Figure 1a shows a typical ESR spectrum of 1 observed at 50 K, exhibiting a pattern characteristic of the $\Delta M_s = \pm 1$ allowed transitions from the undetect spin sublevels. This fine structure has been related to $M_s$ as $A_1 (\pm 5.4 \pm 4)$, $B_1 (\pm 4 \pm 3)$, $C_1 (\pm 3 \pm 2)$, $D_1 (\pm 2 \pm 1)$, and $E_1 (\pm 1 \pm 0)$. The relative separations of each pair in Figure 1a are $(A_1-A_1):(B_1-B_1):(C_1-C_1):(D_1-D_1):(E_1-E_1) = 9.4:7.2:5.1:3.0:1.0$, which are close to the ratios of 9:7:5:3:1 expected for the fine structure from $S = 5$ in the high-field limit.

The observed resonance fields, the signal intensities, and their angular dependence of the observed spectra were well described by the effective spin Hamiltonian,

$$\mathcal{H} = g\beta H \cdot S + D(S^2 - S(S + 1)/3) + E(S_x^2 - S_y^2)$$

with $S = 5$, $g = 2.003$, $D = -0.0168$ cm$^{-1}$, and $E = +0.0036$ cm$^{-1}$. The observed resonance fields and intensities in Figure 1a agree with those in Figure 1b, which were calculated from eq 1, assuming the negligible Boltzmann factor at 50 K. The angular dependence in Figure 2 confirms the agreement between theory and experiment, proving 1 to be an undetect molecule. To ascertain the undetected ground state, we examined the ESR spectra in the range 577 K. Only the spectrum arising from the $S = 5$ state of 1 was observed as shown in Figure 1, signals due to the $S = 1, 2, 3$, and 4 states of 1 being undetected. Furthermore, the total intensity of the undetect line decreased with increasing temperature, as quantitatively expected for an isolated undetect ground state. Thus, we concluded that the observed undetected state is the electronic ground state of 1. The negative sign of $D$ was determined by considering the Boltzmann factor at 5 K.

Hydrocarbon 1 has not only five delocalized unpaired $\pi$ electrons due to topological symmetry, as predicted by the simple MO$^1$ as well as VB$^2$-$^4$ theories, but also five localized unpaired electrons in the $\pi$ nonbonding orbitals at the five divalent carbon atoms. The spin-density distribution obtained from the UHF calculation using a generalized Hubbard model$^5$ gives the following picture. There are five net $\pi$ spins which are parallel and distributed over the carbon skeleton with changing the sign of spin densities alternately from carbon to carbon, while the other five localized spins are exchange coupled ferromagnetically to the $\pi$ spins at each divalent carbon atom. Since the $\pi$ spin densities have the same sign at each of the divalent carbon atoms as determined from topological symmetry, all 10 unpaired spins in 1 are ferromagnetically coupled with each other, leading to the $S = 5$ ground state. The realization of such an organic high-spin molecule as 1 strongly suggests the possible occurrence of organic superparamagnetism originating from properly designed macro-molecules with extremely large spins.

Acknowledgment. The present work was supported by a Grant-in-Aid for General Research on Priority Areas from the Ministry of Education, Science and Culture.

Observation of a New Low-Energy Fluorescent $1(e,r^*)$ Excited State in Strongly Coupled Porphyrin Dimers
Osman Bilisel, Juan Rodriguez, and Dewey Holten*
Department of Chemistry, Washington University
St. Louis, Missouri 63130

Gregory S. Girolami,* Stanley N. Milam, and Kenneth S. Suslick*
School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801
Received December 19, 1989

