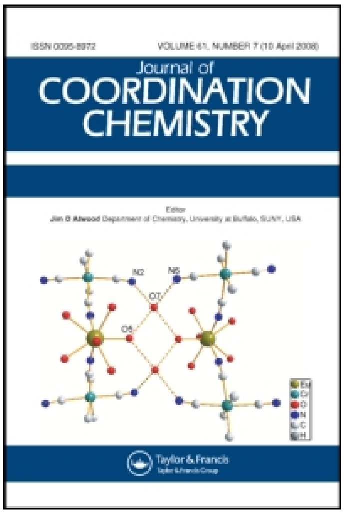

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Vaijayanthimala, G. , D'souza, Francis and Krishnan, V.(1990) 'Synthesis and Structure of Ferrocene-Linked Schiff Base Porphyrins', Journal of Coordination Chemistry, 21: 4, 333 — 342

To link to this Article: DOI: 10.1080/00958979009408196

URL: http://dx.doi.org/10.1080/00958979009408196

J. Coord. Chem. 1990, Vol. 21. pp. 333–342
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SYNTHESIS AND STRUCTURE OF FERROCENE-LINKED SCHIFF BASE PORPHYRINS

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(Received January 3, 1990)

A series of mono ferrocene Schiff-base porphyrins in which the ferrocene unit is disposed in different orientations to the porphyrin core have been synthesized from *meso*-5(*o* or *p*)aminophenyl-10,15,20-triphenyl-21,23-H-porphyrin and ferrocenealdehyde. The optical and magnetic resonance spectral features of these derivatives reveal weak interactions between ferrocene and porphyrin units. The kinetics of metal incorporation into the free-base ferrocenyl porphyrins indicate the steric features induced by the ferrocene unit. Electrochemical redox behaviour of the compounds shows that the ferrocene and porphyrin entities behave as independent units. Steady-state photolysis experiments reveal no internal electron-transfer, although the energies of the CT state of porphyrin-ferricenium ion indicate the feasibility of electron transfer in these systems.

Keywords: Ferrocene, porphyrins, Schiff base, redox behaviour, kinetics

INTRODUCTION

Synthesis and study of metal complexes containing multiple metal centres as models for biological systems are of current interest. Metalloporphyrins with well defined molecular structure offer a great advantage in this respect. A few reports dealing with porphyrins containing chelating sites for metal ions have appeared in the literature.[1–4] These systems are of interest in the study of intramolecular electron transfer reactions. Electron transfer reaction from photoexcited porphyrin to ruthenium(III)pentaamine has been reported in a dinuclear complex meso-tritolyl[N-(pentaamineruthenio)pyridyl]porphyrin.[2] Copper(II) complexes of meso tetra-(nicotinamido-phenyl)zinc(II)porphine is found to be nonfluorescent. The quenching of the fluorescence in this compound has been attributed to electron transfer.[3]

Ferrocene being a stable organometallic compound with well defined redox states is a suitable centre for the study of intramolecular light driven electron transfer reactions. A few interesting ferrocenyl porphyrin systems have been reported in which one or more ferrocene units are covalently linked to the porphyrin entity directly[5] or through bridging groups.[6,7] A slow electron transfer reaction has been observed between the porphyrin and ferricenium ion in the oxidized meso-tetrakis(4-ferrocenyl)porphyrin. The lower magnitude of the rates of electron transfer reaction in these systems have been traced to the metal acceptor orbitals. Kadish *et al*[8] have reported two interesting ferrocenyl gallium and germanium porphyrins, in which the central metal ion in the porphyrin cavity is directly linked to a ferrocene unit. It is found that in these compounds the life-time of the porphyrin triplet state is quenched by the ferrocene unit apparently due to excited state energy-transfer.

