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$S_2 \rightarrow S_0$ Fluorescence of Some Metallotetraphenylporphyrins[†]

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The fluorescence spectra from the Soret band of the metallotetraphenylporphyrins AlClTPP, ZnTPP, and CdTPP were measured in acetonitrile at 296 K and their yields were determined to be 6.7×10^{-4}, 3.7×10^{-4}, and 1.0×10^{-4}, respectively. The rates of radiative transition from the second excited state (S_2) of these compounds were estimated with the Strickler–Berg equation. The radiationless transition from S_2 was discussed in terms of the energy gap law.

Introduction

Porphyrins, in general, have a relatively large energy gap between the first (Q band) and the second excited singlet (Soret band) states. According to the theory of radiationless transitions, the Franck–Condon factor for the S_2–S_1 internal conversion of porphyrins is considered to be smaller than those of usual aromatic compounds. In addition, the Soret band is a strongly allowed transition so that the radiative transition from the second excited singlet state to the ground state has to be very fast. For these reasons, porphyrins are expected to fluoresce from the Soret band. Fluorescence from the Soret band of porphyrins was first observed by Bajema et al.[1] for zinc tetrabenzporphyrin (ZnTBP) in octane containing 0.5% pyridine. The yield was determined to be 1.6×10^{-3} and the lifetime was estimated to be about 2.4 ps.[1] Martarno et al.[2] found also Soret fluorescence for Y^{III}, Lu^{III}, and Th^{IV} complexes of TPP and determined their yields as 1×10^{-3}, 1×10^{-3}, and 4×10^{-4}, respectively. However studies on the fluorescence from the Soret band of porphyrins are still very few.

In the present work, the yield and the lifetime of the Soret fluorescence for $Al^{III}Cl$ TPP, ZnTPP, and CdTPP are reported together with the result of Bajema et al., and the radiationless transition from the second excited singlet state of these compounds is discussed.

Experimental Section

Absorption spectra were recorded with a Hitachi 330 spectrophotometer. All emission spectra were measured with a fluorometer constructed in our laboratory. The excitation light source is a CW He–Cd laser at 325 nm. The detection system consists of a combination of either a HTV 7102 or a R 562 photomultiplier tube cooled to −20 °C and a Nikon G 250 monochromator with either a G 12-50 (blaze wavelength, 500 nm) or a G-6-75 (blaze wavelength, 750 nm) grating. The spectral response of the instrument was corrected by use of a standard bromine lamp whose spectral irradiance was calibrated at the Electrotechnical Laboratory.[3] The fluorescence quantum yield was determined by use of quinine bisulfate in 1 N H_2SO_4 ($\phi_F = 0.55$ at 296 K[4]) or perylene in cyclohexane ($\phi_F = 0.87$ at 297 K[5]) as a standard. The fluorescence lifetime was measured with a phase fluorimeter modulated at 10.7 MHz.

Metal-free tetraphenylporphyrin (H_2TPP) was prepared from pyrrole and benzaldehyde by the method of Adler et al.[6] ZnTPP was prepared by reflux of H_2TPP and zinc acetate in dimethylformamide.[7] AlClTPP was prepared by vigorous reflux of H_2TPP and anhydrous aluminum chloride in dry benzonitrile. The details of purification of H_2TPP, ZnTPP, and AlClTPP will be published elsewhere. CdTPP was synthesized by Mr. M. Arakawa and purified by the method of Rothemund and Menotti.[8] Acetonitrile (extra pure grade, Nakarai Chemicals) was treated with Na_2CO_3 and fractionally distilled on a trace of P_2O_5. Sample solutions, except for CdTPP, were degassed by freeze–pump–thaw cycles. The CdTPP solution was not degassed because CdTPP was bleached during the degassing process.

TABLE I: S_2-S_0 Fluorescence Properties of Some Metal Complexes of TPP in Acetonitrile at 296 K

	$\phi_F{}^Q$	$\phi_F{}^S$	$10^9 k_F{}^S$, s^{-1}	$10^{12} k_d{}^S$, s^{-1}	$\Delta E(S_2$-$S_1)$, cm^{-1}
AlClTPP	1.4×10^{-1}	6.7×10^{-4}	1.4	2.2	7100
ZnTPP	3.3×10^{-2}	3.7×10^{-4}	1.5	4.1	6900
CdTPP	1.0×10^{-3}	1.1×10^{-4}	1.1	9.6	6700
ZnTBP[a]	0.35	1.6×10^{-3}	0.67	0.42	7400

[a] See ref 1.

