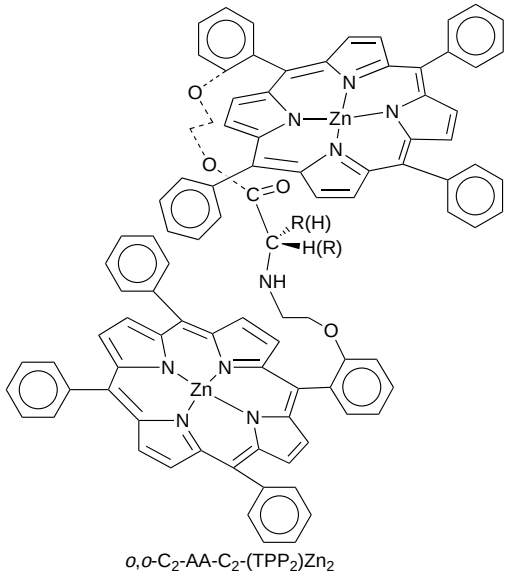
Chiral linear assembly of amino acid bridged dimeric porphyrin hosts

Hai-yang Liu,[a] Jin-wang Huang,[a] Xuan Tian,[b] Xiang-dong Jiao,[a] Guo-tian Luo,[a] and Liang-nian Ji*[a]

[a] *Department of Chemistry, Zhongshan University, Guangzhou 510275, China*
[b] *National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*

Chiral linear zinc porphyrin arrays are constructed from amino acid bridged zinc porphyrin dimers and ethylenediamine *via* self-assembly in $CHCl_3$; the induced CD sign and shape of the array are different from that of the porphyrin subunit.

In photosynthesis, plant cells utilize arrays of up to three hundred porphyrin molecules (chlorophyll) for light capture.[1] These porphyrin chromophores are fixed spatially and orientationally by the skeleton material of the cells. The design and synthesis of artifical molecular systems aimed at mimicking the structure and/or function of photosynthetic centres has attracted much recent interest.[2] In order to construct large porphyrin arrays, a 'building block' strategy has been developed.[3] It was considered that unidimensional porphyrin arrays were particularly well-adapted to accommodate multistep electron-transfer (ET) reactions, eventually leading to long-lived and spatially-remote charge separation states. Each module consists of a porphyrin covalently attached to a chelate and transition metals have been used for making these one-dimensional multicomponent molecular systems.[4] We have synthesized a number of amino acid bridged chiral zinc porphyrin dimers *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$,[5] and here we report a facile approach to the construction of chiral linear zinc porphyrin arrays from these zinc porphyrin dimers and a bidentate ligand (ethylenediamine) in $CHCl_3$. Our 'module–linker' strategy for making one-dimensional porphyrin arrays is illustrated in Fig. 1.



o,o-C_2-AA-C_2-$(TPP_2)Zn_2$

R = H (AA = Gly)
R = Me (AA = Ala)
R = CH(OH)Me (AA = Thr)
R = Bn (AA = Phe)

UV–VIS spectra of metal-free porphyrin dimers *o,o*-C_2-AA-C_2-$(TPP)_2$ exhibited the usual free base porphyrin bands and the λ_{max} values were close to those of tetraphenylporphyrin. However, Q band red-shifting (*ca.* 10–15 nm) occurred for zinc

