Pergamon

Tetrahedron Letters 41 (2000) 4781–4786

TETRAHEDRON
LETTERS

Synthesis and fluorescence behavior of novel $Ru(bpy)_3$–porphyrin conjugates

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Received 13 March 2000; revised 20 April 2000; accepted 21 April 2000

Abstract

No emission of photoexcited $Ru(bpy)_3$ was found in Fe and Mn porphyrin–$Ru(bpy)_3$ conjugates. In the case of free-base and Zn porphyrin–$Ru(bpy)_3$ conjugates, quenching of $Ru(bpy)_3$ emission and the appearance of considerable free-base and Zn porphyrin emissions were found. The excitation spectra of these emissions revealed however that these emissions originate from the corresponding excitation of free-base and Zn porphyrin moieties. These observations suggest efficient intramolecular electron transfer from the photoexcited $Ru(bpy)_3$ moiety to the free-base, Zn, Fe and Mn porphyrins. © 2000 Elsevier Science Ltd. All rights reserved.

Iron porphyrin containing monooxygenase enzyme cytochrome P450, has been the center of interest of numerous research groups in recent decades. Model studies of cytochrome P450's catalytic oxygenation properties have played a major role in the detailed understanding of the mechanistic steps involved in its catalytic cycle.[1] In one of the crucial steps, binding of dioxygen, the reduction of Fe^{3+} to Fe^{2+} is required. In model systems this is typically achieved either electrochemically, or by using external chemical electron donors. On the other hand, several investigations show that the reduction of Fe^{3+} to Fe^{2+} in porphyrins can be done by photoinduced electron transfer (ET) from electron donors to Fe^{3+}, but so far only very few studies have applied this approach to mimics of the cytochrome P450 oxygenation catalytic cycle.[2–5] Herein, we report the synthesis, and the ET properties as studied by steady-state fluorescence spectroscopy of porphyrin–$Ru(bpy)_3$ conjugates **1**–**4** (Scheme 1).

The synthesis of $Ru(bpy)_3$ moiety (**5**) (yield 74%) was achieved by mixing **7**[6] and *cis*-bis(2,2′-bipyridine)dichlororuthenium(II) hydrate, followed by anion exchange. The free-base porphyrin–$Ru(bpy)_3$ (**1**) was obtained by complete amidation of **6**[7] with the acid chloride of **5**. The quantitative metal insertions into **1** were based on the reported procedures.[8] The porphyrin–$Ru(bpy)_3$ framework provides a basis for building versatile porphyrin–$Ru(bpy)_3$ conjugates: the three α-amino

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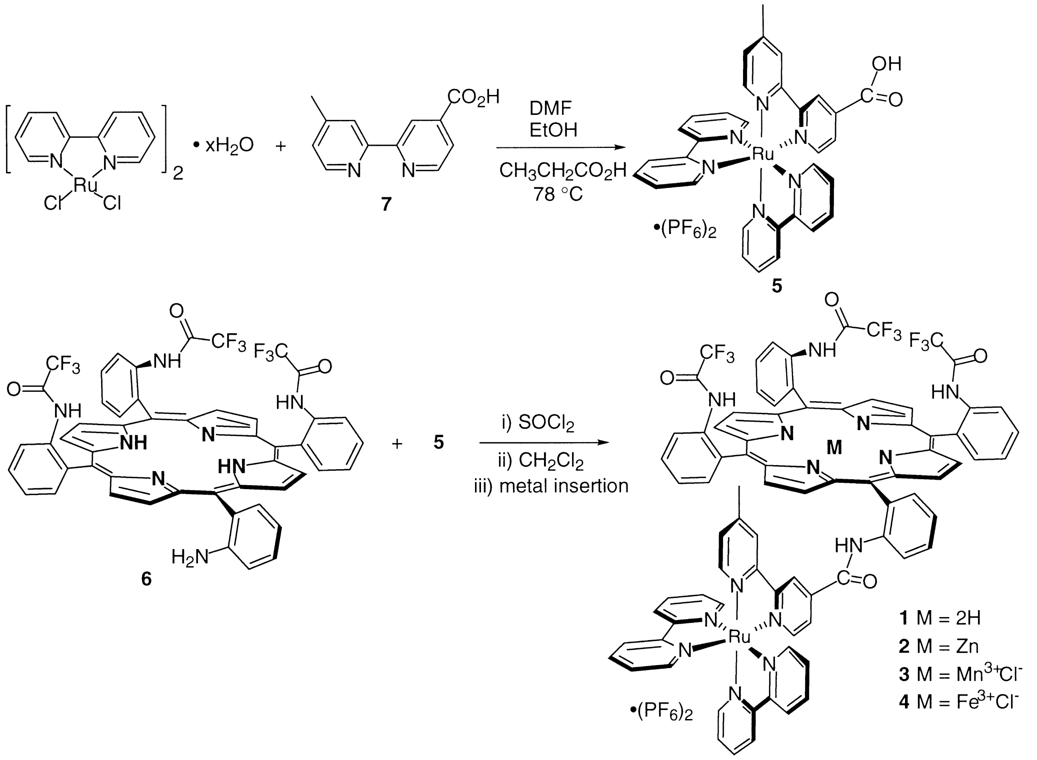
PII: S0040-4039(00)00673-0



