# Solid-State Supramolecular Chirogenesis: High Optical Activity and Gradual Development of Zinc Octaethylporphyrin Aggregates

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Aggregation processes leading to chirality transfer or induction or amplification phenomena are currently one of the "hot topics" of modern chemical science. The investigation of such processes has influenced research in many areas including studies on the origin of the homochirality of life, various biomimetic systems, materials and polymer science, nonlinear optics, molecular devices, molecular recognition, and the determination of absolute configuration.[1] In the course of our investigations on supramolecular chirogenesis phenomena in porphyrin chromophores,[2] we recently discovered a new type of highly optically active aggregates based on bis(zinc porphyrin) upon interaction with chiral amines in the solid state.[2a] Extension of this research revealed that not only more structurally complex bisporphyrins form chiral aggregated species in the solid state, but that even a conventional and simple monomeric zinc porphyrin may generate chiral aggregates under certain conditions. Here we describe the time-dependent formation of chiral aggregates of zinc octaethylporphyrin (ZnOEP, Figure 1) upon interaction with enantiopure chiral amines in the solid state. This results in the highest optical activity ever reported for a supramolecular chirogenic system based on porphyrin chromophores.

Recently it was shown that ZnOEP exhibits either no or only negligible optical activity in the porphyrin absorption region upon interaction with chiral amines in solution[2d] and in the solid state.[3] However, and exclusively for the case of enantiopure 1-cyclohexylethylamines (CHEAs), further analysis of the solid-state mixture with ZnOEP revealed the gradual development of a supramolecular chirogenic process. The solid-state samples were prepared according to the standard procedure for obtaining a glassy KBr matrix.[4] Then the process of supramolecular chirogenesis was monitored by UV/Vis and circular dichroism (CD) spectroscopy over time.

In the beginning the UV/Vis spectrum of freshly prepared ZnOEP·L (L = (*S*)-CHEA) in a KBr matrix closely resembles that in $CH_2Cl_2$ (Figure 2b, see also ref. [2d] and the Support-

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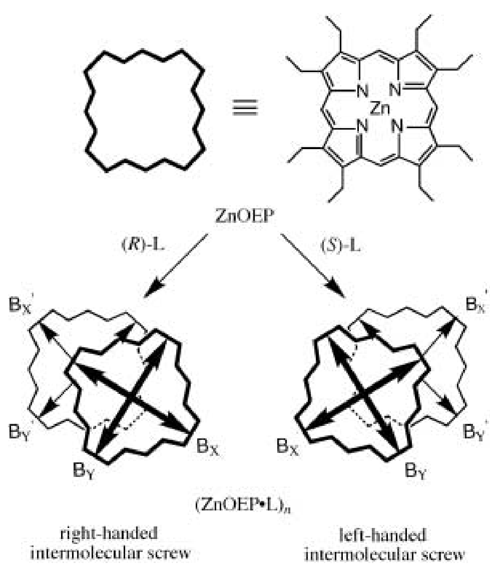

directions of the coupling transitions

| coupling transitions | right-handed screw | left-handed screw |
|---|---|---|
| $B_X/B_X'$ | clockwise | anticlockwise |
| $B_Y/B_Y'$ | clockwise | anticlockwise |
| $B_X/B_Y'$ | clockwise | anticlockwise |
| $B_Y/B_X'$ | anticlockwise | clockwise |

***Figure 1.*** Schematic representation of the formation of chiral aggregates $(ZnOEP{\cdot}L)_n$ upon interaction of ZnOEP with chiral ligands L in the solid state and the directions of the corresponding coupling transitions. The structures of $(ZnOEP{\cdot}L)_n$ are drawn schematically to show the opposite orientation of the transition coupling directions (other stacked orientations are possible as a result of rotations of the ZnOEP·L monomers against each other).