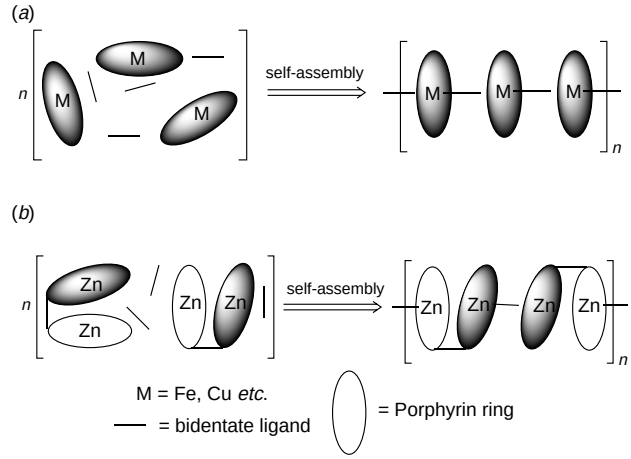


Fig. 1 'Module–linker' strategy used to assemble one-dimensional porphyrin arrays. The basic module is metalloporphrin monomer (*a*) or zinc porphyrin dimer (*b*) and the linker is a suitable linear bidentate ligand.

porphyrin dimers *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ (Table 1). As the π–π interaction between two porphyrin chromophores is enhanced by metallaton,[6] the red shift indicated π–π attraction made the two zinc porphyrins adopt a head to tail arrangement in the dimer and an intramolecular exciton coupling interaction[7] existed between the two zinc porphyrins.

Split induced circular dichroism (ICD) at the soret absorption band was observed for chiral amino acid (Ala, Thr, Phe) bridged zinc porphyrin dimers *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ and the L- and D-amino acid bridged zinc porphyrin dimers constituted pairs of enantiomers (Fig. 2). No significant ICD was observed for the corresponding free base porphyrin dimers. This strongly suggested that the ICD of these complexes was correlated to the chiral π–π stacking of the zinc porphyrins in the dimers. Namely, the observed ICD was caused by chiral exciton coupling interactions.[8]

Molecular orientation in porphyrin-based aggregates can be conveniently monitored by CD spectroscopy.[9] Here CD titration methods were used to detect the formation of the chiral porphyrin array. The ICD spectra of chiral zinc porphyrin dimers *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ is dramatically reduced upon the addition of propylamine; this suggests that the coordination of propylamine to *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ blocked much of

Table 1 Electronic absorption spectrum data of *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ (in $CHCl_3$, room temp.)

	UV–VIS λ_{max}/nm		
Zinc porphyrin	Soret	Q	
(TPP)Zn[a]	418.3	547.1	583.9
o,o-C_2-Gly-C_2-$(TPP)_2Zn_2$	418.5	557.1	599.3
o,o-C_2-Ala-C_2-$(TPP)_2Zn_2$	419.9	556.1	598.1
o,o-C_2-Thr-C_2-$(TPP)_2Zn_2$	421.9	554.9	594.5
o,o-C_2-Phe-C_2-$(TPP)_2Zn_2$	420.1	553.3	595.3

[a] This work.

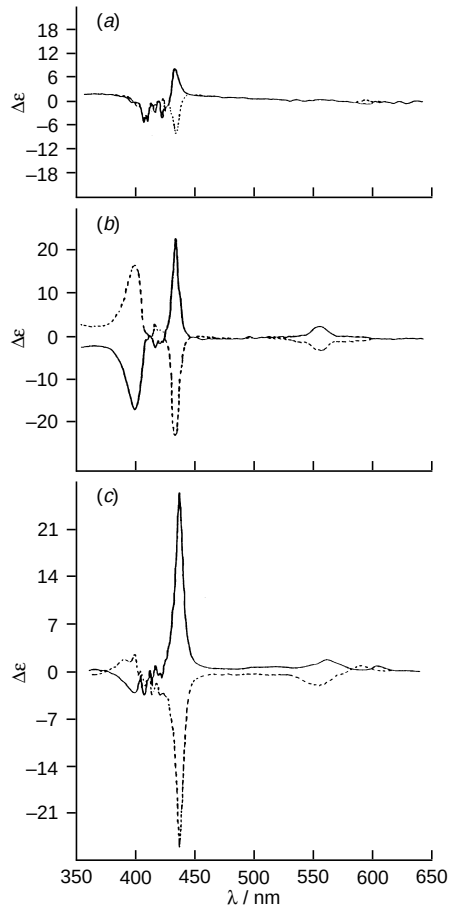


Fig. 2 CD spectra of *o,o*-C_2-(L-AA)-C_2-$(TPP)_2Zn_2$ (——) and *o,o*-C_2-(D-AA)-C_2-$(TPP)_2Zn_2$ (- - -) in $CHCl_3$ at room temperature: (*a*) *o,o*-C_2-Ala-C_2-$(TPP)_2Zn_2$, (*b*) *o,o*-C_2-(Thr)-C_2-$(TPP)_2Zn_2$ and (*c*) *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$

