

Metal Bisporphyrinate Double-Decker Complexes as Redox-Responsive Rotating Modules. Studies on Ligand Rotation Activities of the Reduced and Oxidized Forms Using Chirality as a Probe

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Abstract: Reduction of a chiral cerium bisporphyrinate double-decker complex Ce(MOFPP)₂ (MOFPP = 5,15-bis(3,5-dimethoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin dianion) with sodium anthracenide in dioxane at 20 °C resulted in acceleration of the porphyrin ligand rotation (= racemization) by a factor of more than 300. Photoreduction of Ce(MOFPP)₂ in dioxane also resulted in enhancing the ligand rotation activity of the complex. On the other hand, oxidation of a chiral zirconium complex Zr(DTP)₂ (DTP = 5,15-ditylporphyrin dianion) with phenoxathiinium hexachloroantimonate (Phen⁺SbCl₆⁻) or FeCl₃ resulted in deceleration of the acid-induced racemization in tetrahydrofuran (THF), where monocationic and dicationic forms of the complex racemized 21 and 99 times more slowly than the neutral complex, respectively.

Introduction

Molecular and supramolecular modules which perform restricted motions such as shuttling (linear motion) and rotation (circular motion) have attracted attention in view of the design of molecular machines, devices, and recognition systems.^{1,2} In particular, π -electronic systems whose dynamics can be switched in response to external electro- and photochemical stimuli have become of great interest.³ In the present paper, we wish to report that metal bisporphyrinate double-decker complexes serve as novel stimuli-responsive rotating modules, in which the rotation activity of the porphyrin ligands around the metal center can be switched by redox reactions.

Metal bisporphyrinate double-decker complexes have attracted attention as model compounds of the special pair in the photosynthetic reaction center.⁴ In relation to a possible π -electronic interaction between the two facing porphyrin rings, the ligand rotation activities of the double-decker complexes are interesting. As for zirconium and cerium complexes, variable-temperature ¹H NMR (VT-NMR) studies have been conducted, in which no rotation of the porphyrin ligands has been concluded.^{5,6} On the other hand, we have reinvestigated the ligand rotation activities of some double-decker complexes

using chirality as a probe.⁷ Double-decker bisporphyrinate complexes of cerium⁸ and zirconium^{9,10} take a square antiprismatic coordination geometry and should be chiral with a symmetry group D_2 when the porphyrin ligands are of D_{2h} symmetry.¹¹ In fact, we have succeeded in optical resolution of some D_2 -chiral bisporphyrinate complexes of cerium and zirconium by chiral HPLC. In such D_2 -chiral complexes, the ligand rotation corresponds to racemization (Figure 1). Therefore, the optical activity of the enantiomers can be used as a probe for investigating the rotation dynamics of the porphyrin ligands around the metal center. From the circular dichroism (CD) spectral studies we have found that, in the double-decker complexes of cerium, it is easy to rotate their porphyrin ligands, whereas such a thermal-induced ligand rotation hardly occurs in zirconium complexes.

In the bisporphyrinate double-decker complexes, the π -electronic interaction between the porphyrin ligands and, therefore, their rotation activities should depend on the redox states. In the present paper, we report results of studies on the ligand rotation activities of the reduced and oxidized forms of some D_2 -chiral cerium and zirconium bisporphyrinate double-decker complexes. Here, the method utilizing optical activity as a probe

(1) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995; Chapter 8. (b) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611.

(2) (a) Anelli, P. L.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 5131. (b) Medina, J. C.; Li, C.; Bott, S. G.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 366.

(3) (a) Bissell, R. A.; Códova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133. (b) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N. *J. Am. Chem. Soc.* **1997**, *119*, 7605.

(4) Buchler, J. W.; Ng, D. K. P. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol. 3, Chapter 20.

(5) Girolami, G. S.; Gorlin, P. A.; Suslick, K. S. *Inorg. Chem.* **1994**, *33*, 626.

(6) (a) Buchler, J. W.; Eiermann, V.; Hanssum, H.; Heinz, G.; Rüterjans, H.; Schwartzkopf, M. *Chem. Ber.* **1994**, *127*, 589. (b) Buchler, J. W.; Heinz, G. *Chem. Ber.* **1996**, *129*, 201.

(7) (a) Tashiro, K.; Konishi, K.; Aida, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 856. (b) Tashiro, K.; Fujiwara, T.; Konishi, K.; Aida, T. *Chem. Commun.* **1998**, 1121.

(8) (a) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.* **1986**, *108*, 3652. (b) Buchler, J. W.; De Cian, A.; Fischer, J.; Hammerschmitt, P.; Löffler, J.; Scharbert, B.; Weiss, R. *Chem. Ber.* **1989**, *122*, 2219.

(9) Kim, K.; Lee, W. S.; Kim, H.-J.; Cho, S.-H.; Girolami, G. S.; Gorlin, P. A.; Suslick, K. S. *Inorg. Chem.* **1991**, *30*, 2652.

(10) (a) Buchler, J. W.; De Cian, A.; Fischer, J.; Hammerschmitt, P.; Weiss, R. *Chem. Ber.* **1991**, *124*, 1051. (b) Buchler, J. W.; De Cian, A.; Elshner, S.; Fischer, J.; Hammerschmitt, P.; Weiss, R. *Chem. Ber.* **1992**, *125*, 107.

(11) Shinkai et al. have utilized D_2 -chiral cerium bisporphyrinate complexes for chirality sensors: Sugasaki, A.; Ikeda, M.; Takeuchi, M.; Robertson, A.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3259.

