Iron(III) and copper(II) complexes of *trans*-bis(ferrocenyl)porphyrin: Effect of metal ions on long-range electronic communication

DIPANKAR SAHOO and SANKAR PRASAD RATH*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208 016, India
e-mail: sprath@iitk.ac.in

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Abstract. A series of complex with a general formula of $M(\text{Fc}_2\text{Ph}_2\text{P})$ [$\text{Fc}_2\text{Ph}_2\text{P}$ = 5,10-bisferrocenyl-15,20-bisphenylporphyrin (2-); M = Fe(III)Cl $\text{Fe(III)(ClO}_4\text{)}$ and Cu(II)] have been synthesized and characterized. The single crystal X-ray structure of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ has been reported in which two ferrocene moieties are in *anti* form with respect to each other. The ferrocenyl groups of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ are more easily oxidized via a single two-electron quasi-reversible process compared to the free base ligand in which two 1e-oxidative response separated by 0.23 V are observed. Electrochemical study of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ revealed ferrocene-based two-electron quasi-reversible oxidation at 0.72 V indicating no observable coupling of the ferrocene moieties. The higher oxidation state of Fe(III) reduces the electron releasing tendency of the porphyrin ring and thus make the ferrocene oxidation difficult. The porphyrin, however, lack substituents at the β -pyrrolic positions, and the ferrocenyl moieties are therefore free to rotate. The observed electrochemical analyses thus demonstrate that the oxidation of the ferrocene subunit is strongly affected by porphyrin ring as well as the central metal through extended π -conjugation.

Keywords. Ferrocenylporphyrin; electrochemistry; spectro-electrochemistry; electrochemical conjugation; X-ray structure determination.

1. Introduction

The multiple redox active centers are of fundamental importance for the development of molecular-based electronic devices or molecular electrogenic sensors.¹ Ferrocene-porphyrin conjugates have great potential in such areas due to their donor-acceptor complementary and electrochemical activities. Their ability to reversibly accept and/or release several electrons at distinct potentials is particularly interesting in multi-electron redox catalysis and can be used for multi-bit information storage at the molecular level.^{1–4} The peripheral substitution around the porphyrin ring along with the nature of the organic linkage between these redox active centers have been shown to drastically influence their ‘communication’ and numerous studies are aimed at characterizing and understanding these interactions.

A large variety of ferrocene-appended porphyrins or porphyrin analogues have been reported in the literature.⁴ The outstanding thermal and chemical stability as well as the possibility of tuning the macrocyclic redox potentials make porphyrins and related compounds outstanding candidates as π -conjugated

skeletons, which are able to connect several redox-active ferrocenyl substituents at various available positions.⁵ Ferrocene linked by olefin bridges show larger metal–metal interactions than those linked by analogues of saturated carbon. Two redox active ferrocene units linked by π -conjugation can be expected to show intramolecular and intermolecular interactions, so-called electrochemical communication, of the ferrocenyl groups. When one of the two ferrocenyl groups is oxidized to the monocation, the delocalization of the cationic charge between ferrocene and ferrocenium ion may occur to give a mixed valence state.^{6,7} Recent studies identify at least some of the factors that influence electrochemical interaction between connected ferrocene moieties, including the nature, type and length of the connector and the orientation of the two ferrocene moieties. Examples of strong, long-range (> 10 Å) metal–metal coupling are already reported for the metal-free and nickel and manganese complexes of α , α -5,15-bis(ferrocenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrins.⁵ In these cases, pure atropisomers of the metal-free and transition-metal α , α -5,15-bis(ferrocenyl)-2,3,7,8,12,13,17,18-octaalkylporphyrins demonstrated long-range metal–metal coupling between two ferrocenyl substituents. In the present work, we report the synthesis, structure and

*For correspondence

properties of Fe(III) and Cu(II) complexes of *trans* diferrocenylporphyrin in which the ferrocenyl groups are free to rotate due to lack of substituent at the β -pyrrolic positions. The effects of central metal ions have been explored in details.

2. Experimental

2.1 Materials

5,15-bisferrocenyl-10,20-bisphenylporphyrin (*trans*-H₂Fc₂Ph₂P) was prepared by literature methods.^{6a} Grade-III basic alumina was used for column chromatography. Reagents and solvents are purchased from the commercial sources and purified by standard procedures before use.

