Electronically Asymmetric Bis(porphyrin) Sandwich Complexes

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Bis(porphyrin)metal(IV) complexes (M(porph)$_2$) have been extensively studied in recent years due to their structural, chemical, and spectroscopic similarity to the "special pair" found in the reaction center of photosynthetic bacteria.[1] Strong interactions arise in the bis(porphyrin) complexes due to the short inter-porphyrin separation (< 3 Å), which results in properties not seen in mono(porphyrin) analogs.[2–6] For example, the bis(porphyrin) complexes are considerably easier to oxidize than analogous mono(porphyrin) species, and the M(porph)$_2^{n+}$ cations (n = 1, 2) exhibit near-IR absorptions not found in simple mono(porphyrin) cations. As part of our continuing effort to understand the factors that govern the electronic structures of bis(porphyrin) supermolecules, we now describe the synthesis of a series of zirconium sandwich complexes that are substituted at the porphyrin β-pyrrolic positions; these are the first examples of substituted sandwich complexes. Introduction of electron-withdrawing or -donating groups on the β-pyrrole position considerably affects the electronic properties of these molecules *without* altering their steric parameters. Thus, peripheral substitution allows us to modify the inter-porphyrin π interactions while keeping the inter-porphyrin separation constant. Previous studies have changed the identity of the central metal, but the electronic structure and the interplanar distance could *not* be varied independently.

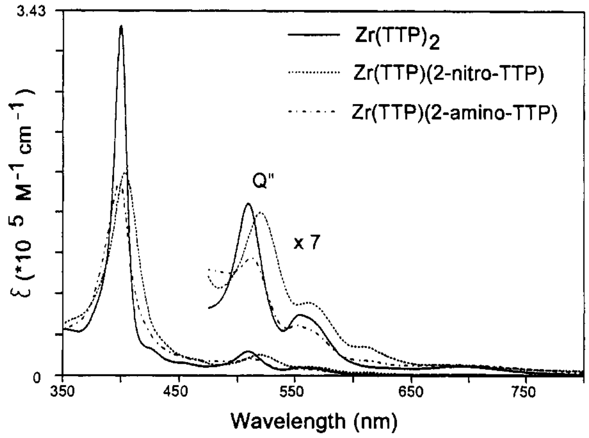

Figure 1. UV–visible spectra of Zr(TPP)(TPP-X) (X = H, NO$_2$, NH$_2$) in toluene.

Treatment of the zirconium tetraphenylporphyrin complex[7] Zr(TPP)$_2$ with I$_2$ and AgNO$_2$ in CH$_2$Cl$_2$/CH$_3$CN followed by flash column chromatography on silica gel affords the mononitro complex[8] Zr(TPP)(TPP-NO$_2$). Reduction of this complex in CH$_2$Cl$_2$/CH$_3$OH with NaBH$_4$ in the presence of 5% Pd on carbon results in the formation of the monoamino complex Zr(TPP)(TPP-NH$_2$). This method of nitration and subsequent reduction of mono(porphyrin) species has been previously employed by Baldwin and co-workers.[9] The TTP analogs of the mononitro and monoamino complexes have been synthesized similarly.[10] Treatment of Zr(TPP)$_2$ with 3 equiv of AgNO$_2$ results in the formation of a mixture of dinitro isomers, several of which have been isolated as pure fractions via chromatography. The π-radical cations and dications of the nitro and dinitro complexes have been prepared by chemical oxidation with phenoxathiinylium hexachloroantimonate in CH$_2$Cl$_2$ followed by recrystallization from toluene or pentane.[11]

The UV-visible spectra of Zr(TTP)(TTP-X) (X = H, NO$_2$, NH$_2$) are shown in Figure 1. Although the spectra of the substituted complexes generally resemble that of Zr(TTP)$_2$, the Soret band red-shifts and decreases in intensity upon nitration

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(7) The syntheses of Zr(porph)$_2$ have been described in ref 2c and 3e.

(8) Abbreviations used: TPP = 5,10,15,20-tetraphenylporphyrinate(2–), TTP = 5,10,15,20-tetra-*p*-tolylporphyrinate(2–).

