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Modulation of vectorial energy transfer in the tetrakis[tris(bipyridine)ruthenium(II)]porphyrinate zinc complex

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Abstract

Reported are the synthesis and photophysical properties of a new supermolecular zinc porphyrin containing four tris(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II) complexes as substituents at the *meso* position. In this system, the lowest energy singlet excited state of the zinc porphyrin is energetically close to the tris(bipyridine)ruthenium(II) triplet MLCT excited state. The fact that the zinc porphyrin states are sensitive to ligand coordination effects, in contrast with the ruthenium(II) moieties, has allowed a selective tuning of the ruthenium complex and porphyrin excited states, providing an efficient control of the vectorial energy transfer process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supramolecular porphyrin; Energy transfer; Photophysics; Ruthenium complexes; Flash-photolysis

1. Introduction

One of the most important features responsible for the great efficiency of photosynthesis is the energy transfer process from the neighboring chromophores to the special pair, through the so-called antenna effect [1–19]. Because of their key role, energy transfer processes have been extensively studied for a number of systems. For example, Lehn [20] has shown that the luminescence from Eu^{2+} ion is enhanced by the energy transfer from the criptate ligand containing three 2,2′-bipyridine subunits, especially when excited in the intra-ligand $p\pi \rightarrow p\pi^*$ transition. Supermolecules constituted by porphyrins and tris(bipyridine)ruthenium(II) derivatives have already been studied, but no clear evidence of energy transfer process has been found [21,22].

In the last 10 years, we have been studying a novel class of supermolecules constituted by porphyrins and ruthenium complexes [1,6,23–41]. Their remarkable photochemical and photophysical properties, particularly, in the case of the free-base and zinc porphyrins coordinated to four $[Ru(bipy)_2Cl]^+$ groups, are reflected in their luminescence and capability to interact strongly with calf thymus DNA [1,25,31,34], inducing the strand damage by in situ generation of singlet oxygen. Now, we report a new zinc porphyrin species particularly suitable for exploiting the occurrence of vectorial energy transfer [3,6,10,42]. In our molecular design, the porphyrin ring was modified with four tris(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II) complexes covalently bound at the *meso* positions (Fig. 1). In this system, the excited triplet MLCT states of the ruthenium complexes are energetically close to the lowest singlet excited state of the zinc porphyrin. This feature makes possible the tuning of the vectorial energy transfer process between those moieties by perturbing the porphyrin energy levels via metal–ligand coordination effects.

2. Experimental

The precursor species 4′-methyl-4-(2,2′-bipyridylcarboxaldehyde) was obtained by refluxing 4.9 g (26.6 mmol) of 4,4′-dimethyl-2,2′-bipyridine with recently prepared and recrystalized SeO_2 (5.0 g, 45 mmol) in dioxane for 140 h [43]. The reaction mixture was filtered while hot through a celite bed and purified by column chromatography in silica gel, using ethyl acetate as eluent. ^1H-NMR in $CDCl_3$: 2.43 (s, 3H); 7.17 (dd, 1H, $J = 5.1$ and 1.5 Hz); 7.69 (dd, 1H, $J = 4.6$ and 1.0 Hz); 8.35 (d, 1H, $J = 1.0$ Hz), 8.54 (dd, 1H, $J = 5.1$ and 1.0 Hz); 8.87 (dd, 1H, $J = 1.5$ and 1.0 Hz); 8.92 (dd, 1H, $J = 4.6$ and 1.0 Hz); 10.17 (s, 1H).

5,10,15,20-Tetra{4′-methyl-4-(2,2′-bipyridyl)}porphyrin, $H_2TBipyP$, was prepared by refluxing 5.6 g (28.3 mmol) of 4′-methyl-4-(2,2′-bipyridylcarboxaldehyde) and 2.0 g of

