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Spectroelectrochemical and photophysical properties of a (3,4-pyridyl) porphyrazine supermolecule containing four $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ groups

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Abstract

Tetra(3-pyridyl)porphyrazine has been modified with four peripheral $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ groups, yielding a novel, dark green supramolecular species. The spectroscopic and electrochemical properties of the tetraruthenated porphyrazine have indicated a significant electronic interaction between the central and peripheral groups. In addition, fluorescence emission from the porphyrazine center has been observed at room temperature either by direct excitation at the Soret and Q bands, or by excitation at the peripheral ruthenium–bipyridine complexes, evidencing an efficient antenna effect. The generation of $^1\text{O}_2$ species from the porphyrazine excited triplet states has also been demonstrated. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Porphyrazine; Supramolecular photochemistry; Vectorial energy transfer

1. Introduction

The antenna effect [1] is very important in the photo-synthetic systems, accounting for the high light harvesting efficiency of the green plants. Because of its strategical relevance, many studies have been performed in order to understand and exploit the factors associated with energy transfer, particularly in supramolecular systems [2–13]. For instance, Sauvage and co-workers [2] have shown that the phenylene spacers are excellent connectors for intramolecular energy transfer in ruthenium/osmium binuclear complexes, and that the efficiency of this process is very much dependent on the relative position of the excited electron and the energy acceptor group, in a ruthenium–osmium terpyridine bridged binuclear complex. If the excited electron is localized in the inner terpyridine bridge, energy transfer proceeds much faster than if it is localized in the outer terpyridine ligand. In addition to the distance traversed by the electron, the electronic coupling between the donor and the acceptor groups also plays an important role in the process.

In our previous publications, we reported on the spectroscopic and luminescence properties of tetraruthenated porphyrin species constituted by four $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ groups coordinated to the pyridyl substituents of the meso-tetra(4-pyridyl)porphyrin center [7,14,15]. The electronic and redox

properties of this type of supramolecular species were consistent with a weak interaction between the central and peripheral groups. The efficiency of the intramolecular energy transfer process from the peripheral ruthenium complexes was found to be very small, as a possible consequence of the poor orbital overlap between the orthogonal bridging pyridyl group and porphyrin ring. In order to improve the understanding of the electronic and photophysical properties of this type of supramolecular complex, we investigated the (3,4-pyridyl)porphyrazine species modified with four $[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ complexes (Fig. 1). In this novel species, here denoted TRuPyPz, the pyridyl group is fused to the porphyrazine ring, forming a π -extended system. The study of the chemistry of this type of supramolecular complexes was pursued based on spectroelectrochemical and photophysical techniques, including the generation of $^1\text{O}_2$ from the excited states, having in mind a possible application in photodynamic therapy processes.

2. Experimental

The free-base porphyrazine (TPyPz) compound was synthesized and purified as previously reported in the literature [16]. Elemental analysis for $\text{C}_{28}\text{H}_{20}\text{N}_{12}\text{O}_3$ exp. (calc.): C=59.4 (58.7), H=3.6 (3.5), N=28.1 (29.3). The supramolecular species TRuPyPz was prepared by refluxing 100 mg of TPyPz and 359 mg of $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ in trifluoroethanol,

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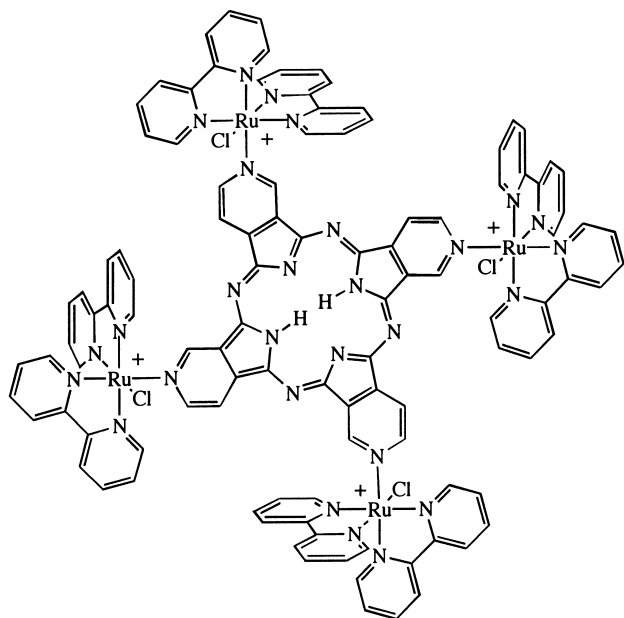


