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Single-component films of different generations of dendrimers bearing a diphenylanthracene core

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Abstract

Different generations of carboxyl-terminated poly(aryl ether) dendrimers bearing a diphenylanthracene core were designed and synthesized. It is interesting to see that not only two-generation dendrimers but also one-generation dendrimers can be fabricated into thin films by self-deposition. Fluorescence spectra indicate that increasing the generation number of a dendrimer can effectively control the quenching of the fluorescence. Moreover, the fluorescence property of the diphenylanthracene core of the dendrimers in a solid film is quite similar to that of one in a solution, which is important for designing light-emitting materials.

Keywords: Dendrimer; Self-deposition; Fluorescence; Single-component film

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1. Introduction

In 1991, Decher and Hong first reported that a polyelectrolyte multilayer film was constructed by alternating deposition of a polycation and a polyanion on a charged surface [1]. This method has attracted much attention because it is a convenient and effective way to produce complex layered structures with precise control of the composition and thickness [2–5]. In addition, the driving force for multilayer assembly has been extended from electrostatic force [6] to other interactions such as charge-transfer interaction [7], hydrogen bonding [8,9] and stereocomplex formation [10]. Recently, we have reported that carboxyl-terminated poly(aryl ether) dendrimers can form a single-component film by self-deposition, since it is a hydrogen-bonding acceptor as well as a hydrogen-bonding donor [11]. This research is significant because we can apply it to construct a *single-component* thin film with controllable thickness, which is different from conventional layer-by-layer assembly. Dendrimers have a number of advantages over linear polymers: controllable exterior groups, identical size, perfectly branched three-dimensional structure, etc. As a result, dendrimer films may significantly enrich the application of thin solid films [12,13].

Herein, we designed and synthesized two generations of carboxyl-terminated dendrimers with a diphenylanthracene core. On the one hand, we would like to know

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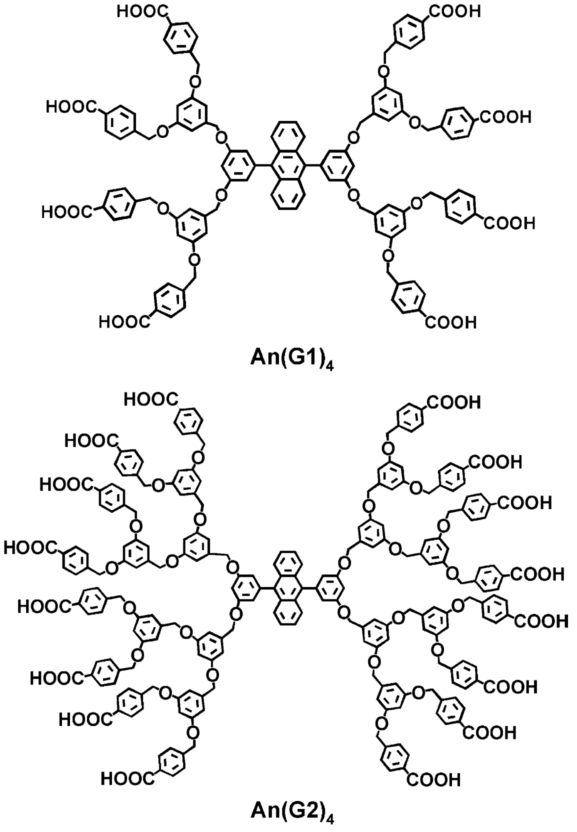
if low-generation dendrimers could also form a single-component film by self-deposition. On the other hand, a chromophore encapsulated by dendrons will allow us to fabricate a functional thin film, since the isolation effect of dendrimers can improve the fluorescence properties of dye molecules in the solid state.

2. Experimental

2.1. Synthesis and characterization of dendrimers

Two dendrimers were synthesized according to the literature [14], and named $An(G1)_4$ and $An(G2)_4$ (Scheme 1).

