Sterically-Hindered Zinc Porphyrins for Solar-Energy Conversion

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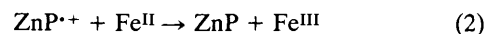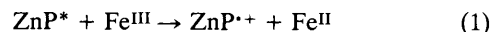
Zinc porphyrins (1) and (2), their triplet excited states and their cation and anion radicals, are remarkably stable in 1 M nitric acid: the consequences for photosensitised water reduction, oxidation, and the photogalvanic effect, are discussed.

Synthetic porphyrins have played an important part in the development of photochemical systems for solar-energy conversion and storage[1] and in modelling the natural photosynthetic process.[2] This is because of their superior light-absorbing properties, long triplet-state lifetimes, and favourable redox properties. Water-soluble zinc porphyrins, in particular, photosensitise water reduction[1] and oxidation,[3] and exhibit a photogalvanic effect.[4] However, one of the shortcomings of these photosystems is the chronic instability towards protonation and bimolecular processes, of zinc porphyrins, their excited states, and the important reactive intermediates derived from them. For example, zinc porphyrin π-radical anions[5] and cations[6] rapidly and irreversibly disproportionate in water to give, respectively, phlorin anions and π-dications. Also, the ground state[7] and the radical anion[5] are readily attacked by protons. Finally, zinc porphyrin excited-state behaviour is modulated by several competing phenomena, such as ground-state aggregation and quenching, triplet–triplet annihilation, ion pairing, and ionic strength effects.[8] If full advantage is to be taken of the beneficial aspects of porphyrin photophysics, ways must be found to inhibit these side reactions by sterically blocking the zinc porphyrin reactive sites[2] (the meso-positions and the metal cation). In photosynthesis, nature accomplishes this task by embedding chlorophyll in the protein–lipid matrix of chloroplast membranes.[9] In this paper, we describe a simple strategy for achieving steric blocking and its consequences for solar-energy storage.

Zinc tetrakis(2-pyridyl)porphyrin, prepared and purified by a literature method,[10] was quaternised in warm N,N'-dimethylformamide, by addition of 1,2-oxathiolane 2,2-dioxide[8] or 1-bromohexane, to give the tetrasubstituted zinc porphyrins, (1) and (2), respectively. The porphyrins were separated and purified as before[8,11] and exhibited typical absorbtion spectra in water ($\lambda_{max.}$ = 427, 553, and 590 nm).† There was no evidence of complexation between the zinc ions and the sulphonate groups in (1).

Both compounds (1) and (2) were stable in aqueous nitric acid solutions at pH = 0, showing no signs of zinc demetallation after one week. This compares very favourably with the short half-lives for zinc demetallation found for the less sterically-hindered porphyrins, (3), (4), and (5) in 1 M nitric acid[12] (see Table 1).

Porphyrins (1) and (2) both gave long-lived triplet excited states [(1) = 1.5 ms; (2) = 0.9 ms, in out-gassed 1 M nitric acid], that were quenched by Fe[III] with a bimolecular rate constant, $(3.6 \pm 0.2) \times 10^8$ dm^3 mol^{-1} s^{-1} (Table 2). This is very close to the diffusional limit. Flash photolysis studies showed that the quenching reactions, in both cases, form zinc porphyrin π-cation radicals with almost unit quantum efficiency [Figure 1, equation (1)]. The reverse reaction {i.e., reduction of the radical cation to the ground-state zinc porphyrin by Fe[II] [equation (2)]} occurred slowly at pH = 0 with pseudo-first order kinetics (Figure 1), for which the rate constant was a linear function of the concentration of added Fe[II]. This gave a bimolecular rate constant (Table 2) $(3.2 \pm 0.2) \times 10^5$ dm^3 mol^{-1} s^{-1} for both (1) and (2).