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We report here the synthesis and properties of mono-ferrocene Schiff-base porphyrins in which the ferrocene unit is disposed at different orientations. The choice of linking single ferrocene unit to the porphyrin is preferred since photoinduced electron transfer reaction involves only one acceptor entity. Metallation reactions of the free-base porphyrin bearing differently linked ferrocene have been carried out to study the effect induced by the ferrocene unit on the rates of metal incorporation into the porphyrins. Electronic and magnetic resonance spectral studies of the free-base and its metal [zinc(II) and copper(II)] derivatives have been investigated to probe into the nature of interaction between the porphyrin ring and ferrocene moiety. Cyclic voltammetric studies of the free-base and the metallated porphyrin derivatives reveal the existence of different redox sites in these systems.

EXPERIMENTAL

meso-5(*o* or *p*)aminophenyl-10,15,20-triphenylporphyrin was prepared according to the methods described in the literature.[9] [UV/Visible in $CHCl_3$: (λmax in nm), 648, 590, 548, 514 and 417. ^1H nmr in $CDCl_3$, δ in ppm (position of the resonance, nature of the multiplet, number of protons involved in the given group). 8.83 (m, 8H, pyrrole H), 7.70 (m, 9H, meta and para protons of triphenyl entity), 8.19 (m, 6H, ortho protons of triphenyl entity), 8.00, 7.03, (d, 4H, amino substituted phenyl protons), −2.76 (s, 2H, imino H)].

Ferrocenealdehyde was prepared[10] by treating a cold mixture of N-methylformanilide and $POCl_3$ with ferrocene. [UV/Visible in $CHCl_3$: (λmax in nm) 475, 322, 278. ^1H NMR in $CDCl_3$ (δ in ppm) 9.95 (s, 1H, aldehyde proton), 4.75, 4.61 (d, 4H, substituted C_p ring), 4.22 (s, 5H, unsubstituted C_p ring)].

Preparation of the ferrocene Schiff-base porphyrins, (H_2PFc):

Figure 1 depicts schematically the preparation of the ferrocene Schiff-base porphyrins. A mixture of meso 5-(*o* or *p*) aminophenyl-10,15,20-triphenylporphyrin (100 mg) and ferrocenealdehyde (90 mg) was refluxed for 6 h in dry benzene using a Dean–Stark apparatus. At the end of the reaction, the solvent was removed under reduced pressure. The compound thus obtained was separated over a dry neutral alumina column using CH_2Cl_2 as eluent. The first fraction was found to contain the desired product. [^1H NMR in $CDCl_3$: (i) *o*-H_2PFc: 8.91 (m, 8H, pyrrole H), 8.42 (s, 1H, Schiff-base H), 8.22 (m, 8H, ortho protons of triphenyl entity), 7.76 (m, 9H, meta and para protons of triphenyl), 7.17, 7.57 (m, 4H, substituted phenyl ring), 4.18 (s, 5H, unsubstituted Cp ring), 4.15, 3.54 (d, 4H, substituted Cp ring). (ii) *p*-H_2PFc: 8.85 (m, 8H, pyrrole H), 8.66 (s, 1H, Schiff-base H), 8.20 (m, 8H, ortho protons of trisphenyl), 7.72 (m, 9H, meta and para protons of trisphenyl entity), 7.16, 7.50 (d, 4H, substituted phenyl H), 4.90 (s, 5H, unsubstituted Cp ring), 4.50, 4.31 (d, 4H, substituted Cp ring), −2.76 (s, 2H, imino H)].

The zinc(II) and copper(II) derivatives of the porphyrins were prepared according to the procedure described in the literature.[11]

The absorption spectral measurements were carried out using a Hitachi-3400 UV/Visible spectrophotometer and the fluorescence spectra were measured using a Hitachi model 650–60 spectrofluorimeter. The porphyrin metal insertion kinetics were carried out using metal acetates as metal carriers in CH_2Cl_2:CH_3OH (1:1 v/v) solvent mixture containing 0.1 M sodium perchlorate. Hi-Tech stopped-flow

