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## **Spectroscopy Letters**

Publication details, including instructions for authors and subscription information:

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### **Resonance Raman Spectra of a Supramolecular Species Containing Four Ruthenium(II)-Bipyridine Complexes Attached to Zinc-Tetrapyrridyl Porphynate**

Koiti Araki<sup>a</sup>; Paulo S. Santos<sup>a</sup>; Luiz F. C. de Oliveira<sup>a</sup>; Henrique E. Toma<sup>a</sup>

<sup>a</sup> Instituto de Química - Universidade de São Paulo, São Paulo, SP, Brazil

**To cite this Article** Araki, Koiti , Santos, Paulo S. , de Oliveira, Luiz F. C. and Toma, Henrique E.(1995) 'Resonance Raman Spectra of a Supramolecular Species Containing Four Ruthenium(II)-Bipyridine Complexes Attached to Zinc-Tetrapyrridyl Porphynate', *Spectroscopy Letters*, 28: 1, 119 — 126

**To link to this Article:** DOI: 10.1080/00387019508011660

**URL:** <http://dx.doi.org/10.1080/00387019508011660>

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**RESONANCE RAMAN SPECTRA OF A SUPRAMOLECULAR SPECIES  
CONTAINING FOUR RUTHENIUM(II)-BIPYRIDINE COMPLEXES  
ATTACHED TO ZINC-TETRAPYRIDYL PORPHYRATE.**

Key words: Resonance Raman spectra, zinc porphyrin, supramolecular porphyrin

Koiti Araki, Paulo S. Santos, Luiz F.C. de Oliveira and Henrique E. Toma

Instituto de Química - Universidade de São Paulo, Caixa Postal 20780  
CEP 01498-970, São Paulo, SP, Brazil

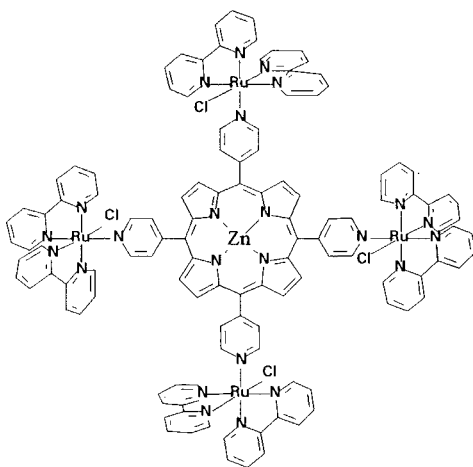
**ABSTRACT**

The chromophore selective resonance Raman (rR) effect was employed in the spectroscopic characterization of a supramolecular species containing four  $\text{Ru}(\text{bipy})_2\text{Cl}^+$  groups (bipy = 2,2'-bipyridine) coordinated to the peripheral pyridine residues of meso-tetrapyridylporphynatezinc(II) (ZnTPyP). The electronic spectrum exhibits strong absorption bands at 441, 568 and 612 nm ascribed to the ZnTPyP Soret,  $Q_{10}$  and  $Q_{00}$  transitions, respectively, and a broad absorption shoulder around 490 nm. Four types of rR excitation profiles can be observed in the range of 457 to 514 nm. The vibrational peaks associated with porphyrin skeletal modes, e. g. at 1352, 1252 and 389  $\text{cm}^{-1}$  are selectively enhanced at the Soret band, while the bipyridine vibrational peaks, e.g. at 1491 and 1321  $\text{cm}^{-1}$  exhibit maximum enhancement at 496 nm, coinciding with the Ru(II)-to-bipy charge transfer transition (MLCT). A third group of peaks, e.g. at 1217 and 1004  $\text{cm}^{-1}$ , corresponding to pyridine or porphyrin vibrations strongly coupled with the py ring, exhibit additional enhancement around 466 nm and supports the existence of a Ru(II) $\rightarrow$ py(TPyP) charge transfer band in this region. A fourth group of peaks, e.g., at 1609 and 1557  $\text{cm}^{-1}$  involves accidentally degenerate modes of the

bridging pyridine and bipyridine groups enhanced in resonance with the Soret,  $\text{Ru}^{\text{II}} \rightarrow \text{py}(\text{TPyP})$  and  $\text{Ru}^{\text{II}} \rightarrow \text{bipy}$  charge-transfer bands.