Results and Discussion

Figure 1 shows the fluorescence spectra of ZnTPP, AlClTPP, and CdTPP in acetonitrile at 296 K. Their Soret fluorescence spectra are good mirror images of their Soret absorption bands. The Soret fluorescence yield $\phi_F{}^S$ for these porphyrins was determined by comparison with the $S_1 \rightarrow S_0$ fluorescence yield $\phi_F{}^Q$. The values for $\phi_F{}^S$ and $\phi_F{}^Q$ are given in Table I.

To estimate the lifetime τ_S of the Soret fluorescence of ZnTPP experimentally, we measured the fluorescence polarization. As shown in Figure 2, the Perrin equation[9] (1) holds for the $S_1 \rightarrow S_0$ fluorescence of ZnTPP in liquid paraffin as well as in 1,2-ethanediol at various temperatures:

$$\frac{1}{P} - \frac{1}{3} = \left(\frac{1}{P_0} - \frac{1}{3}\right)\left(1 + \frac{k}{v}\frac{T}{\eta}\tau\right) \qquad (1)$$

where P is the degree of fluorescence polarization, k is the Boltzmann constant, v is the apparent molecular volume, T is the absolute temperature, and η is the viscosity of solvent. The value for the lifetime τ_Q of the $S_1 \rightarrow S_0$ fluorescence was determined

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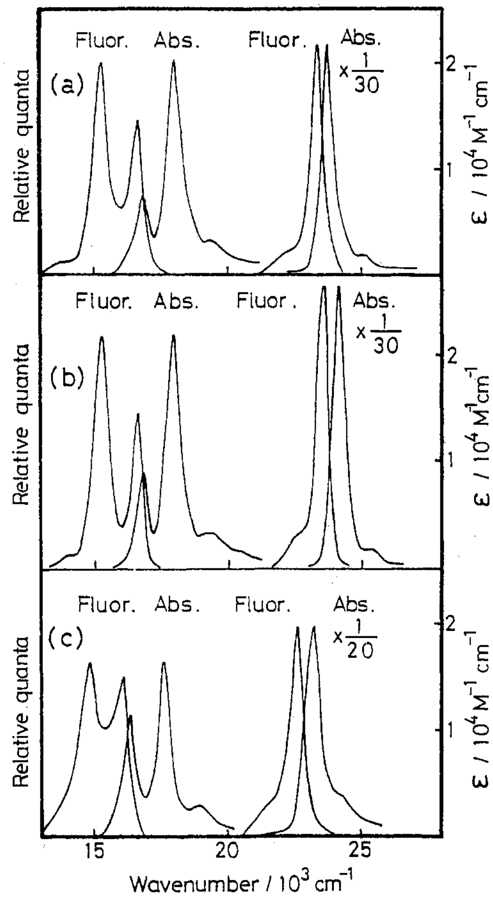

Figure 1. Absorption and fluorescence spectra of (a) ZnTPP, (b) AlClTPP, and (c) CdTPP in acetonitrile at 296 K.

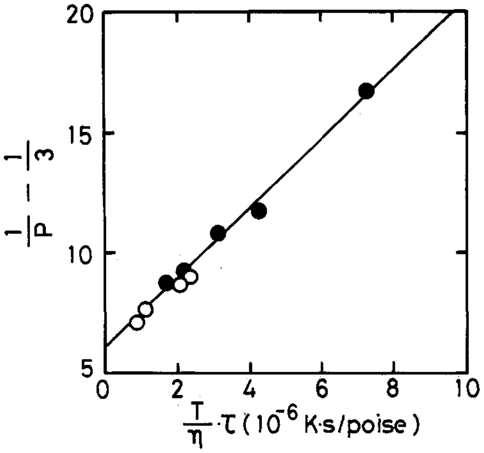

Figure 2. The plot of $(1/P - {}^1/_3)$ vs. $(T/\eta)\tau$ for the $S_1 \rightarrow S_0$ fluorescence of ZnTPP.

to be 2.5 ns in both solvents at 296 K. The limiting polarization P_0 was estimated to be 0.15, which was close to the expected value of 0.13 for degenerated electronic transitions.[10] From the slope of the plot shown in Figure 2, the value for v was estimated to be 5.5×10^{-28} m^3. The values for P of the Soret fluorescence in isopentane, acetonitrile, 1,2-ethanediol, and liquid paraffin agree with one another within the experimental error limit. Therefore, only the upper limiting value for τ_S was evaluated as 3 ps by assuming that the value for v obtained above holds for the Soret fluorescence polarization.

