

## Porphyrins. 40.<sup>1</sup> Electronic Spectra and Four-Orbital Energies of Free-Base, Zinc, Copper, and Palladium Tetrakis(perfluorophenyl)porphyrins

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Absorption and emission spectra and emission quantum yields are given for free-base ( $H_2$ ), Zn, Cu, and Pd derivatives of tetrakis(perfluorophenyl)porphyrin (TFPP). The four-orbital model is used to rationalize differences in the optical properties among the derivatives of TFPP and the same derivatives of porphine (P), octaethylporphyrin (OEP), and tetraphenylporphyrin (TPP). It is concluded from absorption data that the energy difference between the two excited singlets, i.e.,  ${}^1E(a_{2u},e_g) - {}^1E(a_{1u},e_g)$ , decreases along the series Pd > Cu > Zn >  $H_2$  and also along the series OEP > P  $\geq$  TFPP > TPP. The theory and data are reviewed, and it is concluded that the energy difference between the two excited triplets, i.e.,  ${}^3E(a_{2u},e_g) - {}^3E(a_{1u},e_g)$ , also decreases along these series. However the condition of degeneracy, e.g.,  ${}^1E(a_{2u},e_g) - {}^1E(a_{1u},e_g) = 0$ , occurs for different molecules in the singlet and triplet cases. Theory also suggests that if  ${}^3E(a_{2u},e_g) > {}^3E(a_{1u},e_g)$ , the molecule should form a  ${}^2A_{1u}$  cation radical and if  ${}^3E(a_{2u},e_g) < {}^3E(a_{1u},e_g)$  the molecule should form a  ${}^2A_{2u}$  radical.

### Introduction

Longo, Finarelli, and Kim reported the synthesis of new porphyrins, tetrakis(perfluorophenyl)- and tetrakis(perchlorophenyl)porphyrin, 10 years ago<sup>2</sup> and noted that the most interesting features of the new compounds were their unusual electronic spectra, which distinguished them from tetraphenylporphyrins. Further spectral studies were reported by these same workers.<sup>3</sup> Levanon et al. reported transient EPR signals from the photoexcited triplet of free-base tetrakis(perfluorophenyl)porphyrin [ $H_2$ (TFPP)], which were compared to those of the free-base tetraphenylporphyrin [ $H_2$ (TPP)] and to other free-base porphyrins.<sup>4</sup> The catalytic activity of Co(TFPP) has been investigated by Bar-Ilan and Manassen,<sup>5</sup> who were interested in the effect of ring substituents on the electron density at the metal ion. The  ${}^{19}F$  magnetic resonance spectrum of In(TFPP)Cl was measured as part of a study of phenyl-ring rotation in substituted tetraphenylporphyrins.<sup>6</sup>  $H_2$ (TFPP) is included in a study of tautomerism in tetraarylporphyrins.<sup>7</sup>

We became interested in these particular porphyrins because the electron-withdrawing character of the perfluorophenyl substituents strongly raises the redox potentials of these complexes, a feature that might be expected to have effects on film photovoltaic properties.<sup>8</sup> We became further interested in these complexes when it was found that solid films of samples of  $H_2$ (TFPP) and Zn(TFPP) show bright emission when excited by a UV lamp. A report on the emission of solid films of  $H_2$ (TFPP) has appeared.<sup>9</sup> To provide a reference for these solid-state studies we undertook the investigation of the absorption and emission of solutions of  $H_2$ (TFPP) and its Zn, Cu, and Pd derivatives. These three metals were chosen as each represents a different emission type found among metalloporphyrins: *fluorescent* (Zn), *luminescent* (Cu), and *phosphorescent* (Pd). The nature and cause of these three emission types have been defined in a recent review of the electronic structure and optical spectra of porphyrins.<sup>10</sup> This review also describes the four-orbital model for the lower energy excited ( $\pi, \pi^*$ ) states of porphyrin. As we show below,

the four-orbital model allows us to explain differences in absorption among the free-base, Zn, Cu, and Pd derivatives of porphine (P), octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), and the TFPP complexes reported here.

### Synthesis and Experimental Procedures

**$H_2$ (TFPP)** was synthesized according to the method of Longo et al.<sup>2</sup> from pentafluorobenzaldehyde (Aldrich Chemical Co., Inc., Milwaukee, WI 53233) and distilled pyrrole.  $H_2$ (TFPP) made in this way contains considerable chlorine impurity, which is not easily separated from the porphyrin by chromatography. To obtain chlorine-free  $H_2$ (TFPP) we converted the impure  $H_2$ (TFPP) to Zn(TFPP) and purified the latter, as described below. The Zn(TFPP) was demetalated to form  $H_2$ (TFPP) by the dropwise addition of an equal-volume mixture of  $CF_3COOH$  and  $CHCl_3$ , until a color change from red to blue-green, the color of the  $H_2$ (TFPP) acid dication, took place. The mixture was washed with two portions of concentrated  $NH_4OH$  and four times with water. The solvent was evaporated at reduced pressure.

**Zn(TFPP)** was prepared by refluxing 2.5 g of  $H_2$ (TFPP) in 150 mL of dimethylformamide (DMF) to which a 10 times molar excess of  $ZnCl_2$  was added. Zn(TFPP) was precipitated from the cooled mixture upon addition of water. Zn(TFPP) was chromatographed on a column of wet-packed Woelm basic alumina (activity grade I) with benzene as eluant.

