# Stabilisation of tri-valent ions with vacant coordination site at a corrole-metal interface

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# **Electronic Supplementary Information (ESI)**

## **1. Experimental methods**

### **Experimental setup**

The experiments were performed in a movable, custom-designed ultra-high vacuum (UHV) chamber with base pressure in the high 10<sup>-11</sup> mbar regime. The Ti metallation experiments on 5,10,15-tris-(pentafluorophenyl)-corrole (3H-TpFPC) and 2H-tetraphenylporphyrin (2H-TPP) were carried out with the chamber connected to the UE56–2 PGM-2 undulator beamline at the BESSY II storage ring in Berlin (Germany), to exploit tunable soft X-ray radiation in the range 150 – 1000 eV. Soft-X-ray Photoelectron Spectroscopy (SXPS) and Near-Edge X-ray Absorption Fine Structure (NEXAFS) measurements were performed utilizing a SPECS Phoibos 100 CCD hemispherical analyser mounted at 90° to the beam direction. During the SXPS measurements, synchrotron radiation impinged at grazing incidence (7°) with respect to the sample surface, and photoelectrons were collected with the electron energy analyser at normal emission (NE). The Ti L-edge NEXAFS experiments were conducted in the same NE geometry, monitoring decay electrons around the Ti LMM Auger transition at ~380 eV (kinetic energy), whereby the light polarisation was varied from linear horizontal (corresponding to out-of-plane polarisation,  $\theta$  = 7° from the surface normal) to linear vertical (corresponding to in-plane polarisation,  $\theta$  = 90° from the surface normal) while keeping the sample orientation fixed. To minimise detrimental effects from radiation damage during the measurements, the photon flux was appropriately reduced and the sample was moved laterally for each new spectrum. The photon energy scale of the Ti L-edge NEXAFS spectra was corrected by recording Fermi level XP spectra at different photon energies, with the work function of the analyser measured at the known Mg Klpha energy.

Conversely, the V metallation experiments where performed with the same chamber mounted off-line at the Physics TUM-E20 laboratories in Garching (Germany), using as photon source a twin-anode X-ray tube with polychromatic Al K $\alpha$  (1486.6 eV) and Mg K $\alpha$  (1253.6 eV) radiation to excite XP spectra at an energy resolution of ~ 0.8 – 0.9 eV. Here, C 1s and O 1s XP spectra were always recorded at normal emission, whereas the N 1s and V 2p core levels were monitored at grazing electron emission (70° from NE) to enhance the surface sensitivity.

Sample heating was carried out using a proportional-integral-derivative controller (Schlichting Physikalische Instrumente HS 130) and monitored by a K-type thermocouple in direct contact with the Ag(111) sample.

### Data analysis

The XP spectra were calibrated in binding energy using the Ag  $3d_{5/2}$  core-level line (368.27 eV) and/or the Fermi edge. The Ti and V 2p spectra are displayed after subtraction of an interpolated background spectrum and (for the grazing emission geometry with Mg K $\alpha$  source) an additional Shirley background. Curve-fitting analysis was performed using the FitXPS software [1]. For the fitted (sub)monolayer N 1s spectra shown in Fig. S4, recorded with Mg K $\alpha$  emission, the complex background shape due to plasmon loss features of the Ag support was removed by modelling the pristine Ag background with two Gaussian peaks superimposed on a straight line.

The Ti L-edge NEXAFS data of Figs. S1, S2 were processed following a standard procedure [2], i.e. normalizing them to the "clean surface" absorption (in this case, the absorption from the corresponding molecular layer without metal centres) and by subsequent normalisation of the edge jump to one with the pre-edge region set equal to zero. Simulations of the resulting Ti L-edge absorption spectra employed the CTM4XAS code (version 5.5) of de Groot and Stavitski [3]. In particular, we used the same methodology applied in our previous work on the Ti-TPP and TiO-TPP molecules [4] to determine the Ti oxidation state in the metallated Ti-TpFPC.

