Electronic Supplementary Information (ESI)

Surface-confined formation of conjugated porphyrin-based nanostructures on Ag(111)

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Methods

Synthesis of H$_2$TFPP

H$_2$TFPP (2) was synthesized according to a published procedure from 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (1) via a bromine-lithium exchange reaction.[1] For purification, the reaction mixture was washed with brine and sodium bicarbonate solutions. Column chromatography (silica) involved first using dichloromethane with 2% diethyl ether to remove impurities and then elution with acetonitrile. Recrystallizations from DCM/MeOH and ethyl acetate/hexane gave the pure product.
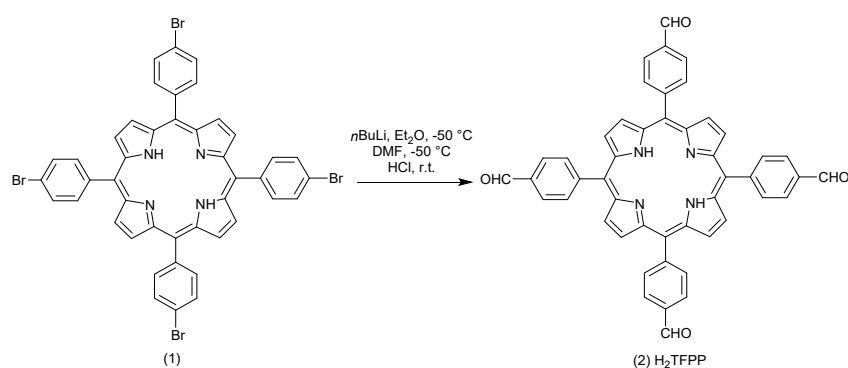
Scheme S1 Synthesis of target compound (2) H$_2$TFPP.

Sample preparation

The Ag(111) and Ag(100) single crystal surfaces were cleaned by repeated cycles of Ar$^+$ sputtering and subsequent annealing to 700 K. The quality and cleanliness of the substrate surfaces were assessed by STM and XPS. H$_2$TFPP molecules were dosed by organic molecular beam epitaxy (at a sublimation temperature of 665 K) onto the substrates held at room temperature. The deposition time was appropriately controlled to attain the desired molecular coverage.

McMurry-type reaction

The reactant molecule, H$_2$TFPP, studied in the present work is a porphyrin containing benzaldehyde functional group. The reaction was carried out on silver single crystal surfaces, Ag(111) and Ag(100), under UHV conditions, which is different from the classical McMurry reaction proceeded in solution.[2] However, the present on-surface reaction, performed in UHV systems, resulted in the formation of C=C, similar to the solution-based McMurry reaction. Therefore, we define the reaction in this work as the 'McMurry-type' reaction.

STM and nc-AFM measurements

STM/nc-AFM measurements were conducted with a commercial instrument (CreaTec) at 4 K at a base pressure below 1×10^{-10} mbar. All STM images were recorded in constant current mode. The tunnelling parameters (tunnelling current, I, and sample bias, V) are given in the respective Figure captions. Nc-AFM measurements were performed at constant height with a qPlus tuning fork sensor (resonance frequency ≈ 31 KHz, oscillation amplitude 80 pm, Q value ≈ 45000 to 75000, stiffness k = 1800 Nm^{-1}) operated in the frequency modulation mode at V = 0 V. The measurements were performed with CO-terminated tips, obtained by vertical manipulation of adsorbed CO molecules that were dosed onto the sample surface at T < 10 K. The determination of the Ag(111) and Ag(100) directions was enabled by STM images revealing the substrate lattice with atomic resolution.

