

Synthesis, Photophysical and Electrochemical Studies on Peripherally Ruthenated Tetraphenylporphyrin

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Ruthenium(II) complexes of 5-(4-hydroxyphenyl)-10,15,20-*tris*-(4-methylphenyl)porphyrin and 5,10,15,20-*tetrakis*-(4-hydroxyphenyl)porphyrin have been synthesized in basic medium and spectroscopically characterized. The complexes show broad bands in the visible region due to overlap of porphyrin transitions with the metal-to-ligand charge transfer (MLCT) transitions arising from *cis*-Ru(bipy)₂Cl₂. ¹H NMR indicates π -electron interactions between the porphyrin ring and bipyridyl rings. The complexes are emissive both at room temperature and at 77 K with two independent emissions at 77 K, one from the excited state of the porphyrin moiety at 650 and 720 nm and the other from the excited state of the ruthenium moiety at 700 nm. No excited state intramolecular energy transfer reactions have been detected. However the quantum yield of the complexes is reduced due to heavy atom effect. Time resolved fluorescence decay analyses show dual life time at 1.5 and 7.7 ns in dichloromethane. The shorter life time is assigned to singlet-excited state of ruthenium and longer life time to porphyrin singlet excited state. Electrochemical analysis of these species in dichloromethane exhibits three anodic peaks at around 0.68, 0.98 and 1.42 V *versus* SCE, analogous to the Ru^{3+/2+} couple and two successive one-electron oxidation processes on the porphyrin ring, respectively. On the other hand, cathodic potentials at around -0.8, -1.4 and -1.54 V *versus* SCE, with first two peaks corresponding to two successive reduction taking place at the porphyrin ring and the third peak corresponding to reduction of bipyridyl unit. All spectroscopic studies reveal perturbation on the electronic levels of both porphyrin ring and ruthenium chromophore.

Keywords: Ruthenated, Porphyrin, Perturbation, Emission, Life time, Electrochemistry.

INTRODUCTION

Supramolecular chemistry, also known as “chemistry outside a molecule” is the heart of the development of chemistry of complex systems, molecular devices, ensembles and nanochemistry [1]. This is the chemistry where molecules are able to self-organize, self-assemble and self-control into systems and the components are often analogues to biological molecules. Metalloporphyrins and metallophthalocyanines are remarkable precursors in supramolecular chemistry and the rapid development of this chemistry led to assemblies possessing various architectures and properties (photo-, electro- and catalytic properties and others). Metalloporphyrins are one of the foundations on which the existence of life is based and major biochemical, enzymatic and photochemical functions depend on the special properties of a tetrapyrrolic macrocycle. However, metalloporphyrins are the only molecules as key elements that require assembly with other elements to form the supramolecular structure.

In natural systems, polypeptides define a given structural organization and hold all the moieties together. Such complex

natural devices are not accessible by direct chemical synthesis so far, but their modeling, using simplified designs, has been actively exploited during the last decades. The rapid development of this new area of chemistry has promoted the understanding of the concepts of design and strategies of self-assembly of structures based on intermolecular interactions to result in natural and synthetic supramolecular complexes of metalloporphyrins. Synthetic metalloporphyrin complexes are often used as analogues of natural systems found in photosynthesis, oxygen carriers and catalysts [2,3]. These studies lead to the discovery of new applications in photodynamic therapy, information storage devices or photoelectrical devices that transform energy in both directions (photocells and lightemitting diodes) [4-6]. An application of increasing importance is the use of metalloporphyrins as receptors, exploiting their ability to selectively form complexes which can sharply change the spectral properties [7,8]. Macrocyclic porphyrin oligomers with cavities suitable for selective molecular recognition [9] and homogeneous catalysis [10] are also known. Most examples deal with porphyrins bearing *meso*-pyridyl groups, since the easy coordination ability of pyridine group

allows large assemblies to be built. In recent times, the physico-chemical properties of tetra-ruthenated metalloporphyrins have been investigated. Its synthesis and photophysical properties of zinc porphyrin and cobalt porphyrin [11-14], electrocatalytic [15-19], analytical application [20] and DNA interactions [21,22] have been studied. The above mentioned results of peripherally ruthenated porphyrins have one common aspect, *i.e.*, all compounds are based on *meso*-tetrapyrrolyl metalloporphyrins. However, three features have not been studied so far, namely, (i) how ruthenium ion can coordinate to other donor atoms at the *meso* position, *e.g.* hydroxy group and what effect it will show on the photophysics, (ii) what will be the effect if ruthenium is coordinated at the periphery of a free base porphyrin instead of a metalloporphyrin, (iii) the above mentioned peripheral compounds indicates that intramolecular energy transfer takes place from $^3\text{MLCT}^*$ of ruthenium(II) to $^3\text{MP}^*$ [23,24]. However no one has studied whether a reverse energy transfer is possible or not by lifting the energy of porphyrin either equal to or above the energy levels of ruthenium chromophore.

Keeping these skin texture, we synthesized *meso* ruthenated porphyrins, namely, symmetrically substituted tetra-ruthenium porphyrin from *meso*-5,10,15,20-tetrakis-(4-hydroxyphenyl)-porphyrin and mono substituted ruthenium porphyrin from *meso*-5-(4-hydroxyphenyl)-10,15,20-tris-(4-methylphenyl)-porphyrin. This type of molecule is particularly interesting, since it coalesce the characteristics and properties of porphyrin and ruthenium bipyridyl species, allowing the preparation of new macromolecular complex. It is to be noted that synthesis of these complexes using hydroxy as one of the coordinating ligand from the porphyrin makes the ruthenium chromophore moiety greatly affected by the porphyrin unit due to greater flexibility of the bent Ru-O bond with respect to the *meso* phenyl group. This makes the ruthenium chromophore disposed spatially closer towards the porphyrin ring unlike that of Anson [16-19], Toma and Araki [21], *etc.* Herein we report the synthesis, spectroscopic and electrochemical properties of the complexes. From the literature survey, we believe that this is the first report on singlet life time data of such type of peripherally ruthenated free base porphyrin monomers and also our observation of dual emission is *hitherto* unknown in these types of complexes.

EXPERIMENTAL

4-Methoxy benzaldehyde, pyrrole and propionic acid were bought from SD fine, India, were used after purification [25]. All the solvents used were analytical grade and were dried further whenever required. The precursor ligands 5,10,15,20-tetrakis-(4-methoxyphenyl)porphyrin (**A**) [26], 5-(4-methoxyphenyl)-10,15,20-tris-(4-methylphenyl)porphyrin (**B**) [27], 5,10,15,20-tetrakis-(4-hydroxyphenyl)porphyrin (**I**) [28], 5-(4-hydroxyphenyl)-10,15,20-tris-(4-methylphenyl)porphyrin (**II**) [29] and *cis*-dichloro-*bis*-bipyridylruthenium(II) (**III**) [30] were synthesized as described in the literature. These ligands have been characterized from ^1H NMR technique and the data are tabulated in Table-1.