Eucidinating the electron interaction between porphyrin macrocycles held in close proximity is crucial to understanding the mechanisms of important biological and chemical processes such as electron transfer in photosynthesis$^1$ and bimetallic catalysis.$^2$ This is evident in the photosynthetic reaction center where the interaction between the bacteriochlorophylls of the dimeric primary electron donor (P) gives rise to unusual features such as the long-wavelength band of P in its neutral form or the near-infrared band in its oxidized form.$^1$ Interestingly, a number of recently synthesized lanthanide and actinide porphyrin sandwich complexes exhibit analogous spectral characteristics, namely, a broad absorption feature immediately to the red of the monomer-like Q bands in the neutral species and a near-infrared band in the oxidized species.$^3$-^5$ We report here the first observation of luminescence from bis-porphyrinate complexes, specifically, the neutral complexes of Th$^{IV}$. The location of the fluorescence identifies the absorption immediately to the red of the Q bands as vibronic transitions to a previously unknown $1(e,r^*)$ state of the dimer. This new $(e,r^*)$ state is the lowest energy excited state in the singlet manifold and apparently arises from substantial porphyrin–porphyrin $\pi$–orbital overlap.


9000-7863/90/1512-4075$502.50/0 © 1990 American Chemical Society
4076

arise from the parent compound. (b) Absorption spectra of Th(OEP), absorption band has been scaled down by a factor of between phosphorescence (dashed line) spectra of Th(OEP)2 in toluene at absorption experiments reveal a phosphorescence emission at 960 nm, in addition to are nonluminescent and deactivate in (dotted line, Figure la).839P Degassed solutions of Th(OEP)2 new, weakly fluorescing fluorescence near 790 nm (dashed line, Figure la). Time-resolved (>85%) to several nanoseconds. The with either a Hamamatsu with (dotted line, Figure la) or an RCA that such an excited state lies at low energy in the Cew complexes, but measured in charge-transfer excited state.2 Details of the time-resolved absorption studies will be reported elsewhere. Chem.

In nondegassed solutions at 295 K, Th(OEP)2 has a broad asymmetric fluorescence emission centered near 790 nm (ϕ~ 10-3) and a short-wavelength tail that extends to near 700 nm (dotted line, Figure 1a).3,4 Degassed solutions of Th(OEP), reveal a phosphorescence emission at 960 nm, in addition to fluorescence near 790 nm (dashed line, Figure 1a). Time-resolved absorption experiments on Th(OEP), (and also on Th(TPP)) reveal an initial transient with a ~10-ps lifetime (probably the new, weakly fluorescent (τ,τ°) state), which decays in high yield (>85%) into a relatively long-lived (τ~ 50 μs) phosphorescent τ,τ° state.5,6 This behavior contrasts with that of the analogous lanthanide porphyrine complexes, Ce(OEP), and Ce(TPP), which are nonluminescent and deactivate in ~2 ps after excitation.10

The fluorescence spectrum of Th(OEP)2 bears a mirror-symmetry relationship to the weak ground state absorption band near 710 nm and the stronger band ~1500 cm-1 to the blue, near 640 nm (solid line, Figure 1). The ~1500-cm-1 spacing is similar to the vibrational spacing typically seen in the absorption and emission spectra of porphyrins,11,12 Including the spacing between the Q(0,0) and Q(1,0) bands in the spectra of the ThIV sandwich complexes (Figure 1b). The strong similarity between the ground state absorption spectra of the ThIV, CeIV, and UIV sandwich complexes suggests that the origin of the lowest energy (Q(π,π°)) excited state in all of these complexes, which we call the Q(π,π°) state, is located in the vicinity of 700 nm. The very small amplitude of the (0,0) transition suggests that it is essentially dipole forbidden. We therefore attribute the stronger absorption near 540 nm to the Q(1,0) vibrionic band (Figure 1b). The fluorescence band at ~790 nm to the Q(0,1) vibrionic transition. Both transitions may derive their strength from vibronic coupling with the higher energy Soret (B) state (and possibly also with Q(-π,-π°)), as is typical in porphyrin spectra.11

