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PHOTODYNAMICS AND ELECTRONIC STRUCTURES OF METAL COMPLEXES

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ABSTRACT

The emitting excited states of $[Ru\ (2,2'\text{-bipyridine})(\text{ethylenediamine})_2]^{2+}$ as well as $[Ru\ (2,2'\text{-bipyridine})_3]^{2+}$ are described as the metal-to-bipyridine charge-transfer triplet state to which a variety of the spin-allowed transitions grant their intensities as deduced by molecular orbital calculations taking into account spin-orbit coupling.

The structure of the lowest excited states of metalloporphyrins are discussed with relevance to the excited state lifetime. A variety of tetraphenylporphyrin metal complexes generate blue light upon red light laser excitation. The pumping up to the second excited singlet is ascribed to a successive two-photon absorption $S_0 \rightarrow S_1 \rightarrow S \rightsquigarrow S_2$.

INTRODUCTION

An electron provided by the reducing reagent to a metalloporphyrin is captured either in the central metal or in the conjugated system of the porphyrin moiety. When a planar Co^{II}TPP (TPP: tetraphenylporphin) is reduced, an electron is trapped in a molecular orbital predominantly localized on the cobalt ion. In this particular planar ligand, the gap between the ligand-field d_σ orbitals, z^2 and x^2-y^2, is so great that the central cobalt(I) is in the diamagnetic ground configuration $(d_\pi)^6(z^2)^2$. A diamagnetic complex $Na[TPPCo^I]\cdot 5THF$ was obtained by reduction of Co^{II}TPP with sodium benzophenone ketyl in THF (ref.1). On the other hand, one-electron reduction of the d^{10} metal complexes yields porphyrin anion radical (ref.2).

One-electron reduction of $[Co^{II}(bpy)_3]^{2+}$ (bpy: 2,2'-bipyridine) yields a complex of Co(I) in the triplet ground configuration $(d_\pi)^6(z^2)^1(x^2\text{-}y^2)^1$ (ref.3). Since the z^2 and x^2-y^2 orbitals are the antibonding orbitals, the electron occupations in the orbitals result in bond dissociations unless an electrostatic attraction between the metal ion and the ligands stabilizes the bonds. $Na[Co^I$-TPP] is not susceptible to accept axial ligands, while $[Co^I(bpy)_3]X$ dissociates one coordinated bipyridine in solution and yields $[Co^I(bpy)_2X]$. On the other hand, $[Fe(bpy)_3]$, isoelectronic to $[Co^I(bpy)_3]^+$, does not dissociate a ligand, since no electron occupation arises in the d_σ orbital. $[Fe(bpy)_3]$ is a complex of Fe(II) in $(d_\pi)^6$ configuration coordinated by two bipyridine anion radicals and one bipyridine molecule (ref. 4).

Reductions of metal carbonyls with the closed d_π shell result in a

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decrease of coordination number formation of a dimer with a metal-metal bond and/or with carbonyl bridges. One-electron reduction of $[Cr(CO)_6]$ yields $[Cr_2(CO)_{10}]^{2-}$ (ref.5), while two-electron reduction results in $[Cr(CO)_5]^{2-}$ (ref.6). The electrons provided by the reducing reagents are in the antibonding d_σ orbitals and thus one of the carbonyl bonds dissociates. However one-electron reduction of $[Cr(CO)_4bpy]$ can be achieved without accompanying evolution of carbon monoxide, and a monomeric open-shell complex $Na[Cr(CO)_4(bpy^-)]$ can be isolated (ref.7 and 8). This complex shows a g=2 ESR signal with a well-resolved superhyperfine structure due to interaction of the trapped electron with the peripheral protons of coordinated bipyridine molecule. It has an electronic absorption spectrum characteristic of the bipyridine anion radical.

