First Observation of the Vibrational Circular Dichroism Spectra of Synthetic Chiral Porphyrazines

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Vibrational circular dichroism (VCD) spectra of (*R*)-(−)- and (*S*)-(+)-camphor-substituted tetrapyrazinoporphyrazines, which show a mirror-image relationship with respect to the line of intensity = 0, were recorded as the first VCD spectra of synthetic porphyrins.

Since the 1970s, circular dichroism (CD) spectroscopy has been used extensively to characterize optically active chromophores in solution, primarily in the ultraviolet and visible regions.[1] Vibrational CD (VCD) which is based on the differential response of a chiral molecule to left and right circularly polarized vibrational transitions in the infrared was first observed experimentally in the mid 1970s.[2] For over a decade, however, the development of VCD spectroscopy was hindered by the fact that a coherent formal theoretical framework for analyzing the spectral data obtained was not developed until the mid 1980s[3] and the necessary instrumentation was not readily available commercially. In the last decade, an increasing number of researchers have shown an interest in VCD probably because of the information that can be readily obtained, since: i) vibrational spectra contain many transitions through which the molecular stereochemistry can be probed, ii) the molecular transitions involve only the equilibrium ground state and hence are easier to calculate from a quantum-mechanical standpoint, and iii) virtually all chiral molecules exhibit a variety of vibrational bands so VCD spectroscopy is not restricted to molecules with a chromophore in the UV–vis region. Even today, however, the application of VCD spectroscopy is in most cases restricted to small rigid molecules,[4] although in a few instances it has been applied to naturally occurring heme protein systems in peptide and protein conformational studies.[5] We report here the first example of VCD spectra for synthetic porphyrins, specifically copper tetrapyrazinoporphyrazine (CuPyZ) fused with four camphor units of *R* or *S* configuration (Figure 1). The syntheses of these complexes and their CD spectra in the UV–vis region have been reported previously.[6]

Figure 2 shows the IR and VCD spectra of CuPyZs,[7] together with calculated spectra (VCD was calculated for the *R* enantiomer).[8] The agreement between the experimental and calculated spectra is very good with respect to both the band intensities and centers. Although some systematic shifts are observed for the energy of the bands, this confirms the validity of the calculations. In the experimental IR spectra (bottom), bands are observed around 1430–1490, 1370–1400, 1200–1300, 1100–1190, and 990–1030 cm^{-1} regions. Of these, the bands in 1200–1300 and 1100–1190 cm^{-1} are the strongest. The calculated IR spectra broadly reproduce these characteristics. The spectra of both enantiomers show curves with a mirror-image relationship with respect to the line of intensity = 0. Although many of the VCD bands that have been reported previously in the literature correspond to bands within the IR spectra for the same molecule, strong VCD bands are not always observed for the most intense IR bands, since the selection rules for IR and VCD spectroscopy are different.[4] The calculated peaks 6 and 7 are very intense with opposite signs but these peaks appear as weak peaks in the experimental spectrum probably primarily due to the cancellation effect resulting from the small energy separation.

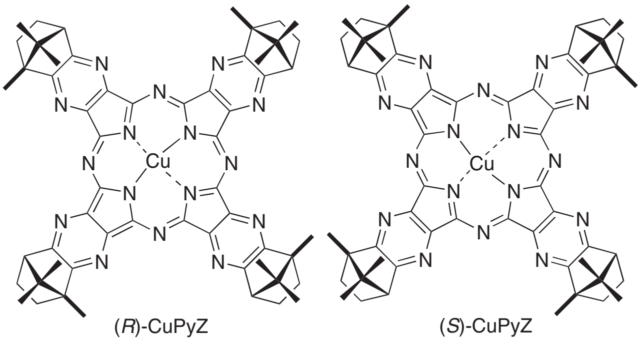

Figure 1. Structures of (*R*)-(−)- and (*S*)-(+)-camphore-substituted tetrapyrazinoporphyrazines.

Figure 3 shows some representative vibrational modes which give strong VCD signals. Two weak positive peaks seen at 1025 and 995 cm^{-1} were calculated at 1008 and 981 cm^{-1} and are tentatively assigned to vibrations spread across the whole molecule, while strong negative VCD peaks observed at 1255 (calculated at 1230) and 1076 cm^{-1} (1062 cm^{-1}) are assigned to vibrations restricted to the camphore-substituted pyrazine moiety. Although they are not all shown individually, most of the strong VCD signals including those at 1255 and 1076 cm^{-1} are found to be due to the camphor moiety.[9] This suggests that rigid small molecules tend to show the most intense VCD signals.

In conclusion, we have reported the first observation of VCD spectra of chiral porphyrins. In our experiments, well-resolved VCD spectra were not obtained for two types of phthalocyanine substituted by optically active binaphthyls.[10] Considering that VCD spectra have previously been reported primarily for rigid, non-aromatic small molecules such as β-pinene, pinane, and menthol, the intensity mechanism of VCD spectroscopy is probably not particularly sensitive to the vibrations of large heteroaromatic molecules with optically active peripheral substituents.

