Electronic States and Optical Properties of Porphyrins in van der Waals Contact: Th IV Sandwich Complexes

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Abstract: Ground-state and time-resolved excited-state absorption spectra and fluorescence and phosphorescence spectra of three Th IV sandwich complexes, Th IV(TPP) 2, Th IV(OEP), and Th IV(OEP)(TPP), are reported (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinate, TPP = 5,10,15,20-tetraphenylporphyrinate). These complexes, in which the nitrogen planes of the two porphyrin macrocycles are ~2.9 Å apart, exhibit a number of prominent optical characteristics: (i) monoporphyrin-like Q and B absorption bands, (ii) a new absorption between the Q and B bands, (iii) a weak, low-energy absorption that is substantially red-shifted relative to the Q bands of analogous monoporphyrin complexes, (iv) fluorescence and phosphorescence emission bands that are even further red-shifted relative to typical emission bands from porphyrin monomers, and (v) a moderately intense near-infrared (π,π*) excited-state absorption not observed in monomeric porphyrins. These characteristic optical properties of the sandwich complexes are all accounted for by a relatively simple molecular orbital configuration-interaction model. Additionally, the spectral data and molecular orbital model identify the energies of charge-transfer configurations and delineate their contribution to the electronic states of these strongly-coupled π systems. These results provide insights into the interactions that can take place between other pairs of chromophores brought within van der Waals contact, such as the bacteriochlorophyll dimer of the photosynthetic reaction center.

Introduction

Investigations of cofacial porphyrin dimers have been motivated by an effort to better understand and mimic the interactions within the dimeric primary electron donor of the photosynthetic reaction center. The two bacteriochlorophyll molecules of the C2-symmetry "special pair" are separated by ~3.3 Å.¹ Electronic interactions within this dimer are thought to be responsible for some of its characteristic properties, such as the ease of porphyrin π-system oxidation and the low energy of the first 1(π,π*) excited state compared to corresponding monomeric chromophores. The latter property produces a bathochromic shift in the long-wavelength absorption band and makes the dimer an effective trap for the harvested photon energy.

Many factors might contribute to the origin of the electronic properties of the special pair. For example, the relative importance of excitation (i.e., dipole–dipole) coupling of the lowest excited states of the bacteriochlorophyll subunits, versus mixing with charge-transfer (CT) configurations, versus energy shifts from protein effects has yet to be established.²,³ The energies of the CT configurations of the special pair (and of dimers in general) are not known and are expected to depend strongly on the interactions between the subunits. Hence, deducing the contribution of CT configurations to the lowest electronic states of a dimer is intimately related to understanding the degree of intermacrocycle orbital overlap.

Recently, several bis(porphyrin) sandwich complexes have been described whose optical characteristics resemble those of the lowest excited states to the special pair²,⁴ and other dimers, such as aromatic exciters¹ and paracyclophanes.² The sandwich complexes also offer advantages as probes of π–π interactions. For example, the separation of the π systems can be tuned in fine (≈0.1 Å) increments via the choice of the central metal ion. In this manner, the mean separation between the nitrogen planes of the two porphyrin subunits can be varied from ~2.9 Å for Th I to ~2.8 Å for Ce and to ~2.6 Å for Zr and Hf,³,⁴ with a mean separation between the core atoms of the two π systems varying correspondingly from ~3.5 to 3.2 Å.

The sandwich complexes show optical characteristics that are not exhibited by porphyrin dimers having larger separations be-

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(≥3000 cm⁻¹) shifted from this new low-energy absorption,¹⁵,¹⁶ and prominent NIR features in the spectra of the (π,π*) excited states,¹⁶ and the π-radical cations generated by oxidation of the sandwicch complexes.⁷,¹²,¹⁷,¹⁸ We have argued that the new red region absorption and fluorescence of the sandwich complexes cannot be explained by exciton coupling. Rather, these properties must be associated with excited states that have significant contributions from CT configurations and, thus, with transitions involving delocalized molecular orbitals of a supermolecule.¹⁴-¹⁶

The NIR, ESR, and Raman spectra of the electron deficient sandwich complexes¹⁶,¹⁷,¹⁸ and the NIR band of the oxidized ZnOEP dimer,¹⁹ have been successfully interpreted using a supermolecule MO approach. However, additional studies of the electronic states and optical properties of the sandwich complexes are needed to help elucidate further the factors that contribute to the electronic structure of these complexes, the special pair in the photosynthetic reaction center, and strongly interacting π systems in general.

In this paper, we report the ground state absorption, fluorescence, and phosphorescence spectra and the time-resolved (π,π*) excited state absorption behavior of the Th⁴⁺ porphyrin sandwich complexes Th(TPP)₂, Th(OEP)₂, and Th(OEP)(TPP).²⁰ We also present in detail a model that accounts for all of the optical characteristics of the sandwich complexes and extends our understanding of strongly-coupled porphyrins.

### Experimental Section

The symmetric complexes Th(TPP)₂ and Th(OEP)₂ were synthesized and characterized as described previously.¹²,²¹ The asymmetric compound Th(OEP)(TPP) was synthesized in a similar manner.²² Samples used for emission studies were further purified by column chromatography on basic alumina (Brockman Activity I, predried under vacuum at -100 °C for 30 min) with toluene as the eluent.

Ground-state absorption spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer. The samples used for emission studies had an absorbance ≤1.0 at the excitation wavelength (normally in the Soret region). Fluorescence measurements utilized a Spex Fluorolog I1 spectrophotometer equipped with an R928 photomultiplier tube and photon counting electronics. Phosphorescence spectra were recorded using an RCA C30956E Si avalanche photodiode and lock-in detection. Detection bandwidths of ~10 nm for fluorescence and ~15 nm for phosphorescence were used.

Time-resolved absorption spectra in the sub-nanosecond regime were recorded on instruments described elsewhere.²¹ Samples having a concentration of ~10 μM in 2 mm path length cells were excited with a 100 fs, 582 nm, 150 μJ pulse and probed as a function of delay times with a broad band (385-965 nm) pulse of comparable duration. Microsecond and longer-time transient absorption measurements utilized an apparatus employing 10 ns, 532 nm, 10 μJ excitation pulses and ~1 μM samples in 1 cm path length cells that were deoxygenated by repeated freeze-pump-thaw cycles on a high-vacuum line. Studies at low temperature employed an Oxford Instruments cryostat system.