Metal carbonyl complexes dissociate the coordinated carbon monoxide upon electronic excitation. In a condensed medium, the relaxation takes place in a very short period down to the lowest excited state. The lowest excited state of $[Cr(CO)_6]$ is the lowest component of the $^3(d,d^*)$ excited states. An electron occupation of the antibonding d_σ orbital in the lowest excited state results in dissociation of the coordinated carbon monoxide. However, excitation of $[Cr(CO)_4bpy]$ yields luminescence instead of the dissociation of carbon monoxide (ref.9). The luminescence is assigned to the lowest "metal-to-bipyridine" charge-transfer excited triplet state rather than the $^3(d,d^*)$ excited state. This implies that reduction and also photoexcitation of $[Cr(CO)_4bpy]$ do not result in the electron occupation of the d_σ orbital which gives rise to dissociation of the coordinated carbon monoxide. In other words, the lowest vacant π^* orbital (LUMO) of the coordinated bipyridine is lower than the antibonding d_σ orbital.

THE LOWEST EXCITED STATE OF $[Ru^{II}bpy(en)_2]^{2+}$

Extensive studies have been achieved on photodynamics and photochemistry of $[Ru(bpy)_3]^{2+}$ and its analogues. However the fine structure of the lowest excited singlet and triplet states of $[Ru^{II}(bpy)_3]^{2+}$ has never been determined exactly even by extensive experimental efforts.

Hanazaki and Nagakura described the lowest (d_π,π^*) excited states of $[Fe(bpy)_3]^{2+}$ as well as $[Fe(phen)_3]^{2+}$ (phen: 1,10-phenanthroline) by the composite-system method in which are superposed the "metal-to-ligand" charge-transfer excited configurations and the ligand (π,π^*) excited configurations (ref.10 and 11). With this model, the promoted electron in the (d_π,π^*) excited state is in one of three ligands and hops around three ligands.
Circular dichroism spectra in the ligand (π,π^*) transitions of the optical isomers are ascribed to an exciton coupling between the excitations in three

ligands (ref.11). The delocalization of electronic excitation over three ligands does not necessarily mean that the promoted electron in the "metal-to-ligand" charge-transfer excited state is in a π^* orbital completely delocalized over all three ligands. The (d_π,π^*) transitions can borrow their intensity from the ligand allowed (π,π^*) transitions by a counter migration of the ligand π electron into the metal d_π hole.

The mixed-ligand complexes such as $[Rubpy(en)_2]^{2+}$ (en: ethylenediamine) and $[Ruphen(en)_2]^{2+}$, in which no interligand exciton coupling is present, exhibit the "metal-to-ligand" charge-transfer bands and emit luminescence which are very similar to those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. Table 1 summarizes the results of our recent measurements on absorption and emission maxima, decay lifetimes and oxidation potentials (ref.12). The resonance Raman spectra taken by use of the argon ion laser lines within the 20~21×10^{3}cm^{-1} band show the skeletal vibrational modes of coordinated bipyridine and phenanthroline. This implies that the lowest excited state is the "metal-to-ligand" charge-transfer excited state.

TABLE 1

Absorption and Emission Maxima, Decay Lifetimes and Oxidation Potentials

Complex	Absorption maxima (10^3cm^{-1})	Emission maxima[a] (10^3cm^{-1})	τ(nsec)	E_p(V) *vs.*Ag/AgClO$_4$
$[Ru(bpy)_3]^{2+}$	21.90, 35.00	17.30, 16.02	610	+0.95
$[Ru(bpy)_2en]^{2+}$	20.53, 34.40	15.15, 13.89	70	+0.62
$[Ru(bpy)_2(NH_3)_2]^{2+}$	20.49, 34.39	13.62, 14.79	33	+0.58
$[Ru(bpy)(en)_2]^{2+}$	19.61, 34.01	15.15, 13.85	64	+0.26
$[Ru(bpy)(NH_3)_4]^{2+}$	19.16, 34.01			+0.21
$[Ru(phen)_3]^{2+}$	22.35, 38.21	16.45, 17.83	870	+0.96
$[Ru(phen)_2en]^{2+}$	20.91, 37.90	15.43, 14.25	250	+0.61
$[Ru(phen)_2(NH_3)_2]^{2+}$	20.96, 37.83	14.86, 13.18	144	+0.57
$[Ru(phen)(en)_2]^{2+}$	21.32, 37.56	15.41, 13.97	154	+0.29
$[Ru(phen)(NH_3)_4]^{2+}$	21.23, 37.64			+0.21

[a] Observed at 77 K.

