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Study of the Suppression of Porphyrin Emission upon Addition of Rare Earth Ions

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Abstract. A topic of constant investigation in recent decades has been the study of electron and/or energy transfer reactions in supramolecular systems. The energy transfer between donor-acceptor depends on the influence of the substituent in the intersystem crossing. The competition between the radiative and non-radiative processes also depends on other factors such as temperature, solvent and energy gap. In this work, we have studied the suppression of the emission of monocarboxyphenyl porphyrins after addition of rare earth ions (RE(III)). The porphyrin emission decreases with the addition of RE(III), no matter which ion is present. When Eu(III) was used, the emission of this ion was not observed either. This suppression happens due to the effect of the heavy atom and not due to the energy transfer through electronic levels between the porphyrin and the RE(III). After the addition of RE(III), the lifetime for $MCTPPH_2$ started to decay biexponentially, indicating the formation of a new species ($MCTPPH_2$-RE(III)) of a shorter lifetime. The presence of NO_2 groups in the ortho mesoaryl positions of $MCTNPPH_2$ and the presence of Zn(II) in Zn(MCTPP) decreased both the porphyrin lifetime and emission due to an increase in the spin-orbit coupling.

Key words: rare earth, porphyrins, energy transfer, luminescence.

1. Introduction

Many model compounds have been prepared in an effort to understand the photosynthetic system and the processes involved in the use of solar energy [1–3]. Investigations of fundamental photochemical and photophysical processes such as electron transfer are being accomplished with great frequency. Such works investigate not only the fundamental principles involved in energy transfer: the separation distance between donor and acceptor, the orientation, the directional forces and the environment [3–10], but also its practical applications. Photo-induced transfer is promising for several industrial, medical and environmental applications. Among its most important practical applications are chemical sensors, which are highly sensitive for the detection of the fluorescence of small molecules [11, 12].

Porphyrins and metalloporphyrins have been used as efficient catalysts in both hydroxylation of saturated hydrocarbons and olefin epoxidation. They have also

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been used in (i) cancer photodynamic therapy, (ii) correction of disorders of the heme metabolism [13, 14], (iii) control of supramolecular structures synthesis [15, 16] and (iv) study of energy/electron transfer [17, 18]. Porphyrins have shown that factors such as the distance of energy transfer, the molecular geometry and the difference in electronic potentials are important for a well-defined electronic transfer to be accomplished. It is known that when the donor and the acceptor are tied up by a rigid spacer, the transfer rates are directly related to the electronic structure and the length of the spacer. The rate of electronic transfer through aromatic spacers is significantly less dependent on the donor-acceptor distance than is the electronic transfer through aliphatic spacers [19]. MacLendon and his research group have observed that the electronic coupling is not large for a supramolecular system containing a free-base porphyrin tied to an iron porphyrin through a phenyl spacer. This suggests that the participation of the phenyl spacer π system in the electron transfer is weak [20]. In this same work, the dependence of the distance between the porphyrin complexes and their preferential orientation are also reported for the two porphyrins tied up by a variety of spacers. When the rings are perpendicular to each other, electron transfer does not occur. It only takes place when the angle between the two porphyrin complexes is less than 45° [8, 9]. Work such as that of Sessler [3, 6, 7] reports a new series of photosynthetic models. These compounds present key biomimetic components which enable the study of orientation, energy and interchromophore effects. They also allow the study of the influence of both the porphyrin rings disposition and the energy of the components of an electron transport chain. A series of porphyrin dimers tied up by a quinone spacer have been used. The rates of electron transfer between the singlet state of the porphyrin and the quinone were shown to be extremely fast, thus facilitating transfer between the two porphyrins.