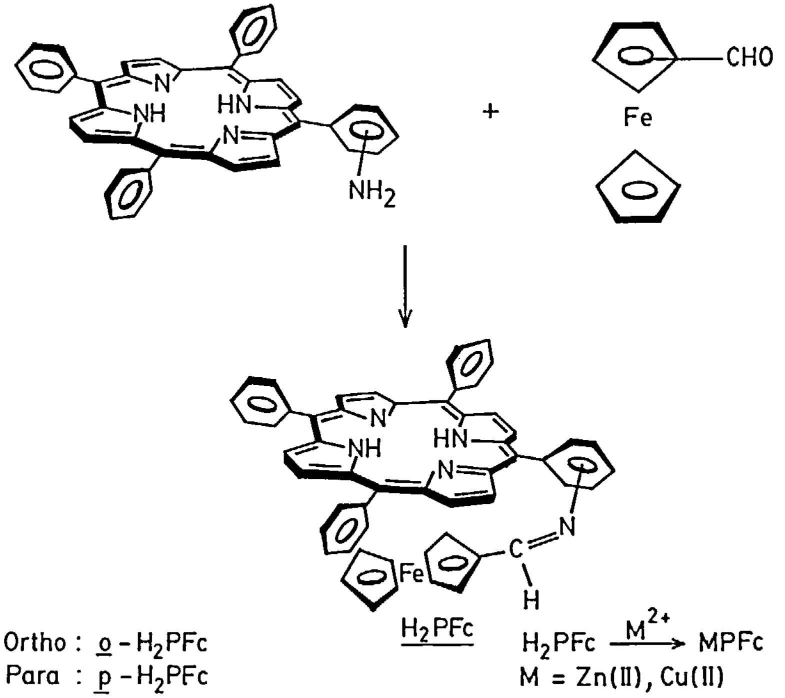

FIGURE 1 Synthetic route for the ferrocene Schiff-base porphyrins.

spectrometer (SF-40), interfaced with Apple-IIe computer was used to monitor the metallation kinetics. The cyclic voltammograms of the synthesized products were recorded on a BAS model 100-A electroanalytical apparatus. Methylene chloride containing 0.1 M tetrabutylammonium perchlorate was used as a supporting electrolyte. A three electrode assembly consisting of a platinum button working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode were used for redox potential measurements. The ^1H NMR spectra were recorded on a Bruker 270 MHz FT-NMR spectrometer using $CDCl_3$ as the solvent. EPR measurements were carried out using a Varian E-109 spectrometer. DPPH was used as a 'g' marker.

RESULTS AND DISCUSSIONS

The ferrocene Schiff-base porphyrin derivatives are highly characteristic and the structural integrity is established by ^1H NMR studies. The assignment of proton resonances and the integrated intensities agree well with the composition of the compounds. The pyrrole protons of the ferrocene Schiff-base porphyrins resonate as a multiplet in the region 8.72–8.93 ppm due to the non-equivalence of the protons as a consequence of meso aryl substitution.[12] The complexity of the multiplet resonance increases from *p* substituted to *o* substituted derivatives indicating the influence of ferrocenyl entity on the β-pyrrole resonance. The presence of ferrocene unit in the para Schiff-base porphyrin unit is revealed by two sets of proton resonances arising from the unsubstituted and substituted cyclopentadiene (C_p) rings. The proton resonance at the lower field 4.90 ppm has been assigned to the unsubstituted C_p ring while the protons of the substituted C_p ring resonates as a doublet at 4.50 and 4.31 ppm. In the ortho substituted Schiff-base porphyrins, the proton resonances of C_p rings are found to occur in higher field relative to the corresponding proton resonances of the para substituted Schiff-base porphyrins. [4.18 ppm for unsubstituted C_p ring and 4.15, 3.54 ppm for substituted C_p ring]. The shielding effect felt by the protons of C_p ring in the *o* substituted derivatives can be rationalized in terms of the proximity of C_p ring to the porphyrin unit. It is reasonable to expect that the ferrocene unit is disposed within the shielding zone of the porphyrin ring current thereby inducing up-field shift in the proton resonance of C_p ring.