The $^1T_1$ and $^1T_2$ states of $[Co(bpy)_3]^{3+}$ and $[Co(phen)_3]^{3+}$ ($^1T_1$: 23×10^{3}cm^{-1}) are in an energy region similar to those of $[Co(NH_3)_6]^{3+}$ and $[Coen_3]^{3+}$ ($^1T_1$: 21×10^{3}cm^{-1}; $^1T_2$: 30×10^{3}cm^{-1}), since the σ donations of ethylenediamine, bipyridine and phenanthroline are not so much different for the cobalt (III) ion. The gap between d_π and d_σ orbitals is substantially increased by the backbonding in $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ in contrast with $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$. A decrease in the oxidation potential is observed in the series, $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2en]^{2+}$ and $[Rubpy(en)_2]^{2+}$ and their ammine analogues. Substitution of bipyridine by ethylenediamine or ammonia lift the d_π orbitals and reduce the energy of the lowest (d,d*) excited state. The "metal-to-bipyridine" charge-transfer absorption maxima of $[Rubpy(en)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ are observed at $20.3\times10^3cm^{-1}$ and $21.9\times10^3cm^{-1}$ and the corresponding luminescence maxima are at $15.2\times10^3cm^{-1}$, $13.9\times10^3cm^{-1}$ and $17.3\times10^3cm^{-1}$, $16.0\times10^3cm^{-1}$, respectively, while the oxidation potentials (E_p) are +0.26V and 0.95V against Ag/0.1M $AgClO_4$. This implies that the ^{3}(d,d*) excited state in $[Rubpy(en)_2]^{2+}$ is much lower than that of $[Ru(bpy)_3]^{2+}$. Thermal activation to the ^{3}(d,d*) excited state results in fast electronic relaxation. For the same reason, the decay lifetime of $[Ru(bpy)_2(NH_3)_2]^{2+}$ (E_p= +0.58V) is as short as 40ns and $[Rubpy(NH_3)_4]^{2+}$ (E_p= +0.21V) analogous to $[Rubpy(en)_2]^{2+}$ emits no phosphorescence. Reduction in the decay lifetimes of $[Rubpy(en)_2]^{2+}$ and $[Ruphen(en)_2]^{2+}$ and the nonluminescent character of $[Rubpy(NH_3)_4]^{2+}$ and $[Ruphen(NH_3)_4]^{2+}$ are attributable to the stabilization of the lowest ^{3}(d,d*) excited state. The nonluminescent complexes are rather sensitive to photolysis. The emitting state is the lowest "metal-to-bipyridine (phenanthroline)" charge-transfer triplet state (^{3}CT) which is lower than the lowest ^{3}(d,d*) excited state. In the case of $[Fe(bpy)_3]^{2+}$, the ^{3}(d,d*) ($^3T_1$) excited state is observed at $12\times10^3cm^{-1}$ (ref.13). Theory predicts that the $^3T_1$ state is in a region not higher than $4000cm^{-1}$ above the ^{3}CT of $[Ru(bpy)_3]^{2+}$. It has been proposed that the upper set of levels, from which photo-induced ligand substitution reaction occurs, is in a region $3600cm^{-1}$ above the lower set which are photoinert (ref.14).

Recently, we calculated the lowest excited states of $[Rubpy(en)_2]^{2+}$ as well as $[Ru(bpy)_3]^{2+}$ by use of the composite system method. The calculation was semiempirical but all the multicentric integrals and overlap integrals were taken into account. The method can reasonably predict a difference in the electronic correlation between the ground and excited states and reproduce the observed spectra not only of benzene, pyridine and pyrazine but also of biphenyl and bipyridine.

The spin-orbit coupling interactions within ruthenium d_π orbitals give rise to mixing of the singlet and triplet manifolds of the metal-to-ligand charge-transfer excited states (ref.15). The present theoretical approach to the nature of the excited state spin-orbit coupling sublevels has been achieved by taking into account configuration interaction between the low-lying states.

