Supplementary Information

Porphyrin metalation providing an example of a redox reaction facilitated by a surface reconstruction†

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Experimental conditions

All experiments have been performed in an ultra-high vacuum (UHV) system with base pressure in the order of 10^{-10} mbar. Cu(001) single crystals were cleaned by Ar^+ sputtering and annealing cycles and their cleanness was confirmed by XPS. The $(\sqrt{2}x2\sqrt{2})R45^o$ O-reconstruction was prepared by dosing 3000 L of O_2 over 1000 s into the vacuum chamber with Cu(001) crystal annealed to ~500 K. 2HTPP molecules (Sigma-Aldrich, ≥ 99% purity) were sublimed onto atomically clean or O-reconstructed Cu(001) substrate kept at ~100 K. Samples were warmed up to RT by switching off the cooling. Rate of evaporation was controlled with a quartz-crystal microbalance. Monochromatised Al Kα line was used for XPS measurements. STM measurements were performed at ~160 K (Fig. 3b) and at RT (Fig. 1c, 1d, 3a and 3c) in constant current mode using electrochemically etched and in situ sputtered tungsten tips. Tunneling parameters used for each figure are given in Tab. S1; positive bias voltage corresponds to tunneling into unoccupied electronic states of the sample. The STM images were processed using WSxM software.[1]

Table S1 Bias voltage and tunneling current used to obtain presented STM images.

Figure	Sample	Bias voltage (V)	Tunneling current (pA)
1c	Cu(001)	-1.31	70
1b (inset)	Cu(001)	-0.034	930
1d	O/Cu(001)	1.03	20
1c (inset)	O/Cu(001)	1.03	10
3a	2HTPP/Cu(001)	0.83	10
3b	2HTPP/O/Cu(001)	2.22	30
3c	2HTPP/O/Cu(001)	2.15	10
S2a	2HTPP/Cu(001)	2.3	10
S2b	2HTPP/Cu(001)	2.1	10
S3a	2HTPP/O/Cu(001)	2.2	20
S3b	2HTPP/O/Cu(001)	2.2	10

Concentration of elements in XP spectra before and after the metalation

Table S2 Concentration of Cu, O, C and N elements before and after metalation showing decrease in the amount of oxygen, while concentrations of other elements did not significantly change.

Element	Cu	O	C	N
Concentration before metalation	87.16	3.06	8.78	1.00
Concentration after metalation	87.49	2.68	8.79	1.03
Change	+0.4%	-12.4%	+0.1%	+3.0%

Metalation of 2HTPP on Ni/Cu(001) and on O/Ni/Cu(001) surfaces

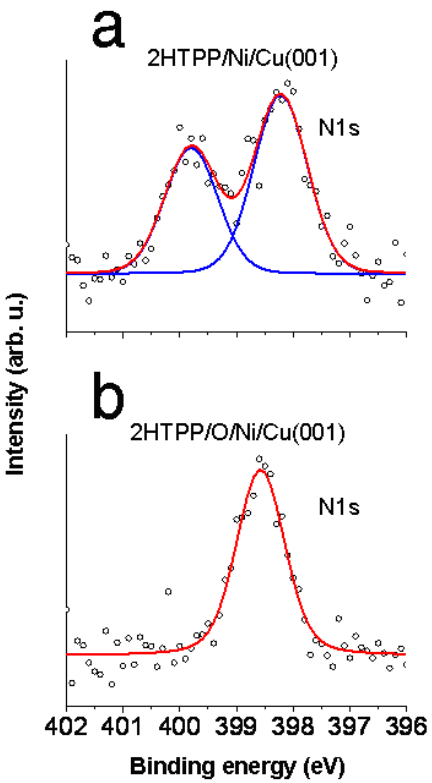

Figure S1 N1s XPS data of 2HTPP put on Ni/Cu(001) and oxygen-reconstructed Ni/Cu(001) substrates. (a) 2HTPP/Ni/Cu(001) at RT; two peaks indicate that molecules did not metalate. (b) 2HTPP/O/Ni/Cu(001) at RT; metalation reaction has been facilitated by the oxygen reconstruction.

Influence of bias voltage and temperature on the appearance of 2HTPP molecules in STM images

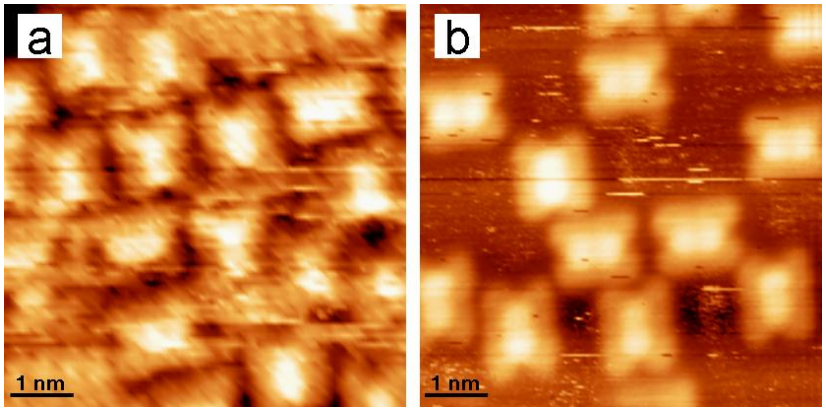

Figure S2 Constant current STM data of 2HTPP on Cu(001) obtained (a) at ~160 K with bias voltage V_b=2.3 V and (b) at RT with V_b=2.1 V. In both cases, not depending on the temperature of the sample or the bias voltage (cf. Fig. 3a), molecules are in saddle shape conformation.

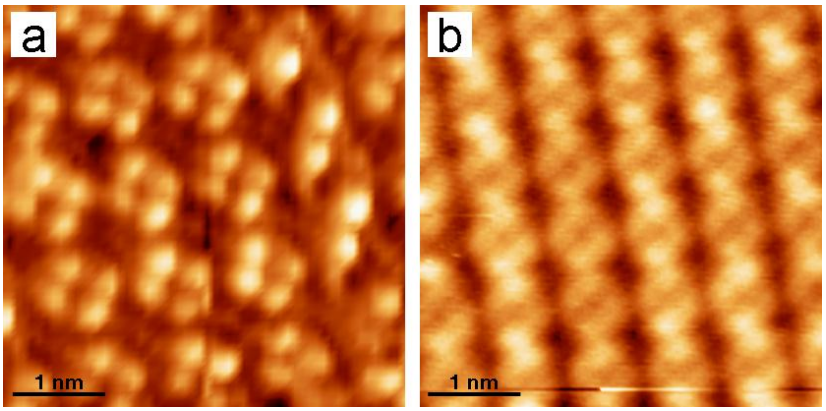

Figure S3 Constant current STM images of 2HTPP put on O/Cu(001) after metalation obtained (a) at ~160 K with V_b=2.2 V and (b) at RT with V_b=2.2 V. The temperature of the sample does not change the conformation of the molecules – in both images molecules appear four-fold symmetric, i.e. are in flat conformation. Please note, that images (a) and (b) were obtained using different scanning directions. They were, however, rotated for the crystallographic directions to match.

Notes and references

[1] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, *Rev. of Sci. Instrum.*, 2007, **78**, 013705.