Electronic Supplementary Information

Stability of bifunctional metallo-porphyrin networks under oxygen reduction and evolution conditions in alkaline media

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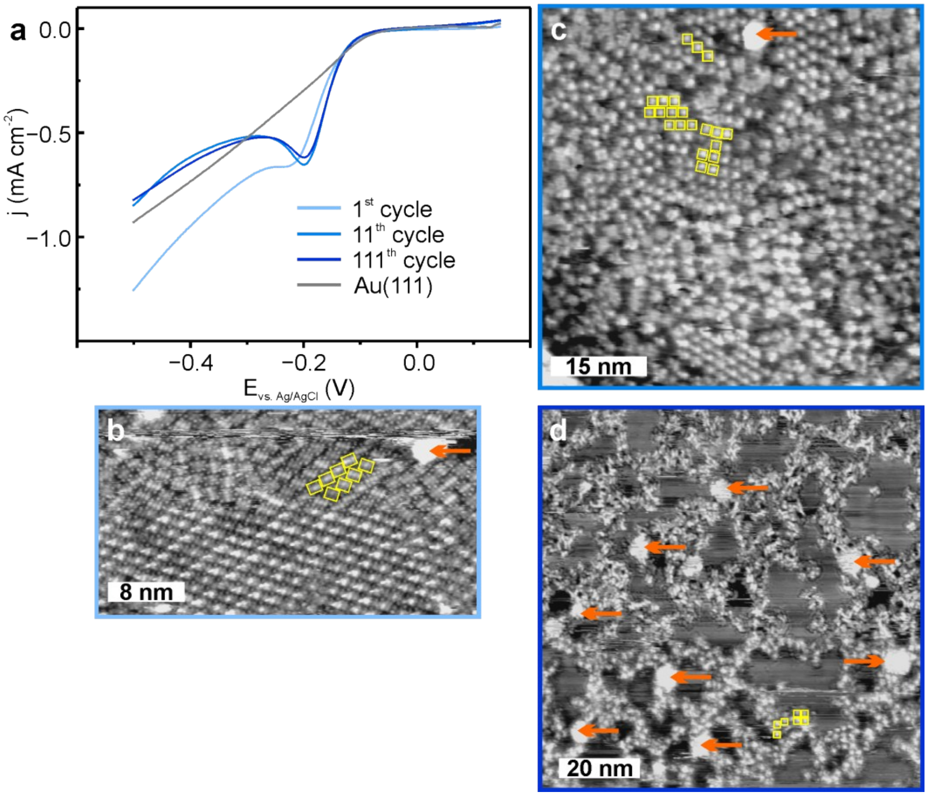

Figure SI 1: Comparison of topography after several LSV in the ORR region. (a) LSV (+0.15 V to −0.5 V, 50 mV s^{-1}, 0.1 M NaOH, O_2 sat.); STM images *post*ORR (b) after the first cycle (I_{tunnel} = 0.4 nA, U_{bias} = 0.9 V); (c) after 11 cycles (I_{tunnel} = 0.3 nA, U_{bias} = 1.2 V); (d) after 111 cycles (I_{tunnel} = 0.4 nA, U_{bias} = 1.3 V). Color code: molecules (yellow rectangles), cluster (orange arrow).