The energy transfer between a donor and an acceptor also depends on the influence of the substituent in the spin-orbit coupling, which in turn facilitates the intersystem crossing. The competition between the radiative and non-radiative processes depends on factors such as temperature, solvent and energy difference [21]. Fluorescence suppression refers to any process that leads to a decrease in the intensity of the fluorescence of a certain compound. A variety of processes can result in suppression. These include reactions in the excited state, energy transfer, formation of complexes and suppression through collision of molecules [11]. In solution, most suppressions happen through diffusion processes. The revenue of the fluorescence of an organic molecule is reduced in the presence of a suppressor molecule such as dioxygen or halogen. The magnitude of the suppression linearly depends on the concentration of the suppressor and obeys Stern Volmer kinetics [11]. The suppression of the fluorescence by halogens, also called the heavy atom effect, is a simpler process than is the suppression by dioxygen. The perturbation produced by the halogen atom induces a larger spin-orbit coupling leading to an increase in the rate of intersystem crossing.

In this work we have studied the equilibrium constant (K) and the suppression of the emission of monocarboxyphenyl-substituted porphyrins after the addition of aliquots of RE(III). The porphyrins used were mono*para*carboxyphenyl*tri*phenylporphyrin ($MCTPPH_2$), its zinc complex (Zn(MCTPP)) and mono*para*carboxyphenyl*tri*orthonitrophenylporphyrin ($MCTNPPH_2$). The porphyrin synthesis and zinc insertion were performed in our laboratory by Gonsalves' [23] and Buchler's methods [24], respectively.

2. Experimental

Zn(MCTPP) and $MCTNPPH_2$ porphyrins were spectrofluorimetrically titrated with Eu(III) and $MCTPPH_2$ was titrated with Eu(III), Tb(III), Gd(III) and La(III), in methanol (MeOH). After each titration, the lifetimes for these porphyrins were determined using a FL 900 – Edinburgh Analytical Instruments spectrometer and its software. The lifetime for $MCTPPH_2$ was also measured in the absence of RE(III). The equilibrium constants (K) between Eu(III) and the porphyrins (interaction between the carboxyphenyl group and Eu(III)) were evaluated with the aid of the computational software SEQS [25] and by the Stern Volmer [11] graphic method (F_0/F *versus* [Eu(III)]).

Methanol solutions of $MCTPPH_2$ (1.75×10^{-5} mol/L) were spectrofluorimetrically titrated with solutions of $EuCl_3$ (1.00×10^{-3} mol/L), $TbCl_3$ (1.00×10^{-3} mol/L), $GdCl_3$ (1.00×10^{-3} mol/L) and $LaCl_3$ (1.93×10^{-3} mol/L). Solutions of Zn(MCTPP) and $MCTNPPH_2$ (6.80×10^{-6} mol/L and 1.89×10^{-5} mol/L, respectively) were titrated with a solution of $EuCl_3$ (1.00×10^{-3} mol/L). The porphyrin solution (3.00 mL) was titrated in a quartz cell of four polished sides (1.00×1.00 cm) with aliquots of 20 μL of the RE(III) solution. The emission spectra were measured in a Spectrofluorometer – SPEX FLUOROLOG II, after each addition. We also obtained the absorption spectrum after each titration in order to verify if the porphyrins had been demetallated or not.

The constants(K) for the equilibrium:

$$P^- + \text{Eu(III)} \leftrightharpoons \text{(PEu)(II)}$$

were calculated for the porphyrins: $MCTPPH_2$, Zn(MCTPP) and $MCTNPPH_2$, through the graphic method of Stern-Volmer and the computational program SEQS. Initially, the K constant was established through the software SEQS [25] using data taken from the titrations and substituting them in to the folowing equations:

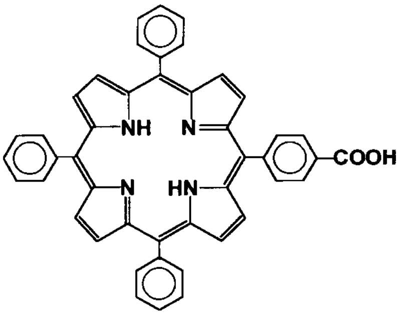
$$K = [PEU1]/([P1]^*[EU1]) \tag{1}$$

$$I1 = (E1^*[P1]) + (E2^*[PEU1]) \tag{2}$$

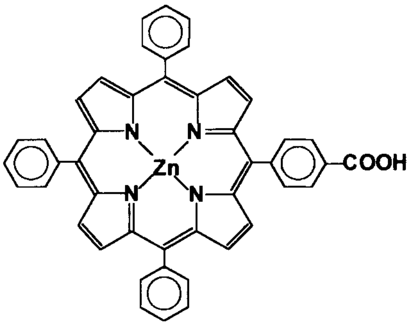
$$[PI1] = [P1] + [PEU1] \tag{3}$$

$$[EUI1] = [PEU1] + [EU1] \tag{4}$$

MCTPPH$_2$



ZnMCTPP



MCTNPPH$_2$

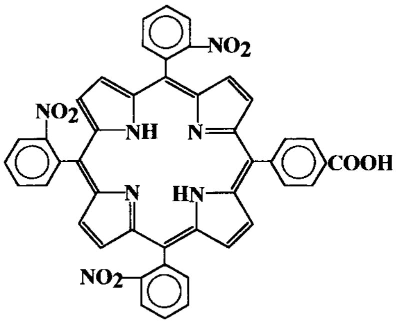


Figure 1. Structures of the porphyrins.

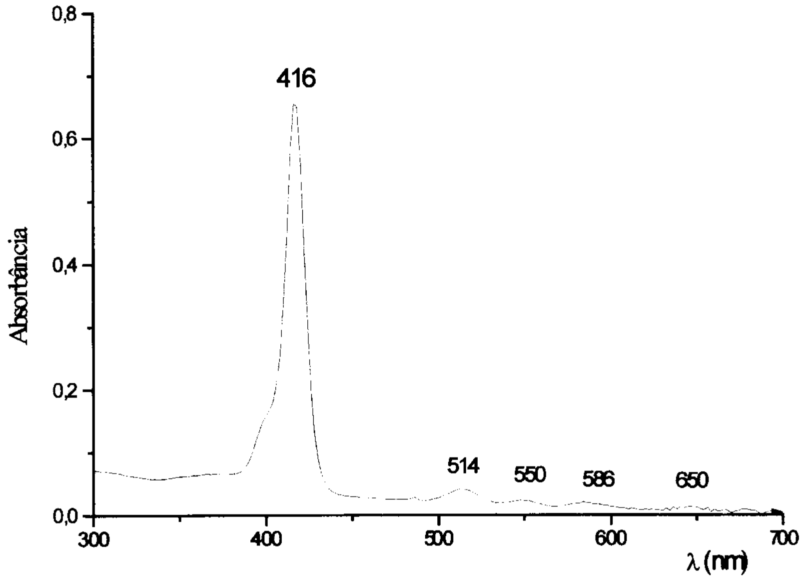


Figure 2. UV-Vis Spectra of MCTPP in MeOH. (9.96×10^{-6} mol L^{-1}).

where the variables are:

K = equilibrium constant;
[PEU1] = concentration of the porphyrin coordinated to Eu(III);
[P1] = concentration of free-porphyrin;
[EU1] = concentration of Eu(III);
I1 = relative intensity of the fluorescence of the porphyrin;
E1 = proportionality parameter of the intensity of the non-coordinated porphyrin;
E2 = proportionality parameter of the intensity of the coordinated porphyrin;
[PI1] = porphyrin total concentration;
[EUI1] = Eu(III) total concentration.

3. Results and Discussion

Figure 2 shows the absorption spectra obtained for MCTPPH$_2$, with bands at 416, 514, 550, 586 and 650 nm. The first excited level for Eu(III) and Tb(III) are at 580 nm (17,240 cm^{-1}, $^5D_0$) and 487 nm (20,530 cm^{-1},$^5D_4$), respectively. The titrations of MCTPPH$_2$ were spectrofluorimetrically followed by exciting the porphyrin to levels below the first excited level of the RE(III) ions: 592 nm (16,890 cm^{-1}) for Eu(III) and 512 nm (19,530 cm^{-1}), 592 nm (16,890 cm^{-1}) for Tb(III).