### Results

#### Ground Electronic State Absorption Spectra

Ground-state absorption spectra of the three Th⁴⁺ bis(porphyrin) sandwich complexes at 295 K are shown in Figure 1. The spectra of

![Figure 1. Ground-state absorption spectra of the three Th⁴⁺ sandwich complexes in toluene at 295 K: (A) Th(TPP)₂, (B) Th(OEP)(TPP), (C) Th(OEP)₂. The 450-800-nm region has been multiplied by the indicated factor and the spectra have been normalized to 1.0 at the Q(1,0) absorption maximum.](image)

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(24) OEP is 2,3,7,8,12,13,17,18-octaethylporphyrinate(2⁻); TPP is 5,10,15,20-tetraphenylporphyrinate(2⁻); TTP is 5,10,15,20-tetratolylporphyrinate(2⁻).
at 575 nm is stronger than the 545-nm Q(1,0) band, whereas, for Th(TPP)2, the Q(0,0) band near 590 nm is barely discernable and much weaker than the 530-nm Q(1,0) band. (ii) The intense near-UV Soret, or B(0,0), band is blue shifted from the position in the corresponding mono(porphyrin) complexes of the same macrocycle. (iii) A broad weak feature which we refer to as the Q' band is observed to the red (600-650 nm) of the monoporphyrin-like Q bands. (iv) A band denoted Q'' is observed to the blue (465-505 nm) of the monoporphyrin-like Q bands. Additionally, there is evidence that additional weak features under the broad absorption between the Soret and Q bands. The Q' and Q'' bands are also present in the spectrum of the non-symmetric sandwich complex, Th(OEP)(TPP). However, for this complex, Ce(OEP)(TPP),14 and Ce(OEP)(TPP)56 the Q(0,0) band is much weaker than expected from the sum of Q bands of typical metallo-OEP and -TPP complexes (Figure 1).

We believe the new Q' and Q'' absorptions to be highly characteristic of strongly-coupled porphyrins. The features are observed for all the "neutral" bis(porphyrin) sandwich complexes (those containing a +4 metal ion and hence filled ring HO-MOs7-14 but not for the corresponding mono(porphyrin) complexes23-24 or bis(porphyrin) complexes with larger macrocycle spacings.25,26 Variations in these features also correlate with the ionic radius of the metal ion and thus the distance between the two rings. First, the Q' absorption maximum shifts to the red as the ionic radius of the metal ion decreases (Figure 2); the Q'' band lies at 615 nm for Th(TPP)2, 630 nm for Ce(TPP)2, and ~700 nm for Hf(TPP)2 and Zr(TPP)2. (Zr and Hf have very similar ionic radii). The metal-metall bonded porphyrin dimers also exhibit red-region absorptions that may be, in part, of Q' origin. Second, the Q'' band red shifts and gains intensity as the separation between the macrocycles decreases (Figure 2).

Several minor changes are observed in the ground-state absorption spectra of the Th16 complexes at 78 K (Figure 3). For Th(OEP)2, the most prominent change is the emergence of two distinct bands in the Q' region in addition to a general sharpening of the spectrum. The Q' band remains considerably broader than the other features in the spectrum, although better resolution of the shoulder near 710 nm is observed. This shoulder may correspond to the Q' transition origin15 and is not resolved in the TPP-substituted sandwich complexes (Figures 1 and 2). The spectrum of Th(OEP)(TPP) at 78 K is similar to that of Ce(OEP)(TPP),14 in that several features to higher energy than the Q(0,0) band are distinguishable that were unresolved at 295 K. The Q' absorption again remains unusually broad at 78 K.

Fluorescence and Phosphorescence. Th(OEP)2 was the first sandwich complex for which Q' fluorescence was observed.15 For this complex and Th(OEP)(TPP) (Figure 4) and Th(TPP)2 (not shown), the fluorescence is found ~3000 cm-1 to the red of the Q' absorption maximum even in the nonpolar solvent toluene. No fluorescence is observed between 900 and 1000 nm region where mono(porphyrin) complexes typically fluoresce (just to the red of the Q(0,0) absorption23-24). Similar fluorescence behavior has also been observed for the Zr and Hf sandwich complexes, except the latter exhibit a larger separation between the Q' absorption and fluorescence maxima.15,28

The emission spectra of all three thorium bis(porphyrin) sandwich complexes in degassed toluene solutions as a function of temperature are shown in Figure 5A-C. The phosphorescence observed between 900 and 1000 nm is spectrally broad and has a maximum significantly to the red of the phosphorescence of typical OEP and TPP monoporphyrin complexes (700-800 nm).23,24 Near room temperature, a shoulder is found ~2000 cm-1

to higher energy for each complex. Two observations indicate that the high-energy shoulder is mainly delayed fluorescence: (i) For a nondegassed Th(OEP)\(_2\) solution at 295 K, not only is the overall emission intensity significantly reduced relative to a degassed sample but the -790 nm emission is also larger by a factor of 3.5

**Table I.** Excited-State Decay Kinetics

<table>
<thead>
<tr>
<th>complex</th>
<th>temp (K)</th>
<th>(T^<em>(\pi,\pi)^</em>)</th>
<th>(1\text{-exp}(\mu s))</th>
<th>(2\text{-exp}(\mu s))</th>
<th>((\pi,\pi)^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(OEP)(_2)</td>
<td>295</td>
<td>13 ± 2</td>
<td>8.9 ± 0.4</td>
<td>3.4 ± 0.5/9.4 ± 0.1</td>
<td>1.09</td>
</tr>
<tr>
<td>Th(OEP)(TPP)</td>
<td>295</td>
<td>27 ± 9</td>
<td>36.2 ± 0.3</td>
<td>26.6 ± 3/40.4 ± 2.0</td>
<td>1.04</td>
</tr>
<tr>
<td>Th(TPP)(_2)</td>
<td>~60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Data at 295 K obtained using degassed toluene solutions; data at low temperatures obtained using 3-methylpentane glasses. The \(T^*(\pi,\pi)^*\) lifetimes were analyzed using single- and dual-exponential functions and the ratio of the \(x^2\) values is given in the last column. *The \(x^2\) ratio for data acquired at the Soret maximum. The ratio is larger when global analysis of the data across the Soret band is used.

![Figure 5](image-url) - Corrected phosphorescence spectra of the three Th\(^{IV}\) porphyrin sandwich complexes in degassed toluene solution. (A) Normalized phosphorescence spectra of Th(TPP)\(_2\) recorded at 180 K (indicated by arrow) followed by spectra at 240, 270, 285, and 300 K with increasing intensity in the 765-nm region. (B) Phosphorescence spectra of Th-OEP(TPP) recorded (in ascending order near the 800-nm region) at 180, 240, 270, 285, and 295 K. (C) Phosphorescence spectra of Th-OEP\(_2\) shown, similarly, at 180, 240, 270, 285, and 295 K. Excitation spectra acquired detecting at the phosphorescence maximum and the high-energy shoulder (at 295 or 300 K) were similar to each other and also to the corresponding absorption spectrum. (D) Phosphorescence spectra of Th(OEP)\(_2\) in silicone oil given as a function of temperature from 295 to 483 K. Temperature readings are correct to ±0.1 K for panels A–C and ±1 K for panel D.

Figure 6. Transient absorption spectra of Th(OEP)\(_2\) in toluene at 295 K recorded ~1 ps (dashed line) and ~60 ps (solid line) after excitation with a 582-nm, 150-fs pulse. The spectrum between 600 and 965 nm has been multiplied by 2.5.

