Synthesis, Characterization and Weak Intramolecular Interactions of Porphyrins Bearing Nucleobases

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5,10,15-Triphenyl-20-{2-[α-(adenine-9) acetylamino]} phenyl porphyrin (1), 5,10,15-triphenyl-20-{2-[α-(cytosine-1) acetylamino]} phenyl porphyrin (2), 5,10,15-triphenyl-20-{4-[α-(cytosine-1) ethoxy]} phenyl porphyrin (3) and their zinc complexes Zn-1, Zn-2 and Zn-3 have been prepared and characterized by ^{1}H NMR spectra, elemental analyses, electronic absorption spectra and mass spectra (FAB). Intramolecular π-π interactions and intramolecular metal-π interaction for 1, 2, Zn-1, and Zn-2 have been investigated by several methods. ^{1}H NMR studies demonstrate that the porphyrin π-system in 1 and 2 is parallel to the adenine and the cytosine aromatic ring, respectively. The electronic absorption spectral properties of free porphyrin derivatives and their zinc complexes have been compared with those of H_2TPP and ZnTPP. The results show that the UV-vis spectra of 1 and 2 are the same as that of H_2TPP, whereas the spectra of their zinc complexes show 7 nm red shifts of the Soret bands compared to that of ZnTPP. The emission spectra of Zn-1 and Zn-2 are independent of excitation wavelength. From combination of the evidence of absorption and emission spectra it is suggested the existence of intramolecular metal-π interaction in Zn-1 and Zn-2. The results of conformational analysis agreed quite nicely with that of experiments, thus it was further to validate the experimental conclusions.

Keywords porphyrin, π-π interaction, spectra, conformational analysis

Introduction

It has been known for many years that noncovalent interactions between aromatic moieties could play a key role in the conformational stability of a wide variety of chemical systems.[1,2] In particular, these interactions have been shown to influence the properties of nucleic acids and binding affinities in host-guest chemistry.[3-6] In the case of porphyrin, three types of interaction have been proposed in connection with π-π interaction before:[7] (i) intramolecular or intermolecular porphyrin-porphyrin interactions,[8] (ii) porphyrin-aromatic solvent π-π interaction, (iii) intramolecular porphyrin-other aromatic grouping interaction. Quinones,[9] phenyl sulfonyl,[9a] and nitrophenyl[10] have been used to study the intramolecular porphyrin-other aromatic grouping π-π interaction.

As a first step towards the construction of model complexes capable of molecular recognition and catalysis, in the present paper, we synthesized three new porphyrins with nucleobases (**1**, **2** and **3**, Fig. 1). **1** and **2** have been so designed that they are adequately constrained to be sufficiently flexible of enabling to fold into a favorable conformation for porphyrin-nucleobase interaction, but there is absence of axial coordination at the metallic complexes. As expected, the intramolecular π-π interaction did take place. In addition, there is another type of weak interaction in the zinc complexes, in particular, this interaction is prosaically called "metal-π interaction".[11-13] Compound **3** was designed to investigate the weak interaction in **1** and **2**.

Experimental

Physical measurements

^{1}H NMR spectra were recorded on a Mercury Vx300 spectrometer and chemical shifts were reported with tetramethylsilane as internal reference. Electronic absorption spectra were recorded on a Beckman Du-8B spectrophotometer with a thermostatic cell compartment. Fluorescence spectra were obtained with a Spex FL-212 spectrometer. Mass spectra (FAB) were performed on a VG-Quattro spectrometer using nitrobenzyl alcohol (NBA) as a matrix. Elemental analyses were performed with a Perkin-Elemer 240 elemental analysis apparatus.

Spectrometric titration

To a solution of 2.1×10^{-6} mol/L of zinc porphyrin derivatives in dichloromethane was added a stock solution