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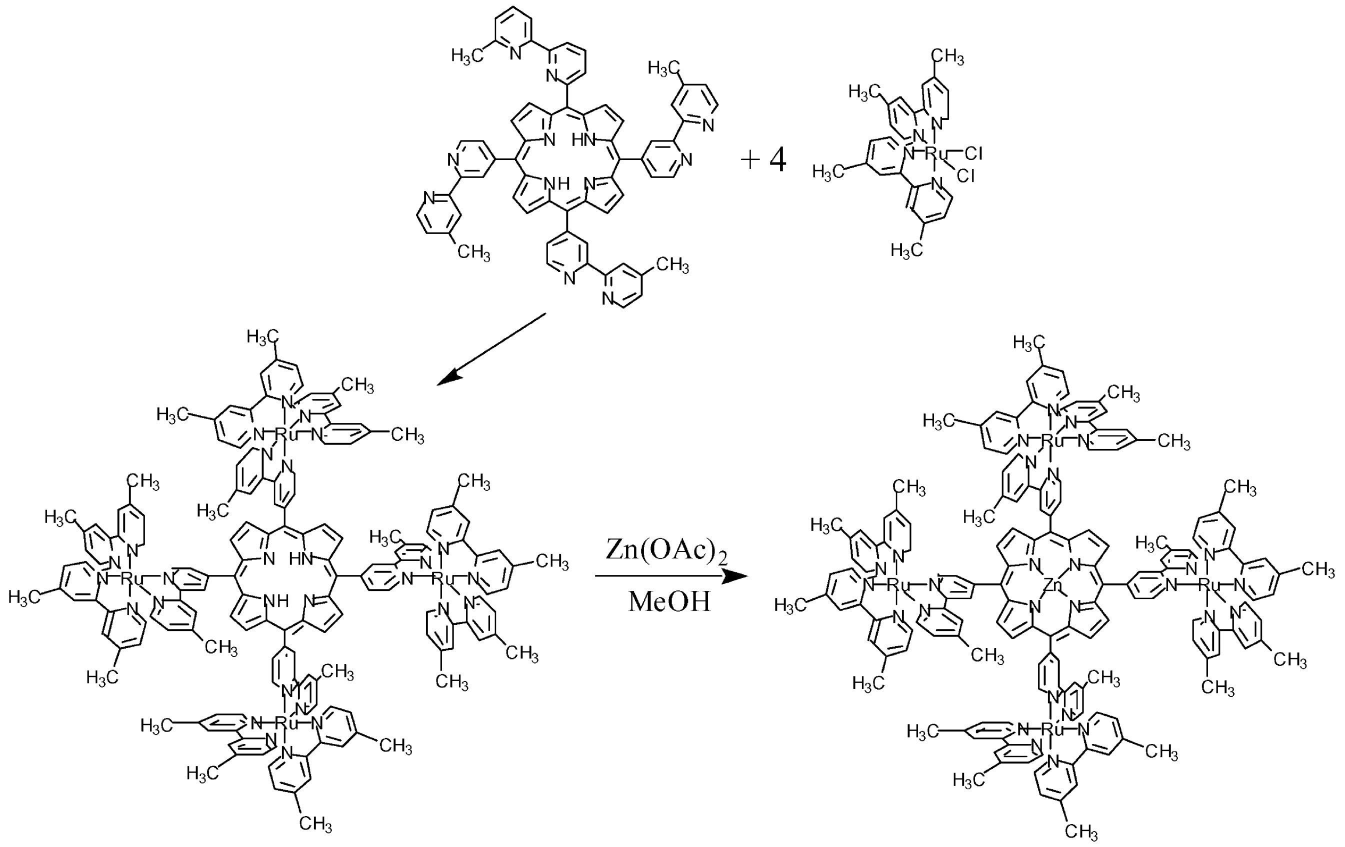

Fig. 1. Scheme showing the assembly of the supramolecular species [H_2TBipyP{Ru(dmbipy)$_2$}$_4$] from the bipyridylporphyrin and [Ru(4,4′-dmbipy)$_2$$Cl_2$], followed by the metallation reaction with zinc acetate to obtain the zinc derivative [ZnTBipyP{Ru(dmbipy)$_2$}$_4$].

pyrrole (29.8 mmol) in propionic acid. The resultant black tar was washed with 2 M HCl and the porphyrin collected as a green solution. This was concentrated in a flash-evaporator and neutralized with NaOAc. The precipitate was centrifuged, washed with water, then with diethylether and dried under vacuum in a dessicator. The yield was 350 mg (5%).