**Excited-State Absorption and Kinetics.** Figure 6 (dashed line) shows the visible/NIR excited-state absorption spectrum of Th(OEP)\(_2\) observed ~1 ps after excitation with a 100-fs 582-nm flash. Since this spectrum is representative of what is observed immediately following the flash, we assign it to the fluorescent state. For comparison, the \((\pi,\pi)^*\) states of monomeric porphyrins show a similarly featureless absorption broken by bleaching of the ground-state absorption bands.\(^{29}\) The 1-ps spectrum evolves with a time constant of 13 ± 2 ps into the spectrum shown at ~60 ps (solid line). Similar behavior is observed for Th(OEP)(TPP) and Th(TPP)\(_2\), except that these complexes exhibit somewhat longer decay times of the \(Q(\pi,\pi)^*\) excited state (Table I).

No appreciable changes occur in the transient spectrum of Th(OEP)\(_2\) after 60 ps up to the 450 nm time limit of the femtosecond spectrometer. This observation suggests that the 60-ps spectrum is due to the lowest \((\pi,\pi)^*\) state. This interpretation is supported by the prominent absorption near 775 nm for Th(OEP)\(_2\), and a smaller absorption ~1500 cm\(^{-1}\) to the blue. The NIR \(Q(\pi,\pi)^*\) spectra of monomeric OEP and TPP complexes generally consist of two such bands built on a featureless background absorption with the longer-wavelength feature having, as is observed here, an intensity about 30% that of the \(Q(1,0)\) ground-state absorption band (i.e., \(log \epsilon \sim 3.7\).\(^{29,30}\)

\(^{(29)}\) Rodriguez, J.; Kirmayer, C.; Holten, D. J. Am. Chem. Soc. 1989, 111, 6500-6506.  \(^{(30)}\) For Th(OEP)\(_2\), the time constant for decay of \(Q(\pi,\pi)^*\) varies from 10 to 15 ps across the 450-500-nm region. As has been found and discussed for other metalloporphyrins,\(^{29}\) including the Ce porphyrin sandwich complexes,\(^{4}\) this may be due to incomplete vibrational equilibration within the electronic excited state.\(^{31}\) (a) Rodriguez, J.; Holten, D. J. Chem. Phys. 1992, 91, 3525–3531. (c) Rodriguez, J.; Kirmayer, C.; Holten, D. J. Chem. Phys. 1991, 94, 6020–6029. (d) Well-resolved NIR \((\pi,\pi)^*\) spectra similar to Figure 6 for Th(OEP)\(_2\) were not obtainable for the other complexes due to their lower solubility.
In addition to the two monoporphyrin-like \(1(\pi,\pi^*)\) features, Th(OEP), shows a much more intense NIR excited state absorption with a peak slightly past 1000 nm (Figure 6). A similarly intense NIR \(1(\pi,\pi^*)\) feature is observed for Zr(TPP) and Hf(TPP),16 and the corresponding OEP compounds. However, for the Zr and Hf complexes, the two monoporphyrin-like features between 700 and 850 nm are not as clearly resolved due, most likely, to spectral overlap with the more intense \(1(\pi,\pi^*)\) band of the sandwich complexes which moves to higher energy as the ionic radius of the metal decreases. We estimate the quantum yield of the \(1(\pi,\pi^*)\) state to be at least 90% in the Th sandwich complexes, based on the minimal decay of bleaching in the ground-state bands as \(1(Q'(\pi,\pi^*))\) evolves to \(1(\pi,\pi^*)\) (e.g., see Figure 6).17

Decay of the \(1(\pi,\pi^*)\) state occurs on the microsecond time scale, as determined by recovery of the bleaching in the Soret band following a 10-ns 532-nm flash. Analysis of the kinetics by local and global nonlinear least-squares methods1 suggests that although the decay of the \(1(\pi,\pi^*)\) state of Th(TPP) in degassed toluene solution at 295 K can be fit well by a monoeponential function (\(\tau = 39.4 \pm 0.5\) ms), it is questionable whether the same holds true for Th(OEP)2, and Th(OEP)(TPP). This is especially true at 77 K, where the lifetimes are also significantly longer than at 295 K (Table I).

Discussion

Comparison with Weakly-Coupled Systems. The sandwich complexes have characteristic optical properties that include (i) monomer-like ground-state absorption features, (ii) a new Q absorption band at a higher energy and a Q absorption band at a lower energy than the monomer-like Q bands, (iii) a broad weak Q fluorescence band substantially red shifted from the Q absorption maximum, (iv) prominent excited-state absorption in the NIR having no counterpart in the spectra of mono(porphyrin) complexes, and (v) a phosphorescence band significantly red shifted from those of typical mono(porphyrin) complexes.

Exciton coupling using the dipole–dipole approximation can be used to rationalize the blue shift of the intense Soret band and the presence, in the symmetric sandwich complexes, of weak Q bands having positions and intensities similar to those of mono(porphyrin) complexes. This approach has likewise provided a satisfactory explanation for the blue-shifted Soret and relatively unperturbed Q bands for porphyrin dimers having larger spacings between the macrocycles (e.g. µ-oxo complexes).25,26 However, exciton coupling of the weak Q transitions of the subunits cannot explain several key spectral characteristics of the sandwich complexes.16 For example, exciton theory cannot account for new Q absorption \(\sim 3000\) cm\(^{-1}\) lower than the monoporphyrin-like Q bands and the significantly perturbed Q bands of the asymmetric complexes Th(OEP)(TPP) (Figure 1), Ce(OEP)(TPP),14 and Ce(OEP)(TPP).50 Furthermore, although simple exciton theory can account for some small absorption between the Soret and Q bands, it cannot account for the intensity of the Q absorption in transition metal sandwich complexes such as Zr(TPP)2 (Figure 2).16

Simple exciton theory neglects overlap of the orbitals of the subunits. The new optical features in the ground-state absorption spectra of the sandwich complexes are not observed in monoporphyrin complexes or dimers with larger ring spacings. In addition, these features vary systematically with the ionic radius of the metal ion (Figure 2). Therefore, the new optical features derive from orbital overlap between the \(\pi\) systems of the subunits and must involve transitions among orbitals that are delocalized over both porphyrins of the complex.15,26 Similarly, the NIR band of electron-deficient sandwich complexes also15,18 and of the ZnOEP dimer cation19 has been assigned by using a delocalized MO approach. In other words, a proper description of the electronic states of the sandwich complexes requires consideration of the wave functions of a supermolecule.

General Approaches for Characterizing the States of Strongly-Coupled Systems. Analysis of strongly-coupled chromophores such as aromatic hydrocarbon excimers, paracyclophanes, and the reaction center special pair24,25 have proceeded in two general directions. One approach is to start with locally-excited configurations (A'B and AB*) of two chromophores (designated A and B) as is done in simple exciton theory. Additionally, due to the non-negligible overlap between the two macrocycles, charge transfer (CT) or ionic configurations (A'B* and A'B) must be considered. In the case where the two chromophores are identical, properly symmetrized wave functions would consist of linear combinations of the respective parent configurations, EX\(^*\) = (A'B \pm AB*)/2\(^{1/2}\) and CR\(^*\) = (A'B \pm A'B* )/2\(^{1/2}\). Consistent with the literature on a variety of systems25b,32c and our previous work on the sandwich complexes,15,16 we refer to the latter as charge-resonance (CR) configurations. If the two chromophores A and B are identical (and in the absence of solvent effects), there is no net transfer of charge from one ring to the other. For non-identical chromophores, a configuration with substantial, but unequal, contributions of the two opposing CT configurations also can be described as having CR parentage. The excited states are then obtained from mixing of the CR and EX configurations under the Hamiltonian of the coupled system.

