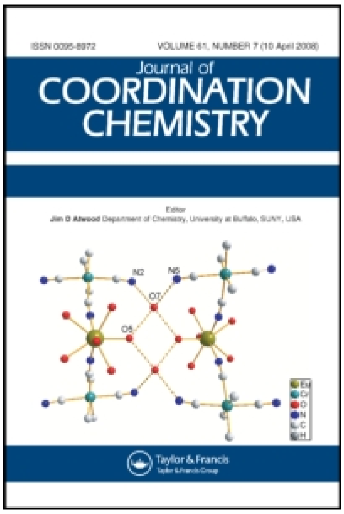

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SYNTHESIS AND CHARACTERIZATION OF A MULTIBRIDGED PORPHYRIN COMPLEX CONTAINING PERIPHERAL BIS(BIPYRIDINE)-RUTHENIUM(II) GROUPS

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The synthesis and characterization of a new *meso*-tetrapyridylporphyrin (TPyP) modified with four $[Ru(bipy)_2Cl]^+$ groups is reported. Cyclic voltammograms of this species in *N,N'*-dimethylformamide exhibit three reversible waves at 0.92, −0.68 and −0.93 V *versus* SHE, ascribed to the ruthenium(III/II) redox couple, and to successive monoelectronic redox processes at the porphyrin ring. Electronic spectra show the characteristic Soret band at 418 nm and the β, α doublets of the porphyrin at 518, 558; and 594, 650 nm, respectively, in addition to the absorption bands of the $[Ru(bipy)_2(pyP)Cl]$ groups at 298 nm (bipy $\pi \rightarrow \pi^*$), 470 nm ($Ru^{II} \rightarrow$ bipy charge-transfer) and 368 nm (ligand field transition). The complex emits around 655 nm, when excited at the porphyrin or $Ru(bipy)_2Cl^+$ absorption bands. The diprotonated species $[H_2TPyP\{Ru^{II}(bipy)_2Cl\}_4]$ displays a new intense band at 690 nm which disappears when the metal ions are oxidized, or when the porphyrin is reduced, suggesting a ruthenium(II)-to-protonated porphyrin charge-transfer transition.

KEY WORDS: Tetraruthenated porphyrin, multibridged complex, ruthenium-porphyrin electrochemistry.

INTRODUCTION

Polymetallated porphyrins are of great interest as new multibridged molecular species,[1–6] displaying unusual chemical and electrochemical properties. Here we describe a new *meso*-tetrapyridylporphyrin (**1**) containing four $[Ru(bipy)_2Cl]^+$ complexes coordinated to the peripheral pyridine groups. The μ-{*meso*-5,10,15,20-tetra(pyridy)porphyrin}tetrakis{bis(bipyridine)(chloride)ruthenium(II)} complex is a prototype of an interesting series of compounds, exhibiting photochemically and electrochemically active groups directly attached to the porphyrin system.

EXPERIMENTAL

The complex $[Ru(bipy)_2Cl_2]$ was prepared as described in the literature.[7] $[Ru(bipy)_2(py)Cl](PF_6)$ was obtained by refluxing the dichloro complex with pyridine

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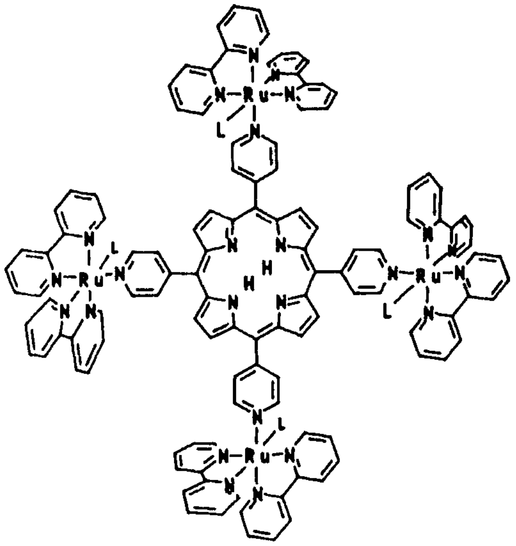

(1:1 molar ratio) in *n,n*-dimethylformamide (DMF), for 60 minutes. The complex was precipitated by adding an aqueous solution of NH_4PF_6.

