

**Figure 2.** Mössbauer spectrum of  $[\text{Et}_4\text{N}][\text{FeCl}(\eta^4\text{-1})]$  in acetonitrile recorded at 150 K in zero field. The solid line results from fitting two Lorentzians (full width  $0.30 \text{ mm s}^{-1}$ ) to the data.

a system. The weakly oxidizing copper(III) complex of Margerum's macrocycle slowly undergoes oxidative ligand decomposition.<sup>15b</sup> Iron(IV) species can be isolated with  $[\eta^4\text{-1}]^{4-}$  because the macrocyclic tetraamide is resistant to oxidative destruction. We are continuing to expand the coordination chemistry of these ligand systems and the reaction chemistry of derivative complexes.

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**Supplementary Material Available:** Tables of data collection information, atom coordinates, Gaussian amplitudes, and bond lengths and angles for  $[\text{FeCl}(\text{C}_{22}\text{H}_{34}\text{N}_4\text{O}_5)][\text{N}(\text{C}_2\text{H}_5)_4]$  (27 pages); a listing of structure factor amplitudes for  $[\text{FeCl}(\text{C}_{22}\text{H}_{34}\text{N}_4\text{O}_5)][\text{N}(\text{C}_2\text{H}_5)_4]$  (9 pages). Ordering information is given on any current masthead page.

### Photoinduced Conformational Ruffling of Distorted Porphyrin. Optical Resolution and Photochemical Behavior of Chiral "Single-Armed" Porphyrin Complexes

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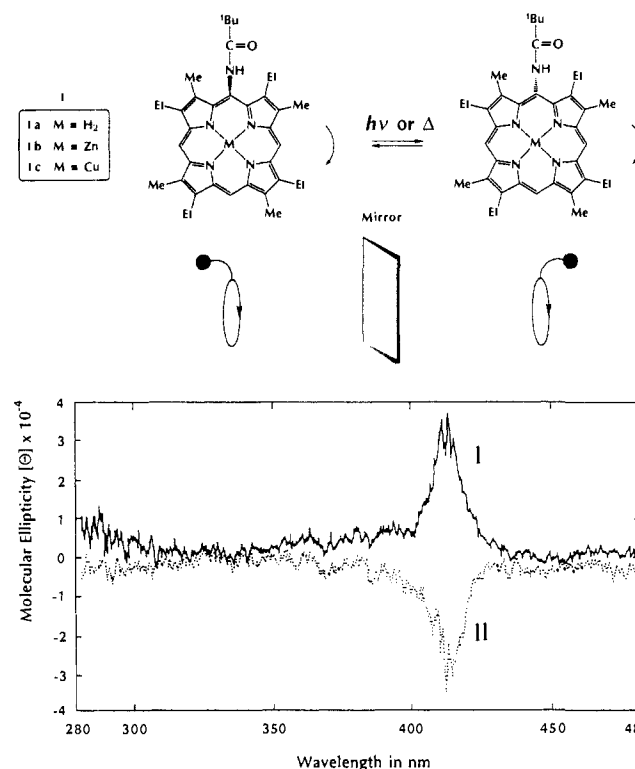
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Photoinduced molecular motions of tetrapyrrole macrocycles continue to be of general interest. Whitten and co-workers have reported the photoinduced atropisomerization of the metal complexes of picket-fence porphyrins.<sup>1</sup> We report herein the flipping phenomena of the meso substituent of porphyrin, as studied by the thermal and photoinduced racemization profiles of the optical antipodes of a chiral "single-armed" porphyrin and its metal complexes (**1**).

(1) (a) Freitag, R. A.; Mercer-Smith, J. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 1226. (b) Freitag, R. A.; Whitten, D. G. *J. Phys. Chem.* **1983**, *87*, 3918.

**Scheme 1**



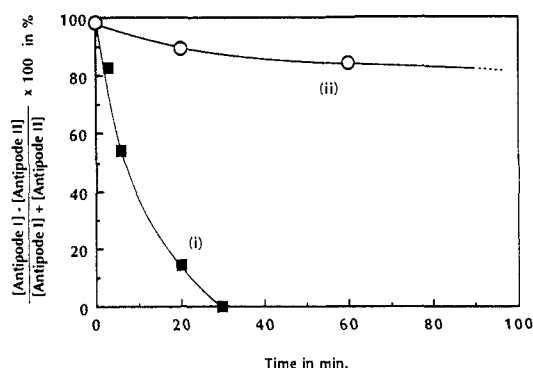
**Figure 1.** CD spectra of the antipodes of  $(\alpha\text{-PivNHETioP})\text{Zn}$  (**1b**) in hexane/EtOH/ $\text{CHCl}_3$  (70/20/10 v/v). I and II correspond to antipodes I and II in the text, respectively. Spectra were measured by using a quartz cell of 1-cm path length.