Fig. 1. Structural representation of the TRuPyPz complex.

for 6 h, under an argon atmosphere. The solvent was eliminated using a flash-evaporator, and the solid was redissolved in 50 dm³ of methanol. The dark solution was filtered, flash-evaporated and the resulting solid washed with acetone. Then, the compound was converted into the trifluoromethanesulfonate (TFMS) salt by dissolving the solid in a minimum amount of DMF and pouring it into a LiTFMS aqueous solution. The product collected on a filter and dried in a desiccator under vacuum already exhibited a reasonable purity, according to the elemental analysis. But, considering the high sensitivity of the photophysical processes to any possible porphyrazine and ruthenium–bipyridine contaminants, a final purification was carried out by column chromatography using neutral alumina (Merck, 200–400 mesh). A minor red violet fraction containing the [Ru(bipy)₂Cl₂] starting material, was eluted with a mixture of acetonitrile:DMF (2:10). The major, dark green fraction containing the polymetalated porphyrazine was eluted next, with pure DMF. After removing the solvent using a flash evaporator, the solid was washed with LiTFMS aqueous solution, distilled water and diethyl ether. Elemental analysis for C₁₁₂H₇₈N₂₈Ru₄F₁₂S₄O₁₂Cl₄, % found (calc.): C=46.6 (46.2); H=3.0 (2.7); N=13.3 (13.5).

The electronic and luminescence spectra were recorded on a Hewlett Packard model 8453A diode array spectrophotometer and a Photon Technology model LS100 spectrofluorimeter, respectively. The ethanol solutions of TRuPyPz were purged with argon for at least 30 min, just before the luminescence measurements.

The electrochemical characterization was carried out by cyclic voltammetry, using the conventional three electrode arrangement, consisting of a platinum disk working electrode, an Ag/Ag⁺ 0.010 M reference electrode (in acetonitrile) and a coiled platinum wire auxiliary electrode.

The measurements were carried out utilizing a Princeton Applied Research model 173 potentiostat coupled to a model 175 universal programmer and a HP 7090A plotter. The spectroelectrochemistry studies were carried out as previously described [7,14,15]. HPLC grade, 99.9+% DMF from Sigma/Aldrich was used in the electrochemistry and spectroelectrochemistry studies. All potentials were referenced to SHE [17] by adding 0.503 V.

The flash-photolysis experiments were carried out using a LP900S1 time-resolved absorption/emission spectrometer from Edinburgh Analytical Instruments, constituted by a Continuum Surelite II-10 pulsed laser (width ≈ 5 ns) excitation source at 90° of the analysis system. The analyser was constituted by a 500 W pulsed Xenon Lamp in line with a Czern–Turner monochromator (250 to 900 nm, maximum resolution=0.05 nm) and a Hamamatsu R955 photomultiplier tube (185–900 nm range). The transient signal from the photomultiplier was captured by a Tektronix TDS 520 digital storage oscilloscope and sent to an IBM/PC computer using an IEEE-488 interface. The ¹O₂ emission decay in acetonitrile was monitored at 1270 nm, as previously described [18].

3. Result and discussion

The tetrapyrrolylporphyrazine is analogous to phthalocyanine except for the substitution of a carbon atom of the condensed phenyl groups for a nitrogen atom. The synthetic procedure employed yields a mixture of geometrical isomers [16,19] exhibiting C_{4h}, D_{4h}, C_{2v} or C_s symmetry as a function of the relative position of the pyridine N-atoms. The isomeric forms, however, are chemically very similar and can be considered equivalent in terms of the coordinating properties of the pyridine N-atoms.

