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Self-assembly of novel tris(*p*-carboxyphenyl) porphyrin monomer and its copolymers with acrylamide in aqueous media

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ABSTRACT

The novel porphyrin monomer 5-(4-acryloyloxylphenyl)-10,15,20-tris(4-carboxyphenyl)porphyrinate zinc(II) (ZnAOTCPP) and its corresponding sodium salt (ZnAOTCPP-Na) were synthesized. The latter compound exhibited a new band in excitation spectra due to formation of porphyrin aggregates in water, which were derived from its surface-activity when the concentration was higher than its critical association concentration (CAC). The porphyrins were copolymerized with acrylamide (AM) to prepare water-soluble copolymers with random and micro-blocky structures, which all displayed very new absorption and fluorescence emission bands in the long wavelength region compared with the porphyrin monomer. Furthermore, the micro-blocky copolymer exhibited an additional new absorption band at even longer wavelength region compared with the random copolymer. The experimental results and analysis showed that the porphyrin units in the random copolymer chains self-assembled to form porphyrin association complexes by hydrophobic association and π–π stacking interactions, and covalent restrictions of polymer chains in the micro-blocky copolymer.

1. Introduction

The photosynthetic system, which converts solar light energy to chemical energy with high efficiency, is the most elaborate nanoscale biological device in nature, and of course, is the most important for the life on earth [1–3]. Light-harvesting (LH) complexes, the most abundant elements of photosynthetic system, achieve absorption of solar light and efficient transport of excitation energy in aqueous media [1–7]. In LH complexes, proteins are employed as rigid scaffolds to anchor chlorophylls in a sophisticated assembly [4–7]. Moreover, effective exciton delocalization in chlorophyll assemblies generates absorption at long wavelength region to afford a large cross section for light absorption, resulting in the efficient and fast energy transfer [5–7].

Porphyrin is an analogue of chlorophyll; both molecules have rigid core structures, intense absorption in the visible region, and similar photochemical properties. Thus, porphyrin assemblies with red-shifts in absorption spectra have attracted considerable attention during the past decades for exploration of the mechanism of LH [8–12]. In practice, using polymers as scaffolds to anchor porphyrin moieties should be a feasible route to artificial LH, though there are many difficulties to overcome [13–20]. Among other challenges is the difficulty of assembling porphyrin molecules into an arrangement that ensures efficient light-harvesting [8–12]. Another problem is the poor solubility of porphyrins in water, which means that assembling a porphyrin-based artificial LH in aqueous media is quite difficult [13–18,21,22].

Many investigations of synthesis of water-soluble copolymers with porphyrin units have been reported, and two approaches have proven to be successful. One approach is to copolymerize porphyrin monomer with water-soluble monomers such as 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) [13–16] and sodium styrenesulfonate (SSS) [17,18]; the other is to bind porphyrin molecules onto water-soluble polymers [19,20]. The corresponding photophysical properties of water-soluble copolymers with porphyrin units have been reported [13–20].

Polyacrylamide (PAM) is very soluble in water, and is therefore a good candidate for the construction of artificial LH systems in aqueous media. In the present study, porphyrin monomer with carboxyl groups was synthesized and copolymerized with AM to form water-soluble copolymers. The effects of self-assembly of the copolymers on the photophysical properties of the porphyrin units were investigated via UV–vis absorption spectra and fluorescence emission spectra. The approach presented here is a new route to

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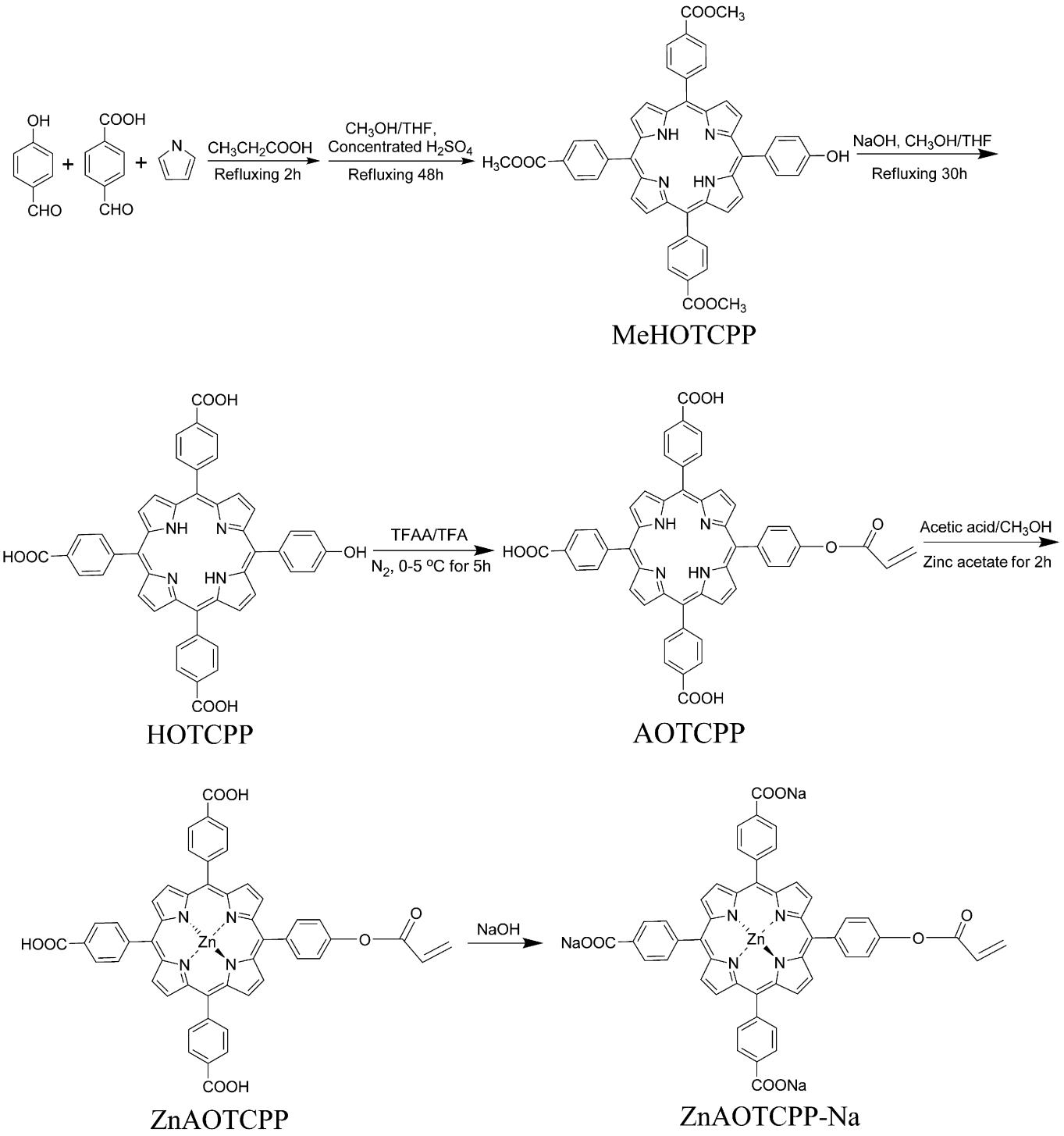


