J. Phys. Chem. **1986**, *90*, 3906–3910

SPECTROSCOPY AND STRUCTURE

Dual Fluorescence from Two Erbium(III) Porphyrins

Youkoh Kaizu, Motoko Asano, and Hiroshi Kobayashi*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

(Received: July 8, 1985; In Final Form: April 1, 1986)

TPPErOH (TPP, 5,10,15,20-tetraphenylporphin) as well as TPPEr(dpm) (dpm, 2,2,6,6-tetramethyl-3,5-heptanedione) fluoresces not only from the lowest excited singlet (S_1) state but also from the second excited singlet (S_2) state, while OEPErOH (OEP, 2,3,7,8,12,13,17,18-octaethylporphin) emits only from S_1 state. TPPEr(dpm) is in two different conformations in methanol/ethanol (7:3 v/v) glass at 77 K; the conformer with the central metal ion displaced out of the porphyrin plane emits no S_2 fluorescence, while the other conformer with the central metal ion in the porphyrin plane does emit S_2 fluorescence. Upon irradiation in the ultraviolet band around 300 nm, TPPEr(dpm) emits from both porphyrin S_2 and coordinated β-diketone T_1 (the lowest excited triplet) states.

Introduction

Upper excited-state emission has been observed for a variety of diamagnetic metal porphyrins.[1,2] Characteristic Q and B (Soret) bands of metal porphyrins in the visible and near-ultraviolet region are assigned as the lowest excited singlet (S_1) and the second lowest excited singlet (S_2) states. Since these excited states are described as a 50:50 admixture of two common $^1(\pi,\pi^*)$ excited configurations $^1(a_{1u}e_g)$ and $^1(a_{2u}e_g)$, the energy surfaces of the lowest excited singlet states are almost parallel. This retards $S_2 \rightsquigarrow S_1$ relaxation and thus the intense S_2 (Soret) oscillator can fluoresce. Since there are no triplet excited states between the S_1 and S_2 excited states,[3] the lifetimes of the S_2 state of diamagnetic metal complexes are goverened by the rate of $S_2 \rightsquigarrow S_1$ internal conversion.

The lowest excited states of paramagnetic metal complexes are attributable to the configuration-interaction admixtures of porphyrin (π,π^*) excited singlet and triplet states and "porphyrin-to-metal" and/or "metal-to-porphyrin" charge-transfer excited states.[4,5] In this situation, T_1 (phosphorescence) emission of paramagnetic metal complexes decays in a very short period. When the charge-transfer excited states are sufficiently low, the S–T absorption bands are observed to the red of Q band instead of the T_1 emission.[6-8] Nickel(II) porphyrins, even if in the diamagnetic ground state, exhibit neither S_1 (fluorescence) nor T_1 emission.[9,10] On the other hand, palladium(II) and platinum(II) porphyrins with isoelectronic outer shells emit intense phosphorescence even at room temperature. The quenching of luminescence in nickel porphyrins has been ascribed to a $^1(d,d^*)$ excited state at lower energy than the S_1 state.[11] The low-lying $^{1,3}(d,d^*)$ excited states of palladium and platinum porphyrins are lifted in between the S_1 and S_2 states. However, this results in quenching of the S_2 emission.

Paramagnetic erbium(III) porphyrins TPPErOH and TPPEr(dpm) (TPP, 5,10,15,20-tetraphenylporphin; dpm, 2,2,6,6-tetramethyl-3,5-heptanedione) show not only S_1 but also S_2 emission, even if a sequence of the sublevels of (f,f^*) excited states ^4I, ^4F, ^4S, ^2H are present below the S_2 state.[12] In this paper, a study of the luminescence properties of erbium porphyrins is presented.

Experimental Section

Materials. $TPPH_2$ and $OEPH_2$ (OEP, 2,3,7,8,12,13,17,18-octaethylporphin) were prepared and purified by methods described elsewhere.[13] TPPErOH and OEPErOH were prepared by the imidazole melt method[14,15] instead of the method proposed by Wong et al.[16-18] The products were purified by chromatography on nonactivated alumina columns and were recrystallized from chloroform/methanol (TPPErOH) or dichloromethane/heptane (OEPErOH).[19]

Anal. Calcd for $C_{44}H_{33}N_4O_3Er(TPPErOH\cdot 2H_2O)$ (mol wt 833.03): C, 63.44; H, 3.99; N, 6.73. Found: C, 63.79; H, 3.67; N, 6.62.

Calcd for $C_{36}H_{47}N_4O_2Er(OEPErOH\cdot H_2O)$ (mol wt 735.06): C, 58.83; H, 6.44; N, 7.62. Found: C, 58.73; H, 6.44; N, 7.81.