The absorption bands at $20\times10^3cm^{-1}$ and $27\times10^3cm^{-1}$ are assigned to the "metal-to-bipyridine" charge-transfer excited singlet states, $^1CT(yz,zx\rightarrow\pi_7)$ and $^1CT(yz,zx\rightarrow\pi_8)$, respectively, where yz, zx and π_7, π_8 are the filled and vacant molecular orbitals in which the metal d_π and the bipyridine π orbitals make a predominant contribution. The band in $34\times10^3cm^{-1}$ followed by the (0,1) vibronic band is ascribed to the bipyridine $^1(\pi,\pi^*)$ excited state $^1LE(\pi_6\rightarrow\pi_7)$. The non-relativistic model predicts two components of $^3CT(yz,zx\rightarrow\pi_7)$ at $17.5\times10^3cm^{-1}$ and

$17.52\times10^{3}cm^{-1}$ and the forbidden and allowed components of $^{1}CT(yz,zx\rightarrow\pi_7)$ at $18.2\times10^{3}cm^{-1}$ and $20.0\times10^{3}cm^{-1}$. The d_{xy} orbital is isolated from the ligand π orbitals in $[Rubpy(en)_2]^{2+}$ and thus $^{1,3}CT(xy\rightarrow\pi_7)$ are strictly forbidden. The backbonding stabilizes only yz and zx orbitals. The oxidation potentials of $[Rubpy(en)_2]^{2+}$ and $[Rubpy(NH_3)_4]^{2+}$ are reduced raising the d_{xy} orbital which is not stabilized by the backbonding.

Spin-orbit coupling interactions mix the spin-forbidden states with the spin-allowed states. However the lowest sublevel of $^{3}CT(yz,zx\rightarrow\pi_7)$ in $[Rubpy(en)_2]^{2+}$ lacks contributions from the allowed excited singlets, while the second and third sublevels can be the emitting states since they are granted an appreciable but less than 10% contribution of the allowed $^{1}CT(yz,zx\rightarrow\pi_7)$ and a variety of ^{1}LE's. An absorption shoulder observed in $17\times10^{3}cm^{-1}$ (ref.13), which is a mirror image of the luminescence band, is a manifold of the weakly allowed sublevels of $^{3}CT(yz,zx\rightarrow\pi_7)$ and $^{1}CT(yz,zx\rightarrow\pi_7)$ origin.

It is also noted that the spin-orbit coupling enhances the intensities not only of $^{3}CT(yz,zx\rightarrow\pi_8)$ but also of $^{3}LE(\pi_6\rightarrow\pi_7)$ in the $25{\sim}30\times10^{3}cm^{-1}$ region.

The exciton coupling in $[Ru(bpy)_3]^{2+}$ is not strong even in the allowed transition and the structure of the lowest excited states of $[Ru(bpy)_3]^{2+}$ must be very close to that of $[Rubpy(en)_2]^{2+}$.

