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Redox Properties of Zinc(II) Tetra-*N*-methyl-2,3-pyridinoporphyrazine in Aqueous Solution

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Abstract

$ZnTMPz^{4+}$ was studied in order to decide if the compound, or its close analogues had any real application in photoredox reactions capable of the storage of solar energy. The compound is reduced easily ($E_{1/2} = -0.02$ V *vs.* NHE). The resultant pi-radical anion undergoes rapid disproportionation in neutral aqueous solution. Oxidation of the compound was very difficult, both electrochemically ($E_{1/2} = >1.55$ V *vs.* NHE) and with conventional oxidants. Altogether, such compounds seem to have little application in solar energy storage devices.

Introduction

During the energy crisis a lot of effort went into trying to find means of utilising solar energy. The idea of mimicing natural photosynthesis became popular. This involved identification of photosensitisers which absorb strongly in the visible region of the spectrum. Metalloporphyrins and metallophtalocyanines received much attention because of their similarity to chlorophyll [1]. Metalloporphyrins were more popular than the phthalocyanines because of their facile synthesis in water-soluble forms and many different molecules were obtainable by varying the central metal ion or the water-solubilising group. Much work was published on the photodissociation of water using zinc(II) porphyrins as photosensitisers [2, 3]. On the other hand, only one method could easily be used to render metallophthalocyanines water-soluble and this involved sulphonation of the compounds. Although these compounds are able to capture a higher fraction of sunlight than can metalloporphyrins (they absorb in the near IR region), they are not so useful because they aggregate easily in water. However, a few attempts were made to photoreduce water to hydrogen with zinc(II) phthalocyanine derivatives [4–6]. In 1981 we synthesized a positively-charged magnesium phtalocyanine which was used with some small success to generate hydrogen from water in a sacrificial photosystem [7]. More recently, positively-charged phthalocyanines were found to have a catalytic effect on the electrochemical reduction of CO_2 [8] and they are known to undergo quite efficient reductive photochemistry [9]. In this work we investigate the ability of zinc(II) tetra-*N*-methyl-2,3-pyridinoporphyrazine ($ZnTMPz^{4+}$) to function as a reductant or oxidant in photochemical electron transfer reactions.

Experimental

Materials

$ZnTMPz^{4+}$ was prepared as before [7] following the method of Scott [10]. Water was deionised and freshly distilled in a Millipore Milli-Q system. For the pulse radiolytic reductions, the phthalocyanine was dissolved in aqueous solution maintained at pH 7 with phosphate buffer (10^{-3} mol dm^{-3}) and containing 10% *v/v* propan-2-ol (Baker). The solution was purged with ultrapure N_2 prior to and during the experiment. For the attempted oxidation by pulse radiolysis, the sources of oxidant radicals (KBr, NaCl and NaN_3) were of the highest available purity and were used as received. For the photochemical experiments, sodium persulphate and ethylenediamine tetraacetic acid (BDH Chemicals) were used as received.

Methods

Luminescence measurements were made with a Perkin-Elmer MPF 4A spectrofluorimeter. Absorption spectra were recorded with a Cary 210 spectrophotometer and a Perkin-Elmer spectrophotometer. Determination of redox potentials for reduction and oxidation of $ZnTMPz^{4+}$ were made with a Rank E611 potentiostat drived by a purpose built triangle wave generator [11]. A glassy carbon working electrode

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was used, together with a Pt counter electrode and a SCE reference. Aqueous solutions containing $ZnTMPz^{4+}$, KCl (0.2 mol dm^{-3}) or Na_2SO_4 (0.1 mol dm^{-3}) for reduction and oxidation respectively, were purged thoroughly with N_2 prior to electrolysis. The carbon electrode was polished between each scan.

Pulse radiolysis studies were made with a Febetron 705 accelerator delivering 50 ns pulses of 2 MeV electrons and full details of the experimental technique have been given previously [12, 13]. The radiation dose was 1160 rad per pulse, as measured by KSCN dosimetry. Optical measurements were made by normal spectrophotometric methods using a 2 cm pathlength irradiation cell, a 300 W Xe monitoring light source, a Bausch and Lomb monochromator and a photomultiplier. The signals were digitised with a Tektronix 7612 transient recorder and analysed with a PDP 11/34 computer. The monitoring beam was filtered to avoid unnecessary photolysis of the solution. Transient absorption spectra of the intermediates were recorded point by point. The triplet lifetime was measured by conventional flash photolysis (Applied Photophysics model 414) after outgassing the solution by the freeze-pump-thaw method. The triplet quantum yield was determined by ns flash photolysis using ZnTPP as standard [14]. The singlet lifetimes were measured by time correlated single photon counting.

