Electronic Supplementary Information

Experimental details

The Ag(111) crystal was cleaned by the normal combination of sputtering and annealing cycles, specifically being sputtered for 30 minute intervals with an emission current of 20 mA and a voltage of 1 kV, before subsequent annealing to 725 K at 5 K/s with the temperature being measured by a K-type thermocouple in physical contact with the crystal.

The Ru-TPP monolayer was formed by subliming Ru(CO)-TPP powder (80% pure by dye content; Sigma Aldrich) with the powder held at 680 K for 20 minutes and the sample held at room temperature to deposit a multilayer of the molecule. Subsequently the sample was annealed to 550 K for 10 minutes resulting in a monolayer coverage of Ru-TPP. Prior to deposition, the powder was outgassed at 620 K and the evaporation temperature for 30 minutes each.

The Ti-TPP monolayer was formed by subliming 2H-tetraphenyl porphyrin (2H-TPP, >99.9% purity; Sigma Aldrich) with the powder held at 550 K for 10 minutes and the sample held at room temperature to deposit a multilayer of the molecule. After evaporation the sample was annealed to 500 K for 15 minutes resulting in a monolayer coverage of 2H-TPP. Titanium (0.01 nm, monitored by a quartz microbalance, corresponding to ~1 Ti atom per adsorbed 2H-TPP molecule on the surface) was then evaporated onto the sample through resistive heating of a Ti-W alloy wire. The cleanliness of the Ti evaporation was checked by XPS from Ti evaporated onto the clean Ag(111) surface. The sample was subsequently annealed to 500 K to facilitate metalation, as observed in the changes to the N 1s XP spectra (Fig. SI 1), of the 2H-TPP to Ti-TPP – the characterisation of which will be more fully discussed in a future publication.[SI1]

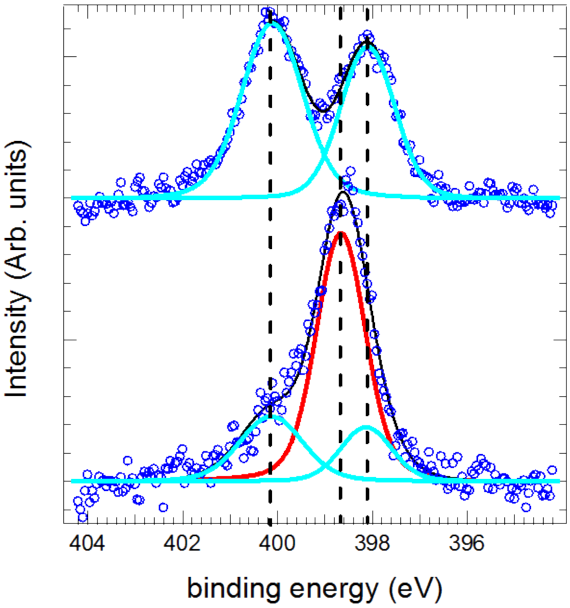

Fig. SI 1 N 1s XP spectra of (top) Ag(111)/2H-TPP and (bottom) Ag(111)/Ti-TPP. The transformation of the N 1s XP spectra from two features to one is the prototypical evidence for on surface porphyrin metalation.[SI2]

Both the Ru-TPP and the Ti-TPP were exposed to oxygen via a needle doser attached to a differentially pumped gas dosing system. The exposure was monitored by a membrane gauge in the gas dosing system and was calibrated to an approximate Langmuir scale by the exposure required to obtain half of a complete monolayer of Ar on Co(0001), ~1.5 L.

Table SI 1 Binding energies of the main peak observed in the Ti 2p XP spectra for Ti deposited on clean Ag(111) before (Ag(111)/Ti) and after (Ag(111)/TiO_x) exposure to 200 L of O_2. Also shown are the same values for the TPP molecule metalated with titanium before (Ag(111)/Ti-TPP) and after (Ag(111)/TiO-TPP) exposure to 75 L of O_2. All four spectra are shown in Fig. 4.

	Ag(111)/Ti	Ag(111)/Ti-TPP	Ag(111)/TiO-TPP	Ag(111)/TiO_x
binding energy	454.7 eV	455.8 eV	457.8 eV	458.2 eV