#### Sample preparation

3H-TpFPC was synthesised following the procedures reported in ref. [5]. It was subsequently purified by preparative High Performance Liquid Chromatography (HPLC) and analysed by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F nuclear magnetic resonance (NMR) spectroscopy. 2H-TPP was instead purchased from Sigma-Aldrich (> 99% purity) and used without further purification.

Prior to molecular deposition, the Ag(111) single-crystal substrate (Surface Preparation Laboratory) was cleaned by repeated cycles of Ne<sup>+</sup> ion sputtering (1 keV) and annealing (725 K). 3H-TpFPC (sub)monolayer films were then prepared by thermal evaporation of the molecules from a quartz crucible kept at 440-450 K, after initial degassing of the latter to this maximum temperature. Upon molecular deposition, the Ag(111) surface was either kept at 300-320 K or at 150 K with subsequent annealing to 300 K, if not otherwise stated. As shown previously [6], under these conditions an ordered layer of singly-deprotonated 2H-TpFPC species forms on Ag(111). Conversely, the 2H-TPP monolayer films were prepared by either annealing at 500 K a condensed multilayer or directly depositing 2H-TPP onto the substrate held at 500 K, in accordance with the standard procedure described in ref. [4]. Note that, while we use the term "monolayer" to indicate a closed monomolecular (single) layer that covers the substrate in the densest fashion, the unit ML refers to the Ag surface density and corresponds, by definition, to one particle (molecule or atom) per Ag surface atom. Considering the size of the porphyrin (corrole) molecules, it is estimated that 0.04 ML of titanium or vanadium are necessary to fully metallate a densely packed porphyrin (corrole) monolayer. Ti was deposited using a custom-built evaporator with a resistively heated Ti–W filament consisting of interwoven titanium and tungsten single wires. For V deposition, the same evaporator was employed, replacing the Ti–W filament with a 0.127 mm thick vanadium ribbon (Alfa Aesar, 99.8% purity). The thickness of the deposited metal was estimated via a quartz crystal microbalance placed at known distance from the metal source assuming a  $1/r^2$ scaling relationship. Neither carbon and oxygen contamination nor other metals were observed on the surface upon Ti/V metal deposition (even in the case of the relatively low purity vanadium ribbon). Ti deposition was commonly performed with the sample held at 300 K; as it is known that the Ti metallation of 2H-TPP proceeds only partially at room temperature, the sample was subsequently annealed to 500 K [4]. For preparing Ti-TpFPC, instead, Ti was deposited with the sample kept at ~300-315 K, without further annealing. In the case of V the optimal conditions were not previously known; accordingly, the sample was held at either 90 K or 300 K during deposition and subsequent annealing steps were carried out to monitor the occurrence as well as the completion of the metallation process (annealing to 460-500 K was used to enhance metallation of TPP, as well as 380 K to enhance metallation of TpFPC). For the preparation of the V-TpFPC multilayer (Fig. 4) alternate depositions of 3H-TpFPC and V at 300 K were carried out, concluded by a final annealing step at 380 K for 10 min to enhance the metalation (as monitored by XPS).

Finally, in the oxidation of Ti-TpFPC, Ti-TPP and V-TPP the metallated layers were exposed to molecular oxygen in a controlled way through a needle-doser. The exposure was monitored by a membrane gauge in the gas dosing system and calibrated to an approximate Langmuir scale by the exposure required to obtain one monolayer of argon on Ag(111), ~2.6 L (1 L =  $10^{-6}$  torr  $\cdot$  sec). The sample was held at 300 K during the O<sub>2</sub> exposure. To fully oxidise the Ti-TPP and V-TPP monolayers on Ag(111) to TiO-TPP and VO-TPP, exposures of 300 L and 3 L, respectively, were used, and for Ti-TpFPC (submonolayer), 600 L; for V-TpFPC exposures up to 1500 L, much larger than the required saturation dose, were used. For reference, we also prepared Ti and V ultra-thin films at 300 K, depositing comparable amounts of Ti and V, respectively. Subsequently, these metallic films were exposed to molecular oxygen at 300 K (here: 6 L of dioxygen for V, 1500 L for Ti).