The electronic absorption spectra of the Schiff-base porphyrins, (H_2PFc)) exhibit *etio* type spectra with the appearance of four bands in the visible region (Q bands) and an intense soret band (B band) (Table I). The presence of ferrocene unit in these derivatives is not discernible in the optical absorption spectra since the absorption by ferrocene in the near visible region (450 nm) is completely masked by the intense absorption of porphyrin unit (B band). The existence of *o* and *p* Schiff-base linkage to tetraphenyl porphyrin does not significantly alter the optical absorption spectra of these derivatives. The fluorescence spectra of the Schiff-base porphyrins are examined. The free-base porphyrin and its zinc derivatives in CH_2Cl_2 exhibit characteristic singlet emissions at 654 and 720 nm and at 596 and 654 nm respectively. The quantum yields of the fluorescence have been calculated using the method of Austin and Gouterman[13] (Table I). It is found that the quantum yield of fluorescence in the intramolecularly linked derivatives is marginally decreased relative to the intermolecular mixtures of porphyrin and ferrocene. Moreover, the quantum yield of the *o* derivatives is lower than that observed for the corresponding *p* derivatives. This seems to suggest that in the *o* derivatives, the ferrocene unit interacts favourably with the porphyrin entity thereby decreasing the fluorescence quantum yield. It is known that the protonation of Schiff-base porphyrins results in the shift of the optical absorption bands of the porphyrins to red region owing to enhancement of π-conjugation.[14-16] However, in these cases we have not observed any shift in the absorption bands on protonation of the Schiff-base porphyrins. This is ascribed to the absence of π-conjugation since the aryl groups of the porphyrins are oriented perpendicular to the porphyrin plane.

TABLE I
Optical absorption data and emission quantum yields of ferrocene Schiff-base porphyrin systems in CH_2Cl_2 at 298K.

Compound	Q_1	Q_2	Q_3	Q_4	B_1	φ_f[a]
H_2TPP	646	592	549	513	417	1.0
o-H_2PFc	648	590	548	514	417	0.90
p-H_2PFc	647	590	551	516	419	0.92
ZnTPP		587	547		420	1.0
o-ZnPFc		586	547		421	0.88
p-ZnPFc		587	548		421	0.91
CuTPP			538		415	
o-CuPFc			539		415	
p-CuPFc			540		416	

[a] These are relative fluorescence quantum yields taking φ_f for H_2TPP and ZnTPP to be 1.0.

We carried out the kinetics of metal incorporation reaction into the free-base porphyrins appended with ferrocene unit in order to illustrate the effect of steric interactions. The change in the optical absorbance at 515 nm of the Schiff-base porphyrins is chosen for monitoring the rate of metallation reactions. It is observed that the absorbance of 515 nm band increases linearly with the increase in the concentration of the porphyrin obeying Beer–Lambert's relationship. Moreover, metallation of Schiff-base porhyrins decreases the absorbance value of the 515 nm band. The change in absorbance of the 515 nm band as a function of time was analyzed to determine the rates of Schiff-base porphyrin metallation reaction. Under pseudo first-order conditions, the rate constant k_{obs} can be expressed as,

$$k_{obs}.t = 2.303 \log A_0/A_t \qquad (1)$$

where A_0 and A_t denote the absorbance values of the porphyrin solution at time zero and time t, respectively. A representative plot for the copper incorporation reactions into free-base porphyrins is shown in Figure 2 and the data is presented in Table II. It is interesting to note that the rates of metallation reaction of Schiff-base porphyrins depend on the nature of the substituent as ortho < para. In the Schiff-base porphyrin derivatives, the relative order of metal incorporation rates depend on the nature of the metal ion as $Cu^{2+} > Zn^{2+} > Co^{2+}$. The smaller magnitude of the metallation rates in the case of Schiff-base porphyrins compared to unsubstituted, H_2TPP, indicates that the ferrocene unit possibly blocks one face of the porphyrin preventing the access of metal ion into porphyrin cavity. The result obtained in the present study is similar to those obtained for pivaloyl and other similar sterically hindered porphyrins.[17–19] The metal ion dependence of the rates can be ascribed to the relative stabilities of metalloporphyrins.