The XP spectra were recorded in a custom built UHV chamber with a base pressure of 3-5×10^{-11} mbar using a SPECS Phoibos 100 CCD hemispherical analyser at a grazing emission orientation with respect to the sample normal and excited by X-ray emission from a polychromatic Al K-α source that was incident along the surface normal. The Ti 2p spectra (figure 3b and 3e) constitute the average of 15 separate near identical preparations. The contour plot of the Ti 2p spectra as a function of exposure (figure 3c) is based on 9 subsequent exposures where the sample was exposed to a certain amount of oxygen, then the XP spectra were acquired, and then the sample was exposed again to a certain amount of oxygen (specifically a total exposure of 0, 0.5, 3, 5.5, 10.5, 20.5, 40.5, 80.5 and 120.5 L). Due to high noise on these measurements the spectra were treated averaging over a 0.2 eV energy range (the same image, without any averaging, is shown in Fig SI 2) and the contour plot was interpolated between points. Binding energies of all spectra were corrected by acquiring a Ag $3d_{5/2}$ XP spectrum (binding energy 368.27 eV) after measuring each Ti 2p or Ru 3d spectra. Additional measurements were also obtained in the Elettra Light Source using the Aloisa (Ru-TPP) and Materials Science (Ti-TPP) beam lines; the results support the reported measurements and conclusions, but are not included in this manuscript.

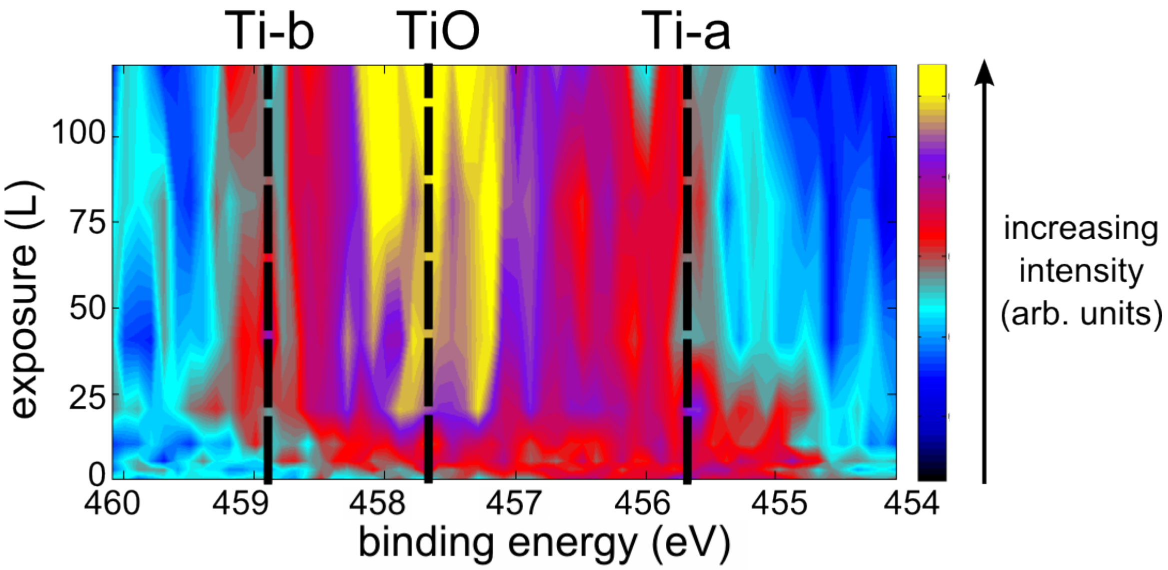

Fig. SI 2 A reproduction of the image in Fig 3c without any smoothing.

The STM images were recorded in a separate chamber, namely in a custom-designed UHV system equipped with a low-temperature CreaTec-STM (www.lt-stm.com). For all measurements, the sample was held at 6 K and the system base pressure was below 3×10^{-10} mbar. The STM images were acquired in constant current mode with an electrochemically etched tungsten tip and the bias applied to the sample. The Ag(111) crystal was cleaned by the same method as described above.

Because of a different distance between the crucible with the powder and the sample, the 2H-TPP molecules were deposited at a higher temperature (600 K) than in the XPS experiments, resulting in a submonolayer coverage with extended 2H-TPP islands. Similar to the procedure described above, <0.01 nm of Ti were evaporated followed by annealing to 500 K. Oxygen was exposed to the sample by back-filling of the chamber through a leak valve while the sample was held at room temperature.

Sticking coefficient calculation details

The calculated values for expected coverage / sticking coefficient were determined using the Hertz-Knudsen formula, which results in a number of adsorbed species per square meter (N_{ads}) by:

$$N_{ads} = \frac{S \cdot P \cdot t}{\sqrt{2\pi m k T}},$$

where S is the sticking probability, P is the pressure (Pa), t is the time (s), m is the molecular weight of the gas (kg), k is the Boltzmann coefficient and T is the temperature (K). Note that 1 L is 1.33×10^{-4} Pa·s. The surface area of one Ag atom was assumed to be 7.21 $Å^2$ (based on density of Ag atoms in a Ag(111) surface), one Ti(II) ion was assumed to be 3.14 $Å^2$ (based on its ionic crystal radius)[SI3] and one Mn(II) ion was assumed to be 2.01 $Å^2$ (based on its ionic crystal radius).[SI3] To compare the number of O atoms expected on the Ag surface after 10,000 L exposure to the number of expected Ru atoms, the Ru-TPP molecule is assumed to cover a surface area of 1.4×1.4 nm^2, such that there are roughly 1 Ru atom per 25 Ag atoms. Note that, per dissociated O_2 molecule, two adsorbed oxygen atoms will be formed.

