Short Communication

Attempted photoproduction of hydrogen using zinc(II) tetrasulphophthalocyanine

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Recent work has demonstrated that irradiation of an aqueous solution containing a chromophore, an electron acceptor such as methyl viologen (MV^{2+}), an electron donor such as EDTA and colloidal platinum can lead to efficient production of hydrogen [1 - 4]. For the system to provide a practical means of storing solar energy, it is necessary to optimize the conversion of sunlight into H_2 and to couple this system to a similar process capable of O_2 production from water [5, 6]. For the former optimization, it is desirable to use chromophores possessing intense absorption in the near IR and, as such, we have studied zinc(II) tetrasulphophthalocyanine (Zn-PcS^{4-}).
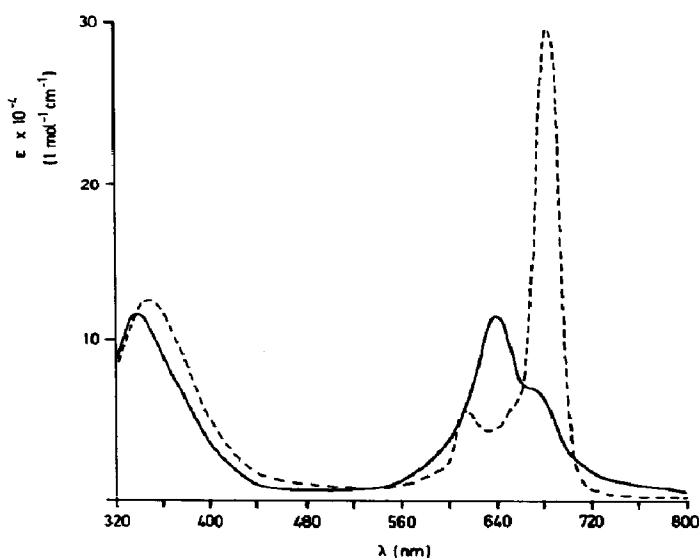

Fig. 1. Absorption spectra of $ZnPcS^{4-}$ (1×10^{-6} M) in water: ———, buffered to pH 7; — — —, containing 3 vol.% DMF.

Absorption spectra of ZnPcS^{4-} in aqueous solution (shown in Fig. 1) are extremely sensitive to changes in concentration. There is a strong negative deviation from Beer's law and the spectra show evidence of dimerization (log K_D = 6) and higher order aggregation. This aggregation can be restricted by the addition of approximately 5 vol.% of organic solvents such as pyridine or N,N-dimethylformamide (DMF). In such solvent mixtures there is intense fluorescence (ϕ_F = 0.32) despite the short singlet state lifetime (τ_S = 2.9 ns) and reasonably high triplet state population (ϕ_T = 0.56, τ_T = 245 μs). Both the singlet and triplet excited states are quenched by MV^{2+} ($k_S \approx (1.0 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}, $k_T = (7 \pm 2) \times 10^6$ M^{-1} s^{-1}) and there is considerable ground state complexation. These quenching rate constants are extremely high considering the modest thermodynamic driving forces involved ($\Delta G° \approx -70$ kJ mol^{-1} and $\Delta G° \approx -15$ kJ mol^{-1} for the singlet and triplet reactions respectively) and are probably a consequence of the strong electrostatic attraction between the reactants.

$$ZnPcS^{4-} + MV^{2+} \underset{}{\overset{h\nu}{\rightleftharpoons}} [ZnPcS^{4-} \ldots MV^{2+}] \rightleftharpoons ZnPcS^{3-} + MV^+$$
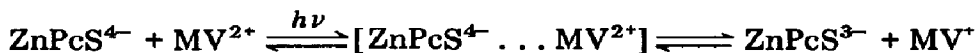
Despite the high quenching efficiency, the yield of MV$^+$ remains very low and this is attributed to poor separation of the ion pair formed initially. Thus geminate recombination competes favourably with radical ion separation, presumably because of the electrostatic attraction between the caged products. Furthermore, the appearance of MV$^+$ occurs on a microsecond time scale, which is consistent with its formation being solely from a triplet reaction, whilst the rate for reverse electron transfer is diffusion controlled. These factors, together with the low rate for reoxidation of ZnPCS^{3-} by EDTA ($k < 10^6$ M^{-1} s^{-1}), greatly restrict the hydrogen-producing capacity of ZnPcS^{4-} in such three-component systems. In fact, upon prolonged irradiation ($\lambda = 670 \pm 50$ nm) of ZnPcS^{4-} in outgassed water buffered to pH 5.5 and containing DMF (3 vol.%), MV^{2+} (5×10^{-3} M), EDTA (5×10^{-2} M) and colloidal platinum, H$_2$ production could not be observed. Replacement of EDTA by neutral donors such as cysteine, triethanolamine or H$_2$S and adjustment of the solution pH and the concentration of reactants gave no apparent improvement in the yield of H$_2$; the real problem remains the strong electrostatic attraction within the ion pair. This can be overcome to some extent by using ZnPcS^{4-} in a two-component system or by using non-sulphonated ZnPc dispersed in neutral micelles [7].

In the two-component system irradiation ($\lambda = 670 \pm 50$ nm) of ZnPcS^{4-} in outgassed water buffered to pH 7 and containing DMF (3 vol.%) and cysteine (2×10^{-2} M) led to irreversible reduction of the chromophore.

$$ZnPcS^{4-} + Cysteine \xrightarrow{h\nu} ZnPcS^{5-} + Cysteine^+$$

$$Cysteine^+ \longrightarrow Products$$
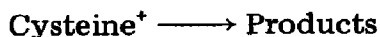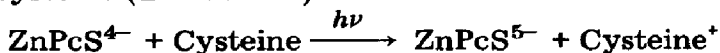
When the irradiation was carried out in the presence of a colloidal platinum catalyst, the reduced phthalocyanine was not observed but production of

H_2 occurred. However, even under optimum conditions the yield of H_2 remained very low ($\phi_{H_2} < 10^{-4}$) and was irreproducible, and there was considerable loss of chromophore.

In summary, it was found that the photoreaction between excited zinc-(II) tetrasulphophthalocyanine and methyl viologen leads to efficient quenching of the excited states and to low yields of redox products. When the chromophore is irradiated in the presence of cysteine and colloidal platinum, inefficient H_2 production takes place. Thus, despite the attractive absorption spectrum, $ZnPcS^{4-}$ appears to be a poor choice as chromophore for two- or three-component systems for the photogeneration of H_2 from water.

1 B. V. Koryakin, T. S. Dzhabiev and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, *233* (1977) 620.
2 J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, *1* (1977) 449.
3 K. Kalyanasundaram, J. Kiwi and M. Gratzel, *Helv. Chim. Acta*, *61* (1978) 2720.
4 A. Moradpur, E. Amouyal, P. Keller and H. Kagan, *Nouv. J. Chim.*, *2* (1978) 547.
5 J. Kiwi and M. Gratzel, *Angew. Chem.*, *90* (1978) 900.
6 J. M. Lehn, J. P. Sauvage and R. Ziessel, *Nouv. J. Chim.*, *3* (1979) 423.
7 J. Darwent, personal communication, 1980.