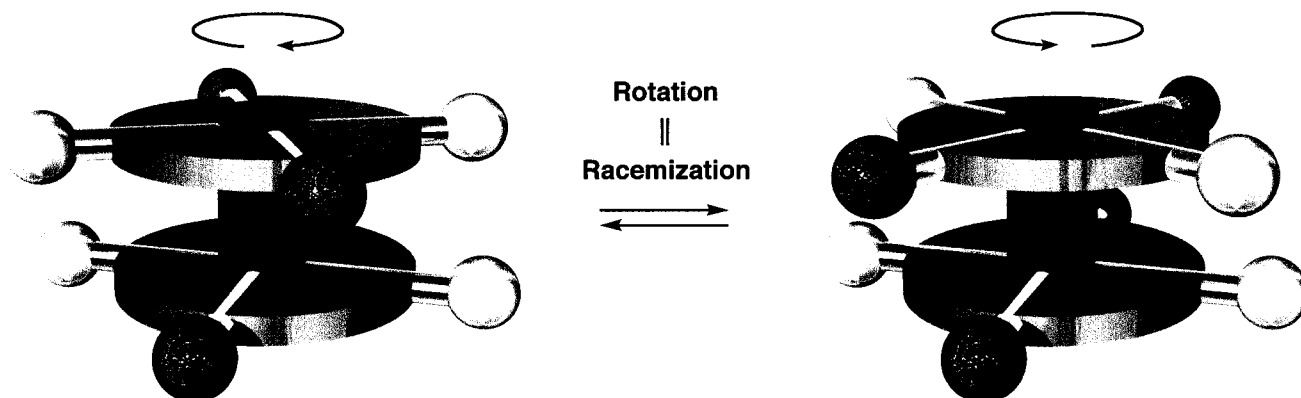
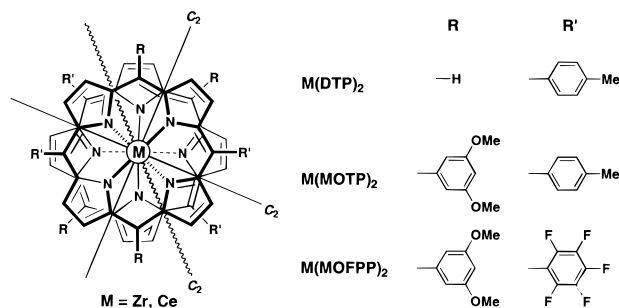


Figure 1. Schematic representation of a D_2 -chiral metal bisporphyrinate double-decker complex and its racemization by rotation of the porphyrin ligands.

is particularly advantageous, since the reduced and oxidized forms of these double-decker complexes are paramagnetic, thereby limiting application of the conventional VT-NMR technique to the investigation on the ligand rotation dynamics.

Results

Synthesis and Redox Properties of Chiral Bisporphyrinate Double-Decker Complexes. Chiral bisporphyrinate double-decker complexes of cerium [Ce(MOTP)₂,¹² Ce(DTP)₂, Ce(MOFPP)₂]



and zirconium [Zr(DTP)₂] were synthesized by the reaction of the corresponding free base or lithiated porphyrins with Ce(acac)₃ and Cp₂ZrCl₂, respectively,^{8,10} and their redox properties were investigated by means of cyclic voltammetry. Similar to reported examples of cerium bisporphyrinate complexes,^{8b} Ce(MOTP)₂ and Ce(MOFPP)₂ underwent a one-step reduction at the metal center (Ce^{IV}P₂ → [Ce^{III}P₂]⁻) and a stepwise two-electron oxidation at the porphyrin ligands (Ce^{IV}P₂ → [Ce^{IV}P₂]⁺ → [Ce^{IV}P₂]²⁺). Ce(MOFPP)₂ exhibited a reduction peak at -0.44 V and oxidation peaks at 0.49 and 0.85 V (versus Fc/Fc⁺), both of which are 0.24–0.30 V more positive than the redox potentials of Ce(MOTP)₂ (-0.74 V for reduction and 0.22 and 0.61 V for oxidation). This is probably due to the electron-withdrawing character of the *meso*-pentafluorophenyl groups of the porphyrin ligands. On the other hand, Ce(DTP)₂ was oxidized at lower potentials (0.14 and 0.53 V) than Ce(MOTP)₂. As for the zirconium complex Zr(DTP)₂, a two-electron oxidation at the porphyrin ligands (Zr^{IV}P₂ → [Zr^{IV}P₂]⁺ → [Zr^{IV}P₂]²⁺) also occurred in a stepwise fashion,¹⁰ where the oxidation potentials (0.00 and 0.43 V) are lower than those of Ce(DTP)₂, indicating that the zirconium complex is more subject to oxidation than the cerium complex.

(12) MOTP = 5,15-bis(3,5-dimethoxyphenyl)-10,20-ditolylporphyrin dianion.

