

Preliminary Note

Light-induced formation of a reversible dioxygen complex of cobalt(II) tetraphenylporphyrin at a micellar interface

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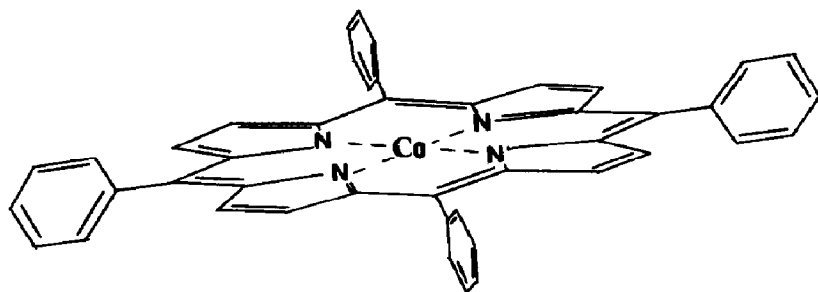
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The binding of molecular oxygen to metal complexes and more specifically to metal porphyrins is a well-documented area [1, 2]. Interest has been mainly spurred by the reversible binding observed in heme proteins. Of all the reversible dioxygen porphyrin systems reported, only a few show the effect at room temperature in solution; most reports describe specific solvent or structural effects [3, 4]. The solvent and structural effects act by restricting the solvation of the complexes by the creation of a hydrophobic pocket [4 - 6]. We know of only one example, which occurs with ruthenium(II) octaethylporphyrin [7], of such a reversible binding in solution. All these processes are ground state reactions, and furthermore they require the presence of a base as a fifth axial ligand to activate the complexes [6, 8, 9].

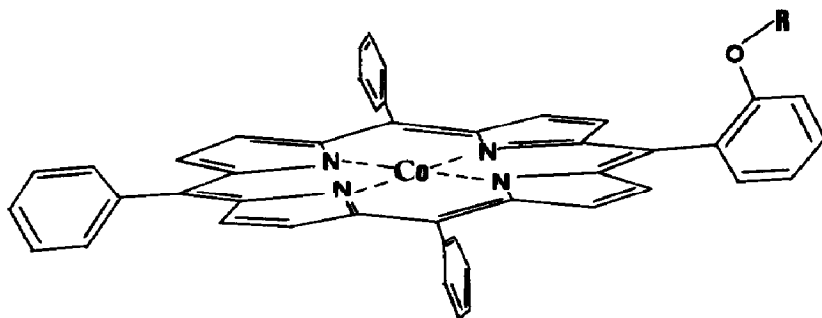
We report here some preliminary results on the visible-light-induced reversible formation of dioxygen complexes of *meso*-cobalt(II)-tetraphenylporphyrin (TPP) (compound I) and its derivatives IIa and IIb shown in Fig. 1. These reactions proceed in aqueous micellar solutions at room temperature.

1. Experimental details

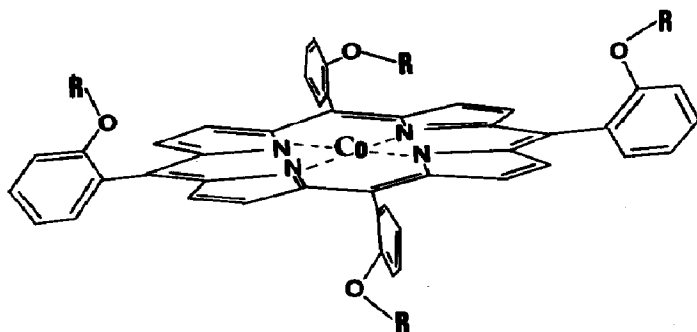
All detergents and especially Triton X were purified before use. The detergent concentration was two to five times the critical micellar concentration, while the porphyrin concentration was in the range 10^{-5} - 10^{-6} . Irradiation was carried out in 10 mm quartz cells fitted to a gas manifold and a vacuum line. A quartz tungsten lamp was used, with a 10 cm water filter and two 3-73 Corning filters. Absorbance was measured on a Varian Superscan III spectrometer.



I



II a



II b

Fig. 1. Structures of *meso*-cobalt(II)-TPP I, of *meso*-cobalt(II)-(2,dodecyloxyphenyl) triphenylporphyrin IIa and of *meso*-cobalt(II)-tetra(2,dodecyloxyphenyl)porphyrin IIb.