5,10,15,20-Tetrakis(4-(hydroxo-chloro-*bis*-bipyridyl-ruthenium(II))phenoxo) porphyrin [IV]: Synthesis of the complex **IV** involves two steps. Firstly, the precursor, **I** (0.34

g, 0.5 mmol) was refluxed with anhydrous potassium carbonate (0.3 g, 2.2 mmol) in 75 mL of dry dimethyl formamide under nitrogen atmosphere for 24 h. Secondly, the metal precursor, **III** (1.17 g, 2.2 mol) was added under nitrogen atmosphere and refluxed for further 24 h. The completion of reaction was monitored using TLC. The R_f value was found to be 0.5 in pure chloroform on an alumina coated plate. The volume of the resultant solution was reduced to one fourth under vacuum and then extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified using column chromatography on basic alumina, initially with chloroform and followed by 2 % methanol in chloroform as eluant to afford 0.150 g (11.5 %) of **IV**. FAB-MS, m/z : calculated for $\text{C}_{124}\text{H}_{106}\text{N}_{20}\text{O}_{12}\text{Ru}_4\text{Cl}_4$: 2612; found: 2010, $[\text{M}-\text{C}_{20}\text{H}_{38}\text{N}_4\text{O}_9\text{RuCl}]^+$. Anal. Calcd for $\text{C}_{124}\text{H}_{106}\text{N}_{20}\text{O}_{12}\text{Ru}_4\text{Cl}_4$: C, 60.3; H, 3.7; N, 11.4 %; found: C, 60.0; H, 3.4, N, 11.8 %.

[5((4(Hydroxo-chloro-*bis*-bipyridyl-ruthenium(II))phenoxo)-10,15,20-tri(4-methylphenyl)]porphyrin [V]: Compound **V** was prepared by following a similar procedure described for **IV** except that **II** (0.35 g, 0.5 mmol) was used instead of **I**. Ratios of anhydrous potassium carbonate (0.085 g, 0.6 mmol) and **III** (0.312 g, 0.6 mmol) were reduced to one fourth instead of the ratio mentioned in **IV**. The R_f value on an alumina-coated plate was found to be 0.45 in 7:3 hexane and chloroform mixture. Pure **V** was obtained by column chromatography on basic alumina using hexane and chloroform as eluant in the ratio of 4:6. Yield 0.184 g (41.8 %). FAB-MS, m/z : calculated for $\text{C}_{67}\text{H}_{53}\text{N}_8\text{O}_3\text{RuCl}$: 1153; found: 881, $[\text{M}-\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_2]^+$. Anal. calcd. for $\text{C}_{67}\text{H}_{53}\text{N}_8\text{O}_3\text{RuCl}$: C, 72.0; H, 4.3; N, 10.0 %; found: C, 71.8; H, 4.1; N, 9.7 %.

Spectroscopic studies: Electronic absorption spectra were obtained with Ocean optics optical fiber (400 μm) spectrophotometer SD1000 using 1 cm quartz cell in dichloromethane. IR spectra were recorded on ABB Bomem MB 104 spectrometer using KBr disks. Elemental (C, H and N) analysis was performed with Heraeus Rapid analyzer. ^1H NMR spectra were recorded on AMX-400 NMR spectrometer in $\text{CDCl}_3/\text{DMSO}$, using TMS as the internal standard. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/Data system using Argon/Xenon (6 kV, 10mA) as the FAB gas.

Fluorescence studies: Fluorescence spectra of the ligands and their ruthenium(II) complexes were recorded in dichloromethane, acetone, ethanol, methanol and acetonitrile using Hitachi F4500 spectrofluorimeter fitted with R928 photomultiplier tube employing right angle detection mode. Fluorescence quantum yields (ϕ_f) were measured by optically dilute method [31] using *meso*-5,10,15,20-tetraphenyl porphyrin as standard ($\phi_f = 0.13$ in benzene) [32]. Spectra at 77 K were obtained by cooling the samples in a quartz Dewar flask filled with liquid nitrogen. The fluorescence decay measurements of were carried out using the time correlated single photon counting technique (TCSPC) with micro channel plate photomultiplier tube (MCP-PMT) as detector and picoseconds laser as the excitation source. The measured fluorescence decay data were analyzed for various fluorescence kinetic parameters (life time, amplitudes *etc.*) using the software provided by IBH (DAS-6) which is based on reconvolution technique using iterative non-linear

TABLE-1
¹H NMR (300/400 MHz) INFORMATION OF LIGANDS AND COMPLEXES WITH TMS AS INTERNAL REFERENCE

Complex	Porphyrins			2,2'-bipyridyl protons (ppm)
	N-H protons (ppm)	β-Protons (ppm)	meso aryl groups' protons (ppm)	
I (DMSO- <i>d</i> ₆)	-2.88, 2H	8.86, 8H	H _{2,6} = 8.0 (8H, <i>J</i> _{2,3} = 8.4 Hz) H _{3,5} = 7.21 (8H, <i>J</i> _{2,3} = 8.4 Hz) H _{4-OH} = 9.94, 4H	
II (CDCl ₃)	-2.77, 2H	8.85, 8H	H _{2,6,2',6'} = 8.10-8.04, 8H H _{3,5} = 7.19 (2H, <i>J</i> _{2,3} = 8.4 Hz) H _{3',5'} = 7.55 (6H, <i>J</i> _{2',3'} = 8.1 Hz) H _{4-OH} = 9.94, 1H H _{4'-CH3} = 2.7, 9H	
III (CDCl ₃)				H _{A6B6} = 8.17, 2H H _{A6'B6'} = 7.6, 2H H _{A5B5} = 7.92-7.85, 2H H _{A5'B5'} = 7.51-7.45, 2H H _{A4B4} = 7.62-7.58, 2H H _{A4'B4'} = 7.31-7.23, 2H H _{A3B3} = 8.13, 2H H _{A3'B3'} = 8.05, 2H H ₂ O = 6.9-7.0, 4H
IV (CDCl ₃)	1.26, 2H	7.79, 8H	H _{2,6} = 8.18, (8H, <i>J</i> _{2,3} = 4.5 Hz) H _{3,5} = 6.75, (8H, <i>J</i> _{2,3} = 4.5 Hz)	H _{A6B6} = 8.65, (8H, <i>J</i> = 8.1 Hz) H _{A3B3} = 8.57, (8H, <i>J</i> = 7.5 Hz) H _{B6'} = 8.39, (4H, <i>J</i> = 8.1 Hz) H _{A4B4} = 8.35-8.31, 8H H _{B5'} & H _{B4'} = 7.88-7.68, 8H H _{A6'} = 7.65, (4H, <i>J</i> = 5.4 Hz) H _{A3'} & H _{A4'} = 7.24-7.13, 8H H _{A5'} = 6.82-6.77, 4H H _{B3'} = 7.5, 4H H ₂ O = 7.1-7.0, 16H
V (CDCl ₃)	0.87, 2H	7.65-7.8, 8H	H _{2,6} = 8.18, (2H, <i>J</i> _{2,3} = 4.44 Hz) H _{3,5} = 6.8, (2H, <i>J</i> _{2,3} = 4.68 Hz) H _{2',6'} = 8.0, (6H, <i>J</i> _{2',3'} = 5.28 Hz) H _{3',5'} = 7.5 (6H, <i>J</i> _{2',3'} = 5.48 Hz) H _{4'-CH3} = 2.2, 9H	H _{A6B6} = 8.9, (2H, <i>J</i> = 8.4Hz) H _{A3B3} = 8.82, (2H, <i>J</i> = 7.92) H _{B6'} = 8.8, (1H, <i>J</i> = 8.0 Hz) H _{A4B4} = 8.39-8.42, 2H H _{A5B5} = 8.10-8.14, 2H H _{B4'} & H _{B5'} = 7.91-7.7, 2H H _{A6'} = 7.64, (1H, <i>J</i> = 5.4) H _{B3'} = 7.49-7.46, 2H H _{A4'} & H _{A3'} = 7.25-7.13, 2H H _{A5'} = 6.89-6.78, 1H H ₂ O = 7.1-7.0, 4H

