Supporting Information

Tunable Interface of Ruthenium Porphyrins and Silver

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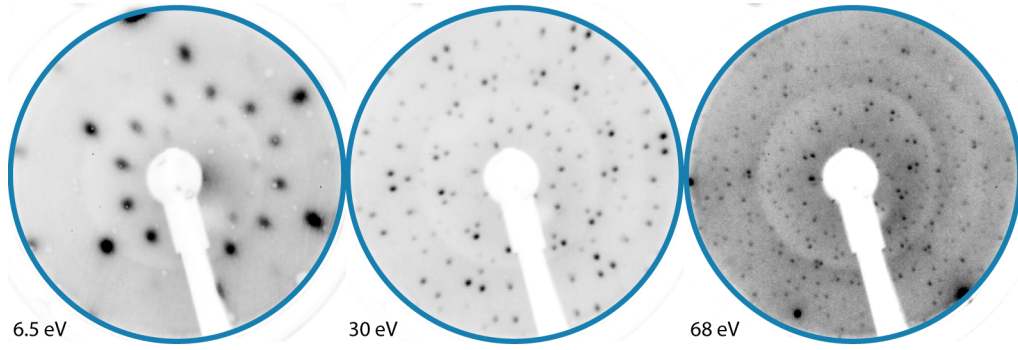
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Figure S1: LEED pattern of square phase of Ru-TPP on Ag(111) at different electron energies.
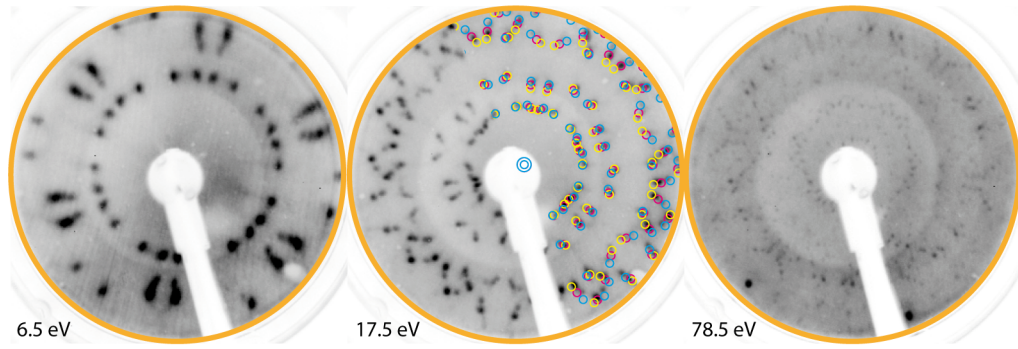

Figure S2: LEED pattern of the compressed phase of Ru-TPP on Ag(111) at different electron energies. At 17.5 eV there are different superstructures overlaid in different colors. Pink: $\begin{pmatrix} 4.00 & 5.00 \\ 3.00 & -2.17 \end{pmatrix}$, yellow: $\begin{pmatrix} 5.17 & 4.04 \\ -2.37 & 2.88 \end{pmatrix}$, blue: $\begin{pmatrix} 3.89 & -0.93 \\ 3.21 & 5.16 \end{pmatrix}$.
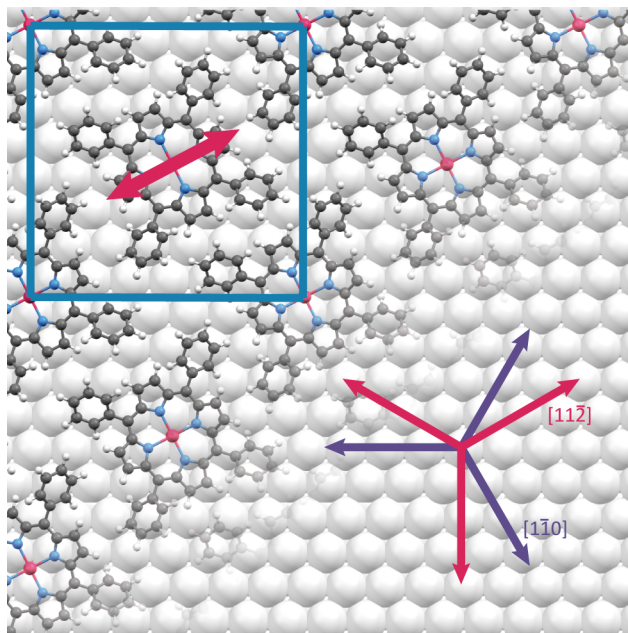
Figure S3: Model of square phase Ru-TPP on Ag(111), elucidating the registry to the substrate. The family of the high symmetry $\langle 1\bar{1}0 \rangle$ directions is marked in violet, the family of the $\langle 11\bar{2} \rangle$ directions in pink. The unit cell of the Ru-TPP is marked in blue, the α-pyr axis of the Ru-TPP is marked in pink according to the substrate alignment.