[TPyP{Ru(bipy)$_2$Cl}$_4$]Cl$_4$.10H$_2$O was synthesized by refluxing [Ru(bipy)$_2$Cl$_2$] and TPyP (4.1:1 molar ratio) in glacial acetic acid for 45 minutes. After removing the solvent in a flash evaporator, the solid was redissolved in a minimum volume of methanol and refluxed for 45 minutes. The product was precipitated by adding acetone saturated with LiCl and collected on a filter. The dark red solid was washed with acetone and dried under vacuum. Anal.; Calcd. for $C_{120}H_{110}N_{24}Cl_8O_{10}Ru_4$: C, 52.67; H, 4.05; N, 12.28%. Found: C, 51.96; H, 4.08; N, 12.32%. Infrared spectrum (cm^{-1}): 3060 w, 3008 w, 1600 s, 1560 w, 1551 w, 1470 sh, 1457 s, 1440 s, 1412 s, 1398 sh, 1380 sh, 1345 w, 1304 s, 1260 m, 1235 w, 1231 sh, 1227 sh, 1225 m, 1207 w, 1183 w, 1150 m, 1098 w, 1015 m, 975 w, 964 s, 879 m, 870 s, 845 w, 795 s, 760 s, 722 s, 652 w, 560 w, 460 w, 420 w, 410 sh, 390 w (s = strong, m = medium, w = weak, sh = shoulder). The corresponding hexafluorophosphate complex was obtained by adding NH_4PF_6 to a methanol solution of the corresponding chloride complex. The precipitate was dissolved in a minimum volume of acetone/methanol (2:1) solution, and the procedure was repeated again, in order to ensure complete exchange of the chloride ions by PF_6^-.

Cyclic voltammetry (CV) measurements were carried out using a 366 potentiostat from EG & G and a Houston XY recorder. The conventional three electrode arrangement was used, consisting of a platinum or glassy carbon disc working electrode, a platinum wire auxiliary electrode and a reference electrode of Ag/AgNO$_3$ (0.010 M) in acetonitrile or of Ag/AgCl (1.00 M KCl) in aqueous solution. The experiments were carried out in doubly distilled DMF containing 0.10 M TEAPF$_6$ (tetraethylammonium hexafluorophosphate) or 0.10 M KCl as supporting electrolyte. Spectro-electrochemical measurements were performed using the potentiostat attached to a Hewlett-Packard model 8452-A diode-array spectrophotometer, as previously described.[3-5] All potentials were referred to SHE by adding 0.503 or 0.222 V in the case of the Ag/AgNO$_3$ or Ag/AgCl reference electrodes, respectively.

The pH measurements were carried out with a combined glass electrode (Orion) and a digital pH meter from Digimed. Fluorescence spectra were recorded on a Perkin Elmer LS-30 spectrofluorimeter.

RESULTS AND DISCUSSION

The modified tetrapyridylporphyrin containing four $[\mathrm{Ru(bipy)_2Cl}]^+$ groups coordinated to the pyridine residues was isolated as a black powder, stable in air. The solid is soluble in a variety of solvents such as water, methanol, acetonitrile and *N*,*N*′-dimethylformamide (DMF), in contrast with the starting porphyrin.

Electronic spectra of the tetraruthenated porphyrin in aqueous solution exhibit absorption bands at 292, 356, 414, 470, 518, 560, 584 and 642 nm, as shown in Figure 1, consistent with the presence of two chromophores located at the peripheral ruthenium complexes and at the porphyrin ring. The bands at 292, 356 and the broad absorption around 470 nm are characteristic of the $[\mathrm{Ru^{II}(bipy)_2(pyP)Cl}]^+$ fragments. The absorption band at 292 nm can be ascribed to a $\pi \rightarrow \pi^*$ transition in the bipy ligands. The absorption band at 356 nm and the broad band at 470 nm was assigned to a ligand field transition and to a Ru(II)→bipy, $d_\pi \rightarrow p_\pi{}^*$ charge-transfer (MLCT) transition, respectively, by analogy with the spectrum of $[\mathrm{Ru^{II}(bipy)_3}]^{2+}$ and related species.[8] The absorption band at 414 was ascribed to the Soret transition; those at 518, 560; and at 584 and 642 nm, respectively, are consistent with β and α transitions in the porphyrin ring.[9-11] A comparison of the electronic bands of modified TPyP species can be seen in Table 1.