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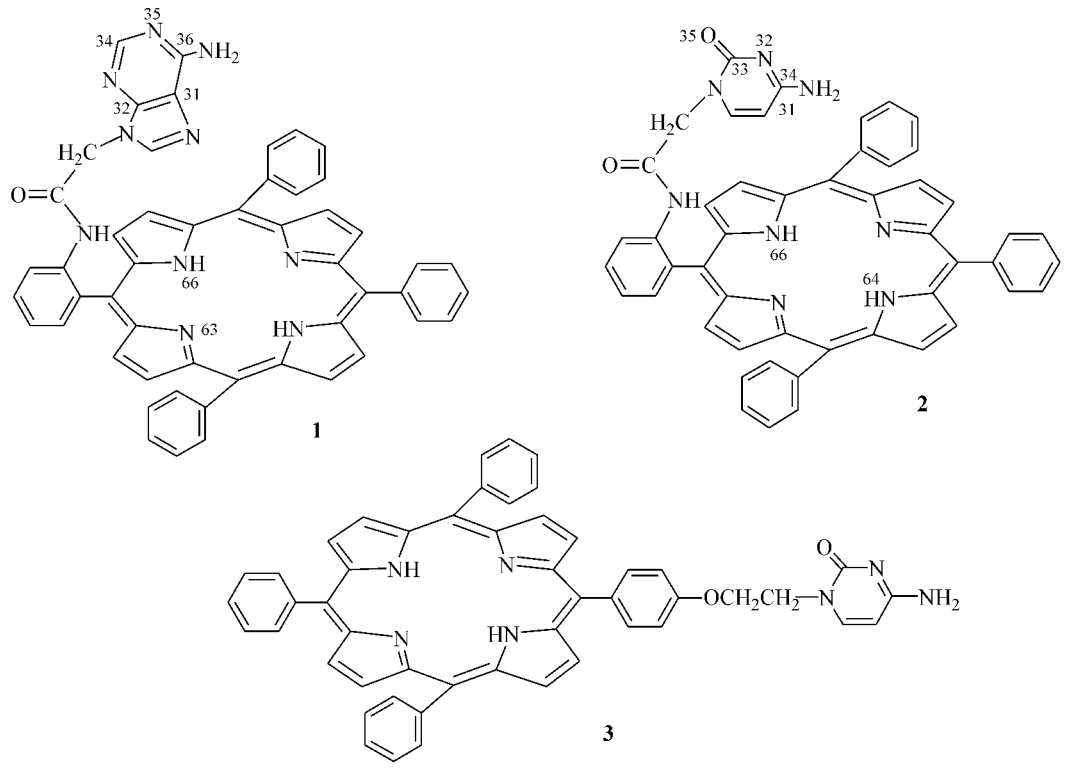


Fig. 1 Structures of free porphyrins.

of guest molecules, *L*-amino acid ester, in dichloromethane at 15 ℃ and the changes in absorption at Soret band were monitored at twelve different concentrations of the guest molecules. The association constants *K* were calculated by means of Origin6.0 based on Rose-Drago method.[14]

Conformational analyses

The conformational analyses were carried out with Random Conformation Search[15] using SYBYL6.3 package implemented on Silicon Graphics working station. The 3D structures of free porphyrin derivatives and their zinc complexes were constructed respectively by using crystal atom coordination of **H_2TPP** (5,10,15,20-tetraphenylporphyrin) and **ZnTPP**. Then the side chain was added with Sketch module and energy minimization was carried out. The optimized geometry was taken as starting conformation. RMS: 0.4184 kJ/mol, convergence range: 0.2092 kJ/mol, max cycles: 1000.

Preparation of porphyrin **1** *and* **2**

General procedure To a solution of 5,10,15-triphenyl-20-{2-[α-bromacetylamino]} phenyl porphyrin (200 mg, 0.27 mmol) prepared according to the reported method[16] in 40 mL of DMF was added nucleobase (1.0 mmol) and 1.5 g of dry powder of K_2CO_3. The mixture was vigorously stirred about 24 h at room temperature, then it was poured into ice water and extracted with CH_2Cl_2. The organic layer was washed with dilute aqueous NH_3 and water successively. The solvent was evaporated and the crude product was purified by column chromatography on silica gel and crystallized from CH_2Cl_2-hexane.

5,10,15-*Triphenyl*-20-{2-[α-(*adenine*-9)*acetylamino*]}*phenyl porphyrin* (**1**) Elution: CH_2Cl_2-CH_3OH (50∶1, *V*∶*V*). Yield 65%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: −3.08 (brs, 2H, inner NH of por.), 2.64 (brs, 2H, $AdCH_2$), 4.17 (s, 2H, NH_2 of Ad), 4.20 (s, 1H, NHCO), 5.24 (s, 1H, 8-H of Ad), 6.93 (s, 1H, 3-H of Ad) 7.50 (t, *J* = 7.5 Hz, 1H, PhH), 7.75—7.82 (m, 9H, PhH), 7.88 (d, *J* = 7.5 Hz, 1H, PhH), 8.18 (t, *J* = 8.0 Hz, 3H, PhH), 8.27 (s, 1H, PhH), 8.36—8.40 (m, 1H, PhH), 8.38 (m, 2H, PhH), 8.53 (d, *J* = 8.0 Hz, 1H, PhH), 8.58 (d, *J* = 4.5 Hz, 2H, β-pyrrole-H), 8.75 (d, *J* = 4.5 Hz, 2H, β-pyrrole-H), 8.88 (s, 4H, β-pyrrole-H); MS (FAB) *m*/*z*: 804 (M^+), 670. Anal. calcd for $C_{51}H_{36}N_{10}O$: C 76.12, H 4.48, N 17.41; found C 75.48, H 4.76, N 16.96.

