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A Versatile Bisporphyrinoid Motif for Supramolecular Chirogenesis

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During the last decade there has been continuously growing interest in the phenomenon of supramolecular chirogenesis, which is a smart combination of chirality and supramolecular chemistry effectively used for investigations of various aspects of living organisms, modern physical and natural sciences, and also for technological applications. Thanks to their spectral, chemical, and physicochemical properties, porphyrinoids have been found to be one of the best suited classes of compounds for study of this subject. Out of a vast number of the porphyrinoid-based supramolecular systems employed for this purpose, a bisporphyrinoid motif has been shown to be the simplest, yet widely applicable, structural element that satisfies the requirements for the desired chirogenic properties and ease of synthetic methodology. The aim of this microreview is to highlight the advantages and versatility of this type of chromophoric arrangement for supramolecular chirogenesis.

1. Introduction

Supramolecular chirogenesis is a smart combination of supramolecular chemistry and chirality science, dealing with different chiral processes – such as asymmetry transfer, induction, modulation, and amplification – under the control of various noncovalent forces in numerous natural and artificial systems. Comprehensive investigation of this phenomenon is important from the viewpoint of fundamental science, allowing better understanding of the activity and functionality of living organisms and evolutionary processes, and also lies behind the smart design of various chiroptical devices, sensors, switches, and molecular machines and the development of modern molecular, supramolecular, and nanotechnologies.[1] It has turned out that, out of a great variety of chromophoric compounds used for chirogenic purposes, porphyrins can play a particularly significant role thanks to their appropriate chemical, physicochemical, and spectral properties, as well as the relative stabilities, readily synthetic accessibilities, and excellent abilities to form supramolecular assemblies. Essentially, porphyrinoids display intense absorption bands (with molar extinction coefficients of up to several hundred thousand) in

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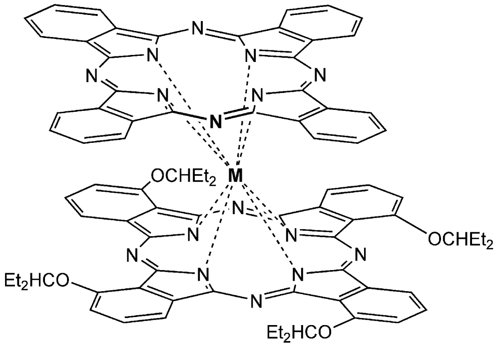
the regions of the high-energy B or low-energy Q electronic transitions (for porphyrins and phthalocyanines, respectively), which is an important prerequisite for efficient chirogenic performance.[2]

According to the exciton chirality theory, at least two strongly absorbing chromophores arranged spatially in a chiral fashion are needed to promote chiroptical events effectively.[3] This makes the bisporphyrinoid's motif a key structural unit for chirogenic processes. Although there are several reviews referring to a greater or lesser extent to bisporphyrinoid-containing systems in relation to the chirality issue,[1,3b,4] there has not to date been a review that comprehensively describes the chirogenic behavior of bisporphyrinoids in various supramolecular systems with a particular emphasis on their versatility and universality in chiroptical applications. To fill that gap, in this microreview we have summarized the most representative examples in this field, including the results of our own and other research groups to illustrate the major developments, current trends, and future prospects in the use of bisporphyrinoid structures in supramolecular chirogenesis in general and the detailed mechanisms and driving forces of chirogenic phenomena in particular, as well as various external and internal controlling factors. For better understanding, the presented data are classified into several categories according to the complexity and versatility of the supramolecular systems and the chirality of the assemble components. In general, the bisporphyrinoid pattern can be constructed by two major approaches, through noncovalent or covalent bonding of the corresponding monomeric units.

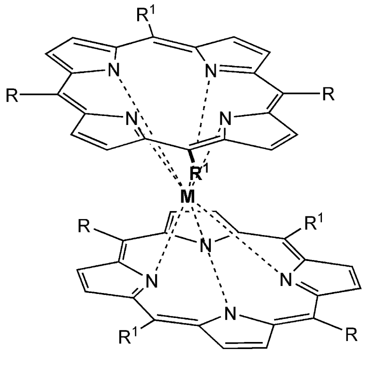
2. Bisporphyrinoid Systems Based on Porphyrinoid Precursors Spatially Fixed by Noncovalent Linkages

Essentially, this methodology can be achieved by two different strategies – either with achiral monomers connected by a chiral bridge, or with chiral monomers connected by an achiral bridge. The basic approach for designing the bisporphyrinoid systems is generally based upon center-to-center fixation of the two macrocycles or the corresponding peripheral substitution.

