

# ANGEWANDTE CHEMIE

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## A Zirconium Bis(porphyrinate) Sandwich Complex with an Appended Quinone\*\*

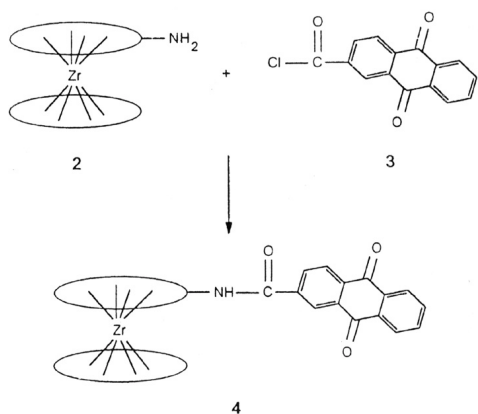
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Kenneth S. Suslick\*

The development of our understanding of the chemical and physical properties of the photosynthetic reaction center (RC) has been greatly assisted by studies of synthetic analogs. For example, remarkably long-lived charge-separated states have been observed in synthetic porphyrin–quinone tetrads and pentads, and the physiological significance of chromophore orientation and donor–acceptor energetics in reaction centers has been addressed through studies of gable porphyrin dimers and porphyrin–quinone complexes, respectively.<sup>[1]</sup> The distinctive structural feature of the RC, however, is the closely stacked “special pair” of bacteriochlorophylls that act as the primary photoelectron donor; unfortunately, no model compounds to date feature such a closely spaced cofacial porphyrin dimer as the primary electron donor. Stacked porphyrin macrocycles constrained by rigid organic tethers do not closely resemble the special pair because their mean porphyrin–porphyrin separation is relatively large, typically 5 Å.<sup>[1,2]</sup> Much better building blocks for synthetic analogues of the RC are bis(porphyrin) metal sandwich complexes in which the porphyrin–porphyrin separations are about 3 Å.<sup>[3]</sup> We now describe the first compounds that combine two key structural features present in the reaction center of photosynthetic organisms: a donor consisting of a cofacial arrangement of two porphyrinic macrocycles held about 3 Å apart, and a quinone electron acceptor.

We have previously developed a method to convert the sandwich complex  $[\text{Zr}(\text{TTP})_2]$  **1** (TTP = 5,10,15,20-tetra(*p*-tolyl)porphyrinato dianion) to the amine-substituted bis(porphyrin) zirconium species  $[\text{Zr}(\text{TTP})(\text{TTP-NH}_2)]$  **2**, in which the amine group is attached to a  $\beta$ -pyrrole site on one of the porphyrin rings.<sup>[4,5]</sup> In such bis(porphyrin) zirconium species, the two porphyrin rings are cofacial with an  $N_4$  mean plane separation of

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Scheme 1.

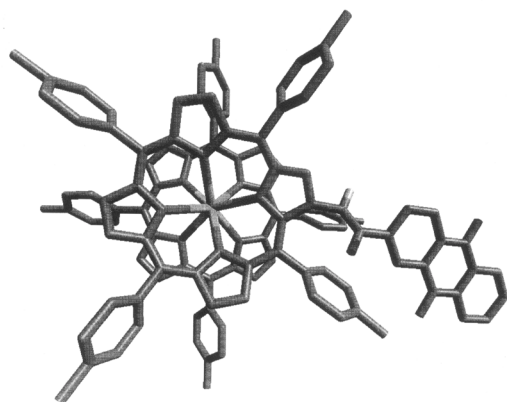


Fig. 1. Schematic representation of **4** (minimum energy configuration) illustrating the proximity of the anthraquinone substituent to two of the *p*-tolyl groups. The structure was calculated by using the programs Quanta and Charm.

2.56 Å; the mean plane separation for all 24 atoms of the porphyrin is 3.28 Å. These strongly interacting porphyrin subunits closely resemble the “special-pair” of chlorophylls in the photosynthetic reaction center, both in their cofacial architecture and spacing and in their electronic properties.<sup>[3]</sup> Condensation of **2** with 2-(chlorocarbonyl)anthraquinone (**3**) (Scheme 1) in excess pyridine yields the quinone-derivatized bis(porphyrinate) complex [Zr(TTP)(TTP-NHCOAQ)] **4** (Fig. 1).<sup>[6]</sup>

The UV/Vis spectrum of **4** contains a Soret band at 400 nm and several Q bands at 511, 557, and 696 nm; these values are essentially unchanged from those obtained for the parent complex **1** (Fig. 2). Holten et al.<sup>[7]</sup> have assigned the Q'' band at 511 nm to a charge-resonance state having a wavefunction described as  $(A^+ B^- + A^- B^+)/\sqrt{2}$ , where A and B represent the two porphyrin rings. The absorption at 557 nm is ascribed to a “normal” metalloporphyrin Q band. The lowest energy absorption at 696 nm, called Q', involves a  $\pi\text{-}\pi^*$  transition that is characteristic of all porphyrin dimers in which the macrocycles are separated by about 3 Å.<sup>[7]</sup> The anthraquinone unit absorbs strongly at 258 nm, and the features seen are again only slightly altered relative to those of 2-(phenylamidocarbonyl)anthraquinone (**5**).

