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Materials Science and Engineering C 10 (1999) 33–38

MATERIALS SCIENCE & ENGINEERING C

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Chiral supramolecular assembly of amino acid bridged zinc bisporphyrin and bidentate ligand

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Accepted 21 May 1999

Abstract

Coordination behavior of bidentate ligand ethylenediamine with amino acid bridged chiral zinc bisporphyrin *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ was investigated by circular dichroism (CD), UV–Vis and ^{1}H-NMR spectroscopy, experimental results suggested that *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ tend to form linear supramolecular assembly with ethylenediamine in chloroform.

Keywords: Chiral zinc bis-porphyrin; Bidentate ligand; Supramolecular assembly

1. Introduction

Multichromophore aggregates in the photosynthetic center [1] and light harvesting antennas [2] are typical examples of self-assembled supramolecular porphyrin species occurring in natural systems. Recently, supramolecular self-assembly of metalloporphyrin has received extensive attention [3–6]. The investigation of artificial biomimetic porphyrin array will not only provide useful insights into the mechanism of the photosynthetic process, but also may revolutionize solar energy technology. Hydrogen bonding [7], transition-metal-templated self-coordination [8], and transition-metal-directed oligomerization [9] are facile methods for the construction of self-assembled multiporphyrin array. We have synthesized several chiral zinc bisporphyrins with flexible bridge containing amino acids *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ (Fig. 1) [10,11]. In a previous communication [12], we have reported that *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ bind bidentate ligand ethylenediamine to form chiral linear zinc porphyrin array via a ''module-linker'' strategy. In this paper, the circular dichroism (CD), UV–Vis titration and ^{1}H-NMR study of the interactions between these chiral zinc bisporphyrins and ethylenediamine are presented and discussed.

2. Experimental

2.1. Materials

Metal-free amino acid bridged bisporphyrin *o,o*-C_2-AA-C_2-$(TPP)_2$ were prepared by the following procedure [10,11]: the mixture of 5-[*o*-(2-bromo-1-ethoxy)]phenyl-10,15,20-triphenylporphyrin (0.27 mmol), L- or D-amino acid (2.42 mmol) and anhydrous potassium carbonate (4 g) was stirred in DMF (50 ml) at room temperature for 72 h. Reaction mixture was then poured into saturated NaCl solution (150 ml). The precipitate was filtered and washed several times with water. Products were purified by means of chromatography on silica gel with chloroform as an eluent. *o,o*-C_2-AA-C_2-$(TPP)_2$ were obtained in 10%–15% yield, respectively. Zinc was incorporated by the standard method [13].

5-[*o*-(2-Bromo-1-ethoxy)]phenyl-10,15,20-triphenylporphyrin was prepared by previous published method [14]. L- and D- Phenylalanine, threonine and alanine were chrom. pure. Chloroform (A.R. grade) was dried with P_2O_5 and distilled before use. Silica gel was C.P. grade (10–40

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PII: S0928-4931(99)00098-3

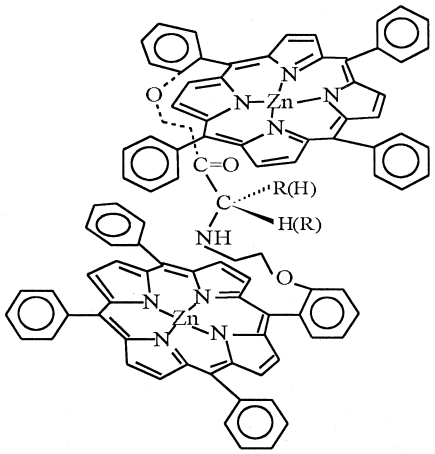

Fig. 1. Structure of amino acid bridged chiral zinc bisporphyrin *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$.

μm). Ethylenediamine (A.R. grade) was distilled before use. Other reagents were A.R. grade chemicals as supplied.

2.1.1. o,o-C_2-Gly-C_2-(TPP)$_2$

^{1}H-NMR ($CDCl_3$): δ −2.96−−2.85 (d, 4H, pyrrole NH), 0.06 (m, 1H, NH), 0.86 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 1.49 (br. s, 2H, CH_2), 2.17 (br. m, 2H, CH_2), 2.94 (br. m, 2H, CH_2), 6.06 (d, 1H, 5-phenyl of TPP), 6.62 (d, 1H, 5-phenyl of TPP), 7.28–7.89 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{94}H_{69}N_9O_4$: C, 81.75 (81.33); H, 5.30 (4.97); N, 9.51 (9.08). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1388 ($M^+ + 1$). UV/Vis (λ_{max}): 417.5, 515.9, 551.1, 587.5, 645.5 nm. IR ($\nu_{C=O}$): 1740 cm^{-1}.