## INTRODUCTION

In a previous paper<sup>1</sup> we described the synthesis, spectroelectrochemistry and photochemical properties of a novel polyruthenated zinc porphyrin, containing four  $\text{Ru}(\text{bipy})_2\text{Cl}^+$  groups attached to the pyridine residues of meso-tetrapyrrolylporphyrinate zinc(II), as shown in (1)



(1)

This multibridged complex exhibits characteristic zinc porphyrin fluorescence (606 and 655 nm) and phosphorescence (770 nm) bands and can undergo at least six redox processes associated with the TPyP, bipy, Ru and Zn moieties. It forms stable films on glassy carbon, displaying reversible photoelectrochemical response when exposed to visible light. Such photochemical and photophysical properties are of great interest in the development of supramolecular devices,<sup>3,4</sup> exhibiting the activity of the zinc porphyrin and ruthenium bipyridine complexes, and the novel properties arising from the interaction between those sites.<sup>5-10</sup> Therefore, the behavior of the supramolecular species is expected to be strongly influenced by the degree of electronic and vibronic coupling between the interacting groups. In order to elucidate this point, we investigated the resonance Raman behavior of the tetraruthenated porphyrin in

the excitation region from 450 to 514 nm, which is strongly complicated by the superimposition of the Soret and the Ru(II)→py(TPyP) and Ru(II)→bipy MLCT bands.

## EXPERIMENTAL

The synthesis and characterization (microanalysis, electrochemistry, spectroelectrochemistry, luminescence and photoelectrochemistry) of the  $[\text{ZnTPyP}\{\text{Ru}(\text{bipy})_2\text{Cl}\}_4](\text{TFMS})_4 \cdot 3\text{H}_2\text{O}$  complex, where TFMS is the trifluoromethanesulphonate anion, have been previously reported<sup>1</sup>.

The electronic spectra of a film of the zinc complex on mirror like finished platinum surface, were recorded on a Guided Wave model 260 fiber optics spectrophotometer. Resonance Raman spectra were obtained for solid samples by using a spinning cell and a Jarrel-Ash model 25-300 Raman double-spectrometer equipped with Spectra Physics argon and krypton ion lasers. The measurements were carried out with the samples dispersed in  $\text{KNO}_3$ ; the nitrate band at  $1050\text{ cm}^{-1}$  was employed as an internal standard for measuring relative intensities.

## RESULTS AND DISCUSSION

The  $[\text{ZnTPyP}\{\text{Ru}(\text{bipy})_2\text{Cl}\}_4](\text{TFMS})_4 \cdot 3\text{H}_2\text{O}$  complex forms stable and uniform films on platinum, exhibiting the Soret,  $Q_{1,0}$  and  $Q_{0,0}$  bands at 441, 568 and 612 nm, respectively, and a broad composite band at 490 nm, as shown in Figure 1. This additional band is similar to that observed at 452 nm in the  $[\text{Ru}(\text{bipy})_3]^{2+}$  complex,<sup>11</sup> corresponding to a ruthenium(II)-to-bipyridine,  $d\pi \rightarrow p\pi^*$ , charge transfer transition.

The resonance Raman spectra of  $[\text{ZnTPyP}\{\text{Ru}(\text{bipy})_2\text{Cl}\}_4](\text{TFMS})_4 \cdot 3\text{H}_2\text{O}$  exhibit strong, well defined peaks in the  $1000 - 1600\text{ cm}^{-1}$  range (Fig. 2), corresponding to totally symmetric zinc meso-tetra(pyridyl)porphyrin and bipyridine ring vibrational modes. The tentative assignment was carried out by comparison with the rR spectra of meso-tetramethylpyridiniumporphynatezinc(II) or  $[\text{ZnTMPyP}]^{4+}$ ,  $[\text{Ru}(\text{bipy})_3]^{2+}$  and related complexes from the literature<sup>12-16</sup>.

