ChemComm

COMMUNICATION

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Cite this: Chem. Commun., 2019, 55, 13665

Received 13th September 2019, Accepted 15th October 2019

DOI: 10.1039/c9cc07170a

rsc.li/chemcomm

Direct synthesis of dilithium tetraphenylporphyrin: facile reaction of a free-base porphyrin with vapor-deposited lithium[†]

Maik Schöniger, (10) ‡ Stefan R. Kachel, ‡ Jan Herritsch, (10) Philipp Schröder, Mark Hutter and J. Michael Gottfried (10)*

A solvent-free dilithium porphyrin was synthesized by direct reaction of free-base *meso*-tetraphenylporphyrin with elemental lithium in ultra-high vacuum. The reaction product dilithium tetraphenylporphyrin was studied by temperature-programmed desorption mass spectrometry (TPD-MS) and hard X-ray photoelectron spectroscopy (HAXPES). The solid-state reaction is thermodynamically favored, according to density functional theory (DFT) calculations.

Porphyrins, the 'colors of life',¹ are widespread in nature and find numerous technological applications.²⁻⁴ While transitionmetal porphyrins can be very stable with respect to metal exchange, alkali metal porphyrins (AMPs) with electron-rich ligands such as meso-tetraphenylporphyrin (TPP) are considered as labile and water-sensitive complexes.⁵ Although AMPs were observed as early as 1938,⁶ they were mainly characterized in solution or as solvates. The lability of AMPs in solution has been used for the synthesis of other metalloporphyrins by metal exchange.⁷⁻¹⁰ The first X-ray structure of an AMP solvate was obtained for the tetrahydrofuran (THF) adduct of dilithium octaethylporphyrin, Li2OEP(THF)4, formed by reaction of octaethylporphyrin (H₂OEP) with LiN(SiMe₃)₂.¹¹ The solid consists of a $[Li(THF)_4]^+$ cation and a $[Li(OEP)]^-$ anion with a square-planar coordination of Li in the center of the porphyrin ring.¹¹ In other AMP solvates such as Li₂TPP(OEt₂)₂, both Li ions are bound to opposite sides of the porphyrin ring in a square-bipyramidal fashion and carry an additional diethyl ether (OEt₂) ligand.¹² This bipyramidal structure has also been reported for dilithium porphyrins in solution and for solid Na and K porphyrins.¹³ Besides these structurally well-characterized solvates, the two solvent-free AMPs Li2TPP and Li2OEP have been obtained from solution, but have not been studied in detail.¹⁴

Here, we report that solvent-free dilithium tetraphenylporphyrin (Li₂TPP) can be prepared by vapor deposition of lithium onto free-base meso-tetraphenylporphyrin (H2TPP) in ultra-high vacuum (UHV), by the reaction shown in Fig. 1. Unlike the very limited reaction depths of transition metals in bulk porphyrins,^{15,16} or the metalation of monolayers,^{4,17-19} we find that Li diffuses readily into the solid porphyrin film, which makes the reaction useful for synthetic purposes. The bulk reaction between metallic Li and organic molecules is also relevant for the field of organic electronics, where metals with low work functions are vapor-deposited onto organic semiconductors as electron-injecting electrodes and intermixing or reaction of the layers is usually not desirable.²⁰⁻²² The reaction of Li with organic materials also plays a role in Li-based electrochemical energy storage, in which the formation of the solid-electrolyte interphase (SEI) and the diffusion of lithium in the SEI is crucial for device performance.^{23,24} Porphyrin-based electrodes have also proven to be efficient electrode materials in lithium batteries.²⁵

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The Li_2 TPP layers obtained by the reaction shown in Fig. 1 were investigated by temperature-programmed desorption mass



Fig. 1 Direct metalation of *meso*-tetraphenylporphyrin (H₂TPP) with two equivalents of elemental Li, resulting in the formation of dilithium tetraphenylporphyrin (Li₂TPP) and H₂. The figure shows the geometry-optimized gas-phase structures calculated by DFT. The distorted square-bipyramidal polyhedron formed by the lithium and nitrogen atoms in Li₂TPP is highlighted.

Department of Chemistry, Philipps University Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany. E-mail: michael.gottfried@chemie.uni-marburg.de † Electronic supplementary information (ESI) available: Experimental and computational details, additional TPD-MS and XPS data, XPS information depths, Born-Haber cycle, additional DFT results. See DOI: 10.1039/c9cc07170a ‡ These authors contributed equally to this study and share first authorship.

spectrometry (TPD-MS) and hard X-ray photoelectron spectroscopy (HAXPES). Complementary density functional theory (DFT) calculations provide insight into the energetics of the reaction.