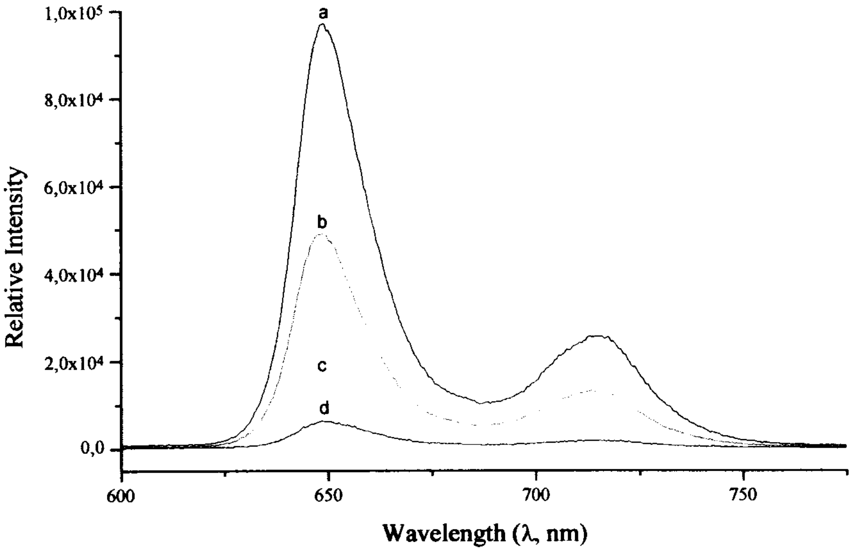


Figure 3. Luminescence spectra obtained in the titration of MCTPP/MeOH (9.96×10^{-6} mol L^{-1}), with $EuCl_3$/MeOH (**a** = 0.00; **b** = 1.00, **c** = 1.96, **d** = 3.85) $\times 10^{-5}$ mol L^{-1}.

The intensity of the bands in the emission spectra of $MCTPPH_2$ (λ_{exc} = 592 nm) decreased after each addition of Eu(III), Figure 3. The same decrease was also observed for Tb(III), (λ_{exc} = 512 and 592 nm).

This experiment leads to the conclusion that deactivation did not take place through the excited electronic energy levels of the porphyrin and RE(III), but it is most probably due to the heavy atom effect.

To confirm the effect of the heavy atom, we titrated $MCTPPH_2$ with Gd(III)and La(III) ions in methanol. In these ions, the first excited energy levels are over 30,000 cm^{-1} and no energy transfer occurs from the porphyrin to the ion. The emission spectra of $MCTPPH_2$ were obtained after each addition of Gd(III) and La(III) and we could observe a decrease in the emission bands of $MCTPPH_2$ (λ_{exc}= 423 nm).

The emission spectra of Zn(MCTPP) in methanol also presented a decrease in the intensity of the bands at 603 nm and 653 nm (λ_{exc} = 420 nm) after each addition of Eu(III), Figure 4. The same was observed for the titration of $MCTNPPH_2$ with Eu(III), for emission bands at 653 nm and 719 nm (λ_{exc} = 411 nm), Figure 5.

Lifetime measurements were performed in the initial methanol solution of $MCTPPH_2$ and after the addition of RE(III) ions, Table I. In Table II, we present the lifetimes obtained for $MCTPPH_2$ and Zn(MCTPP).

In Table I we observe that there are two lifetimes (biexponential decay) after the addition of the RE(III) ion, indicating the formation of a new species. This new species contains an RE(III) ion bound to the porphyrin and presents a lower lifetime due to the effect of the heavy atom. The heavy atom effect can be noticed if