[Ru(dmbipy)$_2$$Cl_2$] complex was synthesized by refluxing $RuCl_3 \cdot nH_2O$, 4,4′-dimethyl-2,2′-bipyridine (dmbipy) and an excess of LiCl in DMF [44]. [H_2TBipyP{Ru(dmbipy)$_2$}$_4$] (TFMS)$_8$ was obtained by refluxing 112.9 mg of H_2TBipyP with an excess (62 mg) of [Ru(dmbipy)$_2$$Cl_2$], in glacial acetic acid [1,25,26,28]. The solvent was removed and the solid dissolved in DCM/EtOH 10:1 and purified by column chromatography using neutral Al_2O_3 as stationary phase. The solvent was removed and the solid recrystallized twice from a dilute lithium trifluoromethanesulfonate aqueous solution. The yield was 80%. Analysis for $C_{168}H_{170}F_{24}N_{28}O_{38}Ru_4S_8$, % exp. (calc.): C = 44.65 (46.86); H = 3.65 (3.98); N = 9.02 (9.11). [ZnTBipyP{Ru (dmbipy)$_2$}$_4$](TFMS)$_8$ complex was obtained by refluxing the free-base with zinc acetate dihydrate (twice its stoichiometric amount) in methanol. The solvent was removed and the product was purified by a similar procedure used for the free-base derivative. The yield was 80%. Analysis for $C_{168}H_{168}F_{24}N_{28}O_{38}Ru_4S_8Zn$, % exp. (calc.): C = 45.95 (46.18); H = 3.92 (3.88); N = 9.08 (8.98).

The cyclic voltammograms were obtained with a Princeton Applied Research model 283 potentiostat/galvanostat, using a Research Electrochemistry Software, version 4.30. A conventional three electrodes cell consisting of a platinum disk working electrode, Ag/Ag$^+$ (0.010 M in acetonitrile, $E = 0.503$ V vs. SHE) reference electrode in acetonitrile and a coiled platinum wire auxiliary electrode, was employed.

UV–visible spectra were recorded on an HP-8453A diode-array spectrophotometer. The spectroelectrochemistry measurements were carried out using a thin-layer cell [1,25,28] and a PAR model 173 potentiostat/galvanostat in parallel with an HP-8453A spectrophotometer. Freshly distilled and dried dimethylformamide was employed for the electrochemistry and spectroelectrochemistry experiments.

The emission and excitation spectra were obtained on a Photon Technology, model LS100 spectrofluorimeter. The triplet state lifetimes and excited state differential spectrum was recorded on an Edinburgh Analytical Instruments, model LP900S1 flash-photolysis equipment, with a Continuum Surelite II-10 pulsed laser (width $\cong$ 5 ns) at 90° to the analyzing beam.

3. Results and discussion

The new supramolecular porphyrin $[H_2TBipyP\{Ru(dmbipy)_2\}_4]^{8+}$ has been isolated, exhibiting consistent analytical data. It possesses 8+ net charge and is soluble in most polar solvents. According to molecular mechanics calculation, the internal rotational barriers are rather small, such that the presence of atropisomers can be neglected. In spite of the high positive charge on the $[H_2TBipyP\{Ru(dmbipy)_2\}_4]^{8+}$ supermolecule, the coordination of Zn^{2+} ion is fast and can be accomplished in few minutes. The resultant $[ZnTBipyP\{Ru(dmbipy)_2\}_4]^{8+}$ species exhibited a characteristic metalloporphyrin spectrum with D_{4h} symmetry (Fig. 2), with absorption bands at 437 (Soret), 570 and 615 nm; in addition to the ruthenium complex bands at 295 ($\pi \rightarrow \pi^*$) and 490 nm (MLCT). The zinc derivative cannot be protonated but its energy levels can be tuned by the coordination of a suitable fifth axial ligand, such as pyridine or imidazole.

All the characteristic porphyrin and $[Ru^{II}(dmbipy)_3]$ complex transitions can be found in the spectra of the supermolecular species shown in Fig. 2. It is interesting to note that the Soret band is broadened and less intense than in conventional or analogous [15,17] supermolecular porphyrins. This behavior was previously [13] ascribed to the coupling between the transition moment vectors of the Soret and $Ru^{II}(d\pi) \rightarrow bipy(p\pi^*)$ transitions. The effectiveness of such coupling depends on two factors: the difference between the transition energies and the oscillator strengths. The coupling is favored when the difference between the transition energies tends to zero and the oscillator strengths are high. In the case of $[ZnTBipyP\{Ru(dmbipy)_2\}_4]$, the porphyrin transitions are sensitive to coordination effects, while the ruthenium complex transitions are virtually insensitive. This characteristic can be used to shift the porphyrin energy levels, and tune the electronic coupling between the central and peripheral subunits.