Exposure of Ag(111)/Ru-TPP to N_2O and CO

Figure SI 3 shows the comparable Ru $3d_{5/2}$ spectra after exposure to N_2O and CO.

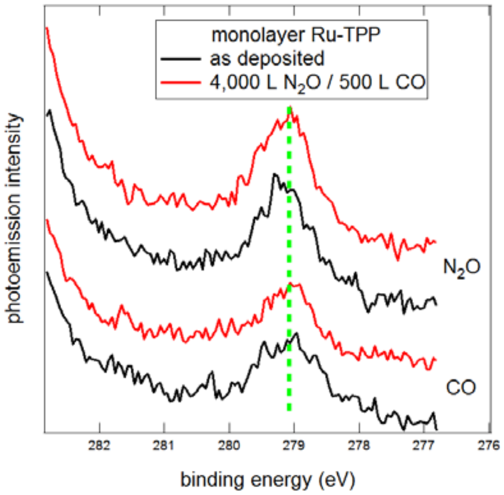

Fig. SI 3 Ru $3d_{5/2}$ XP spectra before (black, lower lines) and after (red, upper lines) exposure to 4,000 L of N_2O / 500 L of CO. The dashed green line indicates the centre of the peak. If a chemical change was present after oxygen exposure, a shift in binding energy should be observed.

Ti-TPP species

The Ti 2p XP spectra from the Ti-TPP results in two observed species, the origin of the higher binding energy species is not fully understood, and will be discussed in a future publication[SI1]. However it does not seem to originate from multiple different species on the surface as only one species was ever observed in the STM as shown in Fig. SI 4.

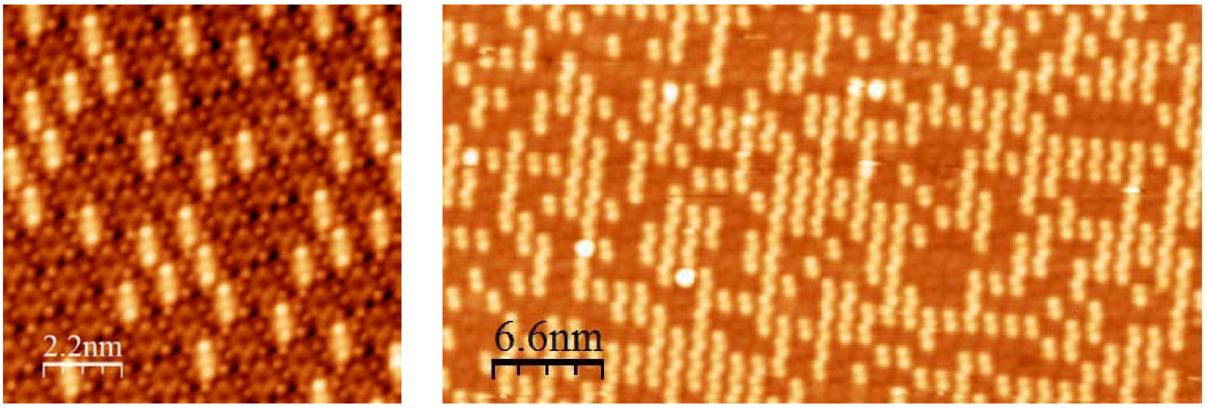

Fig. SI 4 STM images of an intermixed Ti-TPP and 2H-TPP island. The bright protrusions are the Ti-TPP species, with the duller species relating to 2H-TPP species that have not been metallated. Note that in both the (left) medium and (right) large scale images all of the Ti-TPP species are practically identical, it is perhaps notable that the 2H-TPP species show greater variation in the (left) medium scale image.

References

SI1 D. A. Duncan et al., *to be published.*
SI2 J. M. Gottfried et al., *J. Am. Chem. Soc.*, 2007, **128**, 5644; A. Kretschmann et al., *Chem. Comm.*, 2007, **6**, 568; C. M. Doyle et al., *Chem. Comm.*, 2011, **47,** 12134; K. Diller et al., *J. Chem. Phys.*, 2012, **136**, 014705
SI3 R. D. Shannon, *Acta Cryst. A*, 1976, **32**, 751; http://abulafia.mt.ic.ac.uk/shannon/