

Spin Alignment of Orthogonal π -Radicals of Directly *meso-meso* Linked Porphyrin Dimer, Trimer, and Tetramer

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Orthogonally oriented π -planes of directly *meso*-linked porphyrin arrays affords a unique molecular system for spin-alignment based on the exchange interaction between neighboring π -radicals. Directly *meso*-linked porphyrin dimer **ZnP2** was oxidized by the treatment with NaAuCl₄ in chloroform to afford mono(π -radical cation) **ZnP2^{•+}** and bis(π -radical cation) **ZnP2^{2•+}**, successively. On the basis of the magnetic behavior of **ZnP2^{2•+}**, oxidized species of trimer (**ZnP3**) and tetramer (**ZnP4**) have been investigated. Multiplet ESR spectra of the oxidized species of trimer **ZnP3** and tetramer **ZnP4** were interpreted to be derived from quartet tris(π -radical cation) **ZnP3^{3•+}** and quintet tetrakis(π -radical cation) **ZnP4^{4•+}**, respectively. It is suggested that the spin alignment of the orthogonal molecular system can be extended to more longer distances.

Key words: porphyrin, radical, ESR, high-spin

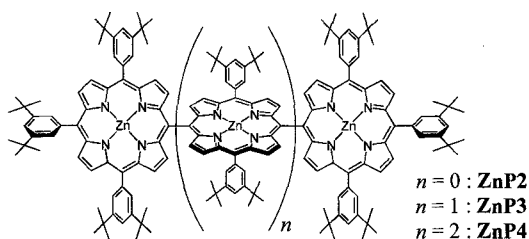
1. INTRODUCTION

Molecule-based magnets are developing from static systems toward controllable dynamic systems; e. g., several switchable spin systems have been reported recently.¹ Among various controllable spin systems, an electronic transformation system would be a most simple one, in which the spins generated through redox processes interact ferromagnetically to afford high-spin states. As another candidate for an electronically transformable system, π -systems connected with ferromagnetic coupler, such as *m*-phenylene, have been reported.² However, large π -systems often cause severe twist to break a simple π -topology effect. If spin alignment is achieved in a twisted π -system, it should work well in larger molecular systems.

On the other hand, the severe twist of a double bond of a π -conjugated molecule should cause breaking of π -bond to afford a biradical state. Spin state of such species has been argued as a "twisted ethylene" system, and some experimental challenges to investigate it have been performed, using bulky substituents.³ The early report on the twist π -systems are π -radical anions of 9,10-anthrylenes.⁴ In this case, π -radicals reside on anthracene π -planes aligned sterically in a nearly orthogonal orientation, and thermally excited high-spin states were observed. In order to realize a high-spin state as a ground state, a perfect orthogonal orientation in which the torsional angle between the spin-carrying π -systems is close to 90° should be accomplished.

From these viewpoints, we have investigated the poly(π -radical cation)s of directly-linked Zn(II) porphyrin arrays.^{5,6} The characteristics of directly *meso*-linked porphyrin arrays are orthogonal orientation of π -systems derived from steric hindrance between adjacent porphyrin macrocycles.⁷⁻⁹ In fact, triplet state of bis(π -radical cation) of directly *meso*-linked

porphyrin dimer (**ZnP2**) was observed in terms of ESR spectroscopy.⁵ It was also found that bis(π -radical cation) of directly *meso*- β -linked Zn(II) porphyrin dimer is a triplet species which obeys Curie law.⁶ In this paper, directly *meso*-linked trimer **ZnP3** and tetramer **ZnP4** were prepared, and their oxidized species were investigated on the basis of the consideration for the magnetic behavior of bis(π -radical cation) of dimer **ZnP2**.



2. EXPERIMENTAL

Directly *meso*-linked porphyrin dimer (Zn(II)₂ 5,5'-bis(10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin) : **ZnP2**) was synthesized by oxidative coupling of Zn(II) 5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin.⁵ In order to synthesize the corresponding trimer (**ZnP3**) and tetramer (**ZnP4**), Zn(II) 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (12.7 mg) and Zn(II) 5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin (16.5 mg) were mixed in dichloromethane-dimethylformamide (10:1 v/v) and oxidized with AgBF₄ (20 mg). Isolation of the products by column chromatography on Bio-Beads S-X3 (Bio-Rad)^{5,7,9} afforded 6 mg (26%) of **ZnP3** and 5 mg (17%) of **ZnP4**, respectively. Chloroform solution of NaAuCl₄, which was used for the chemical oxidation of the porphyrin oligomers, was prepared by dipping NaAuCl₄·2H₂O powder into same

volume of dimethylsulfoxide followed by dilution with chloroform. ESR spectra were recorded on a JEOL JES-TE300 spectrometer, equipped with an RMC liquid helium transfer system and a Scientific Instruments 9650 digital temperature controller. Zero field splitting parameters were evaluated from high field approximation.