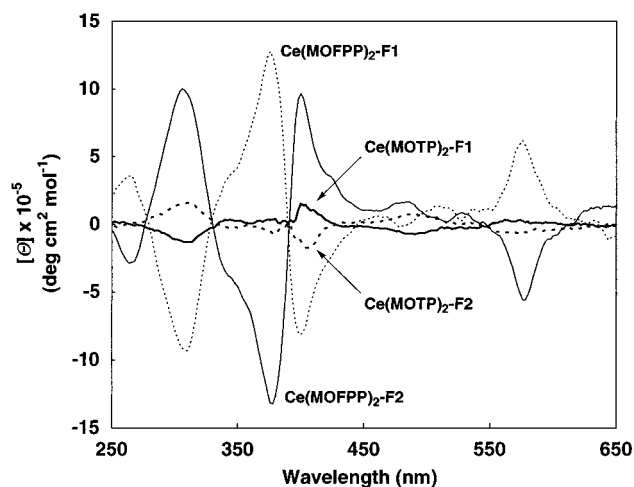


Figure 2. Circular dichroism (CD) spectra of the enantiomers of Ce(MOFPP)₂ in dioxane and Ce(MOTP)₂ in THF at 20 °C. F1 and F2 represent the first and second fractions in chiral HPLC, respectively.

Racemization of Neutral Forms of Chiral Double-Decker Complexes. Zr(DTP)₂, Ce(MOTP)₂, and Ce(MOFPP)₂ were obtained in enantiomerically pure forms by chiral HPLC. For example, HPLC of Ce(MOFPP)₂ on SUMICHIRAL OA-2000 with hexane/CHCl₃ (50/50) as the eluent showed two peaks at 4.54 and 4.72 min with comparable areas. The fractions corresponding to these two peaks displayed perfect mirror-image circular dichroism (CD) spectra of each other at the Soret (350–400 nm) and Q (550–600 nm) bands (Figure 2). Interestingly, the intensities of the CD bands of Ce(MOFPP)₂ were almost one order of magnitude larger than those of Ce(MOTP)₂, bearing two tolyl groups in place of pentafluorophenyl groups. On the other hand, optical resolution of Ce(DTP)₂ by chiral HPLC was not successful, because of a rapid thermal-induced ligand rotation (racemization) during the HPLC process.

As already reported in a previous paper,^{7a} the enantiomers of the zirconium complex Zr(DTP)₂ are highly robust toward thermal-induced racemization in benzene, toluene, and THF. For example, no decrease in intensities of the CD bands was observed, even when the complex was heated in refluxing toluene for 2 h. On the other hand, the enantiomers of Ce(MOTP)₂ and Ce(MOFPP)₂ were both racemized even at 10 °C, indicating their high susceptibility toward the thermal-induced ligand rotation. However, it is also interesting to note that the latter complex carrying π -acidic and π -basic *meso*-aryl groups in benzene at 50 °C racemized with a first-order rate constant of $2.7 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$, which is 1.8-times smaller than that of Ce(MOTP)₂ ($4.7 \pm 0.2 \times 10^{-4} \text{ s}^{-1}$) under the same

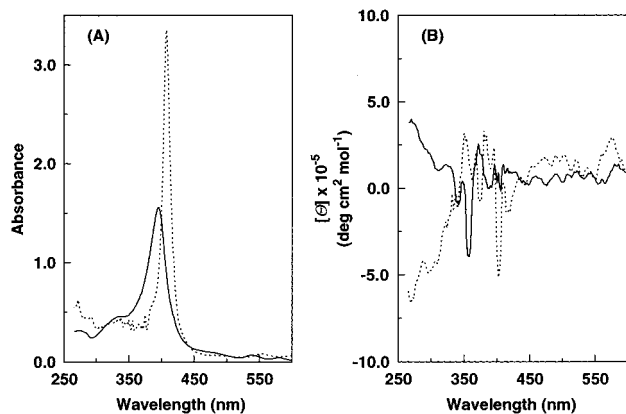


Figure 3. (A) Absorption spectra of Ce(MOFPP)₂ before (solid line) and after (broken line) the reaction with sodium anthracenide (absorption bands of anthracene [product] were subtracted). (B) CD spectra of the reduced forms of Ce(MOFPP)₂-F1 (broken line) and -F2 (solid line).

conditions. Accordingly, the ΔG^\ddagger value of the ligand rotation in Ce(MOFPP)₂ (24.2 ± 0.1 kcal mol⁻¹ at 50 °C)¹³ was slightly but definitely larger than that in Ce(MOTP)₂ (23.9 ± 0.1 kcal mol⁻¹).^{7a}

Racemization of Reduced Forms of Chiral Double-Decker Complexes. As already described, cerium(IV) double-decker complexes undergo a one-electron reduction at the metal center to give the corresponding cerium(III) complexes. Here, the effect of reduction on the ligand rotation activity was investigated for Ce(MOFPP)₂, since the enantiomers of this complex show highly enhanced CD bands (Figure 2). For chemical reduction of Ce(MOFPP)₂, sodium anthracenide was used as a reducing agent. For example, when a dioxane solution (1.0×10^{-5} M) of enantiomerically pure Ce(MOFPP)₂ was mixed with a THF solution of sodium anthracenide (30 equiv) at 20 °C, the Soret absorption band shifted from 396 to 408 nm to give a spectrum (Figure 3A) which is typical of double-decker bisporphyrinate complexes of trivalent lanthanides.¹⁴ On the other hand, the strong CD bands characteristic of Ce(MOFPP)₂ in the neutral form entirely diminished, while a new CD band centered at 270 nm appeared (Figure 3B). However, this band also disappeared completely within 30 min at 20 °C. The CD intensity change at 270 nm provided a rate constant of the ligand rotation of $8.6 \pm 1.6 \times 10^{-4}$ s⁻¹, which is more than 300-times larger than that of the neutral complex under similar conditions ($2.5 \pm 0.6 \times 10^{-6}$ s⁻¹). Thus, the ligand rotation activity of the cerium bisporphyrinate double-decker complex can be greatly enhanced by the chemical reduction at the metal center.

