

Tetraphenylporphyrin picks up zinc atoms from a silver surface

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We demonstrate that adsorbed *meso*-tetraphenylporphyrin molecules can coordinate Zn atoms that are pre-deposited on an Ag(111) surface, forming a complex that is identical to directly deposited tetraphenylporphyrinato-zinc(II); this reaction, which we studied with XPS, is the first example of an oxidative dissolution of a metal by a large organic ligand under ultrahigh vacuum conditions.

Metallation of porphyrins with metal ions in solution is straightforward,¹ but can porphyrins react with solid metals? We recently showed that a monolayer of *meso*-tetraphenylporphyrin on an Ag(111) surface readily coordinates Co atoms from the gas phase.² A stoichiometric amount of the metal is sufficient for a complete metallation of the monolayer, *i.e.*, there is no competitive metal adsorption at other parts of the molecule or at the Ag surface, unless an excess of metal atoms is applied. These findings raise the question of whether the metal atoms impinge on the molecules directly at their coordination centres, possibly guided by steering effects, or whether they adsorb at arbitrary positions and diffuse on the surface until they are coordinated by a porphyrin molecule.

In this paper, we show that *meso*-tetraphenylporphyrin (H₂TPP) can coordinate zinc atoms deposited on an Ag(111) surface *prior* to the deposition of the porphyrin. We chose Zn as the metal, because there is the alternative route to prepare monolayers of *meso*-tetraphenylporphyrinato-zinc(II) (ZnTPP) by direct evaporation deposition of ZnTPP, providing a reference to prove the formation of ZnTPP by reaction between Zn and H₂TPP.

H₂TPP contains two different nitrogen species, pyrrolic (–NH–) and iminic (=N–) nitrogen, which give rise to two separate signals in the N 1s region of the X-ray photoelectron (XP) spectrum.³ The signal of pyrrolic nitrogen is found at a higher binding energy (400.1 eV) than that of iminic nitrogen (398.2 eV, Fig. 1A).^{2,4} ZnTPP, as the final product of the metallation, however, contains four chemically identical N atoms, which lead to a single N 1s signal located between the peaks of pyrrolic and iminic nitrogen (Fig. 1E).²

In the first experiment, we first deposited a monolayer of H₂TPP on the Ag(111) surface and thereafter zinc atoms up to a coverage of $\theta_{\text{Zn}} = 0.031$ (85% of the stoichiometric amount of $\theta_{\text{Zn}} = 0.037$ needed to completely metallate a saturated monolayer of H₂TPP).⁵ This procedure has previously been successfully applied to the metallation of H₂TPP monolayers with Co.² However, here

it does not lead to complete metallation, as can be seen in Fig. 1B by the presence of more than one peak in the N 1s spectrum. Even after deposition of an excess of Zn ($\theta_{\text{Zn}} = 0.064$), the reaction is not complete (Fig. 1C).

However, the metallation reaction is induced by heating to 550 K (Fig. 1D), which suggests the presence of an activation barrier. This behaviour is at variance with that of Co, which was coordinated by the porphyrin at 300 K under otherwise identical

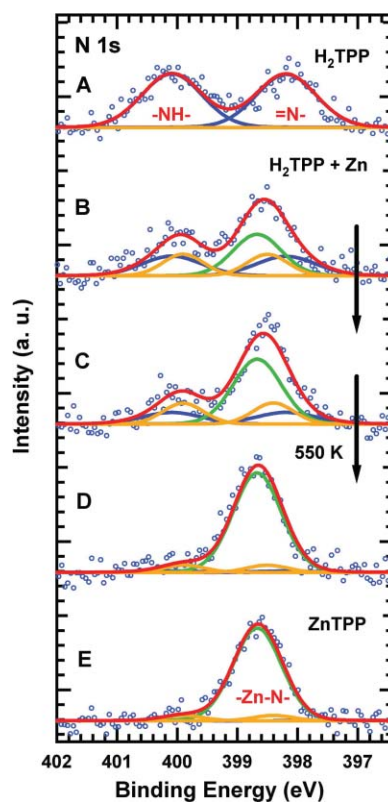


Fig. 1 N 1s XP spectra of (A) a monolayer of H₂TPP on Ag(111) and after subsequent vapour deposition of Zn at 300 K: (B) $\theta_{\text{Zn}} = 0.031$ and (C) $\theta_{\text{Zn}} = 0.064$. After deposition of Zn, the sample was heated to 550 K (D). (E) N 1s XP spectrum of a monolayer of ZnTPP on Ag(111) for comparison. The following colour code is used for the fitting curves: blue = H₂TPP, green = ZnTPP, orange = intermediate (see below) and red = envelope. Note that the spectra B and C are not simple superpositions of the spectra of H₂TPP and ZnTPP, as was the case for the metallation with Co.² This suggests formation of an intermediate complex (probably represented by the orange fitting curves) at 300 K, in which the metal atom is already coordinated, but the pyrrolic hydrogens are still in place. Such intermediates have been observed during metallation in solution (“sitting-atop complexes”, SAT^{12,13}).