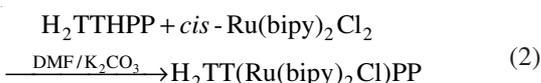
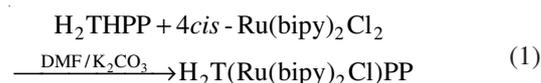
least square methods. The reconvolution is preceded by the series of iterations until a Chi-Square is reduced. The quality of fit is normally identified by the reduced χ^2 , weighted residual and the autocorrelation function of the residuals. The fluorescence decay measurements were carried out using various solvents such as acetone, acetonitrile, methanol, ethanol and dichloromethane.

Electrochemistry: All electrochemical experiments were performed in Ecochemie AUTOLAB PGSTAT 12 using conventional three-electrode setup with saturated calomel electrode as reference, 2 mm diameter platinum disc as working and platinum rod as auxiliary electrodes. Generally all the cyclic voltammogram were performed with scan rate 50 mV/s in dichloromethane/acetonitrile solvent based on the solubility of the substance. For recording square wave voltammogram a constant frequency of 8 Hz with step potential of 4 mV and pulse amplitude of 10 mV was employed.

RESULTS AND DISCUSSION

Synthesis: Reactions 1 and 2 shows the synthetic strategy adopted for the synthesis of ruthenium complexes with 1:4 and 1:1 molar ratios of freebase porphyrin and Ru(bipy)₂Cl₂.

The yield is found to be moderate. The complexes **IV** and **V** are freely soluble in dichloromethane and other low polarity solvents; unlike the free base porphyrin **I/II** and the solution of these complexes are found to be stable in the atmosphere. However, solvation of the chloro group is found to occur rapidly in polar solvents. The space-filling model suggests the possibility of atropisomers, arising out of the disposition of the bipyridyl ring with respect to porphyrin plane. However, we did not attempt to separate the atropisomers. We also believe that all the isomers would show similar spectral properties.



FAB mass analysis first reveals the presence of more than one ruthenium unit in the complex **IV** and one unit in **V**. In complex **IV**, the adduct peak due to loss of [O-Ru(bipy)₂Cl]⁻ fragment from the parent complex is detected as [M+6]⁺ peak at 2010. This observation of [M+6] peak at 2010, strongly

suggests the presence of at least three chlorine atoms and the assignment of loss of one ruthenium complex from **IV** is from the other spectral evidences. Probably, the molecular ion peak is so weak, that escaped notice [33].

Similarly, the FAB mass investigation of complex **V** also resulted only in adduct peak and no molecular ion peak is detected. The adduct peak due to loss of one of the 2,2'-bipyridyl and a pyridyl ring from $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ segment is found at 881. Also loss of remaining pyridyl ring along with chlorine atom and ruthenium resulted in an adduct peak at 666 ion peak.

^1H NMR spectra: The ^1H NMR spectrum of **I** and **II** clearly reveals the resonances characteristic of all the protons in the compound and all the values are in line with the earlier studies [34]. *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ showed characteristic peaks corresponding to various protons in the range of 7 to 10 ppm in CDCl_3 solvent.

^1H NMR of **IV** and **V** in CDCl_3 is reproduced in Figs. 1 and 2, respectively and the resonance positions of various protons are given in Table-1. The notable features of the spectra are (i) shift in the resonance positions of pyrrole protons due to variation in the number of ruthenium moiety coordinated. Thus an upfield shift in the resonances of β -pyrrole protons from 8.8 to 8 ppm in **IV** and to 7.7 ppm in **V**. Also the N-H protons shifts from -2.8 to 1.26 ppm in **IV** and to 0.87 ppm in **V**. These change in the resonance positions clearly indicates interaction of the electronic cloud of bipyridyl present in the $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ fragment with the π -cloud of porphyrin. This also suggest that one of the bipyridyl rings coordinated to ruthenium may be perpendicular to porphyrin ring, so that the ring current of the pyridyl ring is parallel but opposite to the direction of porphyrin ring current. (ii) The *meso*-phenyl protons ($\text{H}_{3,5}$) also shows an upfield shift due to the increased