Fig. 1. Synthesis of the porphyrins.

assembly of the porphyrin molecules with the assistance of polymer chains in aqueous media.

2. Experimental section

2.1. Materials

Acrylamide was purchased from Jiangxi Changjiu Biochemical Engineering Corporation, and 4,4′-azobis(4-cyanovaleric acid) (ACVA) was bought from Alfa Aesar. 2,2′-Azobis(isobutyronitrile) (AIBN), trifluoroacetic anhydride (TFAA), trifluoroacetic acid (TFA), tetrahydrofuran (THF), acetic acid and other A.R. grade reagents were purchased from Beijing Beihua Co., Ltd. Buffer solutions were prepared from hexamethylenetetramine and hydrochloric acid (HCl) for pH 5.37, disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) for pH 6.86, and potassium chloride (KCl) and sodium hydroxide (NaOH) for pH 13.86.

2.2. Synthesis of porphyrins

2.2.1. 5-(4-Hydroxyphenyl)-10,15,20-tris(4-methoxycarboxyphenyl)porphyrin (MeHOTCPP) [23]

4-Hydroxylbenzaldehyde (0.020 mol) and 4-formyl benzoic acid (0.060 mol) were dissolved in propionic acid (0.250 dm^3). The reactant mixture was brought to reflux and freshly distilled pyrrole (0.080 mol) was added over a period of 0.4 h. The reactant mixture was refluxed for further 2.5 h, and then cooled to room temperature and the solvent was removed by reduced pressure distillation. A mixture of THF and methanol (3:2 in volume, 0.500 dm^3) was added into the residual solid, after which concentrated sulfuric acid (0.015 dm^3) was added dropwise in over a period of 0.4 h. This reaction mixture was refluxed for 48 h, and then evaporated under reduced pressure. The cold suspension was filtered to obtain the purple crystals, which were washed with ethanol (0.250 dm^3) three times and dried under vacuum at 318 K. The dried crude product was separated and purified by column chromatography using chloroform/n-hexane mixture (90:10 in volume) as eluent. A purple crystalline solid was obtained in 5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.78$ (s, 2H, pyrrole N–H), 4.13 (s, 9H, methyl), 7.23 (d, $J = 8.0$ Hz, 2H, OH-phenyl-2,6-protons), 8.08 (d, $J = 8.0$ Hz, 2H, OH-phenyl-3,5-protons), 8.30 (d, $J = 8.0$ Hz, 6H, MeCOO-phenyl-2,6-protons), 8.45 (d, $J = 8.0$ Hz, 6H, MeCOO-phenyl-3,5-protons), 8.82-8.92 (m, 8H, β-pyrrole). ESI-HRMS Found: $m/z = 805.26615$ ($[M + H]^+$), requires $m/z = 805.26568$.

2.2.2. 5-(4-Hydroxyphenyl)-10,15,20-tris (4-carboxyphenyl) porphyrin (HOTCPP) [24]

MeHOTCPP (0.002 mol) was dissolved in THF (0.060 dm^3) and a solution of potassium hydroxide (KOH, 10 wt%) in methanol (0.090 dm^3) was added. The reacting mixture was refluxed for 30 h, and then the solvent was evaporated under reduced pressure. The residue was redissolved in water (0.100 dm^3). The pH of the mixture was adjusted to about 7 with 1 mol dm^{-3} aqueous HCl, whereupon a green precipitate was formed. The precipitate was filtered and washed three times with $CHCl_3$ (0.150 dm^3) and three times with acetone (0.150 dm^3), and then dried under vacuum (318 K). A purple crystalline solid was obtained in 90% yield. ^{1}H NMR(400 MHz, DMSO-d_6): $\delta = -2.92$ (s, 2H, pyrrole N–H), 7.21 (d, $J = 8.0$ Hz, 2H, OH-phenyl-2,6-protons), 8.01 (d, $J = 4.0$ Hz, 2H, OH-phenyl-3,5-protons), 8.33–8.40 (m, 12H, COOH-phenyl-2,3,5,6-protons), 8.84–8.89 (m, 8H, β-pyrrole). ESI-HRMS Found: $m/z = 763.21976$ ($[M + H]^+$), requires $m/z = 763.21873$.

2.2.3. 5-(4-Acryloyloxyphenyl)-10,15,20-tris (4-carboxyphenyl) porphyrin (AOTCPP)

HOTCPP (0.001 mol) and TFAA (0.001 dm^3) were dissolved in TFA (0.020 dm^3), and the mixture was stirred under nitrogen atmosphere for 5 h in an ice bath. The solution was evaporated under reduced pressure, and the residual solid was filtered and washed three times with water (0.100 dm^3). A green solid was obtained in 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = -2.95$ (s, 2H, pyrrole N–H), 6.26–6.73 (m, 3H, CH_2=CH-protons), 7.63 (d, $J = 8.0$ Hz, 2H, CH_2=CH-phenyl-2,6-protons), 8.25 (d, $J = 8.0$ Hz, 2H, CH_2=CH-phenyl-3,5-protons), 8.25–8.38 (m, 12H, COOH-phenyl-2,3,5,6-protons), 8.84 (d, $J = 4.0$ Hz, 8H, β-pyrrole). ESI-HRMS Found: $m/z = 817.22929$ ($[M + H]^+$), requires $m/z = 817.23247$.