5,10,15-*Triphenyl*-20-{2-[α-(*cytosine*-1)*acetylamino*]}*phenyl porphyrin* (**2**) Elution: $CHCl_3$-CH_3OH (50∶1, *V*∶*V*). Yield 61%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: −2.84 (s, 2H, inner NH of por.), 3.58 (s, 2H, $CyCH_2$), 5.44 (d, *J* = 7.2 Hz, 1H, 5-H of Cy), 7.08 (s, 1H, 6-H of Cy), 6.91, 7.01 (each 1H, brs, NH_2 of Cy), 7.56 (t, *J* = 7.8 Hz, 1H, PhH), 7.80—7.90 (m, 10H, PhH), 7.99 (d, *J* = 7.8 Hz, 1H, PhH), 8.19—8.30 (m, 7H, PhH), 8.33 (s, 1H, NHCO), 8.73—8.84 (m, 7H, β-pyrrole-H), 9.20 (s, 1H, β-pyrrole-H); MS (FAB) *m*/*z*: 781 (MH^+), 670. Anal. calcd for $C_{50}H_{36}N_8O_2$: C 76.92, H 4.61, N 14.35; found C 76.48, H 4.59, N 14.06.

Preparation of 5,10,15-*triphenyl*-20-{4-[*α*-(*cytosine*-1)*ethoxy*]}*phenyl porphyrin* (**3**)

5,10,15-Triphenyl-20-[4-(2-bromo) ethoxyphenyl] porphyrin (340 mg, 0.45 mmol) prepared according to the established method[16] was added to a solution of cytosine (177 mg, 1.59 mmol) and dry powder of K_2CO_3 in DMF (50 mL) at room temperature. After being stirred for 48 h the mixture was poured into ice water then filtered. The residue was washed with dilute aqueous NH_3 and hot water successively, dried and purified by clumn chromatography on silica gel, eluted with $CHCl_3$-CH_3OH (20∶1, *V*∶*V*). Yield 33%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ∶ −2.93 (s, 2H, pyrrole-NH of por.), 4.21 (t, *J* = 4.8 Hz, 2H, $CyCH_2C\mathbf{H}_2$), 4.48 (t, *J* = 4.8 Hz, 2H, $CyC\mathbf{H}_2CH_2$), 5.76 (d, *J* = 7.2 Hz, 1H, 5-H of Cy), 7.10 (bd, *J* = 27.9 Hz, 2H, NH_2 of Cy), 7.78 (d, *J* = 7.2 Hz, 1H, 6-H of Cy), 7.37 (d, *J* = 8.7 Hz, 2H, PhH), 7.80—7.88 (m, 9H, PhH), 8.10 (d, *J* = 8.7 Hz, 2H, PhH), 8.18—8.25 (m, 6H, PhH), 8.80—8.90 (m, 8H, *β*-pyrrole-H); MS (FAB) *m*/*z*∶768 (MH^+). Anal. calcd for $C_{50}H_{37}N_7O_2$∶C 78.04, H 4.86, N 12.75; found C 78.48, H 5.14, N 12.24.

Preparation of zinc (*II*) *porphyrins*

The zinc complexes of the porphyrin derivatives were prepared with the usual metallization procedure.[17]

Zn-1 Elution∶$CHCl_3$. Yield 90%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ∶3.47 (s, 2H, $AdCH_2$), 3.86 (brs, 2H, NH_2 of Ad), 4.92 (s, 1H, 8-H of Ad), 6.80 (s, 1H, NHCO), 6.82 (s, 1H, 3-H of Ad) 7.62 (t, *J* = 7.2 Hz, 1H, PhH), 7.68—7.84 (m, 10H, PhH), 8.09 (d, *J* = 8.1 Hz, 2H, PhH), 8.20—8.26 (m, 6H, PhH), 8.61 (d, *J* = 4.5 Hz, 2H, *β*-pyrrole-H), 8.80 (d, *J* = 4.8 Hz, 2H, *β*-pyrrole-H), 8.96 (d, *J* = 4.8 Hz, 2H, *β*-pyrrole-H), 8.99 (d, *J* = 4.5 Hz, 2H, *β*-pyrrole-H); MS (FAB) *m*/*z*∶867 (M^+). Anal. calcd for $C_{51}H_{34}N_{10}OZn$∶C 70.56, H 4.56, N 16.14; found C 69.93, H 4.24, N 15.79.