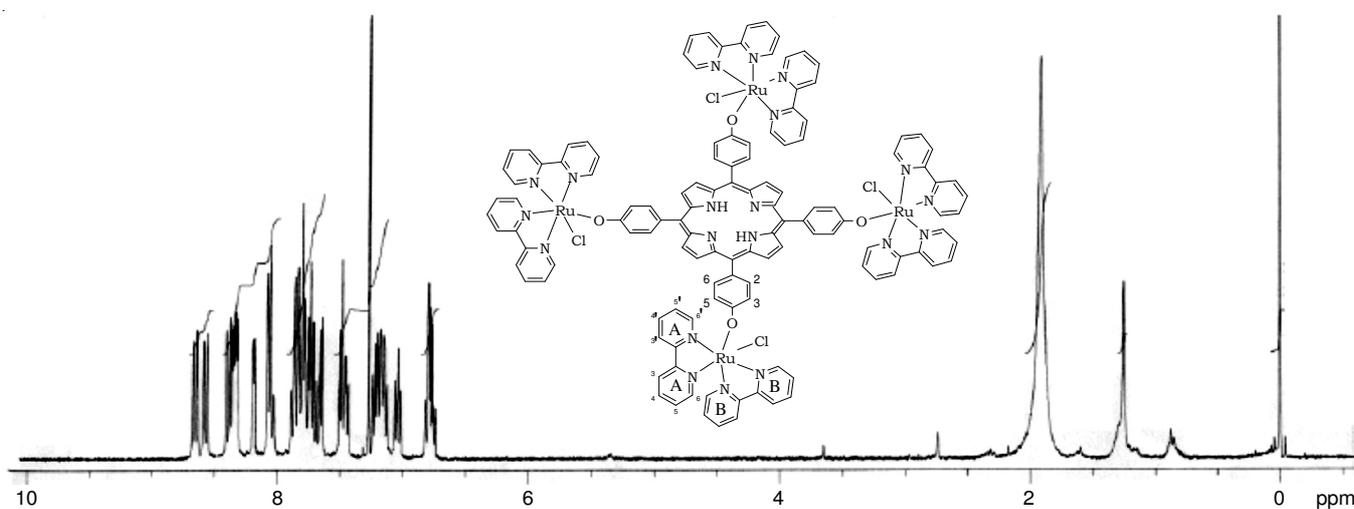


Fig. 1. ^1H NMR (300 MHz, CDCl_3) spectrum of **IV**

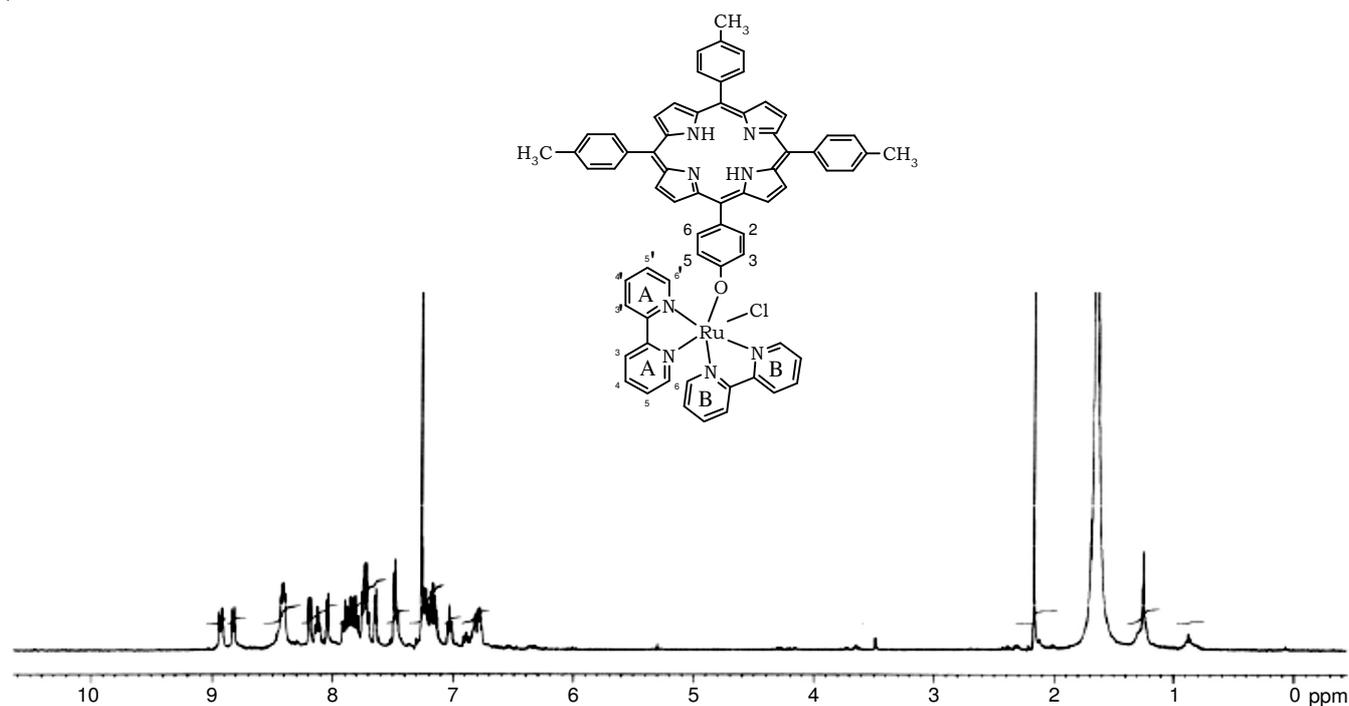


Fig. 2. ^1H NMR (400 MHz, CDCl_3) spectrum of **V**

electron density at 3 and 5 positions, arising as a result of ruthenium complex coordinated at the 4 position of the phenyl ring which facilitate back donation to the phenoxo group [35]. This is further confirmed in the electrochemical behaviour (see later). (iii) Some of the bipyridyl proton is shifted to upfield and some of them to downfield in comparison with the precursor **III**. This is believed to occur due to shielding and deshielding of these bipyridyl protons by the porphyrin π -cloud. Among the upfield shifted protons of the two-pyridyl rings of each bipyridyl show small difference in resonance positions. These variations arise due to the presence of two different electronegative atoms, oxygen and chlorine *trans* to two bipyridyl rings. The pyridyl protons, which are *trans* to oxygen atom, are more downfield shifted in comparison with those *trans* to chloride ion. The shifts in the resonance positions of the various pyridyl protons clearly justify the assumption that one of the bipyridyl rings is perpendicular to the porphyrin ring. The peaks around 7.1 to 7.0 appear from coordinated water [36]. This is further confirmed through D₂O exchange (takes about 90 min for complete disappearance of the peak in CDCl₃). Also the peak disappears in DMSO-*d*₆ due to DMSO coordination.

Absorption spectra: The de-convoluted absorption spectrum of **IV** and **V** in dichloromethane is shown in Fig. 3. The wavelengths of the absorption bands of all the complexes investigated are shown Table-2. The absorption spectrum of the complex **IV** and **V** shows broadened features both in Soret and Q band regions of porphyrins, due to overlap of absorption characteristic of a porphyrin and *cis*-Ru(bipy)₂Cl₂ units. The smeared peaks have been de-convoluted and the absorption spectra of the complexes, **IV** or **V**, are dominated by strong ligand-centered π - π^* transitions at around 290 and 350 nm on *cis*-Ru(bipy)₂Cl₂. The extinction coefficients of these transitions, π - π^* , in **IV** are found to be four times and are equal to in **V** than in *cis*-Ru(bipy)₂Cl₂. The absorption bands arising from ruthenium fragment in the complexes **IV** and **V** are found to show a blue shift in comparison to *cis*-Ru(bipy)₂Cl₂. This indicates that there is increase in energy of the LUMO of

