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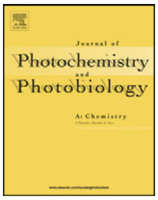

The formation of a slipped cofacial dimer of zinc (II) tripyridylporphyrin in water-soluble polymer

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ABSTRACT

A novel tripyridylporphyrin monomer, 5-[4-[2-(acryloyloxy)ethoxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin (TrPyP), and its zinc (II) complex (ZnTrPyP) were synthesized. It was copolymerized with acrylamide to prepare water-soluble polymer P(ZnTrPyP-AM). The aggregation behavior of P(ZnTrPyP-AM) in aqueous solution was investigated by UV–visible absorption spectra. The red shift of Q band and the significantly enhanced relative intensity ($\varepsilon_\alpha/\varepsilon_\beta$) indicated that the ZnTrPyP was axially coordinated. Meanwhile, Soret band of porphyrin split into two bands, suggesting exciton coupling of aggregates. The porphyrin pendants of P(ZnTrPyP-AM) were supposed to form a slipped cofacial dimer and the macromolecular matrix helped to create the well-defined porphyrin aggregates. This finding was helpful for the assembly of artificial light-harvesting systems in aquatic environment to mimic the dimeric structure in natural LHC.

1. Introduction

Porphyrin assemblies are of fundamental importance since they are not only used as building blocks for the construction of functional molecular devices, but also to mimic the natural systems, particularly the antenna complex and reaction center in the photosynthesis [1]. The simplest antenna system in nature is the core light-harvesting antenna (LH1) of the photosynthetic purple bacteria, in which bacteriochlorophyll-a (Bchl-a) molecules form highly symmetric ring structure with the aid of coordination bonds from peptide matrices and energy is stored by extremely rapid energy migration within the ring [2]. The key functional unit of the LH1 consists of a Bchl-a dimer in a slipped cofacial orientation and these dimers are further arranged into a macroring form [2,3].

Numerous porphyrin architectures aimed at mimicking LH complexes have been prepared through either synthesis or self-assembly [3,4] in organic solvents, but these media are largely different from the microenvironments provided by protein matrices in nature. Water is the only solvent in living systems and surrounding medium for biological macromolecules [5]. Meanwhile, it is an effective pH buffer and a reactant in some biological reactions, such as photosynthesis. For future application, water is also a harmless solvent to conduct other photoredox reactions driven by visible light.

Recently, lots of porphyrin aggregates induced by association in some heterogeneous systems like dendrimers [6], LB films [7], micelles [8] and so on [9] have attracted much attention, among which the driving forces in aggregation process are always hydrogen bonds, coordination bonds, electrostatic interactions, etc. Water-soluble macromolecules could provide a matrix, an environment more similar to the natural system, for side groups to associate and the aggregation behavior of pendants can be affected by main chain greatly. So water-soluble polymer containing porphyrin molecules as its pendant groups is a good scaffold to research the aggregation and photophysical properties of porphyrin molecules for artificial photosynthesis, and construction of noncovalent porphyrin complexes with a well-defined structure within water-soluble macromolecules is a meaningful and challenging target.

Several polymers containing porphyrins in their side chains have been studied [10], among which the derivatives of tetraphenylporphyrin were used most frequently and they aggregated randomly. Pyridine is a good candidate for coordination and forming hydrogen bond and shows versatile solubility in both polar and apolar solvents, such as, water and cyclohexane [11]. As is well known, linking the large and rigid groups to the polymer backbone via a flexible spacer can alleviate steric hindrance and reduce the entropy loss in association [12]. Therefore, in this work, a novel tripyridylporphyrin monomer, 5-[4-[2-(acryloyloxy)ethoxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin (TrPyP), and its zinc (II) complex (ZnTrPyP) (Scheme 1) were synthesized. The monomer ZnTrPyP was