**Cu(TFPP)** was made by refluxing  $H_2$ (TFPP) in DMF with a 25 times molar excess of cupric acetate. The dried product was chromatographed on a dry column of Fisher A-540 alumina with a continuous stream of  $CHCl_3$  as eluting solvent.<sup>11</sup>

**Pd(TFPP)** was made from  $H_2$ (TFPP) and a 10 times molar excess of  $PdCl_2$  refluxed 1 h in DMF. The product was a mixture of  $H_2$ (TFPP) and Pd(TFPP) which could not be resolved chromatographically. When this mixture was chromatographed, redissolved in DMF, and refluxed with  $ZnCl_2$ , a mixture of Zn(TFPP) and Pd(TFPP) was obtained. This mixture was resolved on a Woelm basic alumina column with  $CH_2Cl_2$  as eluant.

[Note: Emission and excitation spectra taken on the Pd(TFPP)- $H_2$ (TFPP) mixture showed unusual effects, which suggest the existence of a complex. The emission of the mixture was substantially weaker than that expected from a sum of the components. Furthermore, when the sample was excited with 583-nm light, an absorption peak of  $H_2$ (TFPP) but not Pd(TFPP), an emission is observed at a novel wavelength, 655 nm, typical of neither  $H_2$ (TFPP) nor Pd(TFPP). In the excitation spectrum ( $\lambda_{det} = 655$  nm) the band at 583 nm appears; but much more intense is a spectrum of Pd(TFPP) blue-shifted about 10 nm relative to the peaks observed for Pd(TFPP) alone.]<sup>12</sup>

**Absorption spectra** were taken on a Varian SuperScan 3 spectrophotometer; all absorption spectra were taken with neat solvent as reference. Absorption spectra were taken at room temperature with

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Table I. Absorption Peaks of Tetrakis(perfluorophenyl)porphyrins (nm)<sup>a</sup>

compd	L	N	B(0,0)	other	Q <sub>y</sub> (1,0)	Q <sub>y</sub> (0,0)	Q <sub>x</sub> (1,0)	Q <sub>x</sub> (0,0)
H <sub>2</sub> (TFPP)	262	309	410 (264)		505 (18.5)	535 (2.2)	582 (5.9)	635 (0.92)
Zn(TFPP) <sup>b</sup>	257	317	412 (479)	~350	543 (20.9)	578 (5.4)		
Cu(TFPP) <sup>b</sup>	~265 sh <sup>d</sup>	314	407 (294)	470, 495	535 (13) <sup>c</sup>	570 (6.1)		
Pd(TFPP) <sup>b</sup>	280	313	406 (192)	~481	519 (18.2)	552 (15.5)		

<sup>a</sup> All spectra at room temperature in CH<sub>2</sub>Cl<sub>2</sub>. In parentheses is  $\epsilon$  in units of 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>. <sup>b</sup> For metal complexes Q<sub>y</sub> and Q<sub>x</sub> bands coincide. <sup>c</sup> Absolute value for  $\epsilon$  of Q(1,0) band taken from ref 2. <sup>d</sup> Shoulder.

Table II. Luminescence Parameters of Tetrakis(perfluorophenyl)porphyrins<sup>a</sup>

compd	solvent <sup>b</sup>	Q(0,0)	Q(0,1)	T(0,0)	T(0,1)	$\phi_f$	$\phi_p$	$\tau_p$
H <sub>2</sub> (TFPP)	3-MP	631	698	806 <sup>c</sup>		0.07	<i>c</i>	
Zn(TFPP)	3-MP	585	641	729	816	0.014	0.008	48 ms
Cu(TFPP)	3-MP			687	738, 768		0.05	205 $\mu$ s
	3-MP <sup>d</sup>			700	728, 779			
Pd(TFPP)	CH <sub>2</sub> Cl <sub>2</sub> <sup>e</sup>	564	610			<i>e</i>		
	3-MP			663	738		0.21	1.65 ms

<sup>a</sup> Taken at 77 K unless noted otherwise. Peak wavelengths in nm. <sup>b</sup> 3-MP is 3-methylpentane. <sup>c</sup> Obtained with 50% ethyl iodide; unobserved in its absence. <sup>d</sup> Taken at liquid-helium temperature. <sup>e</sup> Taken at room temperature; weak. See text.

solvent which had been run over a column of basic alumina.

Molar extinction coefficients ( $\epsilon$ ) for H<sub>2</sub>(TFPP) and Cu(TFPP) have been reported.<sup>2</sup> We determined the molar extinctions for H<sub>2</sub>(TFPP), Zn(TFPP), and Pd(TFPP) by weighing about 10 mg of each on a Mettler balance and dissolving the weighed sample in 10.00 mL of CH<sub>2</sub>Cl<sub>2</sub>. These solutions were then diluted to an appropriate absorbance range.

Emission spectra and lifetimes were taken as described recently.<sup>13</sup> Excitation spectra showed that the reported emission peaks come from the main absorbing species. The solvent for emission studies was 3-methylpentane, which forms a glass at liquid-nitrogen temperature. All compounds discussed here were examined for emission in liquid nitrogen in the spectral range 560–840 nm with an RCA 8852 photomultiplier tube.

Quantum yields were determined relative to Zn(Etio-I), the absolute fluorescence quantum yield of which was taken to be 0.04 at 77 K.<sup>14</sup> Note that the Zn(Etio-I) was in an EPA glass.

