Electronic Supplementary Information (ESI) for

Direct Synthesis of Dilithium Tetraphenylporpyhrin: Facile Reaction of a Free-Base Porphyrin with Vapor-Deposited Lithium

Maik Schöniger[‡], Stefan R. Kachel[‡], Jan Herritsch, Philipp Schröder, Mark Hutter, J. Michael Gottfried*

Department of Chemistry, Philipps University Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany. E-mail: michael.gottfried@chemie.uni-marburg.de

‡ These authors contributed equally to this study and share first authorship.

1. Experimental and computational methods

TPD-MS was carried out in a dedicated UHV apparatus with a base pressure in the low 10⁻¹⁰ mbar regime. The apparatus hosts a HIDEN EPIC 1000 quadrupole mass spectrometer (QMS) mounted inside a pumped cryoshroud cooled to 80 K with l-N₂. This version of a lineof-sight mass spectrometer was described elsewhere.¹ Temperatures were measured directly at the sample using a calibrated Type K thermocouple. A polished Au(111) single-crystal surface (diameter 10 mm, purity > 99.999%, roughness < 0.01 μ m, orientation accuracy < 0.1°, from MaTecK/Germany) was prepared by iterated sputtering with Ar^+ ions (1.0 keV, 3-5 μA , 30 min) and annealing (850 K, 3 min). H₂TPP (purity > 98%, PorphyChem) was evaporated from a home-built Knudsen cell (glass crucible) at fluxes of 0.1 to 1.0 nm min⁻¹. The molecular flux was measured using a quartz crystal microbalance (QCM). Unless otherwise noted, the Au(111) sample was held at 100 K during deposition of H₂TPP. Li (purity > 99.9%, Sigma-Aldrich) was evaporated from a home-built Knudsen cell (boron nitride crucible) at fluxes of 0.1 to 1.0 nm min⁻¹. The prepared sample was placed directly in front of the orifice (8 mm diameter) of the cryoshroud. The crystal was heated resistively via tungsten wires with a constant heating rate of 0.1 K s⁻¹. During heating, survey mass spectra from 4 to 10 amu (0.2 amu step width) and from 600 to 650 amu (0.5 amu step width) were recorded together with the temperature. Acquisition of one cycle took around 8 s, leading to a temperature rise of 0.8 K per cycle. With this procedure, the possible products of the reaction of Li with H₂TPP can be detected, including side products or contaminations with higher masses. The results are presented in the form of TPD-MS maps.

Hard X-ray photoelectron spectroscopy (HAXPES) was performed at the HIKE endstation of the KMC-I beamline at BESSY II, Helmholtz-Zentrum Berlin.² The spectra were recorded at 300 K in almost grazing incidence and near normal-emission geometry (incidence angle 77°, detection angle 13°, both relative to the surface normal). Binding energies were referenced to Au 4f_{7/2} (84.00 eV). Photon energies of 2 to 3 keV and 7 keV were obtained from Si(111) and Si(422) monochromator crystals, respectively. The samples were prepared under UHV conditions at a base pressure better than $1 \cdot 10^{-9}$ mbar. H₂TPP was vapor-deposited onto clean Si(001) with a rate of ≈ 1.2 nm min⁻¹, as measured with a QCM. This led to a smooth film (average roughness ≈ 2.20 nm)³ with a thickness of 24 nm. After the measurement of the pristine H₂TPP sample, an excess of Li (≈ 19 nm, purity > 99.9%, Sigma-Aldrich) was deposited at a rate of ≈ 0.3 nm min⁻¹.

Density functional theory (DFT) calculations were performed with Gaussian09, C.01.⁴ A full geometry optimization was carried out using the PBE⁵ functional and the def2-TZVPP⁶ basis set.

2. Additional TPD-MS data



Figure S1. 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 mass region 4 to 10 amu to probe for Li desorption. The heating rate was 0.1 K s⁻¹ and one mass range cycle took 8 s. The spectra were normalized to the maximum intensity of the Li signal (Figure S1c).



Figure S2. Common TPD traces for the relevant species for (a) 1 nm Li on 20 nm H_2 TPP and (b) 10 nm Li on 50 nm H_2 TPP, both on Au(111). The TPD signal of LiTPP (black) was multiplied by a factor of 12 to show that it exactly reflects the TPD signal of Li₂TPP (red), and hence, is the consequence of fragmentation of Li₂TPP in the mass spectrometer. Furthermore, for (b) recrystallization of the Li₂TPP film is observed as indicated by the peak broadening on the low temperature side. Intensities are in arbitrary units.



Figure S3. Arrhenius plot analysis for the first small peak (see Figure 2b) compared to the multilayer peak for 1 nm Li on 20 nm H₂TPP on Au(111). The desorption rate r_{des} was divided by the mass spectrometer unit (counts per second).