THE CHARGE-TRANSFER STATES OF Cr^{III} AND Co^{III} PORPHYRINS

Al^{III}porphyrin is a typical porphyrin incorporated with a tervalent metal ion; characteristic Q and B bands in the visible and near-ultraviolet region, respectively, are the (π,π*) excitations in the porphyrin ring with only minor perturbation from the outer-shell electrons of the central metal ion (ref.16). On the other hand, Cr^{III}, Mn^{III} and Fe^{III} porphyrins show rather complicated spectral profiles attributable to the configuration-interaction admixtures of the porphyrin (π,π*) excited states and the "porphyrin-to-metal" charge-transfer excited states (refs. 17-18). The ground state of Cr^{III} porphyrin is a spin quartet state. The lowest spin-allowed excited states of E symmetry of Cr^{III}porphyrin are described by superpositions of the antisymmetric product wavefunctions $^{4}E[^{3}(1a_1\rightarrow4e)\cdot{}^{4}A]$, $^{4}E[^{3}(3a_2\rightarrow4e)\cdot{}^{4}A]$, $^{4}E[^{1}(1a_1\rightarrow4e)\cdot{}^{4}A]$, $^{4}E[^{1}(3a_2\rightarrow4e)\cdot{}^{4}A]$, $^{4}E[^{2}A_1(1a_1)\cdot{}^{3}E(d\pi)]$ and $^{4}E[^{2}A_1(3a_2)\cdot{}^{3}E(d\pi)]$, where $^{3}(1a_1\rightarrow4e)$, $^{3}(3a_2\rightarrow4e)$, $^{1}(1a_1\rightarrow4e)$, and $^{1}(3a_2\rightarrow4e)$ are the wavefunctions of the lowest porphyrin (π,π*) excited triplets and singlets, respectively, ^{4}A denotes the ground state of the Cr^{III} quartet state and $^{4}E[^{2}A_1(1a_1)\ ^{3}E(d\pi)]$ and $^{4}E[^{2}A_1(3a_2)\cdot{}^{3}E(d\pi)]$ are the wavefunctions of the excited states which arise from the "porphyrin-to-chromium" charge transfer $1a_1\rightarrow d\pi$ and $3a_2\rightarrow d\pi$, respectively. The electronic delocalization between the orbitals d_{π} and 4e connects two excited configurations which differ in a single orbital. The energy of the charge-transfer state varies with the central metal ion but is not so different from those of the lowest porphyrin (π,π*) excited states. The lowest excited states of Cr^{III} and Mn^{III} complexes are mostly of the (π,π*) triplet excited states and the split Soret bands are ascribed to an equivalent admixture of the porphyrin second excited singlet (S_2) and the "porphyrin-to-metal" charge-transfer states (ref.19). On the other hand, the lowest excited states of high-spin Fe^{III}porphyrins are equivalent admixtures of (π,π*) excited triplets and charge-transfer excited states. The observed spectra of Cr^{III}, Mn^{III} and Fe^{III} porphyrins can be theoretically reproduced for the "porphyrin-to-metal" charge-transfer energies $25.0\times10^3cm^{-1}$, $22.0\times10^3cm^{-1}$ and $12.5\times10^3cm^{-1}$, respectively. The electron affinities of d_π orbitals of Cr^{III}, Mn^{III} and Fe^{III} ions are estimated as 28.27eV, 28.93eV and 30.64eV, respectively, from the atomic spectral term values. A plot of the "porphyrin-to-metal" charge-transfer energies against the d_π electron affinities gives a straight line.

$Co^{III}ClTPP$ in non-coordinating media is not necessarily in the diamagnetic ground state $^1A_1(d_\pi{}^6)$. When the axial ligand field is weak, the ground state of Co^{III} ion is switched from $^1A_1$ to either ^3E or $^5B_2$, ^5E. The triplet ground state as well as the quintet has open-shell d_π orbitals. Thus the d_π electron affinities in the ^3E and $^5B_2$, ^5E states are estimated to be 34.04eV and 33.08eV, respectively. An extrapolation of the straight line obtained for Cr^{III}, Mn^{III} and Fe^{III} porphyrins predicts zero or a minus charge transfer energy for the high spin Co^{III}porphyrin. This implies that a spontaneous electron transfer takes place from porphyrin to the central cobalt(III) ion in a high spin state which arises only in a weak axial ligand field.

In non-coordinating media, the following equilibria must be established;

$$Co^{III}(^1A_1)ClTPP \rightleftharpoons Co^{III}(^3E)ClTPP$$
$$Co^{III}(^3E)ClTPP \rightleftharpoons Co^{II}ClTPP^+$$
$$2Co^{II}ClTPP^+ \rightleftharpoons Co^{II}TPP + Co^{III}Cl_2TPP^+$$

In fact, $Co^{III}ClTPP$ in non-coordinating solvents as well as in crystal yields $Co^{II}TPP$ and $Co^{III}Cl_2TPP^+$ (ref.19). Addition of a small amount of a coordinating solvent such as alcohol and pyridine gives rise to a remarkable shift of the equilibrium which allows exclusively the singlet ground state $Co^{III}(^1A_1)ClTPP$. The spectrum of Co^{III} in benzene shows a component which is in good agreement with that of the porphyrin cation radical, while the spectrum in alcohol is of a typical diamagnetic metalloporphyrins. The spectrum of the benzene solution also exhibits evidence of the formation of cation dimer.

Al^{III}, Ga^{III} and In^{III} porphyrins exhibit characteristic Q and B bands which are the (π,π^*) transitions in the porphyrin ring. Cr^{III} porphyrins, on the other hand, show a spectrum of complicated profile including the S-T absorption bands to the red of the Q band and the split Soret bands. The lowest excited state of Cr^{III} porphyrin, which is mostly of the lowest (π,π^*) excited triplet state (T_1), decays in a short lifetime (ref.20 and 21).

