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Stoichiometry-Controlled Supramolecular Chirality Induction and Inversion in Bisporphyrin Systems

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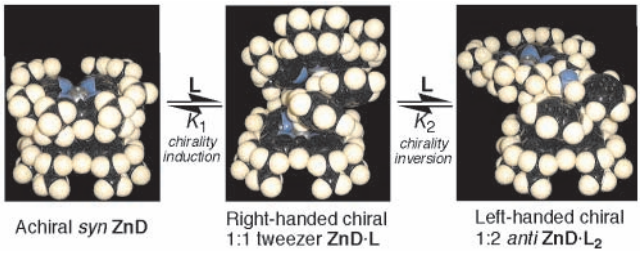
ABSTRACT



Stoichiometry is found to be an effective tool for controlling supramolecular chirality induction and inversion processes. Chirality induction in the achiral *syn* ethane-bridged bis(zinc octaethylporphyrin) is achieved upon interaction with the enantiopure (*R*,*R*)-1,2-diphenylethylenediamine at the low molar excess region, to yield the right-handed chiral 1:1 tweezer complex. Further increase of the ligand concentration results in chirality inversion as the equilibrium shifts toward the extended left-handed 1:2 *anti* complex as a result of switching of the complex helicity.

Chirality modulation includes chirality induction, amplification, reduction, and inversion phenomena and has important implications for understanding the asymmetry in numerous systems. Particularly, chirality induction in supra- and macromolecular systems, which is associated with the conformational changes in intrinsically achiral components upon interaction with a chiral environment, has been well studied to date. Chirality inversion, however, which is caused by a spatial rearrangement of asymmetric single molecules or associates, is more seldom observed.[1] These studies predominantly describe chirality inversion of intrinsically chiral systems, or the switching of the chirality upon asymmetry induction by external controlling factors. Here, by applying supramolecular chemistry and exciton chirality principles, we describe a rarely observed phenomenon of chirality induction and subsequent chirality inversion in a two-component molecular assembly consisting of only an achiral host and a chiral guest that is controlled solely by its stoichiometry.[2]

Our approach to this novel concept grew out of our recent studies of supramolecular chirality induction in the achiral bis(zinc octaethylporphyrin)[3] (*syn* **ZnD**, Figure 1a) upon interaction with chiral monoamines and monoalcohols.[4] The mechanism is based on ligand coordination with the central zinc ion, *syn*-*anti* conformational switching of *syn* **ZnD** to yield the extended *anti* conformation (**ZnD·L_2**, Figure 1c), and unidirectional twisting due to steric interactions between the bulkiest chiral ligand substituent and one of the ethyl

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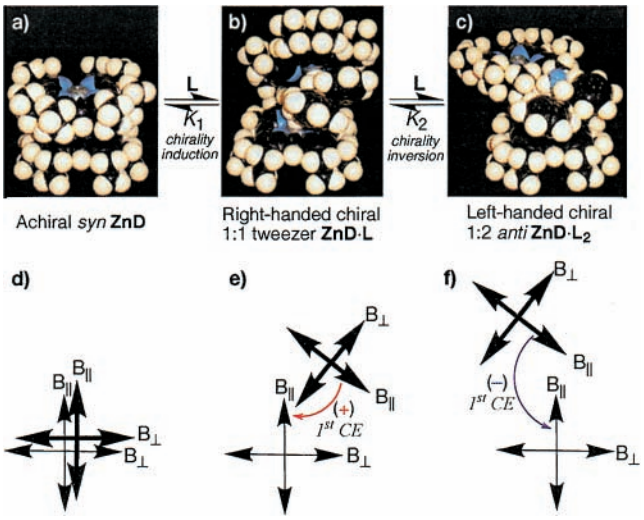

Figure 1. CPK molecular models and coupling electronic transitions of supramolecular chirality induction and inversion in achiral *syn* **ZnD** by (*R*,*R*)-DPEA.

