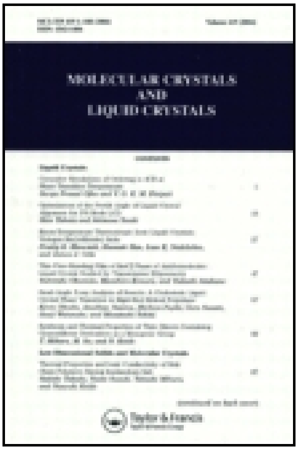

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# Electronic Properties of Bisporphyrin Biradical Dications

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# Electronic Properties of Bisporphyrin Biradical Dications

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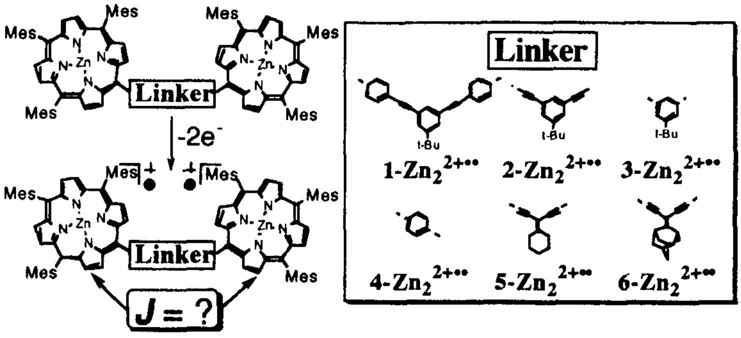
We describe the oxidations of bisporphyrins **1-$Zn_2$** – **6-$Zn_2$**, and present EPR spectra of chemically oxidized species that are consistent with exchange-coupled biradicals.

## INTRODUCTION

Multispin molecular assemblies featuring metalloporphyrins are promising components of molecule-based magnetic materials.[1] Both to strengthen and to extend the spin-spin interactions in magnetic solids composed of porphyrins, we have prepared several bisporphyrins. The bisporphyrins might be oxidized to yield π biradical-dications, in which the unpaired electrons are exchange-coupled by various linker groups.[2] Two common, successful linkers are those in nondisjoint biradicals trimethylenemethane and *meta*-xylylene, known triplet ground-state molecules.[3]

As the first examples of bisporphyrin π dication-biradicals, we describe the synthesis and electrochemical oxidations of bisporphyrins **1-$Zn_2$** — **6-$Zn_2$**, and present EPR spectra of chemically oxidized species that are consistent with an exchange-coupled biradicals.



Bisporphyrins **1-Zn**$_2^{2+\bullet\bullet}$ — **4-Zn**$_2^{2+\bullet\bullet}$ were prepared to examine the efficacy of the *meta*-phenylene coupling fragment. The number of atoms between the radical cation and coupler is systematically decreased from **1-Zn**$_2^{2+\bullet\bullet}$ to **2-Zn**$_2^{2+\bullet\bullet}$ to **3-Zn**$_2^{2+\bullet\bullet}$, while **4-Zn**$_2^{2+\bullet\bullet}$ serves as a "topology check."

Important design elements of **2-Zn**$_2$, **5-Zn**$_2$, and **6-Zn**$_2$ are the mesityl and the ethynyl groups. The nearly orthogonal arrangement of mesityl rings with the porphyrin ring reduces the possibility of aggregation, and after oxidation, increases spin density in the linker fragment by not effectively delocalizing spin density into the mesityl groups. The *meso*-ethynyl groups are important in spatially separating the porphyrin rings to allow linker/porphyrin coplanarity necessary for effective spin-spin coupling in the biradical. Compound **6-Zn**$_2$ has an adamantyl group in place of the cyclohexyl functionality of **5-Zn**$_2$. The increased steric bulk of adamantylidenealkanes is known to inhibit electrophilic addition to C=C. We wished to determine if the adamantane group of **6-Zn**$_2$ could act in a similar capacity to stabilize oxidized ethynyl-porphyrins by providing steric protection near the linker functionality.