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(10) Anal. Calcd for Zr(TTP)(TTP-NO$_2$): C, 78.2; H, 4.86; N, 8.55; Zr, 6.19. Found: C, 78.1; H, 4.72; N, 8.55; Zr, 6.62. IR (Nujol, cm^{-1}): ν(NO$_2$) 1523, 1326. UV–vis (C$_7$H$_8$) [λ, nm (log ϵ)]: 403 (5.29), 520 (4.30), 560 (3.95), 608 (3.55). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): 9.55–9.05 (8 d, *o*-H), 8.76 (s, pyrr-H adj to NO$_2$), 8.70–7.80 (14 d, pyrr-H), 7.82–7.70 (8 d, *m*-H), 7.20–6.80 (8 d, *m'*-H), 6.40–5.95 (8 d, *o'*-H), 2.74–2.55 (8 s, *p*-CH$_3$). Anal. Calcd for Zr(TTP)(TTP-NH$_2$): C, 79.8; H, 5.10; N, 8.73; Zr, 6.32. Found: C, 78.9; H, 5.21; N, 8.71; Zr, 6.44. IR (Nujol, cm^{-1}): ν(NH$_2$) 3485, 3390, 1614, 1514. UV–vis (C$_7$H$_8$) [λ, nm (log ϵ)]: 399 (5.26), 512 (4.21), 552 (3.81), 692 (3.20). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 9.60–9.40 (8 d, *o*-H), 7.90–7.82 (8 d, *m*-H), 8.29–7.73 (14 d, pyrr-H), 7.30 (s, pyrr-H adj to NH$_2$), 7.1–6.9 (8 d, *m'*-H), 6.20–5.97 (8 d, *o'*-H), 4.38 (s, NH$_2$), 2.70–2.63 (8 s, *p*-CH$_3$).

(11) Selected analytical and spectroscopic data are as follows. Anal. Calcd for [Zr(TPP)(TPP-NO$_2$)$^+$][SbCl$_6^-$]·CH$_2$Cl$_2$: C, 60.0; H, 3.23; N, 7.07; Sb, 6.84; Cl, 15.9; Zr, 5.12. Found: C, 60.0; H, 3.35; N, 6.88; Sb, 7.67; Cl, 13.9; Zr, 4.87. IR (Nujol, cm^{-1}): ν(NO$_2$) 1529, 1321; cation marker bands 1418, 1348, 1298, 1274. UV–vis–near-IR (CH$_2$Cl$_2$, nm): 378, 550, 1072 (fwhm = 180 nm). EPR (110 K, 1:1 CH$_2$Cl$_2$:C$_7$H$_8$): g = 2.0087, line width = 5.26 G. Anal. Calcd for [Zr(TPP)(TPP-NO$_2$)$^{2+}$][SbCl$_6^-$]$_2$·CH$_2$Cl$_2$: C, 50.5; H, 2.72; N, 5.96; Sb, 11.5; Cl, 23.5; Zr, 4.31. Found: C, 50.4; H, 2.72; N, 5.74; Sb, 10.5; Cl, 23.9; Zr, 3.70. UV–vis-near-IR (CH$_2$Cl$_2$, nm): 376, 790. IR (Nujol, cm^{-1}): ν(NO$_2$) 1534, 1319; cation marker bands 1385, 1295, 1272.

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Table 1. Electrochemical Potentials of Substituted Bis(porphyrin)zirconium Complexes[a]

complex	$oxdn_2$	$oxdn_1$	$redn_1$	$redn_2$	$redn_3$
Zr(TPP)(TPP-NH_2)	810	391	−1413	−1773	
$Zr(TPP)_2$[2c,3e]	963	501	−1390	−1767	
Zr(TPP)(TPP-NO_2)	1076	639	−1054	−1418	
$Zr(TPP\text{-}NO_2)_2$	1215	811	−931	−1223	−1559

[a] All potentials measured in mV in CH_2Cl_2 vs Ag/AgCl. [Porph] = 1 mM; [$^nBu_4NPF_6$] = 0.1 M. Scan speed = 100 mV/s. $FeCp_2$ oxidation occurs at 489 mV under these conditions. The value of $E_{pc} - E_{pa}$ is approximately 60 mV for all of the redox waves.

and blue-shifts upon amination. Interestingly, the Q″ band, which appears at 510 nm for $Zr(TTP)_2$, is red-shifted in both the nitro (520 nm) and amino (512 nm) complexes. Holten and co-workers have proposed that the excited state associated with this transition is a charge-resonance state; i.e., its wave function can be described as $(A^+B^- + A^-B^+)/\sqrt{2}$, where A and B are the two porphyrin rings.[4] The red-shift observed upon introducing either an electron-donating or an electron-withdrawing group supports the proposed assignment of the Q″ excited state: if the substituted porphyrin is labeled A, then the nitro group will stabilize the A^-B^+ microstate (and increase its contribution to the total wave function), while the amino group will stabilize the A^+B^- microstate. In both cases, therefore, the excited state should be lowered in energy, as observed.