2.1.2. o,o-C_2-Gly-C_2-(TPP)$_2$Zn$_2$

^{1}H-NMR ($CDCl_3$): δ −4.99 (s, 1H, NH), −4.37 (s, 2H, CH_2), −2.25 (s, 2H, CH_2), −0.06 (br. s, 1H, CH_2), 0.84 (m, 2H, CH_2), 1.12 (m, 2H, CH_2), 1.25 (s, 1H, CH_2), 6.17 (d, 1H, 5-phenyl of TPP), 6.74 (d, 1H, 5-phenyl of TPP), 7.24–8.84 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{94}H_{65}N_9O_4Zn_2$: C, 74.23 (74.55); H, 4.57 (4.30); N, 8.42 (8.33). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1514 ($M^+ + 1$). UV/Vis (λ_{max}): 418.5, 557.1, 599.3 nm.IR ($\nu_{C=O}$): 1743 cm^{-1}.

2.1.3. o,o-C_2-Ala-C_2-(TPP)$_2$

^{1}H-NMR ($CDCl_3$): δ −2.94−−2.86 (d, 4H, pyrrole), −0.57 (m, 3H, CH_3), 0.41–2.47 (several m, 10H, bridging chain), 6.08 (d, 1H, 5-phenyl of TPP), 6.20 (d, 1H, 5-phenyl of TPP), 7.13–8.81 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{95}H_{71}N_9O_4$: C, 81.65 (81.37); H, 5.40 (5.07); N, 9.31 (8.99). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1402 ($M^+ + 1$). UV/Vis (λ_{max}): 416.3, 513.7, 549.9, 590.7, 645.3 nm. IR ($\nu_{C=O}$): 1735 cm^{-1}.

2.1.4. o,o-C_2-Ala-C_2-(TPP)$_2$Zn$_2$

^{1}H-NMR ($CDCl_3$): δ −4.12 (br. s, 4H, CH_3, NH), −2.68 (m, 1H, CH), −2.37 (m, 1H, CH_2), −1.91 (m, 1H, CH_2), 0.27 (m, 1H, CH_2), 0.49 (m, 1H, CH_2), 1.62 (m, 1H, CH_2), 1.41 (br. s, 1H, CH_2), 2.36 (br. s, 1H, CH_2), 2.74 (br. s, 1H, CH_2), 6.36 (d, 1H, 5-phenyl of TPP), 6.84 (d, 1H, 5-phenyl of TPP), 7.31–8.82 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{95}H_{67}N_9O_4Zn_2$: C, 74.37 (74.66); H, 4.74 (4.39); N, 8.42 (8.25). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1528 ($M^+ + 1$). UV/Vis (λ_{max}): 419.9, 556.1, 598.1 nm. IR ($\nu_{C=O}$): 1738 cm^{-1}.

2.1.5. o,o-C_2-Thr-C_2-(TPP)$_2$

^{1}H-NMR ($CDCl_3$): δ −2.97−−2.92 (d, 4H, pyrrole NH), −0.33 (m, 3H, CH_3), 0.09–2.88 (several m, 11H, bridging chain), 5.78 (d, 1H, 5-phenyl of TPP), 5.80 (d, 1H, 5-phenyl of TPP), 7.13–8.82 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{96}H_{73}N_9O_5$: C, 80.61 (80.50); H, 5.32 (5.10); N, 8.53 (8.81). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1432 ($M^+ + 1$). UV/Vis (λ_{max}): 415.9, 514.9, 549.9, 591.1, 645.7 nm. IR ($\nu_{C=O}$): 1733 cm^{-1}.