Diamagnetic Ni^{II} porphyrins exhibit normal Q and B bands, however, nonradiative relaxation of the excited states arises in a very short period. Pd^{II} and Pt^{II} porphyrins, which have an isoelectronic outer-shell, emit phosphorescence. The nonluminescent character of Ni^{II} porphyrins has been ascribed to the $^1(d,d^*)$ state lower than the porphyrin T_1 state (ref.22). For the complexes of d^8 ions such as Pd^{II} and Pt^{II} as well as diamagnetic d^6 ion Rh^{III}, in which no $^1(d,d^*)$ and charge-transfer excited states exist lower than the S_1 and T_1 states, strong phosphorescence can be detected even at ambient temperatures (refs.23-27). These complexes, however, exhibit no fluorescence from the second excited singlet. The S_2 fluorescence was observed for a variety of closed-shell metalloporphyrins.

The Q band is of forbidden character but can borrow intensity from the allowed B bands. The intensity of the Q(0,0) band without excitation in the skeletal vibrational modes is rather sensitive to various substituents, while those of the vibronically allowed Q(1,0) bands are less sensitive. The forbidden character of the Q band is attributable to the lowest component of a 50-50 admixture of two excited configurations $^1(a_{1u}e_g)$ and $^1(a_{2u}e_g)$ with almost equal transition dipoles (ref.28). The substituents including the central metal ion remove the accidental degeneracy and the intensity of the Q(0,0) band is enhanced. It is followed that

$$\varepsilon(0,0)/\varepsilon(1,0) \sim [E(^1(a_{2u}e_g)) - E(^1(a_{1u}e_g))]^2 \sim \Delta E^2.$$

Table 2 shows characteristic ratio $\varepsilon(0,0)/\varepsilon(1,0)$ observed for zinc porphyrins. The ratios $\varepsilon(0,0)/\varepsilon(1,0)$ of ZnTPP and ZnT(p-C_2H_5O)PP (T(p-C_2H_5O)PP:

TABLE 2

Ratio of The Molar Absorption Coefficients of Q(0,0) and Q(1,0) Bands.

Compound	$\varepsilon(0,0)/\varepsilon(1,0)$
ZnTPP	0.16
ZnT(p-C_2H_5O)PP	0.32
ZnTFPP	0.21
ZnP	0.44
ZnOEP	1.81

tetra(p-ethoxyphenyl)porphin) increase upon the axial ligation of pyridine which stabilizes the configuration $^1(a_{2u}e_g)$, while those of ZnTFPP (TFPP: tetra(pentafluorophenyl)porphin), ZnP (P: porphin) and ZnOEP (OEP: octaethylporphin) decrease. The fact that a decrease in $E(^1(a_{2u}e_g))$ results in an increase of $(\Delta E)^2$ in ZnTPP and ZnT(p-C_2H_5O)PP but a decrease in ZnTFPP, ZnP, and ZnOEP indicates that the ΔE's values in ZnTPP and ZnT(p-C_2H_5O)PP are negative while those of ZnTFPP, ZnP, and ZnOEP are positive.

A variety of relative rates of the intersystem crossing $T_1 \rightsquigarrow S_0$ are well explained by the energy-gap law (ref.29). In fact, the lifetime of the OEP phosphorescence is much longer than that of the red-shifted TPP phosphorescence. However, this must be ascribed to the T_1 state of $^3(a_{1u}e_g)$ in OEP complexes. The longer lifetime of ZnTFPP is attributable to a relatively high contribution of the $^3(a_{1u}e_g)$, while the shorter lifetimes of ZnTPP and ZnT(p-C_2H_5O)PP to the T_1 state of $^3(a_{2u}e_g)$.

The metal complexes of TPP fluorescence from the S_2 excited state (ref.30). The excitation spectrum of the S_2 fluorescence is in good agreement with the ultraviolet absorption spectrum. Some of the S_2 fluorescence yields observed in the present work are presented in Table 3. The yields are rather independent of the central metal ion. Theoretical calculations of the porphyrin excited states concluded that there is no orbitally allowed excited triplets between S_1 and S_2 (ref.31).