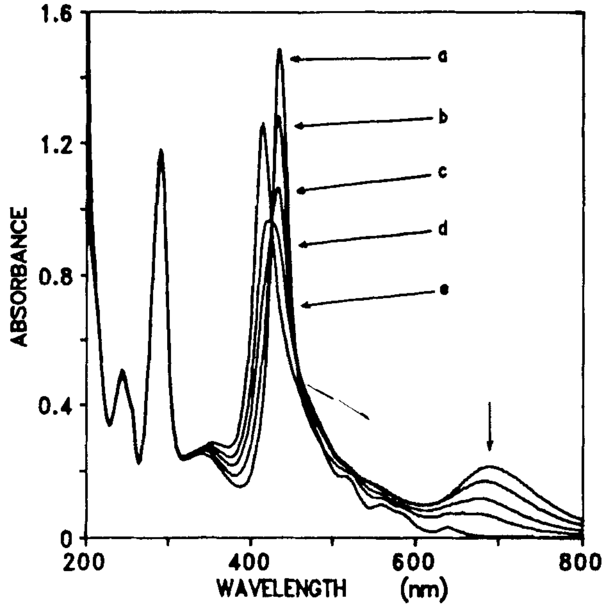

Figure 1 Electronic spectra of aqueous solutions of 5.8 μM $[\mathrm{TPyP\{Ru(bipy)_2Cl\}_4}]\mathrm{Cl_4}$, at pH a) 1.24, b) 1.71, c) 1.98, d) 2.2 and e) 5.30.

Table 1 Electronic spectroscopic data for tetrapyridylporphyrins

	Wavelength (nm)								
Complex	$\pi \rightarrow \pi^*_{bipy}$		LF	Soret	MLCT	β		α	
$[TPyP]^{a}$				417		513	547	588	643
$[H_4TPyP_4]^{4+b}$				420		518	553	585	638
$[H_6TPyP]^{6+b}$				442			588		640
$[TMPyP]^{4+b}$				422		518	554	586	643
$[H_2TMPyP]^{6+b}$				446			588		642
$[TPyPRu_4^{II}]^{b}$	292		356	414	470(br)	518	560	584	642
$[TPyPRu_4^{II}]^{c}$	298		368	418	470(br)	518	558	594	650
$[TPyPRu_4^{III}]^{c}$	304	316	370	424		516	552	590	648
$[H_2TPyPRu_4^{III}]^{b}$	296	314	358	444			596		650
$[H_2TPyPRu_4^{II}]^{b}$	292		350	440	470(sh) 690	546(br)		masked	

[a] In $CHCl_3$. [b] In aqueous solution. [c] In DMF.

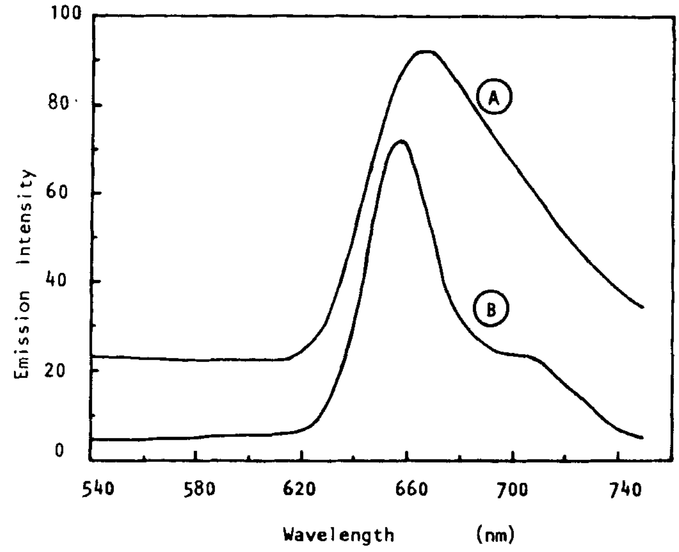

Figure 2 Fluorescence spectra of aqueous solutions of 10 μM $[TPyP\{Ru(bipy)_2Cl\}_4]Cl_4$ at A) pH 1, and B) pH 6.