Before the reaction between H_2TPP and Li was studied, reference TPD-MS measurements were performed with pristine H_2TPP . For this purpose, a film of H_2TPP with a thickness of 20 nm was vapor-deposited onto a clean Au(111) surface. Subsequently, a TPD-MS experiment was performed by heating the sample with a constant rate of 0.1 K s⁻¹ between 300 and 700 K while rapidly recording mass spectra, as described in the ESI.† The resulting temperature-resolved mass spectra are shown as TPD-MS maps in Fig. 2a and Fig. S1a in the ESI.† Around 485 K a dominant peak is observed in a mass range that indicates desorption of intact H_2TPP (614 amu). Arrhenius plot analysis of the zeroth-order desorption trace (Fig. 2e) yields a desorption activation energy of 200 kJ mol⁻¹, which is in the range of literature values for the sublimation enthalpy (between 111 and 240 kJ mol⁻¹).²⁶

To study the reaction between H_2TPP and Li, a fresh 20 nm thick film of H_2TPP was deposited onto the clean Au(111) surface, followed by the deposition of 1 nm Li at 300 K. This thickness of Li is close (within 5%) to the stoichiometric amount required for complete conversion of the H_2TPP film to Li₂TPP. After this preparation, a TPD-MS experiment was performed. The results in Fig. 2b show a dominant signal around the mass of Li₂TPP (626 amu), indicating the formation of the dilithium complex in high yield. The peak temperature



Fig. 2 TPD-MS maps for (a) 20 nm H₂TPP, (b) 1 nm Li on 20 nm H₂TPP, and (c) 10 nm Li on 50 nm H₂TPP, each on Au(111), in the relevant mass region from 600 to 650 amu. Data for other mass ranges are shown in the ESI.† The spectra were normalized to the maximum intensity of the H₂TPP signal (a). The heating rate was 0.1 K s⁻¹ and one mass range cycle took 8 seconds (see the ESI† for further experimental details). Arrhenius plot analysis for (d) Li₂TPP and (e) H₂TPP, with the desorption rates r_{des} divided by the mass spectrometer unit (counts per second, for further details see the ESI†), yields desorption energies of 234 and 200 kJ mol⁻¹, respectively.

of 565 K, which exceeds that of H₂TPP by 80 K, and the higher desorption energy of 234 kJ mol⁻¹ (Fig. 2d) reveal increased intermolecular interactions, compared to H₂TPP. The H₂TPP signal has completely disappeared, which shows that the freebase porphyrin reacts completely. Weak additional features appear at 619 and 637 amu. These masses correspond to LiTPP and LiTPP·H₂O, respectively. The LiTPP is most likely formed by fragmentation of Li₂TPP in the mass spectrometer, because the desorption traces of Li2TPP and LiTPP have the same temperature dependence (see Fig. S2 in the ESI[†]) and their intensities have a constant ratio of $\approx 12:1$. The LiTPP·H₂O adduct ($\approx 5\%$ of the Li₂TPP signal) is attributed to reaction with residual water. The small Li2TPP-related signal around 500 K is due to the formation of small crystallites with lower desorption energy (see Arrhenius analysis in Fig. S3 in the ESI⁺), in agreement with previous work.²⁷ It is worth mentioning that the LiTPP·H₂O adduct is only observed at temperatures where the crystallites desorb.

To investigate whether even thicker H_2 TPP films can be fully converted, 10 nm Li were deposited onto a 50 nm H_2 TPP film. An over-stoichiometric amount of Li was chosen to ensure complete reaction. The TPD-MS map in Fig. 2c shows that the main product is again Li₂TPP, with the water adduct Li₂TPP·H₂O (644 amu) as a side product (\approx 13%). Analysis of the individual TPD traces (see Fig. S2b in the ESI†) indicates that the film substantially recrystallizes during the heating,²⁷ which leads to the observed broadening of the Li₂TPP peak. Again, no traces of residual H₂TPP were found, indicating complete reaction.

The mass spectra presented above show that free-base H_2TPP reacts completely with Li forming Li_2TPP . However, it remains unclear whether the reaction occurs already at room temperature or is induced by the elevated temperatures during the TPD-MS experiment. To clarify this question, additional experiments with X-ray photoelectron spectroscopy (XPS) were performed.

The XPS measurements were carried out with synchrotron radiation in the hard X-ray regime between 2 and 7 keV, to take advantage of the increased information depth of photoelectrons with high kinetic energies.^{16,28} In this way, the composition of the film can be probed over the entire thickness and not only at the surface, as is the case for conventional XPS. At the highest photon energy (E_{ph}) of 7 keV, the information depth of N 1s photoelectrons is 33.6 nm for H₂TPP and 32.7 nm for Li₂TPP, as was calculated by the Gries approach.16,29 The details of the calculation and the information depths for the other photon energies are given in the ESI.† The XPS measurements were performed with a H₂TPP film of 24 nm thickness, which is substantially smaller than the maximum information depth. By variation of E_{ph} (and thus, the information depth), the depth homogeneity of the reacted film can additionally be examined. This film was prepared on a Si(001) surface, as is described in detail in the ESI.†