XPS measurements

XPS measurements were carried out in a SPECS GmbH UHV system (base pressure of 3×10^{-10} mbar). A XR50 X-ray source with ellipsoidal crystal FOCUS 500 monochromator provided monochromatic Al Kα radiation ($h\nu$ = 1486.71 eV). Spectra were recorded with a PHOIBOS 150 hemispherical analyzer in normal emission geometry with the samples held at 300 K. The binding energies were calibrated against the Ag $3d_{5/2}$ – the main photoelectron line position of silver at 368.3 eV. Peak indentation and fitting were processed using CasaXPS software. The spectra were deconvoluted and fitted using a Shirley background. The C 1s peaks were fitted with FWHM of 1.0 to 1.4 and O 1s with 1.35.
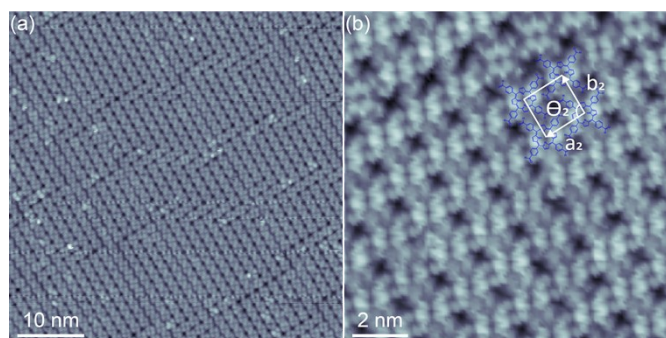
Experimental supplement

Figure S1 Self-assembled structure of H_2TFPP on Ag(111) upon annealing the sample at 455 K. (a) The close-packed self-assembled structure. (b) The molecular model is overlaid on the close-up image, with the lattice vectors of a_2 = 1.61 ± 0.02 nm, b_2 = 1.56 ± 0.02 nm and an angle of Θ_2 = 92 ± 1°. This is comparable with the self-assembled structure obtained at 300 K (Figure 1, see the main text). Scan parameters: (a) I = 10 pA, V = 1 V, (b) I = 30 pA, V = 30 mV.
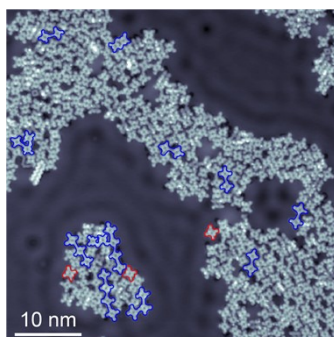

