

## Formation of Amino Acid Bridged Zinc Bisporphyrin-ethylenediamine Linear Supramolecular Array: UV-visible and $^1\text{H-NMR}$ evidence

Hai Yang LIU<sup>1,\*</sup>, Xiao YING<sup>1</sup>, Xi Ming HU<sup>1</sup>, Yun Li GU<sup>1</sup>, Yi LIU<sup>1</sup>, Jin Wang HUANG<sup>2</sup>,  
Liang Nian JI<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry, Department of Physics, South China University of Technology,  
Guangzhou 510641

<sup>2</sup>Department of Chemistry, Zhongshan University, Guangzhou 510275

**Abstract:** Coordination behavior of bidentate ligand ethylenediamine with a new chiral zinc bis-porphyrin  $O,O\text{-C}_2\text{-AA-C}_2\text{-(TPP)}_2\text{Zn}_2$  was investigated by Uv-Vis titration and  $^1\text{H-NMR}$  spectroscopy, which further evidenced that  $O,O\text{-C}_2\text{-AA-C}_2\text{-(TPP)}_2\text{Zn}_2$  tends to form linear assembly with ethylenediamine in chloroform.

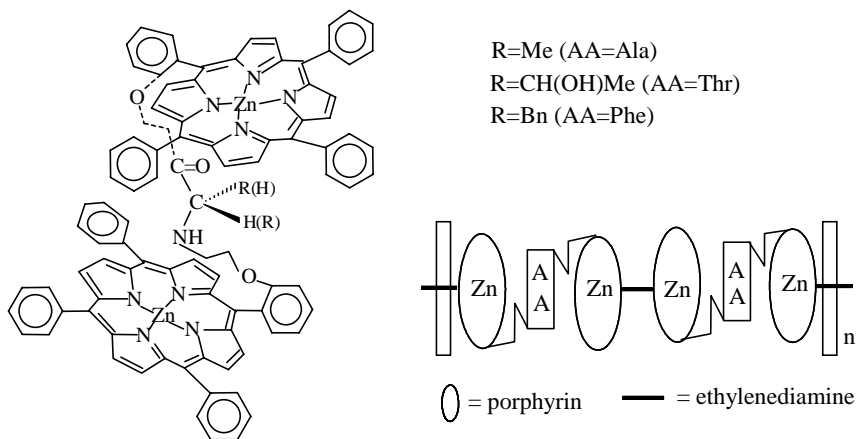
**Keywords:** Chiral zinc bisporphyrin, bidentate ligand, supramolecular assembly.

Multichromophore aggregates in the photosynthetic center<sup>1</sup> and light harvesting antennas<sup>2</sup> are typical examples of self-assembled supramolecular porphyrin species occurring in natural systems. Investigation of artificial porphyrin array will not only provide useful insights into the mechanism of the photosynthetic process but also may revolutionize solar energy technology. Previously we have shown that a new chiral zinc porphyrin dimer with flexible bridge containing amino acids  $O,O\text{-C}_2\text{-AA-C}_2\text{-(TPP)}_2\text{Zn}_2$ <sup>3</sup> binds bidentate ligand ethylenediamine to form chiral linear zinc porphyrin array<sup>4</sup>, and the formation of the array was investigated by circular dichroism (CD) spectroscopy. Herein, we report the Uv-vis titration and  $^1\text{H-NMR}$  characteristics of the formation of linear  $O,O\text{-C}_2\text{-AA-C}_2\text{-(TPP)}_2\text{Zn}_2$ -ethylenediamine array (**Figure 1**).