### Electronic Absorption

The data for absorption by the four TFPP's investigated are presented in Table I. The absorption spectra are shown in Figure 1. The nomenclature for porphyrin absorption and emission bands has been recently reviewed.<sup>10</sup> Typically porphyrin absorption includes an intense near-UV band, called B or Soret, and two visible bands: Q(0,0) represents excitation from the lowest vibrational level of the ground-state singlet to the lowest vibrational level of the first excited singlet electronic state, and Q(1,0) has one quantum of vibration in the first excited singlet electronic state. In metalloporphyrins with square symmetry these bands are due to degenerate excited states with *x* and *y* polarization. In the free base the Q<sub>x</sub>(0,0) and Q<sub>y</sub>(0,0) bands are no longer degenerate due to the proton axis. Thus while metalloporphyrins typically show two clear, visible bands, the free base shows four.

The absorption spectrum of H<sub>2</sub>(TFPP) (Figure 1A) shows the near-UV Soret and four visible bands typical of free-base porphyrins.<sup>10</sup> The Q<sub>x</sub>(0,0) and Q<sub>y</sub>(0,0) bands are weak, as in free-base porphine.<sup>10</sup> Reasons for this weakness are given below. Note that the moderately intense band at 659 nm reported by Longo et al.<sup>2,3</sup> was found to be a chlorin impurity.

Several other features of these absorption spectra can be noted.

(1) The principal electronic bands of the free-base and metallotetrakis(perfluorophenyl)porphyrin are intermediate in energy between the corresponding OEP at higher energy and the corresponding TPP at lower energy.

(2) The Q(0,0) band of Zn(TFPP) is ligand sensitive. Nappa and Valentine<sup>15</sup> report the effect of axial ligands on the visible absorption of Zn(TPP). Similarly, we dissolved Zn(TFPP) in solvents of varying Lewis basicity. The energy of the Q bands and the relative absorbance of Q(0,0)/Q(1,0) varies. These results are shown in Figure 2.

(3) Petke et al.<sup>16</sup> have recently carried out ab initio SCF-MO calculations on Mg(P). They predict bands as follows (oscillator strengths in parentheses): 584 nm (0.092), 382 nm (3.602), 340 nm (0.0706), and 320 nm (1.482). Zinc porphyrins are similar to magnesium porphyrins with respect to optical absorption and ligand binding. In the spectra (Figure 1) it can be seen that Zn(TFPP), unlike Cu(TFPP) and Pd(TFPP), shows a clear extra band at ~350 nm, between the N band at 317 nm and the Soret band at 412 nm. It is tempting to identify the band observed at ~350 nm with the band calculated by Petke et al. for 340 nm.

(4) As with other copper porphyrins, Cu(TFPP) showed a slightly hypso (i.e., blue-shifted) absorption. We also note unusual bands occurring between the B and Q bands at 470 and 495 nm. Their intensity is approximately 0.1 times the intensity of the Q(1,0). These bands occur in all luminescence excitation spectra. In recent studies of silver(II) porphyrins, charge-transfer transitions,  $d_{x^2-y^2} \rightarrow e_g(\pi^*)$ , are identified in the near-infrared spectra.<sup>17</sup> Similar transitions are expected at higher energy in copper(II) porphyrins. Tentatively we identify these extra bands as of such character.

(5) As expected,<sup>10</sup> the Pd(TFPP) shows more pronounced hypso absorption. Also, an unusual band at 481 nm appears in absorption and in all excitation spectra. This band as well as the broadness of the Soret band first suggested the presence of porphyrin dimers. However, a spectrum taken on a sample 0.1 times the original concentration in a cell 10 times as long was exactly the same. While the 481-nm band might be a Q(2,0) band, the energy gap between it and Q(1,0) is rather larger than expected for a vibration. We tentatively identify this band as  $d \rightarrow \pi^*$  in origin. It is possible that the broadness of the Soret band arises because of other underlying  $d \rightarrow \pi^*$  bands.

### Electronic Emission

The wavelengths of emission and other data for the TFPP compounds are presented in Table II. In each case the TFPP's