Photochemical reductions and oxidations were performed with a 100 J flash lamp filtered to remove light of wavelength less than 350 nm. Solutions for photoreduction contained EDTA (2.7×10^{-2} mol dm^{-3}) and for photooxidation persulfate (10^{-4} mol dm^{-3}). All solutions were purged well with N_2 prior to irradiation.

Results and Discussion

Photoredox Properties

Figure 1 shows the structure of $ZnTMPz^{4+}$. Phthalocyanines are attractive photosensitisers in the respect that they possess intense absorption in the near IR region (Fig. 2) such that when used in conjunction with additional chromophores that absorb in the blue–green region (e.g. porphyrins, carotenes) they can collect up to 50% of the energy available in sunlight. The main absorption band of $ZnTMPZ^{4+}$ is situated at 681 nm where the molar extinction coefficient is 1.8×10^5 dm^3 mol^{-1} cm^{-1}. The compound fluoresces in water with a maximum centred at 683 nm so that the Stokes shift is practically zero and the energy level of the first excited singlet state is at 1.81 eV. The fluorescence quantum yield was found to be 0.23 and the singlet excited state lifetime in aerated water was measured at (3.4 ± 0.4) ns. The quantum yield for formation of the triplet manifold was measured by ns laser flash photolysis and it was found to be (0.55 ± 0.08). Consequently, the quantum yield for internal conversion from the first excited singlet state must be about 0.2. The absorption spectrum of the triplet state is shown in Fig. 3, together with a typical decay profile measured in outgassed water. The lifetime of the triplet state is (270 ± 50) μs which is considerably shorter than found with the corresponding zinc porphyrins. This reduced triplet lifetime is probably connected with the low triplet energy of the compound, which from low temperature phosphorescence is about 1.12 eV.

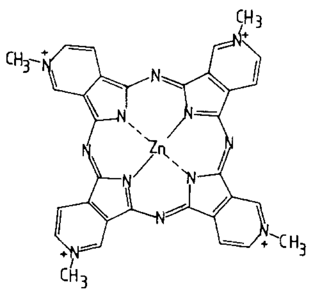

Fig. 1. Structure of $ZnTMPz^{4+}$.

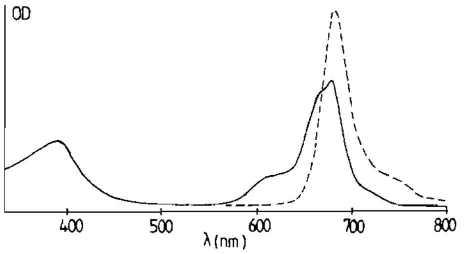

Fig. 2. Absorption (——) and fluorescence (-----) spectra of $ZnTMPz^{4+}$ in neutral aqueous solution.

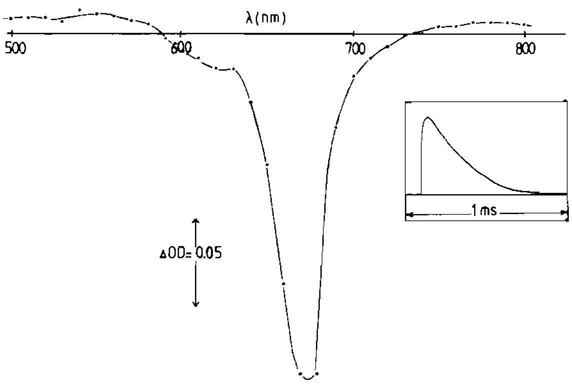

Fig. 3. Difference absorption spectrum of the triplet excited state and profile for its decay at 540 nm in outgassed aqueous solution at pH 5.

