Origin, Control, and Application of Supramolecular Chirogenesis in Bisporphyrin-Based Systems

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ABSTRACT
The rationalization of various aspects of the mechanism of chirality induction in supramolecular assemblies based upon the complexes formed between an ethane-linked bisoctaethylporphyrin and chiral ligands is described. The influence of various controlling factors such as bonding strength, host−guest steric interactions, equilibria and thermodynamic parameters, temperature and solvent effects, role of the center metal ion, stoichiometry, and phase transition on the chirality induction processes have been investigated, and the results and implications are discussed. As a result of such detailed understanding, it is possible to employ this bisporphyrin system as an effective chirality sensor for the determination of absolute configuration.

Introduction

Supramolecular chirogenesis is a modern interdisciplinary field of research based on the principles of supramolecular chemistry and molecular chirality and essentially deals with asymmetry information transfer upon noncovalent interactions. This intriguing phenomenon is widely seen in many natural (such as DNA double helix, the secondary α-helix structure of proteins, and heme proteins) and various artificial systems[1] and is of prime importance not only for fundamental science but also for a number of practical applications in such areas as materials and polymer sciences, enantioselective catalysis and nonlinear optics, chiral memory, and the determination of absolute configuration. Therefore, understanding the mechanisms and various influencing factors is of particular significance for smart control and further effective application of supramolecular chirogenesis. Since noncovalent interactions are the key elements in supramolecular chirogenesis, there are several external (temperature, phase transition, polarity, etc.) and internal (bonding strength, steric and electronic effects, stoichiometry, etc.) stimuli that may affect these interactions and consequently the whole chirality induction process.

Recently porphyrinoids have been shown to be well-suited for studying the processes involved in supramolecular chirality induction owing to their spectral and physicochemical properties, easy handling and versatile modification, great biological importance, and wide applicability.[2] These attractive features prompted us to apply porphyrin compounds for comprehensive investigation of supramolecular chirogenesis; in particular, it was found that the ethane-bridged bisporphyrin (**1**) (Figure 1) may serve as an effective achiral host, forming chiral host−guest assemblies upon noncovalent interaction with chiral guests. Furthermore, these systematic studies led to the development of **1** as an efficient chirality sensor for various classes of chiral compounds and opened up further perspectives for the design of smart chiroptical devices.

Description of Supramolecular System, Equilibria, and Host−Guest Binding

The essential molecular system that has been used in our studies of supramolecular chirogenesis is based on the bisporphyrin **1**, which is comprised of two octaethylporphyrins covalently linked at the meso positions by a flexible ethane bridge (Figure 1).

The key functional features of this system are as follows: first, the center metal, the variation of which allows the coordination of ligands with different functional groups; second, the ethane bridge the flexibility of which allows different coplanar orientations between the two porphyrin moieties upon interaction with external guests while retaining them in close spatial proximity; third, the peripheral ethyl groups, which allow chiral steric interactions with the coordinated ligand (L) and block rotation of the two porphyrins around the ethane-bridge axis.

It was shown that in nonpolar, noncoordinating solvents, **ZnZn** is in a syn face-to-face conformation.[3,4] This spatial arrangement is extremely stable with no observable changes in the conformation even upon heating to 110 °C.[4] This high stability arises from the strong $\pi-\pi$ interactions between the chromophoric moieties, in large part due to the highly planar nature of the zinc porphyrins, which allows very effective interporphyrin interactions. This can be illustrated by comparison of **ZnZn** with **Zn2H**, which has a greater degree of flexibility in the syn-form due to the ruffled, less-planar nature of the free-base porphyrin.[3,5]

The syn-form is found to be changed to the extended anti-form on the addition of a suitable coordinating

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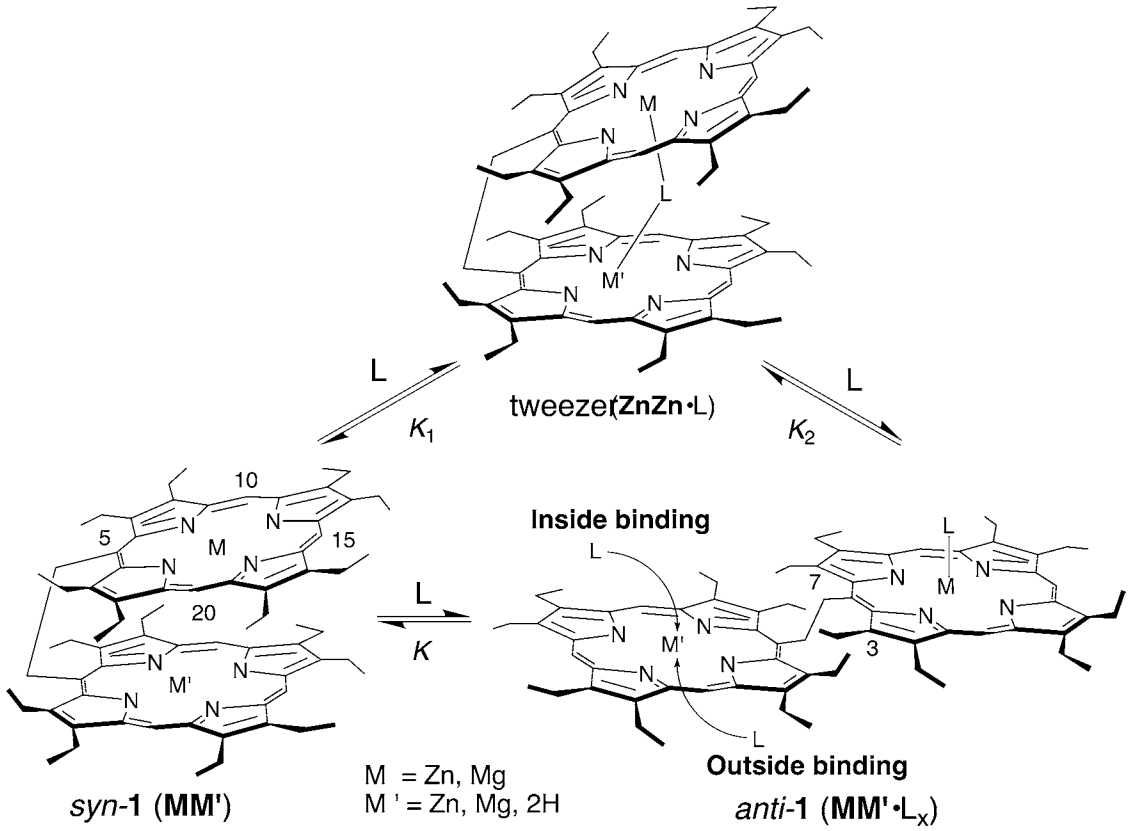