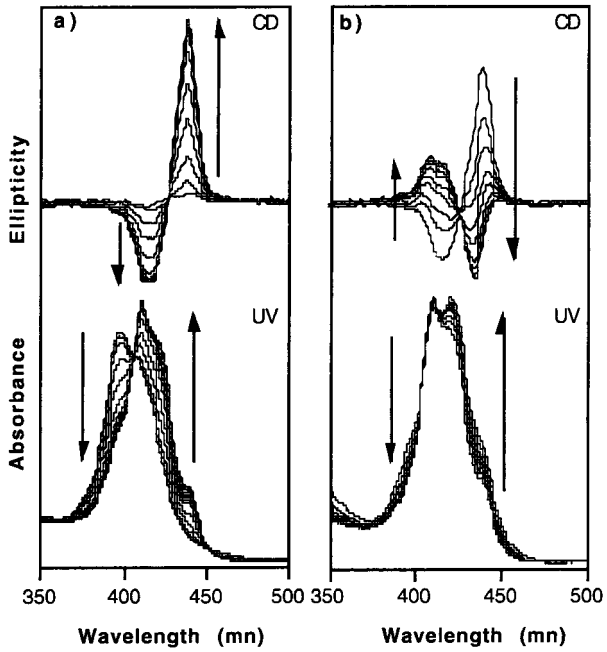

Figure 2. CD and UV−vis changes of **ZnD** upon addition of (*R*,*R*)-DPEA at the low from 1:0.12 to 1:16.5 (a) and high from 1:112 to 1:4866 (b) ligand molar excess regions.

groups of the neighboring porphyrin ring, with the direction of the twist governed by the guest's stereochemistry. Thus, (*R*)-guests produce a left-handed twist and (*S*)-guests give a right-handed twist, corresponding to negative and positive chirality, respectively.[4]

Expanding this research to a new class of chiral ligands with two binding sites (diamines and amino alcohols),[5] we have discovered the formation of a new chiral species at the low ligand molar excess region that corresponds to a 1:1 tweezer complex[6] (**ZnD·L**, Figure 1b), which was monitored by UV−vis, CD, ^{1}H NMR,[7] and ESI MS and confirmed by a Job plot.[8] As an example of a bifunctional ligand, enantiopure 1,2-diphenylethylenediamine (DPEA) was studied.[5]

In the UV−vis spectra the intensity of the Soret band of *syn* **ZnD** (397 nm) gradually decreases upon addition of DPEA, and new bathochromically shifted, split spectral bands (411, 420, and 438 nm) associated with the exciton coupled $B_\perp$ and $B_\parallel$ electronic transitions of **ZnD·L** appear at the low ligand molar excess region (Figure 2a). These spectral changes are in good agreement with exciton coupling theory[9] and indicative of the twisted spatial rearrangement of the two B transitions in **ZnD·L** from its initial parallel orientation in *syn* **ZnD** (Figure 1e and 1d, respectively). Simultaneous CD monitoring of this process shows the appearance and stepwise enhancement of bisignate Cotton effects in the porphyrin Soret band region. The observed optical activity of these coupling transitions is as a result of the induced chirality in **ZnD·L**. The position of the first Cotton effect (438 nm) is well matched to the most bathochromically shifted absorption band in the UV−vis spectrum that arises from the lowest energy $B_\parallel$ coupling transitions. The chirality sign that is associated with the sign of the first Cotton effect depends on the absolute configuration of chiral ligands, and hence the (*R*,*R*)-enantiomer of DPEA induces positive chirality (Figure 2a), whereas the corresponding (*S*,*S*)-enantiomer produces negative chirality (not shown).

