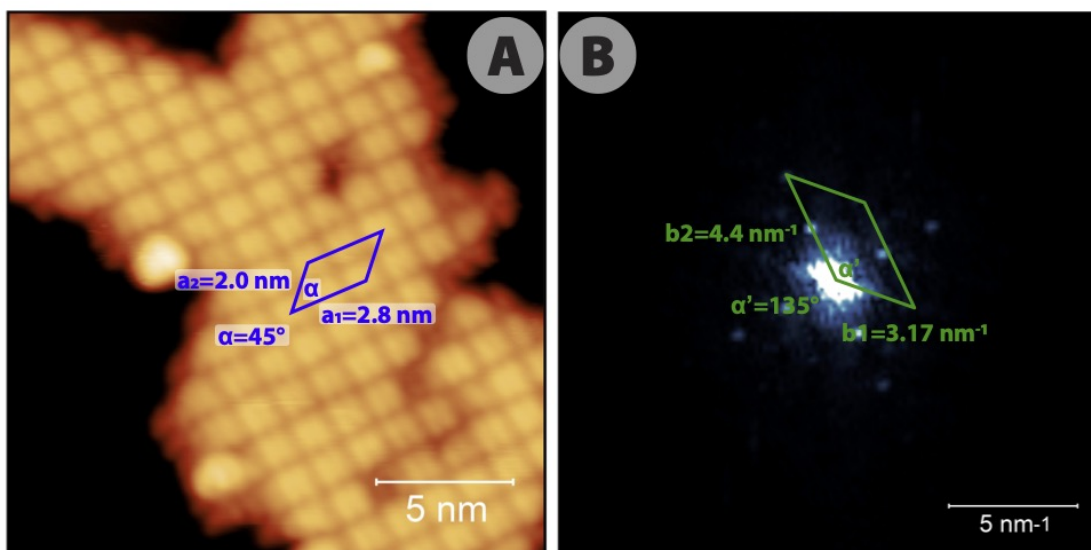


Figure S10: A) STM image of the bimetallic CoTPyPCo/Gr/Ir(111) layer (50 pA/+2.2 V) and in B) the corresponding FFT. Unit cells and parameters are indicated.

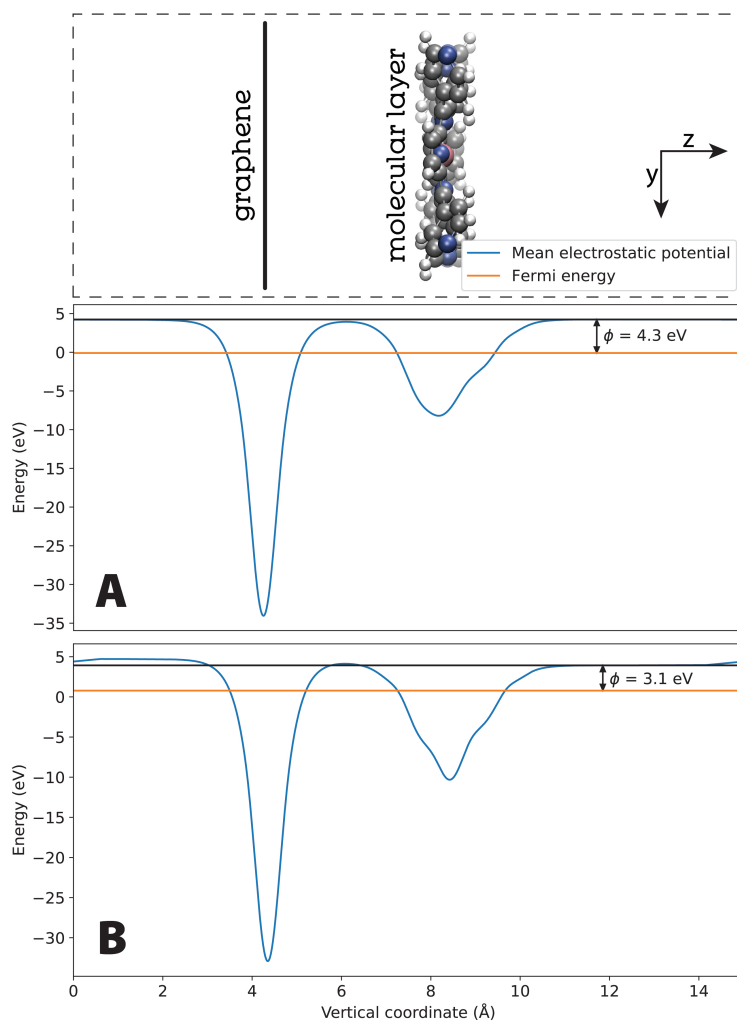


Figure S11: DFT electrostatic potential profile of monometallic CoTPyP (A) and bimetallic CoTPyP-Co (B) molecular layers. The workfunction is extracted from the electrostatic potential profile as the difference between its value in the vacuum region and the Fermi energy. The non-zero slope of the electrostatic potential at the cell edges is due to the application of a dipole correction.