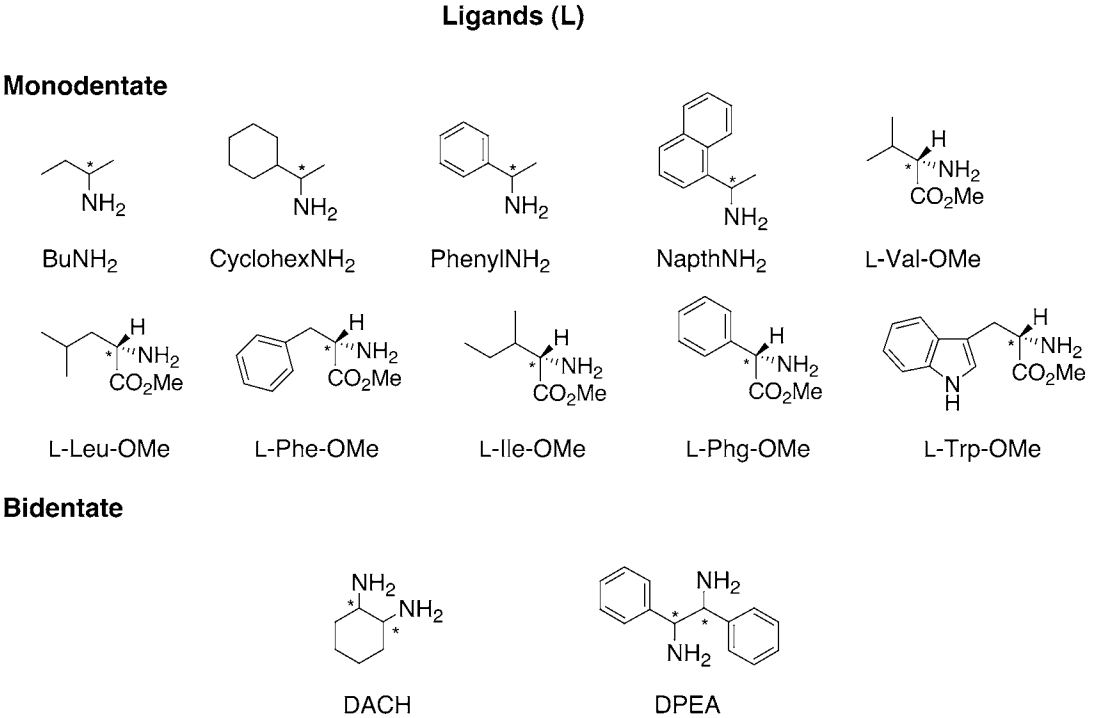

FIGURE 1. The three principal conformations adopted by **1** and the structures of representative ligands.

monodenate ligand, which can be easily monitored by UV−vis and other spectroscopic techniques due to profound differences in the spectral characteristics of the syn- and anti-forms.[4] This syn−anti conformational switching is a general feature for the supramolecular host **1** whether the guest is chiral or not. However, when a chiral guest is used, a new type of structural deformation is observed owing to an effective asymmetry transfer mechanism, which can be detected by circular dichroism (CD) spectroscopy.

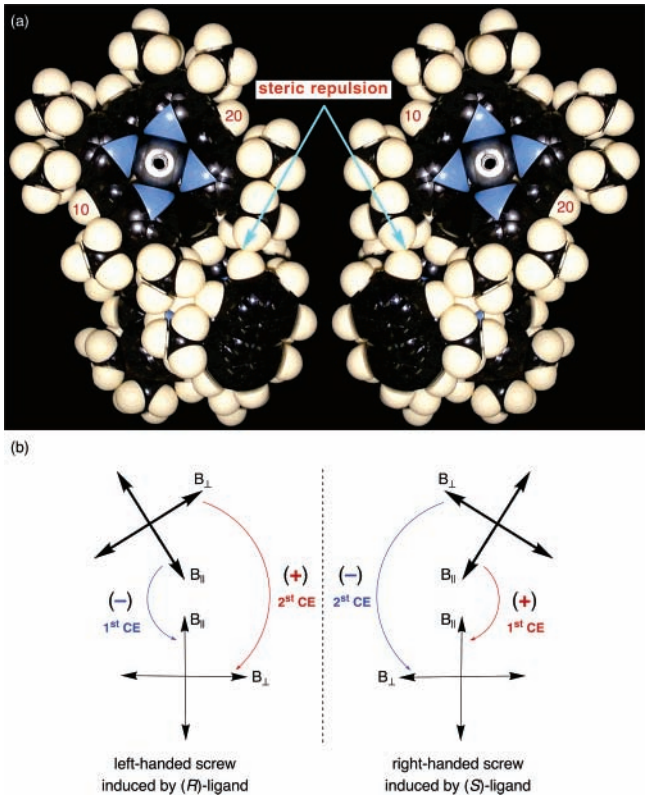

FIGURE 2. (a) The mechanism of chirality induction in **1**, the ligand shown is NaphthNH$_2$ and (b) the orientation of the Soret band electronic transitions in chiral complexes.

Mechanism of Chirality Induction and the Role of the Number of Binding Sites

Upon addition of a chiral ligand, dramatic changes are observed in the associated CD spectra as a result of stereospecific deformations in **1** caused by asymmetry transfer from the chiral ligand to achiral host **1** to yield anti-**ZnZn**·L$_2$.[6] This includes the appearance of pronounced bisignate Cotton effects (which are signals in the CD spectra caused by the differential absorption of right- and left-handed circularly polarized light by a chiral compound) in the region of the Soret band of the porphyrin. The positions of the maxima and minima of the Cotton effect are well-matched to the corresponding split B$_{||}$ and B$_{\perp}$ transitions observed in the UV−vis spectra, which are aligned parallel and perpendicular to the ethane bridge, respectively (Figure 2), indicating a common origin of the transitions. Importantly, the sign and intensity of these bisignate Cotton effects are highly dependent on the absolute configuration and structure of the ligand.