The Arrhenius plot analysis (Figures 2d, 2e and S3) was performed using the Polanyi-Wigner Equation (S1)

$$r_{\rm des} = -\frac{\mathrm{d}\Theta}{\mathrm{d}t} = \mathbf{v} \cdot \exp\left(-\frac{\Delta E_{\rm des}}{RT}\right) \cdot \Theta^n \tag{S1}$$

with the desorption rate r_{des} , the coverage Θ , the time *t*, the pre-exponential factor v, the activation energy of desorption ΔE_{des} , the gas constant *R*, the sample temperature *T*, and the desorption order *n*. In case of multilayer desorption, *n* is zero, hence, the desorption rate becomes coverage-independent. Taking the natural logarithm yields a simple Arrhenius Equation (S2) in the form of y = mx + b. Note that mathematically this is only allowed if the quantities are divided by their units.

$$\ln(r_{\rm des}) = -\frac{\Delta E_{\rm des}}{RT} + \ln(\nu)$$
(S2)

 ΔE_{des} is derived from the slope *m* of a plot of $\ln(r_{\text{des}})$ vs. 1/*T*. The resulting values are shown in Table S1.

Table S1. Fit results of the Arrhenius plot analysis for the spectra in Figures 2d, 2e and S3. The preexponential factors v were not calculated because multilayer experiments have been performed.

Spectra	Species	Slope (m) / K	$\Delta E_{\rm des}$ / kJ/mol
Figure 2d	Li ₂ TPP	-28131	234
Figure 2e	H ₂ TPP	-24095	200
Figure S3	Li ₂ TPP (cryst.)	-22343	186

3. Additional XPS data



Figure S4. Si 1s XP spectra of H_2 TPP (bottom) and Li₂TPP formed by deposition of Li onto a 24 nm thick H_2 TPP layer (other spectra). The spectra were taken with the indicated photon energies.



Figure S5. XP spectra of the Li 1s region of (a) a clean Au(111) crystal, (b) Li deposited onto Au(111) and (c) Li₂TPP on Au(111). Subtraction of the Au $5p_{3/2}$ signal at 57.1 eV (a) from the spectra (b) and (c) led to the Li 1s peaks in the graph on the right-hand side. Al K α (1486.71 eV) was used as X-ray source. It can clearly be seen, that the Li 1s peak of (c) Li₂TPP (56.9 eV) is shifted to higher binding energies compared to that one of (b) metallic Li (54.6 eV). The value for the metallic Li 1s peak is in agreement with the literature (54.8 eV).⁷

4. Information depth of the XPS experiments

The probability that a photoelectron, created at a depth z below the solid/vacuum interface, actually reaches this interface without energy loss decreases exponentially with increasing z. The ratio between the initial flux of photoelectrons at a depth $z(I_0)$ and the flux measured at the solid/vacuum interface I is given by:

$$\frac{I}{I_0} = \exp\left(-\frac{z}{\lambda\cos\theta}\right)$$
(S3)

Equation (S1), in which θ is the angle between the electron trajectory and the surface normal, also provides the precise definition of the inelastic mean free path (IMFP) λ .⁸ Because of the exponential dampening of the signal with increasing *z*, approximately 95% of the total signal of a given photoelectron line emerge from a near-surface layer with a thickness of $3\lambda \cdot \cos\theta$. This value is typically referred to as *information depth*. For most materials, λ increases monotonically with the kinetic energy for energies above 100 eV.⁸ As a consequence, the relative contribution of the electrons originating from deeper layers to the total signal increases for larger photon energies.

In accordance with the results by Seah and Spencer,⁹ we will use the Gries G1 equation^{10,11} to calculate the IMFPs and information depths for H₂TPP and Li₂TPP. In the G1 equation, the energy-dependent inelastic mean free path (IMFP) λ is expressed as:

$$\lambda(E_{\rm kin}) = k_1 \left(\frac{V_{\rm a}}{Z^*}\right) \frac{E_{\rm kin}}{\log_{10}(E_{\rm kin}) - k_2} \tag{S4}$$

The kinetic energy E_{kin} in Equation (S4) is given in eV and the IMFP λ in nm. For a certain compound, the parameter V_a is determined by the stoichiometry and density ρ of the material, while Z^* depends only on the stoichiometry.¹⁰ The parameters k_1 and k_2 also depend on the material; for organic compounds, k_2 is unity and k_1 depends on the H/C ratio of the material: $k_1 = 0.0017$ at H/C = 1 and $k_1 = 0.0023$ at H/C = 2.^{9,10} Seah and Spencer found that a linear interpolation of k_1 for materials with H/C ratios different from either 1 or 2 leads to excellent results for the calculated IMFPs.⁹ Table S2 summarizes the parameters for H₂TPP and Li₂TPP. V_a and Z^* are calculated according to Gries.¹⁰ Due to the lack of actual data, the density of the *in-situ* prepared Li₂TPP was calculated under the simplifying assumption that its molar volume is identical to that of H₂TPP.

Table S2. Material parameters and coefficients for H_2 TPP and Li_2 TPP that are used for the calculation of the IMFP with Equation (S4).

