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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 (H_2TPP) 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 H_2TPP.

H_2TPP 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 H_2TPP on the Ag(111) surface and thereafter zinc atoms up to a coverage of $\theta_{Zn} = 0.031$ (85% of the stoichiometric amount of $\theta_{Zn} = 0.037$ needed to completely metallate a saturated monolayer of H_2TPP).[5] This procedure has previously been successfully applied to the metallation of H_2TPP 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 ($\theta_{Zn} = 0.064$), 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

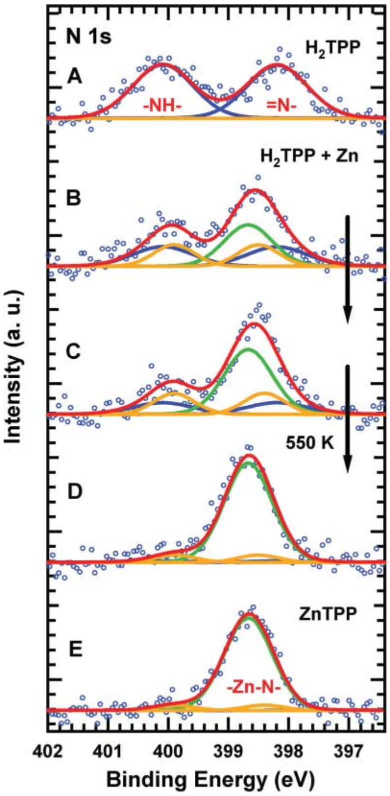

Fig. 1 N 1s XP spectra of (A) a monolayer of H_2TPP on Ag(111) and after subsequent vapour deposition of Zn at 300 K: (B) $\theta_{Zn} = 0.031$ and (C) $\theta_{Zn} = 0.064$. After deposition of Zn, the sample was heated to 550 K (D). (E) N 1s XP spectrum of a monolayer of ZnTPP on Ag(111) for comparison. The following colour code is used for the fitting curves: blue = H_2TPP, green = ZnTPP, orange = intermediate (see below) and red = envelope. Note that the spectra B and C are not simple superpositions of the spectra of H_2TPP 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 (θ_{Zn} = 0.11, *i.e.*, three times the stoichiometric amount) and then approximately one monolayer of H_2TPP. 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 H_2TPP, 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 ZnTPP 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 H_2TPP 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 ZnTPP 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 ZnTPP 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 kJ mol^{-1}, as was estimated from temperature programmed desorption (TPD) data.[9] The bond energy of Zn in ZnTPP can be calculated from the heats of combustion or formation of H_2TPP and ZnTPP. These values, however, are not available for ZnTPP. A recent DFT calculation of the reaction between H_2TPP and Zn atoms in the gas phase predicted a total reaction energy of 318 kJ mol^{-1},[7] which is indeed much larger than our estimated Zn–surface bond energy of $\sim$150 kJ mol^{-1}.

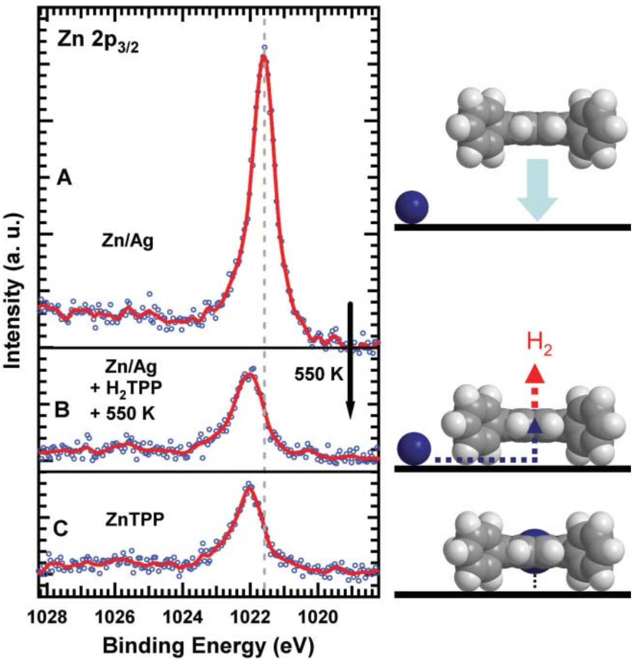

Fig. 3 Zn $2p_{3/2}$ spectra of (A) Zn on Ag(111) (θ_{Zn} = 0.11) and (B) after deposition of Zn (θ_{Zn} = 0.11) followed by approximately one monolayer of H_2TPP and subsequent heating to 550 K. (C) Zn $2p_{3/2}$ spectrum of a directly deposited monolayer of ZnTPP on Ag(111) for comparison.[14]