2.1a $Fe^{III}(Fc_2Ph_2P)Cl$: 100 mg of H₂Fc₂Ph₂P (0.12 mmol) was dissolved in 100 mL dimethylformamide; excess FeCl₂ was added and the mixture was refluxed for 2.5 h under nitrogen atmosphere. The resulting solution was then cooled and transferred to a separatory funnel. 100 mL dichloromethane was added to the mixture which was then washed with 0.2 (N) HCl (3 x 200 mL). Organic layer was separated and dried over anhydrous Na₂SO₄. The resulting solution was evaporated to complete dryness and purified by column chromatography using silica gel. The major fraction, eluted with chloroform, was collected and vacuum dried to obtain brown solid. Yield: 80 mg (72 %). Anal. Calcd (found): C, 67.88 (67.97); H, 3.95 (4.10); N, 6.09 (6.18). UV-vis(dichloromethane) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 420 (7.5 x 10⁴), 486 (4.5 x 10²), 632 (9.9 x 10¹). ¹H NMR (CDCl₃, 295 K): β - H: 7.8; α -Cp: 13.24; β -Cp: 12.27; Cp-H: 9.16 ppm. EPR data: in dichloromethane (120 K), $g_{\perp}$ = 5.96 and $g_{\parallel}$ = 1.99. E_{1/2}, V (ΔE_p , mV): 0.72 (70).

2.1b $Fe^{III}(Fc_2Ph_2P)ClO_4$: 100 mg of Fe^{III}(Fc₂Ph₂P) Cl (0.109 mmol) was dissolved in 100 mL benzene. A saturated acetonitrile solution of AgClO₄ (24 mg, 0.12 mmol) was added to the resulting solution which was then stirred for an hour under nitrogen atmosphere. After the removal of AgCl by filtration, heptane (10 mL) was added, and the solution was then allowed to stand overnight. The purple crystalline products were collected by filtration, washed with hexane, and dried in vacuum at room temperature to give the compound. Yield: 70 mg (65 %). Anal. Calcd (found): C, 63.46 (63.53); H, 3.69 (3.74); N, 5.70 (5.63). UV-vis (dichloromethane) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 397 (7.3 x 10³), 619 (6.5 x 10¹). ¹H NMR (CDCl₃, 295 K):

β - H: 3.6; α -Cp: 13.24; β -Cp: 12.27; Cp-H: 9.16 ppm. EPR data: in dichloromethane (120 K): $g_{\perp}$ = 5.64 and $g_{\parallel}$ = 2.00.

2.1c $Cu^{II}(Fc_2Ph_2P)$: A solution of Cu(OAc)₂ (87 mg, 0.48 mmol) in methanol (20 mL) was added to a chloroform solution (100 mL) of H₂Fc₂Ph₂P under nitrogen. The mixture was then refluxed for 2 h, cooled to room temperature and was dried in vacuum. The solid residue was then purified by column chromatography on silica gel. The major fraction, eluted with chloroform, was collected and vacuum dried to obtain brown solid of the complex. Yield: 78 mg (73 %). Anal. Calcd (found): C, 69.99 (70.01); H, 4.07 (4.12); N, 6.28 (6.24). UV-vis (dichloromethane) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 415 (5.8 x 10⁴), 550 (7.2 x 10¹), 625 (6.3 x 10¹). EPR data: in dichloromethane (120 K), $g_{\perp}$ = 2.06 and $g_{\parallel}$ = 2.21. E_{1/2}, V (ΔE_p , mV): 0.44(75); 1.0(65); 1.3(60).

2.2 Instrumentation

UV-vis spectra were recorded on a PerkinElmer UV/vis spectrometer. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400II elemental analyzer. ¹H NMR spectra were recorded on a JEOL 500 MHz instrument. The spectra for paramagnetic molecules were recorded over a 100 kHz bandwidth with 64 K data points and a 5 μ s 90° pulse. For a typical spectrum, between 2000 and 3000 transients were accumulated with a 50 ms delay time. The residual ¹H resonances of the solvents were used as a secondary reference. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMX EPR spectrometer. Cyclic voltammetric studies were performed on a BAS Epsilon electrochemical workstation in dichloromethane with 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAH) as supporting electrolyte and the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The concentration of the compounds was in the order of 10⁻³ M. The ferrocene/ferrocenium couple occurs at E_{1/2} = +0.45 (65) V versus Ag/AgCl under the same experimental conditions.

2.3 X-ray structure solution and refinement

A suitable crystal of Cu^{II}(Fc₂Ph₂P) was coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of Bruker SMART APEX CCD diffractometer equipped with CRYO industries low-temperature apparatus. Intensity data were collected using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) while SAINT software⁸ was used for data integration

Table 1. Crystal data and data collection parameters of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$.

