

Synthesis and Circular Dichroism of Tartrate-linked Porphyrin Dimers

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Abstract: Synthesis, characterization and circular dichroism of two tartrate-linked porphyrin dimers are described. Circular dichroism of zinc dimers and pyridine complexes is also reported. Copyright © 1996 Elsevier Science Ltd

Porphyrins in a chiral environment have been shown to exhibit induced circular dichroism (CD). Structural information related to the orientation of porphyrins in a supramolecular assembly¹ or a protein such as hemoglobin² can be obtained from CD spectra. Small molecular systems containing porphyrins in a chiral environment^{3,4} are needed to elucidate the complex CD spectra observed for hemoglobin and other systems. We report here the synthesis, characterization and CD of tartrate-linked porphyrin dimers.

5,10,15,20-(tetraphenyl)porphyrin was prepared by standard methods⁵ and nitrated using red, fuming nitric acid⁶ (0°C, 3 hrs.) to yield 5-(4-nitrophenyl) 10,15,20-(triphenyl)porphyrin. Reduction using stannous chloride produced 5-(4-aminophenyl)10,15,20-(triphenyl)porphyrin (MATPP). 1R,2R-disuccinimidyltartrate (0.15 mmol) and MATPP (0.3 mmol) were refluxed in dry dichloromethane for five hours. The purple precipitate was recrystallized from chloroform/methanol to yield the pure dimer **1** (64%). To restrict rotation in the tartrate linkage, the cyclic carbonate **2** was formed using carbonyldiimidazole⁷ (10 equiv., rt., 18 hrs.) in 76% yield. Zinc derivatives (**1a** and **2a**) of **1** and **2** were prepared with zinc acetate in chloroform.⁸

Bisignate CD signals are typically observed as a result of chiral exciton coupling in systems of two or more chromophores.^{9,10} For systems with two identical chromophores, a conservative couplet (rotational strengths of equal magnitude) is expected. Rotational strength is proportional to peak area; therefore, a peak area ratio of 1:1 is predicted for positive and negative components of the couplet.¹⁰ CD in chiral porphyrin dimers has been attributed to exciton coupling of the Soret band transitions. Specifically, Matile et al.³ and Erna et al.⁹ have associated the CD of porphyrin dimers with exciton coupling of the B_x transitions (defined as the 5, 15 direction, Figure 1).

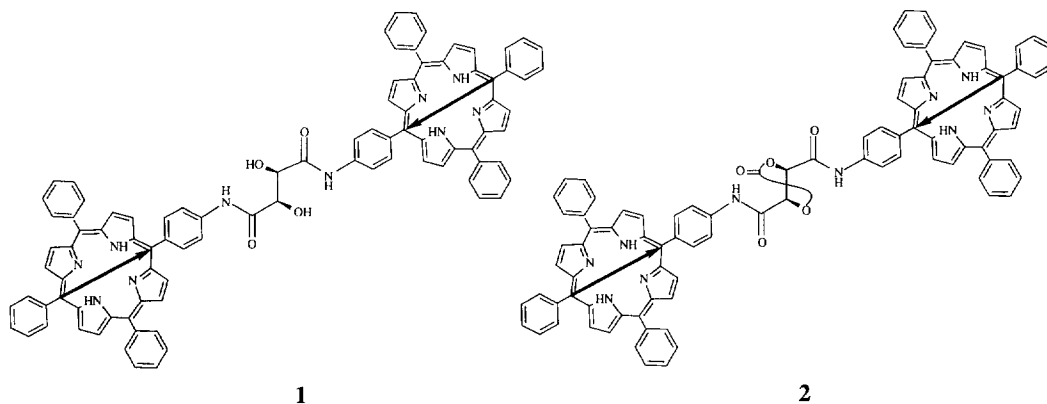


Figure 1. Tartrate-linked dimers (**1** and **2**). The arrows represent the B_x electronic transitions related to CD signals in these systems.