The first approach was successfully applied in the construction of a series of the chiral double-decker bisporphyrinoids **1**–**5**, bound through multivalent metal ions.[5,6] Whereas **1** was obtained as a racemic mixture that was not resolvable,[5] the enantiomer pairs of **2**–**5** were successfully separated and confirmed by their corresponding mirror-image circular dichroism (CD) spectra, each of which corresponded to several bisignate Cotton effects (CEs) due to the exciton coupling of the electronic transitions of chirally arranged porphyrins.[6] The effects of the central metal and its oxidation state on the chiroptical properties were investigated: acceleration and deceleration of the racemization process, for example, were observed for the reduced **5** and the oxidized **2**, respectively, because of modulation of the interporphyrin π-electronic interactions.



1: M = Sm, Eu, Gd



2: M = Ce, Zr, R = Tol, R^1 = H

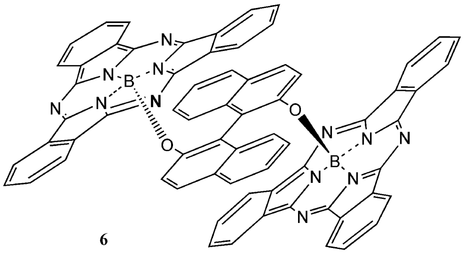
3: M = Ce, Zr, R = 4-iPr-C_6H_4, R^1 = H

4: M = Ce, Zr, R = 3,5-$(OMe)_2$-C_6H_3, R^1 = Tol

5: M = Ce, Zr, R = 3,5-$(OMe)_2$-C_6H_3, R^1 = C_6F_5

Another type of center-to-center bisporphyrinoid bonding, through chiral bidentate binaphthyl and hematoxyline bridges, was achieved in **6** and **7**, respectively.[7] The observed CD signals consisted of several exciton couplets in the Q and Soret band regions, reflecting the electronic structures and spatial arrangements of two interacting chromophores and thus allowing stereochemical assignment of the chiral linkers between the porphyrinoids. Geometry optimization and subsequent Kuhn–Kirkwood coupled oscillator analysis were elegantly achieved for **7**, allowing the absolute configuration determination of hematoxyline as (6a*S*,11b*R*).

Peripheral substitution at the porphyrinoid *meso* position is an alternative approach to chromophore fixation in a chiral fashion that was effectively employed in the cases of **8**–**11**.[8,9] In particular, electrostatic interactions between anionic **8** and cationic **9** resulted in a dimeric 1:1 complex, which in the presence of glucose and xylose exhibited optical activity due solely to supramolecular binding of the boronic acid residues of the porphyrins and the saccharide hydroxy groups.[8a] The chirogenic versatility was considerably enhanced upon application of the monofunctional **10**, two molecules of which interact with one molecule of various sugars, thus yielding bisporphyrin structures that exhibit strong CD exciton couplets in the Soret band region.[8b]



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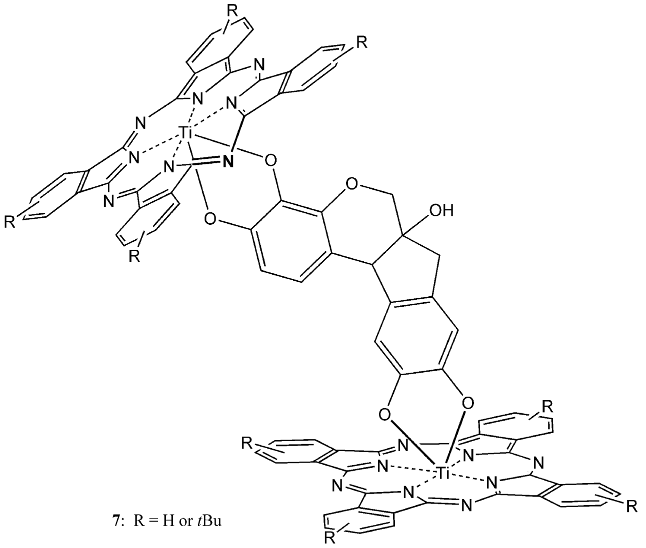
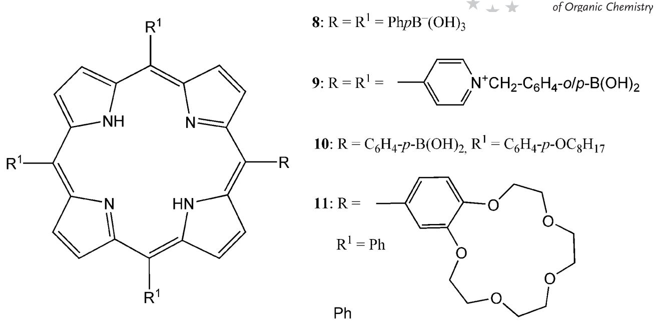