$An(G2)_4$: The brief route of synthesis is shown in Scheme 2. A mixture of $(MeO_2C)_4$-[**G2**]-Br(5.0 equiv), 9,10-Bis(3,5-Dihydroxyphenyl)anthracene (1.0 equiv), anhydrous K_2CO_3 (10.0 equiv), 18-crown-6 (0.1 equiv) and acetone was heated to reflux and stirred vigorously under nitrogen in darkness for 144 h. Then the acetone was evaporated, and the residue was put in a mixture of water and CH_2Cl_2 for partitioning. The organic layer was dried with anhydrous Na_2SO_4 and then evaporated. The crude product was purified by silica gel column chromatography with mixture of ether and CH_2Cl_2 as the eluent. Poly(aryl ether) dendrimers with a diphenylanthracene core and carboxyl methyl esters at the periphery were successfully synthesized (yield 75%).



An(G1)$_4$

An(G2)$_4$

Scheme 1. The molecular structures of dendrimers.

Hydrolysis of the methyl ester was performed in a solution of water (60 ml), ethanol (120 ml), and potassium hydroxide (0.6 g). It was then heated at reflux and vigorously stirred under nitrogen in darkness for 8 h. Next, the ethanol was evaporated and the residue was acidified with dilute hydrochloric acid to form a precipitate. The precipitate was filtered and washed with water to remove all potassium salts. The carboxyl methyl esters were successfully changed to carboxyl groups, i.e. $An(G2)_4$ was synthesized.

$An(G1)_4$ was synthesized with the same route.

$An(G1)_4$: ^1H NMR (500 MHz, DMSO-d6): δ 7.93 (16H, d, ArH), δ 7.57 (4H, m, core ArH), δ 7.51(16H, d, ArH), δ 7.32 (4H, m, core ArH), δ 6.88(2H, s, ArH), δ 6.75 (8H, bs ArH), δ 6.68 (4H, bs, ArH), δ 6.66 (4H, s, ArH), δ 5.15 (16H, s, OCH_2), δ 5.10 (8H, s, OCH_2), MALDI-TOFMS: Calc. for $C_{118}H_{90}O_{28}$ $[M + H]^+$: m/z 1956.96 Found $[M + H]^+$: m/z 1956.4.

$An(G2)_4$: ^1H NMR (500 MHz, DMSO-d6): δ 7.90(32H, d, ArH), δ 7.58 (4H, m, core ArH), δ 7.47 (32H, d, ArH), δ 7.32 (4H, m, core ArH), δ 6.88 (2H, s, ArH), δ 6.68 (24H, bs, ArH), δ 6.66 (4H, s, ArH), δ 6.60 (8H, s, ArH), δ 6.58 (4H, s, ArH), δ 5.10(32H, s, OCH_2), δ 5.06 (8H, s, OCH_2), δ 4.96 (16H, s, OCH_2), MALDI-TOFMS: Calc. for $C_{238}H_{186}O_{60}$ $[M + Na]^+$: m/z 4028.99 Found $[M + Na]^+$: m/z 4028.7.

2.2. Instruments

^1H NMR spectra were recorded on a Bruker Avance-500 NMR Spectrometer (500 MHz) using tetramethylsilane as an internal standard. UV–Vis spectra were collected on a Perkin–Elmer Lambda 800 UV–Vis spectrometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC spectrometer. Atomic force microscopy (AFM) images were taken with an atomic force microscope (Dimension™ 3100, Digital Instrument).

2.3. Fabrication of self-deposition films

A self-deposition film of $An(G1)_4$ was fabricated as follows. A quartz substrate was modified with 4-aminobutyldimethylmethoxysilane in advance. The modified substrate was immersed into methanolic solution of $An(G1)_4$ (7.5×10^{-6} mol/l) for 2 min to adsorb the first layer. Then, it was rinsed in methanol and dried in the ambient atmosphere. Simply repeating the above process leads to the formation of a self-deposition film of $An(G1)_4$. We fabricated a self-deposition film of $An(G2)_4$ in the same way.