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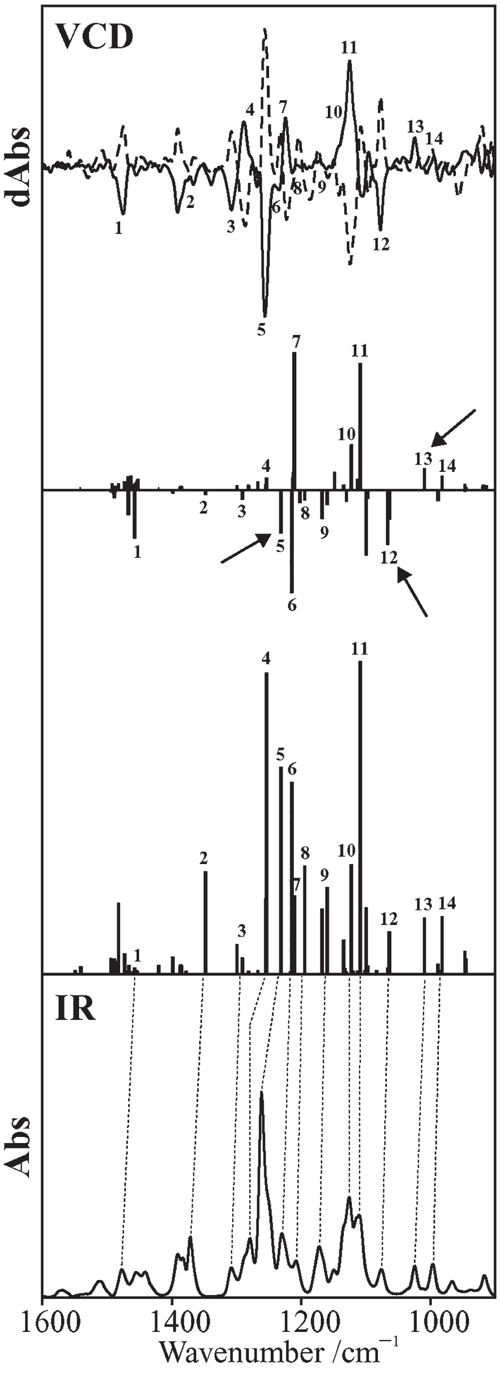

Figure 2. Experimental IR (bottom) and VCD (top) spectra of (*R*)- (solid lines) and (*S*)-CuPyZ (broken lines) and their calculated spectra (bars) in the 900 and 1600 cm^{-1} region. In the calculated and experimental spectra, the peaks and troughs with the same numbers correspond to each other. Vibrations shown by arrows are shown in Figure 3.

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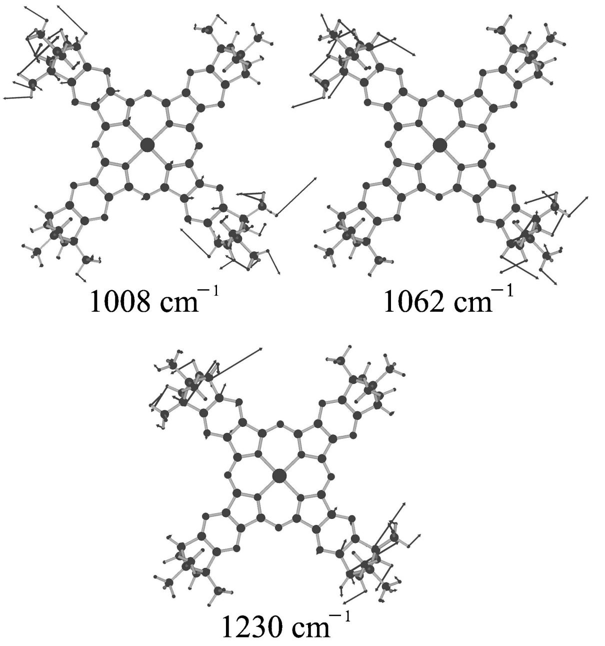

Figure 3. Atomic motions at the selected predicted frequencies.

References and Notes

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7 Spectra were recorded using a Jasco JV-2001 VCD system with a PV-type MCT detector at a scan speed of 4 mm/s under nitrogen. 5 mg of CuPyZ was dissolved in 0.1 mL of CCl_4 and the solution was sandwiched between two BaF_2 plates (cell path length = 50 μm).

8 The GAUSSIAN 98 program running on a NEC TX7/AzusA computing system was used to perform DFT calculations. The B3LYP with 6-31G(d) basis set was used for both geometry optimization and frequency calculations, since studies with a variety of basis sets demonstrated that this set was optimal in terms of cost-to-benefit ratio (P. J. Stephens, F. J. Devlin, C. S. Ashvar, C. F. Chabalowski, and M. J. Frisch, *Faraday Discuss.*, **1994**, 103; C. S. Ashvar, F. J. Devlin, K. L. Bak, P. R. Taylor, and P. J. Stephens, *J. Phys. Chem.*, **100**, 9262 (1996)). The copper was simply replaced with a nickel in order to simplify the calculations. An optimum scaling factor of 0.9613 was applied to the calculated frequencies in order to compare with the experimental data (M. W. Wong, *Chem. Phys. Lett.*, **256**, 391 (1996)).

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