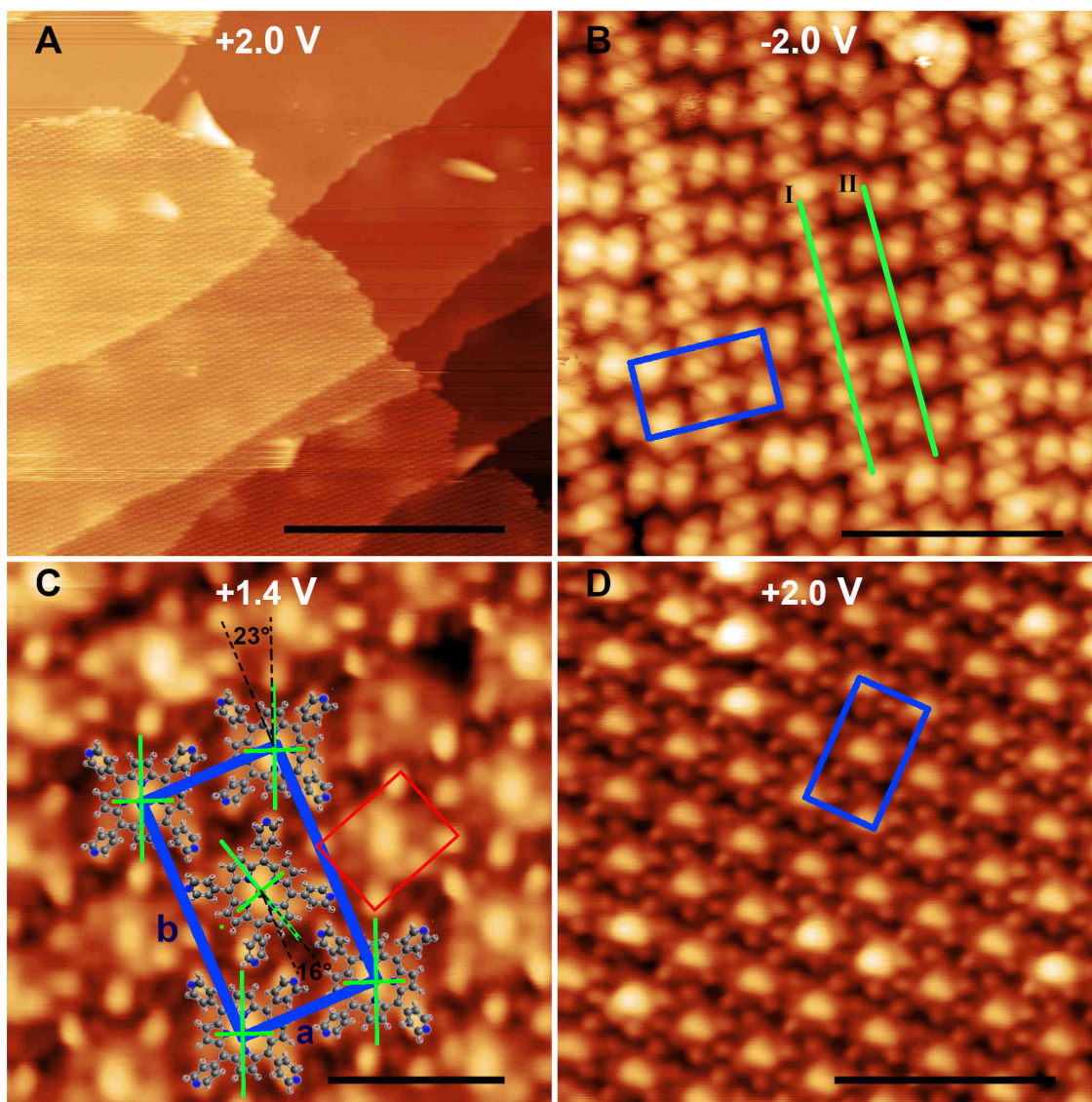


Figure S12: STM images at 77 K of ~ 0.5 ML of CoTPyP/Gr/Ir(111) at different bias and scales. The unit cell is indicated with blue lines. A) On a large scale, large CoTPyP islands are visible, indicating the high porphyrin mobility on graphene during the growth of the molecular layer (scale bar = 50 nm, $I = 0.1$ nA, $U_{\text{bias}} = +2.0$ V); B) At negative bias, where the HOMO is visible with a four lobes shape, the CoTPyPs are packed into two rows (green lines) (scale bar = 5 nm, $I = 0.1$ nA, $U_{\text{bias}} = -2.0$ V); C) With a bias closer to the HOMO-LUMO gap, the topography of the layer is more evident, with the CoTPyPs' two-fold symmetry due to saddle-shape adsorption configuration, the alternatively rotated pyridyl groups yielding a rectangular appearance (red rectangle), and the chirality of the cell originating from a misalignment between the molecule