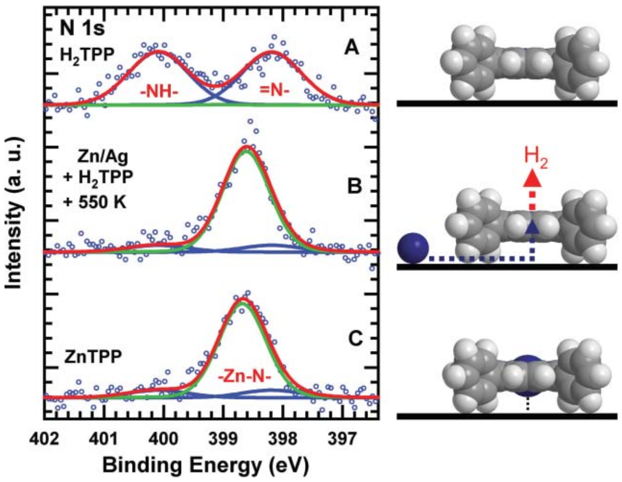

Fig. 2 N 1s XP spectra of (A) a monolayer of H_2TPP on Ag(111) and (B) after deposition of Zn (θ_{Zn} = 0.11) followed by approximately one monolayer of H_2TPP and subsequent heating to 550 K. (C) N 1s spectrum of a directly deposited monolayer of ZnTPP on Ag(111) for comparison.[14]

We note that there is apparently no reaction between H_2TPP and Ag atoms of the substrate. Heating to higher temperatures than needed to start the Zn metallation reaction (>600 K) leads, in the absence of Zn, eventually to decomposition of H_2TPP (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 Ag^{2+} compounds do exist).[10] This fact is also reflected by the gas phase ionisation potentials of the two elements, 17.96 eV for Zn^{2+} and 21.48 eV for Ag^{2+}.[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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Notes and references

1 J. K. M. Sanders, N. Bampos, Z. Clyde-Watson, S. L. Darling, J. C. Hawley, H.-J. Kim, C. C. Mak and S. J. Webb, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000.
2 J. M. Gottfried, K. Flechtner, A. Kretschmann, T. Lukasczyk and H.-P. Steinrück, *J. Am. Chem. Soc.*, 2006, **128**, 5644.

3 All experiments were performed with a commercial X-ray photoelectron spectrometer (Scienta ESCA-200) equipped with an Al-Kα X-ray source (1486.6 eV) with monochromator and a hemispherical energy analyzer (SES-200). The overall energy resolution amounts to 0.3 eV. The binding energies are referenced to the Fermi edge of the clean Ag surface ($E_B \equiv 0$). The base pressure in our UHV system is below 1×10^{-10} mbar.

4 D. K. Sarkar, X. J. Zhou, A. Tannous, M. Louie and K. T. Leung, *Solid State Commun.*, 2003, **125**, 365.

5 The coverage θ is defined as the number of adsorbed molecules or atoms divided by the number of substrate atoms; "monolayer" denotes a closed adlayer of molecules in direct contact with the substrate surface. *E.g.*, monolayers of H_2TPP and ZnTPP correspond to $\theta = 0.037$. This value was determined using a combination of XPS (which proves the existence of a complete monolayer) and low-energy electron diffraction (which provides the ratio of the lattice constants of adsorbate and substrate in this monolayer). Well ordered monolayers of H_2TPP and ZnTPP were prepared by evaporation deposition of multilayers at 300 K and subsequent annealing at 525 K as described in detail in ref. 6. The porphyrins (purity > 98%, Porphyrin Systems) were degassed *in vacuo* for 24 h at 420 K prior to use. The sample was a $10 \times 10 \times 2$ mm^3 Ag single crystal (purity > 99.999%) with a polished (111) surface, which was aligned to <0.1° with respect to the nominal orientation.

6 T. Lukasczyk, K. Flechtner, L. R. Merte, N. Jux, F. Maier, J. M. Gottfried and H.-P. Steinrück, *J. Phys. Chem. B*, accepted for publication.

7 T. E. Shubina, T. Clark, A. Kretschmann, K. Flechtner, M.-M. Walz, J. M. Gottfried and H.-P. Steinrück, in preparation.

8 M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, Toronto, London, 1958.

9 C. Ammon, G. Held, J. Pantförder and H.-P. Steinrück, *Surf. Sci.*, 2001, **482**, 886.

10 F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Brochmann and R. Grimes, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1999.

11 *Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Cleveland, 2003.

12 E. B. Fleischer and J. H. Wang, *J. Am. Chem. Soc.*, 1960, **82**, 3498.

13 Y.-W. Hsiao and U. Ryde, *Inorg. Chim. Acta*, 2006, **359**, 1081.

14 The amount of H_2TPP deposited for the spectra in Fig. 2B and 3B may have slightly exceeded monolayer coverage. However, this has no influence on the result, since multilayers of H_2TPP desorb around 500 K and therefore vanish during heating to 550 K (ref. 6).