Figure S2 The overview STM image upon annealing the sample at 475 K. The ordered self-assembled structure transformed into small islands, which consist of oligomers (marked with the blue outline) and monomers (marked with the red outline). Statistical analysis shows that 65% of the molecules (out of 500 counted molecules in two STM image) have undergone coupling reactions, and 32% of the terminal aldehyde groups had reacted. In another word, the fraction of formed -C=C- connections is 32% of the theoretical maximum. Of the reacted molecules, about 25%, 26%, and 49% formed dimers, trimers, and oligomers (some of them with branches) consisting of more than four units, respectively. Scan parameters: (a) I = 12 pA, V = 50 mV.
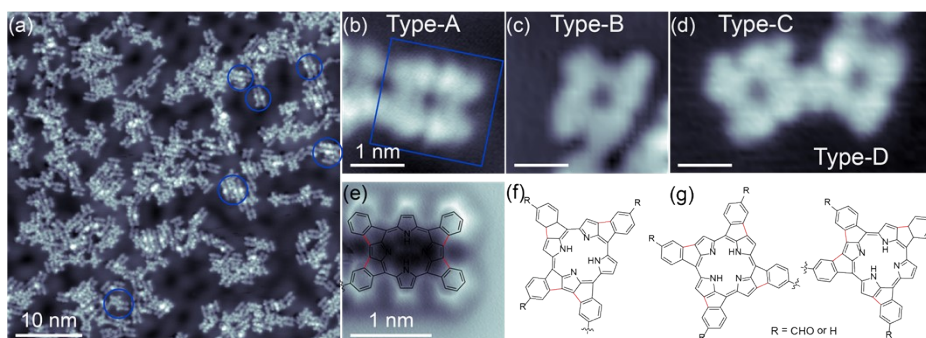
Figure S3 STM and AFM images upon annealing the sample at 515 K. (a) The large scale STM image shows no changes in molecular coverage (≈ 35%) compared to the sample annealed at 475 K, indicating no molecular desorption upon annealing. The small islands observed at 475 K underwent a further phase transition towards more disordered structures. Extended oligomeric or polymeric structures are not observed, potentially due to the loss of terminal aldehyde groups (see the main text). In addition to the -C=C- linked oligomers, other possible coupling motifs were also observed,[3] marked with the blue circles. (b) - (d) STM images of four planarized H_2TFPP derivatives, Type-A, -B, -C, -D, respectively. (e) AFM image of a Type-A molecule with the chemical structure overlaid. The terminal alkyne groups appear cleaved off. (f) The chemical structure of a Type-B molecule, corresponding to image (c). (g) The chemical structure of Type-C and Type-D molecules, corresponding to image (d). Note that none of the images exhibit bright features in their center (observed for self-metalated porphyrins), originating from thermally induced self-metalation by substrate Ag atoms.[3a, 3b, 4] STM scan parameters: (a) - (c) I = 12 pA, V = 50 mV, (d) I = 10 pA, V = 50 mV.
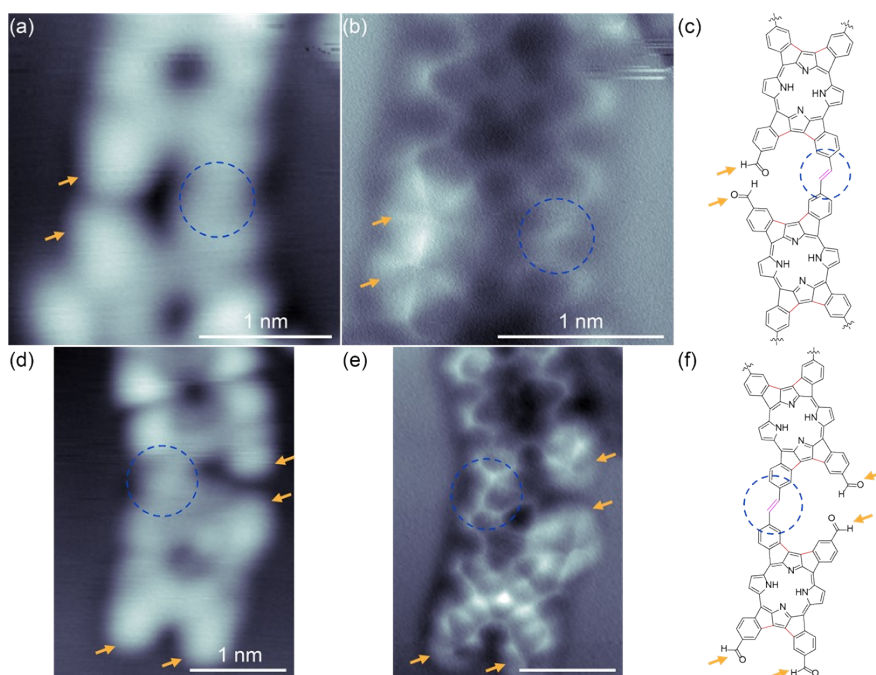