principal axis (green lines) and the unit cell (scale bar = 2 nm, $I = 0.3$ nA, $U_{\text{bias}} = +1.4$ V); D) At +2.0 V, the LUMO appears as a spherical protrusion centered on the cobalt atom (scale bar = 5 nm, $I = 0.2$ nA, $U_{\text{bias}} = +2.0$ V)

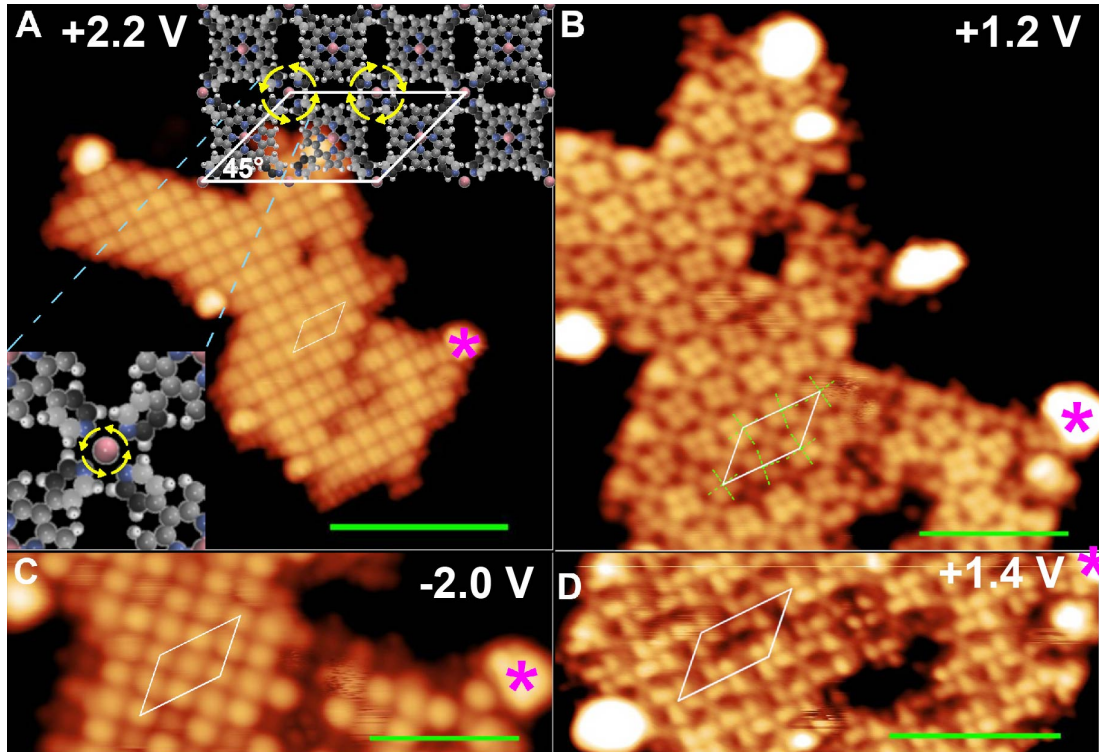


Figure S13: STM images at 77 K on a saturated CoTPyPCo island at different scales and bias. A unit cell with sides 2.84 nm and 2.02 nm² is drawn (white line). A purple asterisk indicates in the different images the position of the same physical spot on the sample. A) The alternating orientation of the pyridinic terminations are indicated with yellow circular arrows (scale bar = 10 nm, $I = 50$ pA, $U_{\text{bias}} = +2.2$ V), B) (scale bar = 5 nm, $I = 50$ pA, $U_{\text{bias}} = +1.2$ V), C) (scale bar = 5 nm, $I = 50$ nA, $U_{\text{bias}} = -2.0$ V), and D) (scale bar=5 nm, $I = 50$ pA, $U_{\text{bias}} = +1.4$ V).