2.1.6. o,o-C_2-Thr-C_2-(TPP)$_2$Zn$_2$

^{1}H-NMR ($CDCl_3$): δ −2.83 (m, 1H, CH), −2.71 (m, 4H, CH_3, NH), −1.05 (m, 1H, CH), −0.45 (m, 1H, CH_2), −0.21 (m, 1H, CH_2), −0.07 (m, 1H, CH_2), 2.07 (m, 1H, CH_2), 2.12 (m, 1H, CH_2), 2.28 (m, 1H, CH_2), 2.94 (m, 2H, CH_2), 6.63 (d, 1H, 5-phenyl of TPP), 6.77 (d, 1H, 5-phenyl of TPP), 7.23–8.84 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{96}H_{69}N_9O_5Zn_2$: C, 73.80 (73.99); H, 4.65 (4.43); N, 8.19 (8.09). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1558 ($M^+ + 1$). UV/Vis (λ_{max}): 421.9, 554.9, 594.5 nm. IR ($\nu_{C=O}$): 1736 cm^{-1}.

2.1.7. o,o-C_2-Phe-C_2-(TPP)$_2$

^{1}H-NMR ($CDCl_3$): δ −2.90−−2.70 (t, 4H, pyrrole NH), 0.46–4.02 (several m, 12H, bridging chain), 5.22 (m, 2H, phenyl of Phe), 6.05 (m, 2H, phenyl of Phe), 6.12 (m, phenyl of Phe), 6.20 (m, 1H, 5-phenyl of TPP), 6.31 (m, 1H, 5-phenyl of TPP), 7.4–8.84 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{101}H_{75}N_9O_4$: C, 81.55 (82.06); H, 5.38 (5.08); N, 8.63 (8.53). FAB-MS (3-nitrobenzyl alcohol) *m/z*: 1479 ($M^+ + 2$). UV/Vis (λ_{max}): 416.9, 514.1, 549.3, 590.5, 644.9 nm. IR ($\nu_{C=O}$): 1736 cm^{-1}.

2.1.8. o,o-C_2-Phe-C_2-(TPP)$_2$Zn$_2$

^{1}H-NMR ($CDCl_3$): δ −2.71 (s, 1H, CH), −2.32 (br. s, 1H, NH), −2.23 (t, 2H, CH_2), −1.81 (m, 1H, CH_2), −0.90 (m, 1H, CH_2), 0.52 (m, 1H, CH_2), 0.86 (m, 1H, CH_2), 1.02 (m, 1H, CH_2), 1.25 (br. s, 1H, CH_2), 1.49 (br.

s, 1H, CH_2), 2.73 (m, 1H, CH_2), 2.98 (m, 2H, phenyl of Phe), 4.96 (m, 2H, phenyl of Phe), 5.49 (m, 1H, phenyl of Phe), 6.55 (d, 1H, 5-phenyl of TPP), 6.90 (d, 1H, 5-phenyl of TPP), 7.25–8.93 (several m, 52H, TPP skeleton). Anal. found (Calcd.) for $C_{101}H_{71}N_9O_4Zn_2$: C, 75.17 (75.61); H, 4.59(4.43); N, 8.48 (7.86). FAB-MS (3-nitrobenzyl alcohol) m/z: 1604 ($M^+ + 1$). UV/Vis (λ_{max}): 420.1, 553.3, 595.3 nm. IR ($\nu_{C=O}$): 1737 cm^{-1}.

2.2. Measurements

CD spectra were recorded on a JASCO-20C Automatic Recording Spectrapolarimeter. UV–Vis spectra were recorded by MPS-2000 spectrophotometer. Proton NMR spectra were taken at 400 MHz in $CDCl_3$ on a Bruker AM-400 NMR spectrometer. Chemical shifts were determined with reference to TMS. IR spectra were obtained on a Nicolet FT-5DX spectrophotometer. Elemental analyses were performed with a Perkin–Elmer 240 element analyzer. FAB-MS was measured by VG ZAB-HS mass spectrometer.