2.2.4. 5-(4-Acryloyloxlphenyl)-10,15,20-tris(4-carboxyphenyl) porphyrinate zinc(II) (ZnAOTCPP)

AOTCPP (0.001 mol) was dissolved in acetic acid (0.030 dm^3), followed by dropwise addition of a solution of zinc acetate (5 wt%) in THF (0.025 dm^3). The color of the reacting solution changed from green to red. The reaction mixture was stirred for 4 h at room temperature. The solution was then evaporated under reduced pressure, THF (0.100 dm^3) was added to the residual solid, and the mixture was ultrasonicated for 0.5 h to promote the dissolution of zinc acetate in THF. The resulting insoluble ZnAOTCPP was separated by filtration and washed three times with THF (0.100 dm^3). A red solid was obtained in 91% yield; the structure of product is shown in Fig. 1. ^{1}H NMR (400 MHz, D_2O-NaOH): $\delta = 5.62$–6.14 (m, 3H, CH_2=CH-protons), 6.97 (d, $J = 8.0$ Hz, 2H, CH_2=CH-phenyl-2,6-protons), 7.90 (d, $J = 8.0$ Hz, 2H, CH_2=CH-phenyl-3,5-protons), 8.14 (d, $J = 8.0$ Hz, 6H, COOH-phenyl-2,6-protons), 8.23 (d, $J = 8.0$ Hz, 6H, COOH-phenyl-3,5-protons), 8.75–9.06 (m, 8H, β-pyrrole). ESI-HRMS Found: $m/z = 879.14382$ ($[M + H]^+$), requires $m/z = 879.14279$. The content of Zn in ZnAOTCPP was 7.57 wt% determined by inductively coupled plasma optical emission spectrometry (ICP-OES), which was close to the value calculated from its chemical formula (7.40 wt%).

2.2.5. Sodium 5-(4-acryloyloxlphenyl)-10,15,20-tris(4-carboxyphenyl)porphyrinate zinc(II) (ZnAOTCPP-Na)

ZnAOTCPP (0.002 mol) was dissolved in aqueous NaOH solution (1 mol dm^{-3}, 0.010 dm^3), and then the mixture was dropped into acetone, immediately forming a grey-green precipitate. The precipitate was filtered and vacuum-dried (318 K) overnight to afford a brown solid powder, which was mixed with NaOH and ZnAOTCPP-Na. The mixture was added in ethanol, and then was ultrasonicated for 1 h to promote the dissolution of NaOH in ethanol. The resulting insoluble ZnAOTCPP-Na was isolated by filtration. These procedures were repeated several times until the pH of ZnAOTCPP-Na (with the concentration about 10^{-5} mol dm^{-3}) in water decreased to about 7. A red solid powder was obtained in 70% yield, with the structure shown in Fig. 1. The ^{1}H NMR and ESI-HRMS spectra of ZnAOTCPP-Na in D_2O were consistent with ZnAOTCPP mixed with NaOH in D_2O. The contents of Na and Zn in ZnAOTCPP-Na determined by ICP-ES were 7.61 wt% and 6.96 wt% respectively, which were close to the values in theory (7.29 wt% for Zn and 6.86 wt%). Moreover, the Na/Zn ratio for ZnAOTCPP-Na could be calculated and its value was about 3.0.

2.3. Preparation of copolymers

Copolymer P-O was obtained by copolymerization of ZnAOTCPP (5.26×10^{-3} mol dm^{-3}, 0.50 mol% in monomer) and AM (1.05 mol dm^{-3}, 95.5 mol% in monomer) in a mixture of dimethyl sulfoxide (DMSO) and acetic acid (3:2 in volume). AIBN (1.05×10^{-3} mol dm^{-3}) was used as initiator. Polymerization was performed at 333 K for 12 h after purging with nitrogen for 0.4 h. A green precipitate was formed during polymerization.

Copolymer P-W was prepared from ZnAOTCPP-Na (1.05×10^{-2} mol dm^{-3}, 0.50 mol% in monomer) and AM (2.10 mol dm^{-3}, 95.5 mol% in monomers) in water. ACVA (2.10×10^{-2} mol dm^{-3}) was used as initiator [25–27]. Polymerization was performed at 348 K for 4 h after purging with nitrogen for 0.4 h. A dark green solution was obtained after polymerization.

The procedure for the purification for P-O and P-W was the same and the details are as follows. The reaction mixture after polymerization was poured into excess of methanol (0.300 dm^3) and a green precipitate was formed. The precipitate was isolated by filtration and washed three times with fresh methanol (0.150 dm^3). The solid product was dried under vacuum (318 K) overnight, and then dissolved in the minimum volume of water about 0.010 dm^3. This purification procedure was repeated several times as described above until the porphyrin content of the copolymer, which was monitored by UV–vis absorption spectrophotometer, became constant. The yields of copolymers P-O and P-W were 85.7% and 75.2% respectively.