Zn-2 Elution∶$CHCl_3$-CH_3OH (50∶1, *V*∶*V*). Yield 88%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ∶3.52 (s, 2H, $CyCH_2$), 5.42 (d, *J* = 6.9 Hz, 1H, 5-H of Cy), 6.98 (s, 1H, 6-H of Cy), 6.90, 6.94 (each 1H, brs, NH_2 of Cy), 7.54 (t, *J* = 7.6 Hz, 1H, PhH), 7.75—7.84 (m, 10H, PhH), 7.94 (d, *J* = 7.5 Hz, 1H, PhH), 8.14—8.24 (m, 7H, PhH), 8.32 (s, 1H, NHCO), 8.67—8.76 (m, 7H, *β*-pyrrole-H), 8.97 (s, 1H, *β*-pyrrole-H); MS (FAB) *m*/*z*∶844 (M^+). Anal. calcd for $C_{50}H_{34}N_8O_2Zn$∶C 71.07, H 4.30, N 13.27; found C 71.38, H 4.45, N 13.01.

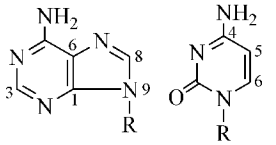
Zn-3 Elution∶$CHCl_3$-CH_3OH (30∶1, *V*∶*V*). Yield 90%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ∶4.21 (t, *J* = 4.8 Hz, 2H, $CyCH_2C\mathbf{H}_2$), 4.48 (t, *J* = 4.8 Hz, 2H, $CyC\mathbf{H}_2CH_2$), 5.76 (d, *J* = 6.9 Hz, 1H, 5-H of Cy), 7.10 (bd, *J* = 18 Hz, 2H, NH_2 of Cy), 7.78 (d, *J* = 6.9 Hz, 1H, 6-H of Cy), 7.34 (d, *J* = 8.7 Hz, 2H, PhH), 7.79—7.85 (m, 9H, PhH), 8.06 (d, *J* = 8.1 Hz, 2H, PhH), 8.12—8.22 (m, 6H, PhH), 8.73—8.83 (m, 8H, *β*-pyrrole-H); MS (FAB) *m*/*z*∶832 (MH^+). Anal. calcd for $C_{50}H_{35}N_7O_2Zn \cdot H_2O$∶C 70.58, H 4.63, N 11.52; found C 70.64, H 4.57, N 11.02.

Amino acid methyl ester hydrochlorides and esters were prepared from the corresponding amino acids on documented methods.[18]

Results and discussion

^{1}H NMR *spectra*

The most remarkable feature of ^{1}H NMR spectra of **1** and **2** is the up-field shifts for the nucleobase protons (Table 1). The up-field shift of adenine moiety in **1** is relative to ethyl 9-adeninebutanoate, and the shifts of cytosine moiety in **2** and **3** are relative to ethyl 1-cytosinebutanoate[19] (see Fig. 2 for numbering of the protons). The observed up-filed shifts are explained by an appreciable contribution of a conformation in which the nucleobase moieties are folded over the porphyrin ring plane in **1** and **2** (Fig. 1). The protons of these nucleobase groups undergo an up-filed shift as a result of the porphyrin ring current. Compound **3** also carries a cytosine group in the *β*-position of an ethoxy side chain, but it is attached at the *para* (*meso*) aryl position. The ^{1}H NMR spectrum of this compound showed no up-field shift for the cytosine moiety protons. The lack of up-filed shift demonstrated that the base group is not located at the upper zone of the porphyrin ring plane. Comparing the up-field shifts of **Zn-1**, **Zn-2** with those of **1** and **2**, respectively, it was found that the protons of these nucleobase groups in **Zn-1** and **Zn-2** have greater shifts than those of in **1** and **2**. It showed that in addition to the π-π interaction, there is another interaction-meta-π interaction in **Zn-1** and **Zn-2**. The results of conformational analyses seem to corroborate these pictures.



R = $(CH_2)_3COOC_2H_5$

Fig. 2 Numbering of the protons of ethyl 9-adeninebutanoate and ethyl 1-cytosinebutanoate.