It should be noticed that the neutral porphyrin and phthalocyanine compounds are rather insoluble in a majority of the solvents, e.g. water, methanol, ethanol, acetone, acetonitrile, *N,N'*-dimethylformamide (DMF), dimethylsulfoxide (dmsO), dichloromethane and toluene. This limitation has imposed a great difficulty in the synthesis of the polymetallic complexes, which required the use of acidic solvents to increase their solubility as a consequence of the protonation of the N-atoms. But, at the same time this reaction competed with the coordination of the metal complexes and the reactions were carried out with much more difficulty [7,14,15]. Recently, however, we found out that 2,2,2-trifluoroethanol is particularly useful in dissolving porphyrin like species, showing a surprising efficiency when all other neutral solvents fail [15,20]. From this point of view, this extraordinary mild solvent provides a real breakthrough in the synthesis of polymetallic derivatives of tetrapyrrolyl porphyrins and porphyrazines [15,20].

In accord to our expectation, TPyPz was soluble in trifluoroethanol, enabling the smooth coordination of the

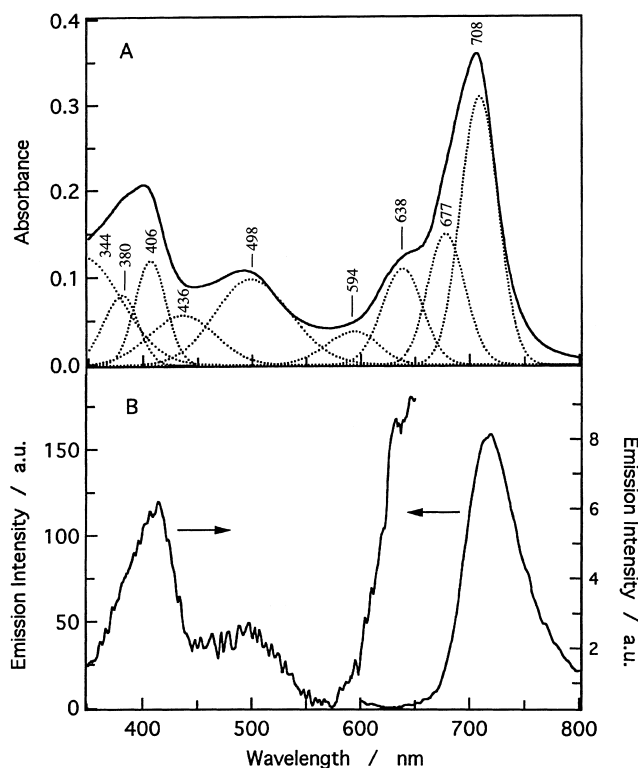


Fig. 2. (A) Electronic spectrum (deconvoluted) of the TRuPyPz complex (room temperature, ethanol solution, $2.6 \mu\text{mol dm}^{-3}$) and the corresponding (B) emission spectrum recorded at $\lambda_{\text{exc}}=400 \text{ nm}$, and excitation profile recorded at $\lambda_{\text{em}}=725 \text{ nm}$.

$[\text{Ru}(\text{bipy})_2\text{Cl}]^+$ groups to its pyridyl nitrogen atoms. The success of the polymetallation procedure was readily apparent, since the modified porphyrazine products exhibited a contrasting solubility imparted by the ruthenium–bipyridine groups, becoming very soluble in organic solvents such as methanol, acetone, acetonitrile, dmsO and DMF, or even in water, when in the form of the chloride salt.

The electronic spectrum of the starting TPyPz compound in trifluoroethanol exhibited the characteristic Soret and Q bands around 330 and 610 nm, respectively; however, the absorption profiles were dependent on the concentration, reflecting the occurrence of association processes [21]. In contrast, no evidence of association was observed in this work for the TRuPyPz species, at least in the concentration range of $1\text{--}1000 \mu\text{mol dm}^{-3}$. A typical electronic spectrum of the TRuPyPz species in ethanol can be seen in Fig. 2(A). The deconvoluted spectrum based on bigaussian functions, exhibited the porphyrazine bands at 380 (B_{0-1}), 406 (B_{0-0} , $\log \epsilon=4.89$), 594 ($Q_{y 0-1}$), 638 ($Q_{x 0-1}$, $\log \epsilon=4.65$), 677 ($Q_{y 0-0}$) and 708 ($Q_{x 0-0}$, $\log \epsilon=5.12$) nm. The remaining bands at 294 ($\log \epsilon=5.32$), 344, 436 and 498 ($\log \epsilon=4.61$) nm were attributed to the $\text{bipy} (p\pi \rightarrow p\pi^*)$ and $\text{Ru}^{\text{II}} (d\pi) \rightarrow \text{bipy} (p\pi_2^*)$, $\text{Ru}^{\text{II}} (d\pi) \rightarrow \text{py} (p\pi^*)$ and $\text{Ru}^{\text{II}} (d\pi) \rightarrow \text{bipy} (p\pi_1^*)$ MLCT transitions, respectively. The band at 436 nm has also been observed in the analogous tetra-ruthenated TPyP complex, and assigned to a charge-transfer transition from the per-