TPPEr(dpm) was prepared from $TPPH_2$ and $Er(dpm)_3$ by the imidazole melt method. The product melt was dissolved in a small amount of methanol. The residual TPPEr(dpm) was washed with water and then recrystallized from dichloromethane/methanol.[19] $Er(dpm)_3$ was made by the literature method.[20]

Anal. Calcd for $C_{55}H_{49}N_4O_3Er(TPPEr(dpm)\cdot H_2O)$ (mol wt 981.28): C, 67.32; H, 5.03; N, 5.71. Found: C, 67.64; H, 4.94; N, 5.97.

---

(1) Kurabayashi, Y.; Kikuchi, K.; Kokubun, H.; Kaizu, Y.; Kobayashi, H. *J. Phys. Chem.* **1984**, *88*, 1308.

(2) Ohno, O.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1985**, *82*, 1779.

(3) Sekino, H.; Kobayashi, H., to be submitted for publication.

(4) Kobayashi, H.; Yanagawa, Y.; Osada, H.; Minami, S.; Shimizu, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1471.

(5) Kobayashi, H.; Higuchi, T.; Kaizu, Y.; Osada, H.; Aoki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3137.

(6) Gouterman, M.; Hanson, L. K.; Khalil, G. E.; Leenstra, W. R.; Buchler, J. W. *J. Chem. Phys.* **1975**, *62*, 2343.

(7) Harriman, A. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2727.

(8) Kobayashi, H.; Tsuji, K.; Kaizu, Y.; Misu, N., to be submitted for publication.

(9) Ake, R.; Gouterman, M. *Theor. Chim. Acta* **1970**, *17*, 408.

(10) Kim, D.; Kirmaier, C.; Holten, D. *Chem. Phys.* **1983**, *75*, 305.

(11) Kobayashi, T.; Straub, K. D.; Rentzepis, P. M. *Photochem. Photobiol.* **1979**, *29*, 925.

(12) Dieke, G. H. *Spectra and Energy Levels of Rare Earth Ions*; Wiley: New York, 1968.

(13) Kaizu, Y.; Misu, N.; Tsuji, K.; Kaneko, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 103.

(14) Gouterman, M.; Schumaker, C. D.; Srivastava, T. S.; Yonetani, T. *Chem. Phys. Lett.* **1976**, *40*, 456.

(15) Srivastava, T. S. *Bioinorg. Chem.* **1978**, *8*, 61.

(16) Wong, C. P.; Venteicher, R. F.; Horrocks, W. DeW., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7149.

(17) Wong, C. P.; Horrocks, W. DeW., Jr. *Tetrahedron Lett.* **1975**, *31*, 2637.

(18) Wong, C. P. *Inorg. Synth.* **1983**, *22*, 156.

(19) It should be noted that no free-base emissions were detected at any stage of purification until after condensation, and the compounds yielded no free base even if they were washed with water. Condensation of solutions for recrystallization yields only a trace of the free base which can be detected by emission but not absorption measurements. Better emission data were obtained on eluates of TPPErOH and OEPErOH from chromatographic columns and on solutions of TPPEr(dpm) prepared by dissolving the product melt after added imidazole was extracted.

(20) Eisentraut, K. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 5254.

0022-3654/86/2090-3906$01.50/0

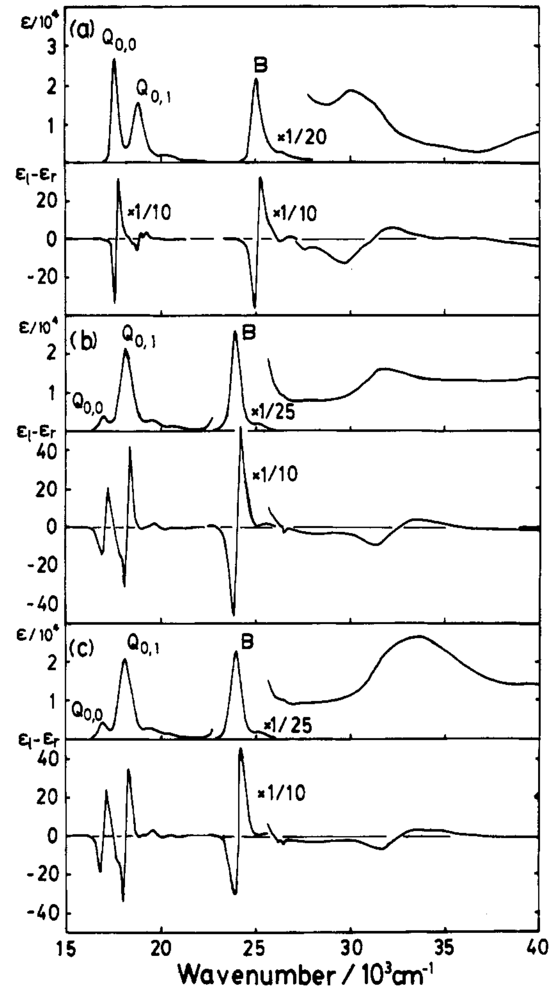

Figure 1. Absorption and MCD spectra of OEPErOH (a), TPPErOH (b), and TPPEr(dpm) (c) in methanol.