Conformational analyses

As a first step in the theoretical investigation of the structure features, we have analyzed the conformations of porphyrin derivatives **1**, **2** and **3** and their zinc complexes using Random Search. The relative small conformational freedom of porphyrin and Random Search Procedure used make us confident that the molecular structures obtained

correspond to the lowest energy minima. Some of those structures are shown in Fig. 3.

We defined the plane of nucleobase as P1, and that of the porphyrin as P2. The angles between two planes are summarized in Table 2. It is apparent from Fig. 3 and Table 2 that there are intramolecular π-π interactions between porphyrin and nucleobase rings in **1**, **2** and as well as in their zinc complexes. Restrained by the side chain, the cytosine ring can not stack in the way of face-to-face with porphyrin ring in **3** and **Zn-3**. The geometry of the intramolecular π-π interactions is not significantly affected by the presence of central zinc ion. It is important to note that the coordination of Zn^{2+} with the porphyrin derivative in **Zn-1** and **Zn-2** produces no dramatic conformational changes. The existence of axial ligand, such as amino acid ester, does not influence the weak intramolecular interaction between porphyrin ring and nucleobase aromatic ring. Therefore, the amino acid esters could be ligated to the oppose side of nucleobase plane (Fig. 3, Table 2). Considering that the main chemical nature of these compounds is controlled by porphyrin ring, one would expect that the intramolecular π-π interaction in **1**, **2** and their zinc compl-

Table 1 Up-field shift $\Delta\delta$ of the base protons in **1** and **2** and their zinc complexes[a]

Compound	NH_2 of Ad	3-H of Ad	8-H of Ad	Compound	NH_2 of Cy	5-H of Cy	6-H of Cy
1	-1.58	-1.43	-2.57	**2**	-0.02, -0.01	-0.19	-0.44
Zn-1	-1.89	-1.54	-2.89	**Zn-2**	-0.03, -0.08	-0.21	-0.54

[a] For a given proton $\Delta\delta = \delta$(porphyrin) - δ(reference compound)