## RESULTS AND DISCUSSION

The synthesis of diporphyrins **5-Zn**$_2$ and **6-Zn**$_2$ have been reported,[4, 5] and the syntheses of **1-Zn**$_2$ — **4-Zn**$_2$ feature similar Pd-mediated methodologies and will be reported elsewhere.[6]

Diporphyrins **1-Zn**$_2$ — **3-Zn**$_2$ and **5-Zn**$_2$ and **6-Zn**$_2$ were examined by cyclic voltammetry (CV), and the results are displayed in Figure 1. The low solubility of **4-Zn**$_2$ precluded electrochemical experiments. The group of waves near +0.60 V include the Zn(II)porphyrin/Zn(II)porphyrin$^{+\bullet}$ couples, while those near +1 V include Zn(II)porphyrin$^{+\bullet}$/Zn(II)porphyrin$^{2+}$ couples.[7, 8] The first and second oxidations for **1-Zn**$_2$ — **3-Zn**$_2$ occur a nearly identical potentials since only a single wave is observed, suggesting little coulombic interaction between the two radical cations.

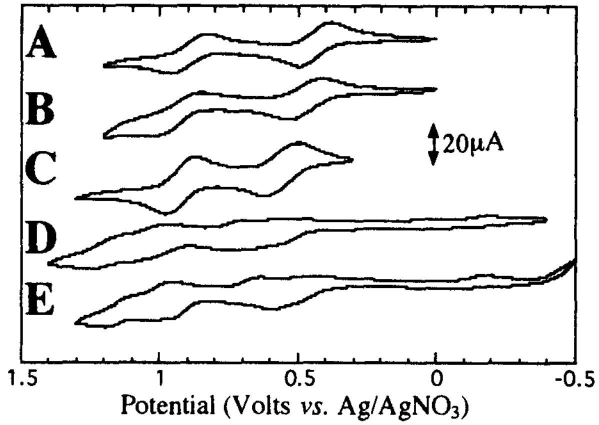


FIGURE 1 Cyclic Voltammograms of **1-Zn$_2$** — **3-Zn$_2$** (**A** — **C**, respectively) and **5-Zn$_2$** and **6-Zn$_2$** (**D** and **E**, respectively) as 1 mM solutions in $CH_2Cl_2$. The supporting electrolyte is tetra-*n*-butylammonium hexafluorophosphate (100 mM). Scan rate = 200 mV/s. Potentials are in V *vs*. Ag/AgNO$_3$.

The appearance of several unexpected oxidations for **5-Zn$_2$** and **6-Zn$_2$**, and the fact that the cathodic:anodic peak current ratios deviate substantially from unity indicate high reactivity of the oxidized species compared to **1-Zn$_2$** — **3-Zn$_2$**, and *e.g.*, Zn(II) tetraphenylporphyrin.[8, 9] Also notable is that voltammogram of **5-Zn$_2$** (A in Figure 2), recorded between +0.81 and -0.50 V *vs*. Ag/AgNO$_3$, is quasi-reversible indicating reactivity of the $\pi$ cation-radical oxidation state of the porphyrin. The quasi-reversibility of the oxidation couples for **5-Zn$_2$** compared to other Zn(II)porphyrins indicates reactivity of the linker group.

Compound **6-Zn$_2$** has an adamantyl group in place of the cyclohexyl functionality. The increased steric bulk of adamantylidenealkanes has been used to slow electrophilic addition to C=C making mechanistic studies more straightforward.[10, 11] We wished to determine if the adamantane group of **6-Zn$_2$** could act in a similar capacity to stabilize oxidized ethynyl-porphyrins by providing steric protection near the linker. The cyclic voltammogram for **6-Zn$_2$** is shown in Figure 1E. Like oxidized **5-Zn$_2$**, oxidized **6-Zn$_2$** shows chemical instability when cycled to potentials greater than *ca*. +0.8 V as indicated by the CV in Figure 1E. However, unlike **5-Zn$_2$**, the $\pi$ cation-radicals of **6-Zn$_2$** are *stable* as indicated by the *reversible* CV in Figure 2B, acquired between -0.5 and +0.8 V. Also evident in

Figure 2B is the splitting of the waves for oxidation of the first and second porphyrin groups to give **6-Zn$_2$**$^{2+\bullet\bullet}$. As suggested by the corresponding CV for **5-Zn$_2$** (Figure 2A), this potential difference implies that the linker is effective at promoting electronic communication by delocalization between the $\pi$ cation-radicals, *i.e.*, **6-Zn$_2$**$^{2+\bullet\bullet}$ behaves as a TMM-type biradical.