The tetraruthenated porphyrin emits around 655 and 700 nm (sh), as shown in Figure 2, when excited in the visible-UV absorption bands. The emission energies are similar to those observed for the (tetra-*N*-methylpyridium)porphyrin free base, and can be ascribed to the decay of the low lying singlet π^*-excited states of the porphyrin centre. The excitation spectrum followed the absorption spectrum shown in Figure 1, reproducing very closely the absorption profile even in the MLCT band of the $[Ru(bipy)_2Cl^+]$ chromophore. Therefore, the π^* emitting state can be pumped either from a direct excitation at the porphyrin centre, or by an intramolecular mechanism involving the peripheral $[Ru(bipy)_2Cl]^+$ groups.

Below pH 3, the modified porphyrin can be reversibly protonated at the pyrrole *N*-atoms, shifting the Soret band from 414 nm to 440 nm, as illustrated in Figure 1. The electronic bands associated with the peripheral ruthenium complexes remain practically unchanged; however, a new intense band appears around 690 nm. The emission band, uncorrected for the photodetector sensitivity, is broad and asymmetric, with a maximum at 665 nm and a shoulder around 700 nm as shown in Figure 2. By monitoring the emission at 700 nm and above, a remarkable increase of intensity was observed when the energy of excitation is in resonance with the new absorption band at 690 nm. The nature of this band will be discussed after the spectroelectrochemical section.

The protonation reaction can be represented by (1).

$$[\mathrm{TPyPRu_4}]^{4+} + 2\mathrm{H}^+ \rightleftharpoons [\mathrm{H_2TPyPRu_4}]^{6+} \tag{1}$$

The linear plot of $\log([\mathrm{TPyPRu_4}]/[\mathrm{H_2TPyPRu_4}])$ *versus* pH gave at the intercept, $\mathrm{pK_a} = 2.0$. The slope of 2.1 is consistent with the involvement of two protons, in agreement with the results previously reported for TPyP[12] ($\mathrm{pK_a} \cong 1.1$) and TMPyP[13] ($\mathrm{pK_a} = 2.2$).

Cyclic voltammetry

Cyclic voltammograms of the tetrametallated porphyrin $[\mathrm{TPyP\{Ru(bipy)_2Cl\}_4}](\mathrm{PF_6})_4$ exhibit three characteristic waves in the potential range −1.2 to 1.2 V, in DMF solutions, as shown in Figure 3. The chloride salt exhibits an additional irreversible anodic wave at 1.1 V, associated with the oxidation of $\mathrm{Cl^-}$ to $\mathrm{Cl_2}$.

The reversible wave at $E^\circ = 0.92$ V follows the Randles-Sevcik equation for a monoelectronic redox process and can be assigned to the $[\mathrm{Ru^{III/II}(bipy)_2(TpyP)Cl}]^{2+/1+}$ redox couple, by analogy with the potential of the $[\mathrm{Ru^{III/II}(bipy)_2(py)Cl}]$ redox couple ($E^\circ = 0.90$ V).[14] The intensity of this wave is four times higher than those observed at cathodic potentials, and provides strong support for the proposed composition based on analysis. It should be noticed that a partial metallation or the presence of the starting ruthenium complex as an impurity can be readily detected by cyclic voltammetry, either from the decrease in the relative intensity of the wave at 0.92 V, or from the presence of an additional wave at 0.52 V corresponding to the unreacted species, $[\mathrm{Ru(bipy)_2Cl_2}]$.