Scheme 1.

groups of the porphyrin unit can be used to construct various environments depending on the desired target reaction and ligands; further, by choosing of the appropriate counter anions for the porphyrin and Ru(bpy)$_3$ units, and/or attaching lipophilic/hydrophilic groups onto the amino moieties of the porphyrin will allow us the use of a large variety of reaction media. Moreover **3** and **4** can be considered as potential photocatalysts for cytochrome P450-type oxygenations.

The high-resolution ^{1}H NMR spectrum of **1** reveals the close proximity of the Ru(bpy)$_3$ moiety to the porphyrin plane. This is seen by clear upfield shifts (ca. 1 ppm) of specific aromatic and methyl protons of Ru(bpy)$_3$ due to the porphyrin's ring current effect as compared to those in the parent compound **5**. All porphyrin–Ru(bpy)$_3$ conjugates reported here were further characterized by FAB mass spectrometry, showing clear molecular peaks.

UV/VIS spectra of **1**–**4** show two major absorption bands, which can be assigned to the LC band of Ru(bpy)$_3$ unit (290 nm) and the porphyrin's Soret band, see Table 1. These bands are located at the same wavelength as the corresponding reference compounds (**5** for Ru(bpy)$_3$ unit and tetraphenylporphyrin (TPP), ZnTPP, MnTPP and FeTPP for the corresponding porphyrin units), whereas comparison of the porphyrin's Q_{00} and Q_{01} bands in **1**–**4** to the corresponding reference porphyrins shows clear shifts of these bands suggesting some level of interaction between the intramolecular porphyrin and Ru(bpy)$_3$ chromophores. In addition, weak absorption of TPP reference compounds is found at the wavelength of LC band of Ru(bpy)$_3$ unit at 290 nm suggesting that the excitation at 290 nm also excites the porphyrin components in the present systems.

Table 1
UV/VIS and steady-state fluorescence spectroscopic data of porphyrin–Ru(bpy)$_3$ conjugates

System	λ_{abs}(nm) $\varepsilon/10^{-6}$ (M^{-1}cm^{-1})^a	λ_{ex}(nm)^b	Q*$_{X00}$ -Band		Q*$_{X01}$ -Band	
			λ_{em}(nm)^c	I_{em} x 10^{-2}(a.u.)	λ_{em}(nm)^c	I_{em} x 10^{-2}(a.u.)
1	420 (1.41), 289 (0.64)	289	647	204	712	241
2	426 (4.12), 290 (1.11)	290	610	52	649	109
3	470 (0.57), 289 (0.73)	289	n.d.	n.d.	n.d.	n.d.
4	417 (0.23), 290 (0.37)	290	649	17^d	n.d.	n.d.

^{a} in CH_2Cl_2 at 295 K. ^{b} λ_{ex} corresponds to the maximum of Ru(bpy)$_3$ unit's LC band. ^{c} originates from direct excitation of the porphyrin moiety at ~290 nm. ^{d} see reference 12.