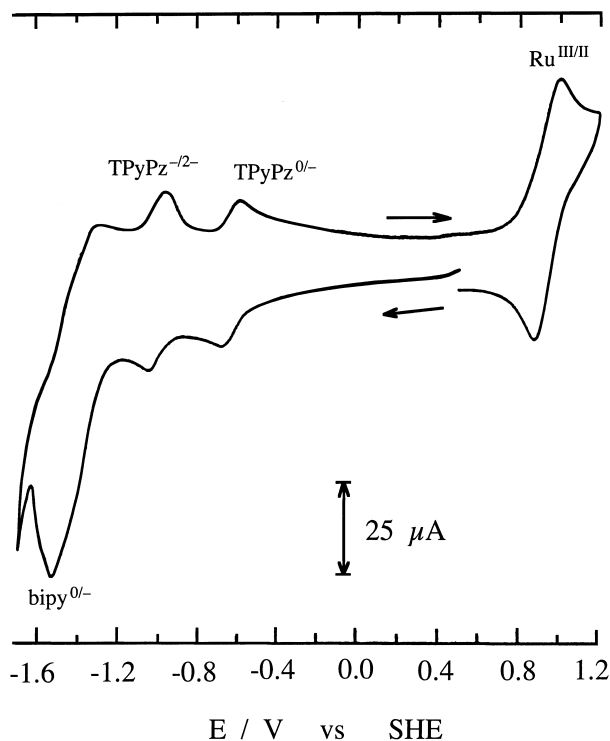


Fig. 3. Cyclic voltammogram of the TRuPyPz complex (2.5 mmol dm^{-3}) in DMF, tetraethylammonium perchlorate (TEAP)= 0.1 mol dm^{-3} , 25°C , scan rate= 200 mV s^{-1} .

ipheral Ru(II) groups to the bridging pyridyl ligand based on resonance Raman measurements [22]. A similar assignment can be proposed for the TRuPyPz complex.

3.1. Electrochemistry and spectroelectrochemistry

The cyclic voltammograms of $[\text{TRuPyPz}](\text{TFMS})_4$ exhibited four redox process in the -1.6 to 1.2 V range, as shown in Fig. 3. By starting at 0.5 V and scanning the potential to the positive side, a reversible wave appeared at 0.94 V vs. SHE. This wave was very similar to those previously reported (around 0.92 V) for related tetra-ruthenated porphyrin species [7,14] and was initially ascribed to the Ru(III/II) redox couple. However, according to the spectroelectrochemical measurements, carried out in parallel for this complex, a composite electrochemical process is involved.

In agreement with the cyclic voltammograms, no spectral change was observed in the -0.30 to 0.50 V range. When the potential was set at 0.90 V the characteristic ruthenium–bipyridine adsorption bands at 297 and 505 nm remained almost unchanged, while the intensity of the Soret and Q bands diminished considerably, as shown in Fig. 4(A). This behavior diverges from that previously observed for the oxidation of the peripheral complexes to ruthenium(III) species, and is rather consistent with the oxidation of the porphyrazine moiety. Unfortunately, the oxidized porphyrazine species was not stable enough to persist in solution without decomposition, during the successive