The rR excitation profiles are particularly useful in the assignment of overlapping bands in species containing several chromophore groups. A careful examination of the spectra reveals the occurrence of four types (here denoted by I

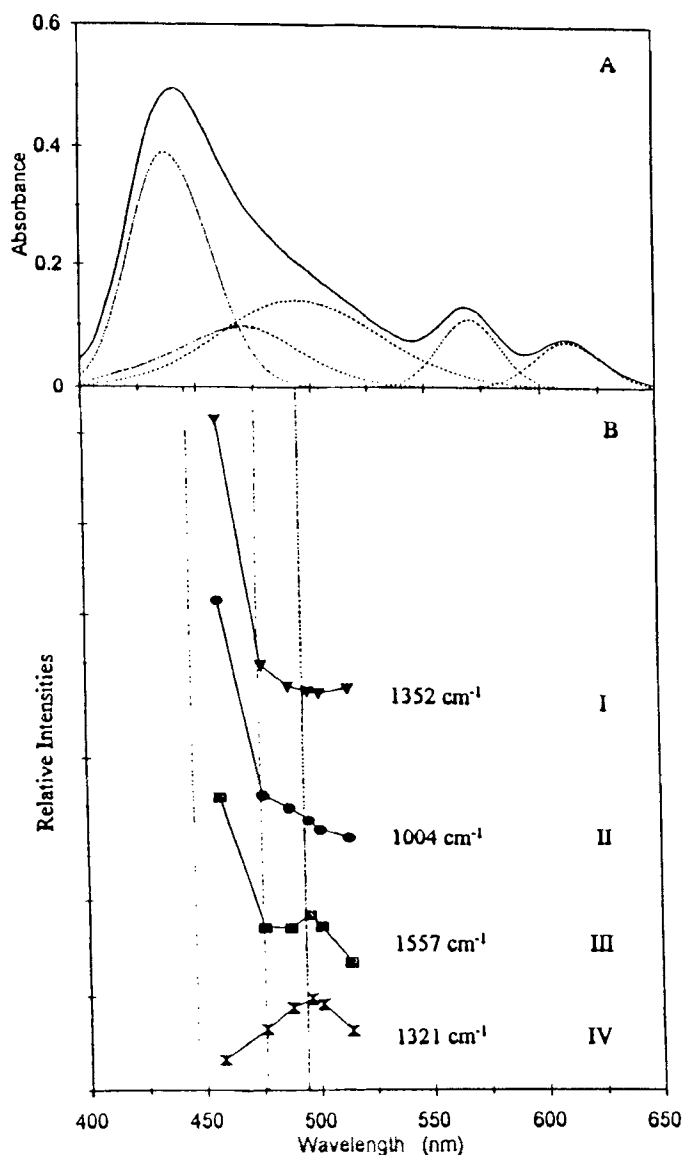


Fig 1: (A) Electronic spectrum of  $[\text{ZnTPyP}\{\text{Ru}^{\text{II}}(\text{bipy})_2\text{Cl}\}_4](\text{TFMS})_4$  and (B) resonance Raman profiles (I) for typical zinc porphyrin vibrational modes; (II) vibronically coupled porphyrin ring and pyridine modes; (III) accidentally degenerate pyridine modes in ZnTPyP and bipy; and (IV) bipyridine vibrational modes.

TABLE I  
Raman frequencies for  $[\text{ZnTPyP}\{\text{Ru}^{\text{II}}(\text{bipy})_2\text{Cl}\}_4](\text{TFMS})_4$  complex.

ZnTMPyP	$\text{Ru}(\text{bipy})_3^{\text{a}}$	$\text{ZnTPyP}\{\text{Ru}(\text{bipy})_2\text{Cl}\}_4^{\text{b}}$	Tentative Assignment <sup>15,16</sup>
1641 s	1608 s	1609 vs	$\nu(\text{C-C}) + \nu(\text{C-N}), \delta(\text{py})^*$
1554 s	1563 s	1557 vs	$\nu(\text{C}_\beta-\text{C}_\beta)^*, \nu(\text{C-C})$ + $\nu(\text{C-N})+\delta(\text{CCH})$
	1491 vs	1491 s	$\delta(\text{CCH})+\nu(\text{C-C})\nu+(\text{C-N})$
1455 vw		1455 w	$\nu(\text{C}_\alpha-\text{C}_\beta)^*$
1353 s		1352	$\nu(\text{C}_\alpha-\text{N})^*$
	1320 s	1321 m	$\delta(\text{CCH})+\nu(\text{C-C})$
	1276 m	1273 vw	$\nu(\text{C-C})+\nu(\text{C-N})$
1253 s		1252 s	$\delta(\text{C}_m-\text{py})^*$
1219 s		1217 s	$\delta(\text{py})^*$
1190 m			$\delta(\text{py})^*$
	1176 w	1173 w	$\delta(\text{CCH})$
1094 w		1090 w	$\delta(\text{C}_\beta-\text{H})^*$
	1067	1070 vw	$\delta(\text{CCH})+\nu(\text{C-C})+\alpha(\text{CCC})$
	1028	1024 s	$\nu(\text{C-C})+\delta(\text{CCH})$
1003 m		1004 s	$\nu(\text{C}_\alpha-\text{C}_m)+\nu(\text{py})^*$
904 w		901 vw	$\delta(\text{porph})^*$
669 vw	668 w	669 m	$\delta(\text{py})^*, \alpha(\text{CCC})$ + $\nu(\text{C-N}) + \nu(\text{Ru-N})$
380 w		389 s	$\delta(\text{porph})+\delta(\text{py})^*$
	370 w	371 vw	$\nu(\text{Ru-N})+\nu(\text{C-C})+\alpha(\text{CCC})$ + $\nu(\text{C-N})$
		320 m	$\delta(\text{porph})+\nu(\text{Zn-N})^*$
		230 w	$\delta(\text{porph})+\nu(\text{Zn-N})^*$