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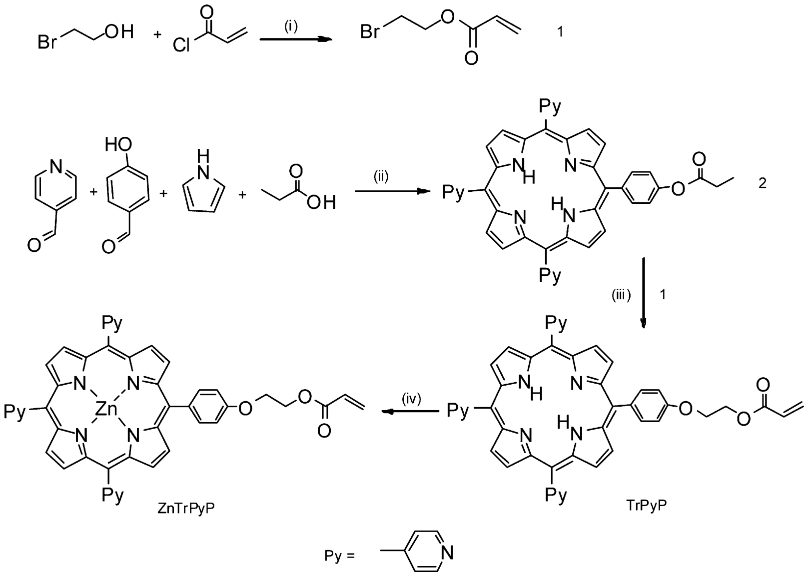


Scheme 1. Preparation of TrPyP and ZnTrPyP. (i) CH_2Cl_2, TEA, 4 h; (ii) propionic acid, Ac_2O, reflux, 3 h; (iii) DMF, NaOH, 3 h, rt; (iv) DMF, $Zn(OAc)_2$, 2 h, rt.

copolymerized with acrylamide to prepare amphiphilic copolymer Poly(ZnTrPyP-co-acrylamide), which is abbreviated as P(ZnTrPyP-AM). Similar copolymers P(TrPyP-AM) and P(ZnTrPyP-NVP) were also synthesized for comparison. The spectral properties of P(ZnTrPyP-AM) and aggregation behavior of porphyrin pendants were discussed.

2. Experimental

2.1. Materials

All reagents not explicitly referenced were obtained from commercial sources and used as received. 2-Bromo-1-ethanol, pyridine-4-carboxaldehyde and acryloyl chloride were purchased from Alfa Aesar Company. Pyrrole was purchased from Sinopharm Chemical Reagent Co., Ltd. and distilled before use. Acrylamide (AM) was purchased from Jiangxi Changjiu Biochemical Engineering Corporation. Acetic anhydride, p-hydroxybenzaldehyde, n-propanoic acid, triethylamine (TEA), 2,2′-azobis (isobutyronitrile) (AIBN), pyridine, N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), zinc (II) acetate dehydrate and other A.R. grade reagents were obtained from Beijing Chemical Works. The aqueous solution was prepared by deionized water.

2.2. Synthesis of porphyrin monomers

2.2.1. Synthesis of 2-bromoethyl acrylate (1) [11]

To a CH_2Cl_2 (25 mL) solution of 2-bromo-1-ethanol (4.25 mL, 60 mmol) and triethylamine (8 mL, 60 mmol), a CH_2Cl_2 (35 mL) solution of acryloyl chloride (4.9 mL, 60 mmol) was added dropwise at 0 °C and then the reaction mixture was stirred at room temperature for 4 h. The white suspension (triethylamine hydrochloride) appeared in the reaction was filtered off and the light yellow filtrate was washed with water. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure, which was then subjected to column chromatography (SiO_2, $CHCl_3$/hexane = 1:3) to give 1 as yellow oil (6.7 g, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.46 (dd, J = 17.3, 1.3 Hz, 1H), 6.15 (dd, J = 17.3, 10.5 Hz, 1H), 5.88 (dd, J = 10.5, 1.3 Hz, 1H), 4.46 (t, J = 6.2 Hz, 2H), 3.55 (t, J = 6.2 Hz, 2H).

2.2.2. Synthesis of 5-[4-[(ethylcarbonyl)oxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin
(2)

It was synthesized by slightly modified Adler–Longo method [13] and confirmed by ^1H NMR and MS. MS (ESI) calcd for M^+ 689.2539, found 690.2640 (M+1).