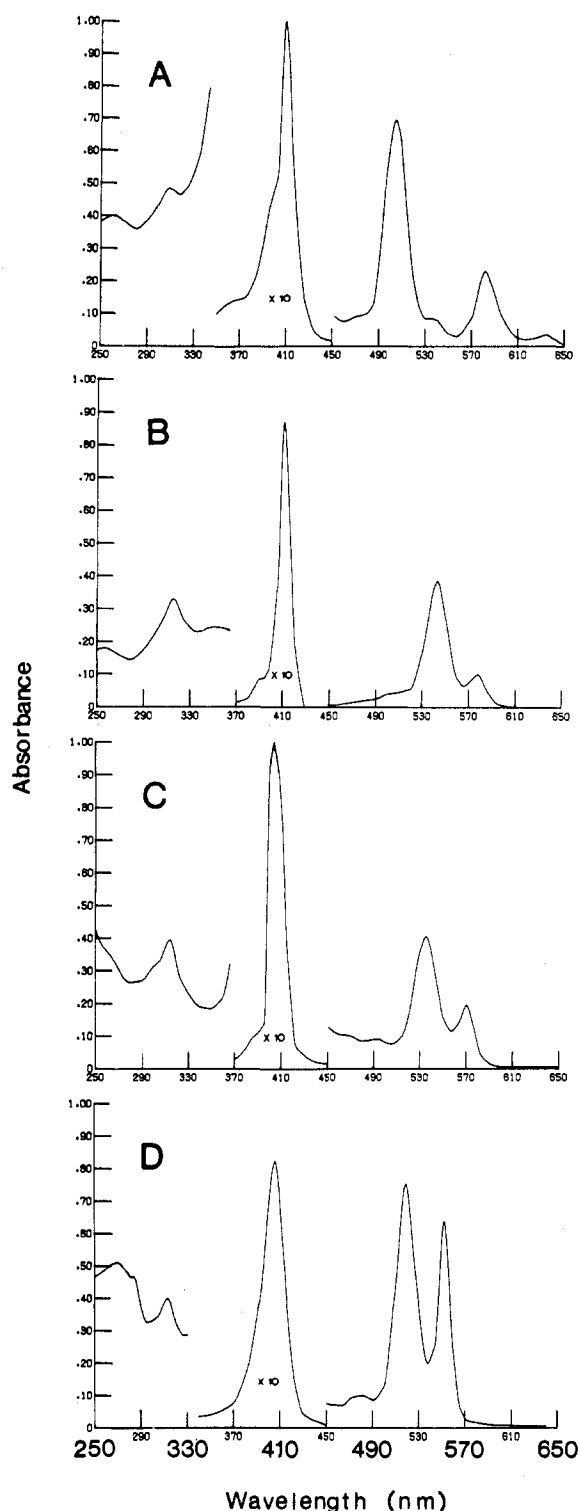
(13) Part 36: A. Antipas, J. W. Buchler, M. Gouterman, and P. D. Smith, *J. Am. Chem. Soc.*, **100**, 3015 (1978).

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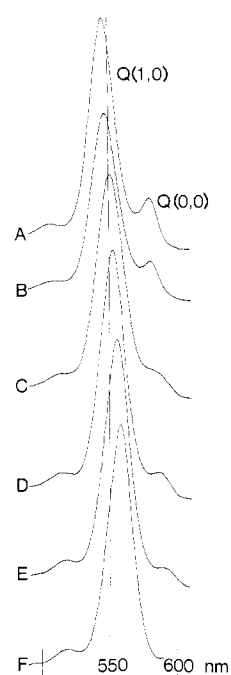
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**Figure 1.** Absorption spectra of tetrakis(perfluorophenyl)porphyrin complexes taken in  $\text{CH}_2\text{Cl}_2$  at room temperature: (A) free base; (B) Zn complex; (C) Cu complex; (D) Pd complex.

emit at wavelengths between those of the analogous OEP at higher energy and those of the analogous TPP at lower energy.<sup>10,12</sup> The emission spectra are presented in Figure 3.

$\text{H}_2(\text{TFPP})$  is a fluorescent emitter. In a heavy-atom solvent, emission from the triplet state is enhanced; we could detect emission at 806 nm in a solvent that was 50% ethyl iodide–50% 3-methylpentane. An excitation spectrum of the phosphorescence showed the characteristic 410- and 505-nm absorption. Heavy-atom solvent phosphorescence has been observed in  $\text{H}_2(\text{P})$  and  $\text{H}_2(\text{OEP})$  but not in  $\text{H}_2(\text{TPP})$ .<sup>18</sup>



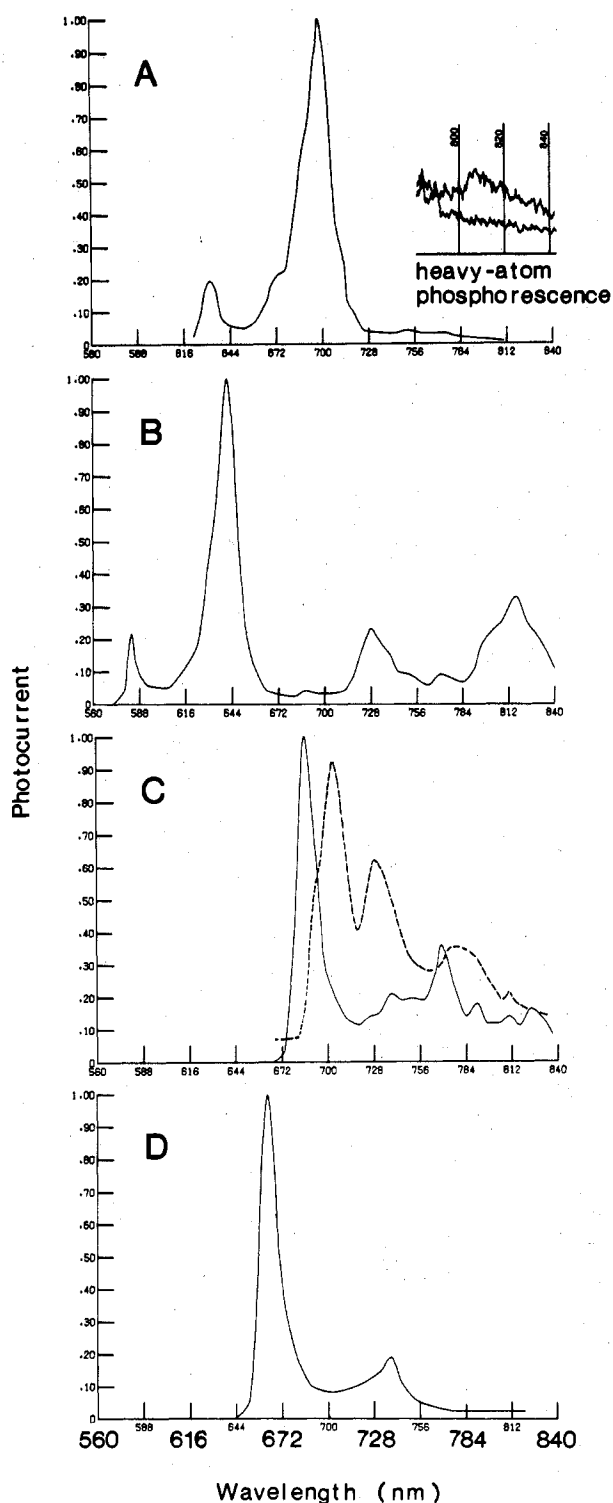
**Figure 2.** Solvent-dependent absorption spectra of zinc tetrakis(perfluorophenyl)porphyrin in visible region: (A) dry toluene; (B) toluene shaken with  $\text{H}_2\text{O}$ ; (C) 75% toluene and 25%  $\text{CH}_3\text{CN}$ ; (D) 75% toluene and 25% ethanol; (E) 75% toluene and 25% pyridine; (F) 75% toluene and 25% triethylamine.