3. RESULTS AND DISCUSSION

3.1 Changes in absorption spectra of *meso*-linked porphyrin arrays in the progress of oxidation

The absorption spectra of the directly *meso*-linked porphyrin arrays showed split Soret-band with two peaks. In all oligomers, the higher energy peak was observed around 420 nm, which is a same wavelength of the Soret-band of the corresponding monomeric zinc

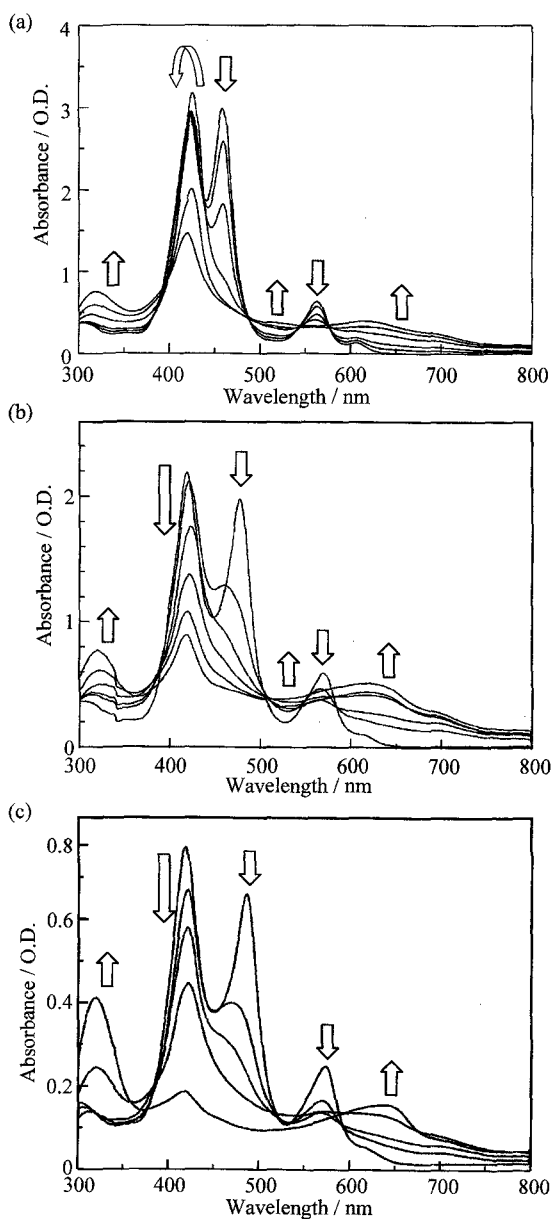


Fig.1 In situ absorption spectral changes due to the progress of the oxidation with NaAuCl_4 in chloroform at room temperature for (a) dimer **ZnP2**, (b) trimer **ZnP3**, and (c) tetramer **ZnP4**.

porphyrin. The higher energy peak is assigned to the transition dipole aligned perpendicular to the *meso-meso* linkage. Since the adjacent porphyrin rings are orthogonal to each other, the neighboring dipoles are also aligned orthogonally, resulting no effective excitonic coupling. On the other hand, the lower energy peak is depending on the number of porphyrins. This absorption is derived from the coupled transition dipole aligned parallel to the *meso-meso* linkage.^{5,7,8}

Oxidation of dimer **ZnP2** was performed by the treatment with NaAuCl_4 in chloroform, which was added dropwise with monitoring of absorption spectrum. When a few drops of NaAuCl_4 in chloroform were added to a chloroform solution of dimer **ZnP2**, the lower energy absorption of Soret-band (450 nm) decreased, whereas the higher energy absorption of Soret-band (410 nm) remained, as shown in Fig.1(a).⁵ The decrease of the lower energy absorption of Soret-band indicates the loss of the coupled transition dipole. The broad absorption band appeared at longer wavelength region (~ 650 nm) is derived from π -radical cation of a porphyrin.⁵ Oxidation of one porphyrin moiety of the dimer to a π -radical cation causes the loss of the exciton coupling. The remaining slightly increased higher energy absorption of Soret-band indicates that the other porphyrin moiety is kept neutral.