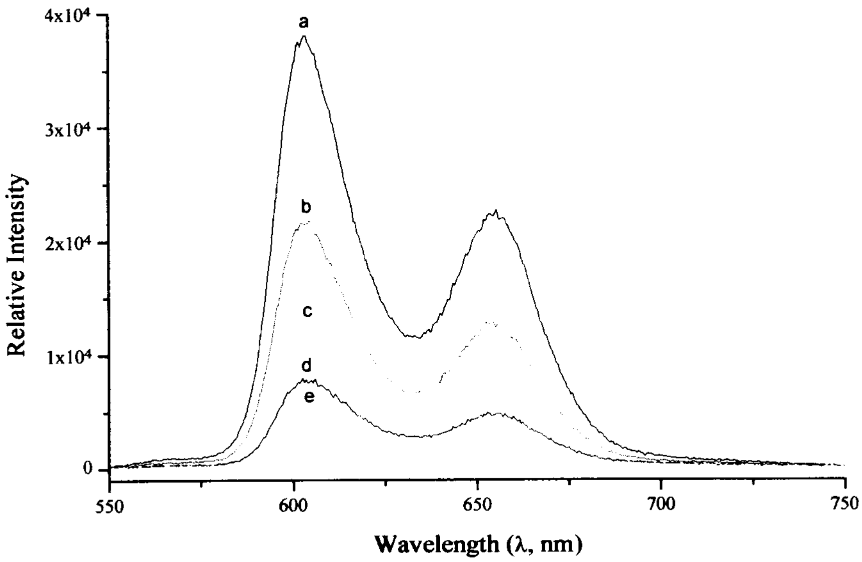


Figure 4. Luminescence spectra obtained in the titration of ZnMCTPP/MeOH (6.80×10^{-6} mol L^{-1}), with $EuCl_3$/MeOH (**a** = 0.00; **b** = 1.00, **c** = 1.96, **d**=2.91; **e** = 3.85) $\times 10^{-5}$ mol L^{-1}.

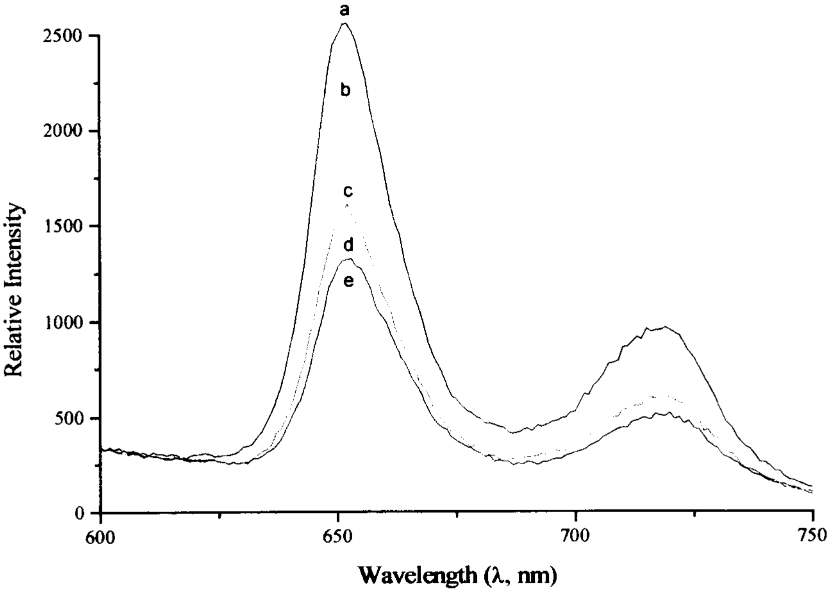


Figure 5. Luminescence spectra obtained in the titration of MCTNPP/MeOH (1.89×10^{-5} mol L^{-1}) with $EuCl_3$/MeOH (**a** = 0.00; **b** = 4.98; **c** = 9.90; **d** = 14.8; **e** = 19.6) $\times 10^{-6}$ mol L^{-1}.

Table I. Lifetimes for $MCTPPH_2$ and $MCTPPH_2$+RE(III) (λ_{exc} = 423 nm, λ_{em} = 650 nm)

Porphyrin	Lifetime (ns)	(%)
$MCTPPH_2$	$\tau 1 = 8.9$	100
$MCTPPH_2$ + Eu(III)	$\tau 1 = 8.7$	86.1
	$\tau 2 = 1.4$	13.9
$MCTPPH_2$ + Tb(III)	$\tau 1 = 8.8$	87.5
	$\tau 2 = 1.1$	12.5
$MCTPPH_2$ + Gd(III)	$\tau 1 = 8.4$	71.0
	$\tau 2 = 1.0$	29.0
$MCTPPH_2$ + La(III)	$\tau 1 = 9.2$	85.8
	$\tau 2 = 2.1$	14.2