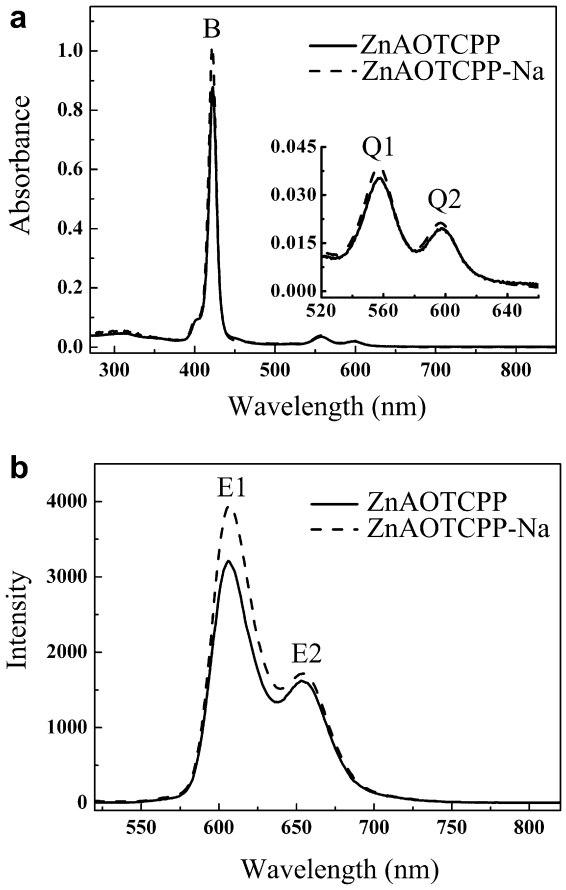


Fig. 2. (a) UV–vis absorption spectra (inset: expanded spectra from 520 nm to 670 nm), and (b) fluorescence emission spectra ($\lambda_{ex} = 422$ nm); of ZnAOTCPP and ZnAOTCPP-Na in water. ($c_{ZnAOTCPP} = 5.24 \times 10^{-6}$ mol dm^{-3} and $c_{ZnAOTCPP\text{-}Na} = 6.02 \times 10^{-6}$ mol dm^{-3}).

UV–vis absorption spectra of the copolymers in water displayed the characteristic absorption bands of the monomers at 422 nm. The content of porphyrin units in the copolymers was calculated from the spectra [19,20]. The molecular weights of the copolymers were measured by static light scattering (SLS). The fluorescence quantum yields (φ_f) of porphyrin monomer and porphyrin units in copolymers, in water, were determined by using tetraphenyl porphyrin (TPP, $\varphi_f = 0.11$ in benzene) as a standard [28].

2.4. Methods

^{1}H NMR spectra were obtained with a Bruker DPX400 spectrometer. Mass spectra were determined with a Buker APEX-IV instructment. UV–vis absorption spectra were recorded with a Hitachi UV-3900 UV–vis spectrophotometer. Fluorescence emission spectra and excitation spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Surface tensions were measured at 298 K using a Drop Shape Analysis System KRüSS DSA100. Static light scattering of copolymers was performed at 308 K with a DAWN EOS (Wyatt) instrument in 0.5 mol dm^{-3} $NaNO_3$ aqueous solution with excitation at 690 nm. Elemental analysis of Na and Zn was performed on an inductively coupled plasma optical emission spectrometry (ICP-OES) instrument (Varian 710-ES).

3. Results and discussion

3.1. Self-assembly and photophysical properties of ZnAOTCPP-Na monomer

Fig. 2 shows that the UV–vis absorption spectra and fluorescence emission spectra of ZnAOTCPP-Na in water were very similar to those of ZnAOTCPP, which means that the ionization of ZnAOTCPP did not affect its photophysical properties. However, the solubility of ZnAOTCPP-Na was more than 10^{-2} mol dm^{-3} in water at room temperature, whereas the saturation concentration of ZnAOTCPP was only about 1.41×10^{-5} mol dm^{-3}.

When the concentration of ZnAOTCPP-Na was changed from 1.48×10^{-3} to 1.72×10^{-2} mol dm^{-3} in water, the UV–vis absorption spectra and fluorescence emission spectra were analogous to the corresponding spectra in Fig. 2. However, when the concentration reached 4.49×10^{-3} mol dm^{-3} a new band (labeled Ex-A3) appeared at 623 nm in the excitation spectrum (Fig. 3a). The structure of ZnAOTCPP-Na comprises a hydrophobic tatrapyrrole macrocycle and hydrophilic carboxylate anions. Consequently, ZnAOTCPP-Na self-aggregates in water, resulting in the electronic interactions of ZnAOTCPP-Na molecules leading to the formation of the Ex-A3 band. CAC determined by this method was 4.49×10^{-3} mol dm^{-3} at room temperature (about 298 K). This value was close to the value, 5.65×10^{-3} mol dm^{-3}, that was obtained by analyzing the relationship between the surface tension and the concentration of ZnAOTCPP-Na aqueous solution (Fig. 3b)

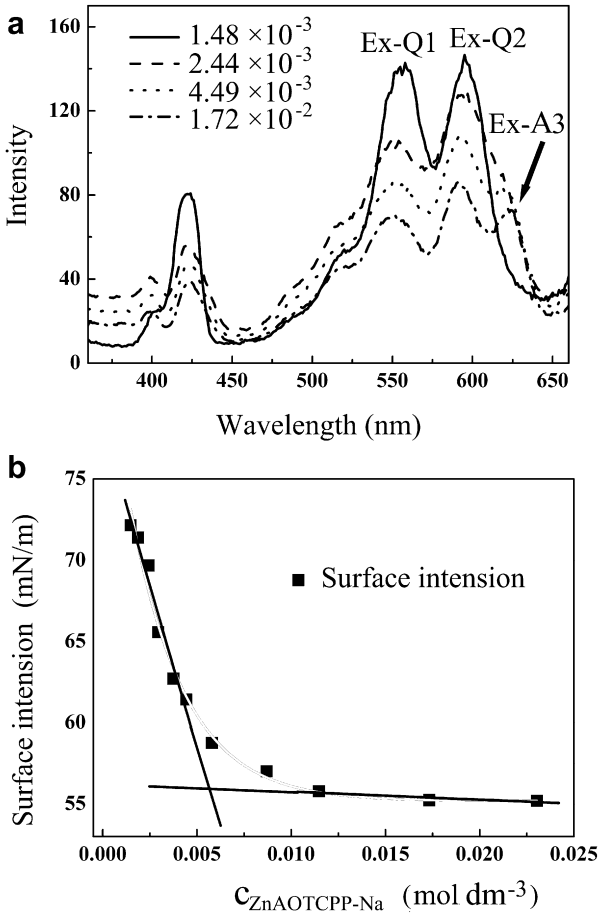


Fig. 3. (a) Excitation spectra ($\lambda_{em} = 680$ nm), and (b) the variation of surface tension at 298 K for ZnAOTCPP-Na in water.

