CD Sensitive Metalloporphyrins for Chiral Recognition and Supramolecular Assemblies: Chiroptical Studies

Nina BEROVA
Columbia University, Department of Chemistry,
New York, NY 10027, USA
ndb1@columbia.edu

During the past few years, porphyrins and metalloporphyrins have attracted widespread attention as receptors for chiral recognition. Various artificial receptors that take advantage of multifaceted properties of porphyrins and metalloporphyrins, e.g., propensity to undergo intramolecular or intermolecular π−π stacking and host-guest complexation, have been synthesized. The application of porphyrins for chiral recognition is favored by the intense and red-shifted Soret band that allows structural studies on completely new concepts to be monitored by circular dichroism (CD) of very high sensitivity. The lecture will focus on a recently developed matalloporphyrin dimers as achiral chromophoric hosts capable of forming in stereocontrolled manner 1:1 complexes with various low-molecular weight chiral guests, such as diamines, aminoalcohols, monoamines, hydroxyacids, as well more complexed natural products.

In general, the formation of 1:1 complexes between matalloporphyrins **3** and chiral bidentate conjugates proceeds as stereodifferentiating process, where the large (L) group at the stereogenic center (assigned based on conformational energies A values) protrudes from the porphyrin binding pocket. This leads to formation of host/guest complexes with a preferred porphyrin helicity which is clearly controlled by the stereogenic center. The preferred chiral sense of porphyrin twist leads to very intense exciton split CD spectra, detectable on microscale.

In order to extend the application to more difficult cases where some ambiguity in the relative steric size of substituents may exist, a molecular mechanics calculation approach using the Merck Molecular Force Field (MMFFs) was developed. Alternatively, a NMR protocol based on porphyrin ring-current induced ^{1}H chemical shift differences for the large and medium size substituents at the stereogenic center has shown a great diagnostic value.

The figure illustrate a recently developed CD exciton chirality protocol for determining the absolute configuration of carboxylic acids with an α-stereogenic center. The acid is reacted with carrier **1** to yield the bidentate amide conjugate **2,** which in turn forms a 1:1 host-guest complex with the porphyrin tweezer **3**, in this case, M = Zn. In addition to a nitrogen coordination to P-1 an amide C=O→Zn coordination to P-2 was identified by shift of the amide C=O stretching frequency (amide I band) to lower IR frequencies. The complexation mode was further studied by Monte Carlo (MC) conformational search with Merck Molecular Force Field (MMFFs), and treating the ligand/Zn coordination within a non-bonded model. In the lowest energy structure calculated by MC/MMFFs, and in all minimum energy conformations within 50 kJ/mol, ligation between the conjugate and the Zn on P-2 occurred through the carbonyl oxygen.

References

1) X. Huang, K. Nakanishi and N. Berova , *Chirality*, 2000, **12**, 237 (review)
2) X.Huang, N. Fujioka, G. Pescitelli, F. E. Koehn, R. T. Williamson, K. Nakanishi, and N. Berova, *J. Am. Chem. Soc*. **2002**, *124*, 10320.
3) G. Proni, G. Pescitelli, X. Huang, N. Q. Quraishi, K. Nakanishi and N. Berova, *Chem. Comm*. **2002**, 1590.