

## Oxidation of a Bis[Zn(II) porphyrin] Yields a Nondisjoint, Exchange-Coupled $\pi$ Dication-Biradical

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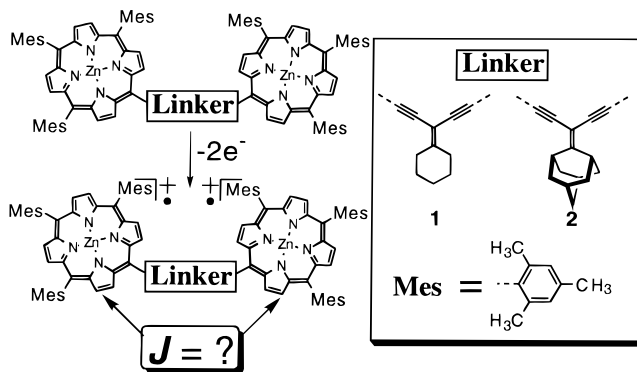
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Multispin molecular assemblies featuring metalloporphyrins are promising components of molecule-based magnetic materials.<sup>1</sup> Both to strengthen and to extend the spin–spin interactions in magnetic solids composed of porphyrins, we have prepared nitroxideporphyrins<sup>2</sup> and several bisporphyrin molecules.<sup>3a–c</sup> The latter might be oxidized to yield  $\pi$  biradical-dications,<sup>4a,b</sup> in which the unpaired electrons are exchange-coupled by various linker groups. Two common, successful linkers are those in nondisjoint<sup>5</sup> biradicals trimethylenemethane (TMM) and *meta*-xylylene, known triplet ground-state molecules.<sup>6</sup>

As the first examples of TMM-type bisporphyrin  $\pi$  dication-biradicals,<sup>4b</sup> we describe the electrochemical oxidations

of bisporphyrins **1** and **2** and present EPR spectra of chemically oxidized  $2^{2+}$  that are consistent with an exchange-coupled biradical.



Important design elements of **1** and **2** are the mesityl and the ethynyl groups. The nearly orthogonal arrangement of mesityl rings with the porphyrin ring<sup>7</sup> reduces the possibility of aggregation and after oxidation does not dilute spin density in the linker fragment by preventing delocalization of spin density into the mesityl groups. The ethynyl groups are important in spatially separating the porphyrin rings to allow linker/porphyrin coplanarity necessary for effective spin–spin coupling in the biradical.

The synthesis of bisporphyrin **1** was described recently,<sup>3a</sup> and **2** was prepared in a similar fashion.<sup>8</sup> Cyclic voltammograms of **1** are displayed in Figure 1A,B. The group of waves near +0.60 V includes the Zn(II)porphyrin/Zn(II)porphyrin<sup>+</sup> couples, while the group near +1.1 V include Zn(II)porphyrin<sup>+</sup>/Zn(II)porphyrin<sup>2+</sup> couples.<sup>9,10</sup> The appearance of several unexpected oxidations and the fact that the cathodic/anodic peak current ratios deviate substantially from unity indicate quasireversibility, suggesting high reactivity of the oxidized species compared to, e.g., Zn(II) tetraphenylporphyrin.<sup>4,10</sup> Most notable is that voltammogram 1B, recorded between +0.81 and –0.50 V vs Ag/AgNO<sub>3</sub>, is quasireversible, indicating that the  $\pi$  cation-radical of the porphyrin is labile. The quasireversibility of the oxidation couples for **1** compared to other Zn(II)porphyrins implicates the linker fragment as being responsible for the reactivity. However, the existence of more than one wave near +0.60 V suggests that the first two oxidations (**1** → **1**<sup>+</sup> → **1**<sup>2+</sup>) occur at different potentials, in turn suggesting nonzero exchange coupling through the TMM-type linker. Unfortunately, the chemical reactivity of oxidized **1** precludes a definitive conclusion.

Compound **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.<sup>11,12</sup> We wished to determine if the adamantane

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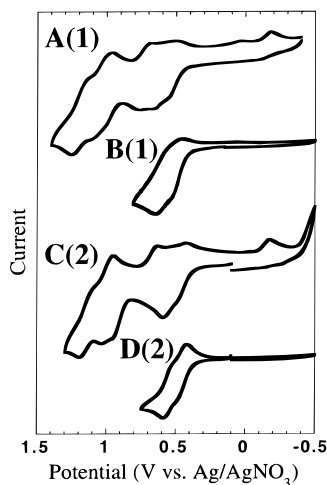
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(8) Procedures for the preparation of all compounds as well as spectral data are contained in the Supporting Information.

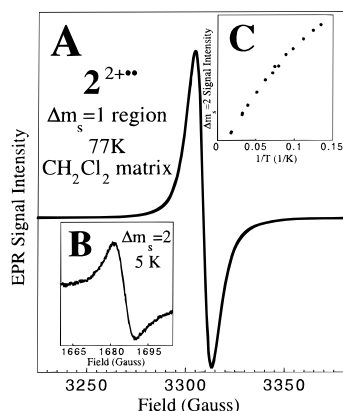
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**Figure 1.** Cyclic voltammograms of **1** (A and B) and **2** (C and D) as 1 mM solutions in  $\text{CH}_2\text{Cl}_2$ . The supporting electrolyte is tetra-*n*-butylammonium hexafluorophosphate (100 mM). Scan rate = 500 mV/s for voltammograms A and C, and 50 mV/s for voltammograms B and D. Potentials are in V vs  $\text{Ag}/\text{AgNO}_3$ .



**Figure 2.** X-band EPR spectra of biradical  $2^{2+}$  as a solution in frozen methylene chloride. A:  $\Delta m_s = 1$  spectrum recorded at 77 K. B (bottom, left inset):  $\Delta m_s = 2$  transition recorded at 5 K. C (top, right inset): Curie plot for doubly integrated  $\Delta m_s = 2$  transition signal intensity.

group of **2** could act in a similar capacity to stabilize oxidized ethynylporphyrins by providing steric protection near the linker functionality. Cyclic voltammograms for **2** are shown in Figure 1C,D. Like oxidized **1**, oxidized **2** shows chemical instability when cycled to potentials greater than ca. +0.8 V as indicated by the CV in Figure 1C. However, unlike **1**, the  $\pi$  cation-radicals of **2** are *stable* as indicated by the *reversible* CV in Figure 1D, acquired between  $-0.75$  and  $+0.8$  V. Also evident in Figure 1D is the splitting of the waves for oxidation of the first and second porphyrin groups to give  $2^{2+}$ . As suggested by the corresponding CV for **1**, this potential difference implies that the linker is effective at promoting electronic communication by delocalization between the  $\pi$  cation-radicals; i.e.,  $2^{2+}$  behaves as a TMM-type biradical.

Biradical dication  $2^{2+}$  was prepared by oxidation of **2** with 2 equiv of tris(4-bromophenyl)ammonium hexachloroantimonate.<sup>13</sup> Frozen solution EPR spectra of the biradical are shown in Figure 2A,B.<sup>14</sup> The spectral feature near 3300 G (Figure 2A) is devoid of fine-structure, precluding calculation of the zero-field-splitting parameter,  $|D/hc|$ , from positions of  $\Delta m_s = 1$  transitions and suggesting that the dipole–dipole

interaction between unpaired electrons is weak. However, clearly visible near half-field is a  $\Delta m_s = 2$  transition, the signature transition of a triplet state, confirming spin–spin coupling in the biradical. The appearance of a  $\Delta m_s = 2$  transition permits estimation of  $|D/hc|$  from the relative intensities of the  $\Delta m_s = 1$  and  $\Delta m_s = 2$  transitions.<sup>15</sup> This calculation gives an upper limit of  $0.0013 \text{ cm}^{-1}$  (14 G) for  $|D/hc|$ .<sup>16</sup> The calculated  $D$  value is clearly an overestimation, as fine structure should be evident for  $|D/hc| = 0.0013 \text{ cm}^{-1}$ . Simulations show that a  $D$  value of 7 G ( $0.0007 \text{ cm}^{-1}$ ), comparable to the spectral line-width in frozen solution, lacks fine structure in the  $\Delta m_s = 1$  region. The interelectronic distance, 12.6 Å, estimated from the  $D$  value<sup>17,18</sup> is slightly less than the interporphyrin-ring separation (ca. 14 Å), calculated from molecular models. At present, we cannot determine whether the smaller interelectronic distance calculated from spectral parameters is the result of crudeness of the point-dipole approximation and errors in measuring the spectral transition ratio, the result of the geometry of the bisporphyrin, or the result of spin-delocalization into the linker fragment.

Figure 2C shows the dependence of the  $\Delta m_s = 2$  signal intensity on temperature. The data follow the Curie law from 12 to 60 K.<sup>19</sup> The slight deviation from linearity below 12 K could be the result of saturation effects; however, our signal saturation plot was linear below the lowest temperature reported (see the Supporting Information). Another possibility is a small, negative exchange coupling constant,  $J$ , resulting from weak antiferromagnetic coupling of the unpaired electrons. The  $J$  value calculated by a line fit is ca.  $-6 \text{ cal/mol}$ . This small value is similar to a typical experimental error, and we feel that the slight curvature does not discount high-spin coupling. Moreover, even when a linear relationship is observed, a singlet/triplet degeneracy is still a possibility.<sup>19</sup>

In summary, we demonstrated exchange coupling in a nondisjoint bisporphyrin-based dication-biradical. The stability of the dication-biradical is affected by the nature of the “protecting group” of the linker fragment. Further study of  $2^{2+}$  and related biradicals is underway.

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**Supporting Information Available:** Synthesis and spectral data (14 pages).

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(13) Porphyrin oxidation was achieved by cannulating 2 equiv of tris(4-bromophenyl)ammonium hexachloroantimonate into a cold ( $-78 \text{ }^\circ\text{C}$ ) methylene chloride solution of bis(porphyrin). After 30 min, solvent was removed on the Schlenk line, and the green solid was taken into a glovebox for EPR sample preparation. Samples were 10 mM in bis(porphyrin) for frozen-solution experiments and 1 mM for fluid-solution EPR measurements. The EPR spectra of solutions of oxidized **2** remain unchanged for several days.

(14) The room-temperature spectrum of  $2^{2+}$  consists of a single line devoid of hyperfine structure; see the Supporting Information.

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