The chiral information transfer is achieved via the influence of the chiral steric field of the coordinated ligand upon the achiral host, resulting in subsequent chiral deformations. On examination of Corey−Pauling−Koltun (CPK) models of anti-**ZnZn**·L$_2$, it is instantly recognizable that the steric interactions between the 3,7-ethyl groups of the porphyrin and the substituents of the ligand bound to the adjacent porphyrin moiety result in induced supramolecular chirality due to unidirectional screw formation in **1** (Figure 2), while other ethyl groups are found to be too distant.[6a] Further, the steric hindrance between the

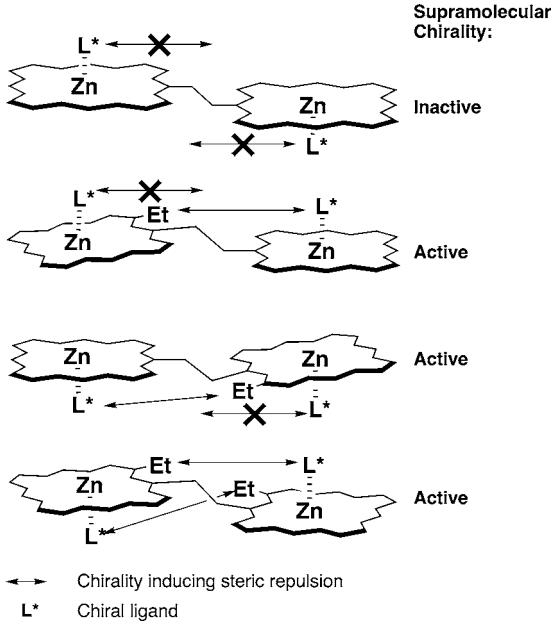

FIGURE 3. Schematic representations of chirogenic activity upon inside and outside binding in anti-**ZnZn**·L$_2$.

3,7-ethyl groups of the two porphyrin moieties makes it impossible for the two porphyrins to rotate around the ethane-bridge axis, which would result in racemization of the induced screw. For monodentate ligands, the more bulky group governs the screw formation due to its closer proximity to the 3,7-ethyl groups.

The formation of the screw structure can be clearly seen in the ^{1}H NMR spectra. The environments of the 10- and 20-protons become nonequivalent, as shown in Figure 2. Depending on the direction of the screw, one of these protons becomes more shielded by the neighboring porphyrin, while the other becomes less affected, thus resulting in the clear split in these signals that are averaged for achiral ligands.

It is important to realize that the size of the induced screw rotation is dependent upon the difference between the magnitudes of the steric repulsions caused by the individual guest substituents and hence is a key factor in the chirogenesis processes. The crucial importance of the substituent's steric effect is further exemplified by the distance dependence of the chiral center to the binding site. When the chiral center is at a position β to the coordinating group, the chirally orientated substituents are further apart from the 3,7-ethyl groups, which correspondingly reduces the steric repulsion effect felt by the neighboring porphyrin and thus reduces the degree of the induced screw resulting in smaller induced CD signals.[6a]

Due to the dynamic, supramolecular nature of this system, there are a number of possible conformations. Thus, there are two basic modes of binding for the ligands in anti-**ZnZn**·L$_2$, inside binding and outside binding (Figures 1 and 3). In the case of inside binding, the ligation occurs from the side that results in a close spatial proximity to the ethyl groups of the adjacent porphyrin, thus allowing chiral supramolecular steric interactions,

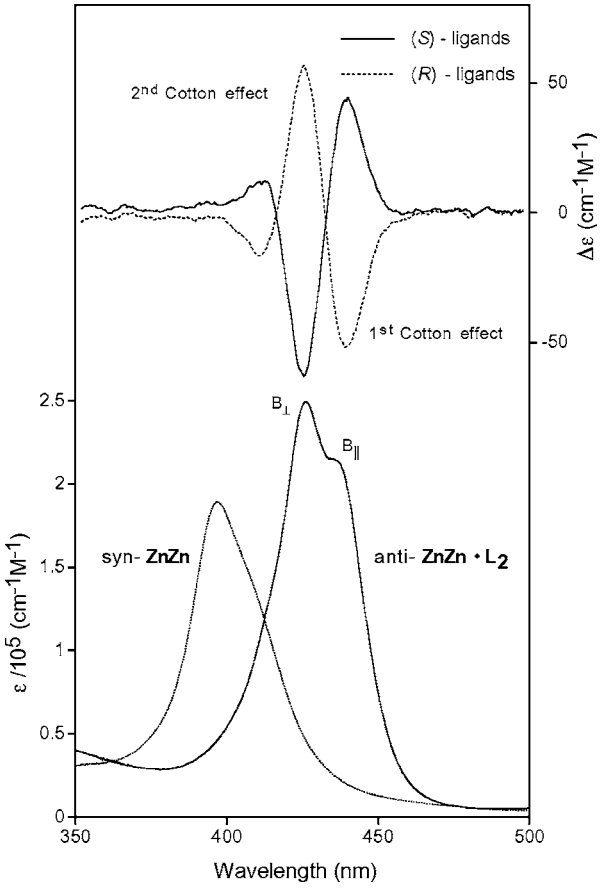

FIGURE 4. The UV−vis and CD spectra of **ZnZn** upon interaction with enantiopure ligands to form anti-**ZnZn**·L_2.

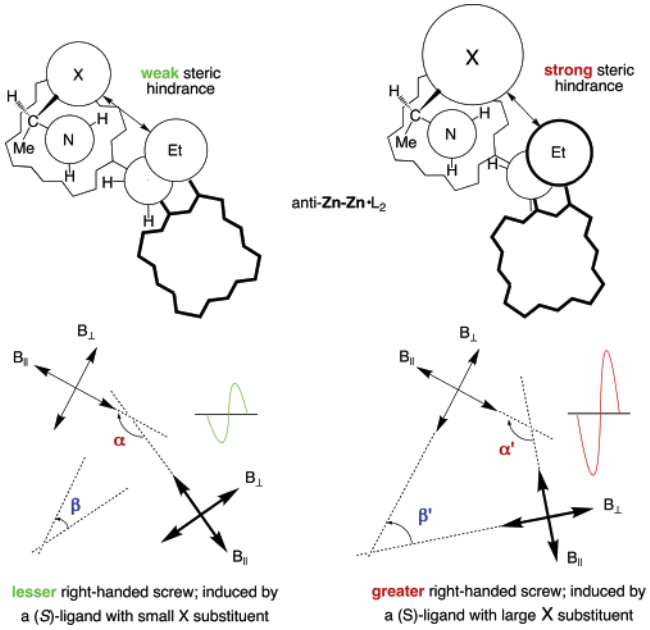

FIGURE 5. Bulkiness effect on the magnitude of the supramolecular chirogenesis in anti-**ZnZn**·L_2.

while for outside binding, these interactions cannot occur because of the distant location of the ligand.

