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Chirality Transfer

Rationalization of Supramolecular Chirality in a Bisporphyrin System**

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Supramolecular chirality is a growing multidisciplinary field of modern research and attracts much attention from the scientific community because of its vital importance for various natural processes and for its attractive possibilities for new smart technologies.[1] Of the vast number of host–guest and self-associated systems, supramolecular assemblies based on porphyrin chromophores are of particular interest for in-depth investigation and potential application as a consequence of them having specific and well-suited physicochemical and spectroscopic properties.[2] However, it is apparent that effective control of any functional system rests upon the comprehensive understanding of the detailed operative mechanisms and the corresponding driving forces. In the case of porphyrin-based supramolecular chiral assemblies (particularly, containing two or more porphyrins) there are two major factors which make such studies an arduous task: the dynamic nature of noncovalent assemblies and the complex electronic structure of these pigments as a consequence of the existence of several differently oriented electronic transitions. Herein, we report for the first time a crystallographic structure of a supramolecular complex con-

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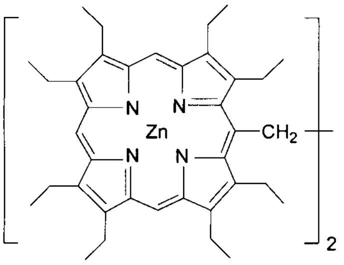
sisting of an achiral bisporphyrin host and a chiral diamine guest which leads to the comprehensive understanding of the origin of transfer of chirality information at the molecular and electronic levels.

It was shown earlier that ethane-bridged bis(zinc octaethylporphyrin)[3] (**1**) is one of the most suitable achiral hosts for the comprehensive investigation of various aspects of supramolecular chirogenesis upon its interaction with different chiral guests (including amines and alcohols).[2a,4] Of the guest compounds studied, bidentate ligands (diamines and amino alcohols) are particularly important and useful for understanding this phenomenon because of their ability to form rigid and stable tweezer-type complexes possessing an extremely high optical activity. The detailed equilibrium mechanism, driving forces, and various controlling factors of tweezer formation have been recently reported.[4c–e] However, such key questions relating to the exact molecular structure and true origin of the induced chirality still remain open. To solve these vital issues (*R*,*R*)-1,2-diaminocyclohexane (**2**) was chosen as the chiral guest, because of its unique property of producing a stable 1:1 tweezer complex exclusively without any further equilibrium steps as a consequence of its remarkably large association constant ($>10^7\,\text{M}^{-1}$).[4c,d]



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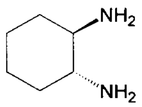

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Slow evaporation of a 1:1 mixture of **1** and **2** in CH_2Cl_2/CH_3CN at room temperature gave needle-shaped metallic-brown crystals, from which an appropriate crystal was chosen for X-ray diffraction experiments (see Experimental Section). The crystal of the chiral supramolecular tweezer complex [(**1**)(**2**)] has a noncrystallographic pseudo-twofold axis through the centers of the bonds C41a–C41b (ethane bridge), C45a–C45b, and C43a–C43b (ligand moiety; Figure 1). The bisporphyrin moiety has a caged or bivalve shape, which opens in the direction of the ligand moiety, with a dihedral angle of 42.8(2)° between the best planes of two porphyrin rings defined by four porphyrin nitrogen atoms. The Zn, C2, C3, and C4 atoms of the corresponding porphyrin rings rise significantly out of these planes, with deviations of up to 0.61 Å. These deviations are apparently a result of the ligand coordination (for Zn atoms) and continuous steric repulsion caused by the proximity of the neighboring porphyrin moiety (for C atoms). The cyclohexane ring of the ligand has a chair conformation in the direction parallel to the two porphyrin rings, thus allowing attractive CH–π interactions between the ligand and porphyrin moieties as an additional stabilizing factor. The two (-*sc*) N atoms of the ligand moiety, which are connected to the porphyrin Zn atoms in the counteraxial directions, are in the equatorial position, thus also shortening the porphyrin···porphyrin distance (the corresponding Zn···Zn distance is 5.604(5) Å). Most importantly, it becomes apparent from the unidirectional screw arrangement of the bisporphyrin moiety in the crystal structure that the effective transfer of chirality information from the enantiomeric guest to the achiral host in the supramolecular complex [(**1**)(**2**)] occurs. This arrangement occurs as a result of the two spatially orientated Zn–N coordination bonds arising from the preorganization of the two amino substituents of the ligand moiety. The porphyrin rings are twisted anticlockwise relative to each other around the ethane bridge, with a torsion angle (Zn1a-C41a-C41b-Zn1b) of −54.1(5)°. These crystallographic data are not only in full agreement with the spectroscopic characteristics obtained previously,[4c,d] but make it possible to unambiguously rationalize many unique properties of these supramolecular systems, particularly the origin of its high optical activity that has so far remained the most outstanding issue of any chirogenic process.