Oxidized bis(porphyrin)metal complexes possess a characteristic near-IR band at *ca.* 1000 nm; this transition has been proposed to involve excitation of an electron from the porphyrin–porphyrin bonding to the porphyrin–porphyrin antibonding orbitals generated from the local HOMO's of each individual porphyrin ring.[5] If this assignment is correct, then the inductive effect of nitro substitutents should lower the energies of the individual porphyrin HOMO's and decrease their mutual overlap integrals. The smaller splitting between the porphyrin–porphyrin bonding and antibonding orbitals (i.e., weaker π interaction between the two porphyrin rings) should then result in a shift of the near-IR band to lower energy. Consistent with this assignment of the near-IR band, in the nitrated and dinitrated π-radical dications this band does appear at lower energy relative to that in the unsubstituted complex. Specifically, the near-IR bands of the dications $[Zr(TPP)_2^{2+}]$, $[Zr(TPP)(TPP\text{-}NO_2)^{2+}]$, and $[Zr(TPP\text{-}NO_2)_2^{2+}]$ are located at 780, 790, and 800 nm, respectively.

The effect of the β-pyrrole substituents on the electronic structures of these sandwich complexes has also been studied by cyclic voltammetry (Table 1). All the redox waves observed are fully reversible. Nitration induces an anodic shift in all the potentials, while amination causes a cathodic shift.[12] The nitro-substituted complexes are some 100–150 mV harder to oxidize, and the amino-substituted complexes some 100–150 mV easier to oxidize, than the unsubstituted bis(porphyrin) complexes. Interestingly, while the reduction potentials of the nitro complexes continue the same trend, the reduction potentials of the amino-substituted complexes are nearly the same as those of the unsubstituted analogs. Because the LUMO of TPP is lower in energy than that of TPP-NH_2, the LUMO in Zr(TPP)(TPP-NH_2) contains more TPP character, while conversely the LUMO in Zr(TPP)(TPP-NO_2) has more TPP-NO_2 character. This effect and the presence of electron–electron repulsions in the bis(porphyrin)metal anions probably are responsible for the invariance of the reduction potentials upon amination. The TTP compounds display similar trends, but the potentials are cathodically shifted by *ca.* 50 mV relative to their TPP analogs.

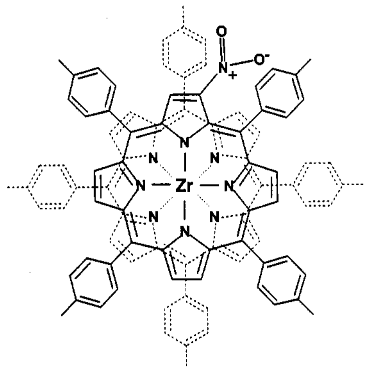

Figure 2. Schematic representation of Zr(TTP)(TTP-NO_2), illustrating the proximity of the nitro substituent to two of the *p*-tolyl groups.

The reduction of symmetry of the bis(porphyrin) complexes resulting from β-substitution is evident in the ^1H NMR spectra of the complexes. For Zr(TTP)(TTP-NO_2), eight singlets of equal intensity are observed in the *p*-Me region at 20 °C. This spectrum demonstrates that the two porphyrin macrocycles are not rotating with respect to one another on the NMR time scale, since rapid rotation would result in a five peak pattern of relative intensity 4:1:1:1:1 due to the exchange of the *p*-Me groups on the unnitrated ring. In fact, no evidence of rotation on the NMR time scale is seen even at temperatures of up to 150 °C. The β-pyrrole resonances, which appear as 14 doublets and 1 singlet (for the hydrogen atom on the nitrated pyrrole ring), also support this conclusion. Presumably, the two porphyrin rings in other bis(porphyrin)metal complexes are also unable to rotate with respect to each other.[13] Interestingly, the variable-temperature NMR spectra of Zr(TTP)(TTP-NO_2) and Zr(TTP)(TTP-NH_2) show that two of the phenyl rings have rotation barriers that are about 4 kcal/mol higher than those of the other six phenyl rings. This suggests that the β-pyrrole substituents sterically interfere with rotation of the two nearest phenyl groups about their C_{meso}–C_{ipso} axes, as illustrated in Figure 2.

In summary, substitution of bis(porphyrin)zirconium complexes with nitro or amino groups at the β-pyrrole position can be achieved, and the resulting species have afforded new insights into the electronic structure of these interesting and biologically relevant supermolecules. The nonlinear optical properties of such complexes should also prove to be of interest, given the inherent "push–pull" character of their electron-donating and -withdrawing substituents.[14]

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(12) In addition to the two commonly observed ring-based oxidations and two reductions, a third reduction is observed in the dinitro complexes. It is likely that this reduction involves the antibonding combination of the mono(porphyrin) e_g^* orbitals.

(13) The inability of the two porphyrin rings to rotate with respect to each other is also shown by the lack of isomerization of single-isomer samples of $Zr(porph\text{-}NO_2)_2$. After such a sample has been heated in refluxing toluene for 2 h the TLC analysis still shows that the same isomer is present.

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