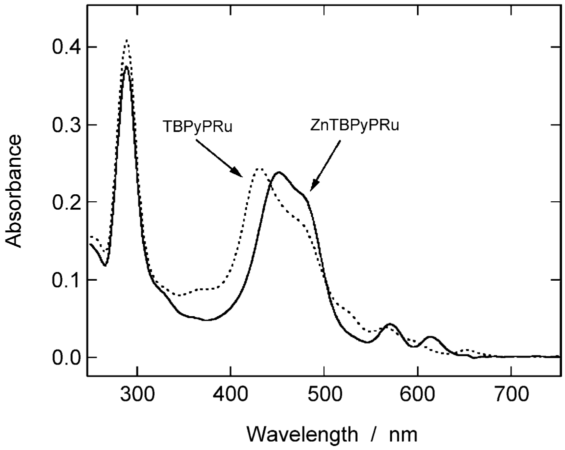

Fig. 2. Spectrum of the free-base supermolecular porphyrin in methanol solution before (dashed line: $[H_2TBipyP\{Ru(dmbipy)_2\}_4]$) and after (solid line: $[ZnTBipyP\{Ru(dmbipy)_2\}_4]$) the addition of zinc acetate.

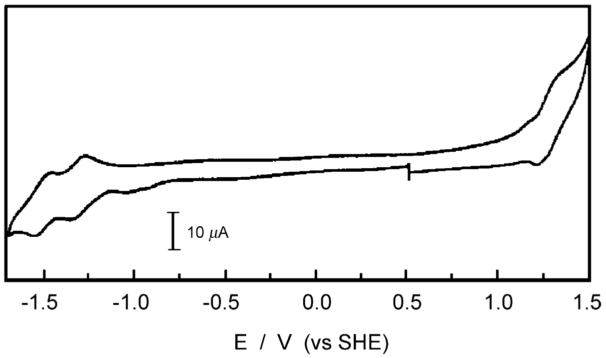

Fig. 3. Cyclic voltammetry of 1.0 mM ZnTDMBipyPRu4 solution in DMF containing 0.1 M $TEAClO_4$ as electrolyte; $v = 50\,mV/s$.

3.1. Electrochemistry and spectroelectrochemistry

A typical cyclic voltammogram of the zinc porphyrin supermolecule is shown in Fig. 3. The cathodic waves associated with the two monoelectronic reductions of the zinc porphyrin ring can be seen at −0.92 and −1.05 V, respectively. At negative potentials, two more waves can be observed at −1.32 and −1.55 V, exhibiting intensities four times greater than the previous one. These nearly coincide with the monoelectronic reduction potentials of the bipyridyl ligands of the peripheral ruthenium complexes in the related $[ZnTPyP\{Ru(bipy)_2Cl\}_4]$ complex [1]. In the positive side, the intense wave at 1.33 V was assigned to the Ru(III/II) process. This wave is preceded by a shoulder around 1.2 V attributed to the oxidation of the zinc porphyrin ring. The above assignment was confirmed by spectroelectrochemistry, as discussed below.

The oxidation of the supermolecule in the 1.00–1.22 V led to the selective decrease of the Soret (442 nm) and Q bands (567 and 612 nm) in comparison with the tris(bipyridine)ruthenium(II) $p\pi \rightarrow p\pi^*$ (287 nm) and MLCT band (~470 nm) of the peripheral complexes (Fig. 4A). At more positive potentials, i.e. 1.50 V, the $p\pi \rightarrow p\pi^*$ band was broadened and had its intensity decreased, while the MLCT band became faint (Fig. 4B), as expected for the oxidation of the $[Ru(bipy)_3]$ complex. The above results confirmed that the Ru(III/II) redox process is preceded by the oxidation of the zinc porphyrin ring.

In the negative side, no significant spectral changes were observed in the 0.0 to −0.7 V range. However, when the potential was shifted from −0.70 to −1.10 V, the Soret and Q bands became less intense while a shoulder and a broad absorption band appeared at 520 and 750 nm (Fig. 5A), respectively. Such spectral changes are consistent with the reduction of the porphyrin ring. The involvement of the bipyridine ligands can be ruled out because the $p\pi \rightarrow p\pi^*$ band at 296 nm remained almost unchanged during that process. Finally, when the potential was stepped further to −2.10 V, the bipyridine $p\pi \rightarrow p\pi^*$ band at 287 nm disappeared while a new broad band rose at 355 nm. Furthermore,