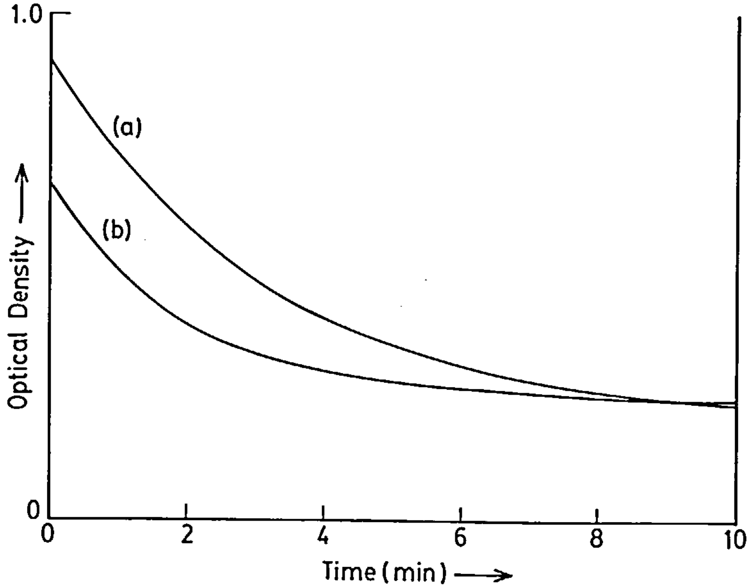

FIGURE 2 Kinetic traces for Cu^{2+} insertion into a) H_2TPP and b) p-H_2PFc in CH_2Cl_2:CH_3OH (1:1 v/v) containing 0.1 M sodium perchlorate. The concentration of the free-base porphyrins was 0.1 mM and the concentration of the copper(II) acetate was maintained at 1 mM.

TABLE II
Rate data[a] for metal incorporation into H_2TPP and Schiff-base porphyrins at 25°C in $CH_2Cl_2:CH_3OH$ (1 : 1 v/v).

porphyrin	metal carrier	$10^3k_{obs}/s^{-1}$
H_2TPP	Cu acetate	3.16
o-H_2PFc	Cu acetate	2.40
p-H_2PFc	Cu acetate	3.14
H_2TPP	Zn acetate	2.14
o-H_2PFc	Zn acetate	1.50
p-H_2PFc	Zn acetate	1.90
H_2TPP	Co acetate	1.52
o-H_2PFc	Co acetate	1.23
p-H_2PFc	Co acetate	1.47

[a] The uncertainty in k_{obs} values is ±10%.