The presence of these steric interactions is nicely demonstrated by comparing the differences in structural rigidity between **ZnZn**·L_2 and **Zn2H**·L, as determined by the full width at half-maximum (fwhm) values of their UV−vis spectra (the smaller the fwhm value, the more rigid the species). Due to the presence of only one binding site in **Zn2H**·L, the percentage of possible conformations with the potential for exhibiting these steric interactions is lower than that for **ZnZn**·L_2, and therefore, the whole system should be more flexible. Indeed **Zn2H**·L displays fwhm values greater than the corresponding **ZnZn**·L_2. This greater number of chiral steric interactions, and consequently enhanced rigidity, directly translates into an increase of ca. 250% in induced supramolecular chirality for **ZnZn**·L_2 over **Zn2H**·L.[5]

Role of the Absolute Configuration of the Guest

As stated above, on coordination of a ligand to **ZnZn** there is syn−anti conformational switching resulting in a pronounced red shift and split of the Soret band in the absorption spectra due exciton coupling in the extended conformation (Figure 4). Furthermore, addition of chiral ligands results in the appearance of bisignate Cotton effects in the CD spectra. Importantly the induced chirality is highly dependent on the absolute configuration and structure of the ligand. For conventional monodentate ligands of which the substituent size order correlates with the Cahn−Ingold−Prelog priority rule system for absolute configuration assignment, it is found that (*S*)-enantiomers give rise to first positive and second negative Cotton effects, while for (*R*)-enantiomers the situation is opposite (Figure 4).[6,7] However, if the substituent size order does not correspond with the priority rule then the opposite Cotton effect order is observed for the same enantiomer.[8] This is because, for example, in the case of (*S*)-enantiomers, the largest substituent (on the right-hand side, Figure 2) interacts with the 7-ethyl group forcing the two porphyrins into a right-handed screw and thus generating positive chirality with (*R*)-enantiomers producing exactly opposite effects.

The chirality of the system is defined as that observed for the lowest energy Soret band transition ($B_{\parallel}$). Therefore, according to the exciton chirality method,[9] in the case of (*S*)-enantiomers the relative orientation between the two $B_{\parallel}$ electronic transitions is clockwise (corresponding to positive chirality), while for (*R*)-enantiomers the sign of the induced chirality is opposite.

Host−Guest Steric Interactions and Substituent Bulkiness Effect

As stated above, the degree of supramolecular chirogenesis has a dependency upon the magnitude of the steric host−guest interactions. This has been further investigated by varying the size of the ligand's substituents. As seen schematically in Figure 5, as the size of the largest substituent of the ligand is increased the steric repulsion between it and either the 3- or 7-ethyl group (depending upon the absolute configuration) is correspondingly enhanced; thus to minimize this repulsion, the screw angle

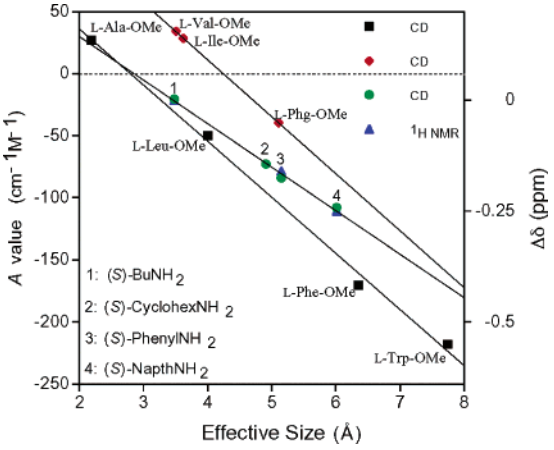

FIGURE 6. Dependence of the *A* and $\Delta\delta$ values on the effective size of the bulkiest substituent for three homologous groups.

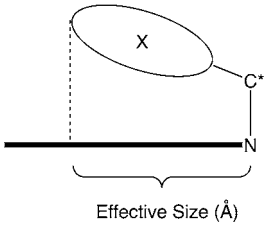

FIGURE 7. Definition of the effective size of the substituents of the ligand.

between the two porphyrins increases. This results in a change of the angle between the respective B band transitions resulting in more intense CD signals. Further, the greater screw induced by bulkier substituents is clearly observed in the ^{1}H NMR spectra; because of their proximities close to the neighboring porphyrin, the 10- and 20-protons are particularly diagnostic, yielding larger splits ($\Delta\delta$) for these signals.[6a]

It is found that there is a direct linear relationship between the total CD amplitude (*A* value) and $\Delta\delta$ values of homologous systems and the size of the largest substituent (Figure 6), even resulting in chirality inversion.[6a,7,8] The size of the substituent is defined by its "effective size", which is obtained by determining the horizontal distance between the amine and the furthest point of the largest substituent in a MM2 minimized molecule (Figure 7), because this correctly represents the steric interactions in anti-**ZnZn**·L_2.

It is crucial to realize that, due to the dynamic nature of the bound ligand (able to rotate around the Zn−N bond), it is not the absolute effective size of the largest substituent that determines the screw size but the difference between the effective sizes of the substituents of the ligand because both are exerting (chirally opposite) steric influences on the adjacent porphyrin. This is exemplified by the chirality inversion phenomena observed in the homologous series of corresponding L-amino acids (Figure 6).[8]

We have seen previously that for "simple" amines and alcohols **ZnZn** can be used as an absolute configuration sensor. As a result of the understanding of how the substituent bulkiness affects the CD intensity and how the observed chirality inversion arises, we are able to extend the sensoric abilities of these compounds; thus, for a homologous series of ligands, if the chirality is known, the magnitude of the induced chirality is a direct measure of the relative bulkiness of the largest substituent.

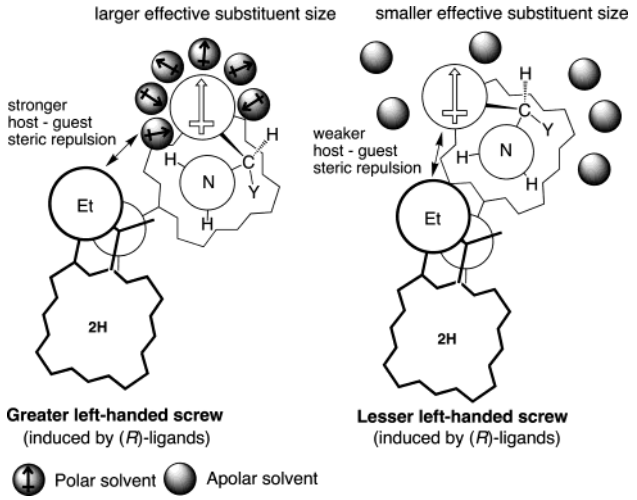

FIGURE 8. Schematic representation of the solvent effect on supramolecular chirogenesis in anti-**Zn2H**·L.