A broad absorption between 600 and 700 nm is characteristic of closely spaced porphyrin dimers. It is seen not only in porphyrin sandwich complexes but also in cofacial Ru11 porphyrin dimers that contain a direct metal-metal double bond.12 In all of these complexes, the core atoms of the two macrocycles are held within ~3.5 Å, and the central nitrogen atoms of the rings are even closer (~2.8 Å).3,13 The new red-region absorption bands are absent in the spectra of porphyrin monomers11 and cofacial porphyrin dimers with larger spacings between the rings, such as those bridged by single atoms (e.g., μ-oxo complexes) and those containing flexible linkages (e.g., face-to-face porphyrins).14 Since excitonic interactions cannot explain the new Q(π,π°) manifold ~3000 cm-1 below the normal Q(π,π°) manifold, we conclude that the new Q(π,π°) state is a manifestation of the strong orbital overlap that must be present whenever porphyrins are brought within ~3 Å of one another.

In a simple one-electron MO picture, the dimer HOMO is the antibonding (i.e., antisymmetric) combination of the HOMOs of the two monomers, and the dimer LUMO is the bonding (i.e., symmetric) combination of the monomer LUMOs.15 The observation of new (π,π°) absorption, fluorescence, and phosphorescence bands that are ~3000 cm-1 lower in energy than those of the corresponding monomers suggests that the interaction energies between the relevant orbitals of the two monomeric subunits are of the order of 103 cm-1. In fact, such strong orbital interactions provide an explanation16 for the appearance of a near-IR band in the ground state absorption spectrum of the oxidized sandwich complexes.16 Strong orbital interactions have also been postulated in recent theoretical studies of other closely spaced cofacial porphyrins16 and of the dimeric primary electron donor in the photosynthetic reaction center.17 It is difficult at present, however, to pinpoint the orbital parentage of the new low-energy Q(π,π°) state, since configuration interaction is likely to be significant.16,17


(20) Some single atom-bridged iron porphyrin dimers have absorptions to the red of 600 nm, but these may be due to d-d or charge-transfer transitions that are also present in iron porphyrin monomers (see: Boxian, D. F.; Findson, E. W.; Hoffman, J. A. Jr.; Schlichter, R. D.; Hendrickson, D. N.; Sudlick, K. S. Inorg. Chem. 1984, 23, 800-807).

(21) As in weakly coupled porphyrin dimers,12,14 excitation coupling of the strong Soret transitions of the monomers can explain the broad Q band in the dimer (and possibly also the appearance of a weak feature near 480 nm) in the sandwich complexes (see Figure 1b). This mechanism cannot, however, explain the presence of the weak Q(0,0) state below the Q(π,π°) state, since excitation coupling of the weak monomer Q(0,0) transitions should be negligible. Similarly, excitation coupling cannot explain the Q bands of Ce(OEP)2(TPP) if these do not resemble the sum of the Q bands of Ce(OEP)2 and TPP monomers, whereas the Q bands of Ce(OEP)2 and Ce(TPP)2 are very similar to the Q bands of the corresponding monomers.


as it is between the four-orbital configurations in the monomer. From an alternative viewpoint, the new low-energy $Q(\pi, \pi^*)$ excited state results from the coupled excitation and charge-resonance states of the dimer. The extent of mixing among these states is of central importance in understanding the properties of the bacteriochlorophyll dimer in the photosynthetic reaction center.

The spectroscopic results presented here for the Th°IV sandwich complexes have identified a new low-energy ($\pi, \pi^*$) excited state that apparently arises from the significant overlap that should be present whenever porphyrin rings are held within ~3 Å of one another. The weak origin and stronger overtone transitions to the exciton states are linear combinations of the local-excited configurations and the charge-resonance states have been discussed recently for the related Sn° phthalocyanine sandwich complex. The relative intensities of these transitions suggest that vibronic coupling is important in these dimers, as has been proposed for the bacteriochlorophyll special pair of the photosynthetic reaction center. Our observations on these simple, well-defined sandwich complexes should aid in evaluating the nature of the lowest excited state of the special pair, where exciton and protein effects may also contribute.