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conditions.² Note that this difference between Co and Zn is in agreement with recent DFT calculations, which predict that the metallation has an activation barrier for the late transition metals Zn and Cu, but not for Co, Fe and Ni.⁷

In a second experiment, we reversed the order of deposition of the two reactants, *i.e.*, we first deposited zinc atoms ($\theta_{\text{Zn}} = 0.11$, *i.e.*, three times the stoichiometric amount) and then approximately one monolayer of H₂TTP. As in the first experiment, the reaction is not complete at 300 K, but can be induced by heating to 550 K. Evidence for the metallation is again provided by the disappearance of the two N 1s signals of H₂TTP, which are replaced by a single peak at 398.6 eV (Fig. 2B). This peak position is almost identical to that of a monolayer of ZnTTP that was directly deposited on the Ag surface as a reference (398.7 eV). (The very small difference of 0.1 eV may be attributed to a work function change caused by some residual Zn atoms on the Ag surface). We conclude that H₂TTP is able to “pick up” and coordinate Zn atoms from the Ag(111) surface. The respective Zn 2p_{3/2} XP spectra are displayed in Fig. 3. They confirm the formation of ZnTTP by showing the higher binding energy of the coordinated Zn ions (1022.0 eV) as compared to that of the adsorbed Zn atoms (1021.6 eV). The Zn 2p_{3/2} spectra also show that the excess of Zn atoms (those not coordinated by the porphyrin molecules) has almost completely vanished from the surface after heating, probably by diffusion into the bulk of the Ag crystal. (Ag dissolves up to 40 atomic percent Zn at 550 K.⁸)

What are the driving forces for this unusual reaction? Apparently, the sum of the bond energies of the four coordinate bonds in ZnTTP exceeds the bond energy of Zn to the Ag(111) surface. A value for the latter has not been reported yet. However, it is probably similar to that of Zn on Cu(111), $\sim 150 \text{ kJ mol}^{-1}$, as was estimated from temperature programmed desorption (TPD) data.⁹ The bond energy of Zn in ZnTTP can be calculated from the heats of combustion or formation of H₂TTP and ZnTTP. These values, however, are not available for ZnTTP. A recent DFT calculation of the reaction between H₂TTP and Zn atoms in the gas phase predicted a total reaction energy of 318 kJ mol^{-1} ,⁷

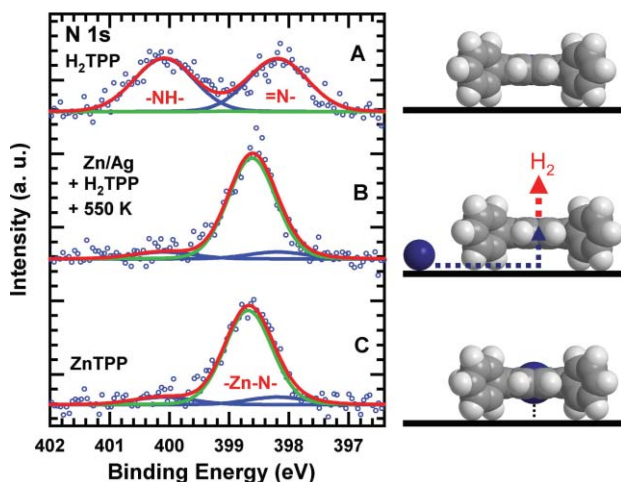


Fig. 2 N 1s XP spectra of (A) a monolayer of H₂TTP on Ag(111) and (B) after deposition of Zn ($\theta_{\text{Zn}} = 0.11$) followed by approximately one monolayer of H₂TTP and subsequent heating to 550 K. (C) N 1s spectrum of a directly deposited monolayer of ZnTTP on Ag(111) for comparison.¹⁴