7: R = H or *t*Bu



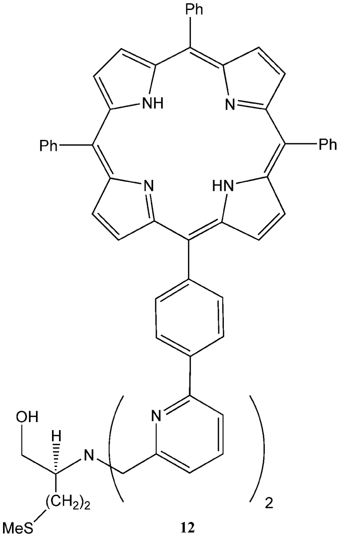
8: R = R^1 = Ph*p*B$^-$(OH)$_3$

9: R = R^1 = N$^+$CH$_2$-C$_6$H$_4$-*o*/*p*-B(OH)$_2$

10: R = C$_6$H$_4$-*p*-B(OH)$_2$, R^1 = C$_6$H$_4$-*p*-OC$_8$H$_{17}$

11: R =

R^1 = Ph



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Further implication of supramolecular chemistry led to the crown ether-appended **11**, the Zn complex of which apparently self-assembles into a sophisticated optically active tweezer-type architecture by clipping a chiral bidentate guest (diamine or amino alcohol) between the two porphyrin moieties in the presence of K$^+$ ions.[9] The generation of optical activity was well documented by the induced excitonic CD signal, with the sign governed by the structure and binding mode of the chiral guest.

Recently, a rather interesting example of a self-organized bisporphyrin system was illustrated in the case of the covalently linked chiral dimer **12**.[10] The assembling process was effectively driven by an excess amount of Cu^{II} ions in the presence of NH$_4$NCS, resulting in a strong negative CD couplet in the region of the Soret absorption as a result of the role played by the metal ion in structural fixation through the chelation mechanism. Whilst the presented approach opens new prospects for designing chiroptical devices, the detailed structural and electronic origin of the observed optical activity in this system is yet to be investigated.

Although the bisporphyrinoids described above are potentially interesting for supramolecular chirogenic systems, their applicability and versatility as chiroptical sensors, as well as comprehensive investigation of various controlling factors, are rather limited, due to the structural complexity (and rigidity in many cases) of the resulting assemblies. In measures directed towards overcoming these shortcomings, the bisporphyrinoids were connected through appropriately flexible covalent or coordination bridges capable of adopting particular chiral conformations upon interaction with chiral guests, and hence of sensing external chiral fields.

3. Bisporphyrinoid-Based Host–Guest Systems Spatially Fixed by Covalent and/or Coordination Linkages

This type of bisporphyrinoid is the most promising from the point of view of chiroptical sensitivity, applicability, and versatility and is widely used for comprehensive investigation of the phenomenon of supramolecular chirogenesis. Generally, these systems can be divided into three major structural categories, in which two porphyrins are variously arranged in face-to-face, tweezer-type, and linearly extended geometries (Figure 1).

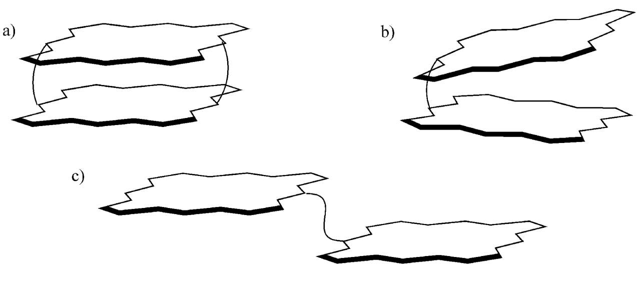
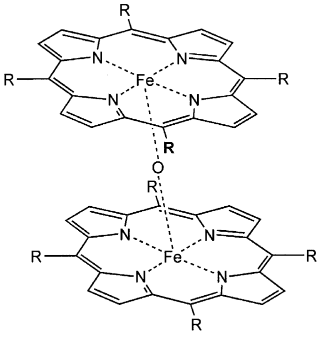


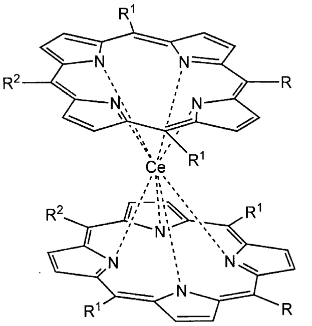
Figure 1. Schematic representation of a) “face-to-face”, b) tweezer, and c) linearly extended bisporphyrinoid geometries.