The CD spectra of **1**, **1a**, **2** and **2a** in chloroform are shown in Figure 2 and summarized in Table 1.¹¹ A monoporphyrin derivative with a diacetyltartrate chain exhibited a negligible CD signal. The bisignate CD bands observed for **1** and **1a** were consistent with exciton coupling of the porphyrin transitions. The negative Cotton effect is clearly weaker for both

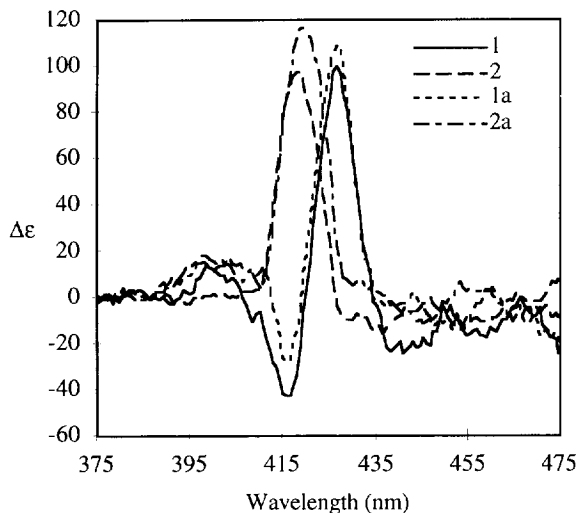


Figure 2. Circular Dichroism Spectra of Dimers

1 and **1a**. Similar nonconservative couplets have been observed for porphyrin dimers exhibiting chiral exciton coupling^{3,9} and could be attributed to interactions of the Soret transitions with other high-energy transitions.⁹ Couplet amplitudes ($A = \Delta\epsilon_{427} - \Delta\epsilon_{416}$, $A_1 = +142$ and $A_{1a} = +139$) were smaller than rigidly linked porphyrin dimers due to conformational averaging.^{3,9}

When the chiral linkage was constrained as a cyclic carbonate, **2** and **2a**, only a positive CD peak was observed for the Soret band. The expected negative Cotton effect was not observed in the visible region.

Chiral porphyrin dimers with short flexible linkages ($<12 \text{ \AA}$) have shown additional evidence of porphyrin–porphyrin interactions.^{3,9,12} Exciton coupling of the Soret transitions in porphyrin dimers typically results in shifting and broadening of the Soret band in the visible spectrum. The Soret bands of **1** and **2** were not shifted or broadened compared to

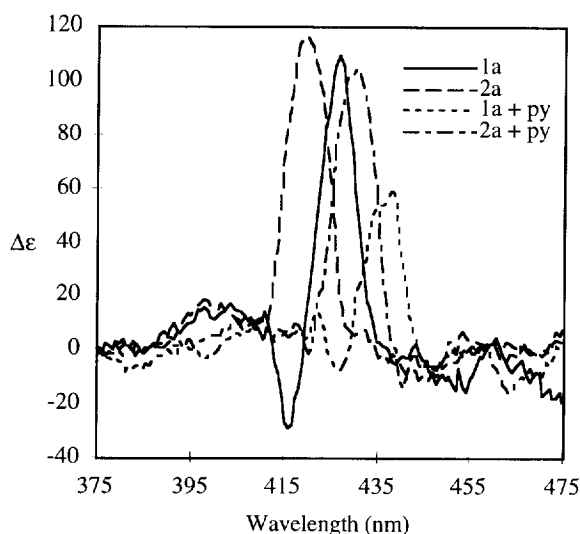


Figure 3. Circular Dichroism Spectra of Metalloporphyrin Dimers and Pyridine Complexes

MATPP. Splitting of the Soret band was not observed. The shoulder at 400 nm in the visible spectrum (Table 1) has been attributed to vibronic fine structure³ and was also observed in MATPP. Ring current shifts in the ¹H NMR spectrum have been linked to close face-to-face porphyrin interactions.^{3, 9, 12} ¹H NMR spectra of **1**, **1a**, **2** and **2a** did not exhibit any unusual shifts associated with porphyrin-porphyrin ring current effects. The internal pyrrole protons were not split and appeared at -2.77 ppm compared to -2.73 ppm for MATPP⁶. The observed circular dichroism was the only indication of interaction between the porphyrin chromophores.