The second general approach involves construction of supermolecule MOs from linear combinations of the subunit MOs. One then obtains excited configurations in the traditional manner by considering electron promotions from the occupied to unoccupied MOs. Configuration interaction among the basis configurations is important in properly describing the excited states of the system (see below).34,66 The supermolecule MO and EX/CR wave functions are related by a basis transformation.

A Model for the Electronic States of the Porphyrin Sandwich Complexes. In a recent study of Zr(TPP) and Hf(TPP), we outlined a simple MO picture and its relationship to the EX/CR description; this model rationalizes the key experimental observations on the neutral sandwich complexes15 and is elaborated in detail here. Supermolecule MO approaches have been used previously to describe the optical properties of the oxidized sandwich complexes, bacteriochlorin dimers,14 the reaction center special pair, aromatic excimers,25 and paracyclophanes.65 Within the supermolecule MO approach, we express the MOs of the sandwich complexes in terms of the \(\alpha(\pi)\) and \(\alpha(\pi^*)\) HOMOs and e3(\(\pi^*)\) LUMOs of the four-orbital model14,15 that has been so successful in describing the electronic states of mono(porphyrin) complexes. For simplicity, the common D4h symmetry notation will be used for the monoporphyrin orbitals although the sandwich complexes have approximate D2h symmetry since the two cofacial macrocycles are rotated about 40° with respect to one another.7,10 Accordingly, the bonding (on the left) and antibonding (on the right) MOs of this eight-orbital model of the bis(porphyrin) are given as follows (Figure 7):

\[
\begin{align*}
\beta_1 &= (a_{1u}^A + a_{1u}^B)/2^{1/2} & \alpha_2 &= (a_{1u}^A - a_{1u}^B)/2^{1/2} \\
\beta_2 &= (a_{2u}^A + a_{2u}^B)/2^{1/2} & \alpha_1 &= (a_{2u}^A - a_{2u}^B)/2^{1/2} \\
\epsilon_{13} &= (e_{g1}^A + e_{g1}^B)/2^{1/2} & \epsilon_{17} &= (e_{g1}^A - e_{g1}^B)/2^{1/2} \\
\epsilon_{17} &= (e_{g1}^A + e_{g1}^B)/2^{1/2} & 
\end{align*}
\]

(1)

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(36) Since the overlap integrals \(\langle\alpha(\pi)|\alpha(\pi^*)\rangle\) and \(\langle\alpha(\pi)|\epsilon(\pi^*)\rangle\) are likely to be comparatively small (\(\sim 0.1\) a.u.), they are omitted in normalizing the MOs. The phases of the supermolecule MOs have been derived using the convention that the positive lobes of the orbitals or equivalent atoms of the subunits point in the same direction and that the overlap integrals are all positive.

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The energy splittings between the bonding and antibonding MOs are twice the respective intermolecular resonance integrals: 
\[ \beta_i = (\alpha_i^A H_{aa} \delta_{ij})_{ab}, \beta_j = (\alpha_j^A H_{bb} \delta_{ij})_{ab}, \text{ and } \beta_k = (\alpha_k^A H_{cc} \delta_{ij})_{ab}, \]
where \( H_{aa} \) is the effective one-electron Hamiltonian and \( H = H_{aa} + \sum \beta_i \). Although the three \( \beta \) integrals are not exactly equal, it is convenient to choose \( \beta_i \sim \beta_j \sim \beta_k \). Hence, the splittings between the bonding/antibonding MO pairs are equal in Figure 7.

In describing the electronic states of the sandwich complexes we use the \( \pi \)-electron approximation and consider only the singly-excited configurations involving the bis(porphyrin) MOs listed above and in Figure 7. There will be 16 possible excited configurations, the irreducible representation of which will be either \( E_1 \) or \( E_2 \) under \( D_{4h} \) symmetry:

\[ E_{1g}: (a_1 e_{1x}), (a_2 e_{1y}), (b_2 e_{2z}), (b_1 e_{2x}) \]
\[ E_{2g}: (a_1 e_{1x}), (a_2 e_{1y}), (b_2 e_{2z}), (b_1 e_{2x}) \]
\[ E_{3g}: (a_1 e_{1x}), (a_2 e_{1y}), (b_2 e_{2z}), (b_1 e_{2x}) \]
\[ E_{3u}: (a_1 e_{1x}), (a_2 e_{1y}), (b_2 e_{2z}), (b_1 e_{2x}) \]

where, for example,

\[ (a_1 e_{1x}) = [(a_{1s} b_{1s} b_{1s} b_{1s} b_{1s} b_{1s}) | + | e_{1s} a_{2s} b_{1s} b_{1s} b_{1s} b_{1s}] ]^{1/2} \]
\[ (a_2 e_{1y}) = [(a_{1s} b_{1s} b_{1s} b_{1s} b_{1s} b_{1s}) | - | e_{1s} a_{2s} b_{1s} b_{1s} b_{1s} b_{1s}] ]^{1/2} \]

and \([a b o d \ldots] \) denotes a properly normalized Slater determinant. Since the LUMOs of the subunits are doubly degenerate, the singly-excited electronic configurations of the supermolecule are doubly degenerate. Thus, in deducing the singlet excited states the problem reduces to consideration of four dipole-allowed configurations having \( E_1 \) symmetry (e.g. the \( E_{1g} \) configurations) and four \( E_2 \) configurations (e.g. the \( E_{3g} \) configurations) which are dipole forbidden in precise \( D_{4d} \) symmetry. We will therefore follow the mono(porphyrin) four-orbital model approach(33) and show explicitly only the \( y \)- and \( y \)-polarized bis(porphyrin) configurations, less the polarization subscripts.

**Singlet Electronic States Derived from the Dipole-Allowed \( E_1 \) Configurations.**

The position, intensity, and macrocycle dependence of the Q bands of mono(porphyrins) are retained in the symmetric sandwich complexes is extremely helpful in assessing the relative energies and mixing of the bis(porphyrin) electronic configurations. For example, it is known that the weak Q(0,0) band of monomeric TTP complexes is a consequence of the near degeneracy of the two excited configurations \( (a_1 e_{1x}) \) and \( (a_2 e_{1y}) \).