TPPGdOH and OEPGdOH were prepared by methods similar to those described for the corresponding Er complexes.

All the solvents used for preparations were commercially available and purified by distillation just before use.

Measurements. Absorption spectra were recorded on a Hitachi 330 spectrophotometer. Magnetic circular dichroism (MCD) spectra were measured on a JASCO J-500C with an electromagnet set at 1 T.

Emission and excitation spectra were taken on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier. The emission and excitation responses were calibrated by use of a concentrated ethylene glycol solution of rhodamine B (8 g/cm³).[21] Emission spectra were also corrected by using standard solutions of 4-dicyano-4′-nitrostilbene (800–600 nm) and *m*-(dimethylamino)nitrobenzene (630–480 nm).[22] Phosphorescence of the dpm moiety in TPPEr(dpm) was detected through a chopper attached to the spectrofluorometer.

Fluorescence lifetimes were determined by the single-photon-counting method on a PRA nanosecond fluorometer system. The lifetimes were determined by fitting the decay curves exponentially using an iterative least-squares method.[2] Quantum yields of emission were measured with reference to the yield of the S_1 emission of TPPZn in benzene ($\phi_f = 0.033$)[23] using optically dilute solutions.[24]

Porphyrin T_1 emission was measured through a Nikon P-250 monochromator by a Hamamatsu R928 photomultiplier upon excitation by an NRG-0.5-5-150/B nitrogen laser. The emission signal was A/D converted on a Kawasaki Electronica transient memory Model M-50E and accumulated on an NEC computer Model PC9801-F2. The lifetimes were determined by the least-squares method.

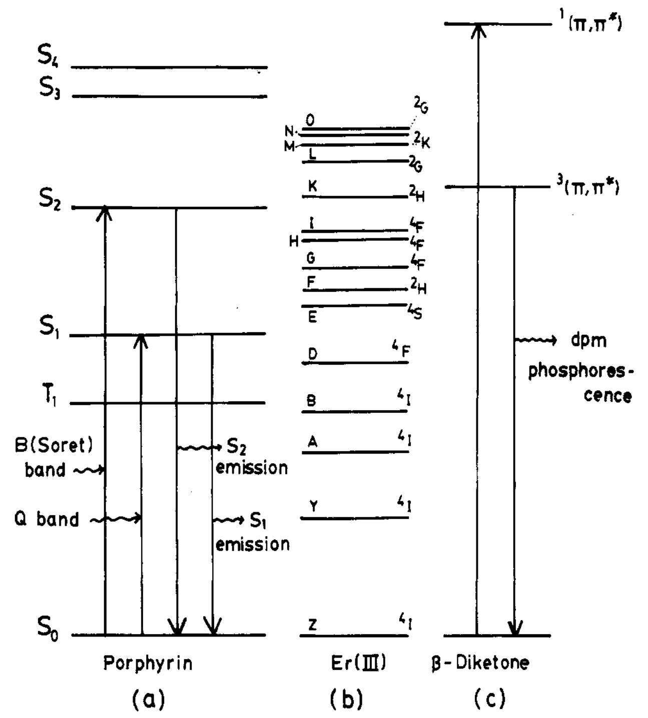

Figure 2. Energy-level diagram of the excited states of erbium(III) porphyrins. T_1, S_1, and S_2 are the lowest porphyrin (π,π^*) excited triplet and singlet states (a), ^4I, ^4F, ^4S, and ^2H are the sublevels of the (f,f*) excited state of the Er(III) ion (b) (ref 12), and $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ are the lowest β-diketone (π,π^*) excited triplet and singlet states (c).

Spectra, decay lifetimes, and quantum yields of emission were measured with methanol solutions. Emission measurements were also carried out in methanol/ethanol (7:3 v/v) at room temperature and in glassy media at liquid nitrogen temperature. Methanol and ethanol used for absorption and emission measurements were commercially available and purified by distillation. Solutions of the porphyrins were sealed in cuvettes after being purged with nitrogen gas just before the emission measurements.

Results and Discussion

Figure 1 shows absorption and MCD spectra of OEPErOH, TPPErOH, and TPPEr(dpm) in methanol. The Q (S_1) band is of forbidden character; however, the Q band can borrow a transition intensity from the allowed B (S_2) band. The intensity of $Q_{0,1}$ band is much less sensitive to peripheral substituents, axial ligands, and central metal ion, while that of $Q_{0,0}$ band is dependent upon the variation of the substituents. MCD spectra exhibit *A* term dispersions in $Q_{0,0}$, $Q_{0,1}$, and B bands. Vibrational structures of the MCD in the $Q_{0,1}$ band are noted. The 34 × 10³ cm⁻¹ band in TPPEr(dpm) is assigned as the $^1(\pi,\pi^*)$ excited state of coordinated dpm. MCD can detect the ultraviolet bands of the porphyrin moiety present beneath the MCD-silent dpm band to the blue of Soret band. In fact almost identical MCD spectra are obtained for TPPErOH and TPPEr(dpm). Figure 2 presents a schematic energy-level diagram of the excited states of erbium(III) porphyrin.

