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Synthesis and characterisation of a bis(silyloxy)tin(IV) porphyrin

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Abstract

Bis(hydroxy)tin(IV) tetraphenylporphyrin (Sn(IV)TPP(OH)$_2$, **2**) condenses with two equivalents of tris(*tert*-butoxy)silanol (HOSi(O^{t}Bu)$_3$, **3**) to form complex **2**.**3**$_2$ in toluene. The product, which is air and moisture stable, has been characterised by ^{1}H, ^{29}Si and ^{119}Sn NMR spectroscopy and mass spectrometry. Application of this reaction in producing novel photochromic glasses is also discussed.

Keywords: Sn(IV) porphyrins; Silanols; Complexations; NMR spectroscopy

Effective conversion of solar energy into electrical energy is important for our sustainable future. Dye-sensitised solar cells have shown promise as an alternative technology to the proven silicon-based, semi-conductor type photovoltaic cells [1]. While the conversion efficiency in both cases is useful at 10–30%, the process is costly [2,3]. Nature adopts a different approach to solar energy transduction. Although the chloroplasts within natural organisms are <1% efficient in sunlight collection, they are >99% efficient in converting the absorbed light into useful chemical energy. Photosynthetic cells overcome the initial energy collection limitation by self-assembling large arrays of (porphyrinic) light harvesting molecules that collect and deliver absorbed light energy to the primary reaction centre via energy transfer mechanisms. Thus, if arrays of organic light harvesters could be prepared so as to offset the comparative loss of initial efficiency in light collection, organic solar cells (either in isolation or in conjunction with existing silicon technologies) could become viable [4].

Of the potential interfaces available for light harvesting, glasses seem the most pragmatic due to their ubiquitous use. In terms of light absorption, glasses that have been surface-modified to produce thin layers of porphyrinic arrays should also be compatible with the strong light absorption properties of the same porphyrinic materials, i.e., allowing 100% of visible light to be absorbed by the porphyrin chromophore. We have been investigating the condensation of bis(hydroxy)tin(IV) porphyrins with a range of structurally varied phenols and carboxylic acids to produce both discrete multiporphyrin assemblies and supramolecular arrays [5–8]. Here, we report on the reaction of tris(*tert*-butoxy)silanol with Sn(IV) tetraphenylporphyrin **2** and describe some qualitative experiments on glass.

Tetraphenylporphyrin **1** was metallated (SnCl$_2$/pyridine) using the method of Arnold to yield the Sn(IV) porphyrin as a mixture containing both hydroxy and chloro axial ligands [9]. In our hands there has become a need to convert the product entirely to the bis(hydroxy) Sn(IV) system using a biphasic mix of THF/H$_2$O in the presence of K$_2$CO$_3$ [10]. Condensation of

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Sn(IV) porphyrin **2** with two equivalents of silanol **3** in refluxing toluene proceeded to yield the bis-product **2.3**$_2$ (Scheme 1) in essentially quantitative yield.