T, K	100(2)
Formula	$\text{C}_{52} \text{H}_{36} \text{Cu Fe}_2 \text{N}_4$
Crystal size (mm^3)	0.26 x 0.22 x 0.18
Formula weight	892.09
Crystal system	Monoclinic
Color	Dark red
Space group	$P2_1/c$
a , Å	9.659(4)
b , Å	10.614(5)
c , Å	18.021(8)
α , deg	90
β , deg	98.445(10)
γ , deg	90
V , Å ³	1827.7(14)
Radiation (λ , Å)	Mo K α (0.71073)
Z	2
d_{calcd} , g cm ⁻³	1.621
μ , mm ⁻¹	1.407
$F(000)$	914
No of unique data	3381
No. of parameters refined	268
GOF on F^2	1.016
$R1^{a[I > 2\sigma(I)]}$	0.0534
$R1^a(\text{all data})$	0.0737
$wR2^b(\text{all data})$	0.1405

$$^a R1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}; ^b wR2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]}}$$

and reduction. An absorption correction was applied.⁹ The structure was solved by the direct method using SHELXS-97 and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97 program package.¹⁰ Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were

treated as riding atoms using SHELXL default parameters. Crystal data and data collection parameters are given in table 1.

3. Results and Discussion

5,15-bisferrocenyl-10,20-bisphenylporphyrin, $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ prepared using the procedure reported previously.^{6a} Free ligand was refluxed with excess FeCl_2 under N_2 atmosphere which upon aerial oxidation and subsequent chromatographic purifications yields dark red 5,15-bisferrocenyl-10,20-bisphenyl chloro Fe(III) porphyrin, $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$. The UV-vis spectrum of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ in dichloromethane shows intense Soret band at 420 nm and two Q bands at 486 and 635 nm. Upon addition of the acetonitrile solution of AgClO_4 into the benzene solution of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$, further change in the UV-vis spectra has been observed due to the formation of 5,15-bisferrocenyl-10,20-bisphenyl perchlorato Fe(III)porphyrin, $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ which was then isolated and spectroscopically characterized. UV-visible spectra of the complex show a Soret band at 397 nm with a Q band at 619 nm. However, the addition of methanolic solution of $\text{Cu}(\text{OAc})_2$ into the CHCl_3 solution of $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ and subsequent chromatographic purifications yields dark-red 5,15-bisferrocenyl-10,20-bisphenyl Cu(II) porphyrin, $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ which was then isolated and structurally characterized. The UV-visible spectrum of the complex shows a Soret band at 415 nm. Scheme 1 shows the synthetic outline of all the complexes reported here along with their abbreviations while figure 1 compares the UV-vis spectra of the representative complexes. However, detailed synthetic procedures

Scheme 1. List of complexes and their abbreviation.

Figure 1. UV-visible spectra in dichloromethane of $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ (green line), $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ (blue line) and $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ (red line) at 295 K.

along with the spectroscopic characterizations are given in the experimental section.

3.1 Crystallographic characterization of $\text{CuFc}_2\text{Ph}_2\text{P}$

Dark-brown crystals of the molecule were obtained *via* slow diffusion of hexane into the chloroform solution of the molecule in air and one such crystals was chosen to mount on the Goniometer head for X-ray structure determination. The molecule crystallizes in the monoclinic crystal system with $P 2_1/c$ space group, a perspective view is shown in figure 2. In the asymmetric unit, 1/2 molecule of the complex is present and Cu metal ion is present at the centre of inversion. Crystal data and data collection parameters are listed in table 1 while the selected bond distances and angles

Figure 2. A perspective view of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ showing 50% thermal contours for all non-hydrogen atoms at 100 K (H-atoms have been omitted for clarity).

Table 2. Selected bond Lengths (Å) and angles (deg) for $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$.