The ratios of intensities of $Q_{0,0}$ and $Q_{0,1}$ bands found for OEPErOH, TPPErOH, and TPPEr(dpm) are 1.74, 0.19, and 0.20, respectively. This suggests that the S_2 state grants more intensity to the $Q_{0,0}$ band in OEPErOH than in TPPErOH and TPPEr(dpm). Figure 3 shows the emission spectra of OEPErOH, TPPErOH, and TPPEr(dpm) in methanol/ethanol (7:3 v/v). The excitation spectra of S_1 emissions are in good agreement with the respective absorption spectra. The spectra of OEPErOH conform to those reported in the literature[14] except that the free-base emission is minimal in the present work. Quantum yields of the

---

(21) Melhuish, W. H. *J. Res. Natl. Bur. Stand., Sect. A* **1972**, *76*, 547.
(22) Lippert, E.; Nägele, W.; Blankenstein, I. S.; Staiger, U.; Voss, W. *Z. Anal. Chem.* **1959**, *170*, 1.
(23) Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111.
(24) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

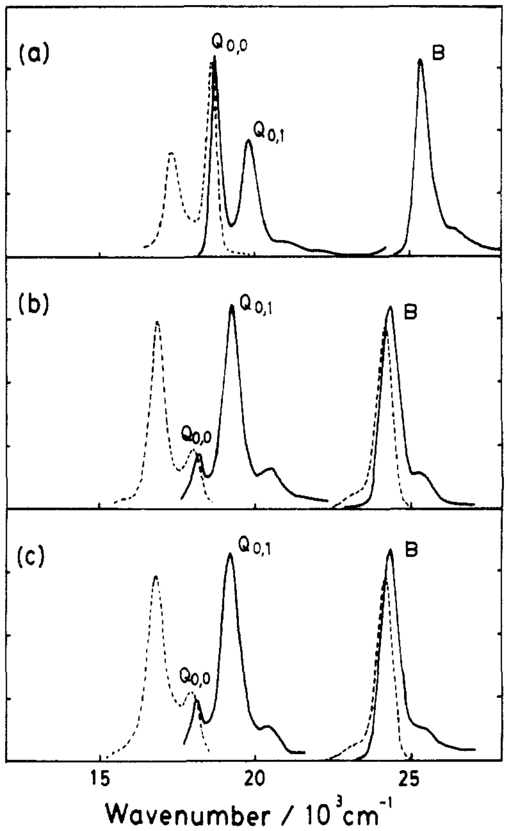

Figure 3. Emission (---) and excitation (—) spectra of OEPErOH (a), TPPErOH (b), and TPPEr(dpm) (c) in methanol/ethanol (7:3 v/v) at room temperature.

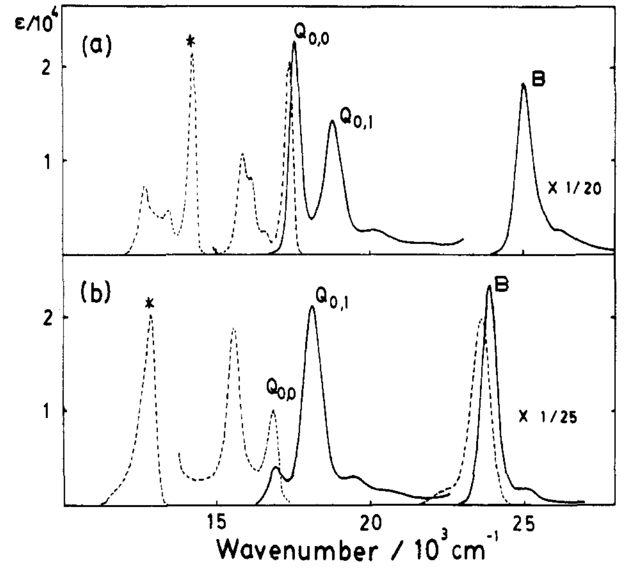

Figure 4. T_1, S_1, and S_2 emission (---) and absorption (—) spectra of OEPGdOH (a) and TPPGdOH (b). T_1 and S_1 emission spectra are those observed for rigid glasses of methanol/ethanol (7:3 v/v) at 77 K. The S_2 emission and the absorption spectra are of methanol solutions at room temperature. The asterisks indicate phosphorescence.