Table II. Lifetimes for $MCTPPH_2$ and ZnMCTPP (λ_{exc}= 423 nm, λ_{em} = 650 nm)

Porphyrin	Lifetime (ns)	(%)
$MCTPPH_2$	$\tau 1 = 8.9$	100
ZnMCTPP	$\tau 1 = 1.9$	100

we consider the decrease in the lifetime from 9 ns to 2 ns for La(III) (139 amu) and from 9 ns to 1 ns for Gd(III) (157 amu). Table II shows there is a more pronounced heavy atom effect when Zn(II) is inserted into the porphyrin ring, lowering its lifetime. We must also mention that the lifetime for $MCTNPPH_2$, with 3 nitro groups, cannot be measured due to its low emission. This probably results in a lifetime in the sub-nanosecond scale. The presence of nitro groups favors the spin-orbit coupling, leading to a deactivation through intersystem crossing [21, 22].

The data from the spectrofluorimetric titrations were used to produce the equilibrium constants K:

$$P^{-} + Eu(III) \leftrightharpoons (EuP)(II)$$

K values obtained by the Stern Volmer graphic method and by the computational software SEQS are shown in Table III.

The values obtained for the equilibrium constants are in the order of 10^5 M^{-1}, indicating a great interaction between the carboxy groups and the Eu(III) ion in methanolic media. The values obtained by the two different methods of calculation are in good agreement.

Table III. Values of the equilibrium constant K for $[Eu(MCTPP)]^{2+}$, $[Eu(MCTPP)]^{2+}$ and $[Zn(MCTPP)\text{-}Eu]^{2+}$

Porphyrins	$[Eu(MCTPP)]^{2+}$	$[Zn(MCTPP)\text{-}Eu]^{2+}$	$[Eu(MCTNPP)]^{2+}$
K (SEQS)	5.9×10^5 M^{-1}	1.5×10^5 M^{-1}	1.8×10^5 M^{-1}
K (Stern Volmer)	4.7×10^5 M^{-1}	1.4×10^5 M^{-1}	1.4×10^5 M^{-1}

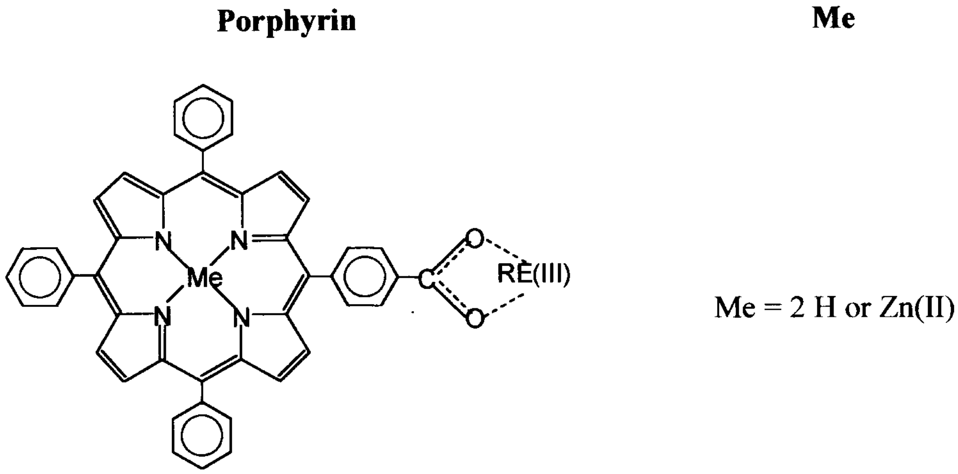


Figure 6. Porphyrin coordinated to the RE(III) ion.

