

## Photoreduction of Iron(II)- and Manganese(II)-Phthalocyanine in the Presence of Azaferrocene

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Irradiation with visible light of iron(II)- and manganese(II) phthalocyanine in the presence of azaferrocene leads to efficient reduction of the macrocycle to iron(I) phthalocyanine–azaferrocene complex and macrocycle-reduced manganese(-I) and -(II) species, respectively.

There is considerable interest in photochemically induced electron-transfer reactions of metal complexes of the phthalocyanine dianion (Pc-2).<sup>1</sup> Both photooxidation<sup>2</sup> and photoreduction<sup>3</sup> can be achieved by irradiation of a phthalocyanine complex in the presence of an electron acceptor or donor.

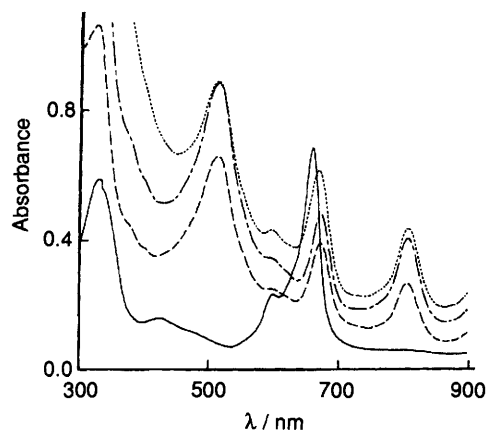
As part of our study on coordination of an organometallic base, azaferrocene (AF),  $[(\eta^5\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]$ , to transition metal macrocyclic complexes,<sup>4</sup> we report here that this complex exhibits especially strong electron-donating properties toward photoexcited phthalocyanines. In particular, iron(II)- and manganese(II)-phthalocyanine,  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  and  $[\text{Mn}^{\text{II}}(\text{Pc-2})]$ , respectively, undergo a photoreduction in the presence of AF, whereas they proved photostable in the presence of organic amines such as pyridine, imidazole or triethylamine.

The electronic absorption spectra showed that both  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  and  $[\text{Mn}^{\text{II}}(\text{Pc-2})]$  coordinate AF in the  $\text{Me}_2\text{SO}$  solution. In the case of  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  we observed equilibrium between 'non base' complex and two other species, presumably  $[\text{Fe}^{\text{II}}(\text{Pc-2})(\text{AF})]$  and  $[\text{Fe}^{\text{II}}(\text{Pc-2})(\text{AF})_2]$ , whereas  $[\text{Mn}^{\text{II}}(\text{Pc-2})]$  gave cleanly only 1:1 adduct,  $[\text{Mn}^{\text{II}}(\text{Pc-2})(\text{AF})]$ . This coordination plays an essential role in the photoreduction of these systems (see below).

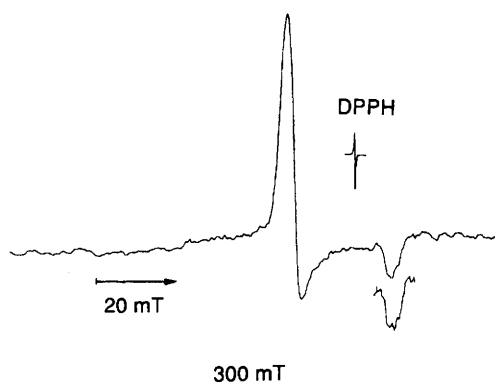
A short irradiation [5–25 s, 250 W Osram xenon lamp and a filter to remove UV ( $\lambda < 400$  nm) radiation] of an argon-saturated  $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  solution of  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  in  $\text{Me}_2\text{SO}$  containing  $8 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of azaferrocene {this solution contained mainly uncomplexed  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  and  $\leq 10\%$  of AF adducts at room temp.} results in a colour change from green to violet. The corresponding changes in electronic absorption spectra are shown in Fig. 1. The phthalocyanine Q band fades and new bands at 805, 668, 511 and 516 nm appear. The species formed is photosensitive and prolonged photolysis results in a very broad band spectrum, without discernible maxima or minima. On the other hand, the photolyte displays at 77 K an EPR spectrum (Fig. 2:  $g_{\perp} = 2.104$ ,  $g_{\parallel} = 1.946$ ,  $a_{\parallel}^{\text{N}} = 0.0013$   $\text{cm}^{-1}$ ) characteristic of five-coordinate amine complexes of iron(I) phthalocyanine.<sup>4</sup> Consequently, we assume that photolysis of  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  in the presence of AF brings about one-electron reduction of the phthalocyanine, leading to  $[\text{Fe}^{\text{I}}(\text{Pc-2})(\text{AF})]$ .

