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COMMUNICATIONS

Published on Web 01/16/2004

Triplet π-Diradical Dication of Directly *meso*−β-Linked Porphyrin Dimer

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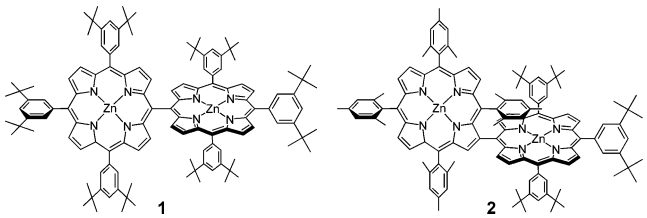
Spin correlation in aromatic molecular systems containing organic radicals has recently captured the spotlight in the field of spin chemistry.[1−7] To achieve a ferromagnetic interaction between the radicals in π-conjugated molecular systems, the molecular topology is widely adopted into their molecular design.[1,2] In this approach, degenerated singly occupied molecular orbitals (SOMOs) determined by the topology successfully provide various high-spin molecular systems.[3] On the other hand, direct exchange interaction between sterically orthogonal π-radicals, which is considered to be an alternative mechanism for spin alignment,[8] has not achieved the high-spin ground state because of the difficulty of obtaining the conditions needed to realize the perfect orthogonal structure of aromatic oligomers. As a representative example of the latter approach, poly(π-radical anion)s of poly-9,10-anthrylenes showed a thermally excited character in the high-spin state.[9]



Recently, our group reported unique high-spin states of poly(π-radical cation)s of directly *meso*−*meso*-linked porphyrin arrays.[10] For a bis(π-radical cation) of dimer **1**, the temperature dependence of the ESR signal intensity of triplet species showed an anomalous feature, that is, an abrupt increase in the triplet signal over 120 K, whereas the intensity change under 120 K was regarded as a summation of plural components of a thermally excited state. Such an anormalous behavior of $\mathbf{1}^{2+\bullet\bullet}$ over 120 K is due to a degeneracy or crossover between singlet and triplet states in the relatively high-temperature region, where a motion around the *meso*−*meso* linkage is activated. These results suggest that the singlet−triplet energy gap of $\mathbf{1}^{2+\bullet\bullet}$ is close to the limiting conditions needed to realize the high-spin ground state. With this in mind, we developed an improved model of directly linked bisporphyrin, $Zn(II)_2$ 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-2-(10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin-5-yl)porphyrin (**2**), and investigated the magnetic property of its bis(π-radical cation). In this dimer **2**, the *meso*−*meso* linkage of dimer **1** was replaced with a *meso*−β linkage.[11−13] Therefore, the overlap integral between neighboring SOMOs of $\mathbf{2}^{2+\bullet\bullet}$ was expected to be smaller than that of $\mathbf{1}^{2+\bullet\bullet}$ since the highest occupied molecular orbital (HOMO) of zinc tetraarylporphyrin is the A_{2u} orbital, which has large coefficients at the *meso* carbons but not at the β carbons. Furthermore, the torsional angle between neighboring π-planes of dimer **2** was kept at nearly 90° by the steric hindrance of a *meso*-mesityl group neighboring the *meso*−β linkage. Consequently, a stable triplet state of the bis(π-radical cation) $\mathbf{2}^{2+\bullet\bullet}$, which obeys the Curie law, was successfully observed.

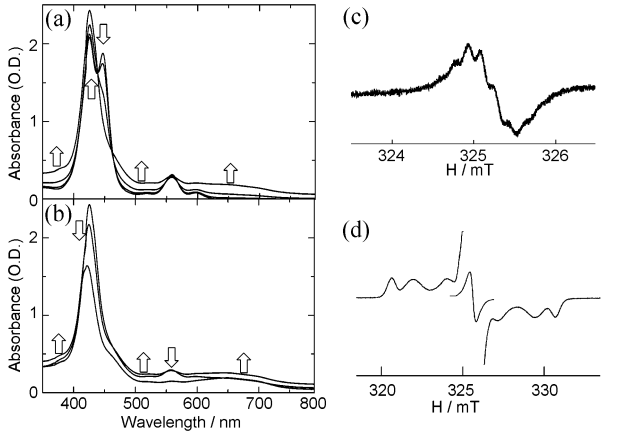


Figure 1. (a,b) In situ absorption spectral changes due to the progress of the oxidation of *meso*−β dimer **2** with $NaAuCl_4 \cdot 2H_2O$ in chloroform at room temperature. (c) ESR spectrum of the monoradical species of dimer **2** at room temperature in chloroform. (d) ESR spectrum of the oxidized species of dimer **2** at 10 K in dichloromethane.