3a. Bisporphyrinoid-Based Host–Guest Systems in Face-to-Face and Tweezer-Type Geometries

Face-to-face arrangements were ensured by using the same double-decker structural motifs as in the cases of **1**–**5**, to yield a series of bisporphyrins **13**–**20** connected by μ-oxo (Fe–O–Fe) and Ce bridges.[11] These bisporphyrins have been successfully applied to chirality sensing with various bidentate compounds, such as sugars, dicarboxylic acids, and dianions, and also to chirality memory. The chirality transfer mechanism is based upon the formation of two noncovalent bonds between two anchor groups of the bidentate guest molecule and two corresponding anchor groups of the neighboring porphyrins in double-decker fashion, thus shifting these porphyrin subunits into a right- or left-handed orientation, depending upon the guest's stereochemistry. This structural reorganization of the host results in induction of the CD signal in the region of the porphyrin electronic transitions, owing to the intercomplex exciton coupling between the porphyrin chromophores arranged in the chiral geometry. The observed optical activities are controlled by various factors, including the guests' structures, the solvents used, and the pH values.



13: R = C_6H_4-*m*-$B(OH)_2$ **14**: R = C_6H_4-*p*-$B(OH)_2$



15: R = R^1 = R^2 = *p*-Py **16**: R = R^2 = *p*-Py, R^1 = Ph

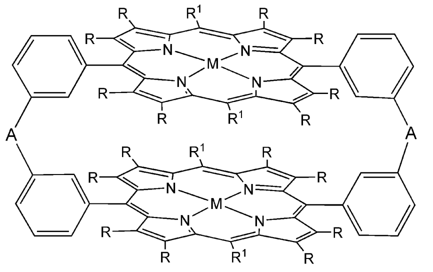
17: R = R^2 = *p*-Py, R^1 = C_6H_3-3,5-$(OMe)_2$

18: R = R^2 = *p*-(N-CH_2-C_6H_3-*p*-$B(OH)_2$)Py, R^1 = C_6H_4-*p*-OMe

19: R = *p*-(N-CH_2-C_6H_3-*p*-$B(OH)_2$)Py, R^1 = R^2 = C_6H_4-*p*-OMe

20: R = R^2 = *p*-(N-Me)Py, R^1 = C_6H_4-*p*-OMe

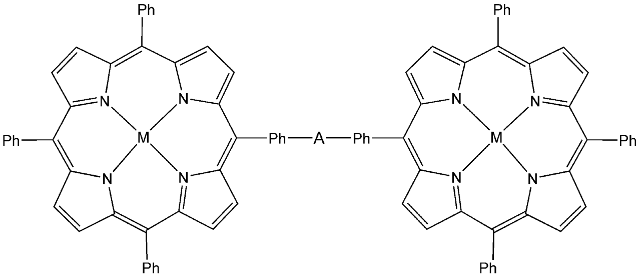
Besides the double-decker approach, cofacial arrangements of bisporphyrinoids could also be ensured by use of two covalent linkages on opposite sides of the macrocycles, as in the cases of **21**–**23**.[12] Through variation of the tether length and the porphyrin structure, various chiral guests (longer bispyridyl derivatives and shorter mandelic acid) form stable 1:1 inclusion complexes with association constants of up to 2.3×10^6 M^{-1}. The chirogenic efficiencies were also governed by the guests' structures, exhibiting considerable enhancement of optical activity relative to the corresponding monomeric porphyrins due to exciton coupling between two porphyrins in the resulting supramolecular assemblies.



