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Optical-gain enhancement of carbosilane dendrimer containing fluorescein groups in the periphery

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ABSTRACT

In this article, a carbosilane dendrimer functionalized in the periphery with fluorescein units was prepared, and the optical property of the fluorescent dendrimer as gain medium was investigated. It was found that the dendrimer consisted of a methylphenylsilane core with 16 fluorescein units in its periphery. The dendrimer exhibits high optical-gain enhancement in methanol solution and laser emission was observed, which is located at 527 nm above the lasing threshold of 0.9 mJ/pulse.

1. Introduction

Dendrimers are well-defined highly branched regular three-dimensional macromolecules, which are characterized by the presence of a large number of functional groups on the surface and the presence of internal cavities [1,2]. Recent investigations have shown that coupling luminescence with dendrimer chemistry can provide systems capable of exhibiting quite unusual and interesting properties [3–5]. In topological viewpoint, dendrimers contain three different regions: core, branches, and surface. Luminescent units can be covalently incorporated in each region of a dendritic structure. For the dendrimers functionalized in the periphery with fluorescent units, cooperation among the photo-active units can allow the dendrimer to perform specific functions such as sensory signal amplification, light harvesting, organic "nanodots", etc. [6–9].

In the previous research, we reported the optical-gain enhancement of silicon-based dendrimer-hosted laser dye in dilute solution and polymer system due to the change of microenvironment around the laser dyes by the site-isolation effect of the dendrimers [10,11]. Continuing our investigations in the field of photoactive dendrimers, a carbosilane dendrimer functionalized in the periphery with fluorescein units was prepared, and its optical-gain enhancement in methanol solution was also studied. The formula of the dendrimer (D) is shown in Fig. 1. The dendrimer consists of a methylphenylsilane core with 16 fluorescein units in its periphery. In order to compare, the behavior of a monofluorescein model compound (M in Fig. 1) was also investigated. The fluorescein group, which shows intense absorption bands and a strong fluorescence band in the visible region, is extensively used for sensing or labeling purposes. The obtained results showed that the dendrimer exhibits high optical-gain as gain medium as well as a laser spectrum was observed above the laser threshold.

2. Experimental

2.1. Synthesis of carbosilane dendrimer (G3)

The dendrimer of the third-generation carbosilane dendrimer (G3) was synthesized according to Refs. [12,13]. The reaction route was given in Scheme 1. The synthesis started from diallylmethylphenylsilane as the core molecule, which was prepared using allylation of dichloromethylphenylsilane with allylmagnesium bromide. The core molecule was hydrosilylated with dichloromethylsilane, and then it was allylated with allylmagnesium bromide to form a growth cycle. The final product with 16 allylic end groups was obtained by repetition of the hydrosilylation–allylation cycles.

^{1}H NMR—0.15–0.35 (m, 45H, CH_3), 0.40–0.70 (m, 28H, Si–CH_2), 0.70–1.00 (m, 28H, Si–CH_2), 1.20–1.40 (m, 28H,–$CH_2CH_2CH_2$), 1.45–1.65 (d, 32H, –CH_2CH=CH_2), 4.75–4.90 (m,

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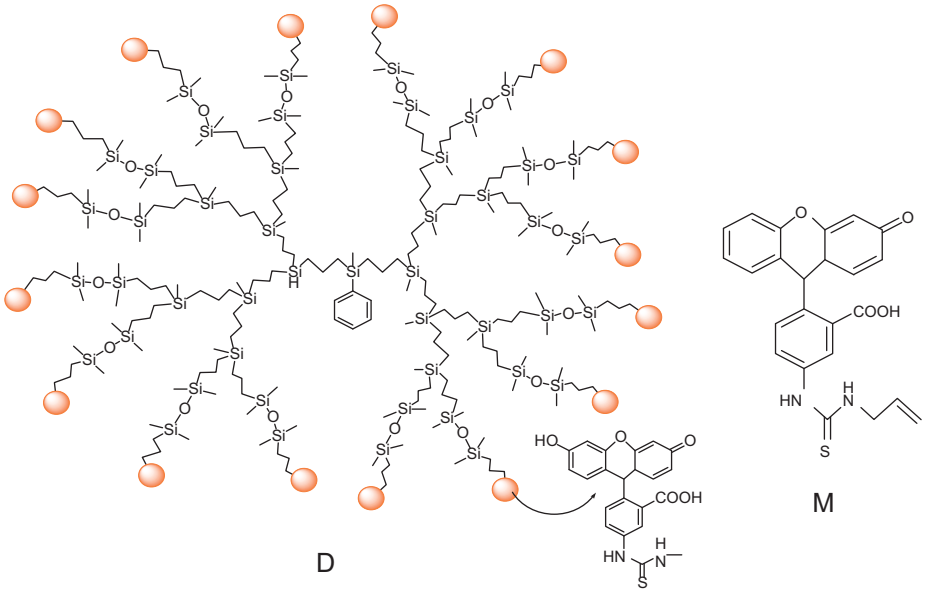
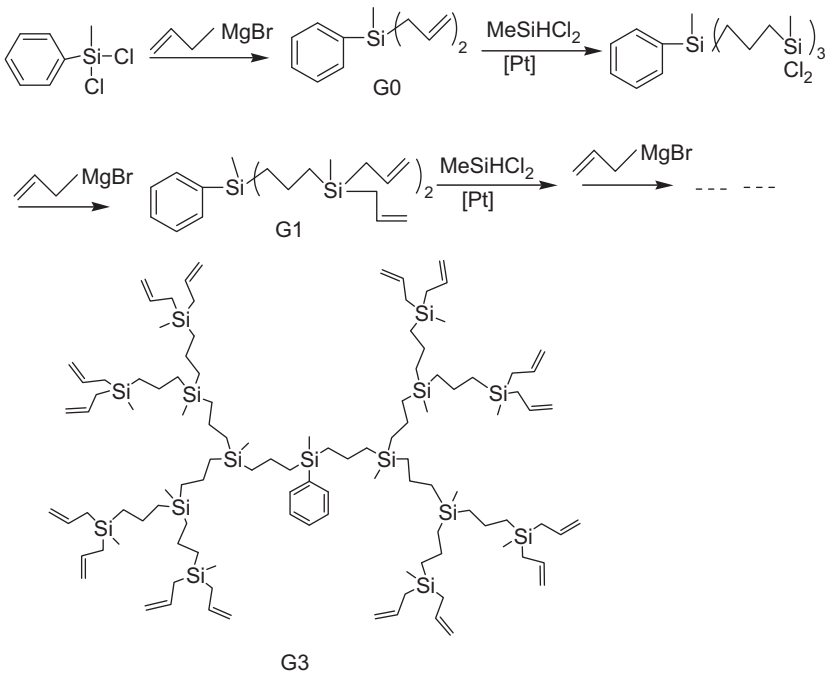