S_1 emission of erbium porphyrins in methanol were determined as 2.1×10^{-4}, 2.0×10^{-4}, and 2.0×10^{-4} for TPPErOH, TPPEr(dpm), and OEPErOH, respectively, and the lifetimes were of the order of 0.1 ns. The yields and the lifetimes of S_1 state are considerably reduced relative to those of diamagnetic metalloporphyrins such as TPPGaCl ($\phi_f = 0.075$, $\tau = 5.5$ ns in ethanol).[2]

TPPErOH emits from both the S_1 and S_2 states, while OEPErOH emits only from the S_1 state. Ultraviolet excitation spectra of both the S_1 and S_2 emissions of TPPErOH coincide with the absorption spectrum. This implies that the internal conversion $S_2 \rightsquigarrow S_1$ must be much faster than intersystem crossing $S_2 \rightsquigarrow T_n$ and internal conversion $S_2 \rightsquigarrow S_0$. The decay of S_2 state is almost entirely governed by the rate of internal conversion to S_1. The energy surfaces of S_1 and S_2 states are almost parallel when the component excited configurations $^1(a_{1u}e_g)$ and $^1(a_{2u}e_g)$ are in an accidental degeneracy. These surfaces, of course, shift from the ground-state surface. This reduces the Franck–Condon overlap and yields only weak $Q_{0,0}$ bands. However, the peripheral substitutions partially lift the accidental degeneracy and give rise to some difference in shift between the S_1 and S_2 surfaces. This prompts the rate of $S_2 \rightsquigarrow S_1$ internal conversion and enhances the intensity of $Q_{0,0}$ band. It should be noted that the green ($^4S_{3/2}$) emission lines of Er(III) ion, which lie between the porphyrin Q and B bands, are completely quenched.

Figure 4 shows emission and absorption spectra of the corresponding OEPGdOH and TPPGdOH. It is noted that S_2 emission is observed for TPPGdOH but not for OEPGdOH. T_1 emission is strong enough in the gadolinium porphyrins that phosphorescence can be detected even at room temperature. The yields and lifetimes of OEPGdOH and TPPGdOH in methanol at room temperature were determined as 1×10^{-2}, 70 μs and 1×10^{-3}, 34 μs, respectively. When the solutions were frozen, however, the lifetimes increased (OEPGdOH 130 μs; TPPGdOH 83 μs in methanol/ethanol (7:3 v/v) at 77 K). On the other hand, porphyrin T_1 emissions have never been detected for Er complexes. In TPPErOH, TPPEr(dpm), and OEPErOH, there are no sizable differences in quantum yields and lifetimes of S_1 emission. An enhanced rate of intersystem crossing, which arises from paramagnetic perturbation by the Er(III) ion, reduces the yields and lifetimes of the S_1 emission. In contrast with enhanced intersystem crossing, which yields strong phosphorescence in gadolinium porphyrins, intersystem crossing in erbium porphyrins results in fast relaxation to the low-lying (f,f*) excited states and, as a result, T_1 emission is totally quenched. So far, however, it has not been possible to detect near-IR emission from erbium porphyrins. In the case of ytterbium(III) porphyrins, near-IR emission from the $^2F_{5/2}$ state of Yb(III) ion, which is lower than porphyrin T_1 state, has been observed.[14,15,25]

Excitation in the B band of TPPEr(dpm) in methanol/ethanol (7:3 v/v) at 77 K yields four emission peaks in the S_1 region (Figure 5). By monitoring each of the four emission peaks, excitation spectra in the Soret region were measured. Two different excitation spectra were obtained for each pair of peaks. This indicates two different species, I and II, present in the medium. In fact, excitation in the two maxima of the excitation spectrum which correspond to the Soret peaks of the two species results in two different S_1 emission spectra. Excitation spectra in the Q band region are also in a mirror-image relationship to the respective S_1 emission spectra of two different species.

Our interpretation is that, in the glassy medium at 77 K, TPPEr(dpm) is present in two conformations. The spectral change observed upon freezing is reversible. At room temperature, a spectrum close to that of TPPErOH is revived. However, TPPErOH itself does not show any spectral splitting upon freezing of the medium. The Q and B bands observed in the excitation spectrum of the species we label II are more red-shifted than those of species I. It is noted that the $Q_{0,0}$ band of species II is much more intense than that of species I.

Figure 5 summarizes the four-peak emission spectra, two different excitation spectra observed by monitoring each pair of the four peaks, and the emission spectra measured upon excitation in the maxima of the excitation spectra of the two presumed conformers I and II.

The metal ion of TPPEr(dpm) in conformation II is shifted out of the porphyrin plane, as suggested by an increase in the intensity of $Q_{0,0}$ band and a comparable red shift of the Q and B bands, while that of conformation I is in the plane, i.e., similar to TPPErOH in methanol/ethanol. The spectral differences between the species I and II might be attributed to a difference in the

---

(25) Tsvirko, M. P.; Stelmakh, G. F.; Pyatosin, V. E.; Solovyov, K. N.; Kachura, T. F. *Chem. Phys. Lett.* **1980**, *73*, 80.