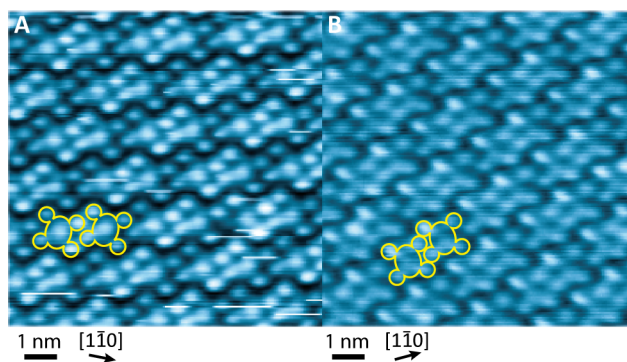

Figure S4: STM image of the square phase of Ru-TPP (A: 1.25 V, 20 pA, 300 K, B: 2.5 V, 90pA, 300 K). The two outlined molecules show one example for a dimer, which can be easily recognized under these imaging conditions.

Estimation of Coherent Fraction and Position from DFT Geometry

For the comparison of NIXSW data with the DFT simulations, we have simulated the coherent fraction f_H and coherent position P_H based on the geometry of the DFT as following:[1]

$$f_H = \sqrt{\left(G_H^c\right)^2 + \left(G_H^s\right)^2} \tag{1}$$

$$P_H = \frac{1}{2\pi} \arctan\left(\frac{G_H^s}{G_H^s}\right) \begin{cases} +\frac{1}{2} \text{ if } G_H^c < 0 \\ +0 \text{ otherwise} \end{cases} \tag{2}$$

$$G_H^c = \frac{1}{N} \sum_{i=1}^{N} \cos\left(2\pi \frac{d_i}{a}\right) \tag{3}$$

$$G_H^s = \frac{1}{N} \sum_{i=1}^{N} \sin\left(2\pi \frac{d_i}{a}\right) \tag{4}$$

Here N denotes the number of atoms that are contributing to the signal, d_i is the adsorption height of the i-th atom and a the lattice spacing of the crystal. It should be emphasized, that the calculated average adsorption height, determined by the coherent position P_H does not necessarily correspond to the actual average adsorption height of the measured atoms. If the adsorption height of two atoms differs by exactly half a lattice spacing, they will not contribute to P_H, which can be seen in the formulas above as a cancelling of their contributions due to the periodicity of the cos and sin functions. In the case of the Ru-TPP, an average adsorption height of the C atoms of 3.53 Å was calculated via DFT. However, calculating the coherent position that would be measured by a NIXSW experiment for this geometry resulted in $P_H = 0.36$, equivalent to an adsorption height of 3.20 Å. For the planarized Ru-TPP and the Ru centres the adsorption height extracted from the coherent position matches the average adsorption height of the corresponding species due to their more uniform adsorption heights, which does not allow the cancelling of single contributions.