$\text{Zn}(\text{TFPP})$  also showed fluorescent emission, including a phosphorescence at 729 and 816 nm. The quantum yields are 0.5–0.1 times those reported for other zinc porphyrins.<sup>14,19</sup>

$\text{Cu}(\text{TFPP})$ , like  $\text{Cu}(\text{OEP})$  and unlike  $\text{Cu}(\text{TPP})$ , showed temperature-dependent luminescent emission. The unpaired Cu(II) electron adds its spin to that of the porphyrin ring. As has been described earlier,<sup>20–22</sup> emission proceeds from tripdouplet and triquartet states. We observed the emission of  $\text{Cu}(\text{TFPP})$  and  $\text{Pd}(\text{TFPP})$  at liquid-helium temperature on an apparatus that has been described.<sup>23</sup> We determined that the spectral response of the apparatus used for the 4 K spectrum was very similar to that used for the 77 K spectrum by showing that the emissions of  $\text{Pd}(\text{TFPP})$  were essentially identical on the two temperature apparatuses. When the shift to 4 K was made, the origin of the  $\text{Cu}(\text{TFPP})$  emission shifted from 686 to 700 nm; some emission at 686 nm persisted as a shoulder on the 700-nm peak. The vibronic structure changed dramatically (Figure 3C). The transition observed at 77 K is thought to be the spin-allowed  ${}^2T_1 \rightarrow {}^2S_0$ , where the  ${}^2T_1$  state is populated by a Boltzmann energy distribution. At the lower temperature, the observed transition is the spin-forbidden  ${}^4T_1 \rightarrow {}^2S_0$ .

Several recent papers concern the nature of the tripdouplet quartet states in copper porphyrin.<sup>24–27</sup> It is then appropriate

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**Figure 3.** Emission spectra at 77 K (solid lines) and at 4 K (dashed line) in 3-methylpentane of tetrakis(perfluorophenyl)porphyrin complexes: (A) free-base fluorescence and (inset) ethyl iodide enhancement of phosphorescence; (B) Zn fluorescence and phosphorescence; (C) Cu luminescence at 77 K and 4 K; (D) Pd phosphorescence.

to compare the emission of Cu(TFPP) with other Cu porphyrins. At 77 K the spectrum of Cu(TFPP) most resembles that of Cu(OEP). Like Cu(OEP) and Cu(P), it clearly

**Table III.** Ratio of Absorbance Peaks  $[Q(0,0)/Q(1,0)]^a$

H <sub>2</sub> (TPP)	0.43	H <sub>2</sub> (P)	0.17	H <sub>2</sub> (TFPP)	0.13	H <sub>2</sub> (OEP)	0.78
Zn(TPP)	0.13	Zn(P)	0.44	Zn(TFPP)	0.26 <sup>b</sup>	Zn(OEP)	1.35
Cu(TPP)	0.095	Cu(P)	0.76	Cu(TFPP)	0.47	Cu(OEP)	1.75
Pd(TPP)	0.11	Pd(P)	1.37	Pd(TFPP)	0.85	Pd(OEP)	2.70
ref	32, 22		34, 35	this paper			36

<sup>a</sup> For free base the ratio of absorbances is  $[Q_x(0,0) + Q_y(0,0)]/[Q_x(1,0) + Q_y(1,0)]$ . <sup>b</sup> 0.22 for Zn(TFPP) in dry toluene.

changes between 77 and 4 K. In this regard it is different from Cu(TPP), which is very broad and structureless at all temperatures reported.<sup>20,22</sup> The broadness of emission in Cu(TPP) has been attributed to the presence of a  $d_{x^2-y^2} \rightarrow e_g(\pi^*)$  triplet in the same region as the usual  $T_1(\pi, \pi^*)$  triplet.<sup>17</sup> The quantum yield of Cu(TFPP) is comparable to those of Cu(P) and Cu(TPP), which are substantially lower than that of Cu(OEP), 0.6.<sup>20</sup>

**Pd(TFPP)** shows phosphorescent emission. In its shape, the Pd(TFPP) is particularly like that of Pd(Etio). Both feature sharp origins followed by considerably less intense vibronic bands. Weak fluorescence from the Pd(TFPP) was observed at 25 °C with a Perkin-Elmer 650-10 fluorescence spectrophotometer (Table II).