Examination of CPK molecular models reveals that the diamines studied are easily accommodated between the two porphyrin planes in **ZnD·L** to yield a stable 1:1 tweezer complex. As a result of the ligand's geometry, upon coordination to minimize the host−guest steric interactions, the two porphyrins in **ZnD·L** form a right-handed twist in the case of (*R*,*R*)-DPEA (Figure 1b). Owing to the spatial proximity between the porphyrins and ligand phenyl groups, host−guest $\pi-\pi$ interactions may also play an additional role in stabilization of the tweezer complex. Because in **ZnD·L** the right-handed twist structure is asymmetric, all of the

(5) Enantiopure 1,2-diphenylethylenediamine, 1,2-diaminocyclohexane, leucinol, and 1-amino-2-propanol have been investigated. Although all of these ligands showed formation of the same 1:1 tweezer complex, only 1,2-diphenylethylenediamine exhibited besides chirality induction the chirality inversion phenomenon.

(6) There are also few examples of the 1:1 chiral tweezer complex formation upon interaction of achiral bisporphyrin hosts with various chiral guests; see: (a) Kurtan, T.; Nesnas, N.; Li, Y.-Q.; Huang, X.; Nakanishi, K.; Berova, N. *J. Am. Chem. Soc.* **2001**, *123*, 5962−5973. (b) Takeuchi, M.; Imada, T.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1117−1123.

(7) The ^{1}H NMR monitoring of the 1:1 tweezer formation has been carried out for the 1,2-diaminocyclohexane-containing system, because of a more clear and well-resolved ^{1}H NMR spectral pattern in comparison to that of 1,2-diphenylethylenediamine and essentially the same UV−vis spectra of these two systems in the low ligand molar excess region (see Supporting Information). This study will be reported elsewhere.

(8) A plot of the Soret band intensity at 411 nm against [**ZnD**]/([**ZnD**] + [**L**]), where **L** is 1,2-diphenylethylenediamine, has a minimum at 0.5 that corresponds to formation of the 1:1 complex at the low ligand molar excess region (see Supporting Information).

(9) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371−392.

porphyrin electronic transitions become optically active. The B_{II} coupling transitions that determine the chirality sign adopt a clockwise orientation that according to the CD exciton chirality method[10] corresponds to positive chirality, which is observed experimentally. In the case of (*S*,*S*)-DPEA, the dipole's coupling directions in the tweezer structure are exactly opposite resulting in negative chirality.

Further addition of (*R*,*R*)-DPEA causes dramatic changes of the UV−vis and CD spectral patterns (Figure 2b) due to a stepwise equilibrium shift toward the 1:2 complex. Correspondingly, in the UV−vis spectra the intensities of the two bathochromically shifted transitions (421 and 436 nm) increase, while the intensity of the higher energy transition (411 nm) decreases. These changes are associated with formation of the extended *anti* **ZnD·L$_2$** species;[4] however, as a result of the high stability of the tweezer complex even at large excesses of (*R*,*R*)-DPEA complete conversion to the 1:2 complex is not achieved. Remarkably, this increase of the ligand concentration results in chirality inversion with a positive CD couplet gradually transforming into a new negative CD couplet (Figure 2b). This reveals an opposite spatial orientation of the coupling electronic transitions in *anti* **ZnD·L$_2$** in comparison to those in **ZnD·L**. Indeed, CPK model analysis clearly reveals that (*R*,*R*)-DPEA induces a left-handed twist in *anti* **ZnD·L$_2$** to minimize steric hindrance between the bulkiest substituent of (*R*,*R*)-DPEA, Ph(NH_2)-CH, and the porphyrin ethyl group (Figure 1c). In the left-handed twist the B_{II} coupling transitions form an anticlockwise turn producing negative chirality in accordance with the CD exciton chirality method[10] (Figure 1f), which is in complete agreement with the obtained experimental data and with the mechanism of the chirality induction.[4]