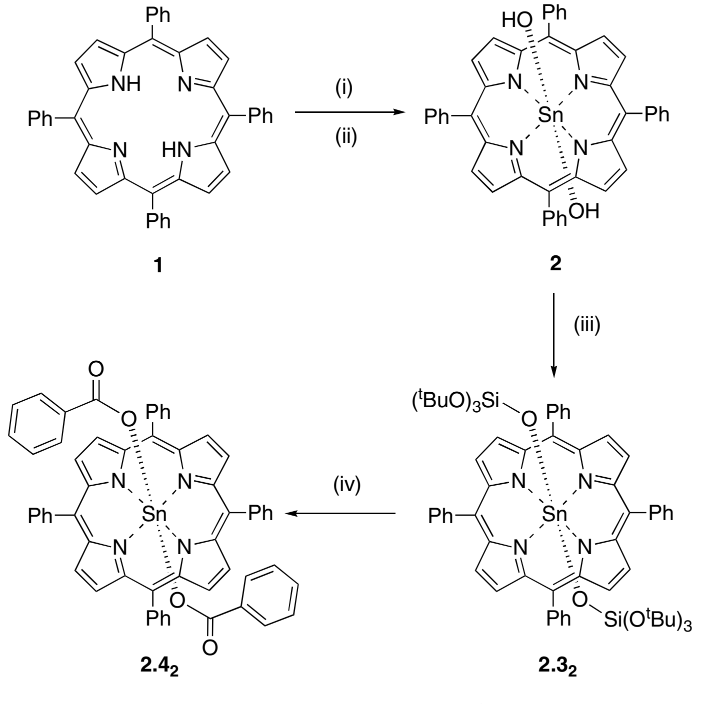
Characterisation of the complex **2.3**$_2$ was possible by ^{1}H, ^{119}Sn and ^{29}Si NMR spectroscopy. As shown in Fig. 1(b), the ^{1}H NMR spectrum of complex **2.3**$_2$ shows a minor but significant upfield shift ($\Delta\delta$ −0.1) of the resonance corresponding to the β-pyrrolic protons of **2** upon complexation. Chemical shift changes of comparable magnitude have been reported for **2** reflecting the exchange of axial ligands from the bis(hydroxy) complex [11]. A more significant change in chemical shift ($\Delta\delta$ −1.8) was observed for the peak corresponding to the *tert*-butyl protons of **3**. The large change in chemical shift is attributed to the close proximity of these protons to the shielding anisotropy of the porphyrin macrocycle upon binding. This shift is not as significant as for other ligands but consistent with the average distance the *tert*-butyl protons reside from the plane of the porphyrin. Associated with this $\Delta\delta$ was the disappearance of the axial hydroxy proton resonance at δ −7.4 as these protons are exchanged for silanol ligands. Satellite signals due to Sn(IV)–H coupling (e.g., **2.3**$_2$ $^4J_{\mathrm{av}} = 12.4$ Hz) were also evident for the β-pyrrolic resonances (see expansions in Fig. 1) although not sufficiently resolved to observe separate coupling to the two tin nuclei (^{117}Sn and ^{119}Sn).

To confirm the formation of **2.3**$_2$ and not just a hydrogen bonded complex, porphyrin **2** and silanol **3** were mixed in $CDCl_3$ and monitored at ambient temperature by ^{1}H NMR spectroscopy. No changes to the spectrum were observed compared to **2** or **3** separately supporting the coordinate covalent nature of the bonding in **2.3**$_2$ rather than non-covalent. Prolonged reaction times (days) revealed some spectral changes indicative of complexation and after four days no resonances corresponding to **2** were observed suggesting condensation was driven toward **2.3**$_2$.

^{119}Sn NMR spectroscopy revealed a resonance at δ −645.4 (Fig. 2(a)) which was assigned to the Sn(IV) centre also diagnostic of **2.3**$_2$. The value was shifted upfield by 76 ppm from the reported Sn(IV) chemical shift of porphyrin **2** (δ −569.6) [10]. The minor resonance observed at δ −607.9 is thought to be attributable to a minor amount of the mono-hydroxy product **(HO)2.3**.

^{29}Si NMR spectroscopy was also used to probe the nature of the complex **2.3**$_2$. The resonance observed at δ −101 (Fig. 2(b)) is attributable to the presence of silicon in complex **2.3**$_2$. This value was shifted upfield by 11 ppm compared to the silicon resonance of uncomplexed **3** (−90 ppm). By acquiring in excess of 50 000 scans, the appearance of satellites due to Sn(IV)–Si coupling (ca. $^2J = 16$ Hz) were also evident in the spectrum (Fig. 2(b)).