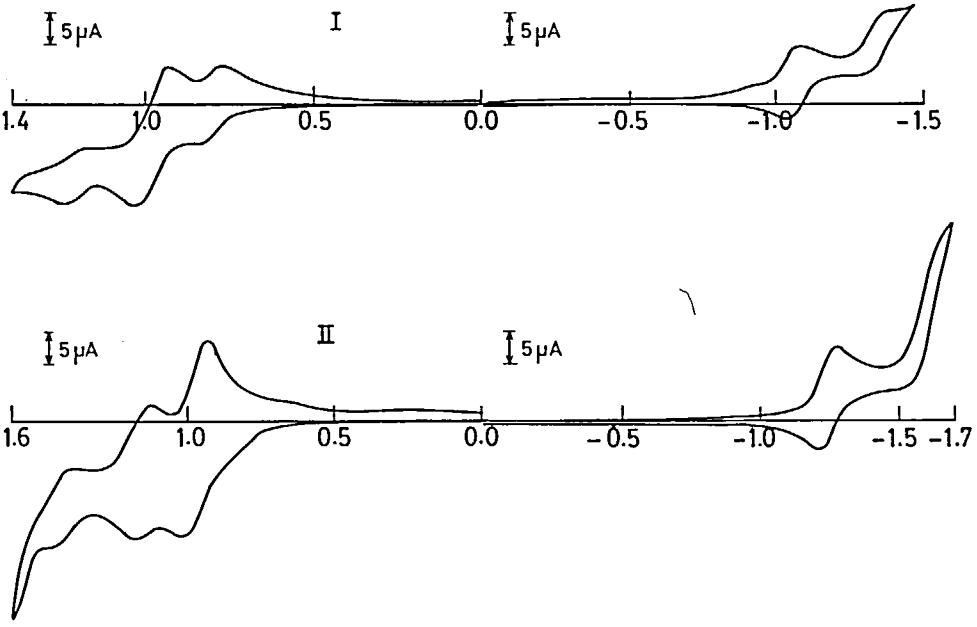

FIGURE 3 Cyclic voltammograms of I) *o*-H_2PFc and II) *p*-CuPFc in CH_2Cl_2 containing 100 mM TBAP at 25°C. Scan rate: 100 mV/s.

The electrochemical redox behaviour of the ferrocene Schiff-base porphyrin derivatives provide interesting results. Porphyrins and their metal [Zn(II) and Cu(II)] derivatives exhibit characteristic two one-electron reversible ring oxidation and reduction peaks corresponding to oxidation and reduction of the π-ring of the porphyrin.[20] The cyclic voltammograms of two representative Schiff-base porphyrin derivatives are shown in Figure 3. It is seen that the Schiff-base derivatives exhibit three distinct oxidation and two reduction peaks. The potentials calculated as the

TABLE III
Electrochemical data for the ferrocene Schiff-base porphyrins in CH_2Cl_2 (in volts).[a]

Compound	$P \rightarrow P^{+\cdot}$	$P^{+\cdot} \rightarrow P^{2+}$	$Fc \rightarrow Fc^{+}$	$P \rightarrow P^{-\cdot}$	$P^{-\cdot} \rightarrow P^{2-}$
H_2TPP	1.00	1.30		−1.11	−1.52
o-H_2PFc	1.02	1.24	0.80	−1.06	−1.43
p-H_2PFc	1.07	1.30	0.87	−1.13	−1.45
ZnTPP	0.79	1.07		−1.12	−1.37
o-ZnPFc	0.96[b]	1.13	0.96[b]	−1.30	−1.53
p-ZnPFc	0.85[b]	1.06	0.85[b]	−1.06	−1.51
CuTPP	1.01	1.26		−1.29	−1.54
o-CuPFc	1.14	1.42	0.92	−1.23	−1.57
p-CuPFc	1.08	1.38	0.89	−1.26	−1.55

[a] The potentials are referenced to the Ag/AgCl couple. [b] Represents overlapping of peaks involving a two electron process.

average of the cathodic and anodic peaks are found to be Nernstian and refer to one-electron transfer. The data obtained for the Schiff-base porphyrins derivatives are presented in Table III. The observed redox potentials are well separated and it has been possible to characterize the peak potentials of the Schiff-base porphyrins according to the electrode reactions by comparison with the cyclic voltammogram of ferrocenealdehyde in the same solvent. The cyclic voltammogram of ferrocenealdehyde in CH_2Cl_2 showed a reversible one-electron oxidation peak at 0.83 V (versus Ag/AgCl) corresponding to the Fe^{2+}/Fe^{3+} couple. The magnitude of this potential is found to be 0.37 V more than that observed for the corresponding couple in ferrocene. The anodic shift in the oxidation potential of ferrocenealdehyde relative to ferrocene is ascribed to the presence of electron withdrawing substituent (formyl) on one of the Cp rings of the ferrocene. It is found that the oxidation of ferrocene unit and the ring oxidations and reductions of the Schiff-base porphyrin unit occur at potentials not significantly different from those observed for the free ferrocenealdehyde and porphyrin units. This suggests that the porphyrin and ferrocene units in the Schiff-base derivatives behave as independent units towards electrochemical oxidation and reduction processes. It has been possible to produce electrochemically a ferrcinium derivative of the free-base porphyrin Schiff-base. The optical spectrum of this compound though does not reveal any absorption at 620 nm corresponding to ferricinium ion,[21] the singlet emission spectrum of this compound reveals a marginal decrease in intensity relative to the unoxidized species (Figure 4). Moreover, the cyclic voltammogram of this oxidized derivative shows a characteristic reduction peak at −0.83 V corresponding to the presence of ferricinium ion in the compound. The complete recovery of this potential in the cyclic voltammogram of the oxidized derivative reveals that there is no significant internal electron transfer between the porphyrin unit and the ferricinium moiety.