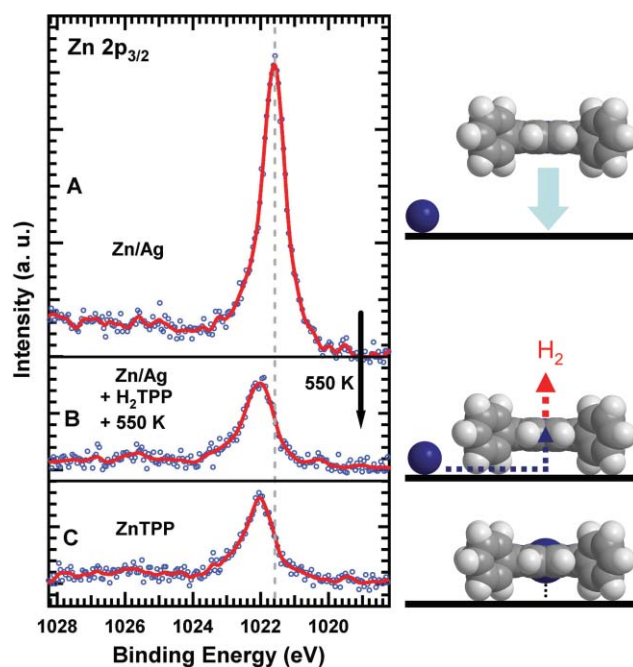


Fig. 3 Zn 2p_{3/2} spectra of (A) Zn on Ag(111) ($\theta_{\text{Zn}} = 0.11$) and (B) after deposition of Zn ($\theta_{\text{Zn}} = 0.11$) followed by approximately one monolayer of H₂TTP and subsequent heating to 550 K. (C) Zn 2p_{3/2} spectrum of a directly deposited monolayer of ZnTTP on Ag(111) for comparison.¹⁴

which is indeed much larger than our estimated Zn–surface bond energy of $\sim 150 \text{ kJ mol}^{-1}$.

We note that there is apparently no reaction between H₂TTP and Ag atoms of the substrate. Heating to higher temperatures than needed to start the Zn metallation reaction ($>600 \text{ K}$) leads, in the absence of Zn, eventually to decomposition of H₂TTP (as, for example, seen by a shift and broadening of the C 1s signal), but no metallation of the porphyrin with Ag is observed. This result is not surprising, because metal ions in metalloporphyrins usually adopt the +2 oxidation state (if no additional axial ligand is present), which is chemically not favourable for Ag (although Ag²⁺ compounds do exist).¹⁰ This fact is also reflected by the gas phase ionisation potentials of the two elements, 17.96 eV for Zn²⁺ and 21.48 eV for Ag²⁺.¹¹

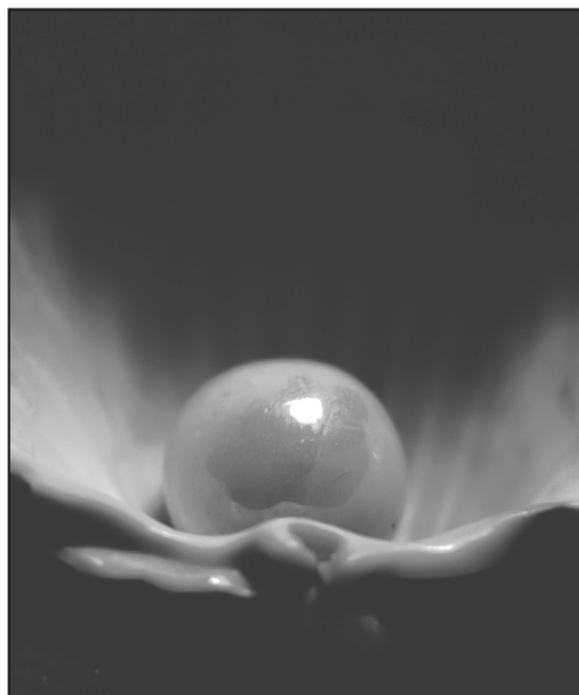
In conclusion, we have demonstrated that adsorbed *meso*-tetraphenylporphyrin molecules on an Ag(111) surface are able to react with Zn atoms, which were deposited on this surface prior to the adsorption of the porphyrin molecules, forming tetraphenylporphyrinato-zinc(II). To our knowledge, this is the first example of a reaction in which a large adsorbed organic ligand removes a metal atom from a metal surface to coordinate and incorporate it in a metal complex.

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