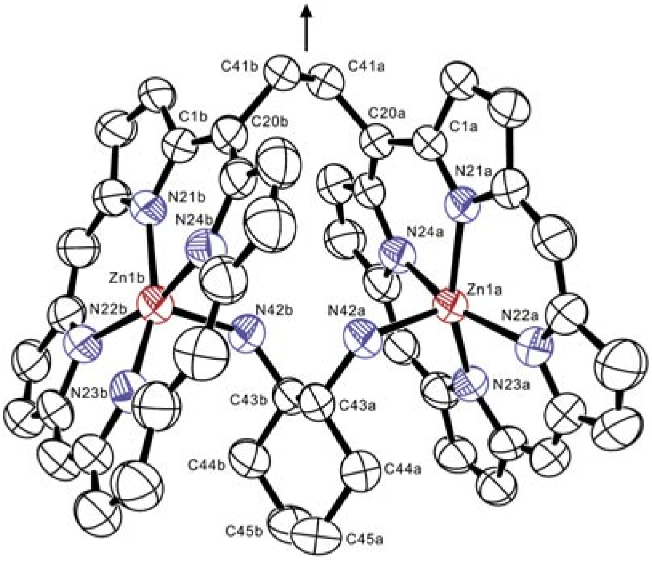

Figure 1. ORTEP-3 representation of [(**1**)(**2**)]. Heavy atoms are shown as 50% probability ellipsoids. The crystallographic numbering is shown excluding the peripheral ethyl groups and all H atoms for clarity. The arrow indicates the noncrystallographic pseudo-twofold axis.

To comprehensively understand the relationship between the supramolecular structure of the tweezer complex [(**1**)(**2**)] and its optical activity its magnetic circular dichroism (MCD) spectrum was measured and compared with the corresponding CD and electronic absorption spectra. It should be noted that CD and MCD analyses are mutually complementary in aiding the interpretation of the excited states, especially in the case of chiral bis- (or multi-) porphyrin systems; CD spectroscopy is sensitive to interchromophoric through-space coupling (that is, exciton coupling), whereas MCD spectroscopy is sensitive to intrachromophoric coupling (that is, coupling occurring between electronic transitions within the same chromophoric unit).[5] The optical spectra of [(**1**)(**2**)] recorded in CH_2Cl_2 in the region of the porphyrin Soret (B) band (Figure 2) clearly show three well-resolved absorption bands at 410, 419, and 436 nm. The position of the MCD peaks coincides very closely with these transitions, thus indicating their nondegenerate character.[6] Importantly, electronic transitions of different polarizations generally exhibit MCD signals of opposite sign and it was found that the two high-energy transitions (at 410 and 419 nm) of the same positive CD sign are indeed of different polarization: the higher energy MCD signal (at 408 nm) is positive, whilst the lower energy MCD signal (at 424 nm) is negative.

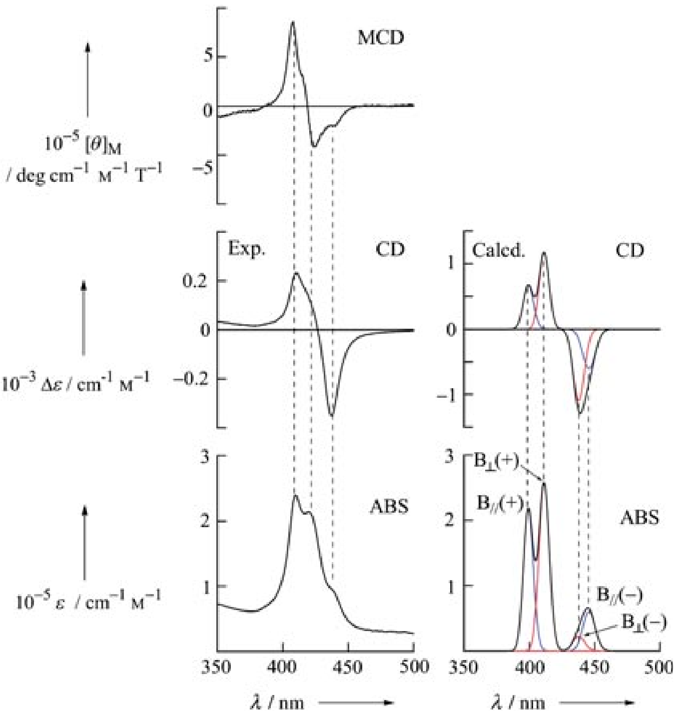

Figure 2. Experimental MCD, CD, and absorption spectra recorded in CH_2Cl_2 at room temperature (left) as well as the calculated CD and absorption spectra (right) of the B-band region of the tweezer. Each calculated exciton band ($B_{\parallel}$: blue, $B_{\perp}$: red) was described by a single Gaussian curve. The notations plus and minus represent the in-phase and out-of-phase transitions, respectively.