Figure S4 Close-up STM and AFM images of planarized *trans*-dimers upon annealing the sample at 535 K. (a) and (d) STM images of two dimers. (b) and (e) AFM images corresponding to (a) and (d), respectively. (c) and (f) The proposed chemical structures corresponding to (b) and (e), respectively. The STM images show a pronounced bright appearance at the unreacted aldehyde groups, in contrast to a more uniform brightness observed for the -C=C- bond. The -C=C- linkage is marked by the dashed blue circles, and the unreacted aldehyde groups are marked by orange arrows. STM scan parameters: (a) and (d) I = 10 pA, V = 50 mV.
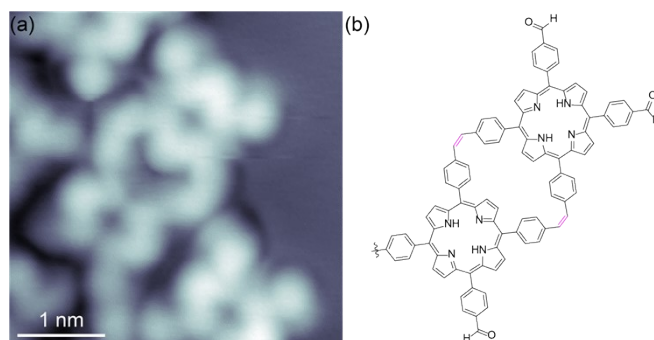
Figure S5 (a) STM image of a *cis*-dimer upon annealing the sample at 475 K. (b) The chemical structure corresponding to (a). Scan parameters: (a) *I* = 10 pA, *V* = 50 mV.
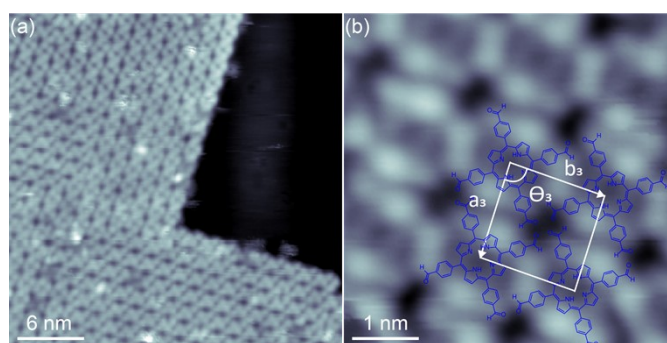

Figure S6 Self-assembled structure of H_2TFPP on Ag(100) after deposition at 300 K. (a) An overview STM image of the self-assembled structure. (b) Zoom-in image of (a) with the chemical structure overlaid. The unit cell can be described by $a_3 = b_3 = 1.56 \pm 0.02$ nm with an angle of $\Theta_3 = 89 \pm 1°$, which is very close to the values measured from the self-assembled structure achieved on Ag(111). Scan parameters: (a) *I* = 10 pA, *V* = 500 mV, (b) *I* = 10 pA, *V* = 100 mV.

Table S1 Contributions of C 1s spectra collected from the H_2TFPP on Ag(111) upon depositing at 300 K and stepwise annealing. All XPS measurements are taken at 300 K.

Temperature	300 K		475 K		515 K	
C1s	Binding energy	Elemental analysis / concentration	Binding energy	Elemental analysis / concentration	Binding energy	Elemental analysis / concentration
-CHO (blue)	287.8 eV	9%	287.8 eV	4%	287.5 eV	2%
C=N, C-N (green)	285.7 eV	17%	285.6 eV	17%	285.5 eV	18%
C-C carbons (violet)	285.2 eV	24%	284.8 eV	25%	284.6 eV	25%
CH=CH of phenyl and pyrrole, and newly formed C=C (red)	284.8 eV	50%	284.5 eV	54%	284.3 eV	55%

In our XPS analysis, the C/O atomic ratio is about 11.6 for precursors adsorbed on the substrate at 300 K, which is very close to the stoichiometric ratio of 12 for intact molecules. Upon thermal annealing the substrate to 475 K, the C/O ratio increases to approximately 25, indicating on the 50% loss of oxygen, which is considerably greater than the reaction yield of 32% obtained from the statistical analysis of the molecular features imaged by STM (Figure S2). It should be pointed out that an accurate statistical analysis of the cleaved aldehyde groups is difficult to perform due to the limited resolution of STM images. Therefore, the 50% loss of oxygen, retrieved from the XPS data, includes the cleavage of aldehyde group and the portion of the molecules that have undergone the coupling reaction.

It should be mentioned that very few XPS spectra for porphyrin-containing compounds have been reported where the carbon peaks have been resolved experimentally (in synchrotron facilities) or fitted accordingly. In most studies, all carbon atoms (except C-N) have been fitted with one peak.[5]

However, based on a few publications where CH=CH carbons and C-C carbons have been fitted separately or resolved,[6] and to illustrate the generation of newly formed C=C in our study, we have fitted accordingly to separate CH=CH carbons from C-C carbons, which can also be supported by theoretical XPS fitting.[7]

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