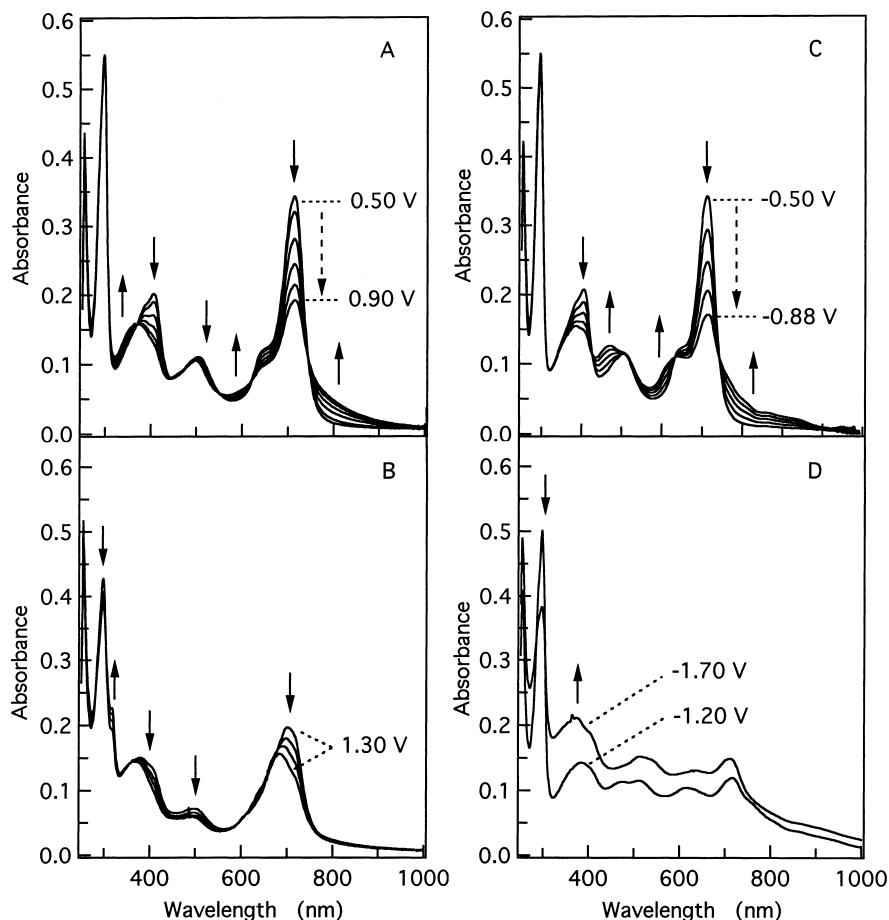


Fig. 4. Spectroelectrochemical changes recorded for the TRuPyPz complex (0.1 mmol dm^{-3}) DMF, TEAP= 0.1 mol dm^{-3} , starting at 0.5 V, showing (A) the initial oxidation of the porphyrzine center at 0.9 V; (B) the successive oxidation of ruthenium moieties at 1.30 V; (C) the first porphyrzine reduction at -0.88 V , (D) the second porphyrzine reduction at -1.20 V and the bipyridine reduction at -1.7 V .

spectroelectrochemical measurements with stepwise increase of potentials. In order to minimize the problem, the working solution was renewed and the potential was stepped from 0.50 to 1.30 V. In this way, the oxidation of the porphyrzine ring was accelerated, and the oxidation reaction of the peripheral ruthenium–bipyridine complexes could be detected from the characteristic decay of the MLCT and bipy ($\pi \rightarrow \pi^*$) bands at 505 and 297 nm, respectively, (Fig. 4(B)) [7,14]. Therefore, according to the spectroelectrochemical results, the voltammetric wave at 0.94 V is actually constituted by the TPyPz $^{0/+}$ and Ru(III/II) redox processes, involving a total of five electrons.

The electrochemical behavior at negative potentials consisted of two reversible waves at -0.63 and -0.99 V , followed by an intense irreversible reduction wave around -1.5 V (Fig. 3). The waves at -0.63 and -0.99 V , exhibited 1/5 of the intensity of the porphyrzine $^{0/+}$ and Ru(III/II) composite wave. The corresponding spectroelectrochemical measurements can be seen in Fig. 4(C)–(D). By applying -0.88 V , i.e., just after the first reduction wave, the intensities of the Soret and Q bands diminished systematically (Fig. 4(C)), while the ruthenium MLCT and bipy ($p\pi \rightarrow p\pi^*$) transitions at 505 and 297 nm, respectively, remained prac-