We also observed a similar acceleration of the ligand rotation upon photoreduction of Ce(MOFPP)₂. For example, when a wet dioxane solution (1% water) of Ce(MOFPP)₂ (1.0×10^{-5} M) at 20 °C was irradiated with a visible light at 390 ± 10 nm, the Soret absorption band of the complex at 396 nm gradually decreased in intensity, while a new absorption band at 414 nm, due to the cerium(III) bisporphyrinate complex, appeared with an isosbestic point at 403 nm and became predominant with irradiation time.¹⁵ Since the photoreduction was accelerated upon an increase in water content in the medium,¹⁶ hydroxy anion

(13) Determined from the rate constants at 10 ($k = 1.5 \pm 0.0 \times 10^{-5}$ s⁻¹), 35 ($k = 7.6 \pm 0.2 \times 10^{-5}$ s⁻¹), and 50 °C. Thermal activation parameters: $\Delta H^\ddagger = 18.0 \pm 0.7$ kcal mol⁻¹, $\Delta S^\ddagger = -19.2 \pm 2.4$ cal K⁻¹ mol⁻¹.

(14) (a) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 339. (b) Buchler, J. W.; Nawra, M. *Inorg. Chem.* **1994**, *33*, 2830. (c) Spyroulias, G. A.; Coutsolelos, A. G.; Raptopoulou, C. P.; Terzis, A. *Inorg. Chem.* **1995**, *34*, 2476.

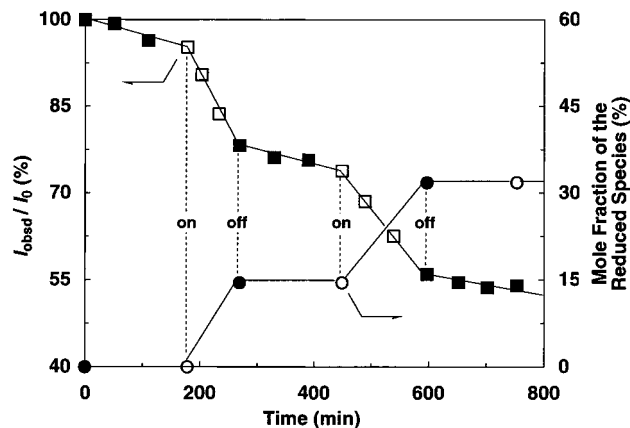


Figure 4. Irradiation of Ce(MOFPP)₂ (1.0×10^{-5} M) with visible light (360–750 nm) in dioxane at 20 °C under Ar. Changes in relative CD intensity [I_{obsd}/I_0] (■ and □) and mole fraction of the reduced species (● and ○, as determined from the absorbance at 396 nm) under light on/off conditions. I represents $| \Theta_{376} - \Theta_{400} |$.

most likely serves as an electron donor. Accordingly, an EPR spectroscopy after photoirradiation of a dioxane solution of a mixture of Ce(MOFPP)₂ and *N-tert-butyl- α -phenylnitron* (PBN) showed the presence of a hydroxy radical trapped by PBN.¹⁷ A lights on/off experiment with enantiomerically pure Ce(MOFPP)₂ indicated that photoreduction of the complex takes place only under irradiation (Figure 4, ○). Furthermore, the CD spectral change of the reaction mixture showed that the enantiomeric purity of Ce(MOFPP)₂ drops off progressively when the light is on (Figure 4, □). Since the racemization and photoreduction profiles appear to coincide with each other, it is again concluded that the reduced form of the cerium bisporphyrinate double-decker complex has an enhanced activity for the porphyrin ligand rotation.

Racemization of Oxidized Forms of Chiral Double-Decker Complexes. As already described, cerium and zirconium bisporphyrinate complexes both undergo a stepwise two-electron oxidation at the porphyrin ligands. To explore the ligand rotation activities of the oxidized complexes, we first investigated the CD spectral change profile of enantiomerically pure Ce(MOFPP)₂ upon oxidation with phenoxathiinium hexachloroantimonate (Phen⁺SbCl₆⁻).¹⁸ However, the complex was found to racemize instantaneously upon mixing with this oxidant. We later found that this is partly due to a very high susceptibility of cerium bisporphyrinates toward acidic impurities of the oxidants. Furthermore, the oxidized form of Ce(MOFPP)₂¹⁹ was labile under the experimental conditions and spontaneously reverted to the neutral form within 1 h at 20 °C. In contrast, the zirconium complex Zr(DTP)₂ was found to behave much better under such oxidation conditions. Thus, Zr(DTP)₂ was successfully converted into the corresponding monocation radical ([Zr(DTP)₂]^{•+}) or dication ([Zr(DTP)₂]²⁺) without racemization. For example, when enantiomerically pure

(15) Photochemical reduction of a cerium double-decker complex with triethylamine as an electron donor has been reported: Radzki, S.; Giannotti, C. *J. Chem. Soc., Dalton Trans.* **1993**, 675.

(16) Quantum yields of the reduction upon selective excitation at 390 ± 10 nm were 1.9×10^{-2} and 3.2×10^{-3} in dioxane/water (99/1 v/v) and dioxane, respectively.