$$ZnP^* + Fe^{III} \rightarrow ZnP^{\cdot +} + Fe^{II} \qquad (1)$$

$$ZnP^{\cdot +} + Fe^{II} \rightarrow ZnP + Fe^{III} \qquad (2)$$

In the absence of added Fe[II], the lifetime of the porphyrin radical cation is determined by the level of Fe[II] impurity in the Fe[III] salt. With concentrations of Fe[III] at the minimum necessary to quench all of the triplet formed (8×10^{-3} mol dm^{-3}) the pseudo-first order rate constants for quenching of the triplet and reduction of the radical cation are 3×10^6 and 85 s^{-1}, respectively, for both (1) and (2). Such a large variation in rate constants ensures a high steady-state concentration of redox products and should allow a photogalvanic effect to be observed. Indeed, visible-light irradiation of (1), in water at pH = 0, containing Fe[III] (1×10^{-2} mol dm^{-3}) in a thin-layer cell (path length, 0.03 cm) and equipped with semi-transparent platinum electrodes, gave an unoptimised photopotential of 26 mV and a photocurrent of 420 μA cm^{-2}.

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† Satisfactory analyses were obtained for these porphyrins.

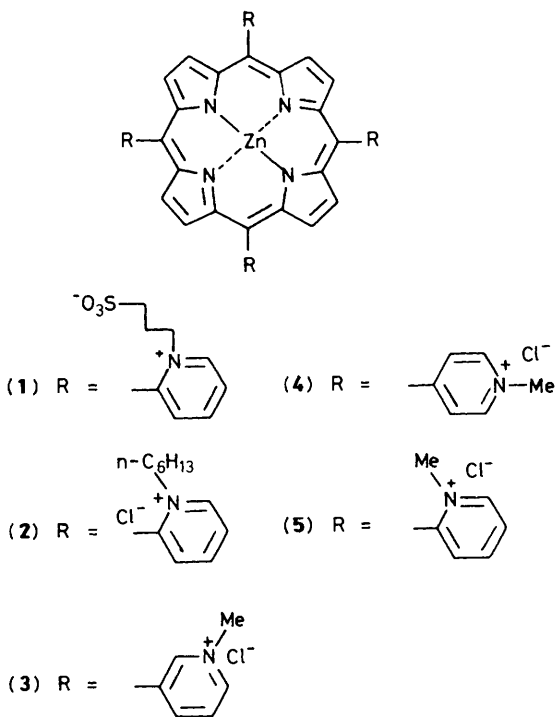**Table 1.** Half-lives of zinc porphyrins in 1 M nitric acid.

Porphyrin	Half-life/s
(1) and (2)	Stable[a]
(3)	89[b]
(4)	165[b]
(5)	6.9×10^{4b}

[a] This work. [b] See ref. 12.

Table 2. Effect of pH on the bimolecular rate constants for zinc porphyrin triplet excited states (k_T) and reduction of π-radical cations (k_R).

Porphyrin	pH	$k_T/dm^3\,mol^{-1}\,s^{-1}$	$k_R/dm^3\,mol^{-1}\,s^{-1}$
(1) and (2)[a]	0	$3.6 \pm 0.2 \times 10^8$	$3.2 \pm 0.2 \times 10^5$
(3)[b]	2	$9.2 \pm 0.7 \times 10^7$	$1.2 \pm 0.3 \times 10^8$
(4)[c]	5	2.2×10^8	2.6×10^9

[a] This work. [b] See ref. 6b. [c] See ref. 15.

Figure 1. Transient absorption spectrum of the π-radical cation recorded 5 ms after flash excitation of (1) in outgassed 1 M nitric acid containing iron(III) nitrate $(8 \times 10^{-3}\,M)$. Insert shows the decay profile observed at 700 nm.

Figure 2. Transient absorption spectrum of the π-radical anion as observed 5 ms after the flash excitation of (1) in outgassed water containing EDTA $(10^{-2}\,M)$.

This corresponds to a light-to-electricity conversion efficiency of 0.005%, a value much higher than those reported previously.[4b,13] This is because of the lower pH that can be used in this work without demetallating the zinc porphyrin.