Solvent Effect on Chirality Induction

For supramolecular chirality-inducing systems, all intermolecular interactions and various external factors have the potential to influence the sign and degree of chirogenesis, and thus, their effect must be considered. The medium in which the chirality induction takes place is often overlooked as a significant contributing factor; however, it has been shown that the chiral characteristics of supramolecular systems can be profoundly affected by the solvent used, even leading to chirality inversion, although these observations have been largely perfunctory in nature.[10] Thus, it should always be kept in mind that the solvent molecules are an active part of the supramolecular system, able to interact with the solute molecules according to their own electrostatic and geometric characteristics, and are able to control supramolecular interactions. Therefore, we have investigated, in detail, the solvent influence on supramolecular chirogenesis using **1** in a suitable host−guest system.

From the previous work and knowledge about chirality induction in **1**, in particular the effects of absolute configuration and bulkiness, it was found that the effect of different solvents on the chirality induction in **Zn2H** could help gain a molecular understanding of the contribution that solvent makes to the overall chirogenesis. To this end, the differences in chirality induction in **Zn2H**·L were observed in both polar CH_2Cl_2 and its nonpolar analogue CCl_4. Particularly, it was found that a dramatic decrease was observed for the induced chirality in CCl_4 with the extent of this reduction averaging 45%. The origin of the chirality enhancement in CH_2Cl_2 arises from the greater ability of this solvent to interact, via its pronounced dipolar electrostatic distribution, with the polar substituents of the ligands (Figure 8).[5]

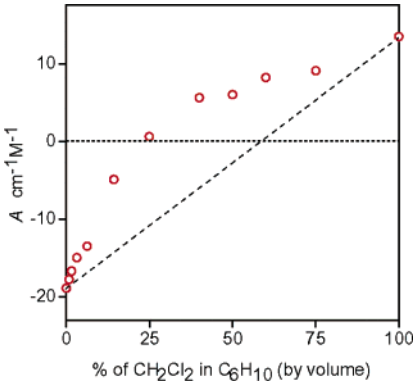

FIGURE 9. The dependence of the induced chirality in anti-**ZnZn**·(L-Ala-OMe)$_2$ on the solvent composition (the dashed line represents the linear dependency expected for no specific solute−solvent interactions).

This is typified, for example, by the greater increase in chirality induction for PhenylNH$_2$ versus CyclohexNH$_2$ in CH_2Cl_2 compared with CCl_4. Due to the quadrupolar electrostatic distribution of the phenyl moiety, it is able to interact with the dipolar distribution of CH_2Cl_2, whereas this interaction is greatly reduced for the cyclohexyl moiety. The result of this is that the effective size of the phenyl moiety is increased upon formation of a specific solvent shell by interaction with the CH_2Cl_2 resulting in an increase in the steric repulsion between this substituent and the 3- and 7-ethyl groups and consequently increasing the screw angle and induced chirality.

This effect of manipulation of the effective sizes of the substituents of ligands via interaction with solvents can be to such a degree that the chirality can even be inverted. By considering **ZnZn**·L$_2$ and the effect of its chirality induction by application of a range of mixed solvents, the true intermolecular origin of the changes in supramolecular chirogenesis can be revealed.[11] To this end, L-Ala-OMe was employed, using differing ratios of polar CH_2Cl_2 and nonpolar hexane as the solvent (Figure 9). In hexane, this system only displays a weak negative bisignate Cotton effect due to the similar effective bulkinesses of the methyl and methyl ester substituents, methyl dominating. As the percentage of CH_2Cl_2 is increased, the negative chirality is reduced and finally undergoes chirality inversion. This transition is dramatically nonlinear with the complex going through the racemic point at only 25% CH_2Cl_2.

This nonlinearity clearly reveals the presence of highly selective solvent−solute interactions. When the solvent is pure hexane, this has only a weak electrostatic distribution and thus does not particularly interact with the ligand, and the bulkiness of the methyl group dominates. However, the polar CH_2Cl_2 is able to interact strongly and specifically with the polar ester group in comparison to the nonpolar methyl group. The mechanism is the same as the observed chirality enhancement in **Zn2H**·L (Figure 8). Clearly then, when steric effects that may alter conformations in achiral supramolecular systems and the optical activity in chiral ones are considered, the general consideration of the interaction of nonpolar/polar solvents with parts, or the entirety, of the complex should be carefully considered, especially in borderline cases where the differences between the competitive steric interactions are small and can be easily shifted by the manipulation of pertinent factors.

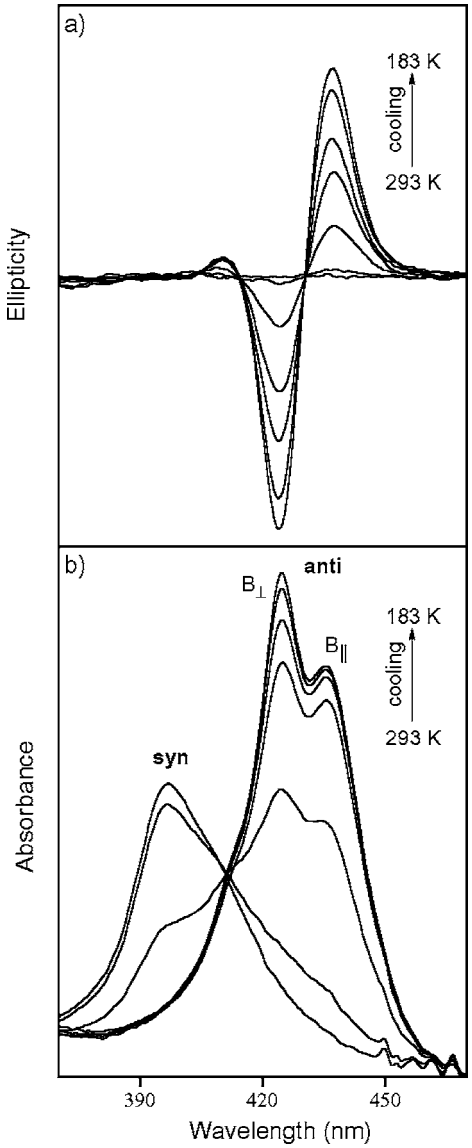

FIGURE 10. The effect of temperature on the UV−vis and CD spectra of the **ZnZn**·L$_2$ system.

Temperature, Thermodynamics, and Enthalpy−Entropy Compensation Aspects

Another factor that may control supramolecular interactions, and thus chirality induction in such host−guest systems, is temperature. For example, it is obvious that changing the temperature directly affects the binding strength of the coordination pair. Thus, temperature control was thoroughly studied in **ZnZn**·L$_2$.[12]

Reduction in temperature results in enhancement of the degree of chirality induction in **ZnZn**·L$_2$ on the application of chiral ligands, Figure 10. This is due to an increase in the percentage of bound ligand and thus an

increase in the degree of chiral steric interactions occurring along with a general reduction in thermal molecular motion.