The "single-armed" porphyrin (**1**),<sup>2</sup> derived from etioporphyrin I (**2**), is considered to be distorted from planarity due to steric repulsion between the meso substituent and neighboring  $\beta$  substituents at the periphery (Scheme 1).<sup>3</sup> Since **2** has enantiotopic faces ( $C_{4h}$  symmetry), the "single-armed" porphyrin (**1**) should be chiral due to the presence of the "amide arm" on either of the two enantiotopic faces of the porphyrin plane. In fact, the zinc complex **1b** (zinc  $\alpha$ -(pivaloylamino)etioporphyrin I, ( $\alpha$ -PivNHETioP)Zn) showed two completely resolved peaks with comparable peak areas (fraction I, retention time 10.9 min; fraction II, retention time 36.5 min) when chromatographed on silica gel coated with cellulose tris(3,5-dimethylphenylcarbamate) with hexane/EtOH/ $\text{CHCl}_3$  (70/20/10 v/v) as eluent.<sup>4</sup> The compounds corresponding to these two peaks, fractionated, were both identical with the original zinc porphyrin (**1b**) in terms of the absorption and  $^1\text{H}$  NMR spectra, while the circular dichroism spectra were perfect mirror images of each other (Figure 1). Thus, the optical antipodes of **1b** were successfully resolved. The antipodes of the copper porphyrin (**1c**) were also resolved perfectly under the same conditions, while those of the free-base porphyrin (**1a**) were only partially resolved (60% enantiomeric purity). The HPLC analysis of **1a** exhibited two peaks (retention times 8.4 and

(2) **1a** was prepared by the condensation of  $\alpha\text{-NH}_2\text{EtiOPH}_2$  with pivaloyl chloride. Treatments of **1a** with metal acetates gave the corresponding metal complexes in quantitative yields. Detailed spectral data of **1a-c** are shown in the supplementary material.

(3) Comparison of the spectral data for **1a** and **1b** with those for etioporphyrin I and its zinc complex shows bathochromic shifts for the electronic absorptions (5-11 nm) and upfield shifts for the  $^1\text{H}$  NMR signals of the meso protons (0.1-0.2 ppm). Such spectral profiles have been claimed to be due to the lack of coplanarity of the porphyrin disk: (a) Abraham, R. J.; Jackson, A. H.; Kenner, G. W.; Warburton, D. *J. Chem. Soc.* **1960**, 853. (b) Burbidge, P. A.; Collier, G. L.; Jackson, A. H.; Kenner, G. W. *J. Chem. Soc. B* **1967**, 930. (c) Gong, L.-C.; Dolphin, D. *Can. J. Chem.* **1985**, *63*, 401.

(4) Conditions: flow rate  $1.0 \text{ mL min}^{-1}$ , room temperature, monitored at 410 nm, the eluates collected in flasks cooled at  $-78^\circ\text{C}$ . The chromatographic conditions have been established for the resolution of the antipodes of chiral N-alkylated porphyrins: Kubo, H.; Aida, T.; Inoue, S.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1015.



**Figure 2.** Racemizations of antipode I of ( $\alpha$ -PivNHETioP)Zn (**1b**) in hexane/EtOH/CHCl<sub>3</sub> (70/20/10 v/v,  $7.1 \times 10^{-5}$  M) at 28.5 °C under irradiation at 410 nm (i) and in the dark (ii). [Antipode I] and [antipode II], as determined by HPLC.

16.9 min) with significant tailing and leading in between, indicating the possibility of concomitant racemization during the HPLC separation.

The antipodes of the metal complexes **1b** and **1c** gradually racemized when stored in hexane/EtOH/CHCl<sub>3</sub> (70/20/10 v/v) at a temperature higher than 20 °C, but no racemization was observed below 0 °C.<sup>5</sup> In contrast, the antipodes of the free-base porphyrin (**1a**) are much easier to racemize, since antipode I with 60% enantiomeric purity, even when stored at 0 °C, gave in only 1 h an almost identical HPLC pattern as observed for racemic **1a**. The rate constants for racemization in hexane/EtOH/CHCl<sub>3</sub> (70/20/10 v/v) were measured as a function of temperature in the range 0–40 °C, which gave activation free energies ( $\Delta G^\ddagger$ ) of 24.2 and 21.7 kcal mol<sup>-1</sup> for the thermal racemization of **1b** and **1c** at 28.5 °C. The racemization takes place via the flipping of the "amide arm" from one side of the porphyrin plane to the other through a coplanar transition state possibly as a consequence of a thermally induced conformational ruffling of the porphyrin skeleton. Thus, the above results imply that the insertion of a metal atom into the porphyrin core provides the porphyrin skeleton with enhanced rigidity, so that the thermally induced ruffling may be much restrained compared with the free-base form. Zinc porphyrins are considered to be conformationally more rigid than copper porphyrins, taking account of the higher  $\Delta G^\ddagger$  value observed for **1b** than **1c**.