The occurrence of a single, reversible wave at 0.92 V in the tetrametallated porphyrin, as well as in the partially metallated species, is consistent with the general behaviour of polynuclear and polymeric systems containing identical, non-interacting redox groups.[15–16] In this case, it has been shown that the current-potential responses exhibit the same shape as that obtained with the corresponding molecule containing a single centre, but the magnitude of the current is enhanced by the presence of additional electroactive centres. The cyclic voltammograms are also coherent with those previously reported for $\mathrm{Ru(EDTA)^{2-}}$, $\mathrm{Ru(NH_3)_5^{2+}}$ (in Nafion) and ferrocene-modified porphyrins.[1–5]

In the cathodic region, a reversible wave is observed at $E^\circ = -0.68$ V. This wave is followed by a second wave at −0.93 V, as shown in Figure 3. They exhibit comparable intensities and are not found in the cyclic voltammograms of the $[\mathrm{Ru^{III/II}(bipy)_2(py)Cl}]$ complex, suggesting consecutive redox processes at the porphyrin ring.

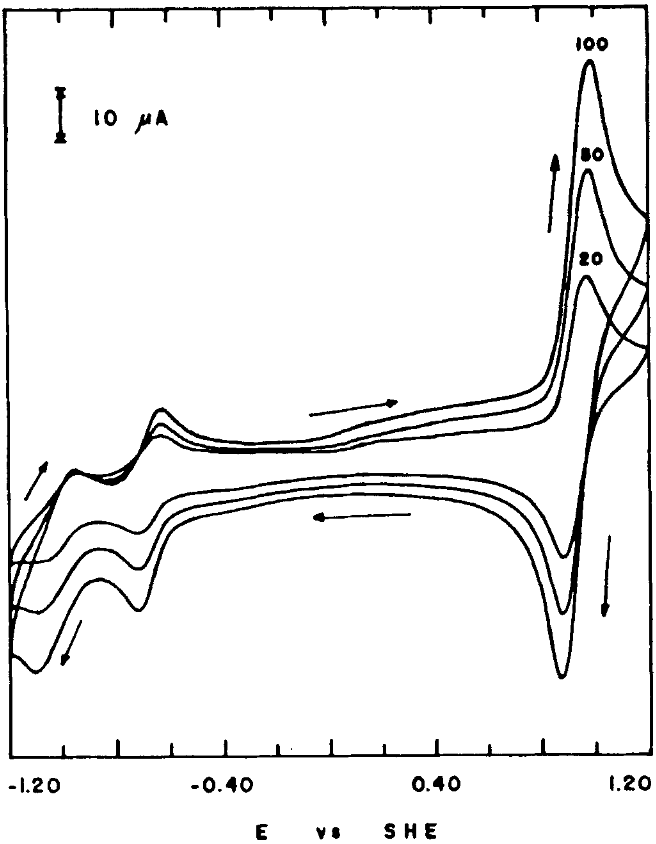

Figure 3 Cyclic voltammograms of 1.2 mM [TPyP{Ru(bipy)$_2$Cl}$_4$} (PF$_6$)$_4$ in DMF, 0.10 M TEAPF$_6$, 25°C.

Cyclic voltammograms for the protonated species were obtained in aqueous solution containing 0.12 M HCl (KCl 0.10 M), leading to a reversible wave at 0.93 V ascribed to the peripheral [Ru(bipy)$_2$LX] groups by analogy to the non-protonated porphyrin. According to Davies and Mullins,[17] the chloride ligand in [Ru(bipy)$_2$LCl] complexes is labile, undergoing substitution by coordinating solvents, such as water. However, the close similarity of the cyclic voltammograms obtained in aqueous and in DMF solutions reaction provided no evidence for this type of reaction for the tetraruthenated porphyrin.

A broad composite cathodic wave at 0 V and a sharp anodic wave at 0.1 V were also observed in acidic solutions. Protonation of the central nitrogen atoms seems to shift the first reduction peak of the porphyrin ring by almost 0.5 V with respect to that of the non-protonated species. The corresponding anodic wave, however, was strongly influenced by the adsorption of the reduced species at the electrode.