Since the Q(0,0) band near 590 nm (Figures 1 and 2) of Th(TPP)\(_2\) is also weak, an essential aspect of our model for the sandwich complexes is a near-degeneracy and considerable interaction of the four \( a_{1u} \) and \( a_{2u} \)-derived dipole-allowed configurations (or \( E_2 \)) configurations. Near-degeneracy of the \( (a_1 e_{1x}), (a_2 e_{1y}), (b_2 e_{2z}), \) and \( (b_1 e_{2x}) \) excited configurations arises from a combination of one- and two-electron terms. In presenting the most mathematically tractable form of the model, we follow calculations on other dimers(34,35) and neglect differential overlap and also adopt a cyclic polyene approximation (e.g. analogous integrals involving the \( a_{1u} \) and \( a_{2u} \) orbitals are equal). Appendix I gives the resulting interaction matrix for the singlet \( E_1 \) configurations. The eigenfunctions of this matrix are

\[ B^+ = [(b_1 e_{1x}) + (b_2 e_{1z})] / 2 \quad (3a) \]
\[ Q^+ = [(b_1 e_{1y}) + (a_2 e_{1z})] / 2 \quad (3b) \]
\[ CR_{1^+} = [(b_1 e_{1x}) - (a_1 e_{1y})] / 2^{1/2} \quad (3c) \]
\[ CR_{2^+} = [(b_2 e_{1y}) - (a_1 e_{1x})] / 2^{1/2} \quad (3d) \]

Expanding in terms of mono(porphyrin) MOs gives in the excitation/CR basis

\[ B^+ = [a_{1s} e_{1x} + a_{2s} e_{1y} + a_{2u} e_{2z} + a_{1u} e_{1z}] / 2 \quad (4a) \]
\[ Q^+ = [a_{1s} e_{1y} + a_{2s} e_{1x} + a_{2u} e_{2z} - a_{1u} e_{1z}] / 2 \quad (4b) \]
\[ CR_{1^+} = [a_{1s} e_{1x} + a_{2s} e_{1y}] / 2^{1/2} \quad (4c) \]
\[ CR_{2^+} = [a_{1s} e_{1y} + a_{2s} e_{1x}] / 2^{1/2} \quad (4d) \]

which makes more transparent the compositions of the states.(39) In eqs 4c and 4d, CT\(_{1^0}^A\), for example, corresponds to a parent CT configuration in which an electron is moved from the \( a_{1u} \) HOMO of subunit A to the \( e_{1x} \) LUMO of ring B.

The corresponding energy eigenvalues of the \( E_1 \) singlet excited states are

\[ E(B^+) = E_m + 2(a_{1s} e_{1x} | b_{2u} e_{1y}) + 4(a_{1s} e_{1x} | a_{2u} e_{1y}) \quad (5a) \]
\[ E(Q^+) = E_m - 2(a_{1s} e_{1x} | b_{2u} e_{1y}) \quad (5b) \]
\[ E(CR_{1^+}) = \Delta - (a_{1s} a_{1s} e_{1x} | e_{2u} e_{1y}) \quad (5c) \]
\[ E(CR_{2^+}) = \Delta - (a_{1s} a_{1s} e_{1y} | e_{2u} e_{1x}) \quad (5d) \]

(38) The weak (0.0) band of monomeric(porphyrin) complexes is understood within the four-orbital model as arising from near-degeneracy of the two \( E_2 \) configurations \((a_1 e_{1x})\) and \((a_2 e_{1y})\). These two configurations add in a \(-1:1\) and out-of-phase fashion yielding a very-weekly-allowed state \( Q = [(a_{1s} e_{1x}) - (a_{1s} e_{1y})] / 2^{1/2} \). The more intense Q(0,0) band of metallo-OEP monomers is understood by a small splitting (loss of degeneracy) of the \((a_{1s} e_{1x})\) and \((a_{2s} e_{1y})\) configurations and incomplete cancellation of the transition moments. The Q(1,0) band of both OEP and TPP monomers gains intensity via vibronic coupling with the strong Soret transition, which represents the allowed in-phase linear combination \( B = [(a_{1s} e_{1x}) + (a_{1s} e_{1y})] / 2^{1/2} \).

(39) Equations 4, and others given later in the text, indicate the major compositions of the states and should not be taken to imply that the true eigenstates of the complexes will contain equal admixtures of the appropriate configurations. For example, the net CT character of the eigenstates will depend on the relative contributions of the opposing CT configurations to the \( E_2 \) configurations, which will differ for the symmetric and asymmetric complexes.

**References**

where the "center of gravity" of the mono(porphyrin) Q and B states is
\[
E_m = \Delta = \left( a_{1u}^4 a_{1u}^4 a_{1u}^4 a_{1u}^4 \right) + 2 \left( a_{1u}^4 a_{1u}^4 a_{1u}^4 a_{1u}^4 \right)
\]
and $\Delta$ is the mono(porphyrin) HOMO-LUMO gap (Appendix 1).

It is seen from eqs 4a and 4b that the B$^*$ and Q$^*$ states represent in-phase excitation components, both being comprised in the simple model solely of locally-excited configurations with no CT contribution. The B$^*$ state gives rise to an intense absorption shifted to the blue of the B band of mono(porphyrin) complexes by the last term in eq 5a. The Q$^*$ energy predicted by our eight-orbital model is the same as that predicted for Q(0,0) by an eight-orbital model of monoporphyrin complexes,
\cite{24,25} thus giving semi-quantitative agreement with the experimental results for the simple ground state absorption spectrum of Th(TPP)$_2$ and validity to the model and its a priori assumptions.

The model also delineates the origin of the Q$^*$ absorption feature located between the mono(porphyrin)-like Q and B bands (Figures 1 and 2). We assign this feature to two CR$^*$ states, CR$_1^*$ and CR$_2^*$. This assignment is consistent with the observation that the Q$^*$ band shifts to the red and intensifies as the rings are brought closer together by decreasing the ionic radius of the metal ion. The barchromatic spectral shift is associated with the increased Coulomb stabilization of the parent CT and hence CR configurations with decreasing macrocycle separation (via the second term in eqs 3c and 3d), and the increased intensity is due to increased orbital overlap.

The existence of two essentially pure CR states (CR$_1^*$ and CR$_2^*$) containing only contributions from the two parent CT configurations and no contribution from the parent locally-excited states is a direct result of the spectrally-determined nature of two states (B$^*$ and Q$^*$) with just the opposite electronic parentage. The formation of these relatively pure states is a direct consequence of the degeneracy for the CT configurations in the E, CI matrix (Appendix 1) which results in the equal contribution of the four basis configurations to the eigenfunctions. Again, near-degeneracy of the a$_{1u}$ and a$_{2u}$ configurations is a good approximation for the symmetric TPP-substituted sandwich complexes such as Th(TPP)$_2$. The degeneracy will be lost to some extent in the symmetric OEP-substituted complexes such as Th(OEP)$_2$ and thus have the effect of introducing increased mixing between the B$^*/Q^*$ and CR$^*$ configurations. Empirically, an intermediate case (i.e., partial recovery of the degeneracy) seems to occur for the asymmetric complexes such as Th(OEP)$_2$ where the intensity of the Q(0,0) band is low and close to that of Th(TPP)$_2$ (Figures 1 and 2).