3. Results and discussion

3.1. Circular dichroism spectra

CD spectra of all synthesized porphyrins were measured in chloroform at room temperature. We found only chiral amino acid bridged zinc bisporphyrins *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ (AA: L- or D-Ala, Thr, Phe) exhibited induced circular dichroism (ICD). L- and D-amino acid bridged zinc bisporphyrin constituted pairs of enantiomers. No significant ICD were observed for the corresponding metal-free

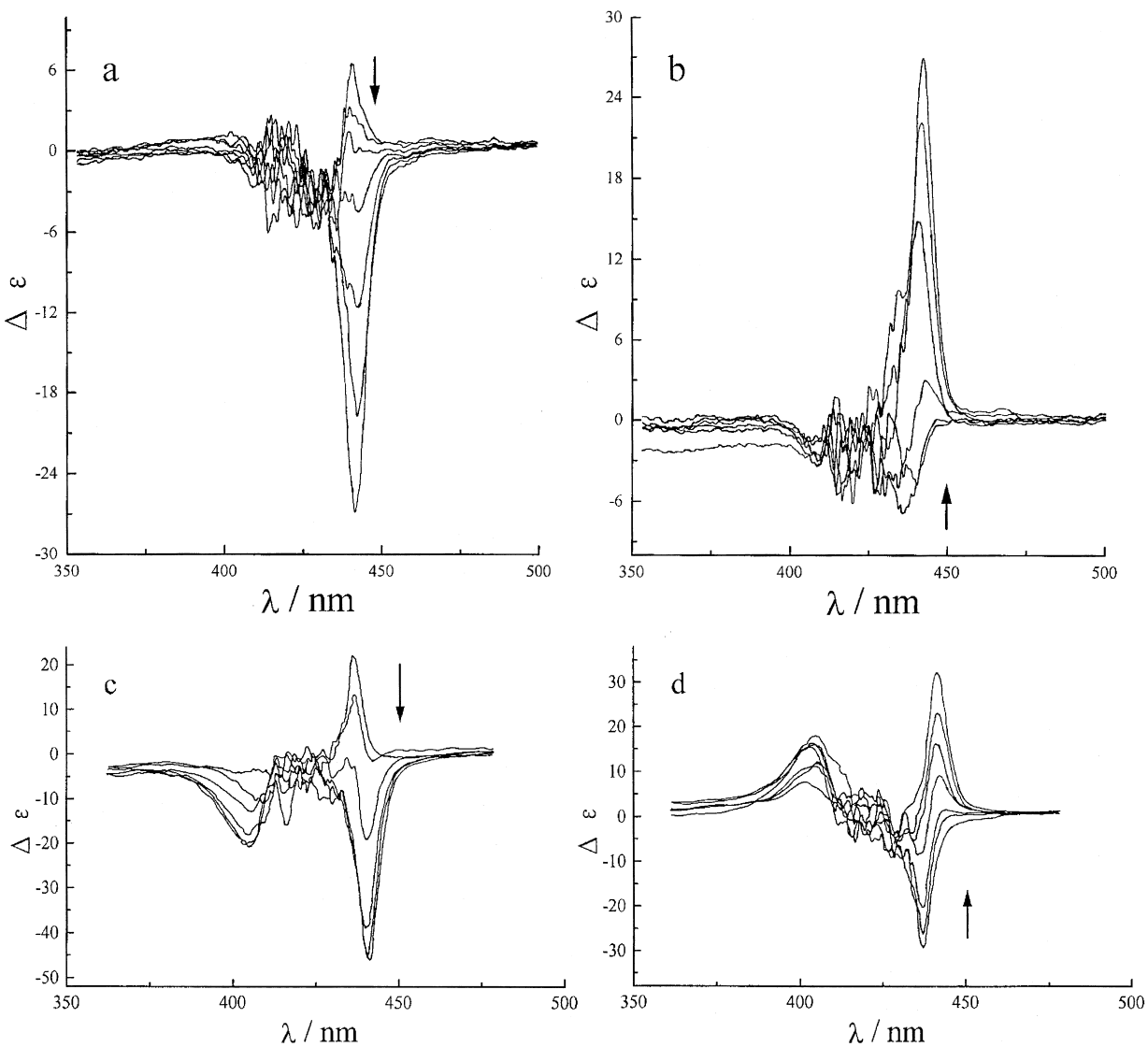

Fig. 2. CD spectra changes of *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ upon the addition of ethylenediamine in chloroform at room temperature (molar ratio: [ligand]:[zinc bisporphyrin] ≤ 1:1). AA: (a) L-Ala; (b) D-Ala; (c) L-Thr; (d) D-Thr; (e) L-Phe; (f) D-Phe.