21: M = Zn, R = H, R^1 = Mes, A = –$CO(NHCMe_2CO)_9NH$–

22: M = Zn, R = H, R^1 = Mes,
A = –$CO(NHCMe_2CO)_3NHC(CHPh)CONHCH_2CONH(CHPh)CO(NHCMe_2CO)_3NH$–

23: M = 2H, R = Me, R^1 = C_6H_3-*o*,*o*-$(OMe)_2$, A = –OCH_2-C_6H_4-CH_2O–

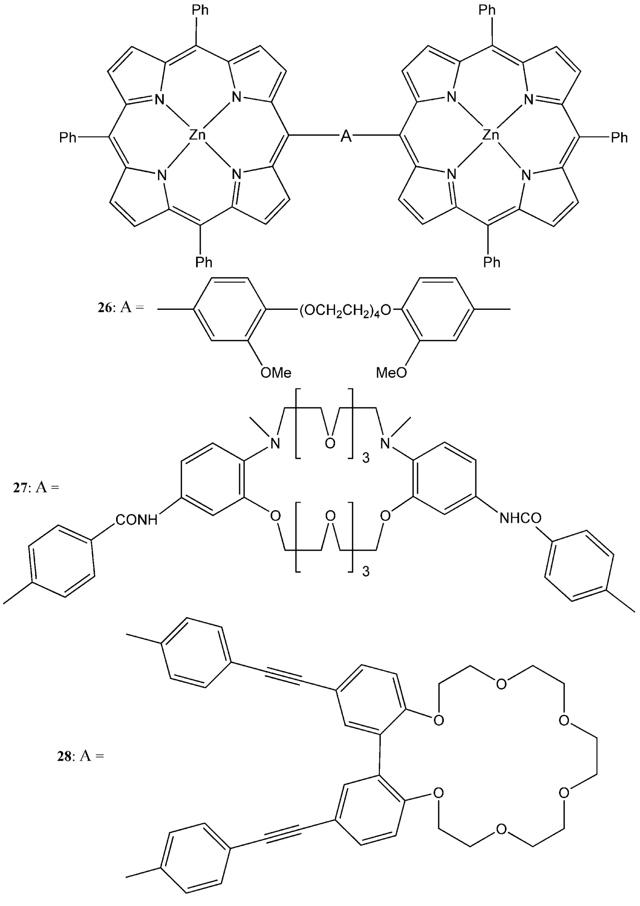


24: M = Yb(acac), Gd(acac), A = –CH_2OCH_2–

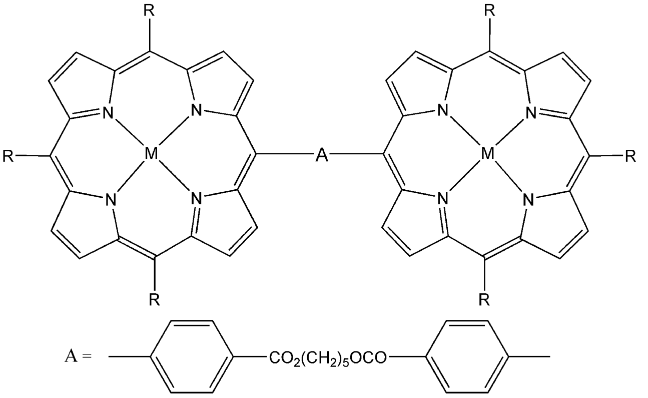
25: M = Yb(acac), Gd(acac), A = –$CH_2O(CH_2)_2OCH_2$–

A different mode of bisporphyrinoid connection is based upon the use of a single covalent bridge between two macrocyclic subunits. This sufficiently enhances the chiroptical functionality of bisporphyrinoid hosts. Through variation of, for example, the linkage length, various types of chiral guests (such as mono- and bidentate compounds) can be used for chirogenic purposes. In particular, ether bridges of different length were used to connect two porphyrins in the lanthanide-containing compounds **24** and **25**.[13] These bisporphyrins exhibited length-dependent selectivity towards cysteine polyions, enabling the shorter **24** [M = Yb(acac)] to bind cysteine more efficiently than cystathionine, homocysteine, and methionine. In contrast, the longer **25** favors homocysteine. The chirogenesis mechanism involves the formation of 1:1 tweezer-type host–guest complexes with accompanying development of optical activity in the region of porphyrin's B transitions.

To ensure preorganized tweezer conformations, crown-ether-type covalent bridges between pairs of porphyrin units were employed in **26**–**28**.[14] In the case of **26**, sodium ions greatly assisted the binding of *trans*-1,2-diaminocyclohexane (DACH) to enhance the corresponding association constant by a factor of two. With use of enantiomerically pure DACH, an exciton-coupled CD signal was induced, the amplitude of which was noticeably enhanced in the presence of Na^+. Similarly, **27**, upon accommodation of a potassium ion in the crown ether ring, displayed allosteric enhancement of the CD couplet induced by the optically active DACH derivatives. However, this bisporphyrin is a more versatile chirogenic receptor than **26**, enabling sensing of the chiralities of potassium salts of chiral carboxylates (camphorates and mandelates) and of aminocarboxylates (unprotected amino acids) through binary-phase extraction. In the case of **28**, Ba^{2+} ions effectively assisted the memory of the chiral tweezer conformation upon replacement of an optically active diamine (used as a chirogenic inducer) with an achiral one, showing only a slight decrease in the CD amplitude after a relatively long period of time, such as one day.



