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Original article

Highly ordered arrangement of *meso*-tetrakis(4-aminophenyl)porphyrin in self-assembled nanoaggregates *via* hydrogen bonding

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ABSTRACT

meso-Tetrakis(4-aminophenyl)porphyrin (TAPP) can self-assemble into nanostructures with different morphologies by a phase-transfer method. The morphologies (nanospheres, nanorods and nanothorns) of porphyrin nanoaggregates could be easily tuned just by changing the concentration of porphyrin in a proper solvent at room temperature. HRTEM images revealed the formation of highly ordered supramolecular arrays of TAPP, *i.e.*, superlattice of TAPP molecules in nanoaggregates, which agreed well with the size of one molecule of TAPP. UV–vis absorption spectra showed an obvious red shift of the Soret band of TAPP, indicating the formation of *J*-aggregates of TAPP in nanoaggregates.

1. Introduction

Self-assembly is a natural and spontaneous process which occurs mainly through non-covalent interactions, such as hydrogen bonding, electrostatic, π–π stacking, van der Waals, metal–ligand coordination bonding and hydrophobic interactions. The self-assembly approach has been widely adopted in the effort for the fabrication of organic functional molecular nanostructures [1]. Based on different non-covalent interactions, various nanostructures, such as cubes, fibers, sheets, rods, and tubes, have been fabricated from different functional molecular materials [2–5]. Porphyrins are particularly attractive building blocks for self-assembly because the intimate packing of these aromatic macrocycles can result in enhanced photophysical and photochemical performances that are important in many technological applications, such as catalysis, optical device, storage, field-effect transistor and photovoltaic [6]. Vesicles of *meso*-tetrakis[(bixinylamino)-*o*-phenyl]porphyrin formed in water at pH 9 can essentially remain intact even on dry solid surfaces [7]. Hao and coworkers reported the formation of vesicles of an amphiphilic manganese complex of Mn(III)TPP(COOH) with four stearic acid groups on one side of the ring plane in the non-aqueous solution [8]. Nanotubes with photocatalytic activity were fabricated by electrostatic interaction between two oppositely charged porphyrins [9]. Twisted supramolecular nanoscrews of a simple porphyrin with tetraheptyl functional groups were fabricated in acetonitrile solvent [10]. Li and coworkers reported on fabricated 2D or 3D structured nanopatterns and arrays *via* the colloidal self-assemble process of a novel porphyrin molecule 5,10,15,20-[1,4-benzodioxane-6-carboxalde]porphyrin (TEOP) [11]. Investigation over the organogel formation properties of a series of porphyrins with amide groups as peripheral hydrogen bonding sites indicated that the aggregation mode of porphyrin stacks can be tuned by hydrogen bonding interaction [12]. Jiang and coworkers found the *meso*-substituted phenyl groups of porphyrin ligand modified by different numbers of hydroxyl groups led to the formation of various nanostructures, clearly indicating the effect of hydrogen bonding interaction in controlling the intermolecular interaction between conjugated molecules in the self-assembly process. Furthermore, studies on conjugated molecules modified by different substitutes, self-assembled at the liquid–solid interface revealed, by scanning tunneling microscope (STM), the ordered molecular packing of porphyrin derivatives [13]. However, to the best of our knowledge, there is still no report on the novel

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morphologies (nanorods and nanothorns) with highly ordered arrangements of porphyrins (TAPP) in nanostructures which were directly imaged by high resolution transmission electron microscopy (HRTEM).

In this paper, porphyrin (TAPP) nanostructures with various morphologies (nanospheres, nanorods and nanothorns) were fabricated. Interestingly, highly ordered arrays of porphyrin molecules in the aggregates of nanorods and nanothorns were directly imaged by HRTEM and detailed investigations revealed that the size of each quadrate supramolecular array agrees well with that of TAPP molecule.

2. Experimental

meso-Tetrakis(4-aminophenyl)porphyrin (TAPP) was synthesized according to published methods [14]. All the solvents were of analytical grade and used without further purification. The molecular structure of TAPP is shown in Fig. 1.

The nanoaggregates of TAPP formed in different concentrations of chloroform solution were fabricated by a phase transfer method according to the following procedure. CH_3OH (1 mL) was injected rapidly into 4 mL chloroform solution of TAPP with different concentrations. After being aged for three days at room temperature, these aggregates were transferred by pipetting to the surface of the carbon-coated grid for the TEM and SEM observations and to a quartz substrate for XRD as well as UV–vis analysis.

The porphyrin aggregates formed in the mixed solvent of $CHCl_3/CH_3OH$ (v/v, 4/1) are characterized by scanning electron microscopy (SEM, JEOL), high-resolution transmission electron microscopy (HRTEM, JEM-2100, JEOL) with an accelerating voltage of 200 kV. The sphere-like nanoaggregates formed at the lower concentration of TAPP were characterized by dynamic light scattering (DLS) (Nano S90 (Red badge) ZEN1960, Malvern). Small-angle X-ray diffraction (SAXRD) measurement was carried out on a Bruker D8 Advance diffractometer using Cu Kα (λ = 1.5418 Å). UV–vis absorption spectra were recorded on a (UV-3200PC) UV–vis spectrophotometer.