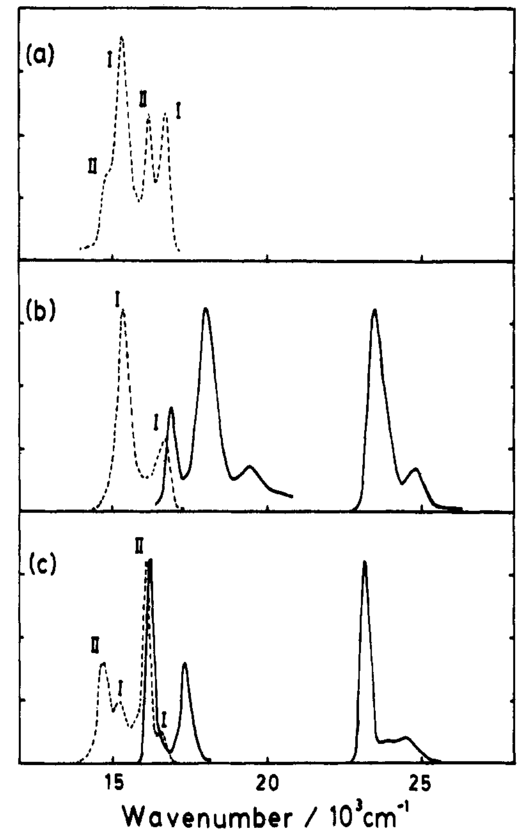

Figure 5. The four-peak emission spectrum (a) obtained upon excitation in the B band of TPPEr(dpm) in methanol/ethanol (7:3 v/v) at 77 K. The excitation spectra (—) in (b) were obtained by monitoring in one of the emission peaks (I) and the emission spectra (---) were taken by excitation at each of the excitation maxima. The spectra in (c) were measured by monitoring at peaks II and by excitation at the respective excitation maxima.

exciton coupling of coordinated dpm and the porphyrin moiety. However, exciton coupling yields a greater shift only in the B band but no sizable shift in the Q band.[13,26] Thus a comparable red shift of the Q and B bands observed in conformer II should be ascribed to an out-of-plane shift of the central metal ion. These assignments for the two conformers of TPPEr(dpm) are also consistent with other metalloporphyrin data. Upon axial ligation by pyridine, which gives rise to an out-of-plane shift of the central metal ion,[27] TPPZn shows a simultaneous red shift of the Q and B bands and an enhancement of the $Q_{0,0}$ band.[28] NMR shifts observed with other rare-earth analogues, TTPEu(acac) (TTP, 5,10,15,20-tetratolylporphin; acac, 2,4-pentanedione) and TTPYb(dpm), indicate that the central metal ions are significantly out of the porphyrin plane.[29]

Excitation spectra of the S_2 emission of TPPEr(dpm) reveal that conformer I exhibits S_2 emission while conformer II does not. A weak $Q_{0,0}$ band of the conformer I implies that the energy surfaces of the Q and B states are parallel and only slightly shifted. It follows that $S_2 \rightsquigarrow S_1$ internal conversion is retarded and the S_2 state emits fluorescence in conformer I. On the other hand, an out-of-plane shift of the metal ion in conformer II results in quenching of the S_2 emission. The displacement of the metal ion yields a difference in shift between the S_1 and S_2 surfaces from the ground-state surface. This enhances not only the crossing of S_1 and S_2 states but also the Franck–Condon overlap of the $Q_{0,0}$ band. A reduction of spin–orbit coupling in the metal ion being shifted out of porphyrin plane may vary the rate of intersystem crossing.[30] However, there is no triplet manifold near the S_2 state and thus intersystem crossing cannot play an important part in the decay of S_2 state.

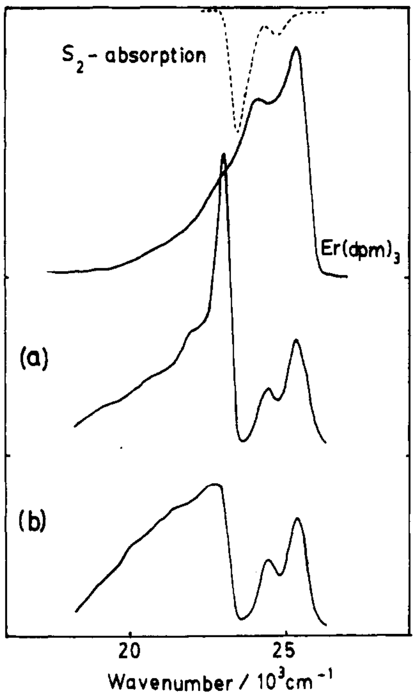

Figure 6. Emission from the upper excited states of TPPEr(dpm). When the $^1(\pi,\pi^*)$ band of coordinated dpm was irradiated around 300 nm, emission spectra a and b were observed. In (b), the porphyrin S_2 emission was excluded by a chopper (~500 Hz) interposed in the detection beam.