### 2. NEXAFS spectra of Ti-TpFPC on Ag(111)

Experimental polarisation dependent spectra of Ti-TpFPC/Ag(111) are shown in Fig. S1.



**Figure S1:** NEXAFS Ti L<sub>2,3</sub>-edge spectra of Ti-TpFPC taken with out-of-plane (black) and in-plane (blue) polarisation, respectively. For reference, the in-plane polarisation spectrum (violet) of TiO-TPP with Ti(IV) is reported, which compares well with the corresponding spectrum of ref. [4] recorded at lower energy resolution on a dipole beamline. The sharp leading peak of TiO-TPP is located at a photon energy of 455.7 eV as found in refs. [4, 7]. The marked difference between the in-plane polarisation spectra of Ti-TpFPC and TiO-TPP clearly excludes the presence of Ti(IV) centres. Note that the Ti-TpFPC/Ag(111) spectrum shown in Fig. 3 of the main manuscript is obtained by averaging over the two perpendicular polarisations here.

# 3. Simulation of the Ti-TpFPC NEXAFS spectra for Ti(III) and Ti(II) ions

Simulations of the NEXAFS spectra of the Ti-TpFPC monolayer on Ag(111) were performed using the CTM4XAS program [3] in a similar way as done in refs. [4, 7] for porphyrin and phthalocyanine molecules with titanium centres. Due to the lower symmetry of the corrole macrocycle, only a moderate agreement is in principle expected by the use of the  $D_{4h}$  symmetry for the metal complexes. The dominant role of the tetrapyrrolic coordination of the central moiety [4, 7], however, suggests that this simplified treatment may be acceptable. Note that the exact orientation of the corrole molecules on the surface as well as deviations from the planarity of the macrocycle are not taken into account in the simulations.

The results reported in Fig. S2 show that the polarisation dependent NEXAFS spectra can be correctly reproduced by assuming a Ti(III) ion (Fig. S2a), unlike the case of Ti(II) (Fig. S2b) which does not match the polarisation dependence of the experimental data. The optimised simulated spectrum averaged over the inplane and out-of-plane polarisations is shown in Fig. 3 of the manuscript. The simulations validate the conclusion that the corrole macrocycle stabilises Ti(III) ions at the corrole-Ag(111) interface, as inferred by XPS (Fig. 1) and by the analysis of the NEXAFS signature (see manuscript, Fig. 3).

Moreover, the CTM4XAS code allows charge transfer effects to be included, combining the ground state configuration of the metal ion with other low-lying configurations. We thus performed tentative simulations combining the  $3d^1$  configuration of Ti(III) with a  $3d^2\underline{L}$  configuration bearing a hole on the macrocyclic ligand, to better handle the complexity of the corrole electronic structure [8, 9]. No substantial improvements were obtained within this scheme, as we were not able to reproduce correctly the polarisation dependence of the experimental spectra, as illustrated in Fig. S3 (green/red vs. blue dashed curves). These findings thus indicate the  $3d^1$  configuration to be the most probable and, although the large parameter space for these charge transfer multiplet calculations may hamper a definitive conclusion, support the description in terms of a Ti(III) formal oxidation state rather than Ti(II) with a  $\pi$ -radical ligand system, which was recently proposed for a Ni corrole species [9].

Finally, the surprisingly good agreement between the calculations utilising a  $D_{4h}$  symmetry and the Ti  $L_{2,3}$ -edge NEXAFS measurements (Fig. 3 of the manuscript and Fig. S2a here), suggests that the Ti atom in the adsorbed molecule is coordinated similarly to all four N atoms of the ligand backbone. While this is not conclusive, it potentially indicates that all four N atoms of the corrole coordinate to the metal centres in a manner that is analogous to porphyrins and phthalocyanines.