2. Results and discussion

Solubilization of long chain substituted cobalt(II)-TPP (compounds IIa and IIb) in air-saturated micellar solutions of sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) leads to the formation of dioxygen complexes at 25 °C. Their formation was monitored optically by the change in optical density with time: the Soret band at 410 nm shifted to 430 nm and the lowest energy transition at 530 nm to 550 nm, with no noticeable change in bandwidth. Clean isosbestic points were obtained (Fig. 2). Pumping over the solution slowly reversed the CTAB

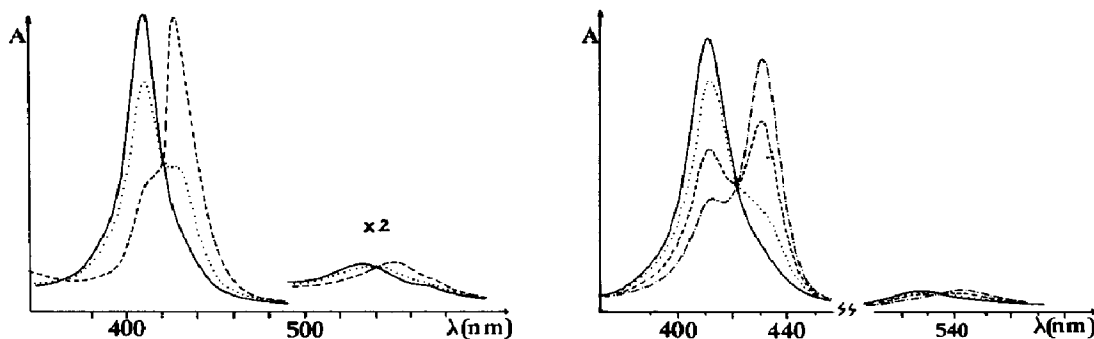


Fig. 2. Evolution of the absorption spectrum of IIb in SDS micellar solution: —, freshly prepared degassed solution; ---, the same after 1 week in the dark, in the presence of air; ····, the solution is then degassed and irradiated for 20 min.

Fig. 3. Evolution of the absorption spectrum of a micellar Triton solution of IIb (air saturated): —, no evolution in the dark; ---, after irradiation for 2 h; ---, partial recovery after 5 h in the dark; ····, the near end of recovery after the fifth cycle has been completed.

system but left the SDS system unaffected. (At the same time that the present work was performed, identical spectral shifts were observed for compounds IIa and IIb in monomolecular layers [10].) However, when a non-ionic detergent such as Triton X100 was used, no such reaction was observed.

We therefore irradiated air-equilibrated micellar Triton solutions of IIa and IIb with visible light. A fast conversion to a species absorbing at 430 and 550 nm, as above, was observed. When this species was kept in the dark it reverted to the starting product with a first-order rate constant of about $5 \times 10^{-5} \text{ s}^{-1}$ at 25 °C. The system was cycled five times using light and dark sequences without showing fatigue (Fig. 3).

Careful degassing of the samples prior to irradiation or the use of a pure nitrogen or argon atmosphere left the starting products unchanged. The changes observed in the presence of oxygen were very similar to those obtained for cobalt porphyrins in organic solvents at low temperatures [6, 8].

We carried out new sets of experiments to differentiate between any effect due to micellization on the one hand and the peculiar "picket fence" structure of IIa and IIb [11] on the other hand. We checked first that neither IIa nor IIb gave any oxygen adduct in organic solvents at room temperature, even under irradiation. Then, using the free bases corresponding to IIa and IIb, we again found no such reactions. Lastly, using the simple molecule I, we obtained the same reversible oxygen binding as with IIa and IIb.

The last result points to the importance of the interface in the process. It has been shown that packing or ordering of chromophores at an interface may lead to cooperative effects [12] or stabilization of some complexes [13]. Here, however, the use of dilute solutions of chromophores (10^{-5} -

10^{-6} M) precludes such effects. Thus we are confident that the reaction we observe must be due only to the adsorption of isolated porphyrins at the interface. In homogeneous solutions, irreversible oxidation of the dioxygen mononuclear complex occurs as a result of protonation or reaction with another metalloporphyrin, leading to a μ -peroxo bridged binuclear complex [14]. The reversibility that we observe could be due to the fact that O_2 is bound to a porphyrin adsorbed at the interface on the hydrophobic side of the interface.

Another interesting fact in these systems is that pumping over the dioxygen complex and then shining visible light totally reverses the systems, even the SDS system.

We are at present probing more deeply into the nature of the dioxygen complexes using electron spin resonance spectroscopy. We are looking for a possible mechanism to explain these unusual photochemical reactions, beginning with quantum yield measurements. The ability of metalloporphyrins to sensitize singlet O_2 formation may provide a lead for this work [15].

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