2.2.3. Synthesis of 5-[4-[2-(acryloyloxy)ethoxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrin
(TrPyP)

To a solution of 2 (0.3 g, 0.43 mmol) in dry DMF (25 mL) under nitrogen was added powdered sodium hydroxide (0.09 g, 2.2 mmol), and the mixture was stirred at room temperature for about 1.5 h (the color of the solution changed from purple to green). Formation of the phenolate form of 2 was checked by TLC. The 2-bromoethyl acrylate (1) (0.42 g, 2.3 mmol) was added to the solution and the mixture was stirred for 3 h at room temperature. The pH of the reaction mixture was then adjusted to 7 with 1 M HCl and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and the organic phase was washed twice with water, dried over Na_2SO_4, and evaporated to dryness. Products were purified by column chromatography on silica with CH_2Cl_2 as the eluent and precipitated from a mixture of dichloromethane–hexane to give TrPyP as a purple solid (0.24 g, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (dd, J = 4.4, 1.5 Hz, 6H), 8.97 (d, J = 4.7 Hz, 2H), 8.87 (s, 4H), 8.84 (d, J = 4.8 Hz, 2H), 8.19 (dd, J = 4.4, 1.5 Hz, 6H), 8.14 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 6.59 (dd, J = 17.3, 1.4 Hz, 1H), 6.31 (dd, J = 17.3, 10.4 Hz, 1H), 5.98 (dd, J = 10.4, 1.4 Hz, 1H), 4.75 (t, J = 6.1 Hz, 2H), 4.55 (t, J = 6.1 Hz, 2H), −2.86 (s, 2H). MS (ESI) calcd for M^+ 731.2645, found 732.2731 (M+1).

2.2.4. Synthesis of 5-[4-[2-(acryloyloxy)ethoxy]phenyl]-10,15,20-tris(4-pyridyl)porphyrinate zinc (II)
(ZnTrPyP)

TrPyP (0.2 g, 0.27 mmol) was dissolved in a mixed solution of $CHCl_3$ (15 mL) and methanol (5 mL). Zinc (II) acetate dehydrate (0.31 g, 1.4 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 2 h. A little of triethylamine was added and the reaction was continued for 2 h. The organic phase was washed three times with water and dried over Na_2SO_4. After removal of $CHCl_3$, the residue was purified by recrystallization ($CHCl_3$/hexane) to give ZnTrPyP as a purple solid (0.2 g,

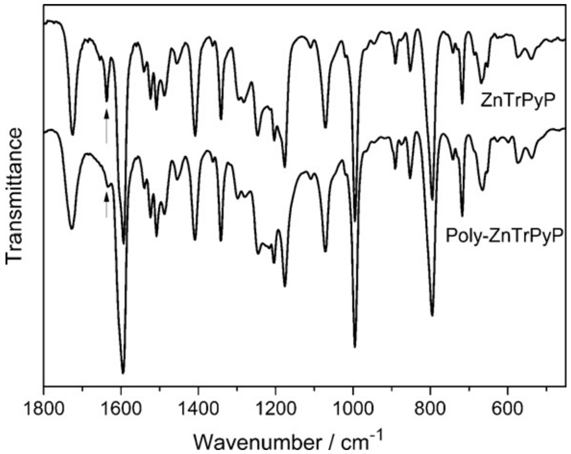


Fig. 1. FT-IR spectra of ZnTrPyP and Poly-ZnTrPyP in KBr.

96%). ^{1}H NMR (400 MHz, DMSO) δ 9.01 (d, J = 5.7 Hz, 6H), 8.88 (d, J = 4.7 Hz, 2H), 8.83 (s, 4H), 8.81 (d, J = 4.7 Hz, 2H), 8.22 (d, J = 5.8 Hz, 6H), 8.09 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 6.47 (dd, J = 17.3, 1.4 Hz, 1H), 6.34 (dd, J = 17.3, 10.2 Hz, 1H), 6.06 (dd, J = 10.2, 1.4 Hz, 1H), 4.64 (t, J = 4.8 Hz, 2H), 4.56 (t, J = 4.8 Hz, 2H). MS (ESI) calcd for M$^+$ 793.1780, found 794.1950 (M+1).