4. Conclusion

The photo-excited emission of porphyrins in methanolic solution is supressed upon addition of RE(III) ions. This suppression happens due to the heavy atom effect [22], and not due to energy transfer between the porphyrin and the RE(III) through electronic levels. The heavy atom effect increases the spin-orbit coupling, leading to a deactivation through intersystem crossing [21, 22]. The presence of a heavy atom (RE(III)) promotes such crossing, increasing the conversion of the singlet to the triplet state, and from this latter state a non-radiative deactivation occurs through vibrational mechanisms. This deactivation only happens due to the coordination of the carboxyphenyl group of the porphyrin to the RE(III) ion [21, 26]. The equilibrium constants for this coordination are ca. 10^5 M^{-1}, in methanol. The presence of Zn(II) in the core of the porphyrin or of nitro groups attached to the phenyl rings results in lower equilibrium constants and lifetimes. In fact, solutions of ZnTPP and $TPPH_2$, which are neutral porphyrins without a coordinating site, were titrated under the same conditions and emission suppression was not observed. This indicates that a non-collisional quenching process occurs for the carboxylic porphyrins.

References

1. E. E. Bonfantini, A. K. Burrell, D. L. Officer, and D. C. Reid: *Inorg. Chem.* **36**, 6270 (1997).
2. S. L. Suib and K. A. Carrado: *Inorg. Chem*. **24**, 200 (1985).
3. J. L. Sessler, M. R. Johnson, S. E. Creager, J. C. Fettinger, and J. A. Ibers: *J. Am. Chem. Soc.* **112**, 9310 (1990).
4. T. J. Meyer: *Acc. Chem. Res.* **22**, 163 (1989).
5. S. Higashida, H. Tsue, K. Sugiura, T. Kaneda, Y. Sakata, Y. Tanaka, S. Taniguchi, and T. Okada: *Bull. Chem. Soc. Japan.* **69**, 1329 (1996).
6. J. L. Sessler, M. R. Johnson, T. Lin, and S. E. Creager: *J. Am. Chem. Soc.* **110**, 3659 (1988).
7. J. Rodriguez, C. Kirmaier, M. R. Johnson, R. A. Friesner, D. Holten, and J. L. Sessler: *J. Am. Chem. Soc.* **113**, 1652 (1991).
8. G. Maclendon: *Acc. Chem. Res.* **21**, 160 (1988).
9. A. Helms, D. Heiler, and G. Maclendon: *J. Am. Chem. Soc.* **114**, 6227 (1992).
10. G. L. Closs and J. R. Miller: *Science* **240**, 440 (1988).
11. J. R. Lakowicz: *Principles of Fluorescence Spectroscopy*, pp. 257–269, Plenum Press, New York (1986).
12. M. Freemantle: *C&EN* **35** (1998).
13. V. E. Yushmanov, H. Imasato, T. T. Tominaga, and M. Tabak: *J. Inorg. Biochem.* **61**, 233 (1996).
14. H. Ogoshi and T. Mizutani: *Acc. Chem. Res.* **31**, 81 (1998).
15. A. K. Burrell, D. L. Officer, D. C. W. Reid, and K. Y. Wild: *Angew. Chem. Int. Ed. Engl.* **37**, 114 (1998).
16. R. K. Kumar, S. Balasubramanian, and I. Goldberg: *Inorg. Chem.* **37**, 514 (1998).
17. X. H. Mu, and F. A. Schultz: *Inorg. Chem.* **29**, 2879 (1990).
18. S. M. B. Costa, M. M. Velázquez, N. Tamai, I. Yamazaki: *Luminescence of Porphyrins* **48**, **49**, 341 (1991).
19. B. Meunier: *Chem. Rev.* **92**, 1411 (1992).
20. D. Heiler, G. McLendon, and P. Rogalskyj: *J. Am. Chem. Soc.* **109**, 604 (1987).
21. N. Filipescu, W. F. Sager, and F. A. Serafin: *J. Phys. Chem.* **68**, 3325 (1964).
22. M. D. Lumb: *Luminescence Spectroscopy*, pp. 130–146, Academic Press, New York (1978).
23. A. M. R. Gonsalves, J. M. T. B. Varejão, and M. M. Perena: *J. Heterocyclic Chem.* **28**, 635 (1991).
24. J. W. Buchler: in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins*, pp. 157–187, Elsevier Amsterdam (1975).
25. Simultaneous Equation Solver – E. E. Tucker: Version 3.1, Licensed to Larry C. Thompson.
26. P. W. Atkins: *Physical Chemistry*, pp. 373–375, 4th edition, Oxford University Press (1990).