

# Radical Induced Intermolecular Linkage and Energy Level Modification of a Porphyrin Monolayer

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## 1 Experimental Procedure and Materials

Au(111) films with well-defined terraces were deposited on mica in a cryo-pumped chamber with a base pressure of  $2 \times 10^{-9}$  Torr. The thickness of each Au film was monitored by a quartz crystal microbalance until the final thickness of  $\sim 1200$  Å was achieved. The gold films were annealed with a hydrogen flame just prior to use, and a new piece of gold was used for each experimental measurement. Cobalt octaethyl porphyrin (97%) was purchased from Aldrich and used as supplied, and toluene ( $> 99.5\%$ ) was supplied by J. T. Baker. The porphyrins were solvated in toluene with a concentration of  $3.7 \times 10^{-4}$  M, and the STM samples were fabricated by placing a 5  $\mu$ L droplet of this solution directly on the gold surface. Once the porphyrin molecules were deposited on the surface and the extra toluene is evaporated (takes about 30 s), the sample was rapidly transferred to the high-vacuum loading dock of the UHV gas-surface system. The main gas-surface reaction chamber consisted of a thermal gas cracker (MANTIS Deposition LTD) and a UHV STM (McAllister Technical Services).<sup>1</sup> Oxygen atoms were produced by thermally dissociating molecular oxygen purchased from Air Liquide, and according to MANTIS Deposition LTD, only O(<sup>3</sup>P) was produced by this pyrolytic method. The O-atom beam was directly aligned to the STM tip-sample junction, and the “beam-on” pressure of the STM chamber was  $\sim 1 \times 10^{-9}$  Torr. Both etched and hand-cut Pt<sub>0.8</sub>Ir<sub>0.2</sub> tips (Nano Science Instruments) were used for STM/STS experiments. For orbital mediated tunneling (OMT) spectroscopy measurements, a 100 Å  $\times$  100 Å STM image was first taken, followed by positioning the tip over one of the CoOEP molecules on the surface. With a fixed tip-sample distance, and the feedback loop was turned off. 50 dI/dV spectra were recorded for each measurement, and the averaged signal values were reported in the main article. Due to thermal drift at room temperature, the averaged data represent OMT signals over an entire CoOEP molecule instead of for a specific sub-molecular unit. All STM images reported were collected in the constant current mode.

## 2 Reflection Absorption Infrared Spectroscopy

Reflection absorption infrared spectra (RAIRS) were collected *ex-situ* and under rough vacuum conditions with a commercially available Bomem DA8 spectrometer.<sup>2</sup> The reported RAIRS spectrum in Figure S1 represents the negative base ten logarithm of the reflectance ratio of the exposed vs. unexposed monolayers with a spectral bandwidth of  $4\text{ cm}^{-1}$ . Since these *ex-situ* infrared measurements required exposure of the modified monolayer to atmosphere, additional STM surface characterization was performed to monitor the surface cross-linking structure after the sample was pumped out from the UHV STM chamber, and no obvious change of monolayer structure was observed. It is important to note that the absence of a peak at  $1645\text{ cm}^{-1}$  indicates the equal amount of atmospheric water molecules on both sample surfaces.<sup>3</sup> One should also keep in mind that RAIRS, as a surface-based technique in comparison to the transmission-based IR measurements, is subject to a surface selection rule that molecular vibrational modes giving rise to the dynamic dipole moments have higher RAIRS signals when perpendicular to the surface.<sup>4</sup> Therefore the negative absorbance peaks in Figure S1 can result from either an actual population decrease of the particular vibrational mode or the reorientation of molecular geometry that makes such vibrational mode more parallel to the surface.

First and most importantly in Figure S1, the broad peak centered around  $3350\text{ cm}^{-1}$  can be directly attributed to intermolecular hydrogen bonding with possible formation of  $-\text{OH}$  groups on the ethyl “arms” of the CoOEP molecules.<sup>5</sup> This and the STM observations together indicate that the intermolecular features are composed of ethyl groups being functionalized by oxygen atoms and are further stabilized via hydrogen bonding between three neighboring CoOEP molecules. Secondly, the weak peak centered at  $2341\text{ cm}^{-1}$  can be assigned to the high-frequency anti-symmetric stretching of an isocyanate ( $\text{R}-\text{NCO}$ ) type structure.<sup>6</sup> This and the observed STM on-the-edge features (Figure 2 of the article) together suggest that O-atoms are directly attached onto the pyrrole moieties of the CoOEP molecules. Furthermore, the positive signal centered around  $1530\text{ cm}^{-1}$ , which can be attributed to the formation of a nitroso  $-\text{N}=\text{O}$  structure, suggests that possibly other oxygen atoms are also attached to the nitrogen atom in the pyrrole moieties. Lastly, the negative peaks centered around  $1140$  and  $1730\text{ cm}^{-1}$  can be attributed to the loss of substituted aromatic structures (*cf.* Table 5 and Figure 9 of Ref. 5) in accordance with the attachment of an O-atom on the pyrrole moiety that disrupts the conjugated system. There is also a possible change of molecular surface orientation that makes the C–N stretch mode more parallel to the surface after the O-atom exposure, which results in the negative peak at  $1270\text{ cm}^{-1}$ .

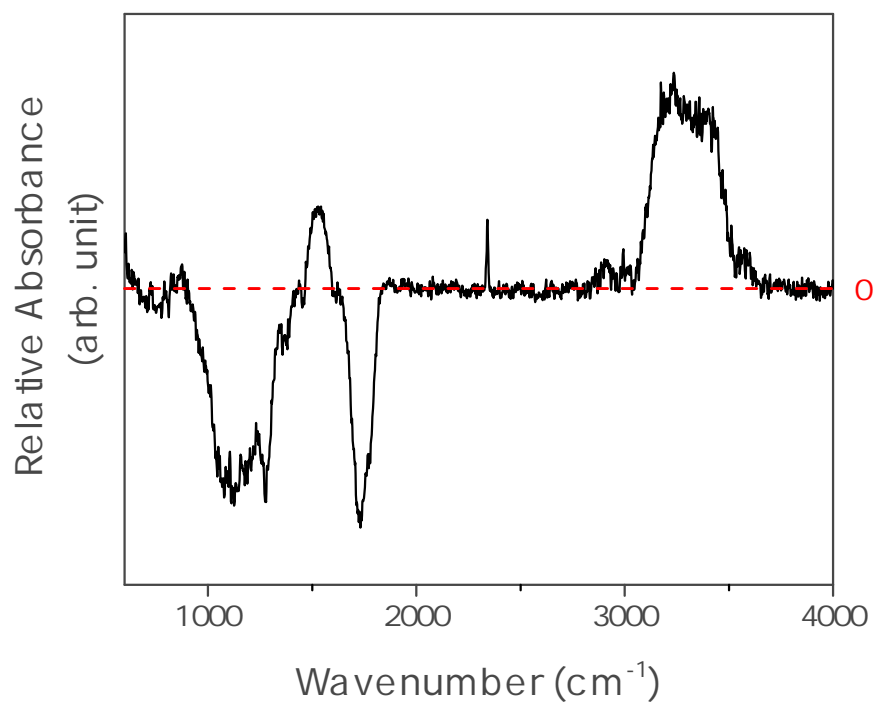


Fig. S1: Direct comparison (the negative base ten logarithm of the reflectance ratio) of the reflection-absorption infrared spectra for the O-atom exposed vs. unexposed CoOEP monolayers.

## References

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