To confirm the presented two-step complexation mechanism and to obtain the equilibria and spectral parameters of the chirality induction and inversion processes, CD titration experiments of **ZnD** with (*R*,*R*)- and (*S*,*S*)-DPEA were carried out at low and high ligand molar excesses. The experimental points show very good correlation with the theoretical 1:1 and 1:2 complexation curves for the low and high ligand concentration regions, which correspond to the chirality induction and inversion processes, respectively (Figure 3). It was also found that tweezer formation (chirality induction) is a highly energetically favorable process with K_1 (19 °C) = 1.44×10^7 M^{-1}, whereas formation of the *anti* form (chirality inversion) is less energetically favorable, K_2 (19 °C) = 1.10×10^3 M^{-1}. The remarkably large K_1 value is due to the optimal geometry of the 1:1 complex, stabilized by two spatially well orientated Zn−N coordination bonds and additional host−guest $\pi-\pi$ interactions (Figure 1b). Additionally, this large difference in the free energy change ($\Delta\Delta G$ = 5.5 kcal mol^{-1}) was found to agree with the molecular peak intensities of the 1:1 and 1:2 complexes in the ESI MS spectrum, with the molecular peak of [**ZnD·L**]$^+$ 4.2 times higher than that of [**ZnD·L$_2$**]$^+$.

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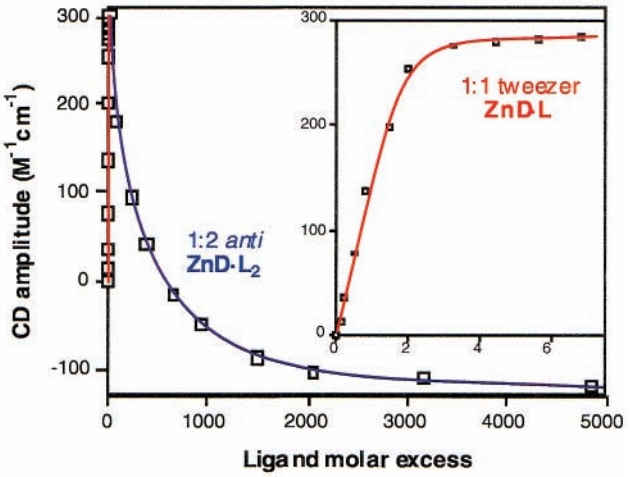

Figure 3. Dependence of the CD amplitude of **ZnD** upon the molar excess of (*R*,*R*)-DPEA. The red line and blue line show the 1:1 and 1:2 complexation processes, respectively. Inset: expanded area of the CD amplitude dependence at the low ligand molar excess region.

The CD amplitudes (*A*) of **ZnD·L** and **ZnD·L$_2$** (where **L** is (*R*,*R*)-DPEA) calculated on the basis of the theoretical complexation curves are +304 and −145 M^{-1} cm^{-1}, respectively. The opposite signs are due to the different twist directions in **ZnD·L** and **ZnD·L$_2$** as discussed above, and the larger *A* value of the 1:1 complex is a result of the enhanced unidirectional rigidity of the tweezer, which arises from the two point interactions that considerably decrease the conformational freedom of **ZnD·L**. The *A* value of **ZnD·L$_2$** falls within the range of the *A* values found experimentally for monoamines containing bulky substituents at saturated ligand concentrations.[4] The spectral and binding parameters evaluated for (*S*,*S*)-DPEA are identical to those for (*R*,*R*)-DPEA within experimental error, while the signs of the *A* value are opposite.

Among the bifunctional ligands studied[5] only enantiopure DPEA exhibits the unique property of both chirality induction and inversion that is discussed in this report. However, for other bifunctional ligands the same *syn* to *anti* changes occurring via the stepwise 1:1 then 1:2 complexation mechanism were observed, and the chirality induction and inversion phenomenon described here is, in principle, possible for other ligands of this type.

In summary, this work demonstrates clearly that the stoichiometry alone can effect supramolecular chirality induction and subsequent inversion control in an achiral host.

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Supporting Information Available: UV−vis, ^{1}H NMR spectra, and Job plot data. This material is available free of charge via the Internet at http://pubs.acs.org.

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