

Research paper

Porphyrin-cored dendrimers consisting of novel siloxane-poly (amido amine) dendron-like arms: Synthesis, characterization, and photophysical properties



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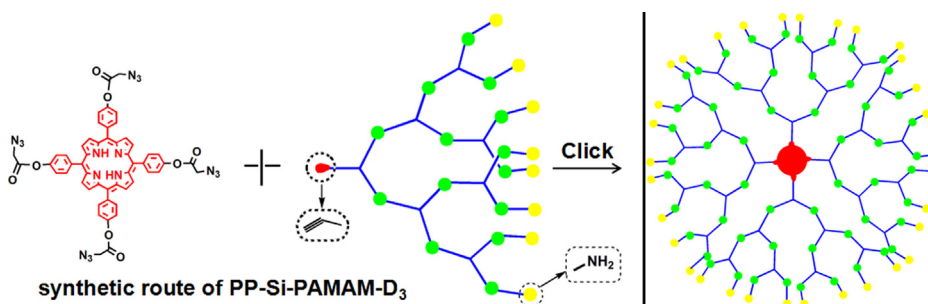
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HIGHLIGHTS

- A versatile strategy to prepare propargyl focal point novel siloxane-poly (amido amine) typed dendrons was described.
- Different generations of porphyrin-cored dendrimers were successfully obtained via click chemistry.
- The synthesized porphyrin-cored dendrimers gave strong and remarkable pH-dependent behaviour in fluorescence emission.

GRAPHICAL ABSTRACT



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ABSTRACT

Different generations of porphyrin-cored dendrimers consisting of novel siloxane-poly(amido amine) dendron-like arms have been synthesized via copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction of azide-modified 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin with different generations of propargyl focal point novel siloxane-poly(amido amine) typed dendron (Si-PAMAM). The used different generations of Si-PAMAM were obtained by the “arm-first” strategy based on the Michael addition reaction and Amidation reaction, orderly. The structure of porphyrin dendrimers is established by ¹H NMR, ¹³C NMR, MALDI-TOF-MS and FT-IR analysis. PP-Si-PAMAM-D_m (m = 1, 2, and 3), not only gave strong fluorescence emission and the intensity increased significantly as the generation growing, but also showed a remarkable pH-responsive in fluorescence emission. These interesting properties indicate that synthesized porphyrin dendrimers may be able to act as pH-responsive probes suitable for biomedical imaging, diagnosis and treatment.

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1. Introduction

During the past two decades, a broad variety of dendrimers has been generated [1]. Among them, poly(amido amine) (PAMAM) and their derivatives are the first complete dendrimer family to be synthesized, characterized and commercialized [2]. Its

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biocompatibility and unique treelike architecture open it up to a significant number of biomedical applications including drug delivery [3], imaging micelles [4] and stimuli-responsive fluorescence probes [5]. Dendrimers consisting of heteroatoms provide several superior characteristics [6,7], such as variable branching multiplicity, high flexibility, and unusual electro-optical properties. Much emphasis to date has been placed on silicon-based dendrimers due to their numerous advantages such as simplicity of the synthetic process to extend the generation, accessibility to a dendrimer with desired molecular weight and adequate number of terminal functions, biochemical stability and biological inertness [8,9]. However, there are scarce literatures on dendritic siloxane structure, only very few dendrimers consisting of siloxane groups are known so far. Niu [10] and co-workers reported the synthesis of Si-based PAMAM dendrimers and the investigation of their luminescent properties. Thus, great efforts have been devoted, taking advantage of unique structural features of Si-based dendrimers, to optimize the delivery efficacy and selectivity of photosensitisers, probes and drug-containing polymeric micelles [11,12].

One of promising approaches is exploration of porphyrin-cored dendrimers [13,14] which had show their potential applications in numerous areas, such as light harvesting, electron transfer, host-guest recognition, photodynamic therapy, and acting as biological sensors [15,16]. Recently, a growing number of researchers show interest in investigating the possibility of using porphyrin-dendrimers as colorimetric and fluorescence pH sensors [17,18]. Compared with the existing commercial dyes, porphyrin dendrimers provide numerous of outstanding features especially act as the pH-responsive probe in the complicated biological systems. The prominent one is the complete membrane impermeability of porphyrin dendrimers, an intrinsic structural property of large dendritic spheres carrying multiple peripheral charges [19]. So, considerable efforts have been contributed to the search of appropriate and convenient synthetic strategies for preparation of porphyrin-dendrimers [20], which could be used as the pH probe for potential application in biological systems.