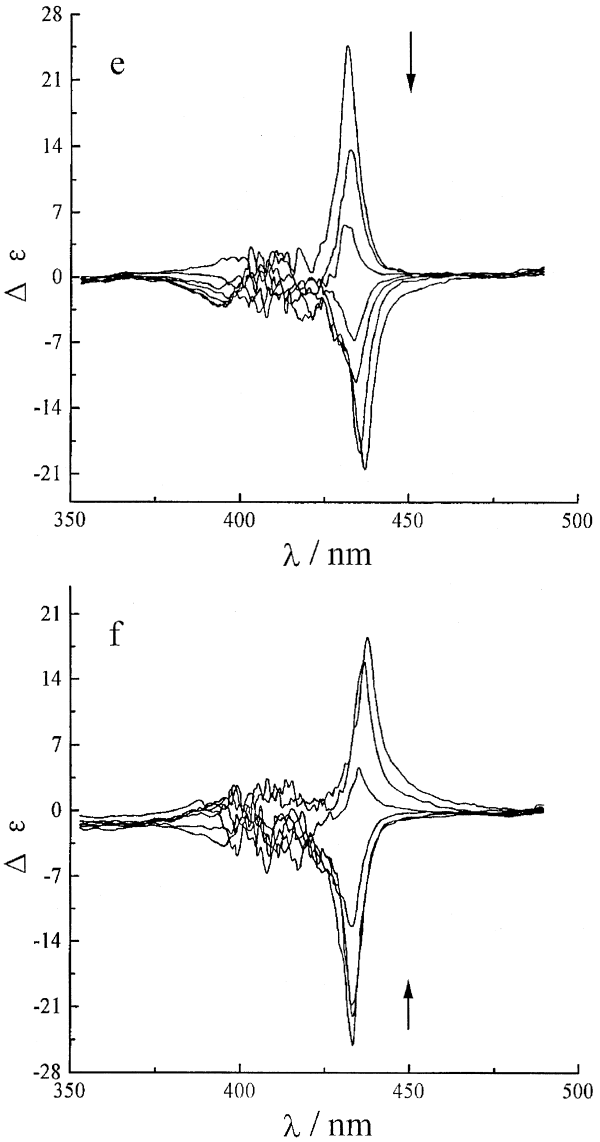

Fig. 2 (continued).

bisporphyrins. ICD of these chiral zinc bisporphyrin can be explained by chiral exciton coupling mechanism [10,11,15,16].

The ICD of chiral *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ decreased sharply with the addition of monodentate ligand propylamine. This suggests that the conformation of zinc bisporphyrin is changed. As coordination of the metal of porphyrin by a ligand would reduce the magnitude of π–π interaction in metalloporphyrins [17]. Fig. 2 shows the ICD changes of chiral *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ zinc upon the addition of ethylenediamine. ICD sign of *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ at about 436 nm reversed gradually with increasing etylenediamine. Reversed ICD reached a maximum when the molar ratio was approximately one-to-one. With further addition of ethylenediamine, the ellipticities gradually decreased and finally disappeared when a large excess of ethylenediamine was added. Fig. 2(a,b) shows that *o,o*-C_2-Ala-C_2-$(TPP)_2Zn_2$ in the presence of ethylenediamine gives reversed exciton coupling CD with larger amplitude. When 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. Following two binding modes are possible when [diamine]:[zinc porphyrin] ≤ 1:1 to form the chiral linear porphyrin array (Fig. 3) or form the species with diamine binding inside the cavity of the zinc bisporphyrin. 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 chiral linear porphyrin arrays, since reversed ICD should have been observed for 1,10-diaminodecane-*o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ complexes if it were due to the later circumstance. Also, Hayashi et al. [18] reported that semiflexible zinc bisporphyrin linked with chiral binaphthyl derivative in the presence of α,ω-diamines gave the same sign coupling CD when diamines were binding inside the cavity of bisporphyrin.