Steady-state fluorescence spectroscopic data revealed very effective quenching of Ru(bpy)$_3$ emission in **3** and **4** compared to mixtures of **5** with MnTPP and FeTPP, respectively, indicating intramolecular ET from the photoexcited state of Ru(bpy)$_3$ moiety to the Fe and Mn porphyrins in these conjugates (Fig. 1). The calculated free energy changes[9] $(-\Delta G)_{calc}$ for *Ru(II)(bpy)$_3$Fe(III)por →Ru(III)(bpy)$_3$Fe(II)por (0.55–1.12 eV) and *Ru(II)(bpy)$_3$Mn(III)por→Ru(III)(bpy)$_3$Mn(II)por (0.64–0.85 eV) processes in different systems[9–11] also suggest that photoinduced ET occurs in **3** and **4**. In contrast to the mixture of **5** and FeTPP, the mixture of **5** and MnTPP shows some quenching of photoexcited **5** hinting at the possibility of a more favorable energy gap in **3** over **4** and indicating that a small contribution of intermolecular ET may occur in **3**. In the case of **1** and **2** efficient quenching of Ru(bpy)$_3$ and the appearance of significant porphyrin emissions were found upon Ru(bpy)$_3$ excitation. The excitation spectra revealed, however, that the emissions

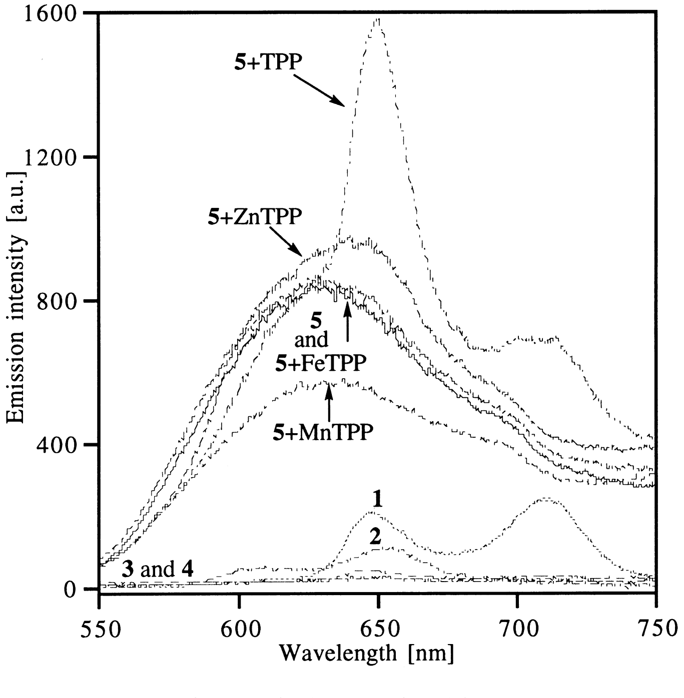


Figure 1. Steady-state fluorescence spectra of **1**–**5** and mixtures of **5** with TPP, ZnTPP, MnTPP and FeTPP (1.44×10^{-6} M) in CH_2Cl_2 at 295 K. Excitation of LC band of Ru(bpy)$_3$ component at 290 nm was performed

were obtained upon photoexcitation of porphyrin moieties at 290 nm, thus ruling out energy transfer as the origin of porphyrin moiety fluorescence in these systems. Also, comparison of the mixtures made of **5** with TPP or ZnTPP showed practically no quenching of photoexcited Ru(bpy)$_3$ emission, suggesting an intramolecular photoinduced ET channel for quenching of the Ru(bpy)$_3$ moiety also in **1** and **2** (Fig. 1). The $-\Delta G_{\mathrm{calc}}$ values for these ET processes are 0.40 and 0.17 eV for **1** and **2**, respectively, from different systems.[9–11]

Excitation of the porphyrin components (Soret region) in **1** and **2** revealed substantial quenching of porphyrin emission when compared to the fluorescence emission intensities with TPP and ZnTPP, respectively (Fig. 2). The $-\Delta G_{\mathrm{calc}}$ values however (–0.70 and –0.17 eV for **1** and **2**, respectively)[9–11] suggest that this quenching is not due to ET from the porphyrin to Ru(bpy)$_3$ moiety, but because of probable ET reducing the singlet porphyrin. The energies of the singlet porphyrins in **1** and **2** are estimated to be close to their corresponding P^-–Ru(III) states (the energy difference, $\Delta E = 0.01$ and 0.06 eV for **1** and **2**, respectively)[9–11] allowing ET/charge recombination (CR) occur between these energy levels.