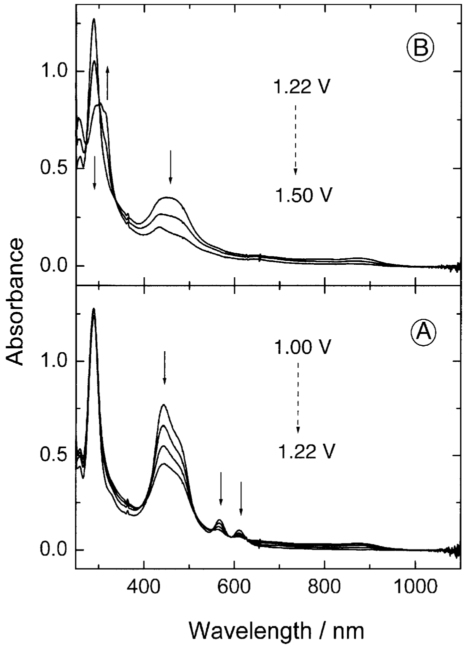

Fig. 4. Spectroelectrochemistry of ZnTDMBipyPRu4 in DMF containing 0.1 M $TEAClO_4$: (A) spectrum at 1.00 V and spectral changes monitored as a function of the time after stepping to 1.22 V; (B) spectral changes as a function of the time after stepping from 1.22 to 1.50 V.

the absorbance increased in the 500–550 nm range where it is located in the ruthenium complexes MLCT band and in the near infrared region, as expected for the formation of bipyridine radical anion (Fig. 5B). Those results are consistent with the monoelectronic reduction of all the bipyridine ligands, generating the respective radical anions. Therefore, the reduction wave of the third bipyridine ligand of the ruthenium complexes would be found around 2 V.

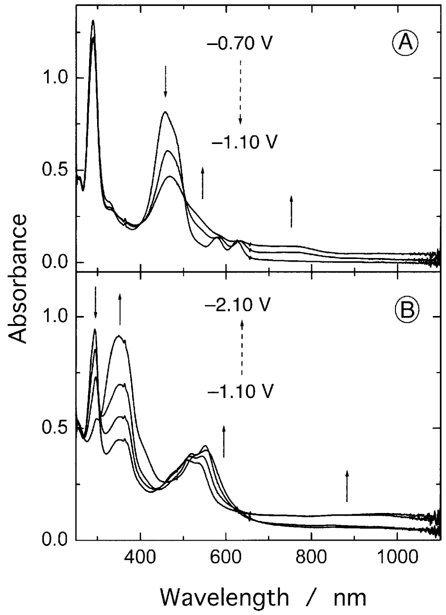

Fig. 5. Spectroelectrochemistry of ZnTDMBipyPRu4 in DMF containing 0.1 M $TEAClO_4$: (A) spectrum at −0.70 V and spectral changes as a function of the time after stepping to −1.10 V; (B) spectral changes as a function of the time after stepping from −1.10 to −2.10 V.

3.2. Excited state properties

The structure of [ZnTBipyP{Ru(dmbipy)$_2$}$_4$] molecule was especially designed for exploiting the occurrence of vectorial energy transfer from the peripheral ruthenium complexes to the porphyrin moiety. It is known that the excited electron in the MLCT state of ruthenium bipyridine complexes is localized in the bipyridine ring with the lowest energy π^* state. On the other hand, the π^* energy level of the 4,4′-dimethylbipyridine ligands in the $[Ru^{II}(4,4'\text{-dmbipy})_3]^{2+}$ complexes is higher than that of ruthenium complexes with non-substituted bipyridine ligands [45,46], such that their emission bands occur at 633 and 613 nm, respectively. In our case, all the bipyridine rings of the peripheral complexes have a methyl substituent, except for the bridging ring that is directly bound to the aromatic porphyrin ring. Thus the excited electron should preferentially be localized on the bridging pyridyl ring, thus facilitating the vectorial energy transfer processes from the ruthenium complexes to the porphyrin ring.