#### Four-Orbital Model—Singlet Excited States

We shall use the four-orbital model described earlier<sup>28</sup> to advance an explanation for the absorption and emission spectra of the TFPP complexes reported here and their relationship to the corresponding P, TPP, and OEP complexes. The four-orbital model describes the low-lying  $(\pi, \pi^*)$  excited states of porphyrins in terms of the transitions between two highest occupied molecular orbitals (HOMO's),  $a_{2u}(\pi)$  and  $a_{1u}(\pi)$ , to two degenerate lowest unoccupied molecular orbitals (LUMO's),  $e_g(\pi^*)$ . For the porphyrin ring, the lowest singlet excited configurations,  $^1(a_{2u}, e_g)$  and  $^1(a_{1u}, e_g)$ , are nearly degenerate, and there is a strong electron interaction between them.<sup>10,28-30</sup> The resulting resonance yields the relatively weak visible Q(0,0) band, in which the transition dipoles of the two configurations nearly cancel, and the intense near-UV (or Soret) B(0,0) band, in which the transition dipoles of the two configurations add. The closer the degeneracy of the configurations  $^1(a_{2u}, e_g)$  and  $^1(a_{1u}, e_g)$ , the weaker is the Q(0,0). In some complexes, e.g., Co(TPP), the Q(0,0) band essentially vanishes.<sup>29</sup>

As a simple measure of the degeneracy of the two configurations, we shall use the ratio of absorbances,  $Q(0,0)/Q(1,0)$ . We do this since the intensity of Q(1,0) arises from vibronic mixing of the Q state with the B state and is relatively constant among porphyrins.<sup>29,31</sup> This picture is somewhat complicated in the free base, because the central protons lift the degeneracy of the  $e_g(\pi^*)$  orbitals, causing the Q(0,0) bands of the metal complexes to split into  $Q_x(0,0)$  and  $Q_y(0,0)$ . To avoid this complication we shall discuss configuration degeneracy in the free base using the ratio of the sum of absorbances,  $A[Q_x(0,0)$

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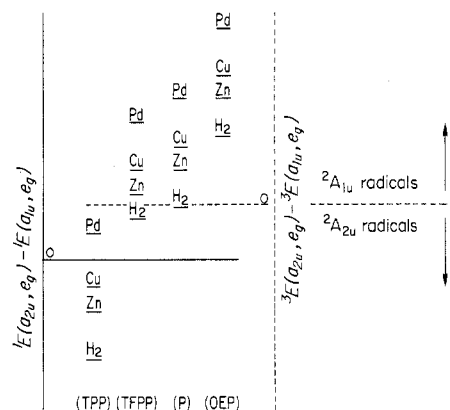
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**Figure 4.** Energy differences: solid lines, between singlet transitions,  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$ ; dashed lines, between triplet transitions,  ${}^3E(a_{2u}, e_g) - {}^3E(a_{1u}, e_g)$ . The triplet energy difference should determine whether the compound gives a  ${}^2A_{1u}$  or a  ${}^2A_{2u}$  cation radical, as shown. See text for derivations.

+  $Q_y(0,0)]/A[Q_x(1,0) + Q_y(1,0)]$ . These ratios are given in Table III for free-base, Zn, Cu, and Pd complexes of TFPP, TPP, P, and OEP; the ratios depend both on the metal and on the ring substituents.

The simplest theory for these intensity ratios can be derived from the four-orbital model.<sup>10,29</sup> The Q and B states of a particular porphyrin are described in terms of states  $Q^0$  and  $B^0$  of an idealized reference porphyrin. In the idealized reference porphyrin we assume that  ${}^1E(a_{2u}, e_g) = {}^1E(a_{1u}, e_g)$ , i.e., that the energies of the two singlet transitions are equal. If we further assume equal transition dipoles,  $\mu(a_{1u}, e_g) = \mu(a_{2u}, e_g)$ , then  $Q(0,0)$  is forbidden for the idealized reference. Vibronic coupling theory and experiment show that the  $Q(1,0)$  band borrows a constant fraction of the  $B^0$  intensity.<sup>31</sup> Under these assumptions, it follows from equations derived earlier<sup>10,29</sup> that the ratio of absorbances,  $A$ , of  $Q(0,0)$  to  $Q(1,0)$  is

$$A[Q(0,0)]/A[Q(1,0)] = (\text{const}) [{}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)]^2 \quad (1)$$

We have used the ratios in Table III to determine  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$  for the free-base, Zn, Cu, and Pd derivatives of the porphyrins TPP, P, TFPP, and OEP, which are shown in Figure 4.

Because of the many assumptions involved in going from the experimental numbers in Table III to the energy differences in Figure 4, this energy difference plot is only of qualitative significance. Nonetheless it nicely shows the effects expected for the various substituents, central atoms, and ligands. Thus, since the perfluorophenyl groups are strongly electron withdrawing, they should act to lower the orbital energy of  $a_{2u}$  relative to that of  $a_{1u}$ , since the latter has nodes at the methine carbon atoms; thus the change from TPP to TFPP should increase  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$ . Since the alkyl groups are electron donating and since  $a_{2u}$  has little electron density at the exo pyrrole positions,<sup>10,29</sup> the change from P to OEP should raise the energy of the  $a_{1u}$  orbital relative to  $a_{2u}$  and hence should increase  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$ . Since  $a_{1u}$  has nodes at the metal, along the series of increasingly electronegative metals,  $Zn < Cu < Pd$ , the energy of  $a_{2u}$  should decrease relative to that of  $a_{1u}$  and hence  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$  should increase. Contrariwise, electron-donating ligands on Zn cause the energy of  $a_{2u}$  to increase relative to that of  $a_{1u}$  and hence should decrease  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$ . Because this difference is positive for Zn(TFPP) and negative for Zn(TPP) (Figure 4), eq 1 shows that along a series of ligands of increasing donor character, the  $Q(0,0)$  band intensity should decrease for Zn(TFPP) and increase for Zn(TPP), as is observed (Figure 2 and ref 15).

