

Remarkable Stability and Enhanced Optical Activity of a Chiral Supramolecular Bis-porphyrin Tweezer in Both Solution and Solid State

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A supramolecular tweezer is defined as a specially shaped type of 1:1 host–guest complex arising from the insertion of a guest molecule between two binding sites of a molecular host through various noncovalent interactions, which lead to a fascinating spatial architecture, resembling a pincer holding an object. Bis-porphyrin derivatives linked by a single covalent tether are well-suited to serve as host compounds for the tweezer structure as a result of their unique physicochemical and spectroscopic properties. Although only a few bis-porphyrin based chiral tweezers have been reported thus far, they are of prime interest not only due to their sophisticated molecular design, but also due to diverse practical applications.¹ Here, we describe a spectacular example of the remarkable stability of a chiral tweezer structure possessing high optical activity in both solution (even upon photoexcitation) and solid state.

Recently it was found that bis(zinc octaethylporphyrin)² (*syn*-**ZnD** in Figure 1) serves as an effective achiral host molecule to form chiral tweezers (**ZnD**·**L** in Figure 1) upon interaction with enantiopure bidentate guests.³ The established binding mechanism includes the initial formation of the 1:1 tweezer complex followed by an equilibrium shift toward the extended 1:2 complex at higher ligand concentrations. We now report our surprising finding that in the case of enantiopure 1,2-diaminocyclohexane (DACH) the 1:1 chiral tweezer structure is formed exclusively, regardless of the amount of ligand used. This process was monitored by UV–vis, CD, ¹H NMR, and ESI MS and studied for the first time by fluorescence spectroscopy. In the sharp contrast to other bidentate ligands³ the extraordinary stability of this tweezer results in the greatest ever reported induced chirality in this bis-porphyrin system.

The UV–vis spectrum of **ZnD**·**L** (**L** = DACH) is essentially the same as that of the reported chiral tweezers,³ while differing drastically from the spectrum of *syn*-**ZnD** (Figure 2). Particularly notable features of the tweezer complexes include a bathochromically shifted and split Soret band associated with the ligation process and exciton-coupled porphyrin B electronic transitions. These spectral changes are in good agreement with exciton coupling theory⁴ and are indicative of the twisted spatial rearrangement of the two pairs of the B transitions in **ZnD**·**L** from its initial parallel orientation in *syn*-**ZnD** (Figure 1). Simultaneous CD monitoring of this process shows the appearance of bisignate Cotton effects in the porphyrin Soret band region (Figure 2, inset). The position of the first Cotton effect (436 nm) well matches that of the most bathochromically shifted absorption band in the UV–vis spectrum that arises from the lowest-energy $B_{||}$ coupling transitions. Thus,

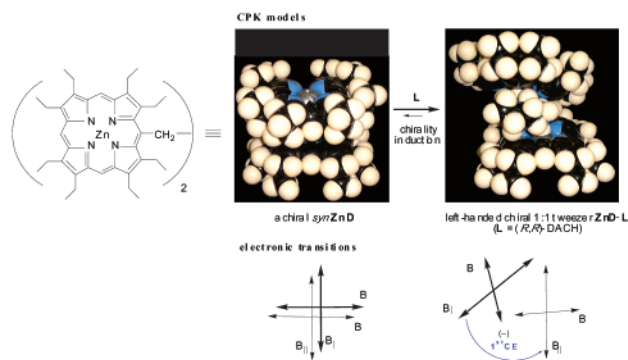


Figure 1. CPK molecular models and coupling electronic transitions of supramolecular chirogenesis in achiral *syn*-**ZnD**.

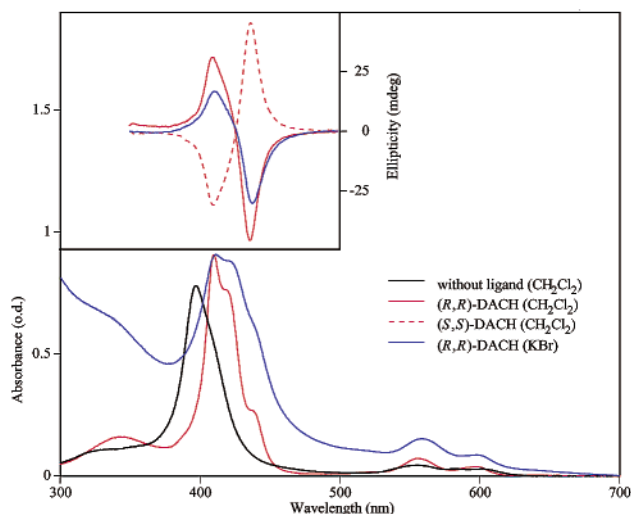


Figure 2. UV–vis and CD (inset) spectra of **ZnD** without ligand and in the presence of chiral ligands in both solution and solid state.

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 DACH induces negative chirality, while the antipodal (*S,S*)-ligand produces positive chirality.

An examination of CPK molecular models reveals that the diamines studied are readily accommodated between the two porphyrin planes of **ZnD**·**L** to yield a stable 1:1 tweezer complex. Following to the ligand's geometry and minimizing the steric hindrances the two porphyrins in **ZnD**·**L** form a left-handed twist upon coordination to (*R,R*)-DACH (Figure 1). As this takes place, the $B_{||}$ coupling transitions that determine the chirality sign adopt an anticlockwise orientation that, according to the CD exciton

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chirality method,⁵ corresponds to negative chirality, which is observed experimentally. In the case of (*S,S*)-DACH the dipole's coupling directions in the tweezer structure are exactly opposite resulting in positive chirality. It is noteworthy that the twist direction, and thus chirality sign, is the same as that induced by enantiopure monofunctional ligands⁶ for the corresponding enantiomer, which is important for the diagnosis purpose.