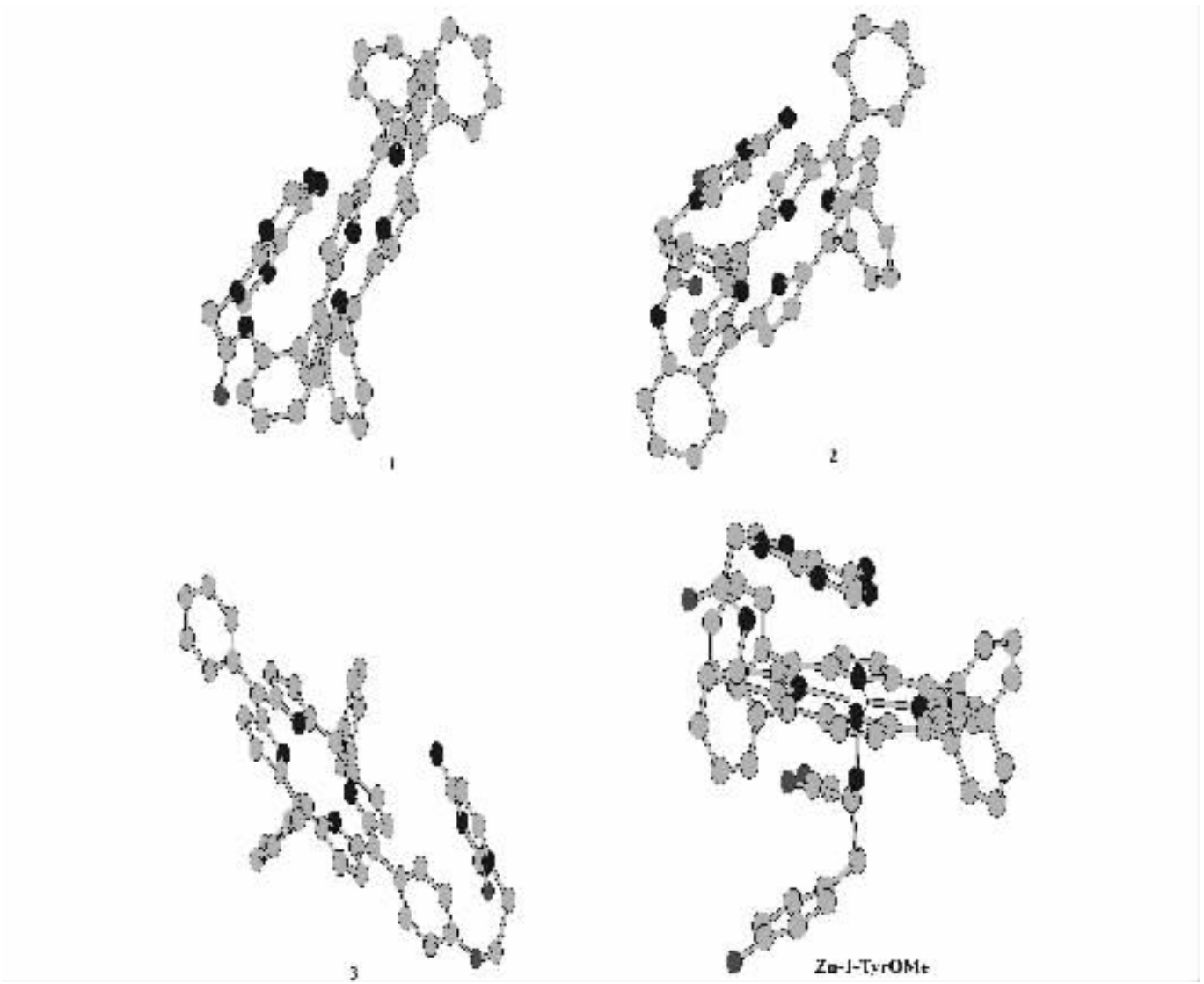


Fig. 3 The conformations of **1**, **2**, **3** and **Zn-1-TyrOMe** corresponding to the lowest energy minima.

exes would cause a significant effect on their characters. This is consistent with the ring current induced shifts observed in ^{1}H NMR experiment.

Table 2 Angles (°) between two planes

	1	Zn-1	2	Zn-2	Zn-1-TyrOMe
P1-P2	4.51	3.02	19.87	16.05	4.32

Some characteristic distances between several atoms in **1** and **2** obtained from the structure analysis are listed in Table 3. It is evident by the data in Table 3 that the van der Waals interactions between the planes of porphyrin and nucleobases are repulsive. According to Hunter's model,[7] the major contributions to the π-π interaction energy come from the electrostatic and van der Waals components. In our case, the face-to-face stacking geometry is controlled by the electrostatic interaction, and the strongly polarization of heteroatoms has a major contribution.

In the geometry of **Zn-1** and **Zn-2**, the distances N(35)—Zn (**Zn-1**) and N(32)—Zn (**Zn-2**) are 0.281 nm and 0.283 nm respectively, shorter than those of van der Waals radii of Zn and N (0.293 nm). Searching of CCSD (Cambridge Crystal Structure Database) indicates that the longest Zn—N coordination bonding distance in the zinc complexes is 0.259 nm, and the average value of Zn—N bonding length is 0.217 nm. We can therefore deduce that the weak Zn···N(35) (**Zn-1**) and Zn···N(32) (**Zn-2**) interactions are not coordination bonding but intramolecular metal-π interaction, and these weak interactions are clearly responsible for the red shifts observed in electronic absorption spectra and spectrometric titration.

Electronic absorption spectra and fluorescence emission spectra

The electronic absorption spectra of **Zn-1** and **Zn-2** show red-shifted absorption bands relative to **ZnTPP** while the absorption spectra of **1** and **2** are almost the same with **H_2TPP** and **3** (see Table 4). It seems clear from the results that π-π interactions in our case can not cause a distortion of visible spectra of free porphyrins. The reason of the red-shifted spectra of **Zn-1** and **Zn-2** is that the central zinc ion induces another type of weak interaction that is metal-π interaction.

In order to confirm that the red shifts are not caused by axial coordination, the emission spectra of **Zn-1** and **Zn-2** were also investigated. Fig. 4 gives emission spectra of **Zn-1** (a and b) at different excitation wavelengths. The emission spectrum excited at 415 nm is similar to that excited at 430 nm. If intramolecular or intermolecular axial coordination took place, we should find two kinds of chromophoric substances, which are the monoporphyrine zinc and its axial complex in the same solution. The emission spectra should be changed with the excitation wavelength. The results indicate that, however, no other chromophoric substance was found over the accessible concentration range (10^{-7}—10^{-2} mol/L). This behavior contrasts markedly with that of 5,10,15-triphenyl-20-{4-[α-(adenine-9) ethoxy]} phenylporphyrin zinc (**ZnPA**) which is used to study the self-assembly.[21] The emission spectra of **ZnPA** are different at different excitation wavelengths (Fig. 4 c and d).