tically unchanged, indicating that the voltammetric wave at -0.63 V is due to the reduction of the porphyrzine ring. The rise of the absorbance at 468, 600, 800 and 900 nm is associated with the internal transitions is the porphyrzine radical. The reduced product generated at more negative potentials can only be detected as transient species, due to their low stability. The solution was renewed before each set of measurements. In this way, it was possible to observe that at -1.20 V , the porphyrzine radical bands in the 600–800 and 300–500 nm range diminished considerably, while the bipy ($p\pi \rightarrow p\pi^*$) band was little affected (Fig. 4(D)). These observations are coherent with a second reduction of the porphyrzine ring, associated with the voltammetric wave at -0.99 V . Finally, the reduction of the complex at -1.70 V led to a pronounced decay of the bipy ($\pi \rightarrow \pi^*$) band at 297 nm, (Fig. 4(D)), supporting the reduction of the bipyridine ligands in polypyridine complexes [7,14].

3.2. Photophysical properties

The TRuPyPz complex emitted at room temperature when excited in the VIS-UV region, showing a well defined band at 720 nm which increased linearly with the concentration,

in the 0.18–1.5 $\mu\text{mol dm}^{-3}$ range (Fig. 2(B)). In contrast, the free TPyPz emission is known to occur at 684 nm, showing a non-linear dependence with the concentration, reflecting the occurrence of an association process [21].

The emission intensity for TRuPyPz did not change either in argon or dioxygen saturated ethanol solutions, at 25°C, showing that the low-lying porphyrazine singlet excited state, S_1 , is not susceptible to dioxygen quenching. In addition to the luminescence decay, the porphyrazine singlet state may undergo intersystem crossing to the triplet state, T_1 , as well as intramolecular energy or electron transfer to the peripheral ruthenium complexes.

The emission of the substituted ruthenium–bipyridine complexes, such as $[\text{Ru}(\text{bipy})_2(\text{py})\text{Cl}]^+$ and $[\text{Ru}(\text{bipy})_2(4\text{-acetylpy})\text{Cl}]^+$ has only been recorded at low temperature [23], i.e. in MeOH/EtOH glass at 77 K, exhibiting $\lambda_{\text{max}}=660$ and 653 nm, (or $\nu_{\text{max}}=15,151$ and $15,314 \text{ cm}^{-1}$) respectively. Therefore, one can assume that the $^3\text{MLCT}$ state in the tetra-ruthenated species lies slightly above the S_1 state of the porphyrazine center.

The porphyrazine fluorescence intensity in TRuPyPz is about 2 orders of magnitude smaller than that for the free porphyrazine molecule in trifluoroethanol. The decrease in the emission efficiency may be due to the efficient intersystem crossing to the triplet state, as well as to the proximity of the $^3\text{MLCT}$ state [2]. Although a redox quenching mechanism cannot be ruled out, a rough calculation neglecting reorganizational effects indicated that the driving force for the oxidative redox quenching of the porphyrazine S_1 state is relatively small ($\sim 0.06 \text{ V}$). On the other hand, the energy difference between the S_1 and $^3\text{MLCT}$ states falls in the vibrational energy scale, i.e. around 1260 cm^{-1} , considering the emissions of the porphyrazine center and ruthenium complexes at 720 and 660 nm, respectively. As a consequence, small changes in the energy levels should lead to large differences in the emission intensities.

In order to test for this hypothesis, the porphyrazine fluorescence was measured as a function of the solvent, taking into account the solvatochromic effects associated with the MLCT transition in the $[\text{Ru}(\text{bipy})_2\text{Cl}(\text{L})]^+$ groups. For instance, a red shift of about 450 cm^{-1} was observed for the MLCT band in the TRuPyPz complex, by changing from ethanol to DMF solutions, while the emission intensity decreased by a factor of about 50 times. This pronounced decrease of the luminescence behavior differs from the typical solvent effects [24], which are normally much smaller. Presumably, in the present case the solvent is tuning the $^3\text{MLCT}$ state of the peripheral ruthenium complex approximating it to the porphyrazine S_1 state, and decreasing the porphyrazine fluorescence efficiency via energy transfer.

