

Switchable photoreduction pathways of antimony(v) tetraphenylporphyrin. A potential multielectron transfer photosensitizer

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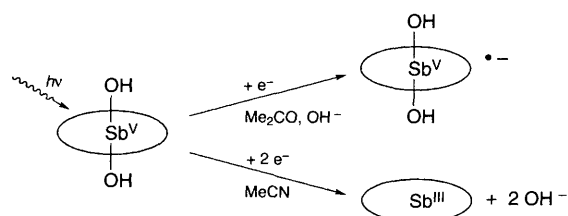
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Photoreduction of [Sb^V(tpp)(OH)₂]⁺ (tpp = dianion of 5,10,15,20-tetraphenylporphyrin) yields either the metastable π -radical anion [Sb^V(tpp^{•-})(OH)₂] or the two-electron reduced [Sb^{III}(tpp)]⁺ complex; product formation can be channelled in the desired direction by an appropriate choice of the reaction medium and dioxygen regenerates the starting compound.

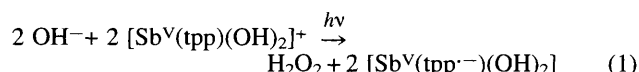
One of the most challenging areas in coordination chemistry remains the design of efficient multiple-electron redox systems^{1–3} capable of performing selective catalytic substrate transformations. Evolution of life on earth has resulted in a diverse array of metalloenzyme prosthetic groups to reach this goal with expertise.^{4,5} A widespread strategy to achieve multielectron transfer reactivity in both natural and artificial systems is the accumulation of redox equivalents by polynuclear transition-metal sites.^{6,7} On the other hand, redoxactive ligands can serve as intermediate charge reservoirs within monometallic multielectron reaction centres.⁸ Following this second approach, it has recently been shown that a single antimony(III) centre coordinated to porphyrin sensitizers can provide an active site for the photochemical transformation of molecular oxygen to water in consecutive two-electron steps.⁹ A reversible photochemical interconversion of the redox couple Sb^{III}–Sb^V could lead to novel systems for homogeneous photocatalysis. It is well known,^{10,11} that antimony(v) porphyrins readily form stable π -radical anions at very high reduction potentials. These compounds can therefore act as powerful photooxidants in their intraligand excited states.^{12–14} A light-induced reaction at the high-valent central metal, however, has never been observed in previous studies. In this context we report the redox behaviour of the complex [Sb^V(tpp)(OH)₂]⁺,[†] where electron transfer routes can be controlled and directed to yield either ligand-based or metal-centred reduction products (Scheme 1).

Upon visible-light irradiation in alkaline acetone solution, the absorption bands of [Sb^V(tpp)(OH)₂]⁺ rapidly disappear (Fig. 1).[‡] The photolysis is accompanied by the development of a NIR spectral pattern which, together with a structureless EPR signal, is diagnostic for the formation of the ligand-centred radical [Sb^V(tpp^{•-})(OH)₂].[§] The starting porphyrin compound is completely restored after aeration of the solution. At an OH⁻ concentration of 3.3 × 10⁻² mol dm⁻³, the quantum yield for the production of the π -radical anion was determined as $\phi = 1 \times 10^{-2}$ ($\lambda_{\text{irr}} = 546 \text{ nm}$).[‡] Under these conditions, the



Scheme 1 Formation of ligand-based vs. metal-centred photoreduction products

photoreduction of the antimony(v) complex yields stoichiometric amounts of hydrogen peroxide,[¶] according to the following endogenic reaction, eqn. (1).