2.3. Preparation of homopolymer of ZnTrPyP

A solution of ZnTrPyP and 2,2′-azobis (isobutyronitrile) (AIBN) in DMSO was placed in a glass tube, degassed, sealed and polymerized at 60 °C for 24 h. The amount of AIBN was 2 wt% corresponding to the monomer. After polymerization, the DMSO was removed under reduced pressure. The residuum could partially dissolve in chloroform. After washed three times by chloroform under ultrasonics, the homopolymer Poly-ZnTrPyP was obtained by centrifugal separation. The IR bands of the monomer at 1636 cm^{-1} are assigned to the vibration of C=C bonds [14], which disappeared in that of homopolymer Poly-ZnTrPyP as shown in Fig. 1. In addition, another peak appeared when polymerized at 1225 cm^{-1} presumably corresponds to the skeleton vibration of carbon–carbon chain. The ^{1}H NMR of Poly-ZnTrPyP in D-substituted pyridine also showed the vanish of H peaks of H_2C=CH–. The results indicated that ZnTrPyP can be polymerized via the double bonds on acryloyl groups.

2.4. Preparation of copolymers

The copolymerization of TrPyP and ZnTrPyP with acrylamide (AM) and N-vinyl-2-pyrrolidone (NVP) was carried out in dimethyl sulfoxide (DMSO) (Table 1). The total concentration of monomers was 0.4–0.45 mol/L, respectively, and the molar ratio of M1 (AM or NVP) and M2 (TrPyP or ZnTrPyP) was 200:1. 4.5 mmol/L of AIBN (1 mol% corresponding to the whole amount of acrylamide and porphyrin) was added as initiator. The polymerization was performed in a sealed tube at 60 °C for 24 h after purging with nitrogen for 20 min.

After the polymerization, the resultant solution keeps homogeneous and it was poured dropwise into excess of acetone with stirring to precipitate the polymers. The precipitates formed in this process were filtered off and dried in vacuum at 45 °C. The polymers were redissolved gradually in a little amount of H_2O–DMSO (1/9 v/v) mixed solvent with stirring, and then precipitated again. The purification process was repeated several times until the porphyrin in filtrate could hardly be detected by UV–vis absorption spectrum, and IR band of C=C bond (1636 cm^{-1}) of the unsaturated ester was not found in the IR spectra of copolymers.

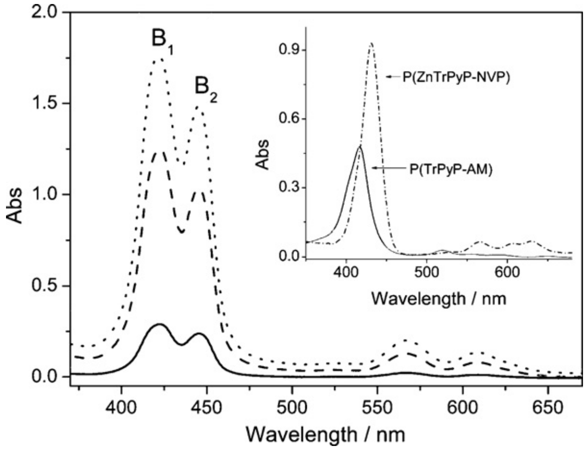


Fig. 2. UV–vis absorption spectra of P(ZnTrPyP-AM) in aqueous solution in different concentration (solid line: 8.0 × 10^{-2}; dashed line: 3.2 × 10^{-1}; dotted line: 4.0 g/L and measured in 1 mm cuvette). Inset: UV–vis absorption spectra of P(TrPyP-AM) and P(ZnTrPyP-NVP) in aqueous solution at 8.0 × 10^{-2} g/L.

The copolymers displayed very similar UV–vis absorption spectra to the corresponding porphyrin monomers in H_2O–DMSO (1/9 v/v) mixed solvent. So the contents of porphyrin units in the copolymers can be estimated from quantitative absorption spectra setting the molar extinction coefficient of Soret band of corresponding monomers in H_2O–DMSO (1/9 v/v) mixed solvent as a standard. The plot of Abs versus concentration of TrPyP and ZnTrPyP in H_2O–DMSO (1/9 v/v) was fitted as $A = 4.0 \times 106\,C$ and $A = 6.4 \times 106\,C$ (A, Abs; C, concentration), respectively. The molecular weights of the polymer were also investigated by static light scattering (SLS). The laser was 690 nm in wavelength where the absorption of copolymer is nearly zero (Fig. 2).