Reduction of $ZnTMPz^{4+}$

$ZnTMPz^{4+}$ was reduced very easily. The half-wave potential ($E^R_{1/2}$) measured for the first electron reduction, by cyclic voltammetry in aqueous solution, was found to be −0.020 V *vs.* NHE. This value is considerably more positive than found for the tetrasulphonated compound ($E^{R}_{1/2} = -0.56$ V *vs.* NHE) [8] and for the nonmethylated compound ($E^{R}_{1/2} = -0.36$ V *vs.* NHE) [8]. Such a finding is consistent with the ability of the methylated aza groups to pull electron density away from the central ring. This facilitates addition of an electron onto the ring but it also makes oxidation quite difficult.

Pulse radiolysis was used to reduce the compound in aqueous propan-2-ol. Radiolysis of water containing 10% *v*/*v* propan-2-ol under an atmosphere of N_2O gives rise to propanoxyl radicals with a radiation yield of $G = 6$. In neutral solution, these radicals are quite powerful reducing species ($E^{R}_{1/2} = -1.20$ V *vs.* NHE [15]) and they will reduce many different metalloporphyrins to the corresponding pi-radical anions. Propanoxyl radicals reduced $ZnTMPz^{4+}$ in neutral aqueous solution. The difference absorption spectrum of the transient species observed some 80 µs after the pulse is given in Fig. 4 and it is assigned to the pi-radical anion. It shows a strong bleaching at 681 nm, corresponding to removal of the ground state compound, and weak absorption centered around 550 nm and some absorption in the near IR region. The spectrum is similar to that of metalloporphyrin pi-radical anions and it shows some resemblance to the spectra of metallophthalocyanine pi-radical anions recorded in nonaqueous solvents [16]. By measuring the pseudo first order rate constant for grow-in of the absorption at 550 nm as a function of the concentration of $ZnTMPz^{4+}$, the bimolecular rate constant for reduction

$$CH_3\dot{C}OHCH_3 + ZnTMPz^{4+} \longrightarrow$$

$$CH_3COCH_3 + H^+ + ZnTMPz^{3+}$$

was found to be $(5.5 \pm 0.8) \times 10^9$ dm^3 mol^{-1} s^{-1}. This value is very close to the diffusion controlled limit and it is consistent with the large thermodynamic driving force for the reaction ($\Delta G^\circ = -114$ kJ mol^{-1}). As shown in Fig. 4, the pi-radical anion decays rapidly. The bimolecular rate constant for decay, as measured at 550 nm, was found to be $(1.7 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1}. Again, this value is close to the diffusion controlled limit (taking into account the strong Coulombic repulsion term) showing that the pi-radical anion is unstable in aqueous solution. The second order nature of the decay process suggests that it involves disproportionation, as found for many metalloporphyrin pi-radical anions in water.

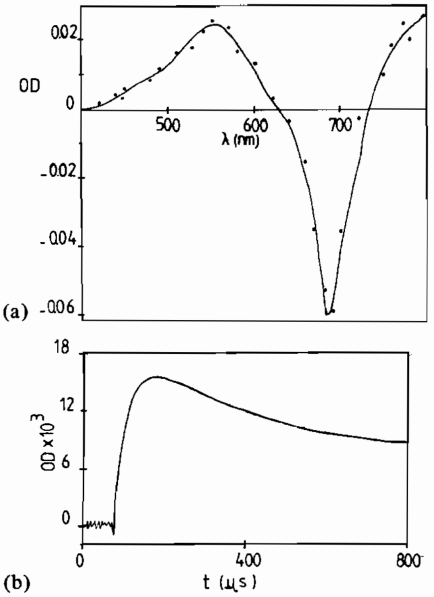

Fig. 4. (a) Difference absorption spectrum of the pi-radical anion of $ZnTMPz^{4+}$ obtained by pulse radiolytic reduction with $CH_3\dot{C}OHCH_3$ at pH 7 and (b) profile of its formation and decay at 550 nm.