To rationalize the experimentally obtained spectral data, and taking into account the assignment of the transition polarization, theoretical absorption and CD spectra were calculated using the geometrical parameters obtained from the corresponding crystal structure and the spectral parameters of the corresponding porphyrin monomer[7] on the basis of the Kuhn–Kirkwood coupled-oscillator mechanism.[8] This tweezer system [(**1**)(**2**)] consists of two identical porphyrin moieties, each having two different transition moments $B_{\parallel}$ and $B_{\perp}$, which are in parallel and perpendicular orientations to the ethane bridge, respectively. This arrangement results in two major types of degenerate exciton interactions ($B_{\parallel}$–$B_{\parallel}$ and $B_{\perp}$–$B_{\perp}$ couplings) and thus leads to four exciton states (see Experimental Section). As can be seen in Figure 3, the relative orientation between these two pairs of electronic transitions is anticlockwise, which according to the exciton chirality method[9] predicts the negative chirality that was observed experimentally. The resulting calculated absorption spectrum has three well-resolved bands that are also similar to the experimental results (Figure 2). The face-to-face conformation and short distance between the centers of the interacting electric dipoles ($r_{12} = 6.23$ Å) results in the higher energy ($B_{\parallel}(+)$ and $B_{\perp}(+)$) and lower energy ($B_{\parallel}(-)$ and $B_{\perp}(-)$) exciton states being well-separated. These pairs of states become optically allowed and partially forbidden transitions, respectively, as a consequence of strong exciton interactions that result in the observed absorption profile. This observation is in line with Kasha's exciton coupling theory.[10] Furthermore, the MCD $B_{\parallel}(+)$ and $B_{\perp}(+)$ bands should theoretically be of opposite sign because of their orthogonal polarizations, which is in full agreement with the experimental results. A minus-to-plus CD pattern was calculated for the both $B_{\parallel}$–$B_{\parallel}$ and $B_{\perp}$–$B_{\perp}$ couplings and results in one intense negative CD signal at lower energy and two partly resolved positive CD signals at higher energy. This calculated CD pattern is in good agreement with that observed experimentally, although the calculated CD intensities somewhat overestimate the experimental values, an observation often seen in the case of a short interchromophoric distance because a point-dipole approximation may overestimate the excitonic interaction energies.[11] Furthermore, the crystallographic structure and the electronic absorption and CD spectra of [(**1**)(**2**)] have been nicely reproduced by TD-DFT calculations at the B3LYP/6-31G(d) level (see Supporting Information).[12]

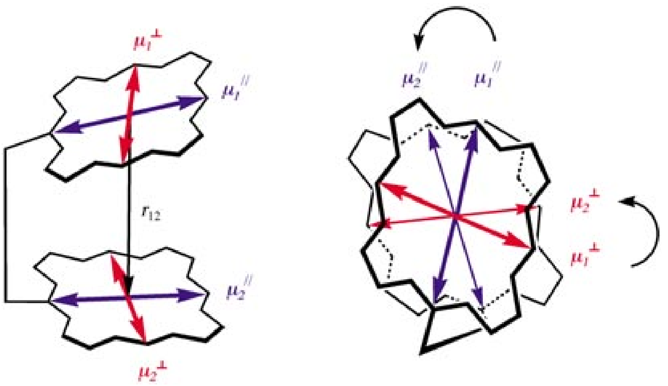

Figure 3. Definition of the direction of the transition dipole moments used in the theoretical analysis. r_{12} is the distance between the centers of gravity of the porphyrin units. The subscripts 1 and 2 (for μ) are used to distinguish between the two chromophores.

In summary, this work gives for the first time full and unambiguous rationalization of the highly efficient transfer of chirality information from an optically active guest to an achiral host in a supramolecular system based on a bisporphyrin. Furthermore, it is a rare example of an explicit crystallographic characterization of a bis(zinc porphyrin) complex with a chiral ligand. Therefore, this approach should have important implications for the complete understanding of the mechanisms and driving forces of various chirogenic phenomena in numerous artificial and natural supramolecular assemblies.

