Photoactivation of a Cobalt(III) Porphyrin by a Redox-active Axial Base-azaferrocene

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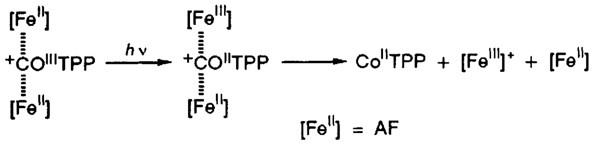
The cobalt(III) porphyrin, [CoTPP(H_2O)$_2$]BF_4 reacts with azaferrocene (AF) to give isolable complex [CoTPP(AF)$_2$]BF_4 which is light sensitive and undergoes photoreduction to CoTPP *via* photoinduced electron transfer from axial ligand AF.

The photoinduced electron transfer (PET) processes of bi- and poly-nuclear transition metal complexes are of intense current interest.[1] On the other hand, much attention is paid to photochemistry of metalloporphyrins.[2] In this context we thought that it would be interesting to synthesize metalloporphyrins containing an organometallic base-azaferrocene (AF)[3] as axial ligand and to look at their photochemical properties.

We have recently reported[4] that cobalt(II) porphyrins (Co**P**) bind AF reversibly in solution and that the adducts formed show unusual photochemistry. For example, complexes Co**P**(AF)(η^1-O_2) are photolabile and lose triplet dioxygen upon irradiation into the Soret or the Q-band, whereas their counterparts, Co**P**(py)(η^1-O_2), are photostable.

In this communication, we report that a cobalt(III) porphyrin, [CoTPP(H_2O)$_2$]BF_4[5] (TPP = dianion of 5,10,15,20-tetraphenylporphyrin) reacts with AF to give isolable complex [CoTPP(AF)$_2$]BF_4 **1**, which is light sensitive and undergoes photoreduction to CoTPP upon irradiation with visible light.

The optical spectrum of [CoTPP(H_2O)$_2$]BF_4 in chloroform is shown in Fig. 1(*a*). The addition of the five-fold excess of AF resulted in spectra changes [Fig. 1(*b*)] very similar to those caused by addition of imidazole (in that case [CoTPP(imidazole)$_2$]BF_4 is formed). When this reaction was carried out in more concentrated solution the complex **1** was isolated and characterized.†



Scheme 1

A short irradiation (~2 min, 800 W tungsten lamp, λ > 350 nm) of a deoxygenated solution of **1** in dimethylformamide (DMF) results in spectral changes presented in Fig. 2. At the same time the initial ESR-silent solution [Co(d^6) low-spin system, diamagnetic] displayed ESR features $g_\perp$ = 2.412, $g_\parallel$ = 2.025, a^{Co} = 5.26 mT, a^{Co} = 10.00 mT at 40 K. These facts clearly indicate that there is a clean photoreduction of **1** to CoTPP (λ_{max} = 414 and 529 nm in DMF). In fact, CoTPP was isolated from the photolyte and identified by comparison (TLC, UV–VIS and ESR) with an authentic sample. The yield of the photoreduction of **1** to CoTPP was nearly quantitative (~95%).

Further experiments showed that photoreduction also takes place in chloroform, but in somewhat lower yield (~80%). There was no reaction in the dark, although subdued daylight was sufficient to produce detectable amounts of CoTPP in solutions of **1**. In contrast to the high photoreactivity of **1** both [CoTPP(H_2O)$_2$]BF_4 and [CoTPP(imidazole)$_2$]BF_4 proved to be photostable under the same conditions.

In the light of these facts the photoreactivity of **1** is clearly due to the presence of coordinated AF. It is known that AF is

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† [CoTPP(H_2O)$_2$]BF_4[5] (44 mg, 0.055 mmol) dissolved in CH_2Cl_2 (2 ml) was treated with azaferrocene (51 mg, 0.272 mmol). The solution was stirred for 5 min, diluted with heptane (3 ml), filtered and concentrated *in vacuo* to afford **1** as a violet, microcrystalline solid. Yield 57 mg (92%). FAB–MS (positive, polyethylene glycol as matrix): *m/z* 672 (100%), (CoTPP + H)$^+$; 858 (8%), CoTPP(AF)$^+$; 1046 (5%) [CoTPP(AF)$_2$–H]$^+$. Electronic spectrum in DMF (λ_{max}/nm, ε/dm^3 mol^{-1} cm^{-1}) 431 nm (22 600), 543 (1955) 580 nm (shoulder) (960).