The photochemical behaviour of  $[\text{Mn}^{\text{II}}(\text{Pc-2})]$  in the presence of AF is more complicated. Similarly, as for

$[\text{Fe}^{\text{II}}(\text{Pc-2})]$  a violet solution is formed upon irradiation [ $\lambda_{\text{max}} = 851, 636, 518$  nm in  $\text{Me}_2\text{SO}$  and 849, 635, 525 nm in dimethyl formamide (DMF)]. However, the EPR spectra of the species formed changed completely on going from  $\text{Me}_2\text{SO}$  to DMF.



**Fig. 1** The changes in electronic absorption spectrum of a solution of  $[\text{Fe}^{\text{II}}(\text{Pc-2})]$  in  $\text{Me}_2\text{SO}$  containing an excess of AF caused by irradiation with visible light: (—) before irradiation, (---) after 5 s irradiation, (-·-·-) after 10 s irradiation, (····) after 25 s irradiation (experimental conditions are given in the text)



**Fig. 2** The X-band EPR spectrum of a photolysed solution of  $[\text{Fe}^{\text{I}}(\text{Pc-2})]$  in  $\text{Me}_2\text{SO}$  containing an excess of AF at 77 K.

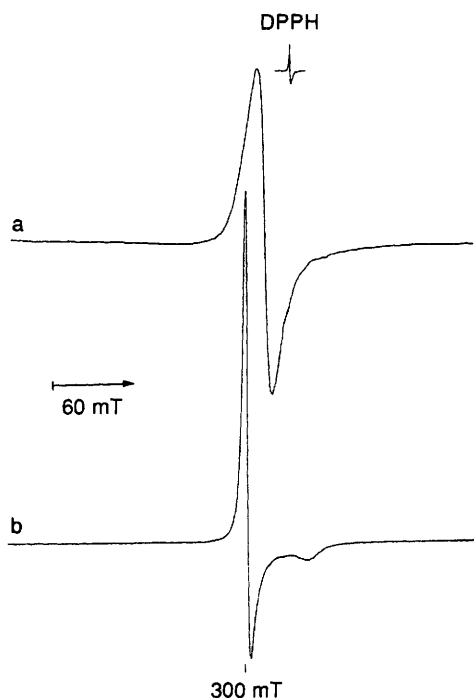


Fig. 3 The X-band EPR spectrum of a photolysed solution of [Mn<sup>II</sup>(Pc-2)] in Me<sub>2</sub>SO containing AF at 77 K (a) and the spectrum of the same solution after annealing to room temp. for 10 min (b)

{It should be noted that although [Mn<sup>II</sup>(Pc-2)] and its complexes with AF are expected to be paramagnetic, we were unable to obtain their EPR spectra at 77 K. By contrast, a short photolysis led to intense EPR features}. The spectrum obtained for a Me<sub>2</sub>SO solution [Fig. 3(a)] displayed a broad isotropic feature at  $g = 2.133$ . Annealing to room temperature for a few minutes resulted in formation of a new species giving an axial spectrum [Fig. 3(b):  $g_{\perp} = 2.208$  and  $g_{\parallel} = 1.884$ ]. The absence in both spectra of a hyperfine coupling with <sup>57</sup>Mn suggests that these species contain an unpaired electron in a macrocycle-centred orbital, and the manganese is reduced to the EPR-silent Mn(I). There can therefore, be a two-electron reduction leading to [Mn<sup>I</sup>(Pc-3)]<sup>2-</sup>. The nature of the second paramagnetic species is uncertain and it may result from a thermal decomposition of the first one. When photolysis was carried out in DMF, the photolyte displayed the EPR spectrum shown in Fig. 4. This spectrum contains a single feature at  $g = 2.001$  and features characteristics for a low spin manganese(II) in axially symmetrical environment ( $g_{\perp}^{av} = 2.185$ ,  $a_{\perp}^{Mn, av} = 0.0013$  cm<sup>-1</sup>,  $g_{\parallel} = 1.875$ ,  $a_{\parallel}^{Mn} = 0.014$  cm<sup>-1</sup>). The relative intensity of the single line increased with prolonged photolysis time confirming its assignment to another species than that giving remaining features. Accordingly, to the study of the electrochemical reduction of [Fe<sup>II</sup>(Pc-2)] by Lever *et al.*<sup>5</sup> we can assign this EPR spectrum to the product of the two-electron reduction of the macrocyclic ligand, *i.e.* [Mn<sup>II</sup>(Pc-4)]<sup>2-</sup>. Consequently, the single feature at  $g = 2.001$  may be due to a product of deeper reduction, *e.g.* [Mn<sup>I</sup>(Pc-5)]<sup>4-</sup>. Unfortunately, in the case of manganese complexes the EPR spectra do not provide direct information about the presence of axial ligands in reduction products (AF, solvent).

The above facts indicate that irradiation of [Fe<sup>II</sup>(Pc-2)] and [Mn<sup>II</sup>(Pc-2)] in the presence of AF leads to one or two-electron reduction of the macrocyclic system. Control experiments have shown that under the same conditions, the organic amines such as imidazole, pyridine and triethylamine, even at concentrations 100-fold higher than that of AF in this study do not cause observable photoreduction of either [Fe<sup>II</sup>(Pc-2)] or [Mn<sup>II</sup>(Pc-2)].