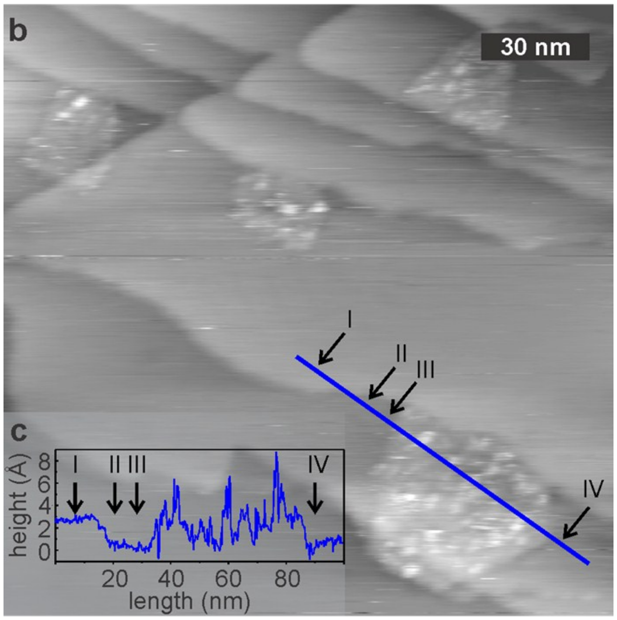

Figure SI 2: 2D topograph of Fig. 3b of the main manuscript (I_{tunnel} = 0.23 nA , U_{bias} = 1.3 V).

XAS N K-edge:

Contamination of the incoming x-ray signal due to N contaminated optics in the beamline leave the XAS at N K-edge inconclusive. However, the subtraction of the two different polarization directions (linear dichroism, XLD) allows sparse insights on the fate of the organic backbone. Subtraction of the signals leads to cancellation of the contamination background.

The similarity of the XLD at the N K-edge after ORR is reminiscent of the *pre*EC signal demonstrating the integrity of the organic backbone (Fig. SI 3a), in agreement with STM results.

In contrast, the lack of XLD after OER is rather difficult to interpret without the corresponding XAS (Fig. SI 3b). It can only be concluded that N components are isotropic. This could be explained by randomly oriented molecules for example in the form of large cluster as demonstrated by STM. However, the lack of XLD can also be explained by the decomposition of the organic back bone. While randomly oriented but intact molecules would demonstrate a XAS signal, this is not the case if decomposition took place. The data for this system cannot conclude whether residual organic components are still present after OER.

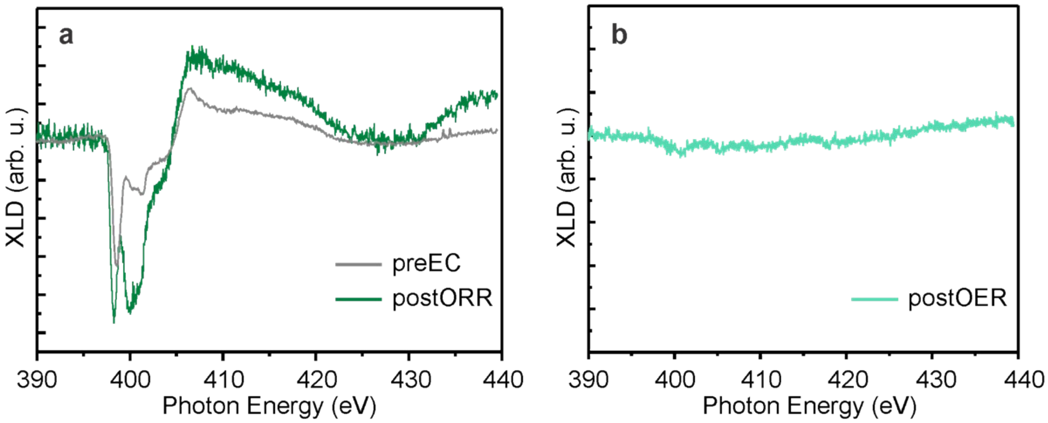

Figure SI 3: XLD ($\sigma^v - \sigma^h$) at N K-edge of FeTPyP+Co. (a) *pre*EC (grey) and *post*ORR (green); (b) *post*OER (light green).