Since the values for $\phi_F{}^S$ of AlClTPP, ZnTPP, and CdTPP are much less than unity, τ_S is expressed as follows:

$$1/\tau_S \simeq k_d{}^S = k_F{}^S\left(\frac{1}{\phi_F{}^S} - 1\right) \qquad (2)$$

where $k_d{}^S$ is the rate constant of nonradiative deactivation from the Soret band. The rate constant $k_F{}^S$ of fluorescence emission from the Soret band can be calculated from the Strickler–Berg equation:[11]

$$k_F = 2.88 \times 10^{-9}\frac{\eta_f{}^3}{\eta_a}\frac{\int F(\tilde{\nu})\,d\tilde{\nu}}{\int \frac{F(\tilde{\nu})}{\tilde{\nu}^3}\,d\tilde{\nu}}\int \frac{\epsilon(\tilde{\nu})}{\tilde{\nu}}\,d\tilde{\nu} \qquad (3)$$

The values for $k_F{}^S$ are listed in Table I. The values for $k_d{}^S$ calculated by using the values for $\phi_F{}^S$ and $k_F{}^S$ are also listed. The value of τ_S for ZnTPP is one order of magnitude smaller than the upper limiting value evaluated from fluorescence polarization.

Soret fluorescence was not observed for H_2TPP and octaethylporphyrins such as H_2OEP, AlClOEP, and ZnOEP, although the absorption intensity at the Soret band for these porphyrins is not so much different from that for AlClTPP, ZnTPP, and CdTPP. Therefore, it is obvious that the $S_2 \rightarrow S_1$ internal conversion occurs much more rapidly in the cases of H_2TPP, H_2OEP, AlClOEP, and ZnOEP.

Intersystem crossing from S_2 to the triplet manifold as well as $S_2 \rightarrow S_0$ internal conversion is not important because the $S_1 \rightarrow S_0$ fluorescence yield for AlClTPP, ZnTPP, and CdTPP does not depend on the excitation wavenumber below 29 000 cm^{-1}. Thus the main route for radiationless transition from the Soret band is internal conversion to the S_1 manifold.

According to the theory of radiationless transitions, the factors which determine the rate k_d of a radiationless transition are as follows:[12] the electronic matrix element C and the energy gap ΔE between two electronic states where radiationless transition occurs, and the frequencies ω_M and the reduced displacements ΔM of the modes of maximum frequency:

$$k_d = \frac{C^2(2\pi)^{1/2}}{h(h\omega_M\Delta E)^{1/2}}\exp\left(\frac{\gamma}{h\omega_M}\Delta E\right) \qquad (4)$$

where

$$\gamma = \ln\left(\frac{2E}{\sum_M h\omega_M\Delta^2 M}\right) - 1$$

In the case of free base porphyrins the N–H stretching vibrations are responsible for the radiationless transition, since the large frequency of the N–H stretching vibration may be an accepting mode of electronic energy from the S_2 state. Similarly, the enhanced rate of radiationless transition for metal-free porphyrins was observed for the decay of phosphorescence emissions and this was also considered to be associated with the presence of central N–H bonds.[13] Metalloporphyrins, in contrast, have no central N–H bond but have N–metal bonds with lower vibrational frequencies, so that the Franck–Condon factor $S_2 \rightarrow S_1$ internal conversion for metalloporphyrins should become smaller than that for metal free porphyrins. As a result, it may be possible to observe fluorescence from the Soret band in metalloporphyrins. The experimental facts for TPP complexes agree with the above qualitative explanation. However, this explanation is not adequate for OEP complexes. The values of ΔE and C for metal–OEP complexes and of corresponding metal–TPP complexes are practically equal. One of the factors which is different is the substituent group on the porphyrin ring. If a C–H stretching mode of an ethyl group in OEP complexes is a better accepting mode for S_2 electronic energy than that of phenyl group in TPP complexes, the internal conversion occurs more rapidly in OEP com-

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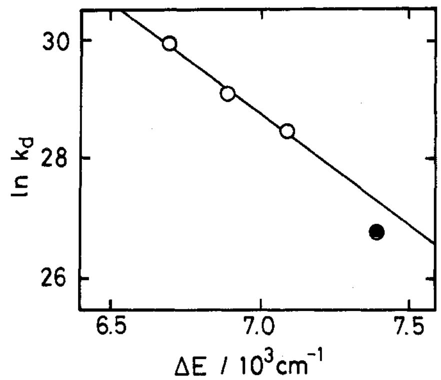

Figure 3. The plot of ln k_d vs. $\Delta E(S_2-S_1)$.

plexes than in TPP complexes. Then, the Soret fluorescence of metal–OEP complexes cannot be observed in contrast to the case of metal–TPP complexes.