(17) The hyperfine splitting constants, a^N and a^H , of the spin adduct were 13.6 and 2.0 G, respectively, which are identical to those of an authentic sample: Bösterling, B.; Trudell, J. R. *Biochem. Biophys. Res. Commun.* **1981**, *98*, 569; Trudell, J. R. *Free Radical Biol. Med.* **1987**, *3*, 133.

(18) Kadish, K. M.; Moninot, G.; Hu, Y.; Dubois, D.; Ibnlfassi, A.; Barbe, J.-M.; Guillard, R. *J. Am. Chem. Soc.* **1993**, *115*, 8153.

(19) Donohoe, R. J.; Duchowski, J. K.; Bocian, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 6119.

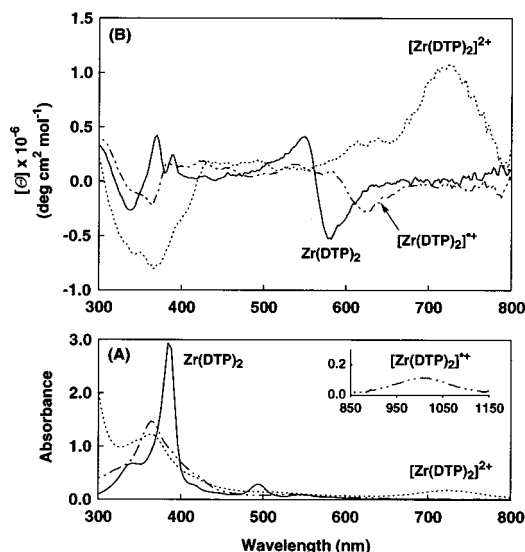


Figure 5. Absorption (A) and circular dichroism (B) spectra of an enantiomer (the first fraction in chiral HPLC) of $\text{Zr}(\text{DTP})_2$, $[\text{Zr}(\text{DTP})_2]^{\bullet+}$, and $[\text{Zr}(\text{DTP})_2]^{2+}$ in THF at 20 °C.

$\text{Zr}(\text{DTP})_2$ (the first fraction in chiral HPLC) was mixed with $\text{Phen}^+\text{SbCl}_6^-$ (1.2 equiv) in CH_2Cl_2 , the Soret absorption band at 385.5 nm disappeared, while a new absorption band at 365.0 nm appeared (Figure 5A) together with a broad near-IR band at 1001 nm (inset). Such a spectral profile is typical of zirconium bisporphyrinate monocation radicals.⁴ Use of a large excess (15 equiv) of $\text{Phen}^+\text{SbCl}_6^-$ for the oxidation resulted in the formation of a dicationic form of the complex $[\text{Zr}(\text{DTP})_2]^{2+}$, in which a significant broadening of the visible absorption bands was observed, together with a blue shift of the near-IR band from 1001 to 722 nm.⁴ FeCl_3 was also usable as the oxidant, which gave a monocation radical $[\text{Zr}(\text{DTP})_2]^{\bullet+}$ selectively, even though it was used in large excess. Figure 5B shows CD spectra of $[\text{Zr}(\text{DTP})_2]^{\bullet+}$ and $[\text{Zr}(\text{DTP})_2]^{2+}$ together with that of the neutral form of $\text{Zr}(\text{DTP})_2$ in THF. $\text{Zr}(\text{DTP})_2$ displayed a split CD band at the Q-band region, whereas $[\text{Zr}(\text{DTP})_2]^{\bullet+}$ showed a monosigned negative CD band. On the other hand, $[\text{Zr}(\text{DTP})_2]^{2+}$ exhibited an essentially different CD spectrum, in which a highly enhanced, positive monosigned CD band was observed at the near-IR region (720 nm). Upon addition of triethylamine (4000 equiv), these oxidized species were reduced to their neutral forms, where the CD spectra in both cases reverted to that of the enantiomerically pure $\text{Zr}(\text{DTP})_2$. This observation indicates no racemization during the oxidation and also subsequent reduction. The oxidized forms of the enantiomers of $\text{Zr}(\text{DTP})_2$ were robust toward spontaneous reduction and thermal racemization, and lasted for a long period of time in THF at room temperature, so long as they were stored under Ar in the dark.

As reported previously, the enantiomer of $\text{Zr}(\text{DTP})_2$, although robust toward thermal-induced ligand rotation, undergoes an H^+ -induced racemization in the presence of a protonic acid, such as *p*-toluenesulfonic acid (*p*-TsOH).^{7a} We found that such an acid-induced racemization of $\text{Zr}(\text{DTP})_2$ is remarkably decelerated upon oxidation. At 25 °C in THF containing *p*-TsOH (100 μM), a monocation radical $[\text{Zr}(\text{DTP})_2]^{\bullet+}$ (6.0 μM), generated by oxidation of $\text{Zr}(\text{DTP})_2$ with FeCl_3 , racemized sluggishly (Figure 6, ●), whereas the neutral form racemized with a decrease in enantiomeric excess from 100 to 51 and 24% in 40 and 90 min, respectively (○). The rate constant of racemization of $[\text{Zr}(\text{DTP})_2]^{\bullet+}$ was evaluated to be $5.6 \pm 0.5 \times 10^{-6} \text{ s}^{-1}$, which is 21-times smaller than that of the neutral form ($1.2 \pm$