Addition of further NaAuCl_4 in chloroform to the solution of dimer **ZnP2** caused the decrease of the higher energy absorption of Soret-band, indicating the loss of the unperturbed transition dipole aligned perpendicular to the *meso-meso* linkage. In this stage, both porphyrin moieties of the dimer are oxidized to π -radical cations.⁵

In the case of the oxidation of trimer **ZnP3** and tetramer **ZnP4**, overall feature of the spectral changes is similar to that of the **ZnP2** but the intermediate species is complicated. When one of the plural porphyrin rings is oxidized to π -radical cation in the porphyrin arrays, different absorption change depending on the oxidation site should be taken into account. If the edge porphyrin ring is oxidized in trimer **ZnP3** and tetramer **ZnP4**, there may be still oligomeric neutral porphyrin moiety in the arrays. Furthermore, oxidation of one of the central porphyrin moiety of tetramer **ZnP4** should divide the array to a single unit and a dimeric neutral unit separated by a π -radical cation unit. At the earlier stage of the oxidation of trimer **ZnP3** and tetramer **ZnP4**, decrease of the longer wavelength Soret-band absorption peak was observed, and the blue-shift of the decreased peak was observed because of the generation of the above mentioned oligomeric neutral unit. Further oxidation caused the decrease of the shorter wavelength Soret-band absorption peak and the increase of the absorption around 650 nm. At this stage, multiple porphyrin units are oxidized to π -radical cations.

3.2 Magnetic behavior of bis(π -radical cation) of dimer⁵

At the earlier stage of the oxidation of dimer **ZnP2**, the ESR spectrum of the oxidized species was observed as a single peak at 10 K, indicating the generation of mono(π -radical cation) **ZnP2^{•+}**. At room temperature, the ESR signal showed a hyperfine-splitting structure due to four equivalent nitrogen atoms. The hyperfine coupling constant and g value ($a_N = 1.57$ G, $g = 2.0037$)

are almost the same as those of the π -radical cation of the corresponding monomer Zn(II) tetrakis(3,5-di-*tert*-butylphenyl)porphyrin ($a_N = 1.51$ G, $g = 2.0031$). These results suggest that the π -radical remains on the single porphyrin ring and hardly penetrates the adjacent porphyrin ring because of the small overlap integral between the orthogonal π -systems.

An additional treatment of the solution of the mono(π -radical cation) of dimer **ZnP2** with NaAuCl₄ caused a spectral change in low temperature ESR. Along with the decreased central monoradical signal, a set of fine-structured signals due to a triplet diradical were observed. Half-field forbidden transition ($\Delta m_s = \pm 2$) signal was also observed at $g = 4.003$. The zero-field-splitting parameters at 110 K were determined to be $|D| = 1.19 \times 10^{-2}$ cm⁻¹ and $|E| = 3.0 \times 10^{-4}$ cm⁻¹, respectively. Although these values slightly deviated with a change of temperature, the spectral line shape was qualitatively kept. The large D value indicates that each component of the diradical resides nearby, and the small E value is due to an axis symmetry. On the basis of the point dipole approximation, the D value is translated as two spins with *ca.* 6.0 Å distance. The distance calculated from the ESR D value is shorter than the center-to-center distance of two porphyrins (8.4 Å). Such tendency may be derived from the contribution of spin density at the *meso*-positions of the nearest neighbor.

3.3 Oxidized species of trimer and tetramer

At the first stage of the oxidation of trimer **ZnP3**, a sharp singlet ESR spectrum was observed at 170 K. This signal corresponds to monoradical species. There are two possible assignments for this monoradical species as shown in Fig.2, *i.e.*, the π -radical cation of the central porphyrin or that of the end porphyrin. Along with the progress of oxidation, the signal showed line broadening from $\Delta H_{p-p} = 9.6$ G to $\Delta H_{p-p} = 10.5$ G, which indicates the appearance of new signals just outer sides of the original one. The fact is interpreted as the generation of triplet diradical species with a remote distance. If two π -radical cations are generated on the porphyrins at the both end of trimer **ZnP3**, the center-to-center distance is longer than 16 Å. Dipole interaction between two radical sites should be very small, but not zero. After further oxidation, distinct two sets of multiplet signals were detected. At this stage, it is preferable to attribute them to a quartet tris(π -radical cation) and a neighboring triplet bis(π -radical cation) as shown in Fig.2. Since the spin distribution of the neighboring bis(π -radical cation) of trimer **ZnP3** is similar to that of bis(π -radical cation) of dimer **ZnP2**, the inner signals were assigned to the neighboring bis(π -radical cation) on the basis of the spectral similarity. The remaining outer signals were assigned to tris(π -radical cation) of trimer **ZnP3**. The splitting width between the most outer signal and the central signal is 166 G, which corresponds to twice of zero-field-splitting parameter ($2D$). The value is larger than one half of the splitting width between two outer signals of the neighboring bis(π -radical cation) of trimer **ZnP3** (240 G) or that of bis(π -radical cation) of dimer **ZnP2** (256 G). The reason for such tendency may be