	Formula	H/C	Density ρ / g cm ⁻³	$\frac{k_1}{\text{eV cm}^3}$	<i>k</i> ₂	$V_{ m a}$ / cm ³ mol ⁻¹	Z*
H ₂ TPP	C44H30N4	0.682	1.274	0.00151	1	6.1863	1.902
Li ₂ TPP	Li ₂ C ₄₄ H ₂₈ N ₄	0.636	1.2986	0.00148	1	6.1863	1.921

The Li₂TPP formation was monitored by recording N 1s core level spectra at photon energies E_{ph} between 2 and 7 keV; the corresponding kinetic energies E_{kin} were ≈ 0.4 keV lower due to the N 1s binding energy. These values result in the following information depths $3\lambda \cdot \cos\theta$ ($\theta_{exp} = 13^{\circ}$) in nm (Table S3):

E . / koV	E., /koV	Information depth / nm			
L _{ph} / Ke v	$L_{\rm kin}$ / KC V	H ₂ TPP	Li ₂ TPP		
2	1.6	10.4	10.1		
2.5	2.1	13.0	12.6		
3	2.6	15.4	15.0		
7	6.6	33.6	32.7		

Table S3. Calculated information depths $3\lambda \cdot \cos\theta$ ($\theta_{exp} = 13^{\circ}$) obtained by application of Equation (S4), for the different photon energies applied for the acquisition of the N 1s XP spectra of H₂TPP and Li₂TPP.

5. Estimation of the reaction energy in the solid state

Gas-phase DFT calculations of the metalation reaction yield a total energy of $\Delta E_{\text{DFT}} = -499.8 \text{ kJ mol}^{-1}$. This gas-phase value is used to estimate the energy for the corresponding solid-state reaction by means of a Born-Haber (BH) cycle (Figure S6), which includes the sublimation enthalpy ΔH_{sub} of metallic Li and the desorption activation energies ΔE_{des} of H₂TPP and Li₂TPP as obtained from TPD-MS. The BH cycle yields an approximate reaction energy of $\Delta E_{\text{R,s}} = -215 \text{ kJ mol}^{-1}$, which means that the solid-state reaction is strongly exothermic.



$$\Delta E_{\rm Rs} = (200 + 318.6 - 499.8 - 234) \approx -215$$

Figure S6. Born-Haber cycle for the estimation of the solid-state reaction energy $\Delta E_{R,s}$ from the reaction energy of the gas-phase reaction obtained by DFT calculations. All energies are given in kJ mol⁻¹. This estimation neglects small numerical differences between the measured desorption activation energies and sublimation enthalpies, as well as the temperature dependence of these quantities. This simplification is justified considering the large uncertainties of related literature values. For example, for the sublimation enthalpy of H₂TPP, values between 111 and 240 kJ mol⁻¹ have been reported.¹²

6. Additional results of the DFT calculations



Figure S7. Geometry-optimized ground state structure of Li_2TPP . The phenyl groups and hydrogen atoms attached to carbon atoms are omitted for the sake of clarity, but were included in the calculations. The Li ions are displaced from the central positions above or below the porphyrin plane and the porphyrin ring shows a slight saddle-shape distortion.



Figure S8. Selected frontier orbitals of Li₂TPP and related energies referenced to the vacuum level.

References

- B. P. Klein, N. J. van der Heijden, S. R. Kachel, M. Franke, C. K. Krug, K. K. Greulich, L. Ruppenthal, P. Müller, P. Rosenow, S. Parhizkar, F. C. Bocquet, M. Schmid, W. Hieringer, R. J. Maurer, R. Tonner, C. Kumpf, I. Swart and J. M. Gottfried, *Phys. Rev. X*, 2019, 9, 011030.
- M. Gorgoi, S. Svensson, F. Schäfers, G. Öhrwall, M. Mertin, P. Bressler, O. Karis, H. Siegbahn, A. Sandell, H. Rensmo, W. Doherty, C. Jung, W. Braun and W. Eberhardt, *Nucl. Methods Phys. Res. A*, 2009, 601, 48.
- 3. M. Schmid, S. R. Kachel, B. P. Klein, N. Bock, P. Müller, R. Riedel, N. Hampp and J. M. Gottfried, *J. Phys. Condens. Matter*, 2019, **31**, 094002.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, 2009.
- 5. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.
- 6. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297.
- 7. S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak and D. A. Shirley, *Phys. Rev. B*, 1973, **8**, 3583.
- 8. M. P. Seah and W. A. Dench, *Surf. Interface Anal.*, 1979, **1**, 2.
- 9. M. P. Seah and S. J. Spencer, Surf. Interface Anal., 2011, 43, 744.
- 10. W. H. Gries, Surf. Interface Anal., 1996, 24, 38.
- 11. W. S. M. Werner, W. H. Gries and H. Störi, Surf. Interface Anal., 1991, 17, 693.
- 12. A. Stefanov, A. Stibor, A. Dominguez-Clarimon and M. Arndt, *J. Chem. Phys.*, 2004, **121**, 6935.