This analysis and the assignment of the CR$^*$ states as giving rise to the Q$^*$ feature in the ground state absorption spectrum provide crucial empirical evidence that the parent CT configurations of porphyrins within van der Waals contact lie close in energy to those of the parent locally-excited configurations. The analysis places the CR configurations ~0.4 eV higher than the Q(0,0) energy of Th(TPP)$_2$ and, furthermore, only ~0.1 eV above the parent a$_{1u}$ and a$_{2u}$ configurations when it is considered that configuration interaction in mono(porphyrin) complexes is responsible for Q(0,0) being energetically below (and B(0,0) above) the energy $E_m$ of these configurations. At the shorter intermacrocycle separation ($R_{mean}$ = 3.2 Å) of Hf(TPP)$_2$ and Zr(TPP)$_2$,
\cite{7,10} the Q$^*$ band lies at 505 nm (Figure 2),
\cite{16} which gives the parent CT configurations an energy slightly lower than $E_m$. These results are important since the lack of direct information on the energies of the CT configurations of the reaction center special pair, simple porphyrin dimers, eximers and para- cyclophanes,
\cite{26,27,28} and other systems has led to uncertainty in assessment of the electronic properties of these molecules. Our findings on the porphyrin sandwich complexes provide support for the proposal that the CR (and parent CT) configurations of the reaction center special pair have energies comparable to the Q$^*$ states of the chromophores.

Singlet Electronic States Derived from the Dipole-Forbidden $E_3$ Configurations: The Low-Energy Q$^*$ and Higher-Energy States. The four $E_3$ (e.g., $E_{3yz}$) configurations do not exhibit the near degeneracy of the $E_1$ configurations (see dashed arrows in Figure 7). In particular, the configurations derived by electron promotion from the antibonding HOMOs (a$_1$ and a$_2$) to the bonding LUMO (e$_1$) should have much lower energy than those involving the b$_1$ and b$_2$ bonding HOMOs and antibonding e$_1$, LUMO. However, near-degeneracy is preserved within the a$_{1u}$ and a$_{2u}$-derived pairs of configurations (a$_1$e$_1$)/(a$_2$e$_1$) (short dashed arrows in Figure 7) and (b$_2$e$_1$)/(b$_1$e$_1$) (long dashed arrows). The resulting singlet $E_3$ CI matrix, eigenfunctions, and eigenvalues are given in Appendix 2. Expressing the eigenfunctions in terms of the exciton/CR basis gives
\[
\phi^+ = \left[ \left( 1 + \lambda_a \right) \right] (B^* - Q^*) / [2(1 + \lambda_a^2)] \]
The discrepancy between the states of the dimer cations and thus to the NIR transition energy. To be estimated transition would increase. The splitting between the supermolecule Soret and Q bands. Indeed, in the spectra of Hf(TPP), Zr(TPP)2 obtained using the CR' and CR- configurations slightly above Q(0,0) in energy. The derived uncoupled exciton and CR states. Our energy and contribute to the broad weak absorption between the states approach having the two a2e-derived configurations that yields relatively pure EX or CR character in the model.

$a_{1u}$-derived basis functions $(a_{2u}, e_u)$ and $(b_{2u}, e_u)$. Thus, the existence of states with mixed parentage can be traced directly to the nondegeneracy of the appropriate $E_1$ basis configurations. For the $E_2$ states it is the degeneracy of the two $a_{1u}$-derived and of the two $b_{2u}$-derived configurations that yields relatively uncoupled exciton and CR states.43

The Empirically-Derived Intermolecular Resonance Intensity $\beta$ and the Energies/Composition of the $E_2$ Eigenstates. In Appendix 3, it is shown that the spectroscopic data combined with our model lead to an estimate of $\beta \sim 0.27$ eV.44 This value of $\beta$ is comparable to those calculated for paracyclophanes thought to have macrocycle spacings similar to the ~3.5 Å distance between the core atoms of the Th sandwich complexes.5e-b This derived $\beta$ permits estimates of the energies and composition of the $E_2$ eigenstates via eqs 7, A11, and A12. The composition of the Q state $\psi$ is found to be roughly 60% Q* and 40% CR-. This shows that the sandwich complexes are indeed strongly-coupled systems. The energies of the eigenstates vary with $\beta$ as shown in Figure 8, and from these plots many of the spectroscopic energies can be estimated in terms of this single parameter. The state energies obtained using $\beta = 0.27$ eV are shown in Figure 9.

On the basis of our analysis, it is likely that the remaining three $E_3$ states $\psi^+$ and $\psi^-$ have energies greater than the Q* = Q(0,0) energy and contribute to the broad weak absorption between the Soret and Q bands. Indeed, in the spectra of Hf(TPP), Zr(TPP), (Figure 2), Th(OEP)2, and Th(OEP)(TPP) at 78 K (Figure 3) several features are observed in this region in addition to the Q* band assigned to the two E1 states CR* and CR'*. Our assignments of the $E_3$ states are self-consistent in placing both the CR* and CR'* configurations slightly above Q(0,0) in energy.

This analysis and the conclusion that the $\psi = Q$ state has substantially mixed Q* exciton and CR- character argues that the red-shift in the Q* absorption from the monomer Q position is due to mixing of the exciton (or parent locally-excited) configurations with the CR (or parent CT) configurations at higher energy. A similar mechanism has been proposed to explain the red-shifted low-energy absorption of aromatic excimers.5w-b This mechanism is also thought to contribute to the reduced energy of the lowest excited state of the reaction center special pair, although exciton splitting is also expected to be significant due to the large dipole strength of the Q transitions of the bacteriochlorophyll subunits.2,3 (Protein effects also may contribute to the red shift.) On the other hand, as noted above, insignificant exciton splitting is expected for the sandwich complexes investigated here due to the weak nature of the Q transitions of the porphyrin subunits. Hence, our observations and analysis of the electronic character of the Q*(e,V) excited state of the simple porphyrin sandwich complexes support the proposal from theoretical studies26,b,8 and Stark-effect measurements44,45 that mixing of the CT and Q* configurations of the special pair contributes substantially to the spectral properties of the photoactive excited state of this complex.

The Absorption/Fluorescence Gap. The substantial (3000–4000 cm⁻¹) shift between the Q* absorption and fluorescence maxima of the sandwich complexes (Figure 4) is explained by the model. The transitions should be weak, as is found, because the $Q^*$ state is assigned as being a dipole-forbidden E3 state $\psi^-$. The main, but weak, absorption/emission intensity may be derived from vibronic coupling of Q' with the intense Soret (B) transition (or possibly with the Q transition) and thus should not occur at the state origin.15,16 Thus, the underlying composition of the Q* absorption and emission is likely to be quite complex in view of the large number of modes that may participate in vibronic borrowing in the sandwich complexes. This may explain in part the breadth of the features.

Another factor may also contribute to the breadth of the absorption/fluorescence gap and to the Q* absorption and emission features. We expect that there will be more π-π bonding between the two porphyrin rings in the excited-state Q' than in the ground state. This is because in the Q* excited state, a first approx-

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43 From another perspective, it is seen that in the weak coupling limit ($\beta \rightarrow 0$ and thus $\lambda_+ \rightarrow \nu_a \rightarrow 1$) $\psi^- \& \& \psi^+$ extrapolate to being relatively uncoupled exciton and CR states. In the strong coupling limit ($\beta \rightarrow \infty$), the states approach having 50/50 exciton/CR character. Thus, as the energetic splitting between the supermolecule HOMOs ($\psi_\alpha$, $\psi_\beta$) and between the LUMOs ($\psi_\gamma$) increases, mixing among the relevant $E_2$ configurations (e.g., $(a_{2u}, e_u)$ and $(b_{2u}, e_u)$) will decrease and the mixed EX/CR parentage of the states will increase.