While there is no doubt that this photoreaction requires OH⁻, the actual role of the hydroxide ion is less clear. Although OH⁻ radicals have not been detected during the reductive quenching of photoexcited antimony porphyrins, it has been proposed¹⁴ that a hydroxide ion might act as the primary electron donor. Formation of H₂O₂ could in fact result from a recombination of photogenerated hydroxyl radicals.¹⁵ Nevertheless, hydrogen peroxide may also originate from a completely different OH⁻-coupled process that avoids the thermodynamically unfavourable formation of hydroxyl radicals as intermediates. The pH dependence of the [Sb^V(tpp)(OH)₂]⁺ absorption spectrum in aqueous solution indicates that one of the axial hydroxo ligands can be titrated with pK_a = 9.7 ± 0.1 at 298 K. In analogy to a recently characterised phosphorus porphyrin,¹⁶ this reversible deprotonation step is suggested to generate a neutral [Sb^V(tpp)(O)(OH)] ground-state species containing an Sb=O oxometallate fragment. Irradiation of this compound might lead to the formation of a binuclear, peroxo-bridged intermediate, that could hydrolyse to form the final products given in eqn. (1).

As previously observed with only a few other metalloporphyrins,¹⁷ the redox site of [Sb^V(tpp)(OH)₂]⁺ can be completely shifted from the porphyrin ligand to the central metal by a variation of the reaction medium. In dry acetonitrile solution, the photochemical or electrochemical reduction of the antimony(v) complex induces spectral changes with characteristic new absorptions at 465 and 644 nm (Fig. 2) that originate

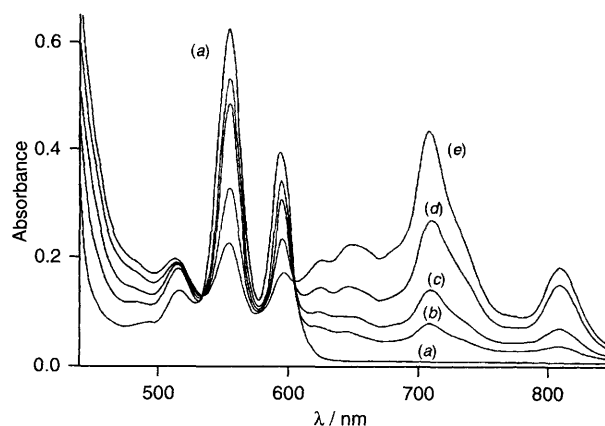
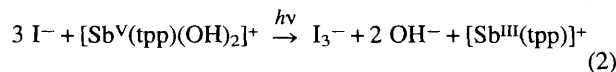


Fig. 1 Spectral variations during the photolysis of 5.4 × 10⁻⁵ mol dm⁻³ [Sb^V(tpp)(OH)₂]⁺Cl⁻ in a mixture of acetone and 0.1 mol dm⁻³ aqueous NaOH (2 : 1 v/v) at 0 (a), 1 (b), 2 (c), 3 (d) and 4 min (e) irradiation times, $\lambda_{\text{irr}} = 546 \text{ nm}$, 1.0 cm cell[‡]

from the formation of antimony(III) tetraphenylporphyrin.⁹ Thus, in acetonitrile containing 10^{-2} mol dm⁻³ NEt₄I, the photolysis of 6.0×10^{-5} mol dm⁻³ [Sb^V(tpp)(OH)₂]⁺ at $\lambda_{\text{irr}} = 546$ nm leads to the production of [Sb^{III}(tpp)]⁺ with a quantum yield of $\phi = 4 \times 10^{-3}$. At the same time, absorption bands of the polyhalide anion I₃⁻ emerge with maxima¹⁸ at 290 and 360 nm. The metal-centred photoreduction of the antimony(v) porphyrin proceeds according to the following stoichiometry, eqn. (2).



