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Self-assembly and supramolecular transition of poly(amidoamine) dendrons focally modified with aromatic chromophores

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Abstract

Three novel series of amphiphiles based on poly(amidoamine) dendrons (from G1 to G3) and having different aromatic chromophores (Cz I, Cz II, and Py) at the focal point were synthesized and studied for their self-assembly behavior in aqueous solution by using electronic microscopies (i.e., SEM and TEM), UV–vis, fluorescence, IR, and ^{1}H NMR spectroscopy. It was found that the generation of dendrons affected significantly the self-assembly of these amphiphiles in aqueous solution and the morphological structures of the resulting assemblies depended greatly on the architecture of the focal chromophores. As a result, the first generation of dendrons assembled readily into vesicles at low concentrations. These vesicular structures subsequently fused to form a stable tubular structure. Similar tubular structures could also be directly obtained through self-assembly of these amphiphilic dendrons at high concentrations. X-ray investigations showed that the resulting tubules possessed a lamellar structure. A head-to-head packing model of amphiphilic dendrons in the assemblies was proposed.

Keywords: Dendrimers; Dendrons; Self-assembly; Morphological transition; Supramolecular chemistry

1. Introduction

Over the past 10 years, self-assembly of dendritic molecules in polar or nonpolar solvents has been intensively explored to construct multidimensional supramolecular structures such as nanoparticles, fibril gels, nanoclusters, nanotubes, and liquid crystals [1,2]. An advantage of such molecules is that a precise structural design and selective structural modification at the focal point, the interior branches, and/or the peripheries are readily achievable, which makes dendrons and dendrimers suitable nanometer-scale building blocks for various functionalities [3]. The driving forces for the assembly are typically noncovalent interactions such as template effect [2a], hydrogen bonding [2b,2c], solvophobic interaction [2d], van der Waals forces [2e], electrostatic interaction [2f], and metal coordination [2g]. In 1985, Newkome et al. [3b] reported their pioneering study on the assembly properties of dendrimers and revealed a unimolecular micelle formation phenomenon. In 1996, Zimmerman et al. [4] reported the first example of self-assembly of dendrons having hydrogen donating and accepting units at the focal point. It has been found that the focal structure has great influence on the supramolecular assembly of dendrons [5]. For example, Smith and co-workers [6] reported a dependence of gelation ability of the dendrons on the length of aliphatic chains at the focal point; Percec et al. [7] found that lattice structures of dendron assemblies in the solid state varied with the number of phenolic moieties at the focal point; and Kim et al. [8] observed a morphological transition of assembling dendrons from vesicles to rods or spherical micelles in aqueous solution as the molecular weight of hydrophilic focal moiety increased.

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On the other hand, organic tubular assemblies represent a unique class of supramolecular structures for their potential use in fields of biology, chemistry, and materials science [9]. Various approaches and substances have been recently developed for construction of organic nanotubes, such as self-assembly of suitable macrocyclic building blocks through noncovalent interactions [9a], solid state self-assembly of two-dimensional sheet-like molecules [9b], preparation of peptide nanotubes from linear peptide monomers [9c], and preparation of covalent organic nanotubes by molding dendritic building blocks around an oligoporphyrin core [9d]. In particular, tubular structures obtained through a supramolecular transition are of great interest. Eisenberg and co-workers [10] systematically studied the self-assembly behaviors of amphiphilic copolymers in aqueous solution and revealed that morphological structures of the resulting assemblies could undergo a change from vesicles to tubules and finally to inverted micelles with an increase of the concentration.