On the theoretical side, it should be noted that early  $\pi$ -electron calculations<sup>30</sup> as well as recent ab initio calculations show that  ${}^1E(a_{2u}, e_g) \approx {}^1E(a_{1u}, e_g)$ ; however, which energy is lower depends on the calculational method and the molecule calculated. The  $\pi$ -electron calculations of Weiss et al.<sup>10,30</sup> on a symmetrized porphine ring show  ${}^1E(a_{2u}, e_g) < {}^1E(a_{1u}, e_g)$ . The recent ab initio calculations by Petke et al.<sup>16</sup> on Mg(P) show  ${}^1(a_{1u}, e_g)$  more heavily weighted than  ${}^1(a_{2u}, e_g)$  in the lowest singlet. [Presumably the more heavily weighted configuration has lower energy.] They find  ${}^1(a_{1u}, e_g)$  more heavily weighted in  $Q_x(0,0)$  and  ${}^1(a_{2u}, e_g)$  more heavily weighted in  $Q_y(0,0)$  in  $H_2(P)$ . The experimental data (Figure 4) suggest that  ${}^1E(a_{1u}, e_g) < {}^1E(a_{2u}, e_g)$  for  $H_2(P)$ , more in keeping with the results of Petke et al.<sup>16</sup> than with the results of Weiss et al.<sup>30</sup> The peel electron calculations of Sundbom<sup>37</sup> on  $H_2(P)$  do not report the composition of the lowest singlet, but they show that  $a_{1u}$  has a lower orbital energy than  $a_{2u}$  by 0.1 eV and by less for a symmetrized calculation. However, for Cu(P), similar calculations<sup>38</sup> show  $a_{1u}$  higher than  $a_{2u}$  by 0.03 eV. Thus the peel calculations suggest that  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$  should increase between  $H_2(P)$  and Cu(P), as shown in Figure 4.

In summary, theoretical calculations agree that  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g)$  is small and will depend on the details of the Hamiltonian. Calculation of the trends shown in Figure 4 can provide a good test of theoretical Hamiltonians.

#### Four-Orbital Model—Triplet Excited States

The energy of excitation for a configuration representing a transition  $a \rightarrow b$  is<sup>10</sup>

$${}^1E(a,b) = \epsilon(b) - \epsilon(a) - J(a,b) + 2K(a,b) \quad (2)$$

$${}^3E(a,b) = \epsilon(b) - \epsilon(a) - J(a,b) \quad (3)$$

Equation 2 gives the energy to form a singlet excited configuration and eq 3 a triplet excited configuration. The terms  $\epsilon(a)$  and  $\epsilon(b)$  are SCF orbital energies,  $J(a,b)$  is the Coulomb integral, and  $K(a,b)$  is the exchange integral between the electron and hole orbitals. By the calculation of Weiss et al.<sup>10,30</sup>  $K(a_{2u}, e_g) = 0.710$  eV and  $K(a_{1u}, e_g) = 0.547$  eV. Thus, as a first approximation we might expect that

$${}^3E(a_{2u}, e_g) - {}^3E(a_{1u}, e_g) = {}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g) - 0.326 \text{ eV} \quad (4)$$

Hence the energy difference plotted for the singlet transitions will hold for the triplet transitions, with  ${}^3E(a_{2u}, e_g) - {}^3E(a_{1u}, e_g) = 0$  for those systems for which  ${}^1E(a_{2u}, e_g) - {}^1E(a_{1u}, e_g) = 0.326$  eV. It should be noted that in  $D_{4h}$  symmetry the electron interaction integral coupling  ${}^3(a_{2u}, e_g)$  and  ${}^3(a_{1u}, e_g)$  vanishes on symmetry grounds.<sup>10</sup> In agreement with this, recent ab initio calculations show that the lowest two triplet states of Mg(P) are relatively pure  ${}^3(a_{1u}, e_g)$  and  ${}^3(a_{2u}, e_g)$  transitions, with the former lower in energy by 0.2 eV.<sup>16</sup> In  $H_2(P)$  these same type of calculations show substantial mixing of the two triplets, as expected for the lower symmetry.<sup>16</sup>

Study of triplet-state resonance would be expected to provide direct evidence of the nature of the lowest excited triplet state. van Dorp et al.<sup>39</sup> conclude from the hyperfine structure that the lowest triplet of  $H_2(P)$  is  ${}^3(a_{2u}, e_g)$  in origin (using  $D_{4h}$  labels). Jansen and van der Waals<sup>40</sup> suggest that the triplet of Mg(P) is  ${}^3(a_{2u}, e_g)$  while that of Zn(P) is  ${}^3(a_{1u}, e_g)$ . On this basis we have drawn between  $H_2(P)$  and Zn(P) a dashed line in Figure 4 to show  ${}^3E(a_{2u}, e_g) - {}^3E(a_{1u}, e_g) = 0$ . Consistent with this line, Leenstra et al.<sup>41</sup> conclude, on the basis of sublevel

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decay rates, that the lowest triplet of Zn(TPP) is  $^3(a_{2u}, e_g)$ .