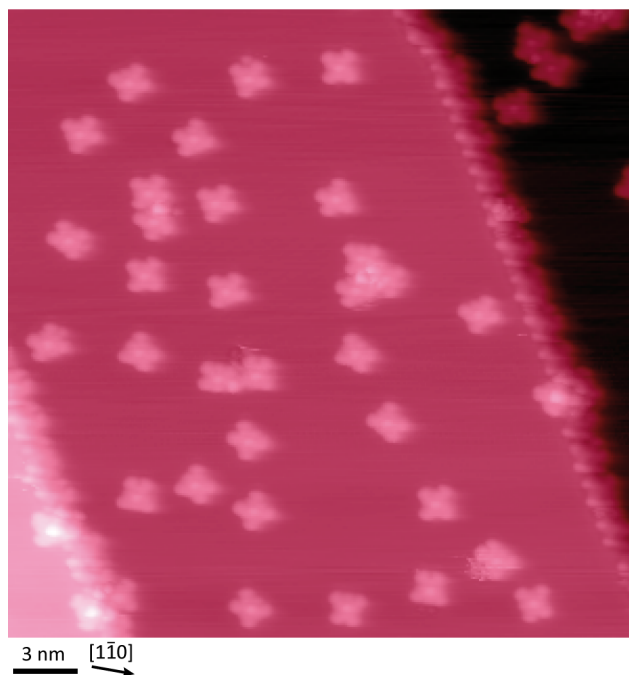[1]J. Zegenhagen, *Surf. Sci. Rep.*, 1993, **18**, S. 202.

Figure S5: STM image (-0.5 V, 50 pA, 5 K) of a low coverage of planar Ru-TPP derivates after annealing to 620 K.
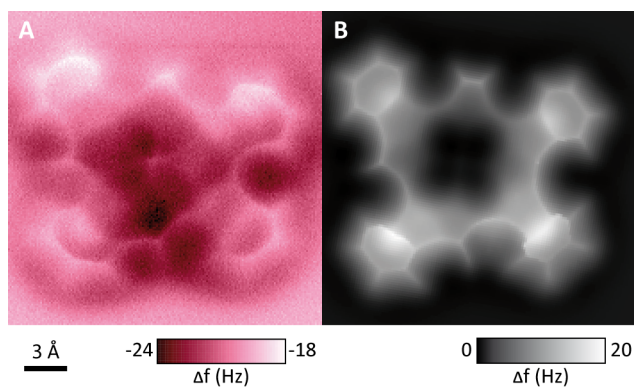

Figure S6: Comparison of nc-AFM frequency shift image (A) and respective simulation based on the DFT model (B) of a planarized Ru-TPP of the most abundant derivate (see Fig. 5B).[2]

[2] P. Hapala, G. Kichin, C. Wagner, F. S. Tautz, R. Temirov, P. Jelínek, *Phys. Rev. B*, 2014, **90**, S. 85421.; P. Hapala, R. Temirov, F. S. Tautz, P. Jelínek, *Phys. Rev. Lett.*, 2014, **113**, S. 226101.
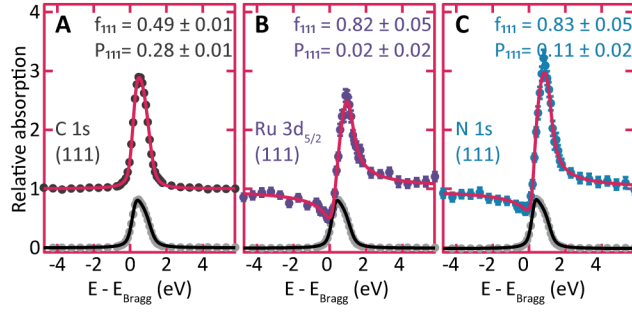
Figure S7: NIXSW fits in (111) reflection for planar Ru-TPP derivates on Ag(111), measured at 300 K. Element and core level with the respective coherent fraction and position are given for each spectrum, the red line shows the fit for the indicated element, the black lines shows the reflection of the silver substrate.

Table S1: NIXSW results: Coherent fractions f_{hkl} and coherent positions P_{hkl} satisfying Bragg conditions from the (hkl) plane of the Ru, C and N signals of planar derivates of Ru-TPP on Ag(111) recorded at 300 K.

	(hkl)	f_{hkl}	P_{hkl}	Adsorption height (Å)
Planarized Ru-TPP at 300 K				
Ru 3d$_{5/2}$	(111)	0.82 ± 0.05	0.02 ± 0.02	2.41 ± 0.05
C 1s	(111)	0.49 ± 0.01	0.28 ± 0.01	3.02 ± 0.02
N 1s	(111)	0.83 ± 0.05	0.11 ± 0.02	2.62 ± 0.05