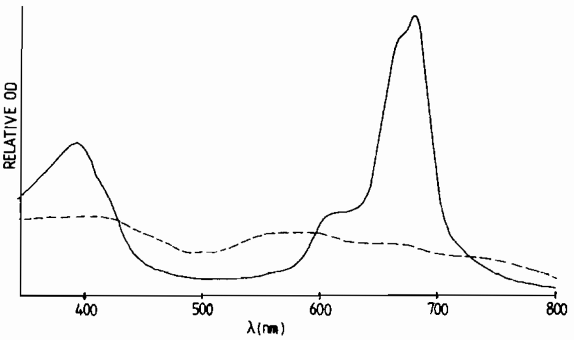

Fig. 5. Absorption spectra following the photoreduction of $ZnTMPz^{4+}$ in aqueous solution at pH 5; $ZnTMPz^{4+}$ (——) and after irradiation (-----) with visible light in the presence of EDTA (2.7 × 10^{-2} mol dm^{-3}).

$$2ZnTMPz^{3+} \longrightarrow ZnTMPz^{4+} + ZnTMPz^{2+}$$

Chemical or photochemical reduction of $ZnTMPyP^{4+}$ in water with EDTA, NADH or ascorbate gives rise to a product having an absorption spectrum somewhat similar to that noted for the pi-radical anion. The bleached nature of this spectrum (Fig. 5), together with the pulse radiolysis results showing the rapid decay of the radical anion, suggests that the final product is some form of protonated, reduced porphyrin analogous to the metallophlorin. These compounds readily air-oxidise back to the porphyrin form.

Oxidation of $ZnTMPz^{4+}$

Oxidation of $ZnTMPz^{4+}$ was found to be very difficult. By cyclic voltammetry in neutral aqueous solution, it was found that the solvent was oxidised before the compound. From the voltammograms, $E^{O}_{1/2}$ must be higher than 1.25 V *vs.* NHE. However, it is possible to estimate the half-wave potential for oxidation of $ZnTMPz^{4+}$ if we accept that the difference between the redox potentials for reduction and oxidation remains constant for similar compounds. For zinc phthalocyanine [17] we have

$$E^{O}_{1/2} - E^{R}_{1/2} = 0.92 + 0.65 = 1.57 \text{ V}$$

and a similar potential difference exists for the tetrasulphonated compound. We assume that the same difference holds for $ZnTMPz^{4+}$ so that $E^{O}_{1/2}$ becomes

$$E^{O}_{1/2} = 1.57 - 0.02 = 1.55 \text{ V } vs. \text{ NHE.}$$

This value is high compared to other phthalocyanines, especially the sulphonated compounds which are easily oxidised. Once again, this can be explained by the fact that the electron density on the central ring is attracted towards the positively-charged aza groups. This makes it hard to remove an electron from the ring and, therefore, the half-wave potential for oxidation is raised.

In the pulse radiolytic experiments, several oxidising radicals were tried, including $Br_2^{\cdot-}$, $Cl_2^{\cdot-}$ and $N_3^{\cdot}$; the redox potentials of which are 1.69, 2.3 and 1.9 V respectively. However, even with the strongest oxidant ($Cl_2^{\cdot-}$ at pH 3) there was no indication of formation of $ZnTMPz^{4+}$ pi-radical cation. There was some ground state complexation between $ZnTMPz^{4+}$ and azide ions, for which the equilibrium constant was found to be 2.85 $dm^3\ mol^{-1}$.

$$ZnTMPz^{4+} + N_3^- \rightleftharpoons ZnTMPz{\cdot}N_3^{3+}$$

Photochemical oxidation with sodium persulphate resulted in complete bleaching of the chromophore. After one hour irradiation with visible light, all the phthalocyanine was bleached but no coloured material was formed. At short irradiations, only the bleaching process could be seen and flash photolysis experiments performed in the presence of persulphate did not show the intermediate formation of the pi-radical cation. Similarly, it was found that methyl viologen (10^{-2} mol dm^{-3}) had no effect upon the triplet state lifetime of $ZnTMPz^{4+}$ in outgassed aqueous solution.

Conclusions

This work has confirmed that positively-charged phthalocyanines are easily reduced but they are very difficult to oxidise. In fact, $ZnTMPz^{4+}$ is highly resistant towards conventional oxidants. Even though it is easy to obtain the pi-radical anion this species does not seem to be useful in photoinduced redox reactions because its lifetime is kept very short by rapid disproportionation and because its $E^{R}_{1/2}$ is close to 0 V *vs.* NHE. This makes hydrogen production unlikely except in strongly acidic solution where the compound is prone to demetallate.

Acknowledgements

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