Our studies of emission show several aspects that may relate to the nature of the lowest triplet: (1) The phosphorescence of  $H_2$ (TFPP) can be brought out through solvent heavy-atom enhancement, as for  $H_2$ (OEP) and  $H_2$ (P) but unlike the case for  $H_2$ (TPP). (2) The phosphorescence of Zn(TFPP) is not strongly red-shifted like that of Zn(TPP), which occurs at 780 nm.<sup>19</sup> These data suggest that the lowest triplets of  $H_2$ (TFPP) and Zn(TFPP) more closely resemble the triplets of the corresponding porphines than those of the corresponding tetraphenylporphyrins. Such a resemblance is in keeping with the energy relations for the lowest triplet diagrammed in Figure 4.

As mentioned above, emission from copper porphyrins comes from the tripdouplet and tripquartet excited states,  $^2T_1(\pi, \pi^*)$  and  $^4T_1(\pi, \pi^*)$ . Measurements reported on Cu(OEP), Cu(TFPP), and Cu(P) show an increasing energy gap between these two states:  $\Delta E_{DQ} = 130, 270, \text{ and } 320 \text{ cm}^{-1}$ . [The first number is from ref 10, the second from Table II, and the third from ref 26.] Initially Ake and Gouterman<sup>21</sup> ascribed the emission of Cu(OEP) to a ring  $^3(a_{1u}, e_g)$  configuration and that of Cu(P) to  $^3(a_{2u}, e_g)$ , since  $\Delta E_{DQ}$  is calculated to be larger for the latter. However, the peel electron calculations of Roos and Sundbom<sup>38</sup> on Cu(P) (in contrast to the ab initio calculations on Mg(P) mentioned above)<sup>16</sup> give states  $^2T_1(\pi, \pi^*)$  and  $^4T_1(\pi, \pi^*)$  that have comparable contributions of the two ring triplet excited configurations. In this light, the data suggest that the contributions of  $^3(a_{2u}, e_g)$  to  $^2T_1(\pi, \pi^*)$  and  $^4T_1(\pi, \pi^*)$  increase along the series  $\text{Cu(OEP)} < \text{Cu(TFPP)} \leq \text{Cu(P)}$ , roughly in keeping with the energy levels of Figure 4. We do not include Cu(TPP) in this series as we attribute its broad, anomalous triplet emission to contributions from charge-transfer states  $d_{x^2-y^2} \rightarrow e_g(\pi^*)$ .<sup>17</sup>

#### Four-Orbital Model—Cation Radical

The energy for the reaction  $2MP \rightleftharpoons MP^+ + MP^-$  is given by<sup>42</sup>

$$\Delta E_{\pm} = \epsilon(e_g) - \epsilon(a) + 2[\Delta E_{\text{solv}}] \quad (5)$$

where  $\epsilon(e_g)$  is the SCF orbital energy of the extra electron of the radical anion and  $\epsilon(a)$  that of the hole in the radical cation (as calculated for the neutral molecule), and  $2[E_{\text{solv}}]$  is the solvation energy for the two ions: By the four-orbital model there are two types of radical cations. Thus the energy differences between them is

$$E(^2A_{1u}) - E(^2A_{2u}) = \epsilon(a_{2u}) - \epsilon(a_{1u}) + [\Delta E_{\text{solv}}(a_{1u}) - \Delta E_{\text{solv}}(a_{2u})] \quad (6)$$

This compares to the energy difference between the excited triplet configurations

$$^3E(a_{1u}, e_g) - ^3E(a_{2u}, e_g) = \epsilon(a_{2u}) - \epsilon(a_{1u}) - J(a_{1u}, e_g) + J(a_{2u}, e_g) \quad (7)$$

Then insofar as the electron-hole interaction integrals cancel as well as the solvation energies, the difference in energy between excited triplet configurations is just that of the difference in energy between the two types of cation radicals. Thus the lower energy of the two excited triplet configurations would determine the hole in the cation radical (Figure 4).

Current data show that Mg(TPP) and Zn(TPP) are  $^2A_{2u}$  radicals and Mg(OEP) and Zn(OEP) are  $^2A_{1u}$ ,<sup>42-44</sup> as expected from Figure 4. It has also been shown that zinc tetraalkylporphyrins are  $^2A_{2u}$  radicals,<sup>45</sup> consistent with alkyl groups being at least as electron donating as phenyls. However, the current identifications of the radical orbital for open-shell metals are not always consistent with Figure 4. For example, on the basis of its optical spectrum, it is claimed that Pd(OEP) forms a  $^2A_{2u}$  radical,<sup>44</sup> which Figure 4 suggests is unlikely. At  $-50^\circ\text{C}$  the Pd(OEP) cation has a narrow ESR line,<sup>46</sup> more suggestive of a  $^2A_{1u}$  than a  $^2A_{2u}$  radical. Hence the ordering of the four-orbital configurations given in Figure 4 provides a rationale for a reinvestigation of the nature of the Pd(OEP) cation. The nature of the cation radical is of some interest, for it has been suggested that the enzymes catalase and peroxidase are respectively  $^2A_{1u}$  and  $^2A_{2u}$  radicals of an  $\text{Fe}^{\text{IV}}$  porphyrin.<sup>47,48</sup> Hence it is important to determine the factors that decide the nature of the hole orbital and how these relate to the factors determining the four-orbital configuration energies shown in Figure 4.

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