It is clear that due to the dynamic nature of supramolecular systems the effect of temperature will be crucially important. Indeed, all intermolecular processes and their function will be, to some extent, affected by temperature, so to rationalize its influence in specific and general terms is highly important. Further variable temperature experiments allowed the thermodynamic parameters of this system to be determined, and a remarkable entropy−enthalpy compensation effect was revealed.

For supramolecular chirogenesis in anti-**ZnZn**·L_2 both the $\Delta H°$ and $\Delta S°$ values are negative. This is a generally observed situation for such complexation processes where the forward equilibrium is driven by the enthalpic gain of ligand coordination, accompanied by the associated negative entropy arising from the reduction in translational and conformational freedom. For ligands with alcohol coordinating groups, it is found that the $\Delta H°$ values are less negative than for amines but with similar entropies; this is expected for the well-known weaker coordination of alcohols to zinc porphyrins and results in positive $\Delta G°$ values at room temperature making the chirogenesis process thermodynamically unfavorable. On the other hand, the stronger binding of amines at room temperature produces comparatively more negative $\Delta G°$ values.[13]

It has been observed in a number of chemical and biological supramolecular host−guest systems that there is a compensatory relationship between the enthalpy and entropy, that is, as the enthalpy becomes more favorable, the entropy becomes less so, and vice versa.[14] Interestingly however this relationship cannot be mathematically derived from fundamental thermodynamics. Nevertheless, when the $T\Delta S$ data are plotted against the ΔH values for a particular host−guest system, good-to-excellent linear relationships are obtained, from which two important insights can be gained. First, the plots provide a measure of the extent to which the enthalpic gain (or loss) is canceled by accompanying entropic loss (or gain) and thus the degree of conformational change on complexation, and second, they serve as a parameter for the extent of desolvation on complexation.

If the $T\Delta S$ and ΔH data of **ZnZn**·L_2 and **Zn2H**·L are plotted in such a manner, two independent linear plots are obtained.[15] Interestingly, these plots are distinguishable not by the host but by the guest type. This suggests separate complexation characteristics primarily due to the different nature of the coordination bonds formed between the amines and alcohols and the differing solvation and geometry of these ligands. In contrast, the differences between **ZnZn** or **Zn2H**, such as the different number of coordination sites and the differing planarity of the porphyrin moieties, appear to be much less influential.

Clearly then, thermodynamic control and entropy−enthalpy compensation are important factors that play significant roles and should be taken into account when studying supramolecular chirogenic processes.

Role of the Center Metal Ion

As seen previously, **ZnZn** and **Zn2H** are highly effective for the study of supramolecular chirogenesis upon interaction with chiral guests such as amines at room temperature and alcohols at low temperature. However, in general, efficient chirality induction can be achieved by using different types of chiral compounds if the correct selection of the appropriate coordination pair is made. One of the attractive features of porphyrins is the relative ease with which different metals can be inserted into its center. Thus, the selection of appropriate metals for **1** raises the prospect of thus being able to generate a range of bismetalloporphyrin compounds tailored to specific coordinating groups, thus extending the range of chiral compounds that can be used to induce supramolecular chirality.

A good example is the corresponding derivative **MgMg**, Figure 1. Thus, with use of **MgMg**, it was possible to induce chirality upon interaction with chiral alcohols even at room temperature, owing to the high affinity of magnesium porphyrins for alcohols.[16] Additionally, as an important implication of this metal replacement, determination of the absolute configuration of alcohols and the assessment the bulkiness of the substituent can also be easily achieved. Further expansion of this approach allows the potential for various compounds with different coordination groups (carboxyl, carbonyl, phosphorus, sulfur, etc.) to be effective for chirogenic processes in **1** by insertion of the suitable corresponding metal ion, thus affording a more versatile chiral sensor.

Stoichiometry Effect on Supramolecular Chirality

Often in supramolecular systems, the stoichiometry between host and guest may play a vital role in forming different association species, especially in the case of multiple binding sites. This will certainly have a great impact on the asymmetry transfer mechanism from the chiral guests to the achiral hosts. The importance of this stoichiometry factor can be elegantly demonstrated using **1** upon interaction with chiral bidentate ligands.[17]

We have already seen that in this system the two porphyrin moieties are necessary for effective chirality transfer via the chiral steric repulsive interactions. However, they may play a different functional role and in so doing generate a new chiral species; thus in **ZnZn**, there are two ligand coordination sites, for which it is energetically favorable for both to be bound. In the previous sections, this has been achieved by formation of the 1:2 complex with monodentate ligands. However, it is found that on the addition of suitable bidentate ligands, a 1:1 supramolecular species can be formed in which each of the functional groups of the ligand is coordinated to one of the zinc centers of the host.[17] This structure is described here as a supramolecular tweezer, in which the guest is held between the two porphyrin moieties in a pincer-like fashion (Figures 1 and 11). If the bifunctional ligand is chiral, the asymmetry is effectively transferred to **ZnZn**

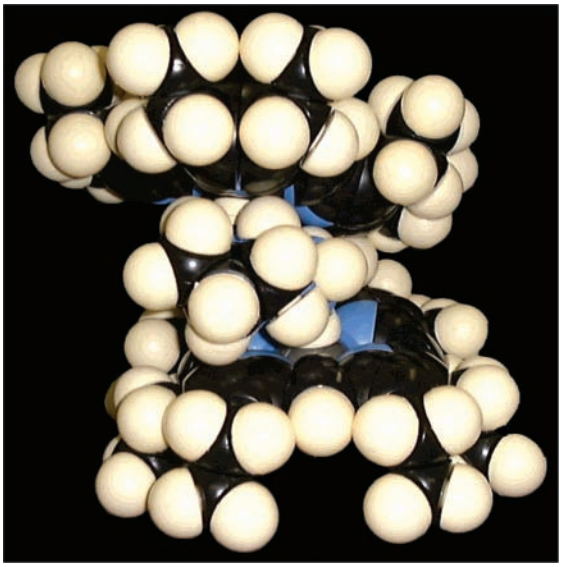

FIGURE 11. CPK representation of the **ZnZn**·[(*R*,*R*)-DACH] tweezer complex.

and is observed to display remarkable and unique chiral and photophysical properties. Only a limited number of porphyrin-based and even fewer chiral porphyrin tweezer complexes have been so far reported[18] but are of significant interest due to their varied applicability.

