Solvent-dependent chiral assembling of two zinc porphyrins in a zinc–free-base–zinc trimeric porphyrin array

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A pair of zinc porphyrins attached to a free-base porphyrin shows a strong split Cotton effect in CH_2Cl_2, in which the leucine esters on the rims lead to chiral assembly.

The functions of multiple porphyrin arrays have attracted attention with regard to the photosynthesis active centre[1] and CD spectra often establish the asymmetric orientation of porphyrins.[2] We also recently reported a chiral porphyrin assembly bound to a designed polypeptide, which was detected by the split CD spectrum.[2c] In the chiral assemblies of porphyrins so-far synthesized, the chiral substituents are directly combined with the aggregated porphyrins and therefore their orientation is tight and does not reflect their surroundings. To explore a multiporphyrin system with a controllable arrangement, we attempted to detach the chiral auxiality from the aggregated porphyrins. We have synthesized a U-shaped and twisted porphyrin trimer **1** (Fig. 1) and here we report our preliminary results.

The Zn(por)–H_2por–Zn(por) trimer **1**, where por denotes the porphyrin dianion, was synthesized in four steps from α,α-5,15-di-*p*-tolyl-10,20-di(2-amino-5-carboxyphenyl) porphyrin.[3] This free-base porphyrin can tether two zinc porphyrins and two chiral groups to the *trans*-phenyl groups. A face-to-face arrangement of the zinc porphyrins may be expected using an α,α-isomeric template. The 2-amino groups of the template link zinc tri-*p*-tolyl-*p*-carboxyphenylporphyrins through the glycine spacers and the 5-carboxyl groups connected L-Leu-OBn. Reference compound **2** with a Zn(por)–H_2por array was also synthesized using zinc tri-*p*-tolyl-*p*-carboxyphenylporphyrin, glycine, tri-*p*-tolyl-(2-amino-5-carboxyphenyl)porphyrin and L-Leu-OBn. All the new compounds gave satisfactory ^1H NMR and FAB MS spectra and synthetic details will be reported elsewhere.

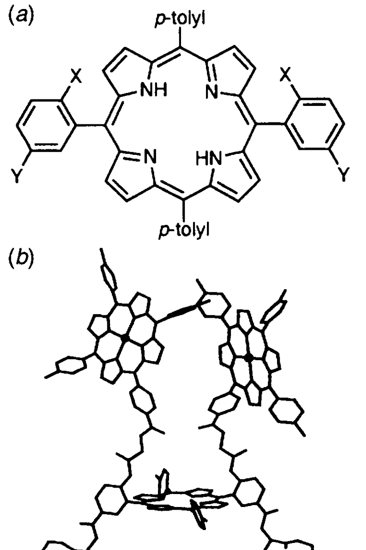

Fig. 1 (*a*) Structure of porphyrin trimer **1**. X = *p*-(zinc tri-*p*-tolylporphyrinato)phenyl-CO-Gly-NH–, Y = –CO-L-Leu-OBn. (*b*) CAChe (MM2)-generated structure of **1** with right-twisted arrangement for the Zn(por) units.

Fig. 2(*a*) shows the UV–VIS spectra of **1** and **2** in CH_2Cl_2 {λ_{max}/nm (log [ε/dm^3 mol^{-1} cm^{-1}]): 427 (5.82), 435 (5.81), 520 (4.36), 558 (4.65), 599 (4.34) and 651 (3.61) for **1**; 420 (5.77), 517 (4.33), 549 (4.47), 589 (3.99) and 648 (3.61) for **2**}. The spectrum of **2** is similar to the sum of its components. However, *ca.* 10 nm red-shifting occurred for **1** and two absorptions appeared in the Soret-band region. These facts suggests the interaction of some porphyrin rings in **1**, probably of the two zinc porphyrins. Since dilution from 1.0 μmol dm^{-3} to 10 nmol dm^{-3} did not change the spectrum of **1**, intramolecular interaction is invoked to explain the red shift.