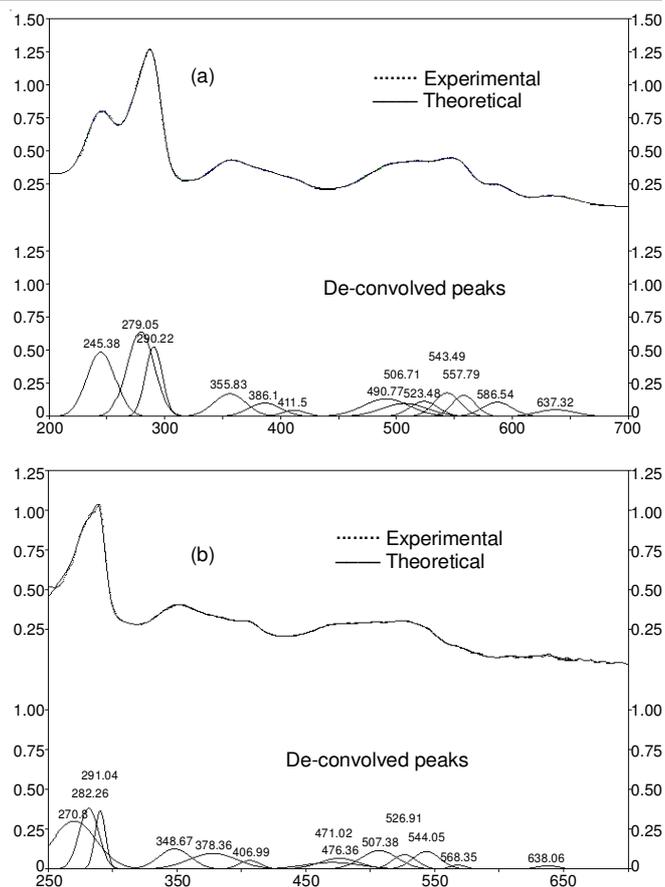


Fig. 3. Electronic absorption spectra of (a) 5,10,15,20-tetrakis((4-hydroxy-chloro-bis-bipyridyl-ruthenium(II))phenyl)porphyrin; (b) 5-((4-hydroxy-chloro-bis-bipyridyl-ruthenium(II))phenyl),10,15,20-tri(tolyl)porphyrin in CH₂Cl₂ at 300 K

ruthenium fragment causing MLCT bands to occur at higher energies.

Emission spectra: Room temperature fluorescence study on ruthenated porphyrins, namely, **IV** and **V**, in solvents such as dichloromethane, acetonitrile, methanol, ethanol and acetone

TABLE-2
ELECTRONIC AND FLUORESCENCE, STEADY STATE AND LIFETIME, DATA OF FREE BASE PORPHYRIN, RUTHENIUM CHROMOPHORE AND *meso* MONO AND *meso* TETRA RUTHENATED PORPHYRIN COMPLEXES

Complex	Absorption maxima ^{1,2} (nm)					Fluorescence data		
						Emission ³	τ ns (A %)	ϕ_f ⁴
I (CH ₃ OH)	642	584	546	508	410	658, 721	8.58, (100)	0.083
	<i>3.62</i>	<i>3.65</i>	<i>3.80</i>	<i>4.17</i>	<i>5.64</i>	644		
II (CH ₂ Cl ₂)	632	574	537	500	412	653, 719	8.123, (100)	0.099
	<i>3.61</i>	<i>3.63</i>	<i>3.79</i>	<i>4.18</i>	<i>5.66</i>	642		
III (CH ₂ Cl ₂)	587	558	501	375	290	701	242	
		<i>3.96</i>	<i>3.96</i>	<i>5.23</i>				
IV (CH ₂ Cl ₂)	<u>557</u>	<u>524</u>	<u>491</u>	<u>356</u>	<u>290</u>	657	1.5, (5.2)	0.004
		<i>4.54</i>	<i>4.54</i>	<i>5.81</i>	<i>279</i>	650, 700		
				<i>5.81</i>	<i>411</i>			
				<i>4.14</i>	<i>5.13</i>			
V (CH ₂ Cl ₂)	637	587	543	506	411	651	0.85, (4.87)	0.001
	<i>3.42</i>	<i>3.45</i>	<i>3.70</i>	<i>4.14</i>	<i>5.13</i>	648, 691,		
	<u>577</u>	<u>535</u>	<u>471</u>	<u>351</u>	<u>290</u>	718		
		<i>3.89</i>	<i>3.89</i>	<i>3.89</i>	<i>5.21</i>			
	634	576	535	531	407			
	<i>3.55</i>	<i>3.54</i>	<i>3.69</i>	<i>4.16</i>	<i>5.25</i>			

¹Values underlined represents the transition from ruthenium fragment in the complexes and normal due to porphyrins unit.

²Values in Italics represent the log ϵ in log (dm³ mol⁻¹ cm⁻¹)

³Values in Bold represents the fluorescence emission at 77 K in ethanol

⁴Fluorescence quantum yield are measured with respect to tetraphenylporphyrin ($\phi_f = 0.13$)

resulted in two fluorescence emission peaks at 650 and 720 nm when excited at 420 nm, similar to that of the parent free base porphyrin. However, the normalized intensity is found to be low in comparison with that of **I/II**, which must arise from the effect of $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ coordination. The quantum yields in **IV** and **V** are found to decrease drastically in comparison with the free base porphyrins. Thus the quantum yield of **IV** in dichloromethane is 0.004 while that of **V** is 0.001. The difference in the values of quantum yield between **IV** and **V** reflects the variation in the number of ruthenium coordinated at the terminal. Thus to summarize, the quantum yield of **IV/V** in various solvents is decreased to about ten times than the free base porphyrins. Even though we observe some trend in the quantum yield on the solvent polarity we cannot give much emphasis to the trend, as the quantum yields are quite low. Since no definite solvent polarity dependence can be established in the spectral pattern, the decrease in the quantum yield is more likely due to heavy atom induced spin orbital coupling instead of any sort of intramolecular charge transfer process [36]. The fluorescence excitation spectrum from these two emission peaks resulted in two types of patterns one corresponding to the absorption spectrum of free base porphyrin ($\lambda_{\text{em}} = 650$ nm) and the other with broadened Q-bands ($\lambda_{\text{em}} = 720$ nm).