Despite the above noted research, studies on self-assembly of tubular structures of amphiphilic poly(amidoamine) dendrons with aromatic focal structures are still less addressed, although such types of dendrons may readily assemble to form various structures [11]. In previous studies [12], we have investigated self-assembly of amphiphilic PAMAM dendrimers peripherally modified with rigid chromophores in aqueous solution. The chemical structure and conformation of chromophores were found to have a great impact on the self-assembly behavior. Herein, we report the self-assembly behavior of a novel series of mono-dispersed amphiphilic poly(amidoamine) dendrons whose focal point was modified with rigid and short aromatic moieties including carbazole I (Cz I), carbazole II (Cz II), and pyrene (Py). These dendritic amphiphiles differ from each other in terms of twist and/or planar structures. Morphological transition from vesicles to tubular structures was observed with a variation of time and concentration. The critical aggregation concentration (CAC) and the molecular packing of the modified dendrons in the assemblies are discussed.

2. Experimental

2.1. Materials

1-Pyrenemethylamine hydrochloride (95%) (from Aldrich), di-*tert*-butyl dicarbonate (97%) (from Alfa Aesar), and trifluoroacetic acid (99%) (from Acros) were purchased and used as received. All other chemical reagents were purchased from Beijing Chemical Reagents Co. and used as received. Dichloromethane, methanol, tetrahydrofuran, diethyl ether anhydrous, acetone, ethyl acetate, dimethyl sulfoxide, *N*,*N*-dimethyl acetamide, acetonitrile, triethyl amine, and ethylene diamine (all from Beijing Chemical Reagents Co.) were purified following the standard procedures. Poly(amidoamine) dendrons were synthesized according to the literature [2a].

2.2. Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer at room temperature using chloroform-*d*, d_6-acetone, or deuterium oxide as the solvents and tetramethylsilane as an internal standard. Elementary analyses were performed on a Vario EL elementary analyzer. FTIR spectra were taken on a Nicolet Magna IR-750 spectrometer in a KBr pellet form or on the surface of glass. A drop of sample solution was placed on the surface of glass and FTIR measurement was performed after water was volatilized naturally at room temperature. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a BIFLE XIII time-of-flight MALDI mass spectrometer. Dithranol (DI), α-nitrile cinnamic acid (CCA), and 2,5-dihydroxybenzoic acid (DHB) were used as the matrices that can give the best resolution. The steady-state fluorescence emission measurements were carried out at room temperature in dichloromethane using a Hitachi F-4500 fluorescence spectrophotometer. The fluorescence decay was performed using the time-correlated single-photon counting technique following excitation by a nanosecond flash lamp (Edinburgh Instruments FL900). Fluorescence decay curves were analyzed using the least-squares interactive convolution method. UV–vis spectra were acquired on a UV–visible scanning spectrophotometer (Schimadzu UV-2101 PC) at room temperature. Transmission electronic microscopy (TEM) measurement was performed on a JEM-100 CXII microscope, operating at an acceleration voltage of 100 kV. Scanning electronic microscopy (SEM) image was obtained on a JEOL JSM-6700F microscope. 1D XRD patterns of the suprastructures were obtained using Dmax/2400 Tigaku at room temperature.

3. Results and discussion

Amphiphilic dendrons D*n*Cz I, D*n*Cz II, and D*n*Py [*n* denotes the generation of poly(amidoamine) dendrons from G1 to G3] were synthesized by the Michael addition reaction of *N*-unprotected poly(amidoamine) dendrons with maleimide-modified chromophores (Cz I, Cz II, and Py) in good yields of 75–88% (Scheme 1). Model compounds (D0Cz I, D0Cz II, and D0Py) were synthesized according to the literature [13] in order to better understand the spectroscopic properties and the structures of focally chromophore-labeled dendrons. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis. The results agree with the proposed structures (supporting information). It should be noted that all the compounds are nonoptically active due to the absence of stereoselectivity in the Michael addition reaction. The detail materials including experimental procedures, synthesis, and characterization of the amphiphilic dendrons are described in the supporting information.

All the resulting amphiphilic dendrons exhibited characteristic absorption and emission properties of the focal chromophores in dichloromethane (Table 1). In comparison with the model compounds, no discernible broadening or shift of the UV–vis absorption bands was observed, indicating the absence