Of greater interest is the photoinduced racemization phenomenon observed for the antipodes of ( $\alpha$ -PivNHETioP)Zn (**1b**). As exemplified in Figure 2, the enantiomeric purity (enantiomeric excess, ee) of the antipode (fraction I) of **1b** decreased rapidly with time when degassed solution of the antipode (solvent: hexane/EtOH/CHCl<sub>3</sub> (70/20/10 v/v),  $7.1 \times 10^{-5}$  M) at 28.5 °C was exposed to monochromatized light with a wavelength of 410 nm corresponding to the Soret band,<sup>6</sup> and complete racemization was attained in only 30 min. In contrast, it took more than 2 days in the dark to achieve complete racemization under the same conditions. A quite similar photoinduced racemization was also observed when the antipode of **1b** was irradiated at the Q band (580 nm).<sup>6</sup> The quantum yields ( $\Phi$ ) at the initial stage upon irradiation at Soret and Q bands were  $3.3 \times 10^{-3}$  and  $2.5 \times 10^{-3}$ , respectively, during the initial 3 min at 28.5 °C.<sup>7</sup> Taking into account the fact that the photoinduced racemization was not quenched at all by admission of oxygen, the almost comparable quantum yields for the Soret band and Q-band excitations indicate that the photoinduced racemization originates from the singlet

excited state. This is in sharp contrast with the photoinduced atropisomerization of a zinc picket-fence porphyrin, for which the triplet excited state has been implicated.<sup>1</sup>

Racemization of the antipodes of the copper porphyrin (**1c**) upon irradiation was also examined under similar conditions, in which however no photoacceleration effect was observed. This difference is possibly due to the short lifetimes of the photoexcited states of copper porphyrins compared with those of zinc porphyrins.<sup>8</sup>

In the present communication, the thermal and photoinduced conformational ruffling of distorted porphyrin skeletons is claimed, taking advantage of the successful resolution of the optical antipodes of chiral "single-armed" porphyrin complexes. Mechanistic studies on the photoinduced racemization process are in progress using other "single-armed" porphyrins with a variety of central metals.

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**Supplementary Material Available:** Experimental details and spectral data for compounds **1a–c** (1 page). Ordering information is given on any current masthead page.

(8) (a) Asano, M.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1988**, *89*, 6567. (b) Kim, D.; Holten, D.; Gouterman, M. *J. Am. Chem. Soc.* **1984**, *106*, 2793. (c) Kobayashi, T.; Huppert, D.; Straub, K. D.; Rentzepis, P. M. *J. Chem. Phys.* **1979**, *70*, 1720. (d) Brookfield, R. L.; Ellul, H.; Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 219. (e) Harriman, A.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1618.

### Evidence for Through-Bond Long-Range Electron Transfer in Peptides<sup>†</sup>

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There are many reports of intramolecular long-range electron transfer (LRET)<sup>1</sup> in proteins and peptides.<sup>2</sup> Efficient transfer between distant donors and acceptors (i) has biological significance in photosynthesis, respiration, and enzyme-catalyzed redox reactions; (ii) may be important in mediating free-radical damage initiated by ionizing radiation and oxygen assault; and (iii) may occur in the radical processes associated with chemical carcinogenesis and cellular aging. We have, therefore, undertaken a systematic study of LRET in proteins and peptides. As part of this program we are studying the intramolecular one-electron oxidation of tyrosine (TyrOH) by the tryptophan radical (Trp<sup>•</sup>). This reaction, first elaborated by Prütz et al.,<sup>3</sup> is initiated with

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(1) Abbreviations: LRET, long-range electron transfer; Lys, lysine; Pro, proline; TrpH, tryptophan; TyrOH, tyrosine; Trp<sup>•</sup> and TyrO<sup>•</sup>, neutral indolyl TrpH and phenoxy TyrOH radicals; TrpH<sup>•+</sup> and TyrOH<sup>•+</sup>, cationic TrpH and TyrOH radicals.

(2) Klapper, M. H.; Faraggi, M. *Q. Rev. Biophys.* **1979**, *12*, 465–519. Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443–517. Guarr, T.; McLendon, G. *Coord. Chem. Rev.* **1985**, *68*, 1–52. Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135–157. Peterson-Kennedy, S. E.; McGourty, J. L.; Ho, P. S.; Sutoris, C. J.; Liang, N.; Zemel, H.; Blough, N. V.; Margoliash, E.; Hoffman, B. M. *Coord. Chem. Rev.* **1985**, *64*, 125–133. Mayo, S. L.; Ellis, W. R.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948–952. Miller, J. R. *Nouv. J. Chim.* **1987**, *11*, 83–89. McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160–167.

(5) The antipodes of the homologue of **1b** with a smaller amide groups such as zinc  $\alpha$ -(acetylamino)etioporphyrin I were also resolved, whose racemization profiles were similar to those for **1b**.

(6) A quartz cell containing **1b** or **1c** in hexane/EtOH/CHCl<sub>3</sub> (70/20/10 v/v), thermostated at 28.5 °C, was illuminated by a 300-W xenon arc lamp from a distance of 4.3 cm through a band-path filter (bandwidth 10 nm) and another filter to cut heat.

(7) Quantum yields were obtained from the change in the enantiomeric purity of **1b** during the initial 3 min, at which the contribution of the thermal racemization was negligibly small (see ii in Figure 2).