44 The value of $\beta \sim 0.27$ eV is about a factor of two smaller than would be estimated on the basis of the ~1200–1300-nm position of the NIR transition in the oxidized sandwich complexes. In the simple model,11,14.15 the NIR transition would occur at an energy corresponding to 20, the gap between the filled bonding HOMO and the half-filled antibonding LUMO of the dimer. The discrepancy between the values is likely due in part to the two-electron terms (Coulomb integrals) that also contribute to the energies of the electronic states of the dimer cations and thus to the NIR transition energy.

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imation, an electron has been transferred from a π-π antibonding orbital to a π-π bonding orbital. This additional π-π interaction in the excited state would cause the two macrocycles to move closer together following excitation, as has been discussed for various oxidized porphyrin sandwich complexes,\(^{17,18}\) aromatic excimers,\(^{28}\) paracyclophanes,\(^{42,43}\) and the reaction center special pair.\(^{44,46,47}\) A shorter porphyrin-porphyrin distance in the excited state vs. the ground state raises the possibility that the Q band may consist of a progression built on one or more low-frequency modes as in the paracyclophanes\(^{44,46}\) and the reaction center special pair.\(^{47,48}\) Although the symmetric inter-porphyrin ‘accordion’ mode, for example, would not be vibrationally active in $D_{4d}$ symmetry, vibronic intensity may result from the slight deviations from $D_{4d}$ symmetry exhibited by the sandwich complexes or via combinations with other modes. Alternatively, the dipole-forbidden $E$ state Q’s may derive intensity from the allowed E states B or Q via vibronic coupling with one or more of the monomer-like out-of-plane deformation modes. Along these lines, the spectra of Th(OEP)$_2$ and Th(OEP)(TPP) in Figure 4 can be simulated reasonably well using a simple Franck-Condon progression built on an origin at ~710 nm with an inter-porphyrin mode having $\nu_{\text{ground}} = 200$ cm$^{-1}$ and $\nu_{\text{cross}} = 250$ cm$^{-1}$, a Huang-Rhys (origin-shift) factor $S = 6.1$ for Th(OEP), and 6.9 for Th(OEP)-(TPP), and an inhomogeneous broadening of 300 cm$^{-1}$ to wash out the progression into the observed broad Q absorption and emission features. These parameters are comparable to those used to describe the NIR vibronic progression of the oxidized sandwich complexes\(^{17b,18}\) and are somewhat larger, as expected, than those derived for the excited special pair.\(^{49}\)

### The Triplet Manifold and Phosphorescence Spectra

The eigenfunctions and energies for the triplet electronic states of the sandwich complexes are similarly derived within our model.\(^{28}\) In fact, the triplet interaction matrices for the sandwich complexes are simpler than those for the monomers, as the orbital interactions are reduced.\(^{24,28}\) Because CI between the analogous triplet $a_{1u}$- and $a_{2g}$-derived configurations is zero in $D_{4d}$ symmetry. For example, the orbitally-allowed $a_{1u}$-derived E$_1$ triplet states are found to be a monomer-like exciton state T$_1$ and a CR state:}

$$T_1 = \left( a_{1u} \right)^2 + \left( a_{2g} \right)^2$$

$$3C_{R}^{+} = \left( b_{1g} \right)^2 - \left( b_{2g} \right)^2$$

Since the $a_{1u}$ and $a_{2g}$ orbitals of the subunits are assumed to be degenerate in the simple model, the corresponding $a_{2g}$-derived exciton and CR triplets, T$_1$ and 3CR$^+$, will be isomeric with T$_1$ and 3CR$^+$, respectively. As in the case of the E$_1$ singlets, it is the degeneracy within the $a_{1u}$- and $a_{2g}$-derived pairs of configurations that is responsible for the formation of relatively pure triplet exciton and CR states. The two 3CR$^+$ states are expected to be essentially isomeric with the two 3CR$^+$ states (Figures 8 and 9), due to negligibly small two-electron intermolecular exchange integrals.\(^{33}\) We have assigned 3CR$^+$/3CR$^+$ as giving rise to the Q$'$ absorption between the Soret and Q bands in the ground-state absorption spectrum. Thus, 3CR$^+$ and 3CR$^+$ are high-energy triplets which should relax rapidly to the lower-energy triplets.

The triplet states T$_1$ and T$_2$ are expected to have energies comparable to those of monoporphyrin triplets since excitation coupling between the subunit triplets is expected to be very small. Since the phosphorescence of lanthanide OEP monoporphyrin complexes occurs near 700 nm,\(^{24}\) and no emission is observed at this short wavelength for the OEP-containing Th bis(porphyrin) sandwich complexes (Figures 5, B and C), it appears that phosphorescence from T$_1$ and T$_2$ is not significant.\(^{49}\)

The main emission from the Th bis(porphyrin) sandwich complexes at ambient temperature is the phosphorescence occurring between 900 and 1000 nm (Figure 5). This emission can be understood by examining the orbitally-forbidden E$_2$ triplet states, in analogy with the low-energy Q$'$ absorption/fluorescence. Again, the problem simplifies to consideration of a pair of $a_{1g}$-derived configurations, \(\{a_{1g},e_3\}\) and \(\{b_{1g},e_3\}\), separated by $\Delta g \approx 48$, and a pair of $a_{2g}$-derived configurations, \(\{a_{1g},e_1\}\) and \(\{b_{1g},e_1\}\), also separated by $\Delta g \approx 48$. This splitting leads to the appearance of red-shifted orbitally-forbidden T'$_1$ and T'$_2$ states (which are degenerate in the simple model), in analogy with the Q$'$($\nu$) state in the singlet manifold. Continuing the analogy, the T' triplets, as well as the higher-energy E$_1$ triplets $\nu$ and $\phi$, have both substantial excition and CR character. With use of $\beta \sim 0.27$ eV obtained above from the red shift of Q$'$ relative to Q in the singlet manifold, the model predicts that the T' states have $\sim 70/30$ exciton/CR character and vice versa for the $\nu$ and $\phi$ states. In further analogy with the singlet manifold, this mixing contributes substantially to the lower energy of T'$_1$ and T'$_2$ compared to the monomer-like T$_1$ and T$_2$ states (Figures 8 and 9).