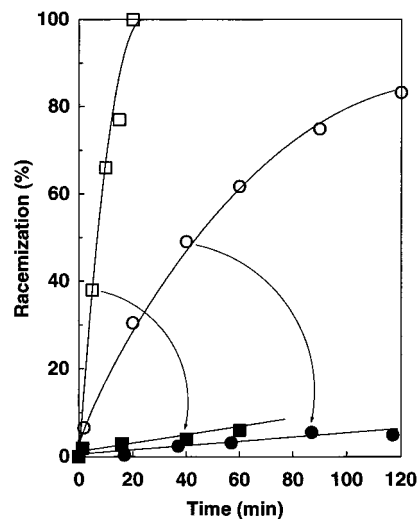


Figure 6. Racemization profiles at 20 °C of $\text{Zr}(\text{DTP})_2$ (○) and $[\text{Zr}(\text{DTP})_2]^{\bullet+}$ (●) in THF (6.0 μM each) containing *p*-TsOH (100 μM), and those of $\text{Zr}(\text{DTP})_2$ (□) and $[\text{Zr}(\text{DTP})_2]^{2+}$ (■) in THF (6.0 μM each) containing *p*-TsOH (900 μM). Racemization of the neutral form was investigated in the presence of hydroquinone ($4.5 \times 10^{-2} \text{ M}$) to prevent acid-driven oxidation of the complex (ref 7a).

$0.0 \times 10^{-4} \text{ s}^{-1}$) under the same conditions. On the other hand, the dicationic form ($[\text{Zr}(\text{DTP})_2]^{2+}$) appeared to be more robust toward the H^+ -induced racemization. Even in the presence of a larger excess amount of *p*-TsOH (900 μM), the racemization of $[\text{Zr}(\text{DTP})_2]^{2+}$ (Figure 6, ■) in THF at 25 °C took place only very slowly, where the rate constant was almost two orders of magnitude smaller ($8.5 \pm 1.1 \times 10^{-6} \text{ s}^{-1}$) than that of the neutral form ($8.4 \pm 0.5 \times 10^{-4} \text{ s}^{-1}$, □) under identical conditions.

Discussion

The redox-responsive switching of the ligand rotation activity, as observed for the cerium and zirconium double-decker bisporphyrinate complexes, is considered to reflect the π -electronic interaction between the two facing porphyrin ligands. As described in previous⁷ papers and also in the present paper, cerium(IV) bisporphyrinate complexes are much more subject than zirconium(IV) complexes to ligand rotation. This is most likely due to the larger ionic radius of Ce^{4+} [0.97 Å]²⁰ (longer porphyrin-to-porphyrin distance)^{8–10} than that of Zr^{4+} [0.84 Å].²⁰ The same may hold true for the enhanced ligand rotation activity of the reduced forms of the cerium complexes, where the π -electronic interaction between the porphyrin ligands is considered much weaker than that of the neutral complexes, due to the larger ionic radius of Ce^{3+} [1.14 Å]²⁰ compared to Ce^{4+} .

As for the zirconium bisporphyrinate complexes of different oxidation states, the ligand rotation activities in the presence of *p*-TsOH appear to be in the following order: neutral form ($\text{Zr}(\text{DTP})_2$) > monocation radical ($[\text{Zr}(\text{DTP})_2]^{\bullet+}$) > dicationic form ($[\text{Zr}(\text{DTP})_2]^{2+}$) (Figure 6). In relation to this trend, X-ray crystal structures of zirconium bis(tetraphenylporphyrinate) complexes⁹ and their oxidized forms have been reported, where the porphyrin-to-porphyrin distance becomes shorter as the oxidation number is increased.²¹ For the significant decrease in ligand rotation activities of the oxidized forms ($[\text{Zr}(\text{DTP})_2]^{\bullet+}$, $[\text{Zr}(\text{DTP})_2]^{2+}$), a possible enhancement of the π -electronic interaction between the porphyrin ligands upon oxidation is

(20) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

(21) Kim, H.-J.; Whang, D.; Kim, J.; Kim, K. *Inorg. Chem.* **1992**, 31, 3882.

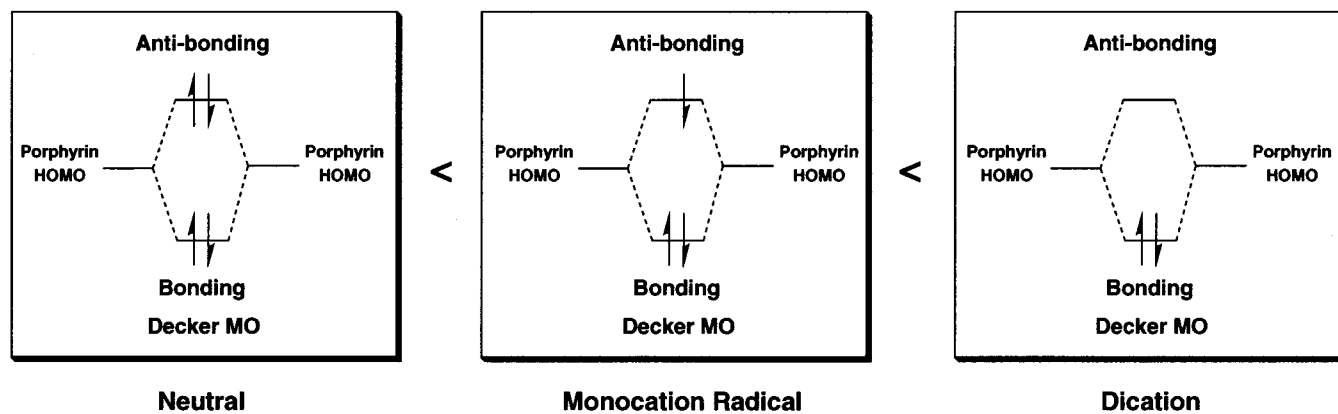


Figure 7. Order of π -electronic interaction force, as expected from simple molecular orbital diagrams for neutral and oxidized forms of metal bisporphyrinates.