Even more versatile chirogenic systems based on the flexibly linked **29** and **30** were developed, and these were also capable of yielding tweezer conformations upon binding bidentate guests.[15] Interaction with chiral compounds resulted in induction of CD couplets in the region of the porphyrins' Soret bands, the signs and intensities of which were dependent upon the chemical structures and stereochemistries of the guests. The chirogenesis mechanism includes the stereospecific differentiation of the relative sizes of substituents at the chiral centers through the two porphyrins in the bisporphyrin systems being forced to adopt, in general, the least sterically hindered conformations. However, it was also shown that other external and internal factors – such as hydrogen bonding, presence of heteroatoms, and solvent – may also affect the overall geometries of the host–guest assemblies and may thus influence the chiroptical outcomes. The directional orientations of the porphyrin subunits in the resulting complexes induced CD exciton couplets in the region of the porphyrin Soret band, reflecting the overall stereochemistries of the supramolecular systems and thus making it possible to use these bisporphyrin hosts as tools for determining the absolute configurations of various bidentate compounds. When the relative sizes of substituents cannot be directly estimated, or when other factors affect the spatial structures of the complexes, molecular mechanics calculations are used for conformational analysis to interpret the observed discrepancies between the predicted and experimental results. Additional functionality was introduced into these chirogenic systems by use of the electron-deficient porphyrins in **30** to increase the Lewis acidity of the host, and therefore to facilitate the binding of hydroxy-containing compounds.



29: M = Zn, Mg, R = Ph **30**: M = Zn, R = C_6F_5

3b. Ethane-Bridged Bisporphyrinoids as One of the Most Versatile Structural Motifs for Supramolecular Chirogenesis

Although the bisporphyrinoids described above are of definite interest for various chirogenesis purposes and potentially applicable to chiroptical sensing, none of them is universal enough to be used for different types of chiral compounds. To fill this gap the ethane-bridged bisporphyrin **31** (Figure 2) was designed as one of the most promising structural motifs for supramolecular chirogenesis in terms of versatility.[1a,1b,4d,16] In sharp contrast to the bisporphyrinoid systems discussed above, **31** is able to exhibit chirogenic responses upon interaction with various classes of chiral guests, including monodentate and bidentate compounds. In particular, this versatility is ensured by the semi-flexible/semi-rigid ethane bridge, which is relatively short but sufficiently flexible to allow twisting of the two directly connected porphyrin moieties. Whereas in nonpolar, noncoordinating solvents the bisporphyrin exists in a *syn* face-to-face spatial arrangement, owing to the strong interporphyr-

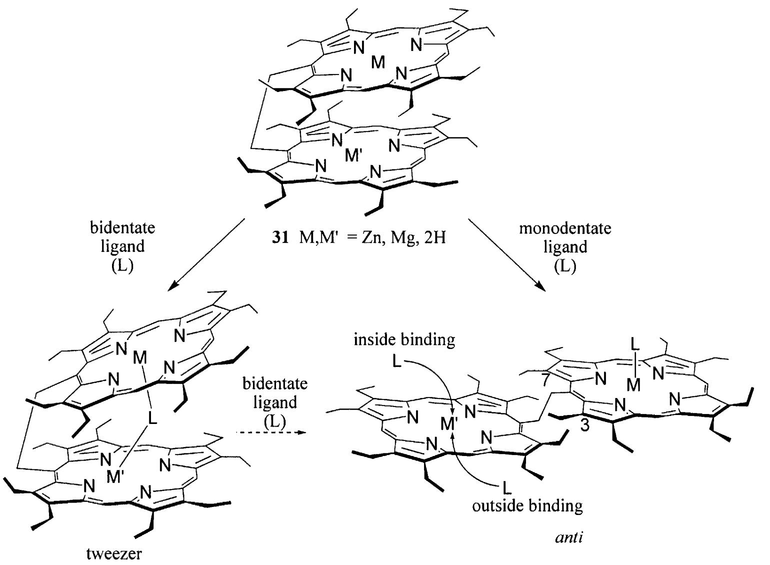


Figure 2. Schematic representation of the conformational changes in **31** governed by the structural type of external ligand: “face-to-face” conformation without ligand, tweezer conformation upon interaction with bidentate ligands, and linearly extended *anti* conformation upon interaction with monodentate ligands.

in interactions, ligation of a coordinating guest induces conformational switching to the extended *anti* form in cases of monodentate guests or to the tweezer structure in cases of geometrically suitable bidentate guests (Figure 2). These binding events are highly cooperative processes, resulting in stable 1:2 or 1:1 host–guest complexes, respectively, with Gibbs free energy changes ranging from –6.7 to –8.4 kcal mol^{-1} for primary amines as monodentate guests, and reaching –9.5 kcal mol^{-1} for DACH, as an example of a bidentate guest. The observed structural transformations (*syn*-to-*anti* and *syn*-to-tweezer) are a general feature of this supramolecular host and occur upon binding of both chiral and achiral guests.