3. Results and discussion

3.1. Morphologies of porphyrin nanoaggregates

Typically, samples were prepared by different dilutions of the original $CHCl_3$ solutions of porphyrin with the mixed solvent of $CHCl_3/CH_3OH$ (5×10^{-4}, 7.5×10^{-4}, 1×10^{-3} and 1.5×10^{-3} mol L^{-1} respectively). The morphologies of the formed aggregates were examined by transmission electronic microscopy (TEM) and scanning electron microscopy (SEM). It can be observed that various morphologies of nanoaggregates were fabricated at different concentrations of porphyrin solutions in chloroform by the phase transfer method. As shown in Fig. 2A, a large amount of nano-scale solid spheres with a diameter from *ca.* 75 nm to 110 nm were formed in the mixed solvent of $CHCl_3/CH_3OH$ (v/v, 4/1) with the concentration (5×10^{-4} mol L^{-1}) of chloroform. Moreover, some nanospheres of several nanometers in diameter can also be found. Further evidence to confirm the formation of solid nanospheres was provided by SEM, as shown in Fig. 2B. Owing to the regular spheres of TAPP nanoaggregates obtained in a mixed solvent of $CHCl_3/CH_3OH$ (v/v, 4/1) with the lower concentration (5×10^{-4} mol L^{-1}) of chloroform, DLS measurements were carried out to investigate the distribution of these regular nanospheres. This is attributed to the spherical nanoparticles with a variety of different diameters, but well-defined shapes [8]. As shown in Fig. 3, two particle size distributions of nanospheres appeared at *ca.* 15 nm and 110 nm, respectively, which is in good accordance with that of TEM and SEM images.

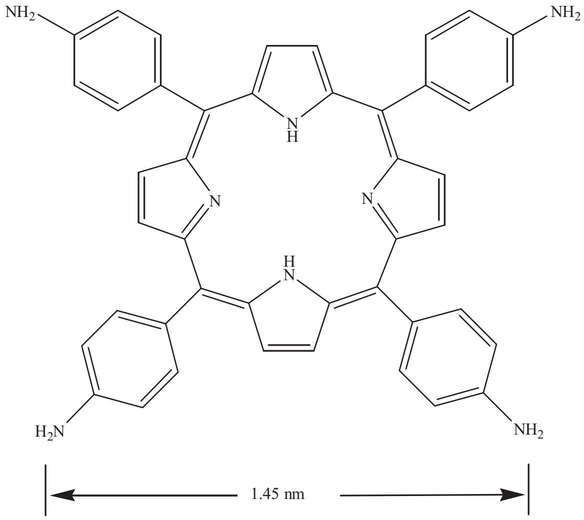

Fig. 1. The molecular structure of *meso*-tetrakis(4-aminophenyl)porphyrin (TAPP).

When the original concentration of TAPP chloroform solution increased to 7.5×10^{-4} mol L^{-1}, nanorods grown from the irregular nanoparticles were found in a mixed solvent of $CHCl_3/CH_3OH$ (v/v, 4/1), as shown in Fig. 4A. However, when the concentration of TAPP chloroform solution was further increased to 1×10^{-3}–1.5×10^{-3} mol L^{-1}, nanothorns appeared in a mixed solvent of $CHCl_3/CH_3OH$ (v/v, 4/1) as shown in Fig. 5A.

The different morphologies of the formed aggregates of TAPP may be explained with the help of the growth mechanism of nanoparticles. As is known, there is a balance between the rate of nucleation and the growth rate of crystal nuclei. If the rate of nucleation is faster than the growth rate of crystal nuclei, the number of crystal nuclei is large, resulting in a relatively smaller size of nanoparticles [15,16]. When CH_3OH solvent was added to

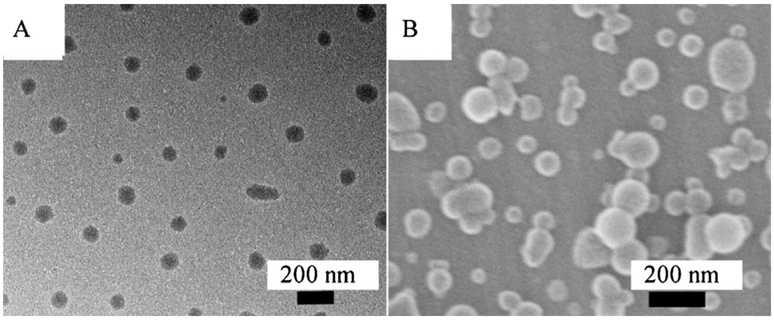

Fig. 2. TEM (A) and SEM (B) images of TAPP nanospheres self-assembled in the mixed solvent of $CHCl_3/CH_3OH$ (v/v, 4/1) with the original concentration (5×10^{-4} mol L^{-1}) of $CHCl_3$ solution.