3.2. UV–Vis spectra

UV–Vis ethylenediamine-titration experiments were carried out at a temperature of 16°C in chloroform. Propylamine-titration study was also performed as control experiment. Soret band changes of *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$ (5.28×10^{-5} mol dm^{-3}) upon the binding of ethylenediamine and propylamine are shown in Fig. 4a and b, respectively. With the addition of ligands, the soret bands were red shifted. This indicated that the amine of ligands were complexed to zinc atoms of *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$. It is noteworthy that the soret band changes of *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$ with the addition of ethylenediamine and propylamine are quite different. Besides a red shift, a clear splitting of the soret band was observable when ethylenediamine was added to solution of *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$ (Fig. 4a). We ascribed the splitting of the soret band is due to the formation of linear *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$-ethylenediamine array (Fig. 3), for the splitting of the soret band is the spectroscopic feature of porphyrin aggregates [19–21] or supramolecular stack of Mg bis (imidazolyl)porphyrin [22]. When a vast excess of

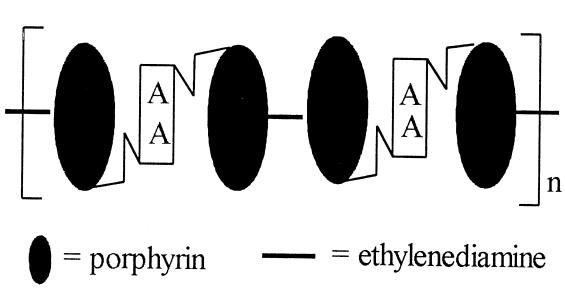

Fig. 3. Linear assembly of *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ and ethylenediamine.

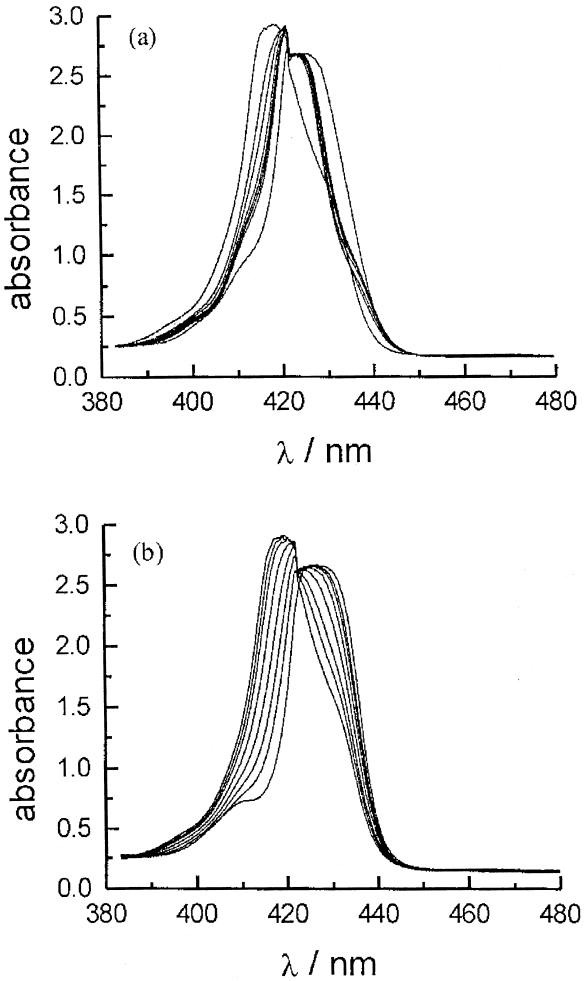

Fig. 4. Optical absorption spectra changes of *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$ (5.28×10^{-5} mol dm^{-3}) in chloroform on successive additions of ethylenediamine (a) and propylamine (b) at 16°C.

ethylenediamine was added, split soret band would become one peak like that of the *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$-propylamine complex (Fig. 4b). This suggests that the higher ethylenediamine content ([zinc porphyrin Dimer]:[ethylenediamine] > 1:1) will cause the dissociation of the array. UV–Vis titration curve of *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$ with ethylenediamine showed an inflection point at ca. 1 equiv. of ethylenediamine added (based upon the change in absorbance at 419.3 nm), indicating that 1:1 supramolecular complex formed as an intermediate. No inflection point was found in *o,o*-C_2-Phe-C_2-$(TPP)_2Zn_2$-propylamine titration curve.