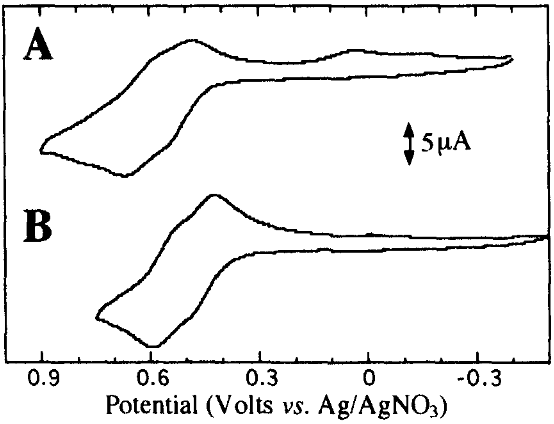


FIGURE 2 Cyclic Voltammograms of **5-Zn$_2$** and **6-Zn$_2$** (**A** and **B**, respectively) as 1 mM solutions in $CH_2Cl_2$. The supporting electrolyte is tetra-*n*-butylammonium hexafluorophosphate (100 mM). Scan rate = 200 mV/s. Potentials are in V *vs.* Ag/AgNO$_3$.

The cyclic voltammograms for **3-Zn$_2$** and **6-Zn$_2$** are shown in Figure 3. The difference in redox wave shape for the first two redox couples (*ca.* +0.52 V) for these bisporphyrins is obvious: splitting is observed for **6-Zn$_2$** (Figure 3B) but not for **3-Zn$_2$** (Figure 3A). The reason this is noteworthy is that the gable bisporphyrin, **3-Zn$_2$**, has non-coplanar porphyrin moieties separated by fewer bonds (four bonds: a shorter distance) that in **6-Zn$_2$** (six bonds). If the separation of the first two redox waves were do solely to through-space coulombic interactions, **3-Zn$_2$** should show greater splitting of these couples since the radical cations produced by oxidation are separated by a shorter distance. We assert that the splitting observed for the first two redox couples of **6-Zn$_2$** indicates effective *through-bond* coulombic interaction of the nearly coplanar porphyrin groups.[12]

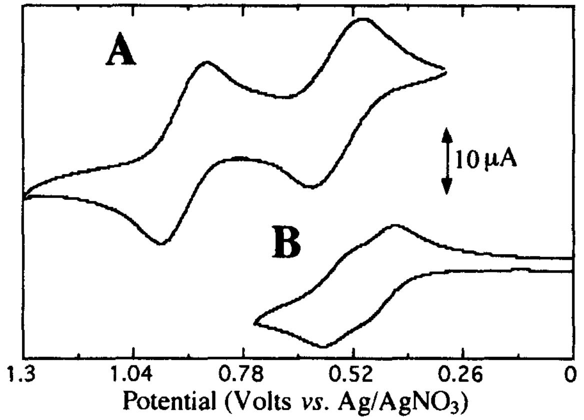


FIGURE 3 Cyclic Voltammograms of **3-Zn$_2$** and **6-Zn$_2$** (**A** and **B**, respectively) as 1 mM solutions in $CH_2Cl_2$. The supporting electrolyte is tetra-*n*-butylammonium hexafluorophosphate (100 mM). Scan rate = 200 mV/s. Potentials are in V *vs.* $Ag/AgNO_3$.

Biradical dications **1-Zn$_2$** — **4-Zn$_2^{2+\bullet\bullet}$** and **6-Zn$_2^{2+\bullet\bullet}$** were prepared by oxidation of the neutral precursors with two equivalents of tris(4-bromophenyl)amminium hexachloroantimonate.[13]

$$\textbf{1-Zn}_2 - \textbf{4-Zn}_2 \textbf{ and 6-Zn}_2 \xrightarrow[\text{CH}_2\text{Cl}_2,\ -78^\circ\text{C}]{\substack{\text{2 equivalents} \\ (p\text{-BrC}_6\text{H}_4)_3\text{N}\bullet\text{SbCl}_6}} \textbf{Biradical Dications}$$