Acknowledgment. This work was supported in part by Grants GM34685 and HL25934 from the National Institutes of Health. Receipt of an NIH Career Development Award (K.S.S.), a Sloan Foundation Research Fellowship (G.S.G. and K.S.S.), and a Dreyfus Foundation Teacher-Scholar Award (G.S.G.) are gratefully acknowledged. We thank L. McDowell for assistance with the phosphorescence measurements and Drs. D. Bocian, C. Kirmaier, R. Friesner, and M. Gouterman for helpful discussions.

(18) The exciton states are linear combinations of the local-excited configurations and the charge-resonance states are linear combinations of the charge-transfer, or ionic, configurations. Charge-resonance states have been discussed recently for the related Sn° phthalocyanine sandwich complex.}


---

**Enzyme-Mediated Asymmetric Decarboxylation of Disubstituted Malonic Acids**

Kenji Miyamoto and Hiromichi Ohta*

Department of Chemistry, Keio University

Hiyoshi 3-14-1, Yokohama 223, Japan

Received December 5, 1989

Transformation of a prochiral molecule to a chiral product is one of the most attractive methods of asymmetric synthesis. Although some efforts have been devoted to enantiospecific decarboxylation of disubstituted malonates, only unsatisfactory results have been obtained so far. Thus, we tried enzymatic decarboxylation of the acids, because some biosynthetic routes, such as fatty acid synthesis, involve decarboxylation steps.

First, we screened for a microorganism that is able to grow by utilizing phenylmalonic acid as a sole source of carbon. It was supposed that the first step of the metabolism is decarboxylation giving phenylacetic acid, which would be further oxidized via benzoylformate. If the enzyme responsible for this reaction also acts on disubstituted malonic acids, then chiral acids are expected to be obtained because further metabolism to $\alpha$-keto acids is impossible.

The absolute configurations of 3a-c were revealed to be $R$ by comparison of the specific rotation with reported values. Chloroform derivative 3d was reduced with $\text{PdCl}_2$·$\text{NaBH}_4$ (90%), to give 3e, which exhibited $[\alpha]_D^{25} = 96^\circ$ ($c 0.82$, ethanol), indicating the absolute configuration to be $R$. Desulfurization (Raney Ni) of 3e followed by hydrolysis and hydrogenation afforded (R)-(−)-$\alpha$-methylcaproic acid (3f).

The absolute configuration of 3a·c is $R$. Optical purity of the products (3) were determined by HPLC analysis (CHIRALCEL OJ) or 400-MHz $^1$H NMR measurements in the presence of a chiral shift reagent [Eu(hfc)$_2$] (3e).

In order to clarify the mechanism and examine the substrate specificity, the racemic monohydrate of 1a was subjected to further metabolism to $\alpha$-keto acids is

---


---

**Table 1. Enzyme-Mediated Asymmetric Decarboxylation**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Substrate Conc., %</th>
<th>Yield</th>
<th>ee, % (config)</th>
<th>$[\alpha]_D^{25}$, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>0.3</td>
<td>87</td>
<td>91 (R)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>0.4</td>
<td>93</td>
<td>96 (R)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>0.5</td>
<td>90</td>
<td>98 (R)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>0.1</td>
<td>48</td>
<td>99 (R)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>0.2</td>
<td>35</td>
<td>97 (R)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>0.3</td>
<td>95</td>
<td>&gt;95 (R)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>0.5</td>
<td>96</td>
<td>&gt;95 (R)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1d</td>
<td>0.3</td>
<td>95</td>
<td>98 (R)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1d</td>
<td>0.5</td>
<td>85</td>
<td>97 (R)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1e</td>
<td>0.3</td>
<td>98</td>
<td>95 (S)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1e</td>
<td>0.5</td>
<td>97</td>
<td>91 (S)</td>
<td></td>
</tr>
</tbody>
</table>

---

(4) Literature: S form, $[\alpha]_D^{25} = +3.3^\circ$ (c 0.96, EtOH). Literature: S form, $[\alpha]_D^{25} = +75.3^\circ$ (c 1.02, CHCl$_3$). Literature: S form, $[\alpha]_D^{25} = +78.4^\circ$ (c 1.05, CHCl$_3$).