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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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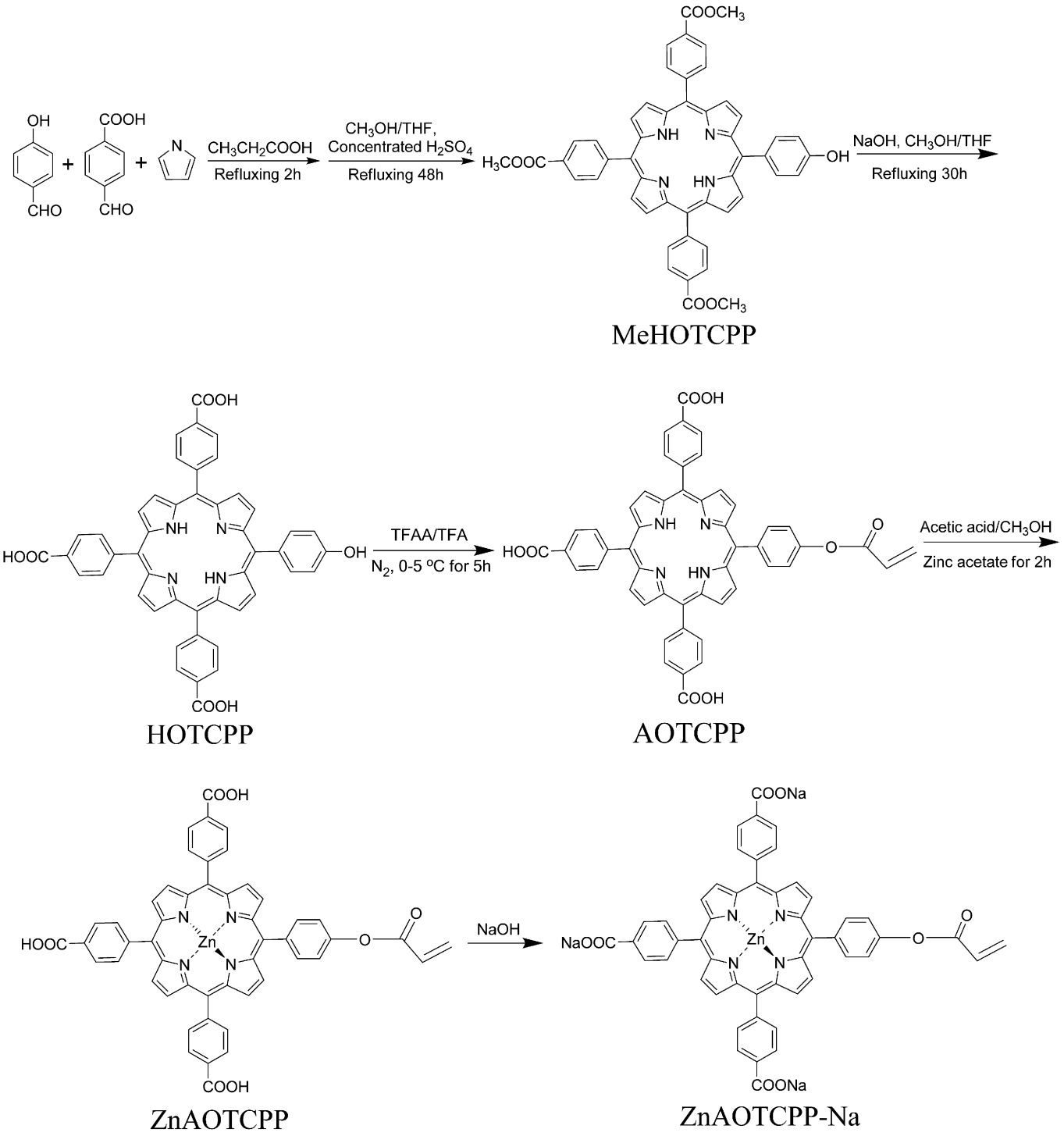

Fig. 1. Synthesis of the porphyrins.

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.