Essentially the same mechanistic pathway is observed for the formation of all these species (Figure 12). That is, initially (at a low ligand molar excess ratio) syn-**ZnZn** transforms into the **ZnZn**·L tweezer, followed by, in most cases, (at higher ligand molar excess ratios) formation of anti-**ZnZn**·L_2 as seen for monodentate ligands. It is possible to characterize and easily follow the progress of these equilibria due to the highly distinct spectral patterns of each species (Figure 13).

Monitoring the corresponding CD changes reveals the efficient transfer of chirality from the bidentate ligands to the host in the tweezer structure. The characteristics of the chirality induction by bidentate ligands fall into two distinct groups: first, **ZnZn**·L tweezer, and second, anti-**ZnZn**·L_2. For the tweezer species, the CD couplet has significantly larger *A* values of ca. 500 M^{-1} cm^{-1}, Figure 13. This arises from the higher structural rigidity and more optimal geometry for chirality transfer experienced by these tweezer complexes in comparison to the anti-species due to the concerted nature of the two coordination bonds in the 1:1 complex, rather than the dynamic single coordination bonds of the 1:2 anti-species. Upon equilibrium shift toward anti-**ZnZn**·L_2, the *A* values are dramatically reduced by ca. 200 M^{-1} cm^{-1}, which is consistent with these significantly more flexible anti-species.

Interestingly, a strong preorganization effect can be seen in the binding of amino alcohols. It has been previously seen that low temperatures are required for alcohol binding; nevertheless, it is clearly seen that for bidentate amino alcohols **ZnZn** tweezer formation occurs. The reason is the preorganization of the host−guest conformation due to the initial amine binding, which allows the subsequent alcohol to more effectively bind to the second zinc site. In the series of bidentate ligands studied, there are two cases that, in particular, result in surprising and powerful insights into chirogenic stoichiometry effects.[17]

First, the remarkable phenomenon of chirality induction and inversion, based solely on the stoichiometry of the complex, is observed upon interaction with enantiomeric 1,2-diphenylethylenediamine (DPEA) and L-Thr-OMe (Figure 12). Thus, on the addition of (*R*,*R*)-DPEA at the low-concentration region, the formation of the tweezer complex is observed with the generation of positive

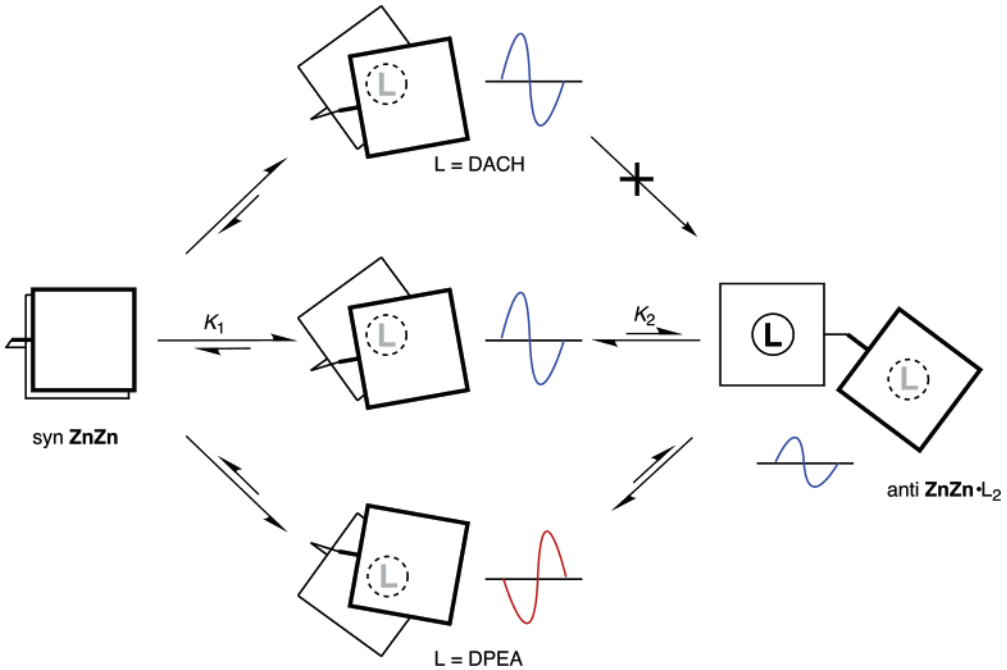

FIGURE 12. Schematic representation of the equilibria between the syn-, tweezer, and anti-**ZnZn** species.

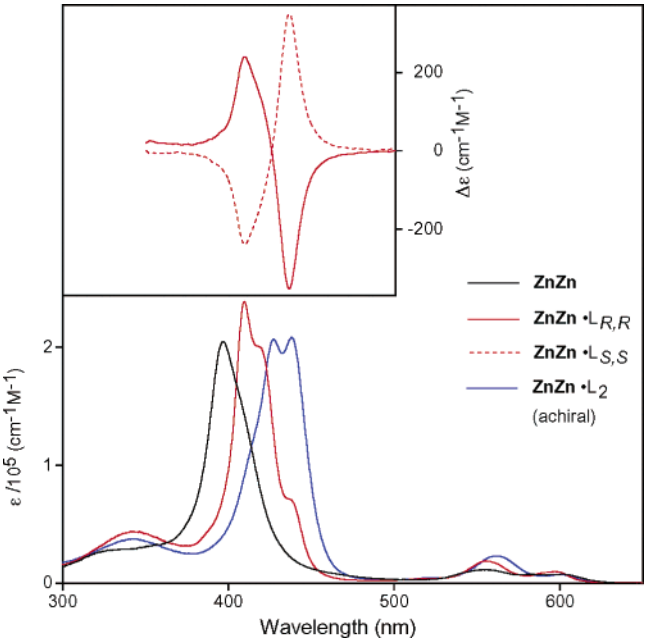

FIGURE 13. The UV−vis and CD spectra of syn-**ZnZn**, **ZnZn**·L tweezer, and anti-**ZnZn**·L_2.