However, when a chiral compound is used as a guest, an additional structural transformation takes place to induce effective chirality transfer from the enantiomeric guest to the achiral host. In particular, in cases of chiral monodentate compounds, upon inside binding (approaching from the side of the ethane bridge; see Figure 2), there are competitive repulsive steric interactions between the two most bulky substituents at the guest’s stereogenic center (such as R and R′) and the ethyl groups at the 3- and 7-positions of the neighboring porphyrin moiety (Figure 3). The bulkier R group forces the neighboring porphyrin ring to move outward as a result of the dominant steric hindrance, thus generating a unidirectional screw twist in **31**. The bisporphyrin’s structure becomes chiral because the steric hindrance between the 3- and 7-ethyl groups of the two porphyrin subunits makes it impossible for the two porphyrins to rotate around the ethane bridge axis, preventing racemization of the induced screw. As a result of this chirogenic event, a moderate-to-strong exciton couplet CD signal is induced in the porphyrin Soret region. The chirality sign correlates unequivocally with the generated helicity, allowing straightforward assignment of the guest’s absolute configuration. In particular, when the bulkiness order of the guest’s substituents around the stereogenic center coincides with the priority order of the relevant substituents determined by the Cahn–Ingold–Prelog rule, the (*R*) enantiomer yields a negative first Cotton effect and a positive second Cotton effect, whereas the (*S*) enantiomer produces a CD couplet with opposite signs, thus allowing this sensing protocol to be effectively used for determining the absolute configurations of different classes of organic molecules. This comprehensive explanation of the host–guest interaction mechanisms has allowed detailed investigations of various external and internal factors governing the chirogenic properties in these supramolecular systems. It has been shown, for example, that the total CD amplitude was linearly dependent upon the size of the largest substituent at the stereogenic center for homologous ligands, hence making it possible to predict the magnitude of induced chirality. Further study of the bulkiness effect revealed a decisive role of solvent as an active component of the overall supramolecular system that considerably influences the chiroptical properties, sometimes even leading to the phenomenon of chirality inversion. This was achieved through judicious analysis of the selective solute–solvent interactions, especially in the borderline cases in which the differences between the competitive chirogenic interactions were small and the substituent’s relative size could be modulated through the formation of a specific solvation shell. Another important factor governing supramolecular interactions, and thus chirality induction, in these systems was found to be temperature. As would be expected, lowering the temperature significantly enhances the host–guest binding, resulting in increasing CD sensitivity, allowing chirality induction in the corresponding Zn complex of **31** by alcohols, which possess well known marginal affinities for Zn porphyrins. However, the alcohol binding and chirogenic capabilities were considerably increased by replacement of the Zn central ions in the porphyrin rings of **31** with Mg ions, making it possible to induce chirality in the bisporphyrin host even at room temperature.

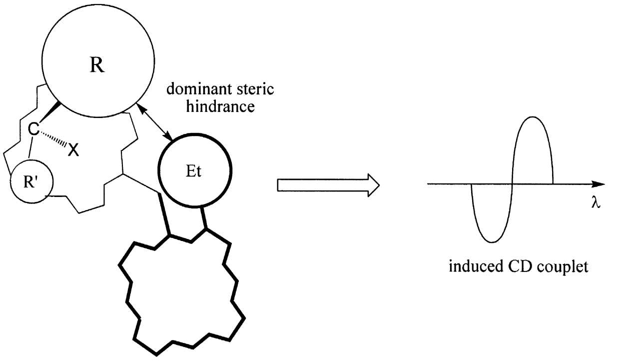


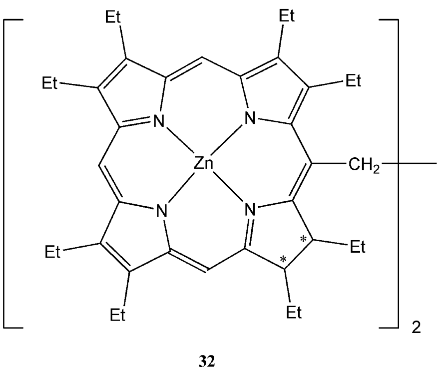
Figure 3. Schematic representation of the mechanism of chirality induction in **31** upon interaction with monodentate guests.