The EPR spectral features of copper(II) derivatives of the Schiff-base porphyrins have been studied to elucidate the nature of interaction between the porphyrin unit and ferrocene moiety. The EPR spectrum of a representative Schiff-base porphyrin derivative in toluene at liquid nitrogen temperature is shown in Figure 5. The EPR spectra are well-resolved displaying characteristic features both in the parallel and perpendicular region. All the spectra were simulated using Gaussian quadrature

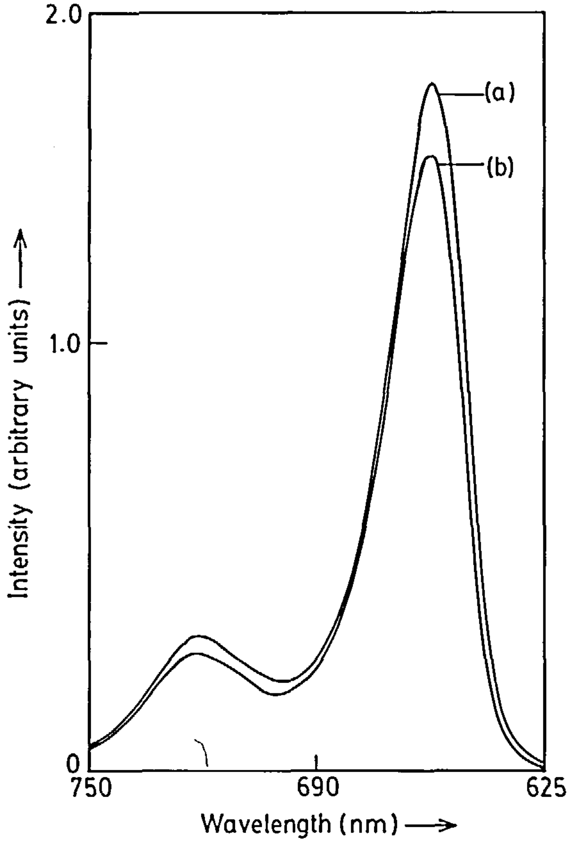

FIGURE 4 Fluorescence spectra of a) *o*-H_2PFc and b) the ferrocene oxidized product of *o*-H_2PFc. The potential was held at +0.9 V in CH_2Cl_2 containing 100 mM TBAP.