The cyclic voltammogram of the quinone-derivatized porphyrin complex **4** contains two oxidation and four reduction waves. The first two reduction waves involve the anthraquinone unit, while the third and fourth involve the bis(porphyrinate)  $\pi$ -electron system, as judged from comparisons with the redox potentials of related species (Table 1). The oxidation potential of the porphyrin  $\pi$ -electron system in **4** is approximately 100 mV

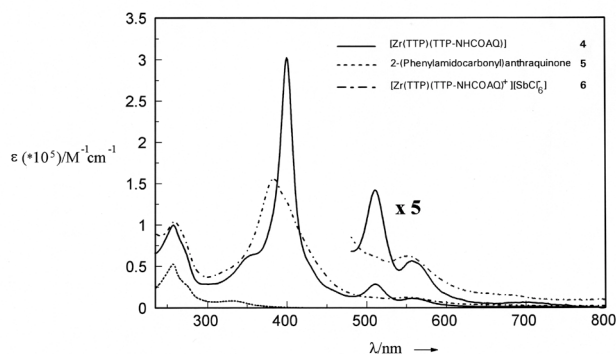


Fig. 2. UV/Vis spectra of complexes **4** and **6** and of quinone **5** in  $\text{CH}_2\text{Cl}_2$ .

Table 1. Electrochemical potentials of the zirconium bis(porphyrinate) sandwich complexes and of the quinone **5** [a].

Compound	Porphyrin		Quinone		Porphyrin	
	Oxid <sub>2</sub>	Oxid <sub>1</sub>	Redn <sub>1</sub>	Redn <sub>2</sub>	Redn <sub>1</sub>	Redn <sub>2</sub>
<b>1</b>	940	515			-1322	-1674
<b>2</b>	836	432			-1357	-1710
<b>4</b>	947	523	-819	-1265	-1363	-1678
<b>5</b>			-782	-1285		

[a] All potentials measured [mV] in  $\text{CH}_2\text{Cl}_2$  vs Ag/AgCl,  $[n\text{Bu}_4\text{NPF}_6] = 0.1$  M. Scan speed = 100  $\text{mVs}^{-1}$ .  $[\text{FeCp}_2]$  oxidation occurs at 493 mV under these conditions.

higher than that of the amine-substituted sandwich complex **2**. Furthermore, the reduction potentials for the anthraquinone substituent in **4** are shifted cathodically by about 40 mV relative to those seen for quinone **5**. These changes in the redox potentials suggest that the quinone substituent is electron-withdrawing. The reduction potentials of the porphyrin  $\pi$ -electron system in **4** remain nearly unchanged.

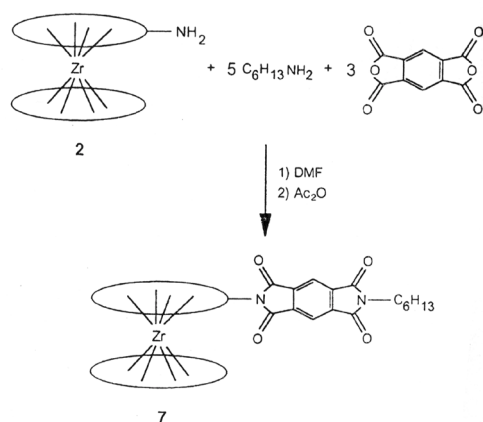
Oxidized dimeric porphyrins exhibit characteristic near-IR absorptions due to electronic transitions between bonding and antibonding molecular orbitals.<sup>[8]</sup> Treatment of **4** with phenoxathiinium hexachloroantimonate<sup>[9]</sup> yields the  $\text{SbCl}_6^-$  salt **6**



of the double-decker quinone monocation. Both chemical and electrochemical oxidation takes place from the porphyrin HOMO. The near-IR absorption band for **6** occurs at 1096 nm compared to that for  $[\text{Zr}(\text{TPP})_2]^+$  at 1075 nm.<sup>[8]</sup> Such electronic transitions are of particular interest since a broad transition (1300 nm) is also found for the special pair of bacteriochlorophyll-b,  $[(\text{BChl})_2]^+$ .<sup>[10]</sup> Oxidation of the bis(porphyrinate)  $\pi$ -electron system increases the extent of  $\pi$ - $\pi$  overlap between the two porphyrin rings; consequently, the Soret band of **6** is shifted to higher energy (Fig. 2).<sup>[11]</sup>

We have also prepared the pyromellitimide-substituted bis(porphyrinate) sandwich complex **7** by treatment of **2** with hexylamine and pyromellitic dianhydride (Scheme 2).<sup>[12]</sup> The mass spectrum confirms the presence of an *N*-hexyl-pyromellitimide group bound to the bis(porphyrinate)zirconium core (*m/z* 1725). The UV spectrum of **7** shows absorptions due to the pyromellitimide substituent at 310 and 320 nm. Porphyrin-pyromellitimide complexes are ideal systems with which to study light-induced charge separation processes because reduced pyromellitimide absorbs strongly at 715 nm, a wavelength at which the bis(porphyrinate) subunit is optically transparent.<sup>[12]</sup>