TABLE 3
The Yields of The S_2 Fluorescence

Compound	Solvent	$\phi_f^{S_2}\times10^4$	$\Delta E_{S_2-S_1}$ (10^3cm^{-1})
AlClTPP	benzene	2.8	6.86
GaClTPP	benzene	3.1	6.69
InClTPP	benzene	3.6	6.81
AlClTPP	ethanol	5.5	7.11
GaClTPP	ethanol	4.6	7.00
InClTPP	ethanol	4.7	7.06
ZnTPP	benzene	3.5	6.69
ZnT(p-C_2H_5O)PP	benzene	3.6	6.61
ZnTFPP	benzene	0.46	6.57
ZnP	benzene	0.73	7.23
ZnOEP	benzene	<0.04	7.21
PbTPP	benzene	0.43	6.24
PbOEP	benzene	0.04	
H_4TPP^{2+}	benzene	0.59	7.51
H_4P^{2+}	benzene	0.56	7.90

The S_2 fluorescence is not observed in any metal complexes of OEP except PbOEP. Since the excitation spectrum of S_1 fluorescence of the complexes, which emit the S_2 fluorescence, is almost identical to the absorption spectrum even in the range of 250 nm the internal conversion $S_2 \rightsquigarrow S_1$ must be much faster than the intersystem crossing $S_2 \rightsquigarrow T_n$ and the internal conversion $S_2 \rightsquigarrow S_0$. A prominent role of the C-H stretching modes of peripheral ethyl groups has been proposed as a more effective accepting mode in the OEP complexes than those of phenyl groups in the TPP complexes (ref.32). However, the lack of the S_2 emission should be ascribed to their much faster internal conversion. ZnTPP and ZnP display the S_2 emission while ZnOEP does not. The yield in ZnTFPP is much lower than that of ZnTPP. The absorption intensity in Soret band is almost the same for ZnTPP and ZnOEP, while the yield of the S_2 fluorescence decreases in the ordering; ZnT(p-C_2H_5O)PP ~ ZnTPP > ZnP ~ ZnTFPP > ZnOEP. This is the reverse of the order found in ΔE. As seen in the intensity of the Q(0,0) band of ZnOEP, an increase of ΔE in ZnOEP enhances admixing of the Q and B states. This promotes an internal conversion $S_2 \rightsquigarrow S_1$ in ZnOEP.

The S_2 emission is observed for PbOEP and PbTPP. Pb(II) porphyrins show "hyperporphyrin" spectra (ref.33). The configuration interaction of the Q and B excited states and the "metal-to-porphyrin" charge-transfer excited states result in a redistribution of spectral intensity and increase the intensity of Q(0,0) in PbTPP but decreases in PbOEP. The detectable S_2 fluorescence of PbOEP is attributable to a decrease in the admixing of the Q and B states.

No S_2 emission was detected in free-base porphyrins such as H_2TPP, H_2OEP and H_2P. As indicated by the enhanced Q_y band in the free bases, a small energy gap and a strong coupling of Q_y and B states are responsible for the fast deactivation of the B state. In contrast with the free bases, diacids H_4TPP^{2+} and H_4P^{2+} emit rather intense S_2 fluorescence.

A variety of TPP metal complexes generate blue light upon red laser-light excitation. According to our measurements using successive laser pulses of two different wavelengths with a varied delay, the pumping to the S_2 excited state is mainly attributable to the successive two-photon absorption, $S_0 \rightarrow S_1 \rightarrow S_n \rightsquigarrow S_2$ but not $S_0 \rightarrow S_1 \rightsquigarrow T_1 \rightarrow T_n \rightsquigarrow S_2$ and a T-T annihilation process (ref.34).

DISSOCIATION OF LIGANDS IN THE EXCITED STATE

Single crystals of Ce^{3+} doped lanthanum(III) ethylsulfate enneahydrate (Ce:La.ES) exhibit five absorption bands in a region between 37 and $51\times10^3 cm^{-1}$. In the crystal, the Ce^{III} ion is surrounded by nine water molecules and forms $[Ce(OH_2)_9]^{3+}$ in a tricaped trigonal prism. The five bands are assigned to five Kramers doublets which are the $^2D(5d^1)$ multiplet split by the ligand-field interaction in $[Ce(OH_2)_9]^{3+}$ and the spin-orbit coupling of a cerium 5d electron (ref.35). Two resolved luminescence bands are detected in 30 and $32\times10^3 cm^{-1}$ at liquid nitrogen temperature. The twin emission bands, which cannot be resolved at ambient temperatures, are ascribed to the transitions to the $^2F_{5/2}$ and $^2F_{7/2}$

substates which are two components of the ground $^2F(4f^1)$ multiplet.