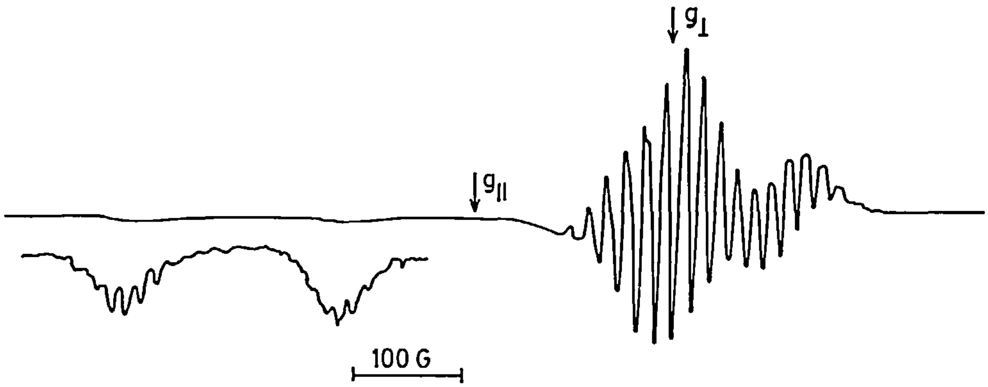

FIGURE 5 EPR spectrum of *o*-CuPFc in toulene at −140°C. The field settings are: time constant, 0.064 s; scan time, 4 min; modulation frequency, 100 kHz; modulation amplitude, 0.4 mT; microwave power, 2 mW; microwave frequency, 9.055 GHz.

method.[22] The EPR parameters g and A are calculated from the spectral features assuming a Spin–Hamiltonian for axial symmetry.[23] The binding parameter (α^2), which is a measure of the covalency of the in-plane π-bonding of the Cu–N bond, was calculated using an expression[24] based on the copper hyperfine tensor $A_\parallel$ as,

$$\alpha^2 = -(A_\parallel/p) + (g_\parallel - 2) + 5/7\,(g_\perp - 2) + c$$

where c is a constant and p = 0.0364 for Cu(II) derivatives of tetraarylporphyrins. The difference in the magnitudes of α^2 values ($\Delta\alpha^2$) for the Cu(II) derivatives of the ferrocene appended Schiff-base porphyrins with CuTPP is given in Table IV. An examination of the Table 4 reveals that in all the Cu(II) derivatives, there is a marginal decrease in $A_\parallel^{Cu}$ and $A_\perp^{Cu}$ values accompanied by an increase in $A_\parallel^{N}$ and $A_\perp^{N}$ values. It is also seen that the magnitude of the α^2 values for CuPFc are found to be lower than that observed for CuTPP. The decrease is significant in case of the ortho derivative relative to the para substituted compounds. The change in the α^2 values of CuPFc derivatives signifies that the M–N bond becomes more covalent relative to CuTPP owing to the intramolecular interaction of the ferrocene unit with the porphyrin.[25] It is to be noted that in the ortho derivatives the interaction is significant possibly due to proximity of the ferrocene unit to the porphyrin moiety.

The Schiff-base porphyrins offer potential systems for the study of photoinduced intramolecular electron transfer reactions. The energy of the CT states o-H_2PFc^+/o-$H_2P^{+\cdot}Fc$ calculated from the electrochemical redox data is found to be ~0.19 V. It is possible to estimate the free-energy change for the excited state electron-transfer reaction (ΔG_{et}) from the algebraic sum of the CT energies of the porphyrins and the excited singlet state energies of the porphyrins. The high exothermicity of ΔG_{et} value (~ −1.7 eV) suggests the feasibility of singlet excited state electron transfer in these systems. However, our attempts to demonstrate the existence of intramolecular electron-transfer reaction in these systems have not been successful. It is worthy to mention here that the steady-state photolysis experiments involving intermolecular mixture of porphyrin and ferricinium ion have also indicated absence of electron transfer from photoexcited porphyrin to ferricinium ion.

TABLE IV
EPR data for the ferrocene Schiff-base porphyrins in toluene at −140°C.

	$g_\parallel$	$g_\perp$	$A_\parallel^{Cu}$	$A_\perp^{Cu}$	$A_\parallel^{N}$	$A_\perp^{N}$	
Compounds	($\times 10^4$ cm^{-1})						$\Delta\alpha^2$
CuTPP	2.785	2.047	202.0	31.6	14.8	15.8	
o-CuPFc	2.170	2.034	195.0	33.2	14.2	16.6	0.0386
p-CuPFc	2.180	2.033	195.5	33.0	15.0	16.5	0.0274

ACKNOWLEDGMENT

This work is supported by the Department of Non-Conventional Energy Sources and Department of Science and Technology, Government of India, New Delhi. One of the authors (V.G.) is thankful to the DNES for a fellowship.

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