# Ti-TpFPC/Ag(111)



**Figure S2:** (a) Comparison of experimental (black) and simulated (blue, dashed) Ti L<sub>2,3</sub>-edge NEXAFS spectra for Ti-TpFPC/Ag(111) in two different polarisation geometries relative to the surface plane: in-plane (top) and out-of-plane (bottom) polarisation. The simulated spectra for a Ti(III) ion ( $3d^1$ ) were multiplied by a common factor for better comparison and shifted by +1.85 eV to align the energy scale. Good agreement is obtained in both geometries. Sticks (in red) correspond to the *d*-orbital split levels as calculated by the CTM4XAS program. Optimised crystal-field parameters: 10Dq = 2.35 eV, Dt = 0.34 eV, Ds = 0.33 eV. Slater integral factors [3]: F<sub>dd</sub> = 1.0, F<sub>pd</sub> = 0.95, G<sub>pd</sub> = 0.95; Lorentzian/Gaussian broadening: 0.2 / 0.25 eV.

(b) Analogous comparison of the experimental Ti L-edge NEXAFS spectra (black) with simulated spectra (coloured) for a Ti(II) ion ( $3d^2$ ) for three different sets of crystal-field parameters. Red: 10Dq = 2.35 eV, Dt = 0.4 eV, Ds = 0.6 eV (energy shift: +3.25 eV). Green: 10Dq = 2.35 eV, Dt = 0.13 eV, Ds = -0.32 eV (energy shift: +3.25 eV). Purple: 10Dq = 2.35 eV, Dt = 0.16 eV, Ds = 0.52 eV (energy shift: +3.6 eV). Slater integral factors:  $F_{dd} = 1.0$ ,  $F_{pd} = 1.0$ ,  $G_{pd} = 1.0$ ; Lorentzian/Gaussian broadening: 0.2 / 0.25 eV. All simulated spectra were multiplied by the same common factor. As illustrated, no simultaneous agreement between experiment and simulation for both experimental geometries could be found in this case.



**Figure S3:** Comparison of experimental Ti L-edge NEXAFS spectra (black) of Ti-TpFPC/Ag(111) at in-plane (top) and out-of-plane (bottom) polarisation of the incident photon beam with simulations *via* the CTM4XAS program. The blue dashed curve represents the best simulation obtained for a Ti(III) ion (3d<sup>1</sup>) in Fig. S2a, whereas the green curve includes charge transfer multiple calculations with charge transfer energy  $\Delta = 3 \text{ eV}$  and U<sub>dd</sub> = U<sub>pd</sub> (U<sub>dd</sub> defines the Hubbard U value and U<sub>pd</sub> the core hole potential [3]) and corresponds to mixed 3d<sup>1</sup> (~60%) and 3d<sup>2</sup>L (~40%) configurations (L describes a hole on the ligand) at unchanged crystal-field parameters. The default hopping terms were used. For the red curve,  $\Delta$  was made negative (-9 eV) to yield a dominant 3d<sup>2</sup>L (weight of ~90%) configuration; to get improved matching with the experimental curves, the crystal-field parameters were re-optimised to Dt = 0.5 eV, Ds = -0.4 eV, but the out-of-plane spectrum is still poorly reproduced. All simulated spectra were multiplied by the same common factor for better comparison and shifted by +1.85 eV to align the energy scale.



### 4. N 1s XP spectra monitoring the metallation of 2H-TpFPC and 2H-TPP with vanadium

**Figure S4:** N 1s XP spectrum (top) of the same submonolayer V-TpFPC/Ag(111) system of Fig. 4 of the main manuscript with the associated curve-fitting analysis. The presence of the pyrrolic and iminic components (labelled) of 2H-TpFPC indicates that the V-TpFPC layer (annealed to 380 K after V deposition) has not been completely metallated. For reference, the spectrum of a partially metallated 2H-TPP monolayer, after V deposition and annealing to 460 K, and the relative curve-fitting analysis are also reported (bottom).