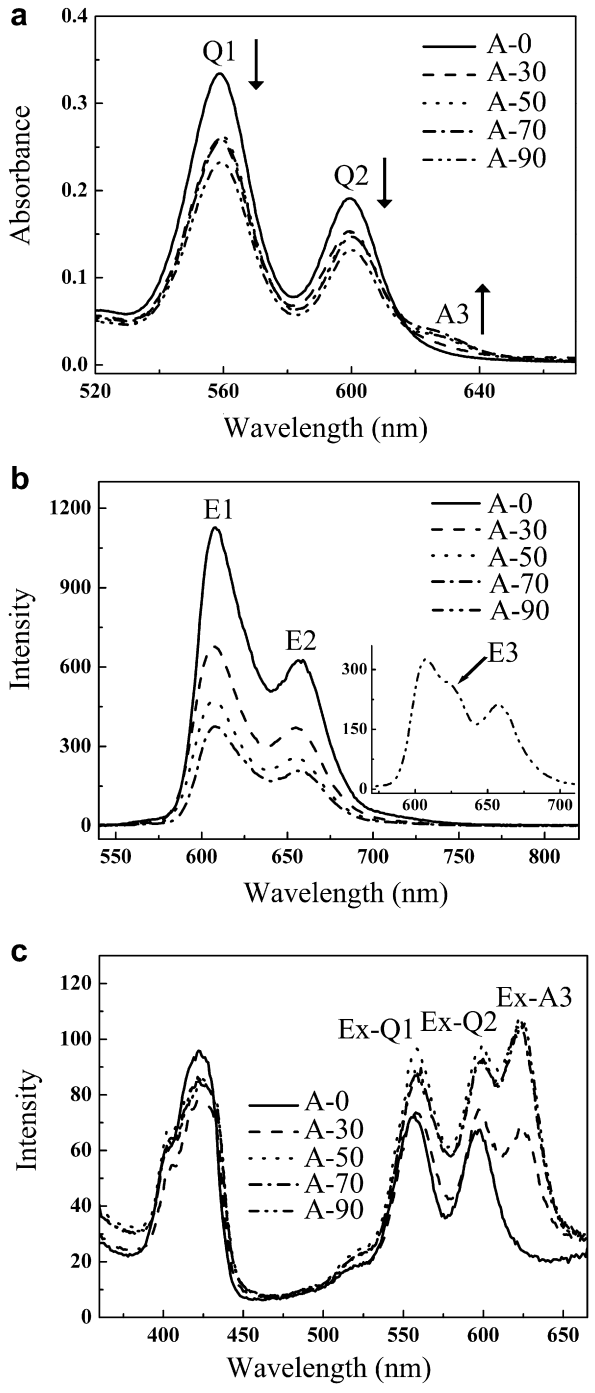


Fig. 4. (a) UV–vis absorption spectra, (b) fluorescence emission spectra ($\lambda_{ex} = 422$ nm, inset: fluorescence emission spectrum of A-90), and (c) excitation spectra ($\lambda_{em} = 680$ nm); of ZnAOTCPP-Na in the mixtures of acetone and water. ($c_{ZnAOTCPP\text{-}Na} = 5.56 \times 10^{-4}$ mol dm^{-3}; A-N: Acetone/(Acetone + Water) = N vol%).

[29]. Moreover, the excitation spectrum exhibited a clear new peak at 625 nm when the concentration reached 1.72×10^{-2} mol dm^{-3}, which means that the aggregation of porphyrins was helpful in decreasing their environmental polarity. However, the interactions between ZnAOTCPP-Na were very weak, because the related signal could only be observed in excitation spectra.

To confirm the observation of the electronic interactions between porphyrins shown by the spectra in Fig. 3a, an experiment to reduce the solubility of ZnAOTCPP-Na in water was performed by addition of acetone, which is a poor solvent for ZnAOTCPP-Na. This was done to enhance the aggregation of ZnAOTCPP-Na and hence the associated spectral effects. Obvious changes were observed in the UV–vis absorption spectra (Fig. 4a) by adding acetone to ZnAOTCPP-Na aqueous solution. As the volume of acetone in the solution was increased, the absorbance of ZnAOTCPP-Na decreased. However, when the ratio of acetone was increased to 50%, a new red-shift absorption band at 625 nm (labeled A3 in Fig. 4a) emerged, as a result of the formation of porphyrin association complex [30]. Moreover, that band became stronger and more

Table 1
Photophysical comparison of porphyrin monomers and copolymers in their dilute aqueous solutions.

	Absorption bands (nm)[a]					Fluorescence emission bands (nm)[a]			$\varepsilon_{Q1/B}$[b]	φ_f[c]
	B	*Q*1	*Q*2	*A*3	*A*4	*E*1	*E*2	*E*3		
ZnAOTCPP	422	557	597	–[d]	–[d]	607	655	–[d]	0.039	0.078
ZnAOTCPP-Na	422	557	597	–[d]	–[d]	607	655	–[d]	0.038	0.079
P-O	422	557	597	622	–[d]	605	654	624	0.040	0.054
P-W	422	566	606	622	752	605	654	624	0.077	0.068

[a] The bands labeled as *B*, *Q*1, *Q*2, *A*3, *A*4, *E*1, *E*2 and *E*3 as shown in Figs. 2 and 5.
[b] The ratio of molar absorption coefficient of *Q*1 band to *B* band.
[c] The fluorescence quantum yield (φ_f) of porphyrins in water using TPP in benzene as a standard ($\varphi_f = 0.11$) [28].
[d] No signal in this wavelength region of the spectrum.

