

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

Janusz Zakrzewski*^a and Charles Giannotti*^b

^a Institute of Chemistry, University of Lodz, 90-136 Lodz, Narutowicza 68, Poland

^b Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette Cedex, France

The cobalt(III) porphyrin, [CoTPP(H₂O)₂]BF₄ reacts with azaferrocene (AF) to give isolable complex [CoTPP(AF)₂]BF₄ 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 reported⁴ that cobalt(II) porphyrins (CoP) bind AF reversibly in solution and that the adducts formed show unusual photochemistry. For example, complexes CoP(AF)(η¹-O₂) are photolabile and lose triplet dioxygen upon irradiation into the Soret or the Q-band, whereas their counterparts, CoP(py)(η¹-O₂), are photostable.

In this communication, we report that a cobalt(III) porphyrin, [CoTPP(H₂O)₂]BF₄⁵ (TPP = dianion of 5,10,15,20-tetraphenylporphyrin) reacts with AF to give isolable complex [CoTPP(AF)₂]BF₄ **1**, which is light sensitive and undergoes photoreduction to CoTPP upon irradiation with visible light.

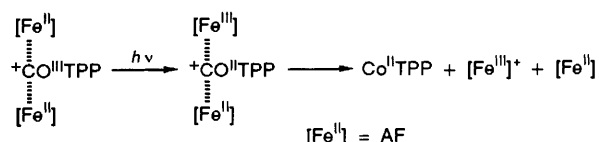
The optical spectrum of [CoTPP(H₂O)₂]BF₄ in chloroform is shown in Fig. 1(a). The addition of the five-fold excess of AF resulted in spectra changes [Fig. 1(b)] very similar to those caused by addition of imidazole (in that case [CoTPP(imidazole)₂]BF₄ is formed). When this reaction was carried out in

more concentrated solution the complex **1** was isolated and characterized.[†]

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(d⁶) low-spin system, diamagnetic] displayed ESR features g_⊥ = 2.412, g_{||} = 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(H₂O)₂]BF₄ and [CoTPP(imidazole)₂]BF₄ 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



Scheme 1

[†] [CoTPP(H₂O)₂]BF₄⁵ (44 mg, 0.055 mmol) dissolved in CH₂Cl₂ (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/dm³ mol⁻¹ cm⁻¹) 431 nm (22 600), 543 (1955) 580 nm (shoulder) (960).

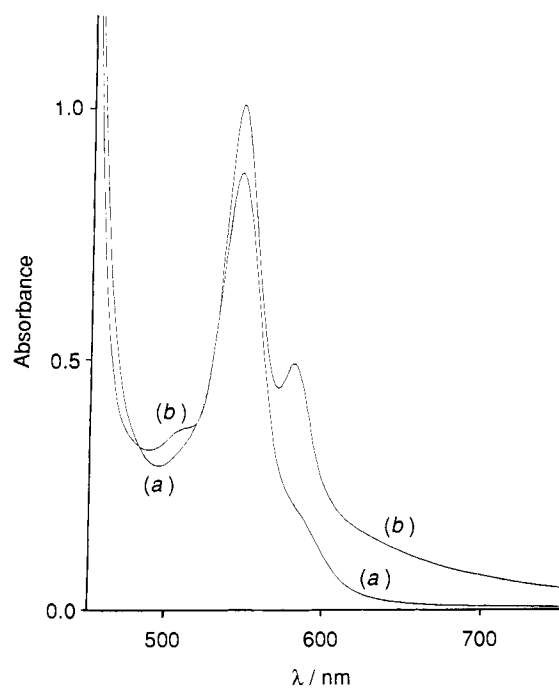


Fig. 1 Optical spectra: (a) $[\text{CoTPP}(\text{H}_2\text{O})_2]\text{BF}_4$ in CHCl_3 , $c = 6 \times 10^{-5} \text{ mol dm}^{-3}$; (b) the solution (a) after addition of 5 equiv. of AF



readily oxidizable to the unstable, putative azaferrocenium cation AF^+ ($E_{1/2} = +0.60 \text{ V}$ in MeCN).⁶ On the other hand, $\text{Co}^{\text{III}}\text{TPP}$ derivatives undergo facile reduction to the corresponding Co^{II} complexes ($E_{1/2} = +0.71 \text{ V}$ for the $\text{Co}^{\text{III}}\text{TPP}/\text{Co}^{\text{II}}\text{TPP}$ couple in CH_2Cl_2).⁵ Even spontaneous, thermal electron transfer between nonbonded molecules of $\text{Co}^{\text{III}}\text{TPP}$ and AF is, therefore, possible but its driving force ($\Delta E \sim 0.1 \text{ V}$) is too small to expect that it would occur with reasonable rate. Furthermore, the coordination of AF to $\text{Co}^{\text{III}}\text{TPP}$ 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 $\text{Co}^{\text{II}}\text{TPP}$ 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 instability of AF^+ 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.