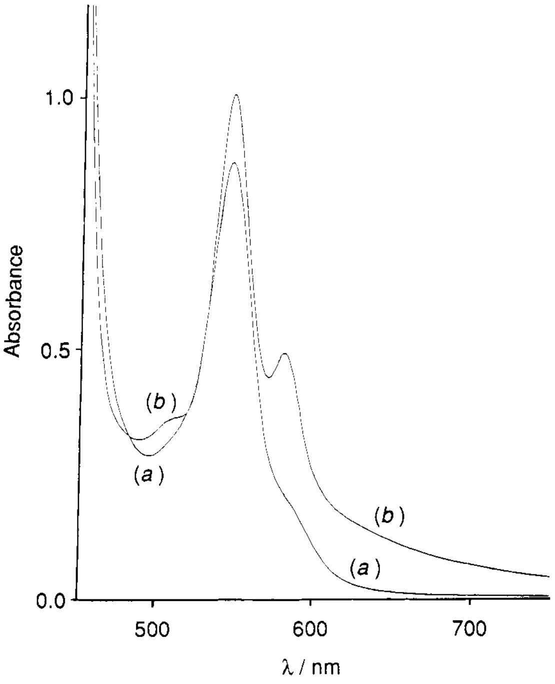
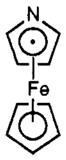


Fig. 1 Optical spectra: (*a*) $[CoTPP(H_2O)_2]BF_4$ in $CHCl_3$, $c = 6 \times 10^{-5}$ mol dm^{-3}; (*b*) the solution (*a*) after addition of 5 equiv. of AF



AF

readily oxidizable to the unstable, putative azaferrocenium cation $AF^{+}\cdot(E_{\frac{1}{2}} = +0.60$ V in MeCN).[6] On the other hand, Co^{III}TPP derivatives undergo facile reduction to the corresponding Co^{II} complexes ($E_{\frac{1}{2}} = +0.71$V for the Co^{III}TPP/Co^{II}TPP couple in CH_2Cl_2).[5] Even spontaneous, thermal electron transfer between nonbonded molecules of Co^{III}TPP and AF is, therefore, possible but its driving force ($\Delta E \sim 0.1$ V) is too small to expect that it would occur with reasonable rate. Furthermore, the coordination of AF to Co^{III}TPP is expected, if σ-donation prevails, to reduce ΔE. The electronic excitation is then necessary to overcome a kinetic or perhaps small thermodynamic barrier.

The tentative mechanism of the photoreduction of **1** to CoTPP is shown in Scheme 1. The first step is the PET from Fe^{II} to Co^{III}. A closely similar process was recently observed in methyl(η^1-AF)cobaloxime by laser flash photolysis.[7] The Co^{II} centre then loses the axial ligands [in fact the complexing ability of cobalt(II) porphyrins is significantly weaker than that of their Co^{III} counterparts],[8] which decompose making decomplexation irreversible. The inherent unstability of $AF^{+}\cdot$ is well established.[6] On the other hand, we have found that AF itself undergoes decomposition to unidentified products upon irradiation in dimethylformamide solution.[9]

The photoreduction of metalloporphyrin *via* a PET from an axial ligand has some precedent in the case of coordinated halides and oxoanions.[2a–d] In this work, we have demonstrated that photoreactivity can be also obtained by the use of a redox-active organometallic axial base—AF. Since axial coordination of bases is a common phenomenon in chemistry of metalloporphyrins the scope of this new approach for redox reactivity may be very wide.

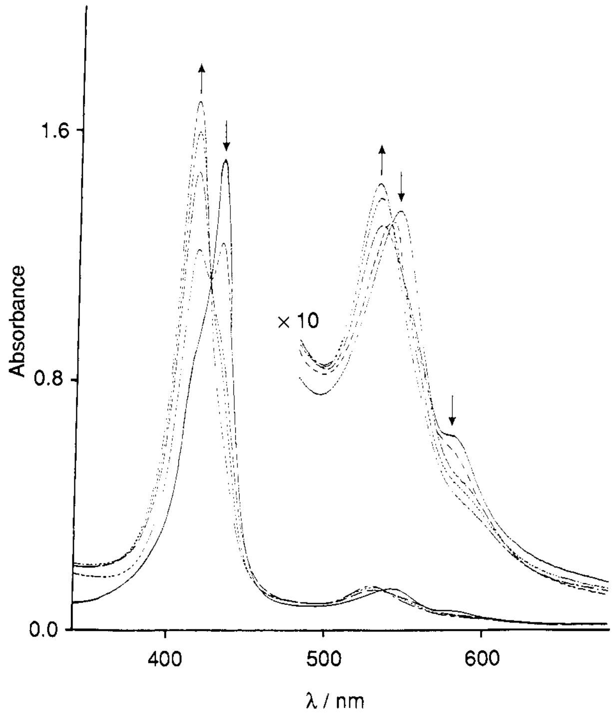


Fig. 2 Photolytic conversion of **1** into CoTPP in dimethylformamide ($c = 6.8 \times 10^{-5}$ mol dm^{-3}). Arrows indicate the change in absorbance during irradiation at λ > 350 nm.

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