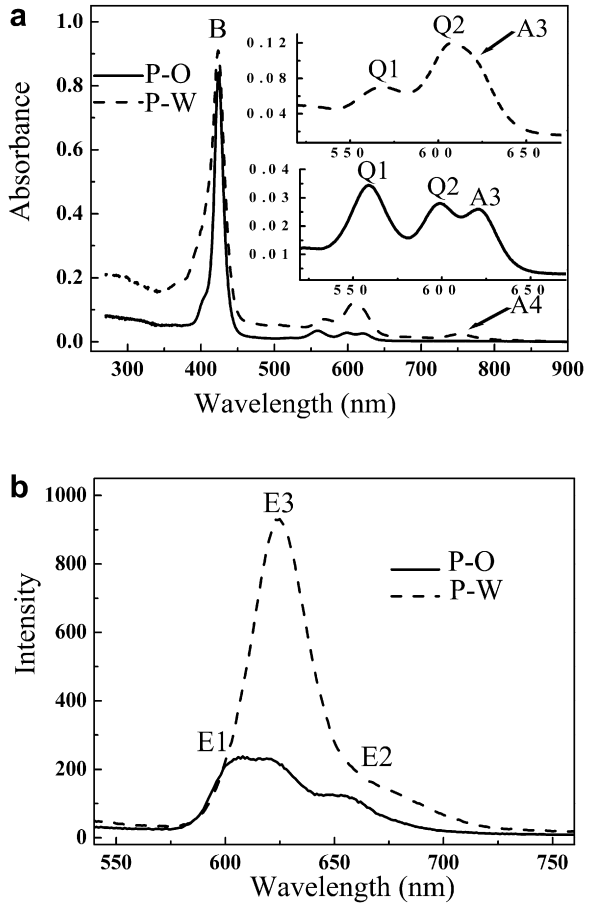


Fig. 5. (a) UV–vis absorption spectra (inset: expanded spectra from 520 nm to 670 nm), and (b) fluorescence emission spectra ($\lambda_{ex} = 422$ nm); of copolymers in water. ($c_{Por} = 5.78 \times 10^{-6}$ mol dm^{-3} for P-O and $c_{Por} = 5.87 \times 10^{-6}$ mol dm^{-3} for P-W).

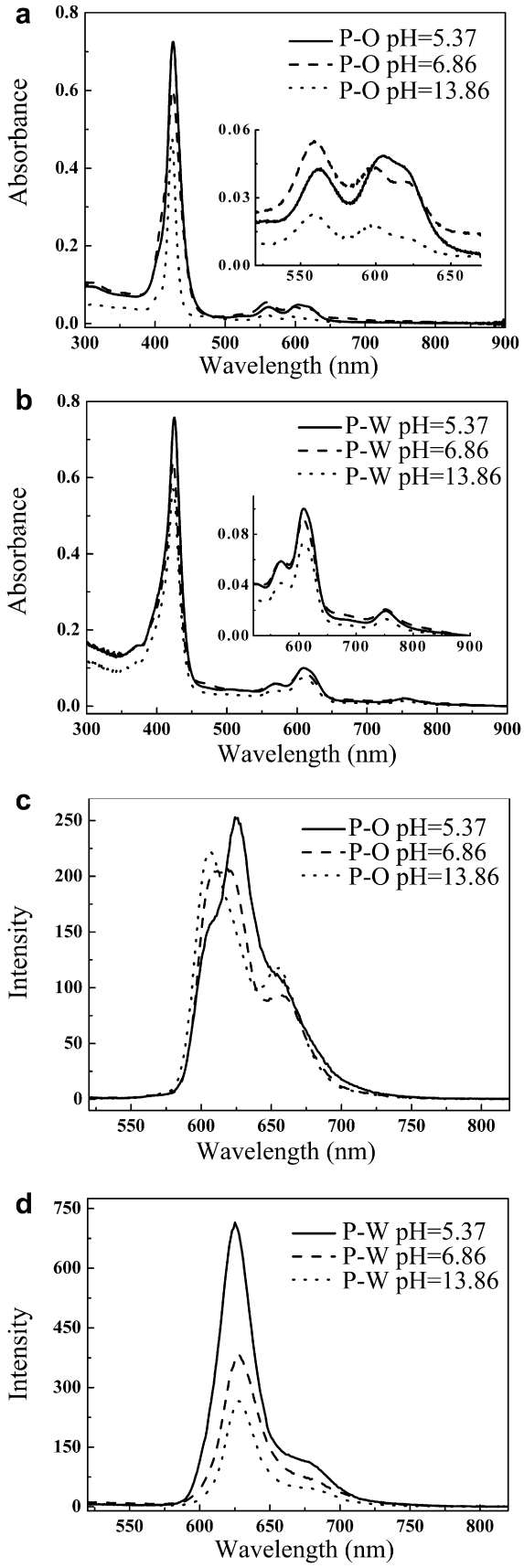


Fig. 6. UV–vis absorption spectra for (a) P-O (inset: expanded spectra from 520 nm to 760 nm), (b) for P-W (inset: expanded spectra from 520 nm to 900 nm); and fluorescence emission spectra ($\lambda_{ex} = 422$ nm) for (c) P-O, and (d) for P-W in various buffer solutions. ($c_{Por} = 5.03 \times 10^{-6}$ mol dm^{-3} for P-O and $c_{Por} = 5.12 \times 10^{-6}$ mol dm^{-3} for P-W).