a) in aqueous solution, b) dispersed in  $\text{KNO}_3$ , \* refers to ZnTPyP vibrations, py = pyridine ring, vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

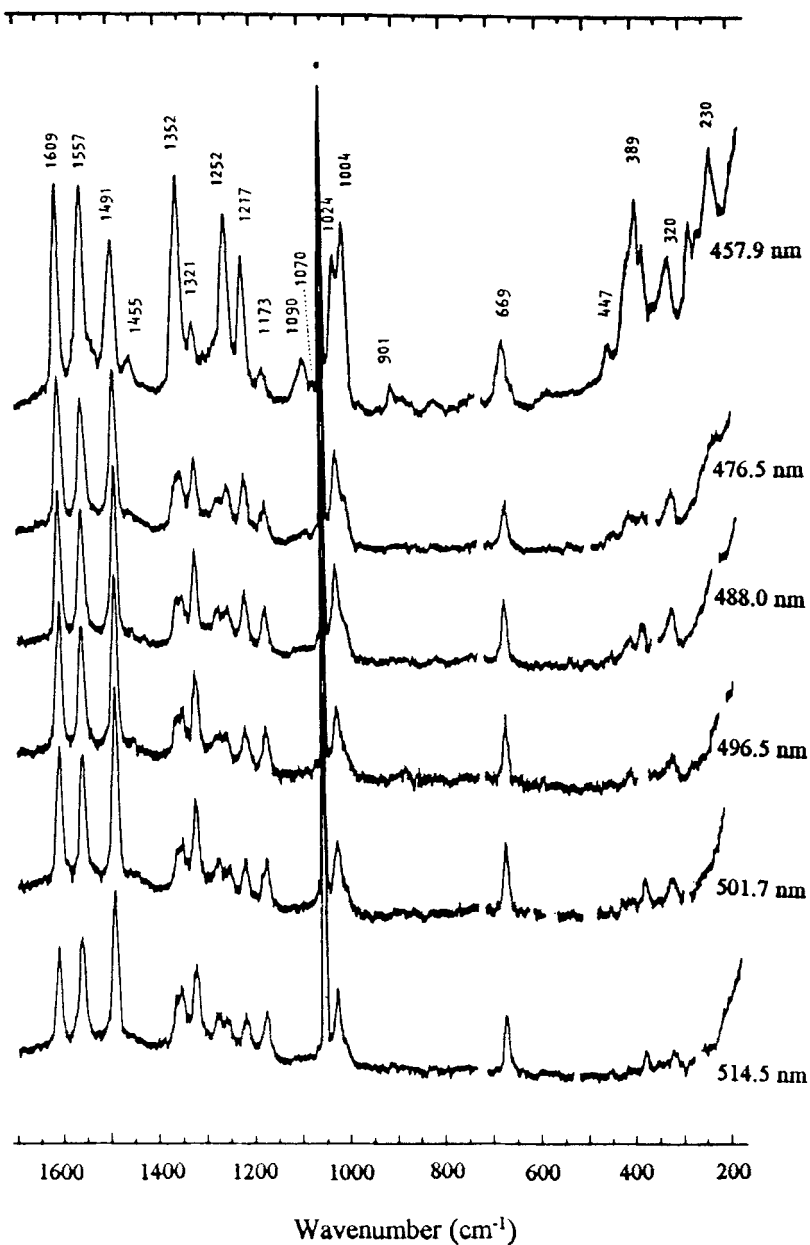


Fig.2: Resonance Raman spectra of the [ZnTPyP{Ru<sup>II</sup>(bipy)<sub>2</sub>Cl}<sub>4</sub>](TFMS)<sub>4</sub> complex dispersed in solid KNO<sub>3</sub>, at several excitation wavelengths. The asterisk indicates the nitrate Raman peak at 1050 cm<sup>-1</sup>; the plasma peaks were omitted.

to IV) of rR excitation profiles for the multibridged porphyrin complex, as shown in Fig. 1.

