Abstract

Chirogenesis in Supramolecular Systems on the Basis of Porphyrinoids †

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Chirogenesis is a phenomenon of symmetry breaking in achiral multi- or unimolecular host systems by chiral guests (and vice versa), and is achieved by the rational application of specific non-covalent interactions via a chirality information transfer mechanism. With supramolecular interactions being responsible for these chiral transformations, they come under the heading of supramolecular chirogenesis, which is a fundamentally novel interdisciplinary field of research—a smart combination of supramolecular/nano chemistry and chiral science.

Recently, a novel and very efficient supramolecular chirogenic system based upon an achiral ethane-bridged bis (metallo- or free base octaethylporphyrin) was developed and well-investigated. Upon interaction with the corresponding chiral guests, ligand-induced structural deformations are produced in this achiral host, resulting in an asymmetric orientation of the two porphyrin subunits and subsequent pronounced and easily detectable spectral changes monitored by various spectroscopies. Particularly, through-space exciton coupling between the porphyrin electronic transitions generates bisignate Cotton effects in the circular dichroism (CD) spectra. Significantly, the sign of the observed CD couplet is unequivocally correlated with the substituents’ bulkiness around the stereogenic center. In turn, this results in the absolute configuration assignment of the chiral ligand used, hence allowing us to develop an absolute configuration sensor for enantiopure amines, alcohols, and acids. This system possesses a high degree of chiroptical activity and sensitivity to various internal and external controlling factors such as the structure of guest molecules, stoichiometry, number of binding sites, solvent, temperature, and phase transition.

Further developments and prospects toward new supramolecular chirogenic systems on the basis of heterometallic bis- and multi-porphyrin structures will be discussed.

References