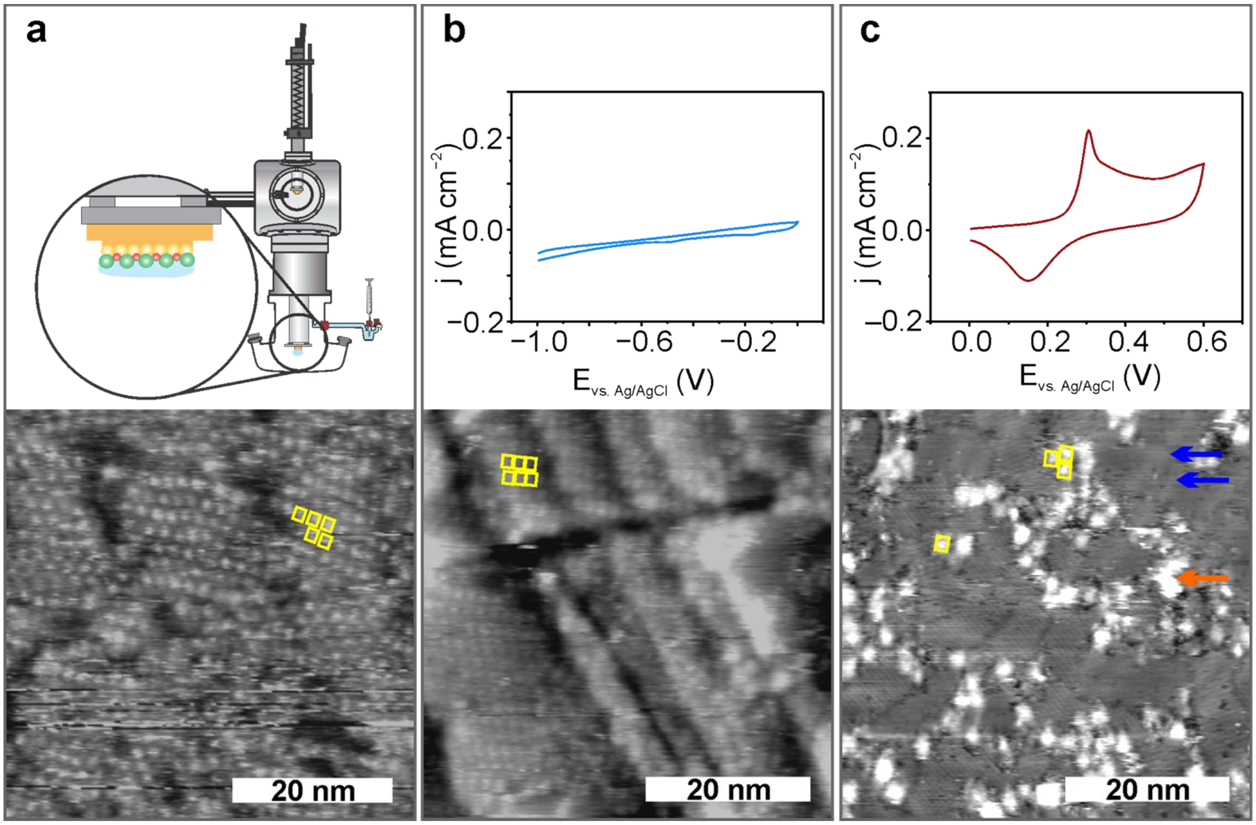

Figure SI 4: Stability depending on the potential window applied to the working electrode. (a) After exposure to a drop of Ar saturated 0.1 M NaOH for 5 min (I_{tunnel} = 0.3 nA, U_{bias} = 0.8 V). This is equivalent to an open circuit of ~0.1V vs. the Ag/AgCl reference electrode if measured in a closed EC set-up. (b) After the negative potential range that is associated with the double layer region of Au(111) (I_{tunnel} = 0.3 nA, U_{bias} = 0.8 V). (c) After the positive potential range that is applied to the working electrode for OER (I_{tunnel} = 0.2 nA, U_{bias} = 0.8 V). Color code: molecules (yellow rectangles), cluster (orange arrow), Au(111) reconstruction lines (dark blue arrow).