

**Direct observation of surface-mediated thioacetyl deprotection:
covalent tethering of a thiol-terminated porphyrin to the Ag(100) surface**

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Supporting Information

Experimental details

The $[\text{SAC}]_4\text{P-H}_2$ was prepared according to the method previously described by Lindsey *et al.*² Experiments were carried out in an Omicron variable temperature UHV STM. Apparent heights were calibrated using the Ag(100) step height. $[\text{SAC}]_4\text{P-H}_2$ was deposited by evaporation under UHV conditions (source temperature 473 K) onto the clean atomically flat Ag(100) surface held at 298 K.

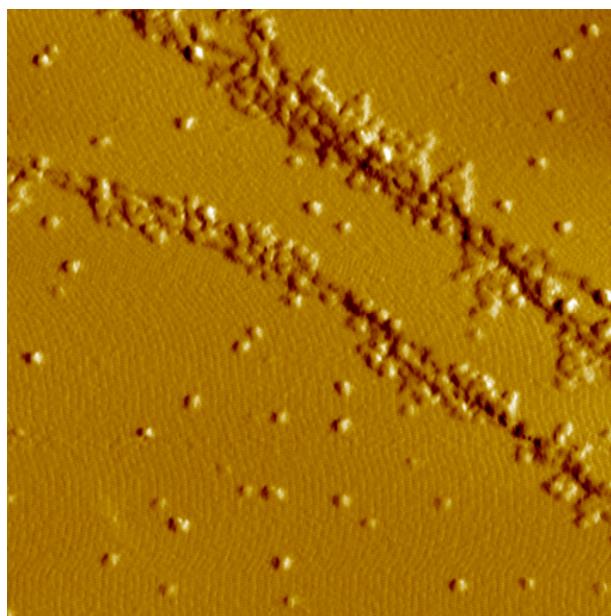


Figure S1 Room-temperature STM image of *deprotected* $[\text{SAC}]_4\text{P-H}_2$ on Ag(100) imaged following exposure to O_2 and elevated temperature of 325 K ($650 \text{ \AA} \times 650 \text{ \AA}$, $V_{\text{tip}} = 1.0 \text{ V}$, $I = 0.1 \text{ nA}$; edge enhanced). This image corresponds to conditions as those applied in Figure 3c, but was taken after cooling to room temperature.

Figure S1 clearly highlights both the absence of acetyl groups, which have been burned off upon heating the O_2 -exposed surface, and the affinity for step edges which is exhibited by the mobilised deprotected porphyrins.

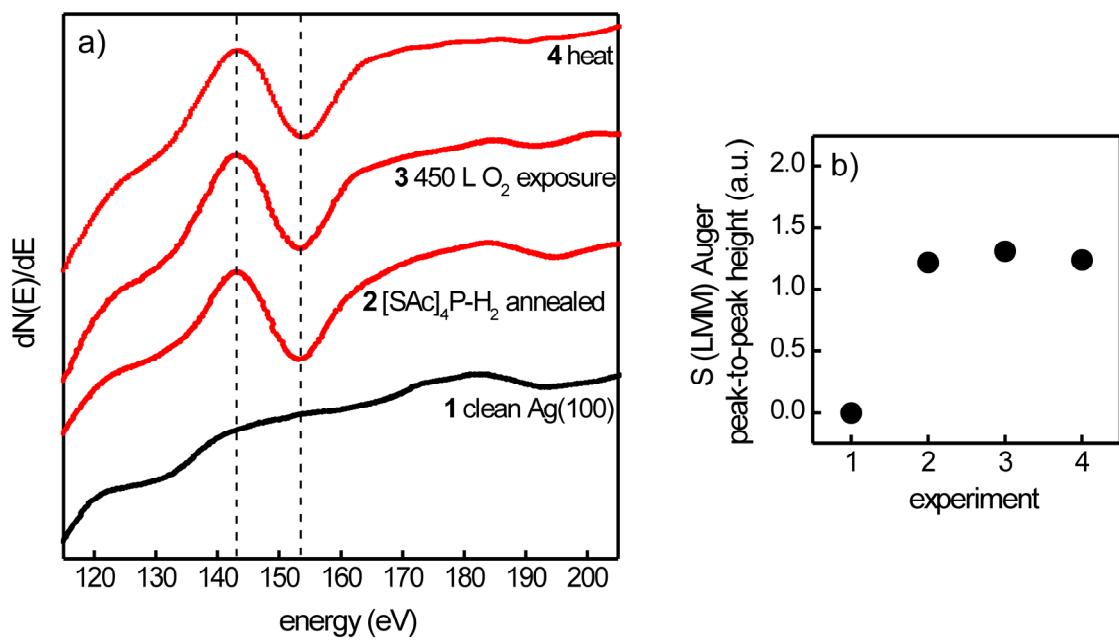


Figure S2 (a) Auger electron spectra acquired at each stage of the experimental procedure as described in the main text, with associated peak-to-peak heights (b) for the sulfur (LMM) transition. It is apparent that the amount of sulfur present on the surface was constant, within the experimental error.