Spectro-electrochemistry

Typical spectro-electrochemical results for the tetraruthenated porphyrin in DMF can be seen in Figure 4. By increasing the applied potentials in the range 0.85 to 1.1 V (Figure 4.A) the broad MLCT transition at 470 nm gradually disappears, and the bipyridine ligand $\pi \rightarrow \pi^*$ transition at 298 nm splits into two bands with maxima at 304 and 316 nm. Similar spectro-electrochemical behaviour has been observed for $[Ru(bipy)_2Cl_2]$; however, the shift of the Soret band from 418 to 424 nm is accompanied by 30% increase in its intensity, reflecting a perturbation of the electronic levels of TPyP by the ruthenium complexes.

The spectro-electrochemical behaviour of the complex in the potential range −0.50 to −0.80 V is similar to that observed when the tetramethylated porphyrin, TMPyP, is reduced under the same conditions (Figure 5). As the Soret band decays, a new band appears at 455 nm and the absorption bands ascribed to the peripheral ruthenium complexes remain unchanged. However, after a few minutes at E = −0.8 V, further reduction takes place, leading to irreversible decomposition of the complex.

The spectro-electrochemistry of the diprotonated porphyrin, $[H_2TPyP\{Ru^{II}(bipy)_2X\}_4]$, in 0.12 M HCl solutions differs from that observed for the non-protonated

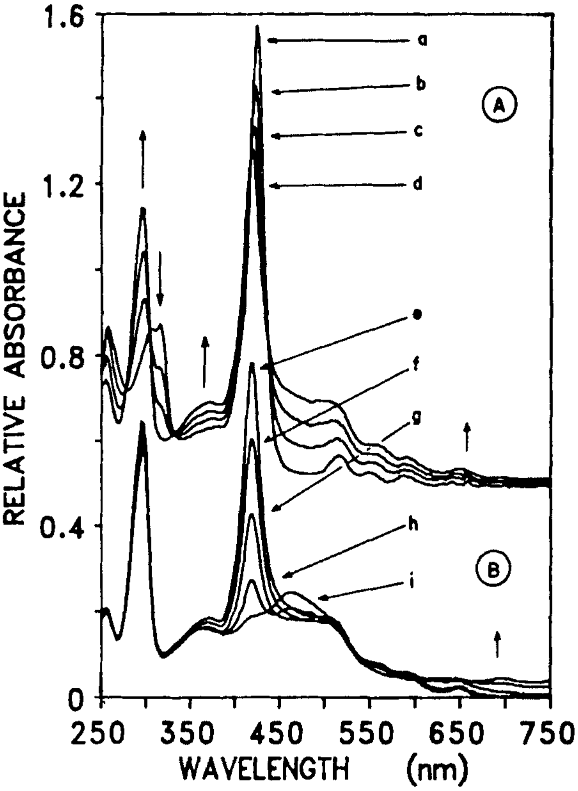

Figure 4 Spectro-electrochemistry of the 0.12 mM $[TPyP\{Ru(bipy)_2Cl\}_4]$ $(PF_6)_4$ complex in DMF, a) 1.10, b) 0.94, c) 0.90, d) 0.50, e) −0.10, f) −0.56, g) −0.62, h) −0.70, i) −0.80 V.

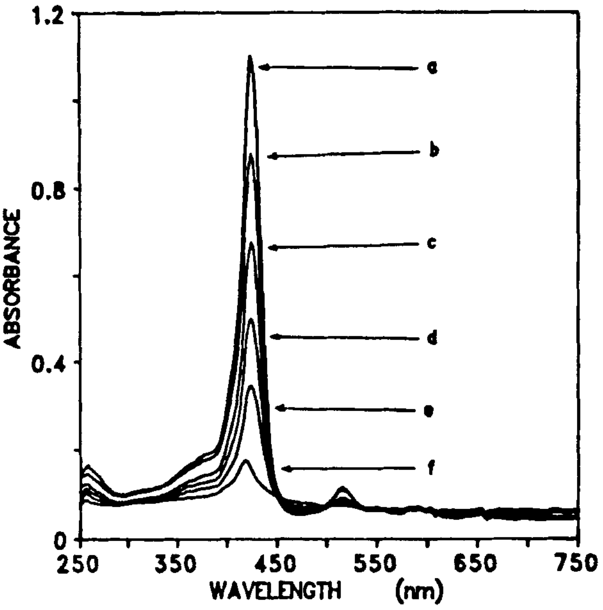

Figure 5 Spectroscopic changes observed during the reduction of 0.2 mM [TMPyP] $(PF_6)_4$ in DMF, 0.10 M $TEAPF_6$, in the potential range a) 0.90 to f) −0.52 V.