The model predicts a red shift of ~0.25 eV (2050 cm$^{-1}$).\(^{28}\) Relative to the 764-nm emission\(^ {23}\) of Th(TPP)(acac)$_{2}$, this places the T' phosphorescence of Th(TPP)$_2$ near 900 nm, in good agreement with the data (Figure 5A). The agreement is not as good for the OEP-containing complexes; this is expected since the assumed degeneracy of the $a_{1g}$ and $a_{2g}$-derived configurations is less valid. Additionally, we suspect that the main phosphorescence between 900 and 1000 nm for the three complexes may not represent the origin of the T' states (Figure 5). The reasoning is analogous to that used above to account for the spectra of the fluorescent Q$'$ singlet state (Figure 4), which is also an orbitally-forbidden E$_2$ state having mixed exciton/CR parentage. Furthermore, the activation energy of $\sim 1700$ cm$^{-1}$ estimated from the temperature dependence of the delayed fluorescence of Th(OEP), along with an electronic origin for the Q$'$ excited state near 710 nm (the average position of the Q$'$ absorption and emission maxima) places the T' phosphorescence origin near 810 nm, which is to the blue of the observed maximum. Additional complexity is expected since there are two close-lying $a_{1g}$- and $a_{2g}$-derived triplets T'$_1$ and T'$_2$. Furthermore, there may be multiple conformers, perhaps derived from the peripheral groups on the macrocycles, as has been suggested to account for the vibronic contour of the NIR band of the oxidized lanthanide sandwich complexes.\(^ {17b,18}\) These factors may contribute to the complexity of (i) the temperature dependence of the low-energy region of the phosphorescence, where a shoulder is seen most clearly for Th(TPP)$_2$ (Figure 5), and (ii) the triplet state decay (ground-state recovery) kinetics, where the OEP-containing complexes show clear indications of nonexponential behavior (especially at 77 K) whereas Th(TPP)$_2$ does not. Despite these complexities, our model provides a very reasonable picture of the triplet manifold and the associated phosphorescence behavior of the sandwich complexes.

### Excited-State Absorption

Finally, the model is successful in explaining the overall characteristics of the excited-state absorption spectra. The most likely visible/NIR transitions initiated from the fluorescent Q$'$ state are to states B$'$ and Q$'$ (Figures 8 and 9). Recall that Q$'$ has Q$'$ exciton and CR$^+$ character, B$'$ is basically an exciton state, and Q$'$ has mainly CR$^+$/CR$^+$ character. The relative strengths of these transition can be evaluated from...
Although these $E_j \rightarrow E_i$ transitions are symmetry allowed (z-matrix), the $Q' \rightarrow B'$ transition is predicted to be very weak due to cancellation of the $a_{1u}$- and $a_{2u}$-derived terms. In view of eqs 10b and 10c, the $Q' \rightarrow Q''$ (i.e., $Q'/CR' \rightarrow CR''$) transition is expected to have an intensity comparable to the NIR band in the oxidized sandwich complexes; the latter is thought to be associated with electron promotion from a bonding HOMO ($b_1$ or $b_2$) to a half-filled antibonding HOMO ($a_1$ or $a_2$). Although the $Q' \rightarrow Q''$ absorption maximum and origin have not been resolved, estimates can be made from the $Q''/Q'$ spacing in the ground-state absorption spectra. For example, the predicted wavelength of 1320 nm for the electronic origin is in accord with the observation that the $Q''$ excited-state absorption spectra of Zr(TPP)$_2$ and Hf(TPP)$_2$ has a prominent absorption past 1000 nm. A difference between the predicted transition origin and the location of the main absorption intensity is unreasonable since the $Q' \rightarrow Q''$ transition may be accompanied by a change in the inter-porphyrin distance, as discussed above and elsewhere. The transition from the ground state to $Q''$ and previously for the NIR absorption of the oxidized species. The $Q' \rightarrow Q''$ transition for the Th bis(porphyrin) sandwich complexes is expected to occur past 1500 nm (well beyond our detection limit), due to the larger spacing between the macrocycles. Hence, our model also accounts for the featureless $Q''$ excited-state absorption spectrum in the visible/NIR region for the Th bis(porphyrin) sandwich complexes. Additionally, the very weak feature seen near 890 nm in the ~1-ns transient spectrum of Th(OEP)$_2$ in Figure 6 is at an appropriate energy for the $Q' \rightarrow B'$ transition and has the low oscillator strength predicted by eq 10a.

The triplet–triplet excited-state absorption spectra may be analyzed in a similar manner. The transition from $T'$ (the phosphorescent state having both exciton and CR' character) to the $2CR'$ states is dipole allowed ($E_2 \rightarrow E_1$), similar to the excited singlet $Q' \rightarrow Q''$ absorption. The energy of the $2CR'$ triplets can be estimated from the position of the $Q''$ ($CR''$) ground-state absorption, since the singlet and triplet CR' states are expected to lie close in energy. Thus, for Th(OEP)$_2$, for example, the $T' \rightarrow 2CR'$ transition is predicted to occur near 1100 nm, in good agreement with the well-defined spectrum of the red of ~1000 nm (Figure 6).
A value of 0.36 eV is estimated for the left-hand side of this equation using $E_Q' = 1.74$ eV from the 710-nm $Q'$ origin (the average of the $Q'$ absorption and emission maxima in Figure 4) and $E_Q = 2.10$ eV from the 590-nm Q(0,0) band position for Th(TPP)$_2$ (Figure 1). The term $(\delta - \alpha)$ on the right-hand side of eq A13 is obtained as follows. Equations A1–A3 may be manipulated to give

$$(\delta - \alpha) = (a_{16}^e a_{2u}^e |a_{16}^e a_{2u}^e>) - [(a_{16}^e a_{1u}^e |a_{2u}^e a_{2u}^e>) - (a_{1u}^e a_{1u}^e |a_{2u}^e a_{2u}^e>)] / 2 - (a_{1u}^e a_{1u}^e |a_{2u}^e a_{2u}^e>)$$ (A14)

The first (intra-porphyrin exchange) integral on the right-hand side of eq A14 is $(a_{1u}^e a_{1u}^e |a_{2u}^e a_{2u}^e>) \sim 0.445$ eV from the difference between the average $Q/B$ energy (-2.51 eV) and the phosphorescence origin (-1.62 eV) for Th(TPP)(acac)$_2$. The last (intra-porphyrin electron repulsion) integral may be estimated from the spacing of the $Q(0,0)$ and $B(0,0)$ bands of Th(TPP)(acac)$_2$ to be $(a_{1u}^e a_{1u}^e |a_{2u}^e a_{2u}^e>) \sim 0.203$ eV. The term in square brackets in eq A14, which is the difference between the intra- and inter-porphyrin Coulomb integrals, is obtained in several steps. In analogy with analysis of mono(porphyrin) spectra, the Th-(TPP)(acac)$_2$ phosphorescence energy allows an estimate of $A\gamma = 1.62$ eV, where $a_{1u}$ is either the mono(porphyrin) $a_{1u}$ or $a_{2u}$ HOMOs and $A\gamma$ is the mono(porphyrin) HOMO/LUMO gap defined in eq A5. Substitution into the expression for the energy of either CR$^+$ eigenstate (eqs 5c or 5d), along with the 2.56-eV estimate for the energy of these (degenerate) states obtained from the 485-nm position of the $Q''$ (CR$^+$) absorption band of Th(TPP)$_2$ (Figure 1), yields $[(a_{1u}^e a_{1u}^e |a_{2u}^e a_{2u}^e>) - (a_{1u}^e a_{1u}^e |a_{2u}^e a_{2u}^e>)] \sim 0.91$ eV. Thus, eq A14 gives $(\delta - \alpha) \sim -0.218$ eV. Substitution into eq 20 along with $E_Q - E_Q' \sim 0.36$ eV given above yields $\beta \sim 0.27$ eV for the intermolecular resonance integral.