

## Supramolecular Chirogenesis in Bis-Porphyrins

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Supramolecular chirogenesis is an important and widely observed event in various natural and artificial systems. This phenomenon is based on “symmetry breaking” in intrinsically achiral uni- or multimolecular systems, or the chirality amplification in supramolecular assemblies consisting of chiral components with a low degree of asymmetry upon noncovalent interactions with a chiral environment via a chirality transfer mechanism. Recently, we have discovered that bis-porphyrins may serve as effective achiral hosts, which become optically active upon interactions with various chiral guests.

Our particular supramolecular systems are based on an achiral ethane-bridged bis-octaethylporphyrin (bis- or monometallated) host (Figure 1), which undergoes a structural transformation from the stacked *syn* to twisted *anti* form upon interaction with chiral amine and alcohol guests. This results in a transfer of the point chirality of the guest molecules into supramolecular helical chirality of the whole system.<sup>1</sup> The origin of the chirality induction is the formation of a screw structure in the bis-porphyrin system (Figure 1). The direction of the screw sense is governed solely by the relative bulk of the substituents around the chiral center, so to minimize the steric hindrance between the largest substituent and the ethyl group in the tethered octaethylporphyrin unit; the critical size discrimination of the substituents allows the practical application of the system to efficient chirality sensing. For example, in the case of simple monofunctional compounds (monoamines and monoalcohols) (*S*)-ligands yield positive chirality due to the formation of a right-handed screw, whilst (*R*)-ligands give negative chirality due to the formation of a left-handed screw (Figure 1 and 2). It was also found that the process of supramolecular chirogenesis is highly sensitive to various internal (binding strength, stoichiometry, steric effects, metal ion type and number, chromophore and ligand structure) and external (solvent, temperature, phase transition, concentration) factors.<sup>1-8</sup>

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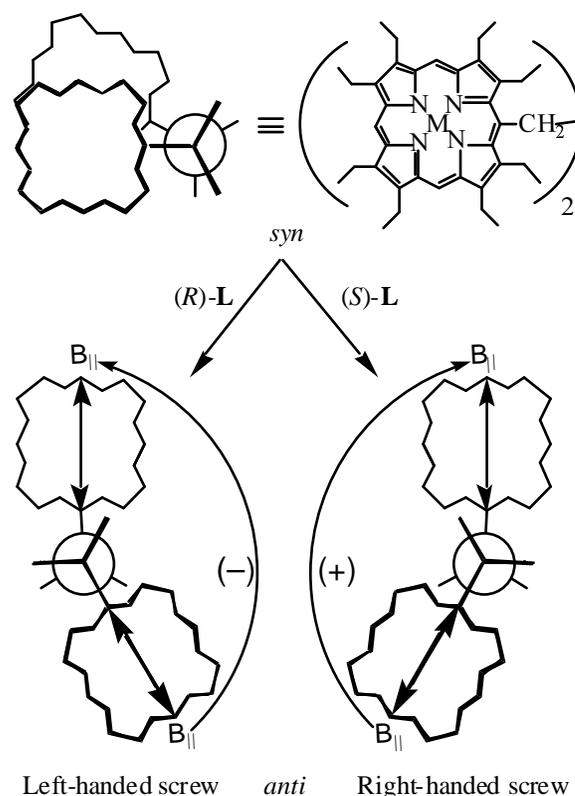


Fig. 1. Supramolecular chirogenesis in bis-porphyrins.

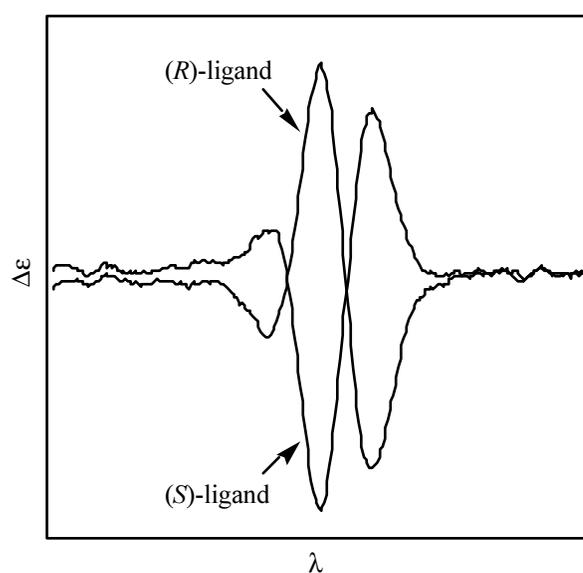


Fig. 2. CD spectra of bis(zinc porphyrin) in the presence of (*R*)- and (*S*)-ligands.