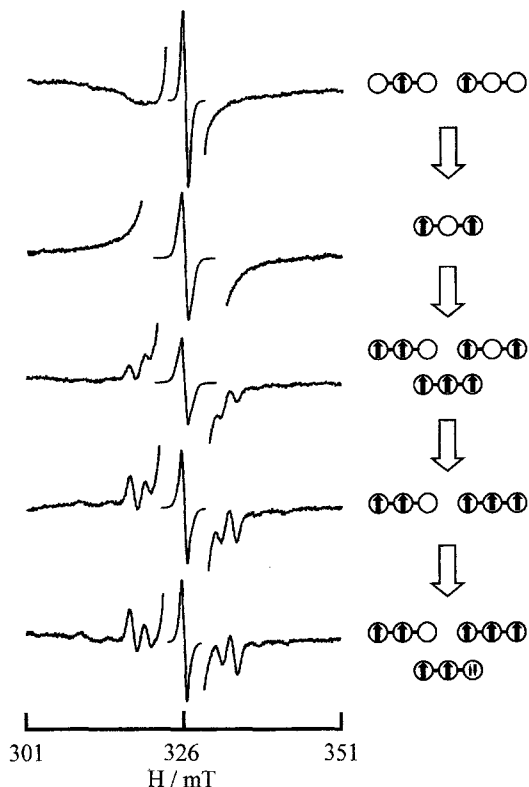


Fig.2 ESR spectral change due to the progress of oxidation stage of trimer **ZnP3** with NaAuCl₄ in chloroform at room temperature. The spectra were recorded at 170 K. The schematic drawings at the right side indicate plausible distribution patterns of π -radicals.

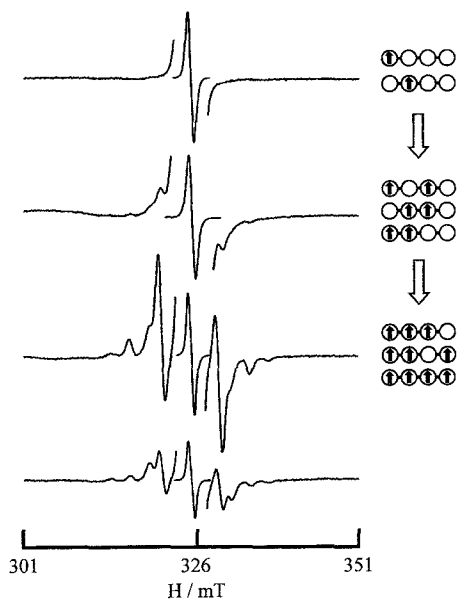


Fig.3 ESR spectral changes due to the progress of oxidation stage of tetramer **ZnP4** with NaAuCl₄ in chloroform at room temperature. The spectra were recorded at 170 K. The schematic drawings at the right side indicate plausible distribution patterns of π -radicals.

also derived from the contribution of spin density at the meso-positions of the nearest neighbor, as seen in dimer. When the oxidation was far progressed, decrease of multiplet signals was observed because of the generation of closed-shell dicationic porphyrin sites.

Similar ESR spectral changes were observed for tetramer **ZnP4** (Fig.3). At the first stage of the oxidation, a sharp singlet spectrum due to mono(π -radical cation) was observed at 170 K. After further oxidation, slightly broadened central singlet signal and a set of multiplet signals were detected. These signals correspond to remote or neighboring bis(π -radical cation) in triplet state, respectively. The nature of these species is similar to bis(π -radical cation) of trimer **ZnP3**. The multiplet signals increased along with the progress of oxidation. At this stage, existence of tetrakis(π -radical cation), neighboring tris(π -radical cation), and remote tris(π -radical cation) is expected as shown in Fig.3. In fact, the major multiplet signals are best rationalized with a quintet axis-symmetrical tetradical model.

Temperature dependence of signal intensity of these multiplet species has a complicated feature since some different states are included in one spectrum. Temperature dependence of signal intensity at earlier oxidation stage was also investigated, and some signals were proved to have different feature in comparison with the highly oxidized state.

4. CONCLUSION

A series of directly meso-linked Zn(II)porphyrin arrays were prepared, and oxidized with NaAuCl₄ in chloroform to afford high spin poly(π -radical cation)s. On the basis of visible absorption spectral change and ESR spectroscopy, the porphyrin arrays are proved to be oxidized stepwise, generating π -radicals on each porphyrin ring. Oxidation of tetramer **ZnP4** afforded quintet tetrakis(π -radical cation). The fact indicates that exchange interaction between adjacent π -radicals is transmitted for longer distances. Extension of this system to longer oligomers is expected to realize much higher spin states.

5. ACKNOWLEDGEMENT

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