considered likely in addition to an expected electrostatic repulsion of these oxidized species with H^+ . Figure 7 shows simplified molecular orbital diagrams for neutral and oxidized forms of double-decker bisporphyrinate complexes.²² In the neutral form, the antibonding orbital is filled with two electrons. On the other hand, when the porphyrin ligands are oxidized, the number of electrons in the antibonding orbital should be decreased, thereby enhancing the bonding character of the π -electronic interaction. On the other hand, the near-IR absorption bands of the oxidized forms of metal bisporphyrinate complexes are informative for the energy gap between the bonding and antibonding orbitals, since the absorption has been assigned to the electronic transition between these two orbitals. $[Zr(DTP)_2]^{*+}$ and $[Zr(DTP)_2]^{2+}$ show the corresponding absorption bands at 1001 and 722 nm, respectively (Figure 5A). Thus, the blue shift (279 nm) of the absorption band, upon oxidation of $[Zr(DTP)_2]^{*+}$ to $[Zr(DTP)_2]^{2+}$, indicates an increased energy gap between these two orbitals.²¹

Conclusion

By using optical activity as a probe, we have demonstrated that the ligand rotation activities of metal bisporphyrinate double-decker complexes can be switched by redox reactions, where reduction of the metal center enhances the rotation activity of the porphyrin ligands, while oxidation at the porphyrin ligands retards the H^+ -induced ligand rotation. The variable-temperature 1H NMR technique, which has been utilized for investigating the ligand rotation dynamics of metal bisporphyrinate complexes, is hardly applicable to the present systems involving paramagnetic species. Therefore, the strategy with D_2 -chiral metal bisporphyrinate complexes is a smart approach, which is applicable not only to dynamic processes slower than the NMR time scale but also to those involving paramagnetic complexes. Finally, molecular devices composed of π -electronic systems have attracted attention, since their dynamics may be controlled by charge transfer or chemical and photochemical electron-transfer reactions. In this sense, the redox-responsive ligand rotation characteristics of the bisporphyrinate double-decker complexes indicate a new potential of these π -electronic systems for the design of molecular machines and devices.

Experimental Section

Materials. Benzene, dioxane, and THF were distilled over sodium benzophenone ketyl under Ar or N_2 . CH_2Cl_2 and 1,2,4-trichlorobenzene (TCB) were distilled over CaH_2 . Tetrabutylammonium hexafluoro-

phosphate (Bu_4NPF_6) was recrystallized twice from ethanol and dried under vacuum overnight. $Ce(DTP)_2$, $Ce(MOTP)_2$, and $Zr(DTP)_2$ were prepared in manners similar to those reported previously.⁷ Phenoxathiinium hexachloroantimonate ($Phen^{*+}SbCl_6^-$) was prepared from phenoxathiin and pentachloroantimony.¹⁸

5,15-Bis(3,5-dimethoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrine (MOFPPH₂). To a 3.2 L round-bottomed flask containing a $CHCl_3$ (3 L) solution of a mixture of pentafluorobenzaldehyde (1.8 mL, 15 mmol), 3,5-dimethoxybenzaldehyde (2.52 g, 15 mmol), and pyrrole (2.1 mL, 30 mmol) was added BF_3 etherate (1.2 mL, 10 mmol) at room temperature under Ar. After the mixture was stirred overnight, *p*-chloranil (5.5 g, 22.5 mmol) was added, and the mixture was stirred for an additional 2 h at room temperature.²³ Then, the resulting black solution was loaded on an alumina column (Merck Art. 1097) and eluted with $CHCl_3$ to allow isolation of a reddish-purple porphyrin fraction. This fraction was further subjected to flash column chromatography on silica gel (Merck Art. 7736), where fractions corresponding to six possible porphyrins were eluted separately with $CHCl_3$ /hexane (2/1). According to FAB-MS and NMR profiles of these fractions, the third fraction was found to contain the desired porphyrin. Recrystallization of this fraction from $CHCl_3$ /MeOH gave MOFPPH₂ as purple crystals (260 mg, 3.8%), R_f 0.4 ($CHCl_3$). 1H NMR ($CDCl_3$): δ 9.04 and 8.78 (d \times 2, 8H, $J = 4.9$ Hz, pyrrole- β), 7.39 (d, 4H, $J = 2.4$ Hz, *o*-H in $C_6H_3(OMe)_2$), 6.92 (t, 2H, $J = 2.4$ Hz, *p*-H in $C_6H_3(OMe)_2$), 3.96 (s, 12H, OCH₃), -2.87 (s, 2H, NH). FAB-HRMS: calcd for $C_{48}H_{29}F_{10}N_4O_4$ (MH^+) m/z 915.2029, obsd 915.2022. Anal. Calcd for $C_{48}H_{28}F_{10}N_4O_4 \cdot 0.5CHCl_3$: C, 59.78; H, 2.95; N, 5.75. Found: C, 60.52; H, 3.28; N, 5.78. UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 417 (5.57), 510.5 (4.32), 544 (3.69), 586 (3.80), 641 (3.48) nm.