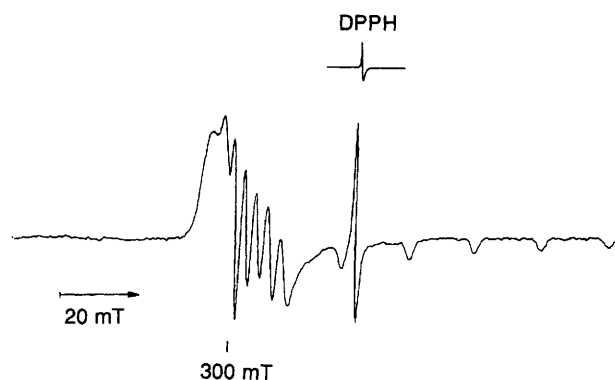


Fig. 4 The X-band EPR spectrum of a photolysed solution of [Mn<sup>II</sup>(Pc-2)] in DMF containing an excess of AF at 77 K

Photoreduction of [Fe<sup>II</sup>(Pc-2)] and [Mn<sup>II</sup>(Pc-2)] necessitates prior coordination of AF to the macrocycle. Ferrocene, which is a stronger reductant than AF (oxidation potentials Fe<sup>II</sup>/Fe<sup>III</sup> of ferrocene and AF are +0.43 and +0.60 V, respectively),<sup>6</sup> but is not capable of coordinating to phthalocyanines, is completely unreactive. We think that coordination of AF to the phthalocyanine enables photoinduced electron transfer from the azaferrocene iron atom to the macrocycle, followed by irreversible destruction of the azaferrocene ligand. A broad, structureless signal of Fe<sup>III</sup> at  $g \sim 6$  was observed in the ESR spectra of photolytes.

The presented data show that photochemistry of metallo-phthalocyanines in the presence of AF offers a new entry to ring-reduced species. The scope and limitation of this approach is currently under investigation.

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## References

- (a) J. R. Darwent, P. Douglas, A. Harriman, G. Porter and M. C. Richoux, *Coord. Chem. Rev.*, 1982, **44**, 83; (b) C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications*, VCH Publishers, New York, 1989.
- (a) H. Ohtani, T. Kobayashi, T. Ohno, S. Tako, T. Tanno and A. Yamada, *J. Phys. Chem.*, 1984, **88**, 4431; (b) H. Ohtani, T. Kobayashi, T. Tanno, A. Yamada, D. Wöhrle and T. Ohno, *Photochem. Photobiol.*, 1986, **44**, 125; (c) T. Nyokong, Z. Gasyna and M. J. Stillman, *Inorg. Chim. Acta*, 1986, **112**, 11; (d) A. B. P. Lever, S. Licocchia, B. S. Ramaswamy, S. A. Kandil and B. V. Stynes, *Inorg. Chim. Acta.*, 1981, **51**, 169; (e) D. K. Geiger, G. Ferraudi, K. Madden, J. Granifo and D. P. Rillema, *J. Phys. Chem.*, 1985, **89**, 3890; (f) T. Nyokong, Z. Gasyna and M. J. Stillman, *Inorg. Chem.*, 1991, **30**, 2301; (g) L. E. Ough, Z. Gasyna and M. J. Stillman, *Inorg. Chem.*, 1987, **26**, 548.
- (a) T. Ohno, S. Kato, A. Yamada and T. Tanno, *J. Phys. Chem.*, 1983, **87**, 775; (b) M. de Baeker, P. Jacquot, F. Sauvage, B. van Vlierberge and G. Lepoutre, *J. Chim. Phys.*, 1987, **84**, 429; (c) G. Ferraudi, *Inorg. Chem.*, 1979, **18**, 1005; (d) J. Zakrzewski and C. Giannotti, *J. Photochem. Photobiol. A: Chem*, 1991, **60**, 289; (e) M. Cesario, C. Giannotti, J. Guilhem and J. Zakrzewski, *Acta Crystallogr. Sect. C.*, 1992, **48**, 798; (f) J. Zakrzewski and C. Giannotti, *J. Chem. Soc., Chem. Commun.*, 1992, 662; (g) J. Zakrzewski, M. Cesario, J. Guilhem and C. Giannotti, *J. Chem. Soc., Dalton Trans.*, 1992, 3059; (h) J. Zakrzewski and C. Giannotti, *J. Chem. Soc., Dalton Trans.*, 1993, 1629.
- A. B. P. Lever and J. P. Wilshire, *Inorg. Chem.*, 1978, **17**, 1145.
- A. B. P. Lever, P. C. Minor and J. P. Wilshire, *Inorg. Chem.*, 1981, **20**, 2250.
- M. G. Peterleitner, L. J. Denisovich, N. I. Pyshnograeva and D. N. Kravtsov, *Metallorg. Khim.*, 1990, **3**, 681.