3.3. ^{1}H-NMR spectra

To further investigate the formation of linear *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$-ethylenediamine assembly, 400 MHz ^{1}H-NMR studies were performed. Fig. 5a shows the ^{1}H-NMR spectrum of *o,o*-C_2-(L-Ala)-C_2-$(TPP)_2Zn_2$. Large ring-current induced upfield shift dimer signals indicated that two zinc porphyrin chromophores were in close proximity. The CH_3 and NH protons of Ala appeared a broad peak at $\delta = \sim -4.12$, While the Ala CH proton appeared at $\delta = -2.68$. The resonances at $\delta = -2.37$ and -1.91 correspond to the $(CH_2)_2$ connecting chain. These assignment were made according to the ^{1}H{^{1}H} COSY spectrum of *o,o*-C_2-(L-Ala)-C_2-$(TPP)_2Zn_2$. Fig. 5b is the ^{1}H-NMR spectrum of *o,o*-C_2-(L-Ala)-C_2-$(TPP)_2Zn_2$ when 1 equiv. of ethylenediamine was added. Surprisingly, we found peaks at $\delta = \sim -4.12$, -2.68, -2.37, and -1.91, corresponding to the Ala and $(CH_2)_2$ connecting chain, were downfield shifted (appeared at $\delta > 0$). The signals at $\delta = -5.66$ and -4.71 correspond unequivocally to NH_2 and CH_2 of ethylenediamine, respectively. Chemical shifts of NH_2 and α-CH of amino acid easter in complexation with zinc porphyrin monomer are at $\delta = -4.57$ and -2.90 [23]. Joost et al. [24] reported the NH_2 and α-CH_2 signals of tetramine binding inside the cavity of Troger's base dizinc bis-porphyrin receptor are at $\delta = -4.68$ and -2.82, respectively. The NH_2 and CH_2 signals of ethylenediamine in present system are apparently at higher field as compared with those of amino acid eater or tetramine zinc porphyrin complexes mentioned above. This strongly suggested that two amino groups of ethylenediamine were complexed to zinc porphyrin and the two porphyrin chromophores were pulled together closely. If the ethylenediamine were binding inside the cavity of *o,o*-C_2-(L-Ala)-C_2-$(TPP)_2Zn_2$, it is unreasonable that proton signals of Ala and $(CH_2)_2$ connecting chain appeared at downfield $\delta > 0$. Thus, ^{1}H-NMR study also evidenced the formation of the linear *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$-ethylenediamine supramolecular assembly (Fig. 3). Systematic NMR investigation will be reported and discussed in a future paper.

Combined observations of these spectroscopies, CD, UV–Vis, and ^{1}H-NMR, suggest that amino acid chiral

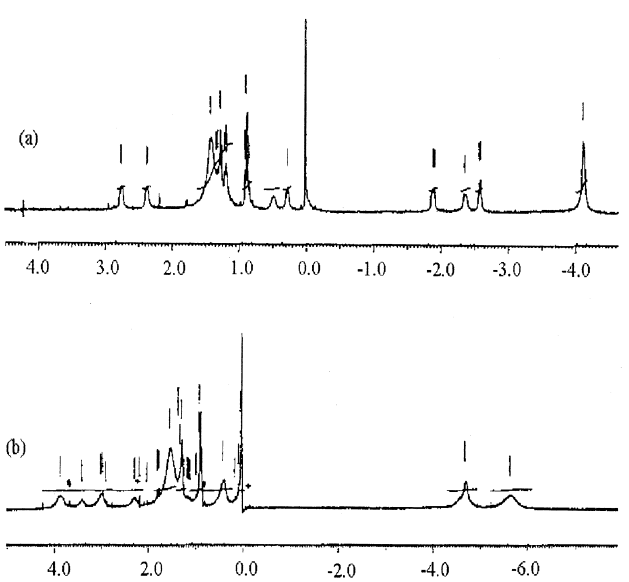

Fig. 5. ^{1}H-NMR spectra of (a) *o,o*-C_2-(L-Ala)-C_2-$(TPP)_2Zn_2$, (b) 1:1 complex of *o,o*-C_2-(L-Ala)-C_2-$(TPP)_2Zn_2$ and ethylenediamine.

zinc bis-porphyrin with flexible connecting chain *o,o*-C_2-AA-C_2-$(TPP)_2Zn_2$ tend to form chiral linear array (Fig. 3) with bidentate ligand ethylenediamine in chloroform. Which is quite different from those rigid and semiflexible zinc bis-porphyrin, as the later are tend to bind bidentate ligand inside the dimeric cavity [24–30]. [1] The present result are surely useful in the design and construction of well-defined porphyrin supramolecular architecture or functional materials.

Acknowledgements

The authors are thankful to the Natural Science Foundation of China, Natural Science Foundation of Guangdong Province and Natural Science Foundation of South China University of Technology for supporting this work.

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