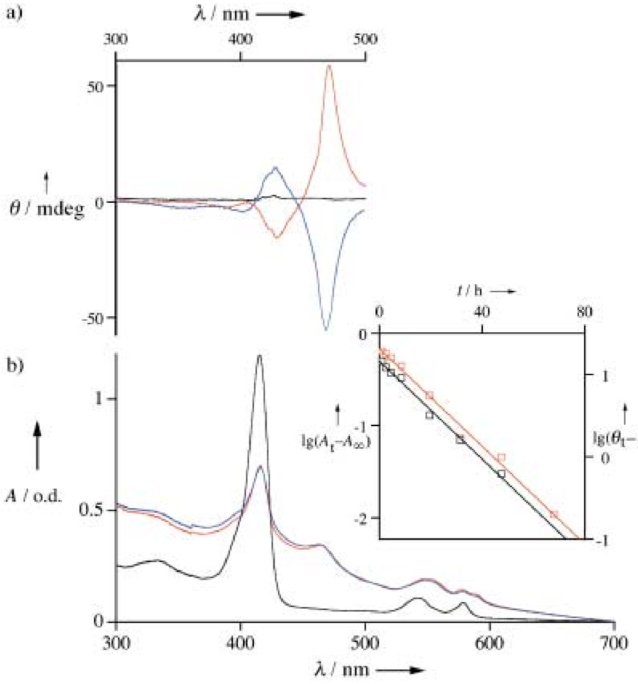

***Figure 2.*** The CD (a) and UV/Vis spectra (b) of ZnOEP in a KBr matrix in the presence of (*S*)-CHEA recorded immediately after preparation (black lines) and after four days (red lines), and (*R*)-CHEA recorded after 4 days (blue lines). The spectra of (*S*)- and (*R*)-CHEA are normalized to the same optical density. Inset: Kinetics data of the UV/Vis (black) and CD (red) spectral changes of ZnOEP in the presence of (*S*)-CHEA in a KBr matrix monitored at the maximum of the B transition ($\lambda = 415$ nm) and the position of the first Cotton effect ($\lambda = 469$ nm). The solid lines represent the best linear fit of the experimental data.

ing Information) and the CD spectrum (Figure 2a) indicates there is only minor optical activity. This indicates clearly that the initial structure and aggregation state of ZnOEP·L in the solid state is very similar to that in solution.

Subsequent measurements of the same sample after four days[5] revealed extensive changes in the UV/Vis and CD spectra. In the UV/Vis spectrum the amplitude of the initial B band was considerably diminished, with a new bathochromically shifted transition appearing at $\lambda = 464$ nm; similar but smaller changes were also clearly observed in the Q absorption region. These observations suggest an intermolecular J-type association of the ZnOEP·L molecules to form a stacked $(ZnOEP{\cdot}L)_n$ species, as they are in good agreement with exciton coupling theory[6] and other literature data on various J aggregates.[1a,f,k,7] Simultaneous CD monitoring of the same solid-state sample showed induction of extraordinarily high optical activity in the aggregated species.[8] Specifically, this includes an intense CD couplet in the region of the new low-energy B band (Figure 2a) and conspicuous monosignate Cotton effects corresponding to the porphyrin Q transitions (see the Supporting Information).

Although the spectral profile of this CD signal somewhat resembles that observed for the bis(zinc porphyrin)/(*S*)-CHEA system under solid-state conditions[2a] and the induced chirality sign is also the same, thus indicating similarity in the structural organization and helical orientation between the chiral aggregates, there are two crucially important differences. These are a considerable low-energy shift of the first Cotton effect ($\lambda^{CD} = 469$ nm) and a remarkable enhancement of the anisotropy ($g$) factor at the wavelength corresponding to the first Cotton effect ($g = -0.015$), which is 10–100 times greater than the $g$ factors reported for typical allowed π–π transitions. This is apparently a result of the formation of larger J aggregates of $(ZnOEP{\cdot}L)_n$ and the amplification of chirality by intermolecular excitonic coupling within the aggregates. In the case of bisporphyrin chromophores the formation of larger aggregates is less probable because of the larger molecular size in comparison to the monomeric porphyrin. Furthermore, the intermolecularly induced chirality is considerably reduced in the bisporphyrin case by intramolecular coupling of opposite orientation.[2a,b] However, all other chiral amines studied to date do not generate any supramolecular chirogenic processes upon interaction with ZnOEP in the solid state.[3]

Although the precise origin of the selectivity of CHEA is not yet well understood, it is likely that the exceptionally high binding ability of these ligands among the amines used[2c] may contribute greatly to the formation of chiral aggregates in the solid state. The strong binding of CHEA may compete successfully with the achiral H-type interporphyrin stacking, thus causing the chiral J-type interporphyrin association. In particular, the approach of the second ZnOEP·L complex to the first ZnOEP·L from the same side as the CHEA ligand forces the former to adopt a screw offset spatial orientation in relation to the latter. The direction of the twist is governed by the relative bulkiness of the substituents at the asymmetric center, which depends upon the absolute configuration of the chiral ligand. For example, in the case of (*S*)-CHEA the screw orientation is left-handed, based on examination of Corey—Pauling–Koltun molecular models, while in the case of (*R*)-CHEA the screw direction is right-handed. Importantly, these spatial arrangements correspond to the negative and positive chirality,[9] which was observed experimentally. Further replication of this process results in formation of the helically twisted J aggregates of $(\text{ZnOEP·L})_n$ inducing the high optical activity.