In accord with this hypothesis, the excitation profile of TRuPyPz resembles the absorption spectrum evidencing the MLCT band (Fig. 2(B)) around 500 nm, which corroborates the occurrence of an efficient transfer process from the ruthenium complexes to the porphyrazine center. This type of behavior has not been observed in the excitation profiles

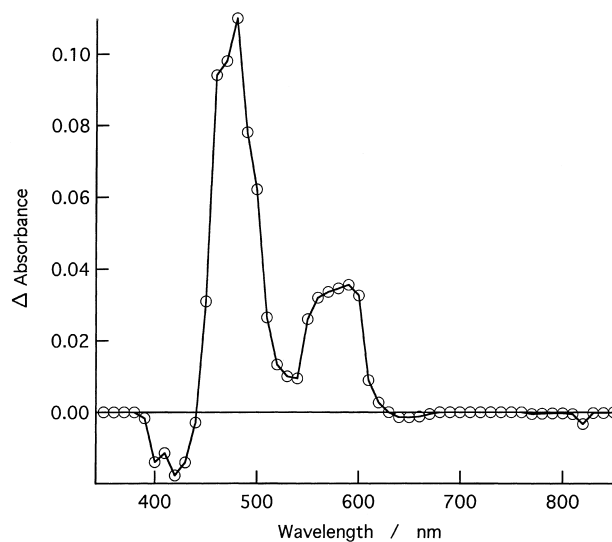


Fig. 5. Differential absorption spectra associated with the TRuPyPz triplet state generated as a transient by flash-photolysis; $[\text{TRuPyPz}]=8.1 \mu\text{mol dm}^{-3}$, in ethanol solution.

of the related TRuPyP complex, which is similar to the porphyrin absorption spectrum, showing little or no evidence of energy transfer between the central and peripheral groups through the orthogonal pyridine bridge.

Based on flash-photolysis measurements, it was possible to characterize the lowest excited state of the TRuPyPz complex from the differential absorption spectrum, as shown in Fig. 5. The observed bands at 474 and 577 nm, and the bleaching of the Soret band at 417 nm are consistent with the porphyrazine triplet state T_1 . The life-time of this state is $5.9 \times 10^{-6} \text{ s}$. In contrast with the S_1 state, the triplet state is efficiently quenched by molecular oxygen, as shown in Fig. 6, exhibiting a second order rate constant of $1.9 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. This result is similar to the $^1\text{O}_2$ generation rate found for tetraphenylporphyrin, a typical photosensitizer for this energy transfer process [25].

The luminescence decay profiles, monitored at 1270 nm after pulsed laser excitation (Fig. 7) of the supramolecular porphyrazine species in the presence of molecular oxygen, led to a lifetime of $\tau=71 \mu\text{s}$ in acetonitrile. This result is analogous to that obtained using TPP as standard, confirming that the quenching of the T_1 state by dioxygen proceeds via an energy transfer mechanism and involves the formation of $^1\text{O}_2$.

4. Final remarks

The electronic conjugation between the pyridine and porphyrazine rings promotes an efficient communication between the peripheral and central groups, which is reflected in the emission spectra and their corresponding excitation profiles. This type of behavior reveals an antenna effect in the TRuPyPz system, contrasting with the photophysical