2.5. Measurement

^{1}H NMR spectrum was obtained on a Bruker DPX400 spectrometer. Mass spectrum was carried out on Bruker APEX-IV. Static light scattering (SLS) measurement of copolymers was performed by the DAWN EOS (Wyatt). FT-IR spectra were obtained from Excalibur 3100 (Varian, USA) infrared spectrometer in KBr disks. UV–vis absorption spectrum was recorded with a Hitachi UV-3900 UV–vis spectrophotometer. Fluorescence emission spectrum was performed on a Hitachi F-4500 fluorescence spectrophotometer. 1 mm colorimetric ware was applied in the test of spectroscopic properties of sample with high concentration.

3. Results and discussion

3.1. Absorption spectra of monomers

Table 2 (the first five lines) lists the steady-state absorption spectral data of monomer TrPyP and its zinc complex ZnTrPyP in some solvents with different coordination ability and polarity. TrPyP exhibits typical spectroscopic features of free base porphyrin and the property of solvent has little influence on it. For the monomer ZnTrPyP, it shows properties of four or five-coordinate zinc tripyridylporphyrin, respectively in different conditions. By increasing the concentration of ZnTrPyP in chloroform, some pyridyl substituents of porphyrin ring could axially coordinate to the central metal ion of others [15] and therefore the new Soret band at 429 nm becomes larger and larger, and the Q band is red shifted and the relative intensity ($\varepsilon_\alpha/\varepsilon_\beta$) increases [16]. Similarly, the fluorescence spectrum is also red shifted and I_α/I_β increases. In the coordinating solvents, such as pyridine and DMSO, the sol-

Table 1
Copolymerization of AM or NVP (M1) with TrPyP or ZnTrPyP (M2).

Copolymer	M1	M2	In feed		In copolymer		$M_w \times 10^{-4}$ g/mol
			[M] mol/L	[M1]:[M2]	[M2] wt%	[M1]:[M2]	
P(TrPyP-AM)	AM	TrPyP	0.40	200:1	2.3	433:1	7.13
P(ZnTrPyP-AM)	AM	ZnTrPyP	0.45	200:1	2.7	394:1	9.72
P(ZnTrPyP-NVP)	NVP	ZnTrPyP	0.45	200:1	2.2	314:1	49.6

vent molecules coordinate to the zinc ion and the solution exhibits typical spectroscopic features of five-coordinate zinc tripyridylporphyrin.

3.2. *Absorption spectra of the copolymer P(ZnTrPyP-AM)*

Fig. 2 illustrates the steady-state absorption spectra of the copolymer P(ZnTrPyP-AM) in aqueous solution at a variety of concentration. It is interesting that the Soret band is split to B_1 (421 nm) and B_2 (445 nm) and the profile of them keeps the same over a wide range of concentration. There are also two *Q*-bands with β band at 567 nm and α band at 609 nm and the intensity ratio of α band over β band ($\varepsilon_\alpha/\varepsilon_\beta$) is up to 0.59 (see Table 2). Compared with that of the four-coordinate ZnTrPyP (in $CHCl_3$), the *Q* bands of the P(ZnTrPyP-AM) in aqueous solution are red shifted by about 20 nm and $\varepsilon_\alpha/\varepsilon_\beta$ is increased considerably, which suggest that the zinc tripyridylporphyrins in copolymer P(ZnTrPyP-AM) are axially coordinated by a certain kind of ligand in aqueous solutions [16].

To investigate the reason of the splitting of Soret band in aqueous solution of P(ZnTrPyP-AM), the reference copolymers P(TrPyP-AM) and P(ZnTrPyP-NVP) were prepared in the same way as P(ZnTrPyP-AM), and their absorption spectra in aqueous solution are shown in the inset of Fig. 2. The Soret band of copolymer P(TrPyP-AM) becomes broad in aqueous solution relative to that of the TrPyP due to their interaction in hydrophobic microdomain, but it is not split. In addition, in the case of reference copolymer P(ZnTrPyP-NVP), the Soret band is not split too. These results demonstrate that the central metal ions in tripyridylporphyrins as well as the polyacrylamide main chain of copolymer play important roles in originating the split Soret band.