In OEPErOH with an intense $Q_{0,0}$ band, $S_2 \rightsquigarrow S_1$ internal conversion is accelerated and as a result no S_2 emission is observed. It should be noted that the enhancement of the $Q_{0,0}$ intensity in this particular case is attributed to the peripheral electron-donating substituents.

TPPEr(dpm) emits not only porphyrin S_2 fluorescence but also dpm phosphorescence upon excitation around 300 nm. The excitation spectrum of porphyrin S_1 emission of TPPEr(dpm) exhibits an ultraviolet band of dpm at 300 nm which is absent in TPPErOH. However, the dpm band in the excitation spectrum is a somewhat weaker than the band detected by absorption measurements. This indicates that all the energy absorbed by the coordinated dpm is not necessarily transferred to the S_1 and/or S_2 states of the porphyrin moiety. A fast relaxation within β-diketone accelerated by paramagnetic perturbation of Er(III) ion yields a rather high population in the lowest dpm T_1 state which is slightly higher than porphyrin S_2 state. This gives rise to dpm phosphorescence.

Figure 6 presents emission spectra which are observed upon excitation in the $^1(\pi,\pi^*)$ band of coordinated β-diketone around 300 nm. TPPEr(dpm) emits not only from the porphyrin S_2 state but also from the β-diketone T_1 state. Emission spectrum (a) in Figure 6 is attributable to a superposition of porphyrin S_2 fluorescence, β-diketone phosphorescence, and also intense Soret reabsorption. Figure 6 also shows phosphorescence of $Er(dpm)_3$ which must be very close to that of the β-diketone moiety in TPPEr(dpm). The porphyrin S_2 emission can be excluded by use of a fast (~500 Hz) rotating sector in front of the detector. Spectrum b represents phosphorescence of the β-diketone moiety 2 ms after excitation which is superposed by intense Soret reabsorption but lacks the porphyrin S_2 emission.

In conclusion, it is noted that TPPErOH and TPPEr(dpm), like many other diamagnetic metal TPP complexes,[2] emit both S_1 and S_2 fluorescence even if a sequence of sublevels of (f,f*) excited

---

[26] Gouterman, M.; Holten, D.; Lieberman, E. *Chem. Phys.* **1977**, *25*, 139.

[27] Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761.

[28] The $Q_{0,0}$ and B bands in benzene and in 1% pyridine/benzene are at 588, 423 and 602, 428 nm, respectively, and the ratios of the intensities of $Q_{0,0}$ and $Q_{0,1}$ bands in benzene and in 1% pyridine/benzene are 0.16 and 0.46, respectively.

[29] Horrocks, W. DeW., Jr.; Wong, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 7157.

[30] Martarano, L. A.; Wong, C. P.; Horrocks, W. DeW, Jr.; Goncalves, A. M. P. *J. Phys. Chem.* **1976**, *80*, 2389.

states are present between the porphyrin S_1 and S_2 states and below the S_1 state, while OEPErOH emits only S_1 fluorescence. Quenching of S_2 emission in OEPErOH, like other diamagnetic metal OEP complexes,[2] is attributed to a fast relaxation to the S_1 state. Since the S_1 and S_2 excited states are a 50:50 admixture of two common $^1(\pi,\pi^*)$ excited configurations in accidental degeneracy, the energy surfaces of the lowest excited singlets are almost parallel. These parallel surfaces, however, are displaced from the ground-state surface. In fact, the Franck–Condon overlap is so small that only a weak $Q_{0,0}$ band is observed in the TPP complexes. In the OEP complexes, on the other hand, the peripheral substituents partially lift the accidental degeneracy and thus yield some difference in shift between the S_1 and S_2 surfaces. This makes an increase in the Franck–Condon overlap, which intensifies the $Q_{0,0}$ band of OEP complexes, and also allows the fast $S_2 \rightsquigarrow S_1$ relaxation.

TPPEr(dpm) exists in two conformations in methanol/ethanol glassy medium at 77 K. Conformer I, with the central metal ion in the porphyrin plane, emits S_2 fluorescence, while conformer II, with the central metal ion displaced out of the porphyrin plane, emits no S_2 fluorescence. The quenching of S_2 emission in conformer II is attributable to an increase in the interaction of S_1 and S_2 states but not to an enhancement of spin–orbit coupling in the central metal ion.