When excited at 500 nm (ruthenium complex MLCT transition) the [ZnTBipyP{Ru(dmbipy)$_2$}$_4$](TFMS)$_8$ exhibited predominantly ruthenium complex emission pattern, but showing significant contribution of the zinc porphyrin emission (Fig. 6A). But, at that excitation wavelength, one still can have some contribution from the direct excitation of the zinc porphyrin (Soret band). The excitation at the Q band farther from the MLCT band, could provide a better insight about the energy transfer process between those components. Consequently, one can have an insight about the relative energies of the zinc porphyrin S_1 and ruthenium complex $MLCT_1$ excited state. In fact, although the spectrum obtained after excitation at 570 nm (only the zinc porphyrin absorbs at this wavelength) is dominated by the zinc porphyrin emission, as shown in the deconvoluted spectrum of Fig. 6A (dotted lines); a significant contribution from [Ru(dmbipy)$_3$] complex emission was found. One can infer from those results that the S_1 and $MLCT_1$ states are rather close in energy, so that the hypothesis of thermally equilibrated excited $MLCT_1$ and porphyrin singlet states is quite plausible.

In order to selectively perturb the energies of those excited states, the fifth ligand coordinated to the zinc porphyrin center was exchanged by imidazole. The coordination of imidazole red shifted the zinc porphyrin bands from 450 (Soret), 570 and 614 nm to 457, 575 and 625 nm, lowering the energy of its excited state. In this case, the emission spectra of that supermolecule exhibited essentially a zinc porphyrin like pattern, when excited at both wavelengths 500 and 570 nm, as can be seen in Fig. 6B. Therefore, the small energy decrease of only about 290 cm^{-1} in the S_1 state was enough to drive the energy transfer from

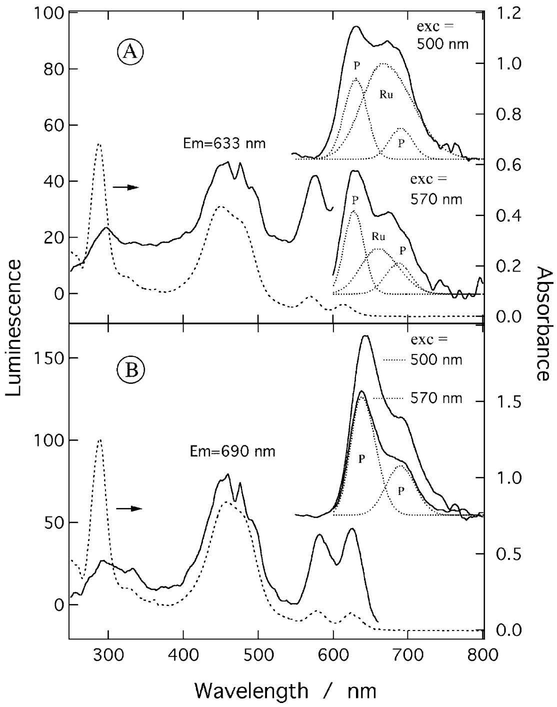

Fig. 6. Emission and excitation spectra (solid lines) of (A) [ZnTBipyP $\{Ru(dmbipy)_2\}_4](TFMS)_8$; (B) [ZnTBipyP$\{Ru(dmbipy)_2\}_4](TFMS)_8$ solution containing 0.28 M of imidazole in nitrogen-saturated EtOH. The absorption spectra (dashed lines) of both species were included for comparison. The deconvolution of the emission spectra are shown in dotted lines, where “P” and “Ru” stands for porphyrin and ruthenium complex emission bands, respectively.

the excited peripheral ruthenium complexes to the central zinc porphyrin moiety. This antenna effect was confirmed by the excitation spectrum, which roughly reproduced the zinc porphyrin and ruthenium complexes absorption bands (Fig. 6B), except at the bipyridine π–π^* transition band. This indicates that only the ^{3}MLCT state has been effective in transferring energy to the zinc porphyrin center. Consequently, the bipy ligand localized π–π^* excited state thermal decay is faster than the energy transfer pathway to the zinc porphyrin center. In addition, the internal conversion from that state to the ^{3}MLCT excited state is not efficient, leading to a poor luminescence response when the supermolecules are excited at bipy(π–π^*) absorption band.

Flamigni and co-workers [13,47] have shown that the strong spin–orbit coupling in the tris(bipyridine)ruthenium (II) complexes can relax the spin selection rule, making the energy transfer from the zinc porphyrin singlet excited state to the triplet $MLCT_1$ state or vice versa, very efficient. In the case of energy transfer from the zinc porphyrin, the rate constant should be sufficiently high to compete with other fast concurrent decay pathways. In the case of an energy transfer from the excited $MLCT_1$ state, the quantum yield is expected to be higher because the life time of this species is inherently longer.