The fluorescence emission spectrum of **IV** at 77 K in ethanol results in two well-defined emission bands at around 650 and 700 nm when excited at 420 nm (Fig. 4). But, the fluorescence emission spectrum of **V** at 77 K for the excitation at 420 nm results in an emission peaks similar to the room temperature fluorescence emissions but with a prominent shoulder like pattern at around 700 nm. The intensity variation between **IV** and **V** is due to the difference in the number of ruthenium chromophores. Interestingly, the fluorescence excitation spectra at these emissions are found to be different. The fluorescence excitation spectrum from 650 nm emission resembles that of ground state absorption spectrum of the free base porphyrin, whereas, the fluorescence excitation spectrum of 700 nm emission results in an spectrum that resembles the room temperature absorption spectrum and fluorescence excitation spectrum (at 77 K) of *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$. Excitation at 380 nm (absorption band of *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$) resulted in only one emission band

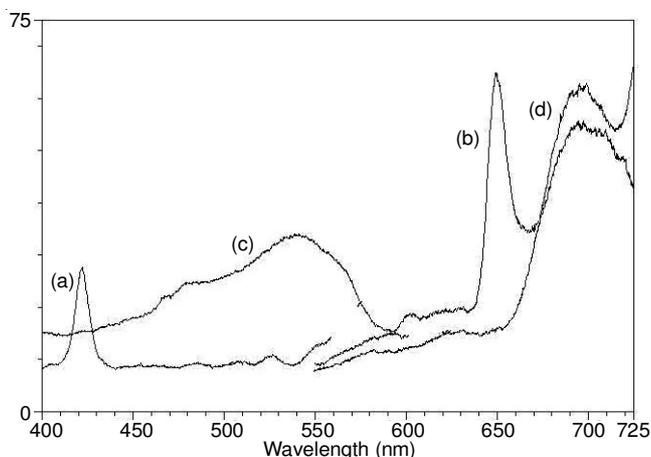


Fig. 4. Fluorescence (a) excitation spectrum of **IV** ($\lambda_{\text{em}} = 650$ nm); (b) emission spectrum of **IV** ($\lambda_{\text{ex}} = 420$ nm); (c) excitation spectrum of **IV** ($\lambda_{\text{em}} = 700$ nm) and (d) emission spectrum of **IV** ($\lambda_{\text{ex}} = 380$ nm) in ethanol at 77 K

at around 700 nm and no emission corresponding to porphyrin is observed for **IV**, however, in **V** we could observe both emissions, 650 and 700 nm, of equal intensities. This intensity discrepancy arises due to lower molar absorptivity of ruthenium chromophore in **V** at 380 nm as compared to **IV** at the same wavelength. Also the excitation spectrum of free base porphyrin, **I**, at 700 nm does not differ from that of 650 nm emission. Since other spectral data rules out the presence of unreacted *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ as impurity, it is clear that the 700 nm emission originates from the excited state of ruthenium group. Excitation at other wavelengths corresponding to $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ group show similar results. All these results suggest that the two emissions are independent of each other suggesting that $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ units do not show any electronic interactions with porphyrin ring. This is quite contrast to the results observed by Araki and Toma [24], where a energy transfer from $^3\text{MLCT}^*$ of Ru(II) to $^3\text{ZnP}^*$ has been observed.

The observation of two different emission properties made us to estimate fluorescence life time measurements through single photon-counting technique. The fluorescence decay of **I** and **II** in acetonitrile shows single exponential decay and the life times are found to be 8.58 and 8.12 ns, respectively. The observed results are in agreement with earlier results [37]. The fluorescence decay of **IV** (Fig. 5e) and **V** (Fig. 5f) in dichloromethane is found to fit to a bi-exponential decay with life times at 1.5, 7.7 ns and 0.85, 7.1 ns with corresponding amplitudes of 5 and 95, respectively. Since all spectroscopic investigation excludes the presence of any impurity, the two life times must originate from the excited states of the complexes.

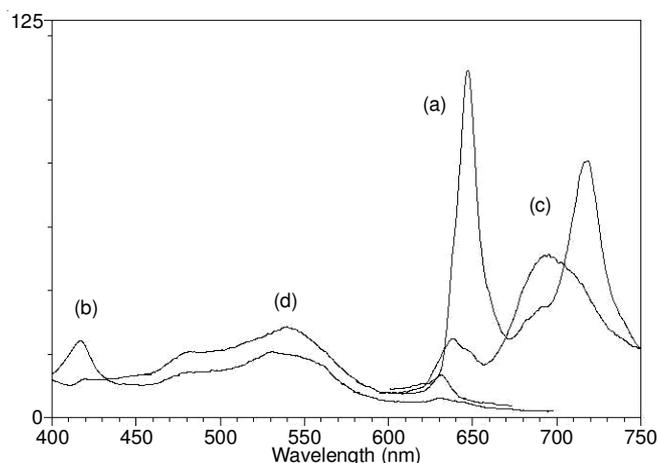


Fig. 5. Fluorescence (a) emission spectrum of **V** ($\lambda_{\text{ex}} = 420$ nm); (b) excitation spectrum of **V** ($\lambda_{\text{em}} = 650$ nm); (c) emission spectrum of **V** ($\lambda_{\text{ex}} = 380$ nm) and (d) excitation spectrum of **V** ($\lambda_{\text{em}} = 700$ nm) in ethanol at 77 K

In addition, bi-exponential decay does not get altered by external addition of *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$. Similar bi-exponential decay is also observed for the emission at 700 nm and at 720 nm. However, 700 nm emission, results in weak emission counts (about 20 %), but shows an increase in the amplitude of the shorter life time without any change in the life time value. This suggests that the shorter life time component has more contribution to the emission at 700 nm. The 720 nm emission characteristic is found to be similar to that of 650 nm emission. In line with the observation of steady state fluorescence emission

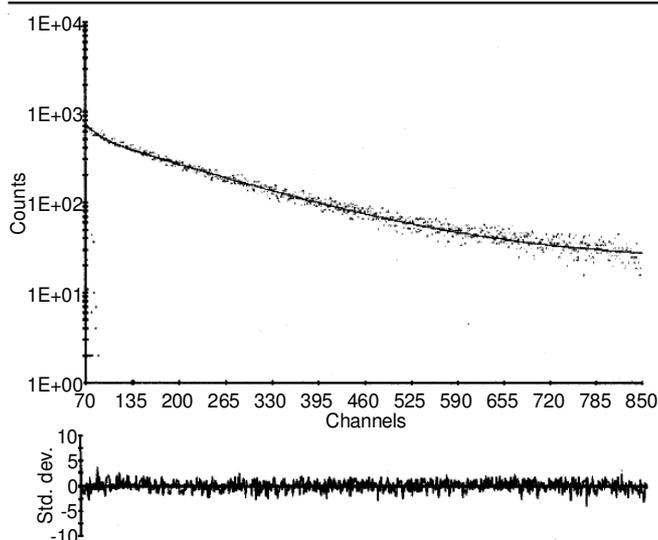


Fig. 5e. Fluorescence decay profile of **IV** in dichloromethane. The solid line represents best fit to $I(t) = A_1 \exp^{-t/\tau_1} + A_2 \exp^{-t/\tau_2}$. $\lambda_{\text{excitation}} = 400$ nm & $\lambda_{\text{emission}} = 650$ nm. $\tau_1 = 1.5$ ns (5.2 %); $\tau_2 = 7.7$ ns (94.8 %)