The chirogenic versatility of this bisporphyrin structure was further demonstrated by interaction of the Zn complex of **31** with chiral bidentate ligands. As mentioned above, in most cases this resulted in the formation of extremely stable 1:1 tweezer complexes with estimated binding constants as high as $>10^{7}\ \mathrm{M}^{-1}$ (Figure 2). However, further increases in the concentrations of some bidentate ligands could shift the supramolecular equilibria towards the extended 1:2 complexes, allowing investigation of the corresponding stoichiometry effects on the chirality transfer mechanism. As an example, upon complexation with enantiomeric 1,2-diphenylethylenediamine (DPEA), a remarkable chirality switching controlled exclusively by the stoichiometry of the supramolecular system was observed and assigned to opposite spatial orientations of the 1:1 and 1:2 complexes. Thus, at low concentrations of (*R*,*R*)-DPEA, the formation of tweezer complex is favored, giving positive chirality. On further addition of the ligand, transformation into the 1:2 *anti* species occurs, with accompanying chirality inversion to the negative sign. This is a unique example of how it is possible to induce supramolecular chirality into an achiral system and then, while keeping the local chiral information of the inductor constant, to invert the overall chirality of the system by simply changing the host/guest ratio.

Another important aspect of chirogenic effects induced by bidentate guests is a comprehensive and unambiguous explanation of the induced optical activity in the bisporphyrinoid-based supramolecular system, achieved for the first time through the use of enantiomeric DACH. In particular, from crystallographic data obtained for the tweezer structure of Zn complex **31** with (*R*,*R*)-DACH and from calculations based on the Kuhn–Kirkwood coupled-oscillator mechanism, the induced CD signal in the region of the porphyrin Soret band was assigned as a combination of the two excitonic homocouplings between the corresponding $B_{\parallel}$ and $B_{\perp}$ electronic transitions orientated along the porphyrin's *meso* 5–15 and 10–20 axes, whilst the contribution of the hetero $B_{\parallel}$–$B_{\perp}$ couplings were found to be negligible. The directions of the two homocouplings were confirmed to be anticlockwise and hence to induce an intense negative CD couplet with an extremely large total amplitude of $-590\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$.

Further chirogenic diversity of these bisporphyrin-based systems was expanded to the solid state, making it possible to use phase transition as an additional stimulus for supramolecular chirogenesis. In this case, besides the inherent chirogenic steric repulsions within the essentially isolated supramolecular system as observed in solution, the intercomplex interactions should be also taken into account. Comparison of the corresponding chiroptical properties revealed a remarkable difference between these two phases. In solution, (*S*) guests induce positive CD couplets in the B band region of Zn complex **31**, corresponding to a clockwise orientation between the low-energy $B_{\parallel}$ electronic transitions. In contrast, the same (*S*) guest yields an enhanced negative bisignate CD signal in the solid state (KBr matrix), indicating anticlockwise orientation of the $B_{\parallel}$ transitions. The observed phenomenon of chirality inversion and amplification is the result of numerous intermolecular electronic transition couplings in the supramolecular aggregates formed in the solid state. A similar amplification of marginal solution-phase chirality in the solid state was also observed even in the case of a zinc octaethylporphyrin monomer system in the presence of enantiopure amines.[17]

Moreover, a simple structural modification of this bisporphyrin motif (i.e., the reduction of one pyrrole ring in each porphyrin subunit to yield the corresponding bischlorin **32**) has opened up new prospective possibilities in the field of supramolecular chirogenesis by allowing effective enantioselective recognition of chiral guests.[18] Thus, enantiopure **32** exhibits reduction in its CD signal upon interaction with chiral guests, due to the induced conformational changes, while the chiroptical response was found to be noticeably different for the corresponding antipodal amines. This makes it possible to use **32** for chiral recognition based solely on a two-point host–guest interaction mechanism combined with the variability of the coupling electronic transitions of the chromophoric host, the chiral orientation of which was controlled by the guest's stereochemistry.



32

4. Conclusions

Supramolecular chirogenesis is one of the most fundamental issues of modern natural and physical sciences and directly affects many innovative molecular and supramolecular technologies. Explanation of the mechanisms controlling this phenomenon and the discovery of versatile structures capable of performing various chirogenic functions are therefore paramount research tasks in the fields of chirality, supramolecular chemistry, molecular sensors, and nanotechnology. This review has detailed recent major advances in the design and use of a bisporphyrinoid structural motif for diverse applications in supramolecular chirogenesis by using the most illustrative examples. Although in some specific cases more sophisticated multiporphyrinoids are necessary for chiroptical purposes,[19] it has been shown that bisporphyrinoids currently serve as the most universal chirogenic units to this end.

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