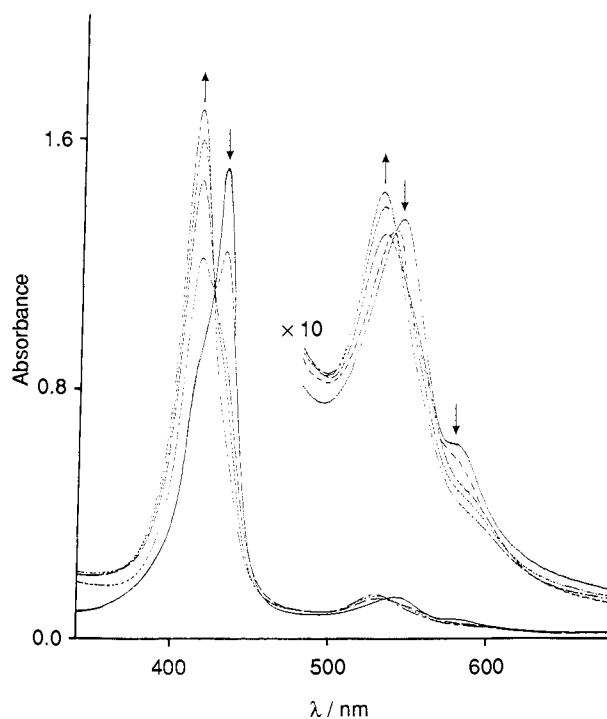


Fig. 2 Photolytic conversion of **1** into $\text{Co}^{\text{II}}\text{TPP}$ in dimethylformamide ($c = 6.8 \times 10^{-5} \text{ mol dm}^{-3}$). Arrows indicate the change in absorbance during irradiation at $\lambda > 350 \text{ nm}$.

We wish to thank NATO Scientific Affairs Division for financial support, (CRG 910552).

Received, 2nd December 1991; Com. 1106097J

References

- V. Balzani and F. Scandola, in *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, Part D, ch. 5.4; A. Vogler, ch. 5.5; V. Balzani and L. Moggi, *Coord. Chem. Rev.*, 1990, **97**, 313.
- Recent leading references: (a) K. S. Suslick, J. F. Battista and R. A. Watson, *J. Am. Chem. Soc.*, 1991, **113**, 6111; (b) K. S. Suslick, R. A. Watson and S. R. Wilson, *Inorg. Chem.*, 1991, **30**, 2311; (c) K. S. Suslick and R. A. Watson, *Inorg. Chem.*, 1991, **30**, 912; (d) D. N. Hendrickson, M. G. Kinnaird and K. S. Suslick, *J. Am. Chem. Soc.*, 1987, **109**, 1243; (e) C. Bartocci, A. Maldotti, G. Varani, P. Battioni, V. Carassiti and D. Mansuy, *Inorg. Chem.*, 1991, **30**, 1255; M. Hoshino and Y. Kashiwagi, *J. Phys. Chem.*, 1990, **34**, 673; M. Hoshino and M. Kogure, *J. Phys. Chem.*, 1989, **93**, 5478; M. Hoshino and T. Hirai, *J. Phys. Chem.*, 1987, **91**, 4510; C. Drew Tait, D. Holten and M. Gouterman, *J. Am. Chem. Soc.*, 1984, **106**, 6653.
- K. K. Joshi, P. L. Pauson, A. R. Quazi and W. H. Stubbs, *J. Organomet. Chem.*, 1964, **1**, 471; J. Zakrzewski and C. Giannotti, *J. Organomet. Chem.*, 1990, **388**, 175.
- J. Zakrzewski and C. Giannotti, *J. Chem. Soc., Chem. Commun.*, 1990, 743; J. Zakrzewski and C. Giannotti, *J. Organomet. Chem.*, 1990, **385**, C-23; J. Zakrzewski and C. Giannotti, *J. Organomet. Chem.*, 1990, **390**, C77; J. Zakrzewski and C. Giannotti, *J. Photochem. Photobiol. A: Chem.*, 1991, **57**, 479.
- H. Sugimoto, N. Ueda and M. Mori, *Bull. Chem. Soc. Jpn*, 1981, **54**, 3425.
- M. G. Peterlietnev, D. I. Denisovych, N. I. Pyshnograeva and D. N. Kravtsov, *Metallorg. Khim.*, 1990, **3**, 581.
- J. Zakrzewski, C. Giannotti and J. Faure, *J. Photochem. Photobiol. A: Chem.*, 1991, **60**, 289.
- F. A. Walker, *J. Am. Chem. Soc.*, 1970, **92**, 4235; D. V. Stynes, H. Cleary Stynes, B. R. James and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 1796.
- J. Zakrzewski and C. Giannotti, unpublished results.