Cu-N(1)	1.995(3)	Fe(1)-C(17)	2.044(5)
Cu-N(2)	2.013(3)	Fe(1)-C(18)	2.049(5)
Fe(1)-C(11)	2.073(4)	Fe(1)-C(19)	2.054(5)
Fe(1)-C(12)	2.069(4)	Fe(1)-C(20)	2.053(5)
Fe(1)-C(13)	2.052(4)	C(4)-C(5)	1.404(6)
Fe(1)-C(14)	2.040(5)	C(5)-C(6)	1.412(6)
Fe(1)-C(15)	2.008(4)	C(5)-C(11)	1.497(6)
Fe(1)-C(16)	2.030(5)	C(10)-C(21)	1.506(5)
N(1)-Cu-N(2)	89.25(14)	C(6)-C(5)-C(11)	120.9(4)
C(4)-C(5)-C(6)	122.3(4)	C(9)-C(10)-C(1)	123.9(4)
C(4)-C(5)-C(11)	116.8(4)	C(1)-C(10)-C(21)	117.3(4)

are given in table 2. The complex has a four coordinate square planar geometry in which the copper (II) atom is displaced by 0.03 Å from the N4 plane of porphyrin. The average Cu-Np distances is found to be 2.004(3) Å which is similar to other four-coordinate Cu(II)porphyrins reported in the literature.¹¹ It is, however, interesting to note that two ferrocene moieties are *anti* with respect to each other. The crystal packing shows the formation of well-separated stacks of molecules as illustrated in figure 3.

The molecule $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$, shown in figure 2, has two ferrocenyl groups in the *anti* configuration. The porphyrin skeleton is essentially planar with only a slight distortion. Phenyl substituents were found to be nearly perpendicular (75.3°) to the porphyrin core while the Cp ring produces a torsion angle of 38° with the porphyrin ring. The C5-C11 distance of 1.497(6) Å is similar with the C10-C21 distance of 1.506(5) Å implying almost no conjugation between the porphyrin ring and the ferrocenyl group. It is interesting to note that all the diferrocenyl porphyrins reported so far^{6,7} aligned in a *syn*-orientation of two ferrocenyl groups while porphyrin rings are much more distorted compared to the same in $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$.

Figure 3. Diagram illustrating the packing of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ in the unit cell. H-atoms have been omitted for clarity.

The porphyrin macrocycle is distorted only slightly in the $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ reported in the present work. This can be best appreciated by turning to figure 4 where the out-of-plane displacements in units of $0.01 \text{ \AA}$ of the porphyrin core atoms are compared and, as can be seen, the porphyrin macrocycle is *wave*-distorted. It is, however, interesting to note that the porphyrin ring distortion is much less in $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ when compared to the similar complexes reported in the literature.

3.2 ^1H NMR

The structure and properties of the iron(III) porphyrins in solution can be obtained from their ^1H NMR spectra in CDCl_3 . The signals are broad and shifted to the downfield regions for the metal complexes compared to the free base porphyrin. The pyrrole-*H* signals of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ are observed at 78 and 36 ppm, respectively. The protons of the substituted Cp ring (α -Cp, β -Cp) are observed as two non-equivalent sets while unsubstituted Cp ring (CpH) shows only one signal, as expected. In $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$, the protons of the substituted Cp ring (α -Cp, β -Cp) are downfield shifted to 12.2 and 13.2 ppm, respectively, compared to unsubstituted Cp ring (CpH) which has been observed at 9.17 ppm. Also, protons from two phenyl substituents of the porphyrin core show a signal at 9.9 ppm. Similar spectral pattern have also been observed in $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$. Figure 5 compares the ^1H NMR spectra in CDCl_3 at 295 K for both the complexes.

NMR spectroscopy serves as a sensitive probe of spin state for paramagnetic heme complexes.^{12,13} Pyrrole-*H* signal of high-spin iron(III) *meso*-tetraarylporphyrin typically appear downfield at ~ 80 ppm. As the iron moves towards the porphyrin mean plane in

Figure 4. Out-of-plane displacements (in units of $0.01 \text{ \AA}$) of the porphyrin core atoms of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ from the mean plane of the C_{20}N_4 porphyrinato core. The horizontal axis shows the bond connectivity between atoms.

Figure 5. ^1H NMR spectra of (a) $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and (b) $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ in CDCl_3 at 295 K.

spin-admixed complexes, pyrrole protons show upfield shift relative to those of the high-spin one. The differences in isotropic shifts between high-spin and spin-admixed complexes can be ascribed to decreased σ -contact shift contribution accompanying partial depopulation of the $d_{(x^2-y^2)}$ iron orbital.¹²

Several factors control the spin states of iron(III) porphyrin complex. Among these, the number and nature of axial ligands are the most important factors.^{12,13} While most of the anionic ligands such as halides and hydroxide lead to the formation of the complexes with high-spin ($S = 5/2$) state, extremely weak ligands such as ClO_4^- give invariably the admixed ($S = 3/2, 5/2$) spin state, as also observed here.