species in DMF, by the presence of a new intense band at 690 nm overlapping the porphyrin α bands, as shown in Figure 6. This band is not observed in the oxidized Ru^{III} species generated at $E^\circ = 0.9$ V, or when the porphyrin is reduced, suggesting a ruthenium(II)-to-protonated porphyrin $d_\pi \rightarrow p_\pi^*$ charge transfer transition (MLCT). The protonated species undergoes reduction at −0.1 V, in agreement with the cyclic voltammograms, leading to the decay of the Soret band at 440 nm and of the LMCT band at 690 nm, and to the appearance of a band at 490 nm, as observed in DMF solutions.

According to the electrochemical and spectro-electrochemical results, the several $[Ru(bipy)_2Cl]^+$ groups attached to the porphyrin behave independently, as weakly interacting redox centres. However, most relevant is their strong interaction with the porphyrin, as deduced from absorption, emission and excitation spectra, ensuring adiabatic conditions for intramolecular electron transfer. As a matter of fact, the spectro-electrochemical evidence of a low lying MLCT band in the diprotonated species corroborates the possibility of photoelectron transfer from the ruthenium complexes to the porphyrin. In addition, the fluorescence observed in the diprotonated species may arise from this low-lying MLCT state, involving a large distance charge-transfer separation between the donor (Ru^{II}) and acceptor (porphyrin) centres. For this reason, detailed studies on the photophysics and photochemistry of this and related multibridged porphyrins are being planned in order to explore their potential usefulness as photocatalyst and in energy conversion processes.

Acknowledgements

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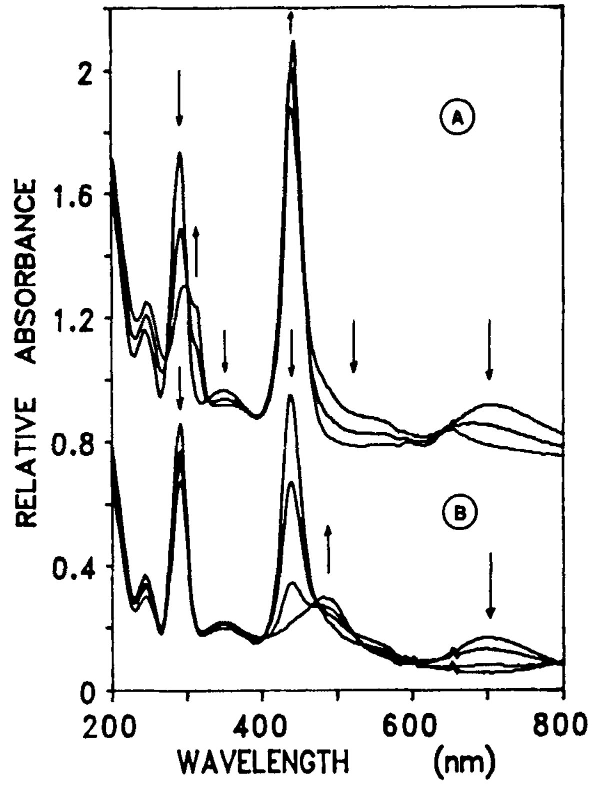

Figure 6 A) Spectroscopic changes observed during the oxidation of 0.64 mM $[\mathrm{TPyP}\{\mathrm{Ru(bipy)_2Cl}\}_4]\mathrm{Cl}_4$ at 1.0 V in aqueous solution containing 0.12 M HCl (KCl = 0.10 M); B) for the reduction of the complex at −0.4 V.

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