### 5. Curve-fitting analysis of V 2p XP spectra of V-TpFPC and V-TPP

**Figure S5:** Tentative curve-fitting analysis of V-TpFPC (top) and V-TPP (middle) XP spectra (Mg K $\alpha$ , 1253.6 eV) after metallation with V of the interfacial layer of the corresponding free-base species on Ag(111). As a reference, the fitting of an ultra-thin metallic vanadium layer is also shown (bottom). All three spectra are the same as in Fig. 4 of the main manuscript. In the fitting, Voigt line shapes were used and the number of components was kept to a minimum. The component coloured in grey, denoted as "satellite", is most likely associated to multiplet effects in the final state or loss features rather than to oxidation states higher than V(III) [10].

The fitting confirms that the dominant oxidation state for V-TpFPC, V(III) (gold), is higher than for V-TPP, V(I/II) (light blue). Note also that the V-TPP monolayer cannot be fully metallated without the presence of a minority of V(0) species (green, dashed). The latter were attributed to partial subsurface V atoms upon annealing to 460-500 K. For the V  $2p_{3/2}$  core level the following, approximate XPS binding energy values are obtained: V(0) – 512.3 eV; V(I/II) – 513.2-513.3 eV; V(III) – 515.3 eV.

#### 6. Comparison of N 1s spectra and binding energies of different molecular systems

Fig. S6 shows that the N 1s binding energy provides limited useful information on the metal oxidation state, as the variations are moderate (< 0.3 eV) and display no clear correlation with the supposed change in oxidation state. Indeed, the interaction with the underlying substrate and the specific molecular structure seem to play a more important role, as further confirmed in Table S1. Importantly, from this table it can be concluded that large shifts (2-3 eV) in the  $2p_{3/2}$  binding energy of the metal centre of various tetrapyrrole complexes are not reflected in the N 1s binding energy. The N 1s binding energy, therefore, is essential for proving the coordination of the metal ions into the macrocycle cavity but cannot be used as a diagnostic tool of the metal oxidation state.



**Figure S6**: Exemplary sets of N 1s core levels for the different molecular systems on Ag(111) considered in this work: (a) after Ti metallation, (b) after V metallation. Submonolayer/monolayer molecular coverages were deposited; generally, full metalation was not sought in order to prevent accumulation of metal adatoms/clusters on the surface. For clarity of presentation, the core-level spectra were normalized to the peak area after background subtraction and vertically stacked. The data in (a) were acquired with synchrotron radiation in normal electron emission, the data in (b) were taken with non-monochromatised Mg K $\alpha$  radiation (thus, at lower energy resolution) in the grazing emission geometry. Dashed lines are a guide to the eye to emphasize minor variations in the binding energy of the peak centroid, which is related to the N-metal coordination (cf. fitting analysis in Figs. 1 and S4).

### Table S1:

Summary of N 1s binding energy values for various metal tetrapyrrole complexes adsorbed at the interface with Ag(111) and Au(111) surfaces, from this and previously published work. The metals considered in the table are Ti, V and Fe.

Molecular	Substrate	N 1s binding	Formal metal	2p <sub>3/2</sub> core-level	References
(monolayer) system		energy (eV)*	oxidation state	binding energy of	
				metal atom (eV)*	
Ti-TPP	Ag(111)	398.6	(11)	455.6-455.8	[4], this work
TiO-TPP	Ag(111)	398.6	(IV)	457.8-457.9	[4], this work
TiO-Pc	Ag(111)	398.8	(IV)	457.9	[11]
Ti-TpFPC	Ag(111)	398.4	(111)	broad: 456-458	this work
Ti-TpFPC + O <sub>2</sub>	Ag(111)	398.3	(IV)	457.7	this work
V-TPP	Ag(111)	398.6	(1/11)	~513.2	this work
VO-TPP	Ag(111)	398.6	(IV)	~516.2	this work
V-Pc <sup>⊥</sup>	Ag(111)	398.5	(1/11)	~513.9	[12]
V-TpFPC	Ag(111)	398.5	(111)	~515.3	this work
V-TpFPC anneal. 430 K	Ag(111)	398.4	(111)	~515.1	this work
V-TpFPC + O <sub>2</sub>	Ag(111)	398.4	-	~516.6	this work
Fe-Pc <sup>⊥</sup>	Au(111)	398.3	(0) and (II)	~707 and >708	[13,14]
Fe-Pc <sup>⊥</sup> + pyridine	Au(111)	398.2	-	~708.2	[13]
Fe-Pc <sup>⊥</sup>	Ag(111)	398.7	(0)	~707	[15]
Fe-TPP	Ag(111)	398.6-398.7	dominantly (0)	~707	[16,17]
Fe-TPP + NO	Ag(111)	398.7	possibly (III)	~709.5	[17]
Fe-OEP <sup>¶</sup> multilayer	Ag(111)	399.4	(11)	~708.5	[18]
Fe-HEDMC <sup>§</sup> multilayer	Ag(111)	399.3	(111)	~708.8	[18]
Fe-OEP <sup>1</sup>	Ag(111)	399.2	[partly (0)]	[~707]	[18]
Fe-HEDMC <sup>§</sup>	Ag(111)	399.1	[partly (0)]	[~707]	[18]