Mass spectrometry (electrospray and laser desorption ionisation) confirmed the presence of the condensation product **2.3**$_2$. The molecular ion was observed at *m*/*e* 995 which compares well to the calculated value less one silanol ligand **3**. The observation of the mono-complexed species in the gas phase is acceptable due



Scheme 1. Reagents and conditions: (i) $SnCl_2$, pyridine; (ii) K_2CO_3, THF, H_2O; (iii) (^{t}BuO)$_3$SiOH **3** (2 equivalents), toluene, Δ, Dean–Stark; (iv) benzoic acid **4** (2 equivalents), $CDCl_3$, Δ.

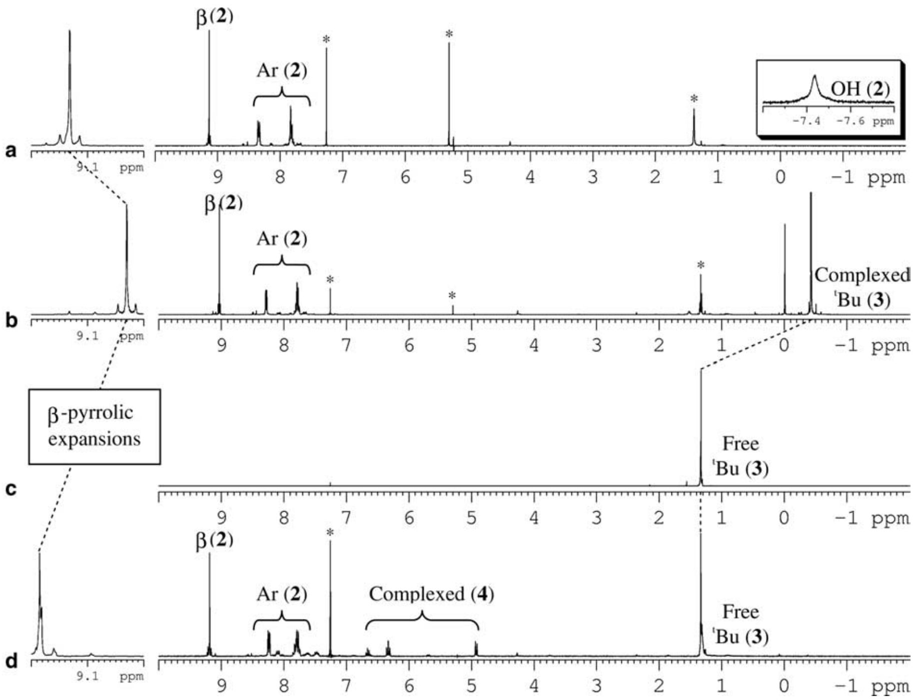


Fig. 1. ^{1}H NMR (CDCl$_3$) spectroscopic comparison between: (a) (300 MHz) Sn(IV) porphyrin **2**; (b) (400 MHz) complex **2.3$_2$**; (c) (400 MHz) silanol **3**; (d) (300 MHz) complex **2.4$_2$** displaying the significant complexation induced chemical shifts. * = solvent peaks, β = β-pyrrolic protons of **2**; Ar = aromatic protons of **2**; ^{t}Bu = *tert*-butyl protons of silanol **3**; inset = resonance attributable to the axial hydroxy protons of **2**.