It seems clear from the UV-visible and emission spectral results that the observed red shifts of UV-visible spectra of **Zn-1** and **Zn-2** are caused not by any kind of axial

Table 3 Some characteristic distances in **1** and **2**

1 (nm)		2 (nm)		Sum of van der walls radii[20] (nm)	
N(63)—C(31)	0.326	N(64)—C(31)	0.324	N—C	0.339
N(63)—C(32)	0.331	N(66)—C(33)	0.332	—	—
N(66)—C(34)	0.304	N(64)—N(34)	0.298	N—N	0.308
N(63)—C(36)	0.308	N(66)—O(35)	0.283	N—O	0.294

Table 4 Absorption spectral data (nm) (The unit of ε is L·mol^{-1}·cm^{-1})

	$Q_{(0,0)}$ ($10^{-3}\varepsilon$)	$Q_{(1,0)}$ ($10^{-4}\varepsilon$)	Soret ($10^{-5}\varepsilon$)		$Q_{x(0,0)}$ ($10^{-3}\varepsilon$)	$Q_{x(1,0)}$ ($10^{-3}\varepsilon$)	$Q_{y(0,0)}$ ($10^{-3}\varepsilon$)	$Q_{y(1,0)}$ ($10^{-4}\varepsilon$)	Soret ($10^{-5}\varepsilon$)
Zn-1	593.0 (4.50)	557.0 (1.50)	426.0 (4.82)	**1**	645.8 (5.70)	590.0 (7.85)	550.0 (9.81)	515.0 (2.16)	419.2 (4.26)
Zn-2	598.0 (3.78)	558.0 (1.01)	426.0 (3.91)	**2**	645.0 (4.60)	590.0 (6.64)	550.0 (8.27)	514.2 (1.86)	418.3 (3.82)
Zn-3	584.0 (1.90)	549.0 (1.26)	419.0 (1.98)	**3**	645.8 (6.86)	590.0 (7.91)	550.0 (11.46)	515.0 (2.15)	417.5 (4.83)
ZnTPP	584.0 (4.01)	548.5 (3.05)	419.0 (6.34)	**H_2TPP**	645.0 (5.30)	590.0 (6.35)	548.3 (8.46)	514.2 (1.52)	416.7 (4.41)