3.3 EPR

The EPR spectral measurements are carried out at 120 K in solution. The spectra are axially symmetric with $g_{\perp} = 5.95$ and $g_{\parallel} = 1.99$ for $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and $g_{\perp} = 5.68$ and $g_{\parallel} = 2.00$ for $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ in dichloromethane. The representative spectra are shown in figure 6. These results are suggestive of high-spin $\text{Fe}(\text{III})$ ($S=5/2$) nature of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and admixed spin state of iron in $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ in solution.

Figure 7 shows the spectrum obtained from $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ in dichloromethane at 120 K. The spectra are axially symmetric with $g_{\perp} = 2.06$ and $g_{\parallel} = 2.21$ for $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ in dichloromethane indicating of low-spin

Figure 6. X-band EPR spectra of (a) $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and (b) $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ in CH_2Cl_2 at 120 K.

Figure 7. X-band EPR spectra of complex $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ in CH_2Cl_2 at 120 K.

($S = 1/2$) state of $\text{Cu}(\text{II})$ which is similar with other Cu^{II} -porphyrins known in the literature.¹⁴

3.4 Electrochemistry

Electrochemistry provides some information on the π -conjugated porphyrin systems. Cyclic voltammetry

were performed at 295 K under N_2 in CH_2Cl_2 using 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAH) as the supporting electrolyte. It has been found that within the solvent electrochemical window, all observed redox processes in the target porphyrins exhibited quasi-reversible behaviour. Also, ferrocene-based oxidation was observed between porphyrin-centered oxidation and reduction waves in all the cases.

Electrochemical properties of $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ and its metal complexes $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ in dichloromethane have been thoroughly investigated. Figure 8 displays the cyclic voltammetry of the complexes while their redox potentials are given

Figure 8. Cyclic voltammogram (selected portions) of (a) $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$, (b) $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and (c) $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ in CH_2Cl_2 (scan rate 100 mV/s) with 0.1 tetrabutylammonium hexa-fluorophosphate (TBAH) as supporting electrolyte at 295 K. The reference electrode was Ag/AgCl .

in the experimental section. The ferrocenyl groups of $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ undergo two quasi-reversible one-electron transfer processes at 0.51 and 0.74 V, respectively. The values of half-wave oxidation potentials indicate that the ferrocenyl groups in the compounds are slightly more difficult to oxidize than that of free ferrocene. The separation of the two ferrocene oxidation waves in $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ indicative of strong coupling of the ferrocene moieties. However, metallation of the diferrocenyl porphyrins also affects the oxidation potential of ferrocenyl groups. Cyclic voltammetry of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ displays a single two-electron oxidative response at 0.44 V related to the oxidation of two ferrocene moieties which is further confirmed using spectro-electrochemistry (*vide infra*). The relatively easier ferrocenyl oxidation might be considered as a consequence of the great electron releasing ability of the porphyrin ring upon metallation with Cu(II). Similar to $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$, the cyclic voltammetry of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ also displays a single quasi-reversible two-electron oxidations at 0.72 V which indicates that two ferrocenyl groups are electrochemically separated. Here the higher oxidation state of Fe(III) is observed to reduce the electron releasing tendency of the porphyrin ring and thus make the ferrocene oxidation difficult. The porphyrin core, however, lacks substituents at the β -pyrrolic positions, and the ferrocenyl moieties are therefore free to rotate. It would be interesting to note that cyclic voltammetric response of 5,15-diferrocenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (H_2DFTTP) and its metal complex $\text{M}(\text{DFTTP})$ [M: Mn(III)Cl, Ni(II) and Zn(II)] displayed two 1e-oxidative response of the ferrocene moieties indicative of strong metal-metal coupling between two ferrocene; however, the ferrocene moieties have been observed to be *syn* with respect to each other while porphyrin ring was highly deformed.^{6,7}

3.5 Spectro-electrochemistry

Spectroelectrochemical studies are very much informative about the coupling between ferrocene units and have been used to obtain spectroscopic signatures of oxidized species originating from the neutral compounds. The ferrocenyl groups of *trans*- $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ displays two one-electron oxidation process at 0.51 and 0.74 V, respectively. The successive removal of individual electrons from the ferrocene substituents, however, confirms the long-distance metal-metal coupling in the *trans*- $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$, which was further supported by the spectroelectrochemical and chemical oxidation

experiments.^{6a} The formation of the mixed-valence *trans*- $[\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}]^+$ species was accompanied by a red-shift in the Soret band from 424 to 448 nm, a loss of Q-band intensity at 623 nm and 697 nm, the appearance of the 650 nm band, and a characteristic IVCT band observed at 854 nm which supports the elimination of an electron from the ferrocene moiety.^{6a} The second one-electron oxidation of *trans*- $[\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}]^+$, however, resulted in the disappearance of the IVCT band, along with the appearance of a band at 708 nm, and the shift of the Soret band to 470 nm.^{6a}