Cyclic voltammetry of (1) and (2) (in aqueous KCl solution, 0.2 mol dm^{-3}, at pH = 5) showed a one-electron reduction step with a half-way potential of -0.87 ± 0.02 V vs. normal hydrogen electrode (n.h.e.). On oxidation scans, a one-electron step occurred with a half-wave potential of 1.02 ± 0.2 V vs. n.h.e. Both processes followed quasi-reversible behaviour, with no sign of the rapid disproportionation that normally follows the production of zinc porphyrin anion and cation radicals in aqueous solution. This stabilisation, on the electrochemical timescale, must arise from steric factors
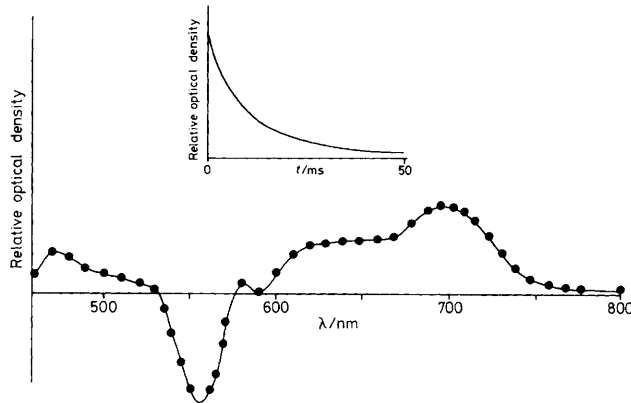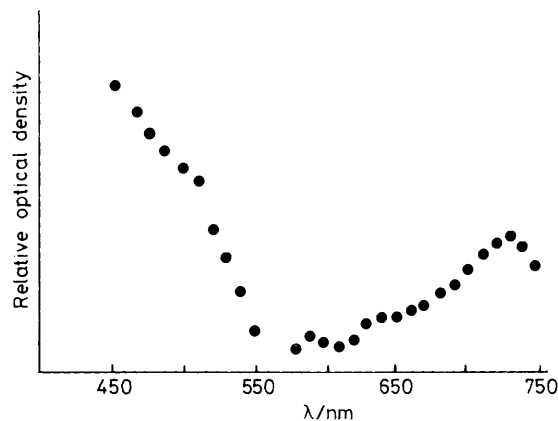
associated with the appended side-chains. Steady-state photolysis of the zinc porphyrins (1) and (2), in the presence of reducing and oxidising agents, did eventually lead to the formation of two-electron reduced or oxidised products, observed electrochemically. The π-radical anions of (1) and (2) were generated by reduction of the zinc porphyrins with ethylenediaminetetra-acetic acid (EDTA)[14] (Figure 2), and each found to have a half-life of 12 ms. Again, this compares very favourably with the half-life of the radical anion of (4) (1—200 μs).[5]

The improved stability of the porphyrin radical cations and anions reported here, suggests that (1) and (2) might function as useful photosensitisers for reversible water oxidation and reduction to oxygen and hydrogen, respectively.[6] According to the half-wave potentials from cyclic voltammetry, however, water oxidation should only be possible at pH > 5, and under such conditions Fe^{III} hydrolyses and will not quench the triplet excited state. Indeed, visible-light irradiation of (1) in water, containing Fe^{III} $(10^{-2}\ mol\ dm^{-3})$ and colloidal ruthenium dioxide $(10^{-4}\ mol\ dm^{-3})$ in the range 1 < pH < 6, did not

generate oxygen. With sodium persulphate (10^{-4} M) as sacrificial electron acceptor at pH = 6, and an excitation wavelength of 560 ± 20 nm, oxygen was generated with a quantum yield of 8%. The total yield of oxygen remained low. At pH = 0, the redox potential of the π-cation radical is too low for oxygen generation.[15] Experiments are in progress to increase this redox potential at low pH, *e.g.*, by using different central-metal cations such as Al^{III}.

Efficient hydrogen generation occurred, on the other hand, when (1) or (2) was irradiated in water containing NADH (2×10^{-3} mol dm^{-3}) and colloidal Pt (10^{-4} mol dm^{-3}). At pH 7, the optimised quantum efficiency for hydrogen formation was 32%. Although this represents a lower value than previously obtained [in systems using (4) as sensitiser[14]], hydrogen generation with (1) continues until all the electron donor (NADH) is consumed, giving a higher overall yield. This contrasts with other systems[14] where the stability of the porphyrin determines the amount of hydrogen generated. Presumably, this is due to the increased stability conferred on the radical anion by steric blocking.

In conclusion, we have shown that a simple strategy of sterically blocking zinc porphyrin reactive sites, effectively counters many of the problems associated with the use of zinc porphyrins as sensitisers of photochemical solar-energy conversion.

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