the exciton interaction.[6] The change in the ICD spectra of the system might also be due to changes in dimer conformation arising from coordination of the metal of the porphyrin, for coordination of the metal by a ligand reduces the magnitude of the π–π interaction in metalloporphyrins and generally leads to disaggregation.[10] When bidentate ligand ethylenediamine was added to a solution of *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$, however, this was not the case (Fig. 3). At the first stage of the addition (ethylenediamine : zinc porphyrin ≤ *ca.* 1 : 1), the CD sign at *ca.* 436 nm was gradually reversed with increasing ethylenediamine. With further addition of ethylenediamine, the ellipticities gradually decreased, and finally disappeared when a large excess of ethylenediamine was added. Surprisingly, when a diamine having a long connecting chain, such as 1,10-diaminodecane, was added to the solution of *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$, the ICD of the system gradually reduced and finally disappeared. No reversed ICD was observed at any [1,10-diaminodecane] : [zinc porphyrin] molar ratio. We suggest that the reversed ICD of ethylenediamine–*o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ complexes is due to the formation of relatively rigid chiral linear porphyrin arrays [Fig. 1(*b*)], since reversed ICD should have been observed for the 1,10-diaminodecane–*o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ complex if it were due to the formation of the species with the bidentate ligand binding inside the cavity of the zinc porphyrin dimer. The CD ethylenediamine titration experiments revealed that the chiral linear zinc porphyrin array [Fig. 1(*b*)] reached a maximum concentration when [ethylenediamine] : [zinc porphyrin] was *ca.* 1 : 1. At higher ethylenediamine content, this bidentate ligand would act as a monodentate ligand and would result in the dissociation of the arrays.

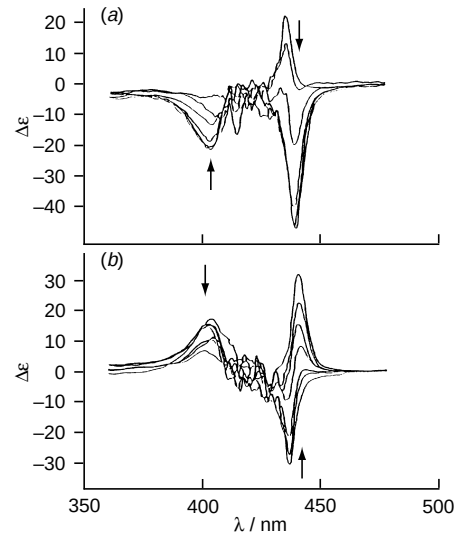


Fig. 3 Changes in the CD spectra upon addition of ethylenediamine to a solution of *o,o*-C_2-Thr-C_2-$(TPP)_2Zn_2$ (in $CHCl_3$ at room temp., [ethylenediamine] : [zinc porphyrin] ≤ 1 : 1); (*a*) *o,o*-C_2(L-Thr)-C_2-$(TPP)_2$ and (*b*) *o,o*-C_2-(D-THr)-C_2-$(TPP)_2Zn_2$

In conclusion, we have demonstrated that chiral linear zinc porphyrin arrays can easily be built with amino acid bridged zinc porphyrin dimer and the bidentate ligand ethylenediamine in solution *via* a 'module–linker' self-assembling strategy. The present study should also be helpful for the investigation of ICD of porphyrins.[8]

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Footnote and References

* E-mail: cesjln@zsulink.zsu.edu.cn

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