The results in Table I can be the test for eq 5. Figure 3 shows the plot of ln k_d vs. $\Delta E(S_2-S_1)$. In Figure 3 the result of Bajema et al.[1] is also shown. It seems that a linear relationship holds for the plot of ln k_d vs. $\Delta E(S_2-S_1)$. The slope of the plot is three times larger than that for azulene and its derivatives.[14] The value for C estimated from this result by assuming $\hbar\omega_M$ = 3000 cm^{-1} for the C–H vibration was too large for the electronic matrix element. This may be due to the small S_2–S_1 energy gap in the porphyrins investigated here. Anyway, the rate of S_2–S_1 internal conversion of metal–TPP complexes depends mainly on the S_2–S_1 energy gap as expected from the energy gap law. Further studies on this subject are necessary to clarify the relation between the radiationless transition rate and the energy gap.

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Registry No. AlClTPP, 71102-37-9; ZnTPP, 14074-80-7; CdTPP, 14977-07-2.

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Systematic Studies of the Semiconductor/Liquid Junction: n-Gallium Arsenide Phosphide Anodes in Aqueous Se^{2-}/Se_2^{2-} Solutions

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Epitaxial layers of n-$GaAs_{1-x}P_x$ ($0 < x < 1$) have been studied as photoelectrodes and as Au Schottky junctions. We observe increases in open-circuit voltage, V_{oc}, with increases in P content for n-$GaAs_{1-x}P_x$ ($x \leq 0.4$) and decreases in V_{oc} for $x \geq 0.6$. Under 88 mW/cm^2 of ELH-type (3350 K color temperature with a dichroic rear reflector) tungsten–halogen irradiation, we observe that n-$GaAs_{0.72}P_{0.28}$ anodes exhibit a V_{oc} of 0.95–0.99 V, short-circuit currents of 15–17 mA/cm^2, and energy conversion efficiencies of 13.0 ± 1.0%. Irradiation at 632.8-nm yields monochromatic conversion efficiencies of greater than 30%, and solar irradiation (85–100 mW/cm^2) yields efficiencies of 11.0 ± 1.0% in 1.0 M KOH/1.0 M Se^{2-}/0.01 M Se_2^{2-} solutions. The n-$GaAs_{0.72}P_{0.28}$ anodes exhibit stable photocurrent for passage of over 3000 C/cm^2 at AM1 photocurrent densities. $Ru(H_2O)_6^{3+}$ ions are effective in improving photocurrent–voltage characteristics for n-$GaAs_{1-x}P_x$ ($0 \leq x < 1$) anodes but have no effect for n-GaP, indicating chemical interactions of the Ru ion with As or As oxide sites at the semiconductor/liquid junction. Direct comparison of V_{oc} for n-$GaAs_{1-x}P_x$/Au junctions with n-$GaAs_{1-x}P_x$/Se^{2-} barriers indicates that liquid junctions have higher V_{oc} values than some Schottky barriers and that pinning of the Fermi level by intrinsic surface states may not play a dominant role in determining interface parameters for these junctions.

There have been very few controlled studies of the properties of a semiconductor/liquid junction with continuous, incremental changes in semiconductor composition. Therefore, models that would enable prediction of junction parameters are difficult to formulate from the data available. This is due, in part, to the substantial differences in experimental conditions, as well as to variations in electronic properties and surface chemistry of the materials that have been compared. Of particular interest is the response of junction properties to substitution of isovalent ions in the semiconductor lattice. Related studies of variation in interface properties with changes in lattice composition have been reported for semiconductor/metal contacts.[1-3] Although the properties of liquid junction systems are often compared to those of Schottky contacts, rarely are the two types of experiments performed under controlled conditions on identical samples. We report studies which indicate that deliberate variation in bulk elemental composition of the electrode can be correlated with the properties of the semiconductor/liquid interface. In addition, we find substantial differences in interfacial behavior of metal and liquid junctions.

A general rule advanced for III–V photoanodes[4,5] suggests that the electronegativity of the lattice anion controls the position of the semiconductor valence band edge.[6-8] This notion has been adopted from a similar proposal in the solid-state Schottky barrier literature which states that the barrier height for holes in Au Schottky barriers will be determined by the nature of the semiconductor lattice anion.[2] The reported values of the open-circuit voltage, V_{oc}, for n-GaAs[9] and n-GaP[5] photoanodes in aqueous

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