Since introduced by Tornøe and Meldal in 2001, Cu(I) catalysis of the Huisgen 1,3-dipolar cycloaddition reaction of organic azides and alkynes has become the most useful and widely employed reaction in the synthesis process of dendrimers in recent years [21–23]. Cu(I) catalyzed click reaction (CuAAC), not only has the unique properties of high yielding, high atom efficiency and selectivity [24], but also character by versatile, clean, requires simple workup and simple purification procedures [25]. Hence, the CuAAC provides an ideal method in the synthesis of porphyrin dendrimers. In the past few years, a number of porphyrin dendrimers possessing different peripheral functional groups have been successfully synthesized via CuAAC. Such as, Divya Kushwaha et al. [26] synthesized a series of glycoporphyrin dendrimers and Stephanie L. Elme et al. reported the synthesis of polyglycerol porphyrin-cored dendrimers via click chemistry [27]. To the best of our knowledge, porphyrin-cored dendrimers consisting of novel siloxane-poly(amido amine) dendron-like arms via click reaction have not been reported.

In this work, we synthesized different generations (from 1 to 3) of porphyrin-cored dendrimers consisting of novel siloxane-poly(amido amine) dendron-like arms (PP-Si-PAMAM-Dm, m = 1, 2, and 3) via the Cu(I)-catalyzed click reaction. In this synthetic strategies, porphyrins caged inside dendritic shell are structurally reminiscent of enzymes, in which the encapsulation of novel siloxane-poly(amido amine) dendrons (Si-PAMAM) itself could be used to increase the solubility of porphyrins and to prevent their aggregation in aqueous solutions [28]. Thus, dendritic Si-PAMAM offers a convenient method to isolating porphyrin moiety from components of biological systems [29]. Three generations of dendrimers were characterized by means of ^1H NMR, ^{13}C NMR, MALDI-TOF-MS, FT-IR, UV-vis and the results demonstrated that

the click reaction performed well. In addition, fluorescence properties of PP-Si-PAMAM also be investigated in this study. In one hand, the fluorescence intensity of synthesized porphyrin dendrimers with the siloxane blocks had greatly enhanced compared with the porphyrin-dendrimers without the siloxane (PP-PAMAM). In another hand, the synthesized PP-Si-PAMAM-Dm (m = 1, 2, and 3) showed a significant pH-responsive in fluorescence emission.

2. Experimental section

2.1. Materials

1,3-bis(3-aminopropyl)-tetramethyldisiloxane (D_0) was obtained as a commercial product and used directly. Parahydroxybenzaldehyde, pyrrole, sodium azide, bromoacetyl bromide, propynylamine, sodium ascorbate, copper sulfate pentahydrate were purchased from Aladdin reagent company or Aldrich, and all of these reagents were used without further purification.

Methyl acrylate (MA), methanol, petroleum ether, propionic acid, acetic acid, nitrobenzen, chloroform and dimethyl sulfoxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol and chloroform were distilled from CaH_2 . Methyl acrylate were distilled under reduced pressure before used.

5,10,15,20-Tetraphenylporphyrin (TPP) were purchased from Shanghai Dibai Chemical Technology Co., Ltd and used as received.

Azide-modified 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (PP- N_3) used in the study was prepared according to the literature [30]. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ (ppm) 8.87 (s, 8H, β -pyrrole-H), 8.00 (d, $J=8.4$ Hz, 8H, m-Ar-H), 7.21 (d, $J=8.4$ Hz, 8H, o-Ar-H), 2.61 (s, 8H, COCH_2N_3), -2.88 (s, 2H, β -pyrrole-NH). FT-IR (KBr, cm^{-1}): 3420 ($\nu_{\text{O-H}}$, ν_{NH}), 2927 (ν_{CH}), 2095 (ν_{NNN}), 1780 (ν_{CO}), 1450–1600 (Ar, VP), 802 (Ar).

2.2. Methods

^1H NMR spectra were recorded with CDCl_3 or $\text{DMSO}-d_6$ as solvent at room temperature on a Varian Mercury-400 spectrometer, chemical shift are reported in ppm downfield from TMS. Ultraviolet-visible (UV-vis) spectra was recorded in DMF or THF solutions at room temperature using a Spectrumlab54 UV-vis spectrophotometer. The FT-IR spectra measurements were conducted on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) at frequencies ranging from 400 to 4000 cm^{-1} , using KBr disks at room temperature (25°C). Fluorescence spectrum was performed at room temperature using a Fluorescence Spectrophotometer (CaryEclipse, AUS). Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker Daltonics-ultraflex II & ultraflex II TOF/TOF using α -Cyano-4-hydroxycinnamic acid (CHCA) as a matrix.

2.3. Determination of the fluorescence quantum yield in organic solution

The fluorescence quantum yields (ϕ_f) of PP-Si-PAMAM-Dm (m = 1, 2, and 3) were found using Eqs. (1) and (2), and TPPH₂ was used as standard ($\phi_f = 0.11$) [28,31,32]. The fluorescence emission of sample was excited at 422 nm, and the concentrations of TPPH₂ and samples were $1.63\ \mu\text{mol L}^{-1}$.

$$\phi_f = 0.11 \frac{A_{\text{TPPH}_2} S_{\text{sample}}}{S_{\text{TPPH}_2} A_{\text{sample}}} \quad (1)$$

$$S = \int_{\lambda_{600\text{nm}}}^{\lambda_{800\text{nm}}} I_{\lambda} d\lambda \quad (2)$$

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