In order to understand the mechanism of this net two-electron photoredox reaction, we studied the electrochemistry of [Sb^V(tpp)(OH)₂]⁺ at 298 K in the absence of iodide. The cyclic voltammetric curve of the metalloporphyrin in dry acetonitrile displays several reduction peaks, the morphology and dependence on scan rate of which suggest the occurrence of chemical reactions coupled to the heterogeneous electron transfers. In particular, the first peak has a peak potential of ca. -0.25 V (vs. SCE) and corresponds to a chemically irreversible electron transfer for scan rates up to the investigated limit (10 V s⁻¹). A controlled-potential coulometric experiment was carried out corresponding to the first reduction, and the electrolysed solution was monitored by UV-VIS absorption spectroscopy (Fig. 2). Exhaustive electrolysis indicates the exchange of two electrons per three molecules of the starting compound. During the electrolysis a gradual decrease of the absorption bands relative to the starting species is observed. At the same time the absorption bands of [Sb^{III}(tpp)]⁺, that is the two-electron reduction product of the starting species, appear and their intensity increases proportionally to the charge exchanged. The final [Sb^{III}(tpp)]⁺ concentration reaches $30 \pm 5\%$ of the amount of the starting compound consumed by electrolysis. The remaining product percentage is ascribed to the deprotonated complex [Sb^V(tpp)(O)(OH)], which is formed from the starting compound by its reaction with hydroxide ions released during [Sb^{III}(tpp)]⁺ production. Since the deprotonated antimony(v) complex obviously is not electroactive at the applied potential,

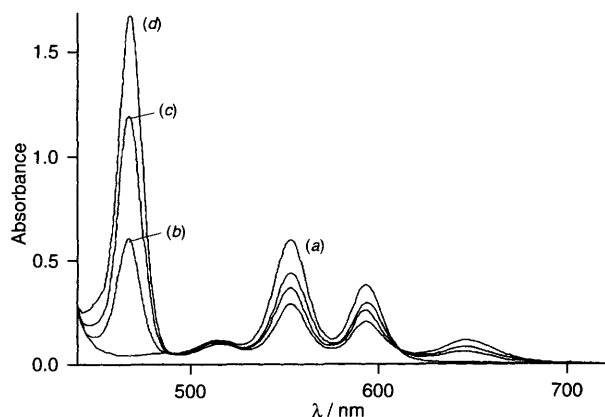
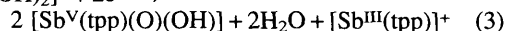


Fig. 2 Spectral changes during the successive electroreduction of 5.0×10^{-4} mol dm⁻³ [Sb^V(tpp)(OH)₂]⁺Cl in dry acetonitrile (a)–(d); 0.1 cm cell. Similar spectra were obtained upon photoreduction in acetonitrile solution (see text).

the exhaustive electrolysis corresponds to the following overall reaction, eqn. (3). Most probably¹⁹ the first reduction of 3 [Sb^V(tpp)(OH)₂]⁺ + 2e⁻ →



[Sb^V(tpp)(OH)₂]⁺ in dry acetonitrile takes place at the porphyrin ligand. However, in this solvent at 298 K the resulting π -radical anion apparently undergoes an efficient intramolecular electron transfer to the central metal. Such a process should lead to a paramagnetic antimony(IV) porphyrin,¹⁹ that can reach the stable Sb^{III} oxidation state either by disproportionation, eqn. (3), or by its reaction with suitable electron donors like iodide, eqn. (2).

Since [Sb^V(tpp)(OH)₂]⁺ is readily formed during visible-light photooxidation of [Sb^{III}(tpp)]⁺ in the presence of molecular oxygen,⁹ this system promises to be of interest for multielectron photoredox catalysis in homogeneous solution.

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Footnotes

† Selected spectroscopic data: FD-MS *m/z* 767.7 (Calc. for C₄₄H₃₀N₄O₂Sb⁺ 767.1). IR (CH₂Cl₂) 3670, 3580 cm⁻¹ ($\nu_{\text{O-H}}$). UV-VIS [EtOH, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)] 314 (12 900), 419 (316 200), 552 (11 800), 591 (6400).

‡ Quantum yields were determined with a Polytec pyroelectric radiometer; experimental details are as previously described.⁹

§ EPR: *g* = 2.004 (62 K, no hyperfine pattern). VIS-NIR [Me₂CO-NaOH, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)] 428 (66 800), 706 (7700), 808 (3200).

¶ An enzymatic assay was used to quantify hydrogen peroxide.⁹

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