A strong split CD at the Soret-band region occurs for **1** in CH_2Cl_2 [Fig. 2(*b*), λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 438 (+638), 428 (−872) and 413 (+106)]. These Δε values are substantial compared with the Δε of +412 and −263 dm^3 mol^{-1} cm^{-1} for bisporphyrin-attached cholesterol.[2b] Such large Δε values with split Cotton effects can be attributed to exciton-coupled CD. On the other hand, dimer **2** showed little induced CD [λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 418 (−4)]. Since Zn(por)–H_2por **2** shows only an induced CD spectrum whereas Zn(por)–Zn(por) **1** showed an exciton-coupled CD, interaction of the two Zn porphyrins in **1** is strongly suggested. Being connected to the 2-phenyl positions, the Zn porphyrins would be closely located in a twisted face-to-face arrangement [Fig. 1(*b*)]. The +/− sense of the split CD for **1** indicates a right-twisted orientation of the Zn(por) excitons.[4] The Leu-OBn group at the 5-phenyl position may incline the phenyl group into a left-twisted mode; consequently the two Zn(por) units can be arranged in a right-twisted manner.

Interestingly, adding toluene to CH_2Cl_2 drastically decreased the CD of **1**, although the UV–VIS spectra differed only slightly; λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 439 (+388), 429 (−505), 414 (+69) in toluene–CH_2Cl_2 (1 : 1, *v*/*v*) and 440 (+39), 433 (−48), 426 (+34) in toluene [Fig. 2(*b*)]. The Cotton effect decreased almost linearly with increasing toluene content in the solvent (Fig. 3); the CD spectra being probably sensitive to remote interactions of the porphyrins.[2b] The higher dipole

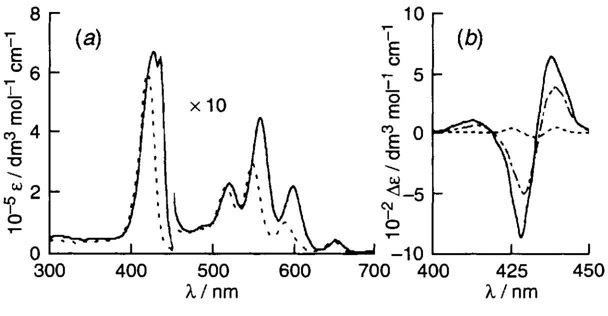

Fig. 2 (*a*) UV–VIS spectra of **1** (—) and **2** (···) in CH_2Cl_2. (*b*) CD spectra of **1** in CH_2Cl_2 (—), CH_2Cl_2–toluene (1 : 1, *v*/*v*, ——) and in toluene (···).

moments (μ/C m; CH_2Cl_2, 5.2; toluene, 1.0) and/or higher relative permittivities (ε_r; CH_2Cl_2, 8.93; toluene, 2.38)[5] of CH_2Cl_2 might stabilize aggregation of the zinc porphyrins.

In conclusion, the U-shaped and twisted porphyrin trimer **1** showed strong a split CD spectrum in CH_2Cl_2. The L-Leu-OBn groups of the template leads to a right-twisted arrangement of the two Zn(por) units and the chiral orientation can be controlled by the solvent. The present finding should be helpful for the study of porphyrin self-assembling under environmental control. Further investigation is in progress to clarify the driving forces for the overlapping of the porphyrin rings.

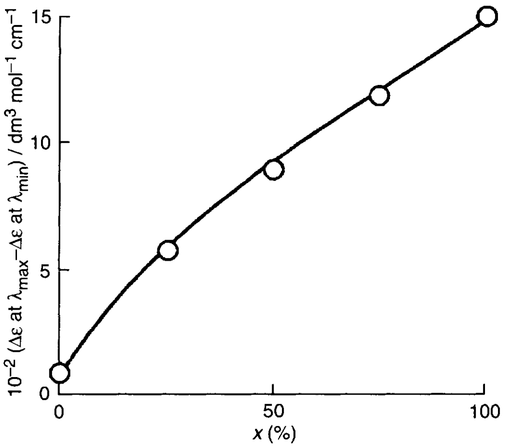

Fig. 3 The intensity of the split Cotton effect of **1** in CH_2Cl_2 (100 − x%)–toluene (x%); $\lambda_{max.}$ is at *ca.* 438 nm and $\lambda_{min.}$ at *ca.* 428 nm

This work was partly supported for T. A. by a Grant in Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan (No. 07780497) and Ogasawara Foundation for the Promotion of Science and Engineering.

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Received, 1st July 1996; Com. 6/04538C