None of the biradicals exhibited fine-structure, precluding estimation of the zero-field-splitting parameters, $|D/hc|$, from positions of $\Delta m_S = 1$ transitions and suggesting that the dipole-dipole interactions between unpaired electrons in the biradicals are weak. However, clearly visible near half-field are $\Delta m_S = 2$ transitions, the signature transition of a triplet state, confirming spin-spin coupling in the biradicals, as shown in Figure 4. The appearance of $\Delta m_S = 2$ transitions permits estimation of $D$-values from the relative intensities of the $\Delta m_S = 1$ and $\Delta m_S = 2$ transitions.[14] These calculations give upper limits of 0.0013 $cm^{-1}$ (14 G) for $|D/hc|$.[15] Clearly, the calculated $D$-values are clearly an over-estimation as fine-structure should be evident for $|D/hc| = 0.0013$ $cm^{-1}$. Simulations show that $D$-values of 7 G (0.0007 $cm^{-1}$), comparable to the spectral line-width in frozen solution, lacks fine-structure in the $\Delta m_S = 1$ region. The interelectronic distances, *ca.* 12 Å, estimated from the *D*-value[16, 17] is close to the interporphyrin-ring separations (*meso*-carbon to *meso*-carbon distances, *ca.* 5 — 14 Å), estimated from molecular models.

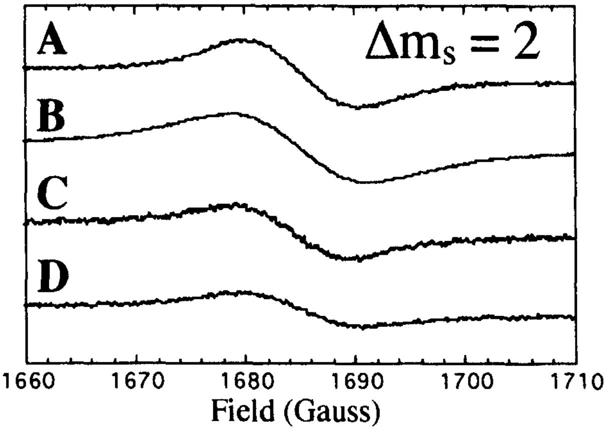


FIGURE 4 X-band EPR spectra ($\Delta m_S = 2$ transitions) of **2-Zn$_2$$^{2+\bullet\bullet}$** — **4-Zn$_2$$^{2+\bullet\bullet}$** (**A** — **C**, respectively) and **6-Zn$_2$$^{2+\bullet\bullet}$** (**D**) as solutions in frozen methylene chloride.

Figure 5 shows the dependence of the $\Delta m_S = 2$ signal intensities on temperature. The data follow the Curie law from *ca.* 12 to *ca.* 60 K.[18] These data are consistent with $J \geq 0$; *i.e.*, with either a triplet ground-state or a singlet-triplet degeneracy.

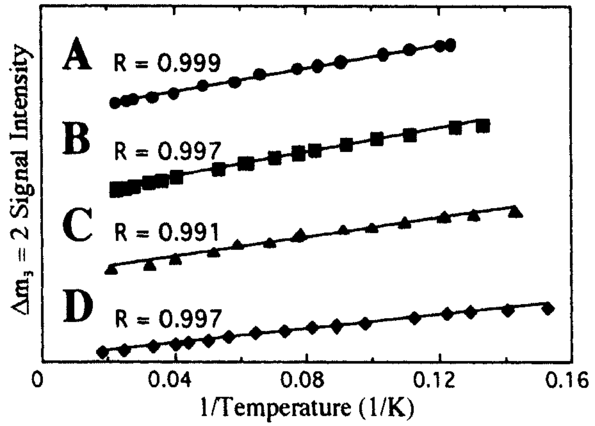


FIGURE 5 Curie plots for doubly-integrated $\Delta m_S = 2$ transition signal intensities of **2-Zn**$_2^{2+\bullet\bullet}$ – **4-Zn**$_2^{2+\bullet\bullet}$ (**A** – **C**, respectively) and **6-Zn**$_2^{2+\bullet\bullet}$ (**D**).

## CONCLUSIONS

In summary, we demonstrated exchange coupling in four nondisjoint bisporphyrin-based dication-biradicals. The stability of the dication-biradical is affected by the nature of the "protecting group" of the linker fragment, and evidence of through-bond interaction of the radical ions was presented. Curie plots are consistent with triplet ground-states and singlet-triplet degeneracies. Further study of these biradicals is underway.

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green solid taken into a glove box for EPR sample preparation. Samples were 10 mM in bisporphyrin for frozen-solution experiments, and 1 mM for fluid-solution EPR measurements. EPR spectra of solutions of the biradicals remain unchanged for several days. Generally, the room temperature EPR spectra consist of single lines devoid of hyperfine structure.

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