Bulk coulometric oxidations of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ were performed in dichloromethane at applied potentials of 0.65 and 0.92 V for two electron oxidations of each complex, respectively, using 0.1M TBAH as supporting electrolyte under nitrogen and the progress of the reactions are monitored by UV-visible spectroscopy which are shown in figure 9. Similar observations have also been obtained during the chemical oxidation. During 2e-oxidations of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ (figure 9A), the Soret band at 415 nm and a Q-band at 652 nm decreases in intensity and revealed a new band at 555 nm, characteristic of the charge-transfer band observed in ferrocenium cations. No intervalence charge transfer (IVCT) band, indicative of mixed-valence compounds are observed during

Figure 9. UV-visible spectral change (in dichloromethane) upon 2e-oxidation of (a) $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ and (b) $\text{Fe}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ at 295 K; arrows indicate increase or decrease of band intensity.

the oxidation process. Similarly, for $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$, the Soret band has blue-shifted from 421 to 414 nm with a loss in intensity. Two new Q-bands at 454 and 635 nm have also appeared during the oxidation process (figure 9b).

Step-wise oxidations of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ were also performed using silver triflate (AgOTf) as chemical oxidants under nitrogen and have been monitored using UV-visible spectroscopy. However, the observations are very similar with the results obtained in spectrochemical studies shown above. The present study suggests that two ferrocenyl moieties are electrochemically separated in the $\text{Fe}(\text{III})$ and $\text{Cu}(\text{II})$ complexes and thus demonstrates the importance of metal ion on the long-range electronic communication for such types of complexes.

4. Conclusions

$\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$, $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$ and $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ have been synthesized and characterized by UV-vis, ^1H NMR, EPR and single crystal X-ray diffraction study for $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$. X-ray structure of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ shows two ferrocene moieties in *anti* conformation with respect to each other for the first time, which is in contrast to all other diferrocenyl porphyrin where the ferrocenyl unit is *syn*. Phenyl substituents were found to be nearly perpendicular (75.3°) to the porphyrin core while the Cp ring produces a torsion angle of 38° with the porphyrin plane of the molecule. It is, however, interesting to note that the porphyrin ring distortion is much less (*wave*-distorted) in $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ when compared to the similar complexes reported in the literature. EPR and ^1H NMR studies confirm the high-spin and admixed-spin of iron in $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ and $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{ClO}_4$, respectively.

The ferrocenyl groups of $\text{H}_2\text{Fc}_2\text{Ph}_2\text{P}$ undergo two quasi-reversible one-electron transfer processes at 0.51 and 0.74 V, respectively. However, the ferrocenyl groups of $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$ are more easily oxidized via a single two-electron quasi-reversible process (at 0.44 V) than ferrocene. The easier ferrocenyl oxidation might be considered as a consequence of the great electron releasing ability of the porphyrin ring. Also, the ferrocene subunits of $\text{Fe}^{\text{III}}(\text{Fc}_2\text{Ph}_2\text{P})\text{Cl}$ are oxidized by a single two-electron transfer process at 0.72 V, indicating that two ferrocenyl groups are electrochemically separated. The higher oxidation state of $\text{Fe}(\text{III})$ reduces the electron releasing tendency of the porphyrin ring and thus make the ferrocene oxidation difficult. Spectro-electrochemical study thus revealed ferrocene-based two-electron quasi-reversible oxidation of the

complexes reported here with no observable coupling of the ferrocene moieties. The porphyrin, however, lacks substituents at the β -pyrrolic positions, and the ferrocenyl moieties are therefore free to rotate. The observed electrochemical analyses thus demonstrate that the oxidation of the ferrocene subunit is strongly affected by porphyrin ring as well as the central metal through extended π -conjugation.

Supplementary Information

CCDC-976062 contain the X-ray crystallographic details in CIF format for $\text{Cu}^{\text{II}}(\text{Fc}_2\text{Ph}_2\text{P})$. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or [from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

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