Upon irradiation in an absorption band of coordinated dpm around 300 nm, we observe not only phorphyrin S_2 emission but also coordinated β-diketone T_1 emission. This implies that the rate of interligand energy transfer from the β-diketone S_1 state to the porphyrin S_2 state is not as fast as intersystem crossing within the β-diketone. Also energy transfer between the β-diketone T_1 and porphyrin S_2 states, even if in an accidental degeneracy, is rather inhibited.

Acknowledgment. The authors are grateful to Professor I. Tanaka for his continuous interest and encouragement.

Registry No. TPPErOH, 102941-86-6; TPPEr(dpm), 102941-87-7; OEPErOH, 60452-84-8; TPPGdOH, 102941-88-8; OEPGdOH, 60452-83-7.

Infrared Spectra of Diacetylene–Hydrogen Fluoride Complexes in Solid Argon

Kenneth O. Patten, Jr., and Lester Andrews*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

(Received: September 6, 1985; In Final Form: February 10, 1986)

Diacetylene–hydrogen fluoride complexes and their deuterated counterparts have been characterized in solid argon at 10 K by infrared spectroscopy. The observation of two new sets of H–F stretching, C–H stretching, and C–H bending absorptions indicates that two primary product 1:1 complexes were trapped in the matrix. These absorption bands characterize a C_4H_2--HF π complex and a C_4H_2--FH σ complex whose relative yields exhibit a deuterium substitution dependence consistent with a preference for deuterium in the bonding position. The relative values of the ν_s (H–F stretching) and ν_l (H–F librational) modes for the diacetylene--HF and acetylene--HF π complexes reveal weaker hydrogen bonding in the diacetylene--HF complex. Annealing produced comparable increased yields of both 1:1 complexes, suggesting comparable stabilities, and a marked increase in a C_4H_2--$(HF)_2$ complex.

Introduction

A variety of techniques have recently been applied to understanding the hydrogen-bonding interaction with π-bonded systems. Infrared spectroscopy was first used to observe alkene–HI complexes in matrix isolation;[1-3] results of later studies on ethylene–HF and acetylene–HF in solid argon indicated T-shaped complexes, with the hydrogen halide attached to the π bond.[4-6] Microwave spectra of ethylene–HF and acetylene–HF confirmed the T-shaped structures deduced from the matrix spectra.[7,8] Analogous complexes between HF and methyl-substituted ethylenes[9] and acetylenes[10] have been studied in matrix isolation, and rotational spectra of propyne–HF suggested that the geometry is slightly distorted by the methyl group.[11]

Interest in conjugated π systems as bases followed from experimentation with localized π bonds. Molecular beam electric resonance spectra of benzene–HF indicated that the average structure placed HF on the C_6 axis perpendicular to the benzene ring,[12] and matrix infrared spectra supported this structure.[13] The weak hydrogen bonding in the complex and the breadth of the potential for the proton apparently favor a complex where HF oscillates markedly from this average position. Infrared spectra of conjugated diene–HF complexes in solid argon suggested a similar oscillation of HF from an average position above the central C–C bond.[14] Conjugation of the two π systems also exists in diacetylene, so that a similar oscillating structure might be expected; however, due to the geometry of this molecule, the distance separating the two π bonds is greater than for conjugated dienes and a greater barrier may exist between the potential minima.

---

(1) Barnes, A. J.; Hallam, H. E.; Scrimshaw, G. F. *Trans. Faraday Soc.* **1969**, *65*, 3172.

(2) Barnes, A. J.; Davies, J. B.; Hallam, H. E.; Howells, J. D. R. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 246.

(3) Kimel'fel'd, Ja.-M. *J. Mol. Struct.* **1975**, *28*, 171.

(4) McDonald, S. A.; Johnson, G. L.; Keelan, B. W.; Andrews, L. *J. Am. Chem. Soc.* **1980**, *102*, 2892.

(5) Andrews, L.; Johnson, G. L.; Kelsall, B. J. *J. Chem. Phys.* **1982**, *76*, 5767.

(6) Andrews, L.; Johnson, G. L.; Kelsall, B. J. *J. Phys. Chem.* **1982**, *86*, 3374.

(7) Legon, A. C.; Aldrich, P. O.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 625.

(8) Aldrich, P. O.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 2126.

(9) Andrews, L.; Johnson, G. L.; Kelsall, B. J. *J. Am. Chem. Soc.* **1982**, *104*, 6180.

(10) Andrews, L.; Johnson, G. L. *J. Phys. Chem.* **1982**, *86*, 3380.

(11) Shea, J. A.; Bumgarner, R. E.; Henderson, G. *J. Chem. Phys.* **1984**, *80*, 4605.

(12) Baiocchi, F. A.; Williams, J. W.; Klemperer, W. *J. Phys. Chem.* **1983**, *87*, 2079.

(13) Andrews, L.; Johnson, G. L.; Davis, S. R. *J. Phys. Chem.* **1985**, *89*, 1706.

(14) Patten, K. O.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 5594.

0022-3654/86/2090-3910$01.50/0