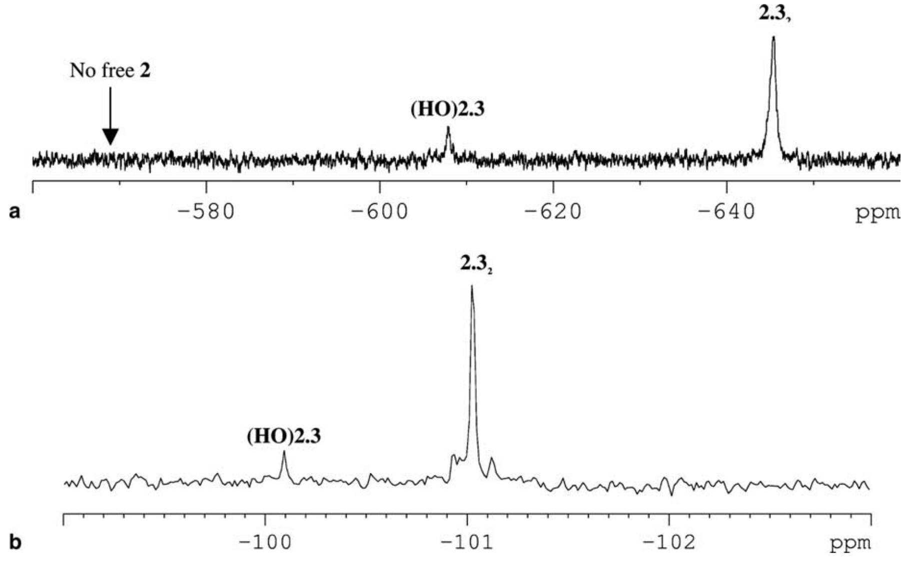


Fig. 2. Selected regions of the: (a) ^{119}Sn and (b) ^{29}Si NMR spectra of **2.3$_2$** in CDCl$_3$.

to the weaker nature of metal coordinate bonds and the conditions of the mass spectrometry experiment.

To assess the stability of the complex **2.3$_2$** towards further ligand exchange a sample was heated at reflux with two equivalents of benzoic acid **4** in CDCl$_3$ (Fig. 1). After three days the bis(benzoic acid) complex **2.4$_2$** was predominately observed by ^{1}H NMR spectroscopy. The expanded region of the spectrum (Fig. 1(d)) clearly indicates the downfield shift of the β-pyrrolic resonance (Δ*δ* 0.05) upon exchange of the axial silanol ligand for acid **4**. In addition to the new resonances observed for the aromatic protons of complexed **4** (*δ* 6.6, 6.3 and 4.9) a peak at *δ* 1.3 indicative of free silanol **3** was observed. This experiment suggests **2.3$_2$** is sufficiently stable and requires forcing conditions for exchange to alternative ligands while importantly still demonstrating the reversible nature of the silanol condensation process.

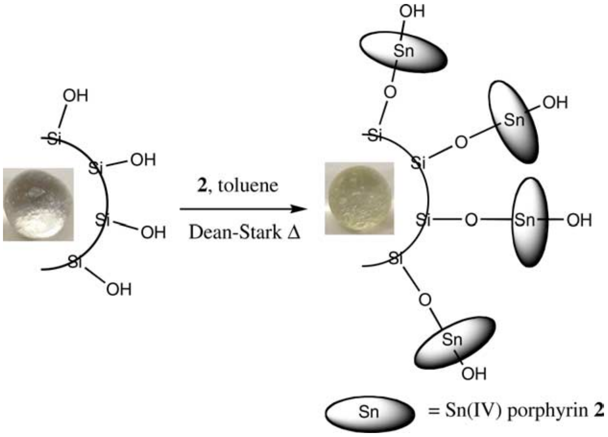


Fig. 3. Schematic representation demonstrating the monolayer coating of Sn(IV) porphyrins to the glass bead surface.

Applying the concept of porphyrin–silanol binding to a more practical system, an experiment was conducted to assess the potential of coating a glass surface under similar conditions. Spherical glass beads were heated with porphyrin **2** under Dean–Stark conditions in anhydrous toluene overnight. After evaporation of the solvent the glass beads were washed with chloroform consecutively to remove excess porphyrin and dried. A photographic comparison of a glass bead before (left bead) and after (right bead) is shown in Fig. 3. The weak colouration of the bead illustrates at least a monolayer coating of Sn(IV) porphyrin on the glass bead. Attenuated reflectance (ATR) IR spectroscopy was used to confirm that the porphyrin coating is at most a few microns thick.

Further experiments involving the binding of Sn(IV) porphyrins to glass surfaces, their functionalisation, orientation and photophysics are continuing in our laboratory and a comprehensive report of these results will be published in due course.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2005.07.005.

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