Fig. 3A shows the changes of absorption spectra after pyridine was added to the solution. The absorption bands of B_1 and B_2 decrease and a new band between them appears rapidly, which becomes very sharp and finally locates at 430 nm when volume fraction of pyridine is up to 10%. This new band is due to five-coordinate zinc tripyridylporphyrin. This result indicates that neither B_1 nor B_2 is resulted from the self-coordination. Contrarily, both of them should be due to aggregated species. Furthermore, the dissociation progress gives isosbestic points in the UV–vis titration spectra, which suggests that there is equilibrium between aggregated species and monomeric species in water–pyridine mixture. The equilibrium shifts toward monomeric species as the addition of pyridine.

$$\text{Aggregated species (displaying split B band)} \leftrightarrow \text{Monomeric species} \tag{1}$$

The fluorescence emission spectra in this process are shown in Fig. 3B. As the volume fraction of pyridine increases, the whole intensity of fluorescence rises greatly due to reducing quenching caused by aggregation, and the intensity ratio of 628 nm over 609 nm decreases continuously as shown in the inset of Fig. 3B. Hence, the fluorescence of monomeric species with *Q* (0, 0) at 609 nm and *Q* (0, 1) at 659 nm is enhanced quickly, whereas the relative fluorescence intensity of the aggregated species (628 nm) becomes lower. The above phenomena are reversible and indicate that the intermolecular forces in the aggregated species can be destroyed by the addition of pyridine.

3.3. *Structure of the porphyrin aggregates in P(ZnTrPyP-AM)*

Some structural information about the porphyrin aggregates can be deduced from the change of absorption spectra. The splitting or shift of absorption bands of covalently linked porphyrin dimer or oligomer models has been explained very well by exciton interactions [18]. According to Kasha's exciton theory [19], when the dipole transition moments of monomer molecules are aligned parallel ("side-by-side") to the line joining the molecular centers in the aggregate, the absorption band will red shift relative to that of the monomer and this kind of aggregate is called *J* aggregate. On the other hand, for the H aggregate, the monomers' dipole transition moments are perpendicular to the line of centers ("face-to-face") leading to a blue-shift electronic transition with respect to the absorption band of the monomer. The dipole–dipole exciton splitting energy, ΔE, in coplanar geometry is given by the equation [19]:

$$\Delta E = \frac{2|\mu_M|^2}{r^3}(1 - 3\cos^2\theta) \tag{2}$$

Table 2
Absorption spectral data of porphyrin monomers and copolymers in different solvents.

	Solvent	Absorption			
		Soret band (nm)	Half-bandwidth (nm)	Q bands (nm)	Peak ratio $\varepsilon_\alpha/\varepsilon_\beta$[a]
TrPyP	$CHCl_3$	419	14	515,550,590,645	
TrPyP	Pyridine	421	16	516,551,591,647	
ZnTrPyP[b]	$CHCl_3$	419	12	547,586	0.13
ZnTrPyP[c]	$CHCl_3$	421,429	22	562,605	0.41
ZnTrPyP	Pyridine	429	10	562,603	0.37
ZnTrPyP	DMSO	428	10	560,600	0.36
P(TrPyP-AM)	H_2O	416	36	520,556,591,651	
P(ZnTrPyP-AM)	H_2O	422,445	44	567,609	0.59
P(ZnTrPyP-AM)	$1H_2O$:9 pyridine	430	11	560,600	0.39
P(ZnTrPyP-NVP)	H_2O	431	31	566,607,630	

[a] The ratio of the molar extinction coefficients of the intensity maxima of α: *Q* (0, 0) and β: *Q* (1, 0) absorption bands [17].
[b] Obtained from a dilute solution (8.0×10^{-7} mol/L).
[c] Obtained from a concentrated solution (8.0×10^{-5} mol/L).