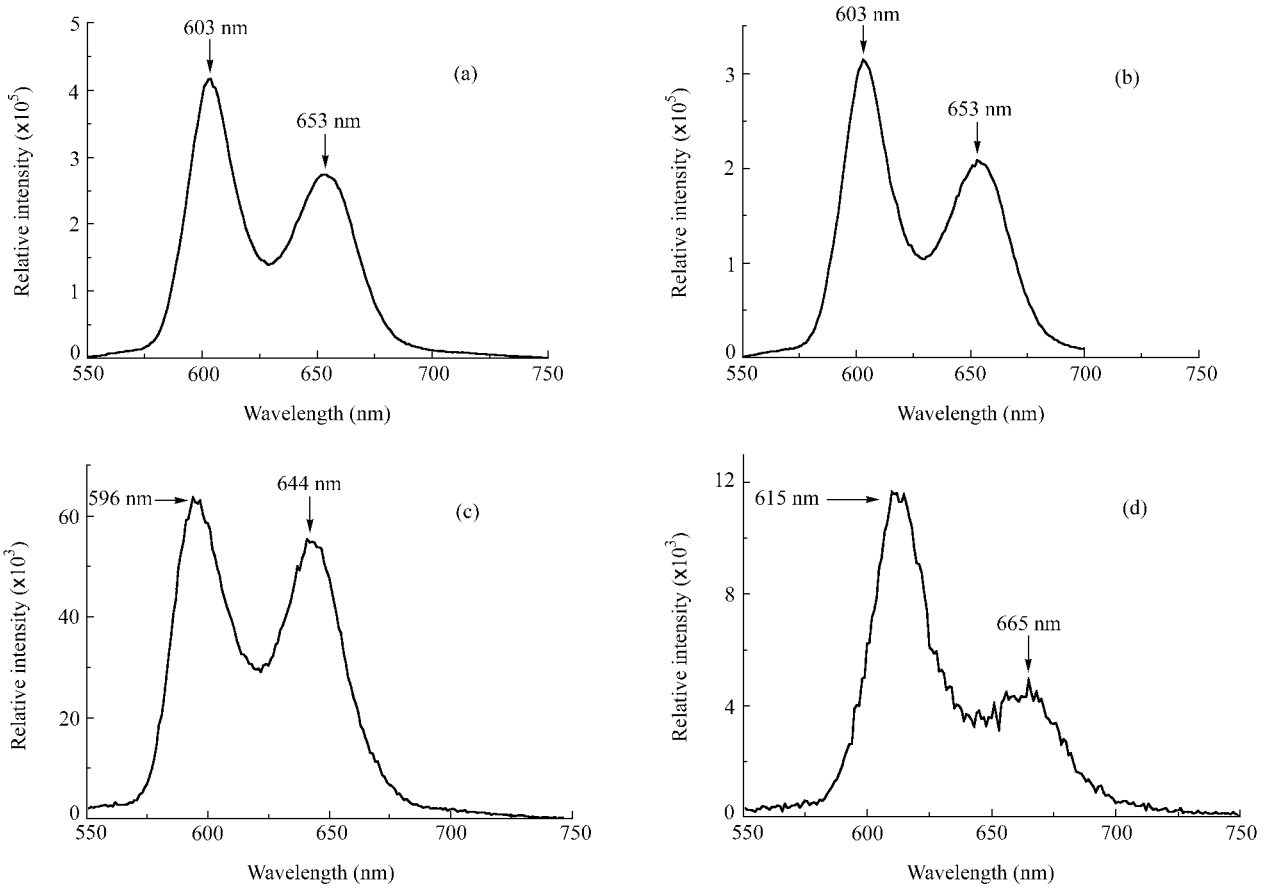


Fig. 4 The emission spectra of **Zn-1** (2×10^{-5} mol/L) and **ZnPA** (2×10^{-7} mol/L) in CH_2Cl_2 solution: (a) **Zn-1**, excited at 415 nm; (b) **Zn-1**, excited at 430 nm; (c) **ZnPA**, excited at 415 nm and (d) **ZnPA**, excited at 437 nm.

coordination but by some kind of weak intramolecular interaction between the central zinc ion and nucleobases.

Another experiment, spectrometric titration, was also done for investigating the weak interaction between zinc ion and nucleobases. The host molecules in this work were **Zn-1** and **Zn-2**. **ZnTPP** and **Zn-3** were employed as the reference compounds. Visible spectral changes of hosts induced by addition of amino acid esters showed clear isosbestic point in Soret band, indicating 1∶1 complex between host and guest. The association constants K were calculated based on Rose-Drago method[14] with Origin. The results are summarized in Table 5.

Table 5 Association constants ($mol^{-1}\cdot L$) for the reaction of zinc porphyrin derivatives with L (amino acid esters) in CH_2Cl_2 at 15 ℃

L	**ZnTPP**	**Zn-3**	**Zn-2**	**Zn-1**
LeuOMe	1.46×10^4	1.48×10^4	2.88×10^3	4.10×10^2
Asp(OMe)$_2$	6.27×10^3	6.36×10^3	2.24×10^3	2.64×10^2
TyrOMe	7.34×10^3	8.25×10^3	2.85×10^3	3.59×10^2
PheOMe	1.82×10^4	2.36×10^4	3.10×10^3	5.56×10^2
IleOMe	1.48×10^4	1.55×10^4	5.05×10^3	4.10×10^2

For all amino acid esters used in this work, the association constants decrease in the order of K (**Zn-3**) > K (**ZnTPP**) > K (**Zn-2**) > K (**Zn-1**), **Zn-3** shows a little more strong affinity to the guest molecules than **ZnTPP** while **Zn-2** shows substantially weaker affinity. This observation indicates that the geometry of host has a significant effect on the binding ability toward amino acid esters. **Zn-3** and **Zn-2** both bear cytosine as mono-substitute in spite of at different substitute site. There is no π-π interaction between porphyrin and nucleobase ring for the restriction in geometry in the case of **Zn-3**. The intramolecular π-π interactions and weak intramolecular interaction between the central zinc ion and nucleobase in **Zn-2** lead to a decrease in the magnitude of association constants. For the case of **Zn-1**, the larger up-field shift for adenine group protons showed its stronger π-π interaction and weak affinity to the guest molecules, so the K is smaller. This agrees with Hunter's π-π interaction model.[7]

Conclusion

In this study, we have prepared and characterized prophyrin bearing nucleobases **1**, **2**, **3**, and their zinc complexes **Zn-1**, **Zn-2** and **Zn-3**. We also have endeavored to investigate the weak intramolecular interactions. The results of experiment and conformational analysis demonstrate that there are intramolecular π-π interactions

in the present porphyrin derivatives. In particular, there is a metal-π interaction in **Zn-1** and **Zn-2**. The π-π interactions hardly cause a distortion of the electronic absorption spectra in the present case. This concurs with the studies of the others.[6] The red shifts, which were observed in UV-visible spectra of **Zn-1** and **Zn-2**, are imposed by metal-π interaction.

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