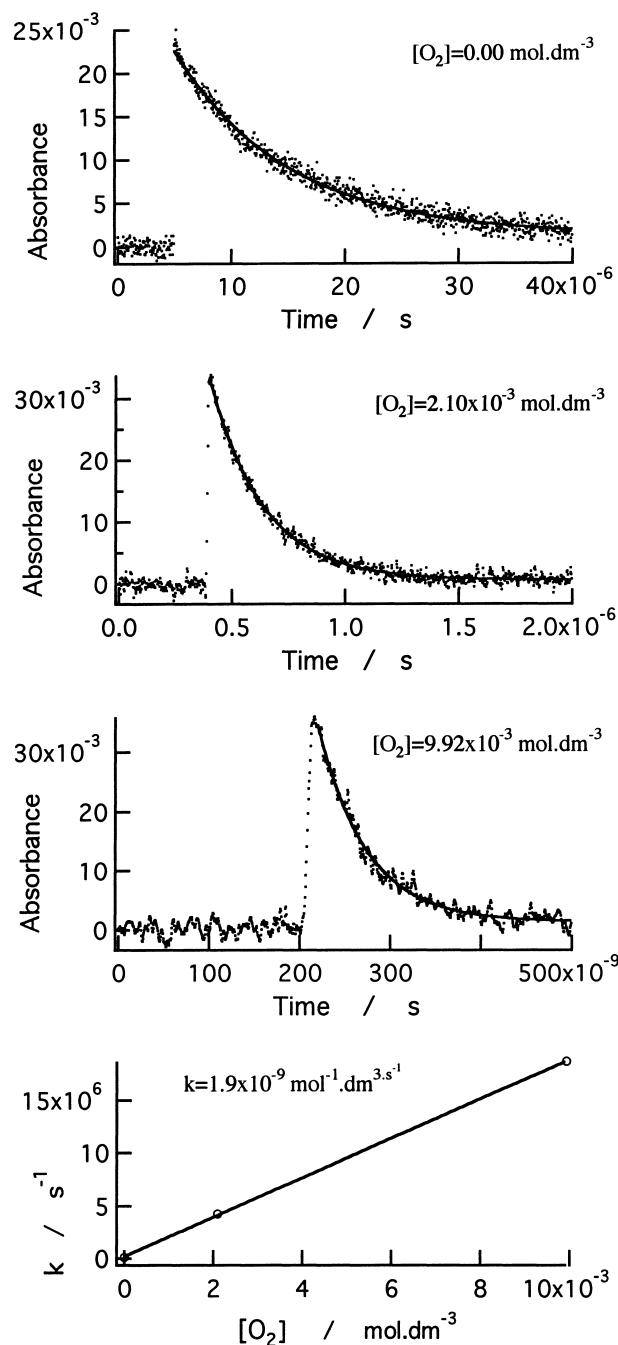


Fig. 6. Kinetic plots illustrating the decay of the TRuPyPz triplet state, and the first order quenching behavior as a function of the concentration of molecular oxygen, in acetonitrile solution, $T=25^{\circ}\text{C}$.

properties of the TRuPyP analogue, where the pyridyl groups are orthogonal to the porphyrin ring. In spite of the strong coupling between the central and peripheral groups, the electronic properties of the ruthenium complexes are preserved, exhibiting similar redox potentials and spectroelectrochemical behavior. In this sense, the tetra-ruthenated porphyrine cannot be regarded as a tetranuclear metal cluster kept by strong metal–metal bonds or exhibiting a completely delocalized electronic structure. In fact, the

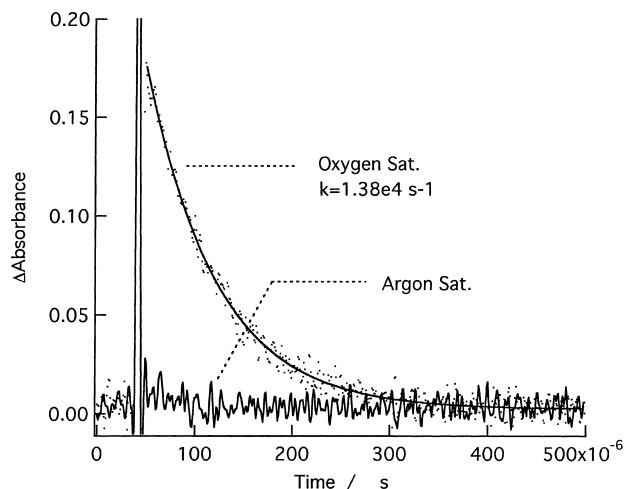


Fig. 7. Luminescence decay monitored at 1270 nm, characteristic of the $^1\text{O}_2$ species generated by flash-photolysis of TRuPyPz ($2.0\ \mu\text{mol dm}^{-3}$) in oxygen saturated acetonitrile solution.

porphyrine center acts as a conjugated bridging unit for assembling the tetra-ruthenated species by means of the strong metal–ligand interactions, which are typical of the metal complexes with N-heterocyclic ligands. The interesting photophysical properties, as related to the antenna effect, reflect the importance of the metal–ligand interactions in the electronic properties of the supramolecular species. This finding provided new insights relative to the structure of compounds which are potentially interesting for PDT and $^1\text{O}_2$ related studies.

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