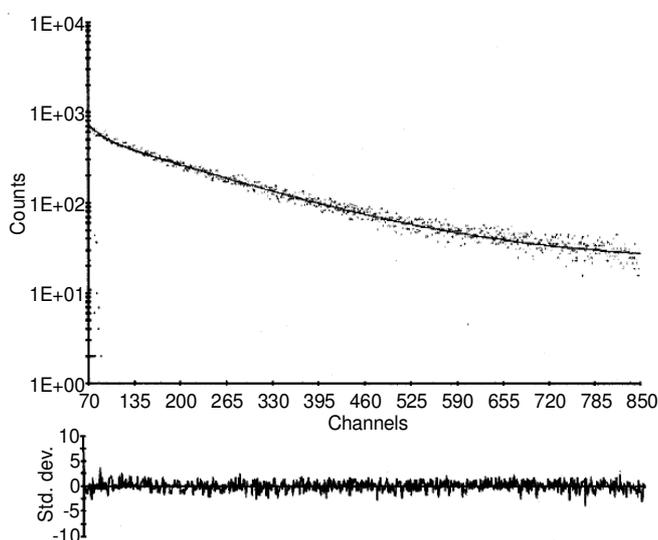


Fig. 5f. Fluorescence decay profile of **V** in dichloromethane. The solid line represents best fit to $I(t) = A_1 \exp^{-t/\tau_1} + A_2 \exp^{-t/\tau_2}$. $\lambda_{\text{excitation}} = 400$ nm & $\lambda_{\text{emission}} = 650$ nm. $\tau_1 = 0.85$ ns (4.87 %); $\tau_2 = 7.1$ ns (95.1 %)

at 77 K, we attribute the shorter life time to $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ unit of **IV** and **V** and the longer life time to the porphyrin emission. Probably due to this short life time, we could not observe distinct emission at room temperature. However, we could not see any definite trend in either life times or amplitudes with solvent polarity. Thus, the decrease in life times of porphyrin group in **IV** and **V** may be attributed to increased non-radiative decay process due to heavy atom coordination.

Electrochemical properties: The cyclic and square wave voltammogram of the complex **IV** in dichloromethane is given in Fig. 6. Thus the three peaks in the potential range of 0 to 1.75 V are attributed to reversible ($i_c/i_a = 0.875$, $\Delta E = 66$ mV) oxidation process of $\text{Ru}^{2+} \rightarrow \text{Ru}^{3+}$ at 0.68 V and two step one electron oxidation of porphyrins ring at 0.985 and 1.421 V. Comparing the current intensity of oxidation of ruthenium centre and porphyrin centre, the former is found to be four times than the latter indicating presence of four ruthenium subunits in the complex. Further coulometry analysis at 0.71 V

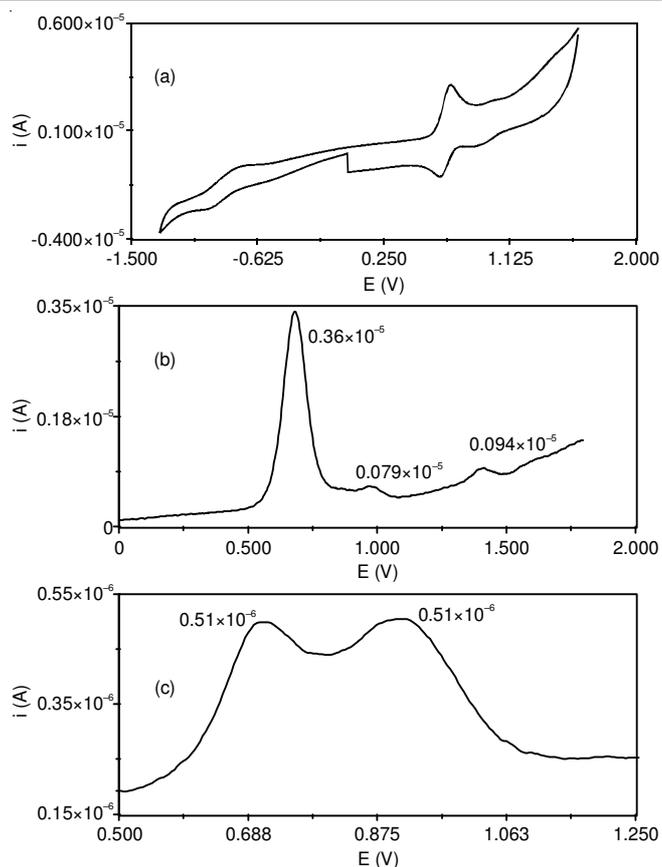


Fig. 6. (a) Cyclic voltammogram of complex **IV**; (b) Square wave voltammogram of **IV** and (c) Square wave voltammogram of **V** measured in 1 mM TBAP in dichloromethane solution at 300 K

confirms the transfer of four equivalents of charges in **IV** and one equivalent in **V**.

The peak potential for the reversible oxidation process of the $\text{Ru}^{3+/2+}$ couple in the ruthenated complexes is 0.68 V (*vs.* SCE), which is more positive than the corresponding value of 0.43 V (*vs.* SCE) obtained for the unsubstituted analog *cis*- $\text{Ru}(\text{bipy})_2\text{Cl}_2$ [38]. This shift is taken as a bench marking for the formation of the ruthenium complex and is attributed to the increased metal to ligand charge transfer after porphyrin coordination. This is also confirmed by intentional addition of *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ to either **IV** or **V**. Any unreacted *cis*- $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ would have shown oxidation at 0.43 V instead of 0.68 V.

The redox potentials are tabulated in the Table-3. On comparing the oxidation potential between the complexes **IV** and **V**, it is observed that the oxidation of ruthenium moiety is slightly difficult in **V** than in **IV**. This variation arises due to difference in the number of metal coordinated to the porphyrin, which in turn affects the planarity and makes porphyrin more electron withdrawing in **V** than in **IV**.

Since, the cyclic voltammetric analysis gave broad peaks we studied the reduction processes taking place in the complexes through square wave voltammetry technique. The voltammetric study of the complexes in the range of 0 to -1.75 V resulted in two peaks at -0.965 V and -1.530 V, corresponding to the reduction processes taking place in the porphyrin unit and the bipyridyl unit of $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ fragment. The coulometric analysis at -1.58 V gave transfer of six equivalents of

TABLE-3
PEAK POTENTIAL FROM SQUARE WAVE VOLTAMMETRIC ANALYSIS AT 300 K, WITH
SCE AS REFERENCE ELECTRODE AND TBAP AS SUPPORTING ELECTROLYTE