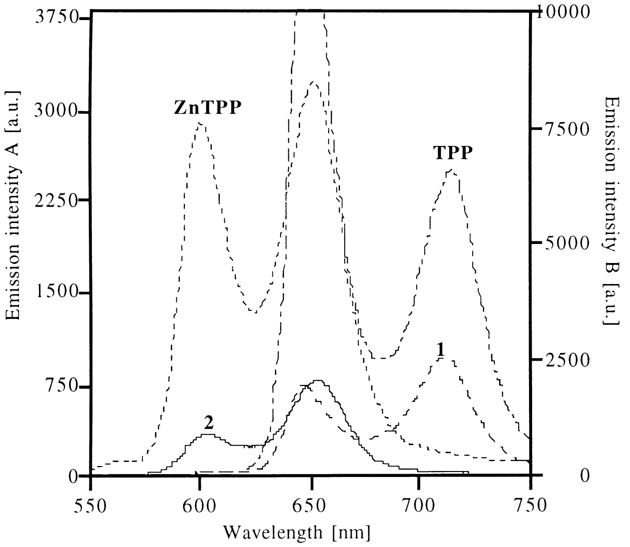


Figure 2. Steady-state fluorescence spectra of **2** and ZnTPP (emission intensity A) and **1** and TPP (emission intensity B) (1.44×10^{-6} M) in CH_2Cl_2 at 295 K. Excitation of porphyrin's Soret band was performed

Schematic representation (Fig. 3) shows the main pathways of ET and CR processes, as well as excitations and emissions in the present porphyrin–Ru(bpy)$_3$ conjugates. The triplet state of Ru(II) was found to reduce the porphyrin units in **1** and **2**. Further, there is a probable ET/CR channel between the singlet porphyrins and corresponding P^-–Ru(III) states in **1** and **2**. Another probable ET/CR pathway exists from the triplet state of Ru(II) to form ZnP^+–Ru(I) ($\Delta E = 0.08$ eV),[9–11] but in the case of H_2P^+–Ru(I) the energy cost for the same process is unfavorable by 0.30 eV. Charge recombination of the ZnP^+–Ru(I) state leads to the singlet porphyrin which may give emission as well.

The triplet state of Ru(II) transfers an electron to Mn and Fe porphyrins in **3** and **4** followed by CR. Thus, only effective quenching of Ru(bpy)$_3$ emissions was found upon Ru(II) excitation.

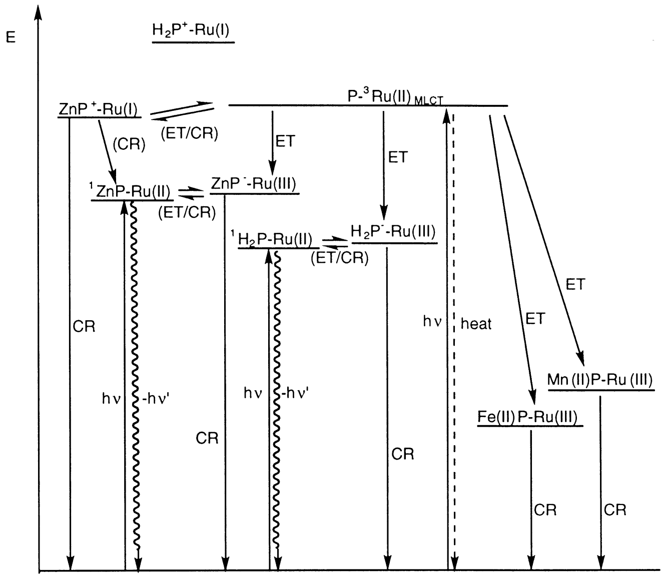


Figure 3. Schematic presentation of relaxation pathways of photoexcited Ru(II)(bpy)$_3$ and porphyrin units in **1**–**4**. Abbreviations: ET = electron transfer, (ET) = probable electron transfer, CR = charge recombination, (CR) = probable charge recombination, hν = excitation, –hν = emission

Further studies, including time-resolved spectroscopic measurements to elucidate the detailed mechanisms of the photoinduced ET processes of these conjugates are currently in progress.

Acknowledgements

We would like to thank Dr. G. A. Hembury for assistance in the preparation of this manuscript.

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9. The free energy values are tentative and obtained from $-\Delta G = E_{00}-(E_{ox}-E_{red})$, where the E_{00} values are based on the intercepts of corresponding absorption and emission bands in **1**, **2**, **5**, and E_{ox} and E_{red} are from cited literature.

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12. The small emission at 649 nm for **4** was found when either the LC band of $Ru(bpy)_3$ component (290 nm) or the Soret band of Fe porphyrin component (417 nm) was excited. The same emission was found from column chromatographically purified commercial FeTPP, suggesting that the origin of this emission is some impurity other than free-base porphyrin ($\lambda_{em} = 651$ and 715 nm).