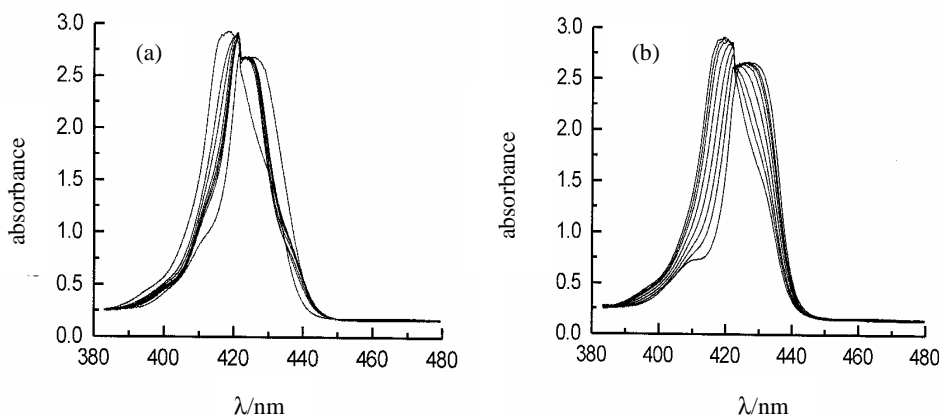
Uv-vis ethylenediamine-titration experiments were carried out at 16°C in chloroform. Propylamine-titration study was also performed as control experiment. Soret band changes of  $O,O\text{-C}_2\text{-Phe-C}_2\text{-(TPP)}_2\text{Zn}_2$  ( $5.28 \times 10^{-5}$  mol/L) upon the binding of ethylenediamine and propylamine are shown in **Figure 2a** and **Figure 2b** 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  $O,O\text{-C}_2\text{-Phe-C}_2\text{-(TPP)}_2\text{Zn}_2$ . It is noteworthy that the Soret band changes of  $O,O\text{-C}_2\text{-Phe-C}_2\text{-(TPP)}_2\text{Zn}_2$  with the addition of ethylenediamine and propylamine are quite different. Besides red shifts, a clear splitting of the Soret band was observable when ethylenediamine was added to the solution of  $O,O\text{-C}_2\text{-Phe-C}_2\text{-(TPP)}_2\text{Zn}_2$  (**Figure 2a**). We ascribed the splitting of the Soret band is due to the formation of linear  $O,O\text{-C}_2\text{-Phe-C}_2\text{-(TPP)}_2\text{Zn}_2$ -ethylenediamine array, for the

splitting of the Soret band is the spectroscopic feature of porphyrin aggregates<sup>5</sup> and supramolecular stack of Mg bis-(imidazolyl) porphyrin<sup>6</sup>. When a vast excess of ethylenediamine was added, splitted Soret band will become one peak like that of the *O,O*-C<sub>2</sub>-Phe-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>-propylamine complex (**Figure 2b**). This suggests that the higher ethylenediamine content ([zinc por. Dimer]: [ethylenediamine]>1:1) will cause the dissociation of the array. Titration curve of *O,O*-C<sub>2</sub>-Phe-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub> based upon the change in absorbance at 419.3 nm on addition of ethylenediamine showed an inflection point at *ca.* 1 equivalent of ethylenediamine, indicating a 1:1 supramolecular complex as an intermediate. No inflection point was found in *O,O*-C<sub>2</sub>-Phe-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>-propylamine titration curve.

**Figure 1.** Structure of *O,O*-C<sub>2</sub>-AA-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub> and its self-assembled supramolecular array



**Figure 2.** Absorption spectra changes of *O,O*-C<sub>2</sub>-Phe-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub> in chloroform on successive additions of ethylenediamine(a) and propylamine(b) at 16 °C



In order to further investigate the formation of *O,O*-C<sub>2</sub>-AA-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub> supra-molecular assembly, <sup>1</sup>H-NMR titration experiments have been carried out. Here we

only discuss *O,O*-C<sub>2</sub>-(L-Ala)-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>-ethylenediamine <sup>1</sup>H-NMR titration (in CDCl<sub>3</sub>) result for the simplicity. In <sup>1</sup>H-NMR spectrum of *O,O*-C<sub>2</sub>-(L-Ala)-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>, The CH<sub>3</sub> and NH protons of Ala appeared as a broad peak at  $\delta = \sim -4.12$ , and the Ala CH proton appeared at  $\delta = -2.68$ . The resonances at  $\delta = -2.37$  and  $-1.91$  correspond to the (CH<sub>2</sub>)<sub>2</sub> connecting chain. These assignments were made according to the <sup>1</sup>H{<sup>1</sup>H} COSY spectrum of *O,O*-C<sub>2</sub>-(L-Ala)-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>. Large ring-current induced upfield shift dimer signals indicated that two zinc porphyrin chromophores were in close proximity. When 1 equivalent of ethylenediamine was added to the solution of *O,O*-C<sub>2</sub>-(L-Ala)-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>, we found all of the four cited peaks were downfield shifted with  $\delta > 0$  and two new peaks at  $\delta = -5.66$  and  $-4.71$  appeared. These new upfield signals correspond unequivocally to NH<sub>2</sub> and CH<sub>2</sub> of ethylenediamine respectively. Chemical shifts of NH<sub>2</sub> and  $\alpha$ -CH of amino acid ester in complexation with zinc porphyrin monomer are at  $\delta = -4.57$  and  $-2.90$ <sup>7</sup>. Crossley<sup>8</sup> *et al.* reported the NH<sub>2</sub> and  $\alpha$ -CH<sub>2</sub> signals of tetramine binding inside the cavity of Troger's base dizinc bis-porphyrin receptor are at  $\delta = -4.68$  and  $-2.82$ . The NH<sub>2</sub> and CH<sub>2</sub> signals of ethylenediamine in the present system are apparently at higher field as compared with those of amino acid ester 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 inside the cavity of *O,O*-C<sub>2</sub>-(L-Ala)-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>, proton signals of Ala and (CH<sub>2</sub>)<sub>2</sub> connecting chain should appear at upfield  $\delta < 0$ . Thus <sup>1</sup>H-NMR study also evidenced the formation of the linear *O,O*-C<sub>2</sub>-AA-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub>-ethylenediamine assembly (**Figure 1**).