The excitation profiles (Fig. 1, type I) for the zinc porphyrin skeletal modes at 1352, 1252 and 389  $\text{cm}^{-1}$  parallel the absorption spectrum of the porphyrin group and are strongly intensified as the excitation wavelength approaches the Soret band at 441 nm.

The 1491, 1321 and 669  $\text{cm}^{-1}$  peaks are related to bipy vibrational modes and exhibit excitation profiles with a maximum around 495 nm (Fig. 1, type IV), following the contour of the MLCT band of peripheral  $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$  groups.

A third type of excitation profile is observed for the peaks at 1609 and 1557  $\text{cm}^{-1}$ . Such vibrational peaks are enhanced by resonance with the Soret band at 441 and the  $\text{Ru} \rightarrow \text{bipy}$  MLCT at 490 nm (Fig. 1, type III). However, an additional enhancement can be observed around 460 nm, consistent with the existence of a new electronic transition in this region.

The presence of this new band becomes evident in the excitation profiles for the 1217 and 1004  $\text{cm}^{-1}$  peaks, where a shoulder appears in between the Soret and the  $\text{Ru}^{\text{II}} \rightarrow \text{bipy}$  charge-transfer bands (Fig. 1, type II). This group of peaks correlates with pyridine modes in the pyridyl(pentaamin)ruthenium(II) complex<sup>16</sup> e.g., at 1608, 1217, 1049 and 1008  $\text{cm}^{-1}$ , or with porphyrin vibrations strongly coupled with the py ring.<sup>2,15</sup> It should be noted that the pyridine ring, is common to both ZnTPyP and the peripheral bis-(bipyridine)ruthenium(II) complexes. Therefore, the occurrence of accidental degeneracy involving py vibrational modes of ZnTPyP and bipy becomes rather plausible in the multibridged complex.

Pyridine modes can be enhanced in two different ways: a) at the Soret band, by vibronic coupling with porphyrin ring skeletal modes and b) by direct excitation at the  $\text{Ru}^{\text{II}} \rightarrow \text{py}(\text{ZnTPyP})$  charge-transfer band. When both mechanisms are effective, the excitation profiles exhibit pyridine modes enhancement at the Soret band and at the  $\text{Ru}^{\text{II}} \rightarrow \text{py}(\text{ZnTPyP})$  charge-transfer band (Fig. 1, type II). Evidence for this type of behavior has been previously reported for the modes at 1609, 1248, 1212 and 1027  $\text{cm}^{-1}$  in the analogous  $[\text{Fe}^{\text{II}}\text{TPyP}\{\text{Ru}^{\text{II}}\text{EDTA}\}_4]^{8-}$  complex<sup>2</sup>. In such case, the peripheral complexes exhibit only the  $\text{Ru}^{\text{II}} \rightarrow \text{py}(\text{ZnTPyP})$  charge transfer band at 470 nm and the enhanced modes correspond to pyridine or porphyrin vibrations strongly coupled with the py ring modes, as in the case of type II vibrational modes of  $[\text{Zn}^{\text{II}}\text{TPyP}\{\text{Ru}^{\text{II}}(\text{bipy})_2\text{Cl}\}_4]$ .



Therefore, the type II and III excitation profiles are consistent with the existence of a  $\text{Ru}^{\text{II}} \rightarrow \text{py}(\text{ZnTPyP})$  charge-transfer transition around 466 nm overlapping with the Soret band at 441 nm and the  $\text{Ru}^{\text{II}} \rightarrow \text{bipy}$  MLCT band at 496 nm, as shown in the deconvoluted spectrum in the figure 1A. This transition is particularly important in the multibridged complex because it is an evidence of a direct interaction between the central and peripheral groups, as expected from the supramolecular photochemical properties observed in the system.

#### ACKNOWLEDGMENTS

This work was supported by FAPESP, CNPq and PADCT.

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Date Received: July 29, 1994

Date Accepted: September 15, 1994