Self-stacking could also contribute to the observed CD spectra. Addition of methanol to dissociate possible π - π stacking of the dimers in chloroform did not change the CD bands. For the zinc dimers, axial ligation would dissociate any self-aggregation. CD spectra of **1a** and **2a** pyridine derivatives in chloroform are shown in Figure 3. The positive CD band of **2a** was retained upon pyridine coordination and shifted to 430 nm. The Soret band for the pyridine complex in the visible spectrum also appeared at 430 nm (Table 1). Interestingly, the CD couplet for the pyridine complex of **1a** appeared with a positive component red shifted to 438 nm and a negative component of considerably weaker rotational strength. Axial coordination of ligands has been predicted to play a role in the induced CD of hemoglobin and myoglobin. Self-organization of **1a** and **2a** with various axial ligands to form supramolecular assemblies is the focus of ongoing study in this laboratory.

Table 1
Summary of Spectral Data

	Visible Spectrum Soret Band (nm)	Circular Dichroism (nm/ $\Delta\epsilon$)
1	400 (sh), 420	416 (-42), 427 (100)
2	400 (sh), 420	418 (97)
1a	400 (sh), 420	416 (-29), 427 (110)
2a	400 (sh), 420	419 (116)
1a + excess py	409 (sh), 430	427 (-8), 438 (61)
2a + excess py	409 (sh), 430	430 (105)

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- 1:** ¹H NMR (400 MHz, CDCl₃): 9.42 (s, 2, amide), 8.85 (m, 16, β-pyrrole), 8.22 (m, 16, *o*-phenyl and 3- and 5-aminophenyl), 8.05 (d, 4, 2- and 6-aminophenyl, J = 8.5 Hz), 7.75 (m, 18, *m, p*-phenyl), 5.35 (broad, 2, -OH, D₂O exchangeable), 4.78 (s, 2, linkage), -2.78 (s, 4, internal NH). ¹³C NMR (400 MHz, CDCl₃): 172.5 (amide), 142.11 (C1), 139.26 (C4'), 136.20 (C1'), 135.24 (C2'), 134.53 (C2), 130.20 (β-pyrrole), 127.72 (C3), 126.68 (C4), 120.28 (meso), 119.08 (meso'), 118.46 (C3'), 70.74 (CH). IR (KBr): 1671 (CO). Visible spectrum (λ (nm) in CHCl₃; ε x 10⁴ cm⁻¹ M⁻¹): 419.5 (95), 516.0 (3.9), 551.0 (1.9), 591.0, (1.3) 646.5 (0.94). C₉₂H₆₄N₁₀O₄·2H₂O Anal: Calcd (%): C 78.39, N 9.94, H 4.86. Found (%): C 78.37, N 9.85, H 4.79. **2:** ¹H NMR (400 MHz, CDCl₃): 8.86 (m, 16, β-pyrrole), 8.81 (s, 2, amide), 8.23 (m, 16, *o*-phenyl and 3- and 5-amino phenyl), 8.08 (d, 4, 2- and 6-aminophenyl, J = 8.5), 7.77 (m, 18, *m, p*-phenyl), 5.67 (s, 2, linkage), -2.77 (s, 4, internal NH). ¹³C NMR (400 MHz, CDCl₃): 163.99 (amide), 151.35 (carbonate), 142.11 (C1), 139.86 (C4'), 135.78 (C1'), 135.34 (C2'), 134.51 (C2), 131.36 (β-pyrrole), 127.75 (C3), 126.70 (C4), 120.29 (meso, meso'), 118.55 (C3'), 76.14 (CH). IR (KBr): 1831 (CO, carbonate), 1689 (CO). Visible spectrum (λ (nm) in CHCl₃; ε x 10⁴ cm⁻¹ M⁻¹): 419.5 (91), 516.0 (3.9), 551.0 (1.8), 590.0, (1.1) 645.0 (0.90). C₉₃H₆₂N₁₀O₅·4H₂O Anal: Calcd (%): C 74.99, N 9.40, H 4.87. Found (%): C 75.51, N 9.40, H 4.87. **1a.** Visible spectrum (λ (nm) in CHCl₃; ε x 10⁴ cm⁻¹ M⁻¹): 420.0 (88), 547.0 (4.0), 586.0 (0.8). **2a.** Visible spectrum (λ (nm) in CHCl₃; ε x 10⁴ cm⁻¹ M⁻¹): 420.0 (91), 547.0 (3.9), 584.0 (0.7).
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