The resulting N 1s XP spectra are shown in Fig. 3. The spectrum of the pristine H_2 TPP film (Fig. 3a) consists of two peaks, which are attributed to the pyrrolic (-N(H)-, 400.2 eV) and iminic (-N=, 398.1 eV) nitrogen species,^{4,30} see Fig. 1. After deposition of Li at room temperature (Fig. 3b–e), a new peak appears at a



Fig. 3 N 1s X-ray photoelectron spectra of (a) H_2TPP and (b)–(e) Li₂TPP formed by deposition of Li onto a 24 nm thick H_2TPP layer, taken with the indicated photon energies.

binding energy (BE) of 399.6 eV, while the two H_2TPP -related peaks disappear. The presence of a single N 1s peak indicates that all four nitrogen atoms are chemically equivalent, which is the case in the metal complex.^{4,18,19} The information depth of the experiment exceeds the film thickness also after deposition of Li, as can be seen from the Si 1s signal related to the Si(001) substrate in Fig. S4 in the ESI.† The formation of Li₂TPP is also supported by the related Li 1s XPS data in Fig. S5 in the ESI,† which show a chemical shift to higher BE in line with the oxidation of metallic Li to Li⁺ ions.

The absence of any H_2 TPP-related signals at a photon energy of 7 keV, where the information depth exceeds the film thickness, proves that the H_2 TPP film reacts over its entire thickness at room temperature. For the photon energies of 2, 2.5 and 3 keV (Fig. 3b–d), the information depths in Li₂TPP are 10.1, 12.6 and 15.0 nm (see Table S3 in the ESI†), respectively, *i.e.*, they are smaller than the film thickness. Still, position and general shape of the N 1s peaks are the same as for the 7 keV spectrum, indicating that the reaction is homogeneous over the entire depth of the film.

The fact that the H_2 TPP film reacts over its entire thickness of 24 nm (or even 50 nm in the TPD-MS experiment) is exceptional when compared to related reactions with transition metals. For example, when Fe or Co are deposited onto H_2 TPP films at room temperature, formation of the related FeTPP and CoTPP complexes is limited to a depth of approximately 1 nm.¹⁶ Additionally deposited metal forms a layer of metallic Fe or Co on-top of the organic film. It can be concluded that the room-temperature mobility of Li atoms in the solid porphyrin is much higher than that of typical transition metals.

To evaluate whether the direct formation of Li₂TPP is thermodynamically feasible, gas-phase DFT calculations were performed.

For the reaction shown in Fig. 1, a total energy of ΔE_{DFT} = -499.8 kJ mol⁻¹ was obtained, indicating that the gas-phase process is strongly exothermic. In the following, we use this gas-phase value to estimate the energy for the corresponding solid-state reaction by means of a Born-Haber (BH) cycle (see Fig. S6 in the ESI[†]), which includes the sublimation enthalpy of Li metal and the desorption energies of H2TPP and Li2TPP as obtained from TPD-MS above. The BH cycle yields an approximate reaction energy of -215 kJ mol⁻¹, which is still strongly exothermic. Another driving force of the solid-state reaction is the entropy gain from the release of gaseous H₂ $(S_{\text{gas,1 bar}}^{\circ} = 130.68 \text{ J mol}^{-1} \text{ K}^{-1} \text{ at } 298.15 \text{ K}).^{31}$ Energetic and entropic contributions add up to a standard Gibbs energy of approximately -254 kJ mol⁻¹, indicating that the formation of Li₂TPP is thermodynamically favored even in the solid state. Vapor deposition should therefore not be necessary to induce the reaction, except to overcome kinetic barriers. The calculated minimum energy structure of the Li₂TPP complex is shown in Fig. S7 in the ESI.[†] The Li ions are located on both sides of the porphyrin ring, but not above (or below) the center of the porphyrin ring, in agreement with previous theory work.³² The frontier orbitals HOMO-1, HOMO, LUMO and LUMO+1 are exclusively localized at the porphyrin ring; the Li ions do not contribute (see Fig. S8 in the ESI[†]).

In conclusion, we have demonstrated that dilithium tetraphenylporphyrin (Li_2 TPP) can be prepared in solvent-free form by direct reaction of *meso*-tetraphenylporphyrin (H_2 TPP) with vapor-deposited metallic Li at room temperature. DFT calculations show that the reaction is strongly exothermic in the gas phase. A negative standard Gibbs energy for the solid-state reaction confirms that the reaction is thermodynamically favored also in the condensed phase. Our results may pave the way to simple solidstate syntheses of alkali metal porphyrins and thus increase the availability of these compounds as reactants for organic and inorganic synthesis. The exceptionally high mobility of Li in the organic material is relevant for the deposition of metal electrodes in organic electronic devices and the transport of Li in electrochemical energy storage.

Financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through project number 223848855 – SFB 1083 is gratefully acknowledged. We thank the Helmholtz-Zentrum Berlin for allocation of synchrotron radiation beamtime at BESSY II and financial support. We thank M. Albus, C. Zülch and F. Fillsack for assistance during the measurements. We thank the HRZ Marburg for computational resources.

Conflicts of interest

There are no conflicts to declare.

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Communication

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