Experimental and Computational Section

X-ray structural analysis and crystal data: The structure was solved by direct methods by using the SAPI91 program.[13] The absolute configuration was established to correspond to that of **2** without Bijvoet analysis.[14] Non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, but finally fixed. All calculations were carried out with the program packages.[15] Crystal size $0.5 \times 0.05 \times 0.05$ mm, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 14.356(2)$, $b = 41.472(5)$, $c = 13.159(2)$ Å, $V = 7834(1)$ Å^3, $d_{\mathrm{calcd}} = 1.13\ \mathrm{g\,cm^{-3}}$, No. of reflections used = 8847, $2\theta_{\max} = 149.9°$ with $\mathrm{Cu}_{\mathrm{K}\alpha}$, $R = 0.060$, $(\Delta/\sigma)_{\max} = 0.0008$, $(\Delta\rho)_{\max} = 0.59$ e Å^{-3}, $(\Delta\rho)_{\min} = -0.86$ e Å^{-3}.

Spectroscopic measurements: MCD spectra were recorded on a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet, which produced magnetic fields of up to 1.09 tesla with parallel and antiparallel fields. Scanning conditions were as follows: scanning rate: 50 nm min^{-1}, bandwidth: 1 nm, response time: 0.5 s, accumulations: 2 scans.

Theoretical calculations: The analysis was based on the Kuhn–Kirkwood coupled-oscillator mechanism. A stealing of CD intensity from the ligand transitions was ruled out because of the absence of chromophores in the ligand. The exciton states energies, oscillator strengths, and rotatory strengths were calculated within the point-dipole approximation using the geometrical and spectral parameters. The geometrical parameters were obtained from the crystal structure. The spectral parameters for the $B_{\parallel}$ and $B_{\perp}$ transitions of the porphyrin monomer were obtained by band deconvolution analysis of zinc octaethylporphyrin with a CH_2OEt substituent at the meso position (ZnOEP-CH_2OEt) ($B_{\parallel}$: excitation energy = 23743 cm^{-1}; band width = 576 cm^{-1}; magnitude of the transition moment = 7.428 D; $B_{\perp}$: excitation energy = 23575 cm^{-1}; band width = 525 cm^{-1}; magnitude of the transition moment = 7.118 D). The values for the exciton interaction energies were obtained from these parameters ($B_{\parallel}$–$B_{\parallel}$: 1300 cm^{-1}, $B_{\perp}$–$B_{\perp}$: 740 cm^{-1}, $B_{\parallel}$–$B_{\perp}$: 250 and 225 cm^{-1}). The contribution arising from nondegenerate couplings ($B_{\parallel}$–$B_{\perp}$) was calculated to be about 1% of the degenerate couplings ($B_{\parallel}$–$B_{\parallel}$ and $B_{\perp}$–$B_{\perp}$), and therefore its contribution was neglected in our calculations. The polarizations of the two major calculated transitions (399 and 411 nm) were perpendicular to each other. Similar spectroscopic properties were also obtained by the ZINDO/S calculations when the geometry of the ground state was regarded as that observed in the crystal structure (see Supporting Information).

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[7] The orientation of the B transitions in the corresponding porphyrin monomer were determined by TDDFT calculations of the model compound zinc(octaethylporphyrin) with a CH_2OCH_3 group at one meso position. The accuracy of the DFT-optimized structure was assessed by comparison with the porphyrin units in the crystal structure. Averaged bond lengths of the calculated porphyrin skeleton are as follows (values in parentheses indicate corresponding bond lengths in the crystal structure): Zn-N_p: 2.06 (2.07), N_p-C_α: 1.37 (1.37), C_α-C_β: 1.46 (1.45), C_β-C_β: 1.38 (1.36), C_α-C_m: 1.40 (1.39). The calculations

indicated that the direction of the dipole moment at lower energy (382 nm, $B_{\perp}$) is perpendicular to the CH_2OCH_3 axis, whereas the direction of the dipole moment at higher energy (375 nm, $B_{\parallel}$) is parallel (see Supporting Information). This situation may arise from the fact that the position of the meso-carbon atom in the DFT-optimized structure deviates from the mean plane of the porphyrin ring as a result of steric repulsion between the CH_2OCH_3 and two adjacent ethyl groups. This observation was also supported by the crystallographic structure (see Figure 1). Indeed, when the ZINDO/S calculations were carried out using the geometries of each monomeric porphyrin unit with a methyl bridge in the crystal structures (the ethane C–C bond was replaced by one hydrogen atom to construct these two monomeric porphyrins), we obtained stick spectra similar to the TDDFT results (see Supporting Information). Since these calculations overestimate the excitation energies of the B bands, the values obtained from a band deconvolution analysis for the absorption spectrum of a model compound, ZnOEP-CH_2OEt, were used for the CD calculations (see Supporting Information and A. Muranaka, A. Ceulemans, N. Kobayashi, V. V. Borovkov, G. A. Hembury, Y. Inoue, unpublished results).

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