To confirm the complex stoichiometry and to obtain the binding and spectral parameters of the chirogenesis process, the corresponding UV-vis and CD titration experiments were carried out (see Supporting Information). In the UV-vis spectra the intensity of the Soret band of *syn*-ZnD (397 nm) gradually decreases upon addition of the enantiopure DACH, while new spectral bands associated with ZnD·L appear simultaneously; in the CD spectra there is stepwise enhancement of the bisignate Cotton effects, which are described above. The monitoring parameters were UV-vis absorbance at the wavelength corresponding to the maximum of the most intense *B* transition (for UV-vis spectroscopy) and total CD amplitude (*A*) (for CD spectroscopy). The observed spectral changes show excellent correlation with the theoretical 1:1 complexation curve, and no indication of any 1:2 binding is detected.⁷ It was also found that tweezer formation is a highly energetically favorable process with an equilibrium constant K (19 °C) = $1.25 \times 10^7 \text{ M}^{-1}$. This remarkably large K value is due to the optimal geometry and enhanced unidirectional rigidity of the 1:1 complex, stabilized synergetically by two spatially well orientated Zn-N coordination bonds arising from the preorganized two amino substituents in DACH (Figure 1). These factors are also responsible for the suppression of the possible 1:2 complex formation that is clearly seen in the case of other bifunctional ligands.³ The *A* value of ZnD·L (where L is (*R,R*)-DACH) calculated on the basis of the theoretical complexation curve is $-589 \text{ M}^{-1} \text{ cm}^{-1}$. This is the largest *A* value ever reported for a chirality induction process involving this bis-porphyrin host,^{3,6} arising from the above-mentioned structural features of ZnD·L. The spectral and binding parameters evaluated for (*S,S*)-DACH are identical to those for (*R,R*)-DACH within experimental error, while the sign of the *A* value is inverse due to the induction of opposite chirality.

Interestingly, reflecting this remarkable stability of the 1:1 tweezer complex, the UV-vis and CD spectral profiles of ZnD·L in the solid state⁸ are essentially the same as those in solution phase (Figure 2). However, substantial broadening of the Soret band and decrease of the anisotropy (*g*) factor observed in the solid state are apparently a result of the formation of intermolecular aggregates of opposite chirality in the solid state, as reported in the case of monoamines.⁹

Investigation of this phenomenon by NMR spectroscopy clearly demonstrates formation of the 1:1 tweezer complex (see Supporting Information). The most intriguing feature of the ¹H NMR spectrum of ZnD·L is the extraordinary large upfield shift ($\Delta\delta = 8.9 \text{ ppm}$) of the $-\text{CH}(\text{NH}_2)-$ protons of L, arising from their proximity to both of the porphyrin subunits and are thus affected strongly by the ring currents. On the other hand, the $-\text{CH}_2\text{CH}_2-$ bridge protons and 10,20-*meso* protons are noticeably downfield-shifted due to conformational changes upon tweezer formation, which results in moving the two porphyrin rings farther apart from each other and subsequently decreasing the shielding effect of the neighboring porphyrin. Furthermore, these protons become nonequivalent in the chiral tweezer as a result of their different exposure to the ring-current effect. Further firm evidence of the tweezer structure is the

observation of the positive NOE cross-peaks in the ROESY spectrum of ZnD·L due to through-space interactions between the ligand's protons and the porphyrin *meso* protons.

The ESI MS spectra of ZnD·L also unambiguously support exclusive formation of the 1:1 complex (see Supporting Information). Thus, in the presence of DACH besides a signal of the molecular ion $[\text{ZnD}]^+$, only a new peak attributed to $[\text{ZnD}\cdot\text{L}]^+$ is observed at 110 °C. Lowering the temperature increases the relative intensity of the $[\text{ZnD}\cdot\text{L}]^+$ signal due to enhancement of the ligand binding strength, while there is no indication of the peak associated with a 1:2 complex.

Important results have been obtained upon investigation of the excited state of ZnD·L by fluorescence spectroscopy (see Supporting Information). The induced chirality sign in the circularly polarized fluorescence spectrum is the same as that in the CD spectrum in the region of the porphyrin Q-bands. Also the fluorescence and absorption *g* factors correlate well with each other (2.7×10^{-3} and 3×10^{-3} , correspondingly). These results clearly indicate at structural similarity of the 1:1 complex in the ground and singlet excited states of ZnD·L due to the enhanced rigidity of the tweezer, which is independent upon the electronic state involved. Additional evidence for the conformational stability of this complex in the excited state is the monoexponential fluorescence decay profile with a lifetime of 1.62 ns, which is distinctly different from that of *syn*-ZnD.

In summary, this work shows clearly that the enhanced conformational stability of the tweezer complex ensures an efficient chirality information transfer from a chiral guest to achiral host via supramolecular association mechanism.

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Supporting Information Available: UV-vis, CD, ¹H NMR, ESI MS, fluorescence spectral data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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