S. No.	Complex	Oxidation potential (V)			Reduction potential (V)		
		$\text{Ru}^{2+} \rightleftharpoons \text{Ru}^{3+}$	$\text{P} \rightleftharpoons \text{P}^+$	$\text{P}^+ \rightleftharpoons \text{P}^{2+}$	$\text{P} \rightleftharpoons \text{P}^-$	$\text{P} \rightleftharpoons \text{P}^{2-}$	$\text{bipy} \rightarrow \text{bipy}^-$
1	A	–	0.916	1.113	-1.272	-1.619	–
2	B	–	0.972	1.224	-1.266	-1.628	–
3	I	–	0.743	1.178	-1.260	-1.680	–
4	II	–	0.789	1.151	-1.258	-1.624	–
5	III	0.425	–	–	–	–	-1.500
6	IV	0.680	0.985	1.421	-0.887	-1.387	-1.541
7	V	0.6969	0.923	–	-0.654	-1.495	-1.542

charges. It is known that the bipyridyl of *cis*-[Ru(bipy)₂Cl₂] reduces in the region -1.8 V. This mean that the higher current observed at -1.54 V in the complexes arises from overlapping of bipyridyl reduction and porphyrin's second electron reduction. Thus, de-convoluted square wave voltammogram of the complex, **IV** (Fig. 7), shows two peaks at -1.387 and -1.541 V. The former corresponds to the second electron reduction of porphyrin and the latter corresponds to the reduction of the bipyridyl ligand. Furthermore, the current ratio between -1.387 and -1.541 V peaks confirms coordination of four ruthenium centers in the porphyrin ring. On the other hand, the de-convoluted square wave voltammogram of the complex, **V** (Fig. 8), shows two peaks of equal intensities at -1.495 V and -1.542 V

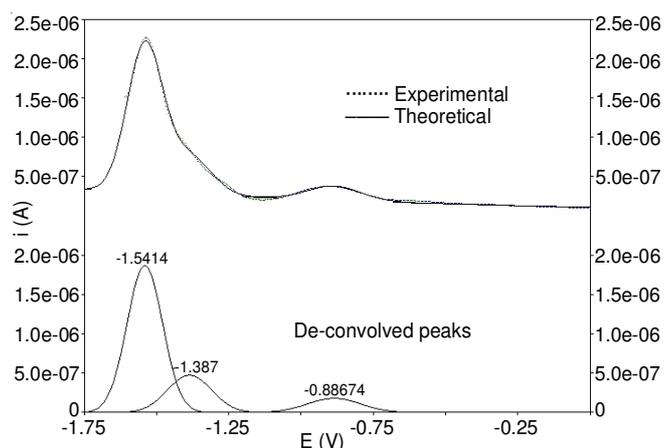


Fig. 7. Square wave voltammogram of complex **IV** (0.1 mM) measured in 1 mM TBAP in dichloromethane solution at 300 K

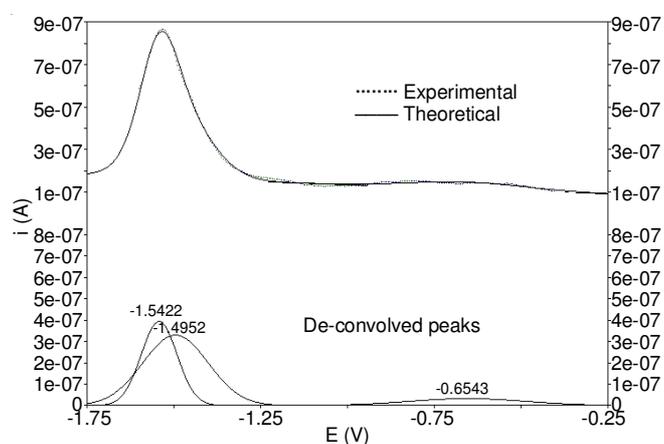
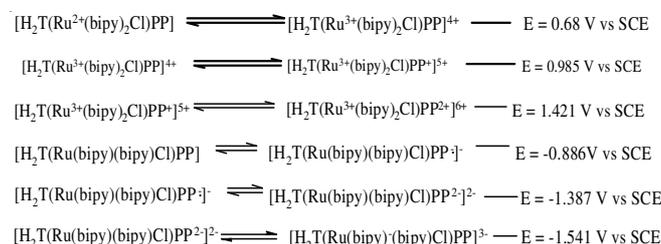


Fig. 8. Square wave voltammogram of complex **V** (0.1 mM) measured in 1 mM TBAP in dichloromethane solution at 300 K

with former corresponding to the second electron reduction of porphyrin and the latter corresponding to the reduction of the bipyridyl ligand. The difference in the intensities between the two complexes at -1.54 V is an indicative of the number of bipyridyl units getting reduced or the number of ruthenium attached to the porphyrins ring.

Thus, when comparing the redox potential of porphyrin ring between the complexes and precursor, it is found that the oxidation is comparatively difficult in the complexes than in the free base porphyrin. On the other hand reduction of the porphyrin ring is easy in the complexes than in the precursor, which is an indicative of the depletion in the electron density in the porphyrin core. It is clear from the Table-3 that the reduction potential of the complexes has shifted towards less negative potential comparing with the free base porphyrin. The electrochemical processes taking place in the complex, **IV**, can be summarized as:



The change in the redox values must occur due to perturbations to HOMO-LUMO energies. We notice a reduction in energy of both HOMO and LUMO, with LUMO showing more stabilization. The stabilization is found to be 0.293 eV for LUMO and 0.196 eV for HOMO in **IV** and in **V** it is 0.393 eV for LUMO and 0.134 eV in HOMO. The larger stabilization energy of LUMO in **V** suggests that distortion is more in unsymmetrical complexes than in symmetrical. One of the reasons for this observation might be occurring due to non-planar distortion of the porphyrin ring, which probably brings the *meso*-phenyl group more in plane with the porphyrin ring than in the corresponding parent free base porphyrin. This in plane distortion of phenyl group would induce increased delocalization of electron towards the porphyrin ring through the phenoxo group and this is also proved by the upfield shift in the β -pyrrole hydrogens in the ¹H NMR spectrum. This delocalization of electron towards the porphyrin ring is also identified in an EPR study on porphyrin substituted with paramagnetic metal ion [31] at the core and at the periphery of the porphyrin ring.

Conclusion

A new class of Ru(II) complexes of the *cis*-Ru(bipy)₂Cl₂ type with phenoxo-porphyrin ligands, (H₂(P)-Ru₄ and H₂(P)-Ru) has been achieved. This resulted in a stable ruthenium oxygen phenolato bridged porphyrin complexes. The electronic spectra shows shift in the absorption, which is due to perturbation of the energy level. The results suggest that the ruthenium orients probably in a perpendicular to the porphyrin plane and also suggest that the *meso*-phenyl group might rotate into the plane of the porphyrin. At room temperature, the fluorescence of the complexes resulted in emission from porphyrin unit alone while at 77 K two emissions one from each chromophore is observed. This is also further confirmed by singlet life time measurement, which resulted in two life times of different amplitudes. The quantum yield measurement resulted in decreased yield than the free base porphyrin. This reduction in quantum yield can be claimed due to heavy atom effect. The electrochemical investigation of the complexes revealed the number of metal coordinated to the porphyrin, which further confirms the formation of the above said complexes. From the various analytical studies we can conclude that these complexes could act as good catalysts for many chemical transformation reactions.

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