Hydrated Ce^{3+} ions present in aqueous solution show absorption bands corresponding to those observed with Ce:La.ES. Thus the hydrated ions in aqueous media must be in a structure of $[Ce(OH_2)_9]^{3+}$ similar to those in the single crystal. However an extra weak absorption band is observed at $34\times10^3cm^{-1}$ with the hydrated ions in aqueous solution. The band can not be detected with Ce:La.ES even if a high concentration of Ce^{3+} and/or a thick crystal are used (ref.36). The ligand splitting of the $^2D(5d^1)$ multiplet gives not more than five Kramers doublets. Elevation of temperature gives rise to an enhancement of the extra band but a decrease in the intrinsic bands of $[Ce(OH_2)_9]^{3+}$. The spectral change is reversible with variation of temperature displaying isosbestic points. The intensity of the $34\times10^3cm^{-1}$ band is independent of the hydrogen-ion concentration in solution. Thus the weak band absent in $[Ce(OH_2)_9]^{3+}$ is assigned to the lowest component band of a ligand-dissociated species such as $[Ce(OH_2)_8]^{3+}$ but not of a proton-dissociated species such as $[Ce(OH)(H_2O)_8]^{2+}$. Recent X-ray studies on the aqueous solutions concluded that the hydrated ions La^{3+} through Nd^{3+} are nine coordinated and those between Nd^{3+} and Tb^{3+} are transitional between nine and eight (ref.37 and 38). For aqueous solutions of Ce^{3+} ion, an emission band is observed at $28\times10^3cm^{-1}$ regardless of the excitation in the band to be assigned to $[Ce(OH_2)_8]^{3+}$ or in the five component bands of $[Ce(OH_2)_9]^{3+}$ (ref.36). This implies that the luminescence is only of the dissociated species. The luminescence of hydrated Ce^{3+} ion in aqueous media decays in a single exponential of 45 ns lifetime regardless of the excitation wavelengths while that of Ce:La.ES decays in a shorter lifetime of 27 ns. No variation of the emission intensity is observed for temperature rise. However the temperature variation of the excitation spectra conforms to that of the absorption spectra. Regardless of the monitoring wavelengths within the emission band, an actually identical excitation spectrum is obtained.

An equilibrium between $[Ce(OH_2)_9]^{3+}$ and $[Ce(OH_2)_8]^{3+}$ exists in aqueous media, where the predominant species is $[Ce(OH_2)_9]^{3+}$. Upon the 5d←4f excitation of the central metal ion, one of the aqualigands of $[Ce(OH_2)_9]^{3+}$ dissociates during the excited state lifetime. The equilibrium is shifted to an exclusive predominance of $[Ce(OH_2)_8]^{3+}$ in the excited state ($*[Ce(OH_2)_8]^{3+}$). In a very early stage after excitation, however, the emissions not only of the long lived excited species $*[Ce(OH_2)_8]^{3+}$ (48 ns) but also of the short lived excited species $*[Ce(OH_2)_9]^{3+}$ (430 ps) are detected in ethylene glycol. The rise transient of emission indicates an increase of $*[Ce(OH_2)_8]^{3+}$ immediately after pulse excitation. The lifetime of $*[Ce(OH_2)_9]^{3+}$ in ethylene glycol is governed by the rate of aqualigand dissociation $k_3=2.3\times10^9s^{-1}$.

The structure of $[Ce(OH_2)_9]^{3+}$ is a tricapped trigonal prism. In the lowest substate of $^2D(5d^1)$, the promoted electron occupies in d_{z^2} orbital which extends in the direction of the C_3 symmetry axis. The excitation results in a shift of the vertex water molecules to the equatorial and thus one of the equatorial waters is eliminated. A calculation based on the angular overlap model taking into account the spin-orbit coupling predicts the lowest 5d←4f excited Kramers doublet of $[Ce(OH_2)_8]^{3+}$ in an energy region much lower than the lowest component of $[Ce(OH_2)_9]^{3+}$. The structure of the excited octacoordinate species in solution must be fluxional between dodecahedron, square antiprism, and/or cube.

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