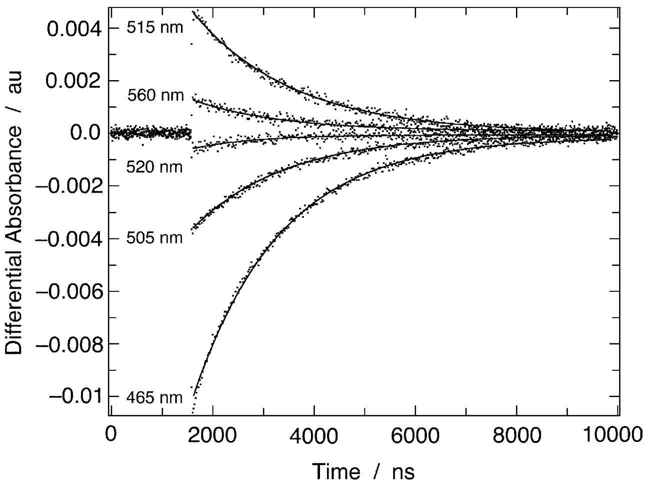

Fig. 7. Characteristic differential FP decay curves (dots) and the respective single exponential fittings (solid lines), obtained for a [ZnTBipyP $\{Ru(dmbipy)_2\}_4](TFMS)_8$ solution in ethanol, monitored at the wavelengths indicated in the figure.

The lifetime and the excited state spectra of the zinc supermolecular porphyrin were obtained by flash-photolysis (FP) in ethanol. All absorbance decay curves in the 350–750 nm range could be fitted by single exponential functions (Fig. 7) with equivalent rate constants, within the experimental error. The calculated decay rate constant and lifetime were $(6.0 \pm 0.1) \times 10^5\,s^{-1}$ and $1.7 \pm 0.1\,\mu s$, respectively. No relevant photochemistry was observed.

The differential spectrum and the corrected excited state spectrum of the zinc porphyrin supermolecules are shown in Fig. 8. The corrected excited state spectrum exhibited the bipyridine $p\pi \rightarrow p\pi^*$ intra-ligand and the $Ru^{II}(d\pi) \rightarrow$ bipy($p\pi^*$) MLCT absorption bands, characteristic of the tris(bipyridine)ruthenium(II) complexes. Nevertheless, the Soret and Q bands of the porphyrin moiety were strongly bleached and are absent in the corrected spectra, indicating that the lowest energy triplet excited state is localized on the porphyrin ring. The bleaching around 450 nm, observed

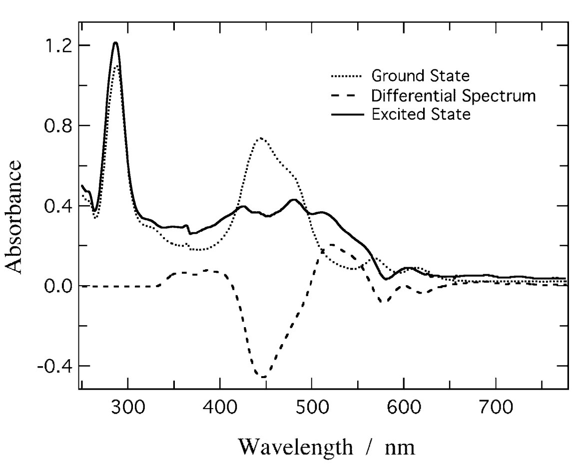

Fig. 8. Absorption (dotted lines), excited state differential (dashed lines) and corrected excited state (solid lines) spectra of [ZnTBipyP $\{Ru(dmbipy)_2\}_4](TFMS)_8$ in ethanol solution.

in the differential spectrum of the zinc derivative, clearly involves a highly broadened Soret band. This is another evidence for the occurrence of a quite strong electronic interaction between the Soret and MLCT states for this species.

4. Final remarks

The singlet excited S_1 state of the zinc porphyrin moiety is very close to the excited $^3MLCT_1$ state of the ruthenium complexes and probably are in thermal equilibrium. However, a small energy decrease in the zinc porphyrin S_1 excited state promoted by axial coordination of imidazole is enough to drive the energy transfer from the ruthenium complexes to the zinc porphyrin moiety. Furthermore, a quite strong coupling between the Soret and MLCT transitions is evidenced by the broadening of the Soret band in the absorption and excited state differential spectra. In conclusion, the ligand coordination effects can provide a fine tuning of the electronic coupling and energy transfer processes in porphyrin-based supermolecular species.

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