\* Typical error bars for N 1s:  $\pm$  0.1 eV.

For the metal  $2p_{3/2}$  core level the much broader shape leads to considerably higher uncertainty.

<sup> $\perp$ </sup> Pc = phthalocyanine.

<sup>¶</sup> OEP = octaethylporphyrin.

<sup>§</sup> HEDMC = hexaethyl-dimethyl-corrole.

### 7. Exposure of Ti-TpFPC to molecular oxygen

To highlight the presence of a vacant axial coordination site for the metallated corrole species we have investigated the ability of the Ag(111)-adsorbed Ti- molecules to bind oxygen upon exposure to  $O_2$  at 300 K. The successful oxidation is proven in Fig. S7 by comparison with the porphyrin counterparts, TiO-TPP.



**Figure S7:** Effect of the exposure of a submonolayer coverage of Ti-TpFPC on Ag(111) to molecular oxygen (600 L at 300 K), compared to a TiO-TPP monolayer ( $O_2$  exposure: 300 L at 300 K; applied conditions similar to ref. [4]). (a) Ti 2p and (b) O 1s XP spectra with synchrotron radiation. The similarity of the peak binding energies is highlighted by the dashed vertical lines. In panel (b) the O 1s spectra before oxidation (dotted lines) are also reported, in order to demonstrate the absence of oxygen following metallation in UHV.

### 8. Exposure of V-TpFPC to molecular oxygen

The experiments shown in Fig. S8 support the presence of a vacant axial coordination site also for the Ag(111)-supported V-TpFPC species. Exposure to  $O_2$  at 300 K causes a clear chemical shift to higher binding energy (~1.5 eV) of the V  $2p_{3/2}$  core-level line for both monolayer and submonolayer coverages (Fig. S8a). This shift can be attributed to the binding of oxygen to the open coordination site of the V atom (Fig. S8b), with the final V  $2p_{3/2}$  binding energy of ~516.6 eV (green curve, top of Fig. S8a) being moderately higher than for VO-TPP (cf. Fig. 4 of the main manuscript: 516.2 eV).



**Figure S8:** Effect of the exposure of V-TpFPC on Ag(111) to molecular oxygen at 300 K, as monitored by XPS. (a) V 2p core levels of a submonolayer film before (black curve) and after (light green) exposure to 15 L of  $O_2$ . The dark green curve, top, is obtained after a large  $O_2$  exposure (~1500 L, much higher than the saturation value) for a similarly prepared V-TpFPC monolayer. (b) O 1s spectrum (dark green) corresponding to the green curve of panel (a); the same region before oxygen uptake, featureless, is shown for reference (grey). Note that the 2H-TpFPC layers in these experiments were annealed to 430 K. While this may induce partial cyclization of the molecules at the periphery [6], it is not expected to have substantial effect on the incorporated V centres, with the V  $2p_{3/2}$  line being located at ~515.1 eV, V(III), before oxidation. These XPS data prove the availability of a vacant axial coordination site for oxygen coordination on the metal ion of the metallated molecules.

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