The free base derivative of dimer **2** was prepared by the BF_3−Et_2O-catalyzed condensation of β-formylated *meso*-tetramesitylporphyrin, *meso*-(3,5-di-*tert*-butylphenyl)dipyrromethane, and 3,5-di-*tert*-butylbenzaldehyde in dry chloroform under a nitrogen atmosphere according to the reported procedure.[10,12,14] The two porphyrin rings were simultaneously metalated with $Zn(OAc)_2$ in chloroform/methanol.[10,12,15] The product showed Soret band absorptions split by excitonic coupling, indicating the orthogonal alignment of the neighboring porphyrin rings.[10−18]

When a chloroform solution of dimer **2** was treated with a small amount of $NaAuCl_4 \cdot 2H_2O$, the lower-energy Soret absorption around 445 nm, assigned to the coupled dipole moment of the dimer, decreased with an increase in the longer wavelength transitions around 650 nm, assigned to an oxidized porphyrin π-radical (Figure 1a). The ESR spectrum of the oxidized species at room temperature was observed as a single peak with a hyperfine-splitting structure due to four quasi-equivalent nitrogen atoms (Figure 1c), indicating the generation of the mono(π-radical cation) $\mathbf{2}^{+\bullet}$. The splitting parameter (a_N = 1.72 G) was more like that of a π-radical cation of Zn(II) tetramesitylporphyrin (a_N = 1.75 G) than that of Zn(II) tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (a_N = 1.60 G) (Supporting Information). Therefore, it is suggested that the generated π-radical resides mainly at the tetramesitylporphyrin site at the first stage and hardly penetrates the adjacent tris(3,5-di-*tert*-butylphenyl)-porphyrin site because of the small overlap integral between the orthogonal π-systems.

As the oxidation progressed, a set of fine-structured ESR signals due to a triplet species was detected at 10 K, along with an increased monoradical signal (Supporting Information). The triplet signals

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10.1021/ja0385989 CCC: $27.50 © 2004 American Chemical Society

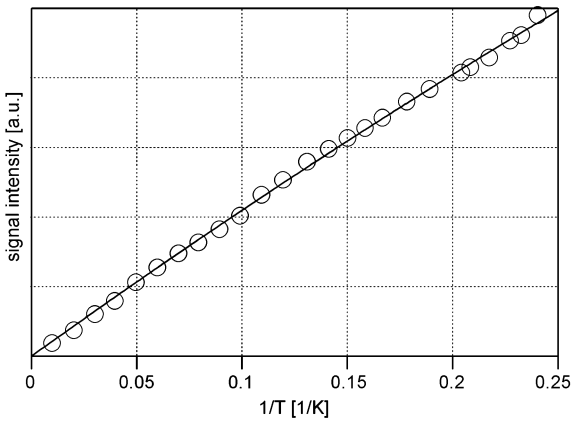

Figure 2. Temperature dependence of triplet ESR signal intensity of $\mathbf{2}^{2+\bullet\bullet}$ in chloroform. The solid line is a fitting curve derived from eq 1 with $\Delta E_{ST} = 2.1$ cal/mol.

increased upon further oxidation while the central monoradical signal decreased (Figure 1d). At this stage, the visible absorption peak around 420 nm also decreased (Figure 1b), indicating the formation of bis(π-radical cation) $\mathbf{2}^{2+\bullet\bullet}$. This second oxidation step of dimer **2** occurs at an earlier stage than that of *meso*−*meso* dimer **1** due to the relatively small Coulombic interaction between two cations on $\mathbf{2}^{2+\bullet\bullet}$.[10] Although the ESR spectral shape deviated slightly from that of a characteristic triplet species, the zero-field-splitting parameters were estimated to be $|D| = 4.6 \times 10^{-3}$ cm^{-1} and $|E| = 7.5 \times 10^{-4}$ cm^{-1}. The *x* and *y* lines were broadened and lowered due to hyperfine coupling. The smaller *D* value and larger *E* value of the *meso*−β diradical $\mathbf{2}^{2+\bullet\bullet}$, in comparison to those of the *meso*−*meso* diradical $\mathbf{1}^{2+\bullet\bullet}$ ($|D| = 1.2 \times 10^{-2}$ cm^{-1} and $|E| = 3.0 \times 10^{-4}$ cm^{-1}),[10] were qualitatively in accord with the molecular structure of *meso*−β dimer **2**, in which the center-to-center distance is longer and the axis symmetry is lower than those in *meso*−*meso* dimer **1**. On the basis of a point-dipole approximation, the spin−spin distance of the diradical $\mathbf{2}^{2+\bullet\bullet}$ was estimated to be 8.2 Å from the *D* value, which is qualitatively consistent with the center-to-center distance of the two porphyrin rings.