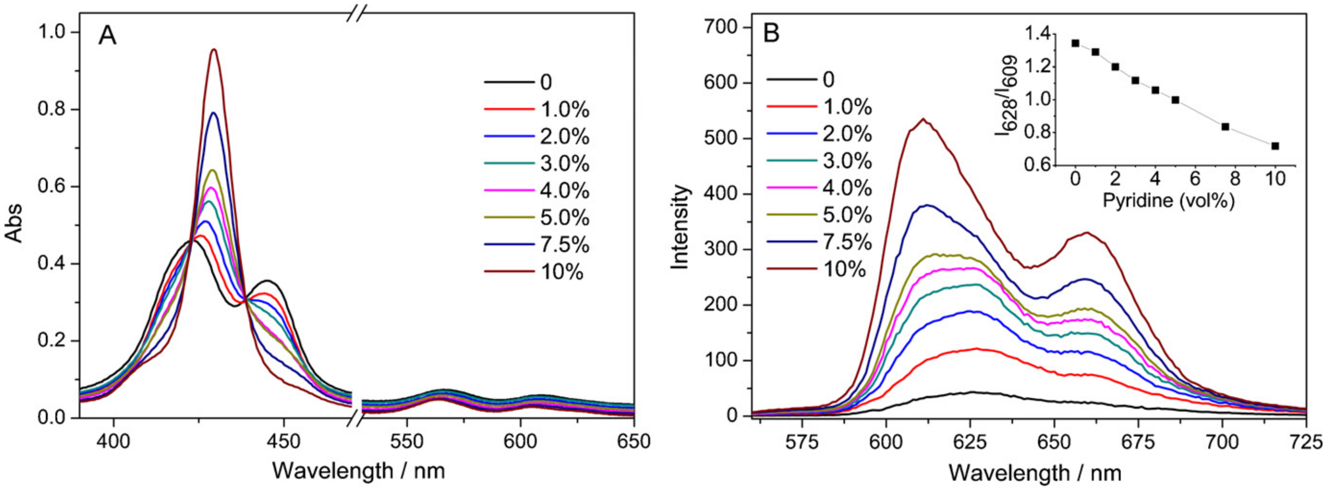


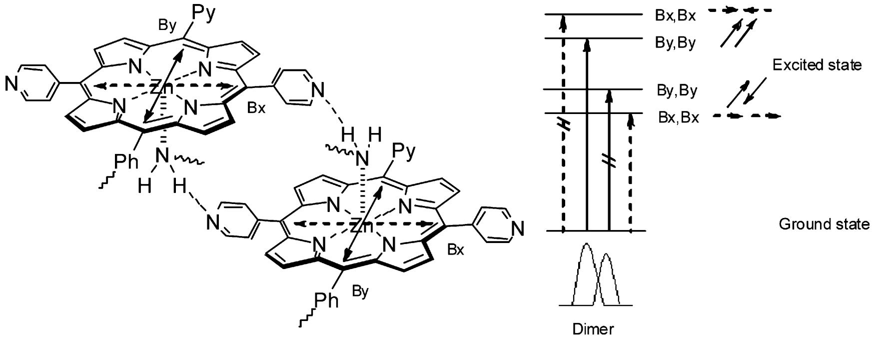
Fig. 3. UV–vis absorption (A) and fluorescence emission (B) spectra of P(ZnTrPyP-AM) in different pyridine volume fractions in water–pyridine mixtures (1.0×10^{-1} g/L). Inset (B): dependence of intensity ratio 628:609 on volume fraction of pyridine.

where μ_M is the transition dipole moment of the monomer, r is the center to center distance of the two dipoles, and θ is the angle made by the dipole with the line of molecular centers. The transition dipole moment used for the calculations can be obtained by integration of the absorption band [20].