The plausible mechanism of chirality induction in $(\text{ZnOEP·L})_n$ can be rationalized on the basis of a simple dimeric subunit (where $n=2$) of the whole chiral aggregate, the schematic structure of which is shown in Figure 1. Interaction of ZnOEP with (*S*)-CHEA produces negative chirality that corresponds to the left-handed interporphyrin screw structure in the solid state as described above and has also been observed for the bis(zinc porphyrin) systems.[2a] In this twisted conformation the coupled porphyrin electronic transitions become optically active. In particular, the two degenerate transitions ($B_X$ and $B_Y$) of the first ZnOEP·L molecule couple with the $B_{X'}$ and $B_{Y'}$ transitions of the second porphyrin complex in a stereospecific manner. Thus, the $B_X/B_{X'}$, $B_Y/B_{Y'}$, and $B_X/B_{Y'}$ pairs adopt an anticlockwise orientation, and the $B_Y/B_{X'}$ pair forms a clockwise orientation, which correspond to negative and positive chirality, respectively, according to the exciton chirality method.[9] As a result of the three negative and one positive couplets in the same B band region, the overall sum of these should be a complex CD signal with a first Cotton effect of negative sign, which is exactly what is observed experimentally (Figure 2a). In the case of the *R* enantiomer the coupling directions of the dipoles are exactly opposite, resulting in the mirror-image CD spectrum of positive chirality.

As noted above, this supramolecular chirogenesis proceeds slowly in the solid state. The course of the aggregation process was monitored at the most intense porphyrin absorption region of the Soret band by UV/Vis and CD spectroscopy (see the Supporting Information). In the UV/Vis spectra the intensity of the Soret band of ZnOEP·L gradually decreases with time, while a new spectral band associated with $(\text{ZnOEP·L})_n$ simultaneously appears. In the CD spectra there is a stepwise transformation of the initial small signal into the bisignate CD couplet induced by the aggregation process as described above. Although the intermolecular porphyrin association is apparently a complex and multistep process, there is a clear pseudo-isosbestic point in the UV/Vis spectrum at $\lambda = 425$ nm which is due to the similarity of the absorption profiles of the porphyrin aggregates and intermediate species. However, in contrast to the UV/Vis spectra the CD spectra do not show an isodichroic point because of the different chiroptical properties of the various chiral species. In the case of UV/Vis spectroscopy the monitoring parameter was the absorbance at the wavelength corresponding to the maximum of the initial B transition ($\lambda = 415$ nm) as this is most affected by the aggregation process. For CD spectroscopy the intensity of the newly developed Cotton effect ($\lambda = 469$ nm) was selected to monitor the corresponding spectral changes. The bathochromically shifted CD transition was chosen to minimize the contribution of the intermediate chiral species, which appear to absorb at higher energies in comparison to the larger chiral aggregates.

Both the UV/Vis and CD kinetic experimental data fit well to a theoretical equation for a first-order processes [Eq. (1)], where $A_0$, $A_t$, and $A_\infty$ are UV/Vis absorbances (in

$$A_t = A_\infty + (A_0 - A_\infty)(-k_{\text{obs}}\,t) \tag{1}$$

the case of CD the ellipticities $\theta$ were used) at the initial, intermediate, and final stages of the aggregation process, respectively. This allows determination of the pseudo-first-order rate constants $k_{\text{obs}}$ by a nonlinear least-square fitting procedure (inset of Figure 2). The $k_{\text{obs}}$ values obtained from both spectroscopic techniques are almost identical ($k_{\text{obs}}^{\text{UV}} = 0.026\ \text{h}^{-1}$ and $k_{\text{obs}}^{\text{CD}} = 0.030\ \text{h}^{-1}$), indicating that the supramolecular chirogenesis is simultaneously generated by slow interporphyrin aggregation.

To prove the absence of any chemical reactions in the solid state that might yield new chiral compounds rather than an aggregated species, the four-day-old KBr sample of $(\text{ZnOEP·L})_n$ was destroyed by treatment with water and then extracted into $CH_2Cl_2$. The UV/Vis spectra of the resulting extract is essentially identical to that of ZnOEP in the same solvent, and the CD spectrum does not show any optical activity (see the Supporting Information). This result clearly demonstrates that the aggregation process is the sole reason for the supramolecular chirality induction in the solid state.

Finally, these $(\text{ZnOEP·L})_n$ solid-state aggregates are remarkably stable over time. Even after storage for over six months in a dark, dry environment, reexamination of the chiroptical properties by CD spectroscopy showed that the integrity of the developed chiral structure was retained.

In summary, this work provides a unique example of a time-dependent, solid-state chirogenesis phenomenon in supramolecular systems based on a simple monomeric porphyrin chromophore by the formation of helical intermolecular aggregates possessing a high degree of optical activity.

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**Keywords:** chirality · circular dichroism · porphyrinoids · solid-state structures · supramolecular chemistry

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[8] Using a solid-state specialized universal chiroptical spectrophotometer UCS: J-800KCM (R. Kuroda, T. Harada, Y. Shindo, *Rev. Sci. Instrum.* **2001**, *72*, 3802 – 3810) it was shown that optical anisotropies of the solid-state samples are negligibly small (see the Supporting Information). For example, linear dichroism, which is the major source of the artifacts observed in the CD signal of solid-state samples, contributes less than 1 % to the total observed amplitude.

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