Combined observations of these spectroscopies, CD<sup>4</sup>, Uv-Vis, and <sup>1</sup>H-NMR, suggest that amino acid chiral zinc bis-porphyrin with flexible connecting chain *O,O*-C<sub>2</sub>-AA-C<sub>2</sub>-(TPP)<sub>2</sub>Zn<sub>2</sub> tends to form chiral linear array 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<sup>8</sup>.<sup>9</sup> The present results are useful in the design and construction of well-defined porphyrin supramolecular architecture or functional materials.

### Acknowledgments

This work was supported by Guangdong Provincial Natural Science Foundation (No. 984041, 960291) and Natural Science Foundation of South China University of Technology (No. B8-124-014).

### References

1. J. Deisenhofer, O. Epp, K. Miki, *et al.*, *J. Mol. Biol.*, **1984**, *80*, 385.
2. G. McDermott, S. M. Prince, A. A. freer, *et al.*, *Nature*, **1995**, *374*, 517.
3. a) H. Y. Liu, J. W. Huang, X. Tian, *et al.*, *Chemical Journal of Chinese Universities*, **1998**, *19*(4), 511. b) H. Y. Liu, J. W. Huang, X. Tian, *et al.*, *Inorganic Chimica Acta*, **1998**, *272*, 295.
4. H. Y. Liu, J. W. Huang, X. Tian, *et al.*, *J. Chem. Soc. Chem. Commun.*, **1997**, 1575.
5. a) I. Inamura and K. Uchida, *Bull. Chem. Soc. Jpn.*, **1991**, *64*, 2005.
6. b) C. Endisch, C. Bottcher, and J. H. Fuhrhop, *J. Am. Chem. Soc.*, **1995**, *117*, 8273.

7. Y. Kobuke and H. Mijaji, *Bull. Chem. Soc. Jpn.*, **1996**, 69, 3563.
8. Y. Kuroda, Y. Kato, T. Higashioji, *et al.*, *J. Am. Chem. Soc.*, **1995**, 117, 10950.
9. J. N. H. Reek, A. P. H. J. Schenning, A. W. Bosman, *et al.*, *Chem. Commun.*, **1998**, 11.
- 9 a) T. Hayashi, M. Nonoguchi, T. Aya, *et al.*, *Tetrahedron letters*, **1997**, 38 (9), 1603.
- 10 H. Imahori, E. Yoshizawa, K. Yamada, *et al.*, *J. Soc. Chem. Chem. Commun.*, **1995**, 1133.
- 11 M. J. Crossley, L. G. Makey and A. C. Try, *J. Chem. Soc. Chem. Commun.*, **1995**, 1925.
  - b) I. P. Danks, I. O. Sutherland and C. H. Yap, *J. Chem. Soc., Perkin Trans. I*, **1990**, 421.
  - c) C. A. Hunter, M. N. Meah, and J. K. M. Sanders, *J. Am. Chem. Soc.*, **1990**, 112, 5773.
  - d) I. Tabushi, S. -I. Kugimiya, M. G. Kinnaird, and T. Sasaki, *J. Am. Chem. Soc.*, **1985**, 107, 4192.

Received 6 October 1998