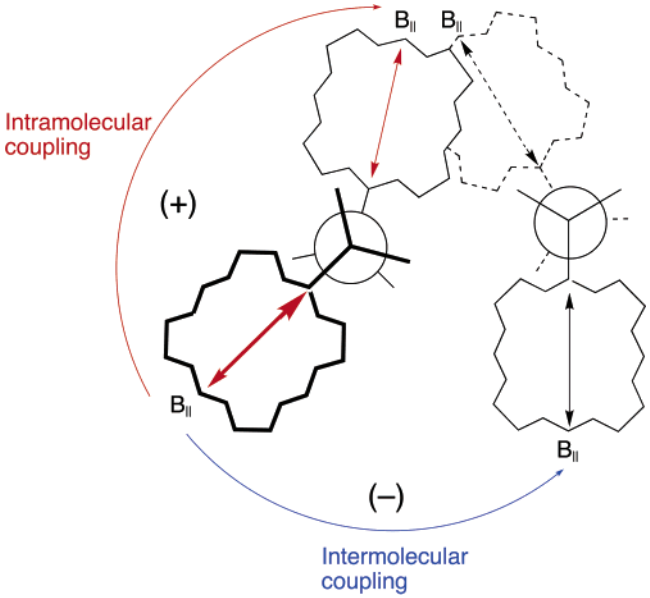

FIGURE 14. Representation of the intra- and intermolecular exciton coupling in the solid-state **ZnZn**·(*S*)-$(L)_2$.

chirality. On further increase of (*R,R*)-DPEA, the transformation to the 1:2 anti-species occurred, accompanied by a remarkable chirality inversion process giving negative chirality. The origin of this unusual chiral activity is due to the geometry and preorganization of the ligand; thus, to minimize the host−guest steric repulsions in each case, the chiral conformation of the host must be opposite. Thus, this is a unique example of how it is possible to induce supramolecular chirality into an achiral system and then, while keeping the chiral information of the inductor constant, invert the overall chirality of the system.

Second is the exceptionally high stability of the tweezers with enantiomeric 1,2-diaminocyclohexane (DACH) (Figures 11 and 12) and a hitherto unseen level of chirality induction with *K* (binding constant) and *A* values of 1.24×10^7 M^{-1} and -590 M^{-1} cm^{-1}, respectively, which exceed all values previously obtained for these related bisporphyrin systems and are among the highest ever reported for any chirogenic supramolecular porphyrin complex. The origin of this remarkable stability is believed to be in the highly favorable geometry with which the DACH can be accommodated within the porphyrin moieties and also via the additional stabilizing factor of numerous CH−π interactions between DACH and the porphyrin, as inferred from the extraordinarily large upfield ^{1}H NMR shifts of the DACH CH protons of $\Delta\delta = 8.9$ ppm. Thus, it was shown that stoichiometry plays a particularly important role in supramolecular chirogenesis.

Phase Transition Effect

Hitherto, we have seen how the chirogenesis in these bisporphyrin systems in solution can be manipulated by a number of internal and external controlling factors. However, chirality induction can also be performed in the solid state, and it possesses properties and phenomena unique to this phase, making it possible to use phase transition as an additional stimulus for supramolecular chirogenesis.

Generally, in solution, the chirality induction is achieved via chiral steric repulsions within the essentially isolated supramolecular complex; in the solid state, however, we must also take into account the intercomplex interactions.

Observation of the solution and solid-state spectral characteristics of anti-**ZnZn**·L_2 revealed significant differences between these phases.[19] On examining the solid-state UV−vis spectra of the host−guest complex, we observed that while the syn−anti conformational switching mechanism is also active in this phase, in contrast to the solution phase, anti-**ZnZn**·L_2 in a KBr matrix is additionally intermolecularly associated with neighboring complexes.

The CD spectra of **ZnZn**·L_2 show induced optical activity in the solid state but with dramatic deviations. The CD profile in the solid state is more complicated than that in solution due to the overlapping of the inter- and intramolecular exciton couplings. However, the CD spectra can be rationalized by a simple dimeric model (Figure 14). In this, it is clear that the direction of the lowest energy intermolecular B_{II} coupling is opposite to the intramolecular B_{II} coupling and that there are multiple intermolecular couplings that result in the observed considerable enhancement of the intensity of the first Cotton effect in the solid state.

Furthermore, the same solid-state intermolecular exciton coupling mechanism is observed to be operating in a related system comprising the formation of a chiral solid-state species between simple zinc octaethylporphyrin and chiral amines in a glassy KBr matrix.[20] In this case, over a period of 4 days, exceptionally high optical activity (g factor $= \Delta\epsilon/\epsilon = 0.015$) is induced, the sign of which was the same as that previously seen for the solid-state **ZnZn**·L_2.

In summary, these results clearly demonstrate that the phase transition of the system can play a crucial role in the outcome and characteristics of chirogenesis in a host−guest system and that it is qualitatively possible to rationalize and understand the chirality and conformation of these systems by consideration of both inter- and intramolecular exciton coupling interactions. These insights may lead to the design of solid-state chirality sensors.

Applications

In the preceding sections, we have gained a high degree of insight into how various external and internal factors contribute to the conformational, photophysical, and chiral properties of supramolecular systems. The consideration and judicious application of these controlling factors can allow the rational production of smart molecular and chiroptical devices designed to perform a particular function.

First, the chirality sensing ability for determining the absolute configuration can be addressed. To this end, it has been shown that **1**·L_x can be used as an effective tool for such determination, allowing a wide range of ligands to be assessed. This compound possesses a number of features that make it attractive for this purpose, in particular, its versatility, the microgram scale required, the rapid and simple protocol, easy compound recovery, and high sensitivity. Second, from this work it can be clearly seen that the effective bulkiness of a molecular component is crucial for determining a system's spatial, photophysical, and chiral properties. However the relative bulkiness of various substituents is often unclear from simple consideration of the covalent makeup; for instance, it was found that for the protected amino acid Phe-OBn, the −Bn substituent has a greater effective bulkiness than the $-CO_2Bn$ substituent and thus dictates the induced chirality in **1**·L_2. The "acid-test" proof of the viability of such smart molecular sensors has been the commercial appearance in recent years of a number of rationally designed compounds, including **ZnZn** discussed here.

Aside from absolute configuration and bulkiness sensors, recent years have seen the development of a number of successful chirogenically active functional molecules in areas such as molecular memory devices, surface chirality and catalysis, chiral organized media, liquid crystals, and thin films.[1,18a,21] All of these depend heavily on and are substantially affected by the kinds of mechanistic, external, and internal factors that have been successfully addressed with the bisporphyrin **1**; thus it should be strongly emphasized that for effective and reliable functioning of molecular chiral and achiral devices consideration and skillful manipulation of these factors are crucially important.

13. Concluding Remarks

In conclusion, novel and simple supramolecular chirogenic assemblies on the basis of **1**·L_x and the rationalization of various aspects of its functional mechanism have been described. As a result of such detailed understanding and their high sensitivity and efficiency, it has been possible to use these systems as sensors for determination of absolute configuration and other purposes. The influences of various external and internal controlling factors have been comprehensively investigated, and the results and implications have been discussed. Finally, these insights open up further intriguing prospects for new applications of supramolecular chirogenic systems in various modern fields of science and technology.

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