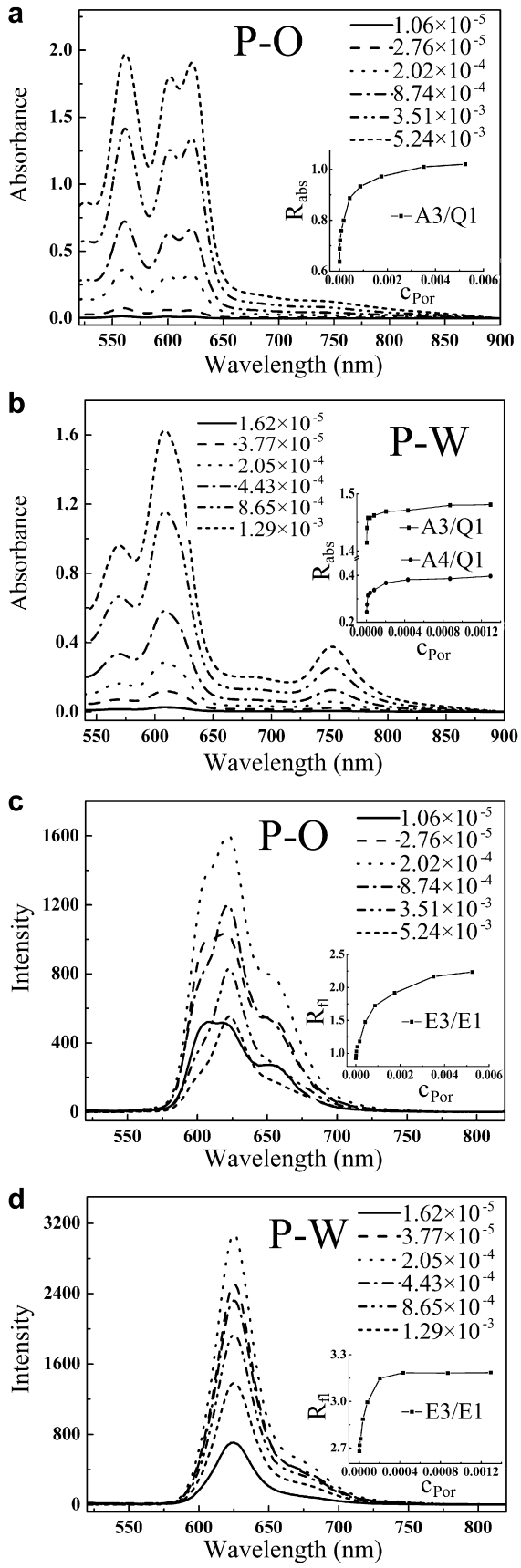
prominent with the increase in the proportion of acetone. Interestingly, there was a new band at 627 nm labeled E3 in the fluorescence emission spectrum of ZnAOTCPP-Na solution with 90% acetone (Fig. 4b), which was also caused by the association complex [31–34]. The excitation spectra of ZnAOTCPP-Na with a low concentration (5.56×10^{-4} mol dm^{-3}) in mixtures of acetone and water are shown in Fig. 4c. The spectra for solution with more than 30% acetone were similar to the spectrum of 1.72×10^{-2} mol dm^{-3} ZnAOTCPP-Na aqueous solution in Fig. 3a, in which the Ex-A3 band was also at 625 nm. The more acetone added in ZnAOTCPP-Na aqueous solution, the greater should be the tendency for porphyrin association complexes to form. Thus, the Ex-A3 band displayed in Fig. 4c increased in intensity with increasing proportion of acetone. All of these results indicated that weak electronic interactions existed between the porphyrin molecules in an aqueous solution of ZnAOTCPP-Na, and they could be tuned by addition of a poor solvent.

3.2. Self-assembly and photophysical properties of the copolymers

In the P-O polymerization system, the monomers AM and ZnAOTCPP distributed uniformly in a mixture of DMSO and acetic acid. Consequently, during the polymerization the initiator AIBN initiated any kind of monomers encountered in solution randomly, i.e. either AM or ZnAOTCPP, to form propagating radicals of polymerized AM and porphyrin units until they were terminated. Under these polymerization conditions nonionic porphyrin units became distributed randomly in the P-O copolymer chains.

In the P-W polymerization system, ZnAOTCPP-Na aggregates were formed in water due to its initial concentration (1.05×10^{-2} mol dm^{-3}) being higher than CAC. In the polymerizing process of P-W, the water-soluble initiator ACVA initiated AM monomer to polymerize in aqueous media and form propagating radicals of PAM at first. When PAM radicals encountered ZnAOTCPP-Na aggregates, they copolymerized with several ZnAOTCPP-Na molecules, which resulted in micro-blocks of anionic porphyrin units being incorporated in the propagating radicals [25–27]. The propagating radicals polymerized with AM monomer again after they had departed from the aggregates of ZnAOTCPP-Na. These steps were repeated many times until the propagating radicals were terminated. Therefore, P-W had micro-blocky sequences of anionic porphyrin units in the copolymer chains. Moreover, there were electrostatic repulsions between the P-W propagating radicals with incorporated anionic porphyrin units and ZnAOTCPP-Na monomer, which resulted in copolymer P-W having a smaller content of porphyrin units (0.34 mol%) than P-O (0.67 mol%), for the same porphyrin monomer/AM feed ratio. Furthermore, PAM has a larger solubility in water than in a mixture of DMSO and acetic acid, so P-W had a higher molecular weight (3.0×10^6 g mol^{-1}) than P-O (5.4×10^5 g mol^{-1}).

When copolymer P-O was dissolved in water, the nonionic porphyrin units anchored in polymer scaffolds would try to aggregate due to their hydrophobicity. Therefore, hydrophobic microdomains were formed by the amphiphilic copolymer chains, where the most of the porphyrin units should be located to escape from water [15–17]. When some of them were located close enough and in favorable orientations, they could interact with each other by π–π stacking interactions to form porphyrin association complexes [30–34]. Consequently, compared with monomer at



approximately equal concentrations of porphyrin molecules (Table 1), copolymer P-O exhibited a red-shift absorption band at 622 nm (labeled A3 in Fig. 5a). This was similar to the band of the solution of ZnAOTCPP-Na with up to 50% acetone (Fig. 4a). In a like manner, there was a new emission band at 624 nm (labeled E3 in Fig. 5b) that was similar to that formed in the solution of ZnAOTCPP-Na with 90% acetone (Fig. 4b). Thus, copolymer P-O enlarged the range of spectral absorption, which was meaningful in the effort to set up an artificial LH system in aqueous media. As observed in absorption and emission spectra (Fig. 5), some of the porphyrin units in P-O did not form association complexes, and displayed the photophysical characteristics of monomers, such as the location of Q1 and Q2 as well as the value of $\varepsilon_{Q1}/\varepsilon_B$, as listed in Table 1.

The copolymer P-W was an anionic copolymer and readily soluble in water, and the porphyrin units were arranged in micro-blocky sequences. In the UV–vis absorption spectra of P-W shown in Fig. 5a, there is a 9 nm red-shift in Q bands (Table 1), which means that the energy level of S_0–S_1 of the porphyrin units in the copolymer was lower than that of monomer. Hence there was a larger transition probability between ground state and excited state of porphyrin units in P-W compared to monomer, because the value of $\varepsilon_{Q1}/\varepsilon_B$ in P-W was 0.076 while the value for monomer was 0.039 [35,36]. Moreover, there was a shoulder at 622 nm (labeled A3 in Fig. 5a) and a new emission band at 624 nm (labeled E3 in Fig. 5b), which arose from the porphyrin association complexes similar to those of P-O in water, and those of ZnAOTPP-Na in mixtures of acetone and water. Interestingly, another new red-shift absorption band appeared at 752 nm (labeled A4 in Fig. 5a) for P-W but not for P-O, which indicated that there was another kind of porphyrin association complex formed in the system. It is noteworthy that this kind of long wavelength absorption by a water-soluble polymer containing porphyrins has not been reported to the best of our knowledge. However, the origin of A4 could not be ascertained in details in this study. In addition, when the concentrations of porphyrin units (c_{Por}) of P-O and P-W were approximately equal, P-W had larger cross section of absorption (400–800 nm) and higher molar absorption coefficient $\varepsilon_{Q1}/\varepsilon_B$ (0.076) than P-O (400–650 nm and 0.041 respectively). These results indicated that the copolymer P-W can more efficiently in absorbing light, compared to P-O, to accomplish light-harvesting in water.