Taking the absorption spectra of P(ZnTrPyP-AM) in aqueous solution into account, the most amounts of zinc tripyridylporphyrins are supposed to be in a slipped cofacial orientation as shown in Scheme 2. In a slipped cofacial dimer [3,21], the neighboring molecular planes are parallel, while the molecular centers are displaced. Soret band of zinc (II) porphyrin monomer has two perpendicular transition dipole moments, Bx and By, that are degenerated in a simple monomer. In the dimer we proposed above, Bx dipole moments are arranged in head-to-tail orientation (the angle between dipole and the line of molecular centers is θ_x), whereas By dipole moment interacts face to face (θ_y is 90°). And then, Bx and By couple, respectively and the Soret bands of dimer are split into a red-shifted Bx component and a blue-shifted By components (Scheme 2). The total splitting energy ΔE in this work corresponds to $1281\,\text{cm}^{-1}$, from which the relationships between geometrical parameters, r (Å) and θ, can be obtained. According to similar works reported earlier, the interplanar distance of the dimer is fixed at 3.5 Å [8d]. So geometrical parameters of the slipped cofacial dimer can be obtained approximately: the center-to-center distance is 9.9 Å, the slipping displacement is 9.3 Å, and θ is about 20.8°. We do not observe the phenomenon derived from the coupling of the Q-bands due to their relative smaller transition dipole moments compared with that of the Soret band.

It is clear that the formation of the dimer in copolymer P(ZnTrPyP-AM) is dependent on some intermolecular interactions. As discussed previously, zinc tripyridylporphyrins are five-coordinated and polyacrylamide main chain is a key factor in originating the split Soret band. So it is safe to consider that amino-groups on the polymer backbone are the fifth coordinates. In fact, since the amphiphilic copolymer contains only a few zinc tripyridylporphyrins, the amount of amino-groups on backbone is numerous compared with the limited pyridyl moieties on porphyrins. Hence, we suppose that the pyridine moieties on zinc tripyridylporphyrins in P(ZnTrPyP-AM) interact with the coordinated amino-groups in the manner of N–H···N(py) intermolecular hydrogen bands which help to form and stabilize the slipped cofacial dimer of zinc tripyridylporphyrin (Scheme 2). This was similar to the reported dimeric structure of aquamagnesium phthalocyanine and protonated meso-tetraphenylporphine, which were stabilized by hydrogen bonds of the bound water molecules [22]. Due to the complexity of macromolecules, it is hard to optimize the proposed structure by calculation. However, according to general bond length and bond angle, the proposed structure well coincides with the above parameters and therefore the conjecture is reasonable. So the water-soluble macromolecular matrix PAM makes the ZnTrPyP display dimeric absorption spectrum in aqueous solution. It is like that Bchl-a molecules are coordinated by peptide matrices and thus their position and orientation are fixed accurately in light-harvesting complex (LHC).

The experimental phenomena can be interpreted well by the proposed structure. For copolymer P(ZnTrPyP-NVP), since tertiary amine on NVP cannot generate hydrogen band, the NVP could not



Scheme 2. Proposed structure of slipped cofacial dimer and the exciton coupling model.

serve as the similar bridge. In the case of P(ZnTrPyP-AM), because there are two N–H···N(py) intermolecular hydrogen bands in every one of the dimers, the dimer has a large association constant, which explains why the dimer still exist even in very dilute aqueous solution. Besides, the four-coordinate zinc tripyridylporphyrin will accept one and only one amino-group to form five-coordinate complex, so this type of aggregate is limited to dimer rather than extends to larger oligomers. With the increase of concentration, it is only the increase in the number of dimers in large aggregates and there are not strong electronic interactions even some extent of hydrophobic association may exist between these dimers. As a result, except the increase of intensity, no other changes are observed in absorption spectra in concentrated aqueous solution of P(ZnTrPyP-AM). The addition of pyridine could destroy the N–H···N(py) intermolecular hydrogen bands by replacing the coordinated amino-groups, and make the amphiphilic copolymer dissolve thoroughly in the mixture of pyridine and water.

4. Conclusions

To construct the porphyrin architectures in the environment closer to that in nature is a challenge. Water-soluble macromolecule containing small amount of porphyrin derivative is a simple and easily understandable model. In copolymer P(ZnTrPyP-AM) in this work, the zinc tripyridylporphyrins were axially coordinated by amino-groups on backbone and self-assembled into slipped cofacial structure with the help of two N–H···N(py) intermolecular hydrogen bands. This is an example for the observation of well-defined porphyrin dimer in water-soluble copolymers containing hydrophobic porphyrin pendants. The slipped cofacial dimer is a building block in artificial photosynthesis, so further investigation about how to regulate the effects, factors and parameters are to be further studied.

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