Cerium Double-Decker Complex of 5,15-Bis(3,5-dimethoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrine ($Ce(MOFPP)_2$). To a TCB (10 mL) solution of MOFPPH₂ (130 mg, 0.14 mmol) was added a hexane solution (2.0 mL) of BuLi (3.4 mmol) under Ar, and the mixture was stirred for 15 min at room temperature to convert MOFPPH₂ into the corresponding lithiated complex. Then, $Ce(acac)_3 \cdot 3H_2O$ (240 mg, 0.50 mmol) was added, and the mixture was heated at 200 °C for 35 h. The reaction mixture was loaded onto an alumina column (Merck Art. 1097), and the second brown fraction eluted with CH_2Cl_2 was collected and evaporated to dryness. Recrystallization of the residue from $CHCl_3$ /hexane gave $Ce(MOFPP)_2$ as a brown powder (10 mg, 7.2%). 1H NMR ($DMSO-d_6$): δ 8.73 (s, 4H, *o*-endo-H in $C_6H_3(OMe)_2$), 8.50–8.28 (m, 16H, pyrrole- β), 6.98 (s, 4H, *p*-H in $C_6H_3(OMe)_2$), 5.61 (s, 4H, *o*-exo-H in $C_6H_3(OMe)_2$), 4.39 (s, 12H, endo-OCH₃), 3.55 (s, 12H, exo-OCH₃). FAB-HRMS: calcd for $C_{96}H_{53}CeF_{20}N_8O_8$ (MH^+) m/z 1965.2721, obsd 1965.2682. UV-vis ($CHCl_3$): λ_{max} (log ϵ) 398 (5.27), 540 (4.08), 581 (3.97) nm.

Optical Resolution by Chiral HPLC. Chiral HPLC was carried out on a JASCO-type 880-PU intelligent HPLC pump equipped with a JASCO-type 875-UV variable-wavelength detector at a flow rate of

(22) Duchowski, J. K.; Bocian, D. F. *J. Am. Chem. Soc.* **1990**, *112*, 3312.

(23) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

1.0 mL min⁻¹ at room temperature. A 4.6 × 250 mm chiral column (Chiralcel OD) was used for the optical resolution of Zr(DTP)₂, while Sumichiral OA 2000 was used for Ce(MOTP)₂ and Ce(MOFPP)₂. Typically, a CHCl₃/hexane (1/1) solution (40 μL) of racemic Ce-(MOFPP)₂ was loaded on the chiral column, and the eluates were collected into a flask wrapped with aluminum foil.

Racemization of Ce(MOFPP)₂ upon Reduction with Sodium Anthracenide. A THF solution (0.5 mL) of sodium anthracenide (2.4 × 10⁻³ M) was added to a quartz cell of 1 cm path length, fitted with a three-way stopcock, containing a dioxane solution (4 mL) of an enantiomer of Ce(MOFPP)₂ (1.0 × 10⁻⁵ M) under Ar, and the mixture was subjected to absorption and circular dichroism spectroscopies.

Racemization of Ce(MOFPP)₂ upon Photoreduction. To a 10 mL flask, fitted with a quartz cell of 1 cm path length and a three-way stopcock, was added a dioxane solution (4 mL) of an enantiomer of Ce(MOFPP)₂ (1.0 × 10⁻⁵ M) under Ar, and the mixture was exposed to a 300 W xenon arc light through a thermal-cut filter and a glass filter to remove light of wavelength shorter than 360 nm and longer than 750 nm. The reduction and racemization were followed by techniques of absorption and circular dichroism spectroscopies, respectively.

Acid-Induced Racemization of Zr(DTP)₂ upon Oxidation with Phen⁺SbCl₆⁻. A THF solution (30 mL) of an enantiomer of Zr(DTP)₂ (6.0 × 10⁻⁶ M) was added at room temperature to a 50 mL flask, fitted with a three-way stopcock, containing Phen⁺SbCl₆⁻ (1.4 mg, 2.7 μmol) under Ar, to generate a dicationic species. To this flask was added a THF solution (0.3 mL) of *p*-TsOH (9.0 × 10⁻² M), and aliquots of the mixture were periodically taken out from the flask and subjected to CD analysis after the addition of a few drops of triethylamine in order to reduce the dicationic species to the neutral form. For the preparation of a one-electron oxidized species (monocationic form), 0.23 μmol of

Phen⁺SbCl₆⁻ (1.2 equiv) or 1.5 μmol of FeCl₃ (8.5 equiv) was used for the oxidation under otherwise identical conditions to those stated above.

Measurements. ¹H NMR spectra were measured in CDCl₃ or DMSO-*d*₆ on a JEOL-type GSX-270 spectrometer operating at 270 MHz at 25 °C, where the chemical shifts were determined with respect to internal CHCl₃ (δ 7.28) or CHD₂SOCD₃ (δ 2.49), respectively. Absorption and circular dichroism spectra were recorded on a JASCO V-570 spectrometer and a JASCO J-720 spectropolarimeter, respectively. FAB-MS spectra were recorded on a JEOL JMS-SX102A spectrometer with a 3-nitrobenzyl alcohol/dithiothreitol matrix. Cyclic voltammetry was carried out on a BAS CV-27 voltammetry controller using platinum-wire working and counter electrodes and a silver-wire pseudoreference electrode. Sample solutions (0.2 mM in CH₂Cl₂) containing Bu₄NPF₆ (0.1 M) as a supporting electrolyte were degassed by several freeze-to-thaw cycles before measurements, and redox potentials were determined with respect to ferrocene as an internal standard.

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