When copolymer P-O was dissolved in buffer solution at pH 5.37, ionization of the carboxylic acid groups of the porphyrin units was reduced, hence the hydrophobicity of porphyrin units increased, and electrostatic interactions between them decreased. These changes favored the formation of porphyrin association complex. However, the carboxylic groups of the porphyrin units were ionized in pH 13.86 buffer, so the solubility and electrostatic interactions of porphyrin units of P-O were increased. As a result, the lower the pH of the buffer solution in which P-O is dissolved, the stronger the absorption and emission of porphyrin association complexes becomes (Fig. 6a and c). In case of copolymer P-W, the micro-blocky sequences of porphyrin units in the copolymer chains, the covalent restrictions of polymer chains, played a more important role in the formation of porphyrin association complexes. Therefore, the spectral changes with pH were less noticeable for P-W (Fig. 6b and d) than for P-O, although the effects of pH on porphyrin units were similar for these two copolymers. The different effects of pH of the

Fig. 7. The UV–vis absorption spectra ((a) P-O, (b) P-W; insets: the variation of the ratio of absorption bands (R_{abs}) with c_{Por}), and fluorescence emission spectra ((c) P-O, (d) P-W; insets: the variation of the ratio of fluorescence emission bands (R_{fl}) with c_{Por}), for the copolymers in water.

aqueous solution on the photophysical properties of P-O and P-W indicated that the formation of porphyrin association complex was caused by weak interactions in P-O while strong interactions in P-W.

As shown in Fig. 7, the solubility of porphyrin units in copolymers in water was improved to 10^{-3} mol dm^{-3} with the aid of the water-soluble polymer chain, thus these copolymers overcome one of the main problems in setting up an artificial LH system in aqueous media. Spectroscopic methods can give good insight into the self-assembly behavior of molecules, especially for molecules that have characteristic photophysical properties. These polymers have porphyrin units that are either aggregated or non-aggregated, with corresponding differences in absorption and fluorescence emission spectra. The non-aggregated porphyrin units in copolymer P-O shows Q1 and Q2 bands in the UV–vis absorption spectra, and *E*1 and *E*2 bands in fluorescence emission spectra, while a new band A3 in UV–vis absorption spectra and band *E*3 in the fluorescence emission spectra was for one kind of porphyrin association complex. In copolymer P-W, there was another kind of porphyrin association complex with absorption band A4. The intensity ratios for absorption or fluorescence emission between the aggregated porphyrin units and non-aggregated porphyrin units in the copolymers can be used to monitor the aggregation of copolymer in the aqueous media [37–40]. In the spectra of P-O (Figs. 7a and c), R_{abs} of A3/Q1 and R_{fl} of E3/E1 increased rapidly with c_{Por} for $c_{Por} < 8.72 \times 10^{-4}$ mol dm^{-3}. However, those ratios changed slowly for $c_{Por} > 8.72 \times 10^{-4}$ mol dm^{-3}. These results indicated that there were two stages of self-assembly of P-O in water, and 8.72×10^{-4} mol dm^{-3} could be taken as the critical concentration of P-O to reach a balance of the self-assembly. Similar behavior was shown by copolymer P-W (Figs. 7b and d), for which its critical concentration thus determined was 2.04×10^{-4} mol dm^{-3}. The first stage of variations of R_{abs} and R_{fl} represents the intermolecular associations of the copolymer chains containing porphyrins in the aqueous media, during which a large amount of porphyrin association complexes is formed [39,40]. The second stage corresponded to the range of c_{Por} in which further addition of copolymer does not greatly change the local environment of porphyrin units to reach a balance of the self-assembly in water, although assemblies of copolymers should continue to grow [37]. P-W had a lower critical concentration than P-O, even though the content of porphyrin units of P-W was much smaller, which indicates that the micro-blocky sequences of porphyrin units in P-W played a primary role in its aggregation in water [39]. The values of R_{abs} and R_{fl} for P-O increased about 2-fold with the increasing c_{Por}, while those for P-W increased not more than 1.2-fold. Thus, there were larger effects of c_{Por} on the formation of porphyrin association complex of P-O than of P-W, suggesting that the complexes are formed by weaker interactions in P-O than in P-W. It is worthy of note that the increase of porphyrin association complex absorbing at 752 nm (1.56-fold) was enhanced much more than the complex that absorbs at 624 nm. That suggests that the increasing c_{Por} of P-W in water is an effective way to afford a large cross section of absorption at longer wavelength region. In general, P-W with micro-blocky sequences of porphyrin units in the copolymer chains is a better candidate for building an artificial LH system in aqueous media due to the porphyrin association complex with absorption at the longer wavelength region.

4. Conclusions

The novel porphyrin monomer ZnAOTCPP and its salt ZnAOTCPP-Na were synthesized and their corresponding copolymers with AM, named P-O and P-W respectively, were also prepared. There were electronic interactions between ZnAOTCPP-Na molecules in water, when its concentration was above CAC or when acetone was added. In copolymers, the solubility of porphyrin was greatly improved by water-soluble AM units in the polymer chains. Moreover, porphyrin association complexes with absorption and emission at long wavelength region were anchored in the polymer scaffolds, especially for the micro-blocky copolymer. To the best of our knowledge, this is the first observation of such absorption or emission of porphyrin association complexes in water-soluble polymers. These results suggest that the water-soluble copolymers containing porphyrin units should be promising materials for the construction of artificial LH systems in aqueous media.

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