Until now, models of the photosynthetic reaction center have all relied on monomeric porphyrins as the electron donor. The



Scheme 2.

two new structural analogs of the reaction center presented here are the first in which an electron acceptor is attached to a porphyrin pair in which the porphyrin planes are held within 3 Å of each other. Comparisons of the electron transfer kinetics and the excited-state lifetimes of **4** and **7** with those of the reaction center are currently under investigation.<sup>[13,14]</sup>

### Experimental Procedure

**4:** A solution of **3** (64 mg, 0.24 mmol) in toluene was added dropwise to a suspension of **2** (140 mg, 0.097 mmol) in toluene and pyridine (2 mL), and the resulting mixture was stirred at room temperature for 2 d under Ar. The solvent was removed and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was purified by thin layer chromatography on silica plates with toluene as the eluting solvent ( $R_f = 0.18$ ). Product **4** was then recrystallized by slow diffusion of hexane into a toluene solution at 25 °C. Yield: 104 mg (66%). Calcd. for [Zr(TTP)(TTP-NHCOAQ)]: C 79.4, H 4.75, N 7.51, Zr 5.44; found: C 79.2, H 4.66, N 7.59, Zr 5.31. IR (Nujol):  $\tilde{\nu} = 1678$  cm<sup>-1</sup> (C=O). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}(\epsilon) = 258$  (98000), 400 (295000), 511 (28000), 557 (11000), 696 nm (1300). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, -80 °C):  $\delta = 9.63$ – $9.3$  (8 d, *o*-H), 9.30 (s, pyr-H adjacent to AQ), 9.0 (br. s, amido N-H), 8.74 (s, AQ H1), 8.49–8.45 (m, AQ H4-H8), 8.43–8.02 (14 d, pyr-H), 8.01–7.62 (8 d, *m*-H), 7.88–7.82 (m, AQ H3), 7.09–6.81 (8 d, *m'*-H), 6.34–5.88 (8 d, *o'*-H), 2.69–2.57 (8 s, *p*-CH<sub>3</sub>). FAB MS (8 kV, 3-nitrobenzyl alcohol):  $m/z$  (%): 1676 (100) [ $M^+ + H$ ].

**6:** Phenoxathiinium hexachloroantimonate (34 mg, 0.064 mmol) was added to **4** (100 mg, 0.060 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL), and the resulting mixture was stirred for 1 h under Ar. The solution was concentrated to about 1 mL and crystals of the salt **6** were obtained by slow diffusion of toluene into the CH<sub>2</sub>Cl<sub>2</sub> solution at -78 °C. Yield: 72 mg (60%). Calcd. for [Zr(TTP)(TTP-NHCOAQ)][SbCl<sub>6</sub>] $\cdot$ 0.5CH<sub>2</sub>Cl<sub>2</sub>: C 65.2, H 3.92, N 6.13, Zr 4.44, Sb 5.92, Cl 12.1; found: C 64.6, H 4.01, N 6.08, Zr 4.35, Sb 6.01, Cl 11.8. IR (Nujol):  $\tilde{\nu} = 1678$  (C=O), 1302 (cation marker band), 1292 cm<sup>-1</sup> (cation marker band). UV/Vis/NIR (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}(\epsilon) = 259$  (104000), 383 (156000), 554 (12000), 1096 nm (fwhm = 1300 cm<sup>-1</sup>). EPR (95 K, 1:1 CH<sub>2</sub>Cl<sub>2</sub>:C<sub>6</sub>H<sub>6</sub>):  $g = 2.0037$ , linewidth = 6.41 G. Electrospray ionization MS: 1675 [ $M^+$ ], 2005 [ $MSbCl_6^-$ ].

**7:** Pyromellitic dianhydride (34 mg, 0.064 mmol) was added to a mixture of **2** (15 mg, 0.01 mmol) and hexylamine (3 mg, 0.03 mmol) in *N,N*-dimethylformamide (DMF) (2 mL). The resulting mixture was heated to reflux for 12 h. The solvent was removed, acetic anhydride (2 mL) was added, and the mixture was allowed to reflux for 1 d. The solvent was removed and the resulting product **7** was purified by thin layer chromatography on silica plates ( $R_f = 0.16$ ). Yield: 1 mg (6%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}(\epsilon) = 310$  (117000), 319 (129000), 400 (295000), 511 (27000), 555 (13000), 689 nm (5000). FAB MS (8 kV, 3-nitrobenzyl alcohol):  $m/z$  (%): 1725 (30) [ $M^+ + H$ ].

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- [13] Whereas the fluorescence intensity of [Zr(TPP)<sub>2</sub>] (**1**) remains relatively unchanged in a range of solvent polarities, excitation of [Zr(TTP)(TTP-NHCOAQ)] (**4**) gives a considerably weaker fluorescence signal with increasing solvent polarity. This suggests that the singlet excited state of **4** undergoes electron transfer to form a charge-separated state (porphyrin<sup>-</sup>quinone<sup>+</sup>). Dewey Holten and Steve Gentemann (Washington University, St. Louis, Mo), personal communication.
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