The plots of the triplet ESR signal intensity versus inversed temperature afforded an almost straight line, in agreement with the typical Curie law, in a temperature range of 4.2−150 K, as shown in Figure 2. In this case, there are two possibilities: (i) a ground-state triplet or (ii) a nearly degenerated singlet and triplet. If (ii) is true, then the energy gap ΔE_{ST} is smaller than 3 cal/mol. This temperature dependence of the triplet ESR signal intensity of the bis(π-radical cation) of the *meso*−β dimer **2** is completely different from those of *meso*−*meso* dimer **1** and poly-9,10-anthrylenes. When dichloromethane was used as a solvent, a similar triplet ESR spectrum was observed, although the plots of signal intensity (*I*) versus inverse temperature were slightly curved and could be fitted with $\Delta E_{ST} = 12$ cal/mol by eq 1:

$$I = (C/T)\exp(-\Delta E_{ST}/RT)/[1 + 3\exp(-\Delta E_{ST}/RT)] \quad (1)$$

Such a delicate solvent dependence may be caused by the solvent-induced conformational change or the difference in the solvation itself of the bis(π-radical cation) $\mathbf{2}^{2+\bullet\bullet}$. It was recently documented that bond-torsion-sensitive exchange interaction (*J*) caused matrix-dependent singlet−triplet bistability of some biradicals.[19] In these cases, the magnitude and the sign of *J* are controlled by the solvent. In the bis(π-radical cation) $\mathbf{2}^{2+\bullet\bullet}$, the rotation of the *meso*−β bond and the solvation of the cationic π-radical moieties are considered to affect the singlet−triplet energy gap slightly. The solvent effect on biradicals has been investigated on the energy levels of a transient radical ion pair of porphyrin−chlorophyll *meso*−β heterodimer.[11] Since the spin−spin exchange interaction in a radical ion pair has fundamental significance in the photoinduced electron transfer,[20] the *meso*−β diradical $\mathbf{2}^{2+\bullet\bullet}$ reported here could be a good object for the examinations of the various spin-carrying π-systems.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of the Japanese Government.

Supporting Information Available: ESR spectra of $\mathbf{2}^{+\bullet}$ and $\mathbf{2}^{2+\bullet\bullet}$, and temperature dependence plots in various solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346−351. (b) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385−415. (c) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893. (d) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109−116.
(2) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999.
(3) (a) Shultz, D. A.; Lee, H.; Kumar, R. K.; Gwaltney, K. P. *J. Org. Chem.* **1999**, *64*, 9124−9136. (b) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, *123*, 5942−5946. (e) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, *294*, 1503−1505.
(4) Tsukagoshi, K.; Alphenaar, B. W.; Ago, H. *Nature* **1999**, *401*, 572−574.
(5) (a) Matsuda, K.; Irie, M. *Chem. Lett.* **2000**, 16−17. (b) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195−7201. (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 8309−8310. (d) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 9896−9897.
(6) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789−793.
(7) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378−4400.
(8) Müllen, K.; Baumgarten, M.; Tyutyulkov, N.; Karabunarliev, S. *Synth. Met.* **1991**, *40*, 127−135.
(9) (a) Hoshino, M.; Kimura, K.; Imamura, M. *Chem. Phys. Lett.* **1973**, *20*, 193−196. (b) Baumgarten, M.; Müller, U.; Bohnen, A.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 448−451. (c) Müller, U.; Baumgarten, M. *J. Am. Chem. Soc.* **1995**, *117*, 5840−5850.
(10) Segawa, H.; Machida, D.; Senshu, Y.; Nakazaki, J.; Hirakawa, K.; Wu, F. *Chem. Commun.* **2002**, 3032−3033.
(11) (a) Wasielewski, M. R.; Johnson, D. G.; Niemczyk, M. P.; Gaines, G. L.; O'Neil, M. P.; Svec, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 6482−6488. (b) Wasielewski, M. R.; Gaines, G. L.; Wiederrecht, G. P.; Svec, W.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 10442−10443.
(12) Susumu, K. Dissertation, Kyoto University, Japan, 1996.
(13) (a) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 176−179. (b) Tsuda, A.; Nakano, A.; Furuta, H.; Yamochi, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 558−561.
(14) Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399−8402.
(15) Wu, F.; Segawa, H. *Photogr. Sci. Photochem.* **1999**, *17*, 316−322.
(16) Khoury, R. G.; Jaquinoid, L.; Smith, K. M. *Chem. Commun.* **1997**, 1057−1058.
(17) (a) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135−136. (b) Yoshida, N.; Shimidzu, H.; Osuka, A. *Chem. Lett.* **1998**, 55−56. (c) Tsuda, A.; Nakamura, T.; Sakamoto, S.; Yamaguchi, K.; Osuka, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2941−2945.
(18) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371−392.
(19) (a) Shultz, D. A.; Boal, A. K.; Farmer, G. T. *J. Am. Chem. Soc.* **1997**, *119*, 3846−3847. (b) Rajca, A.; Lu, K. Rajca, S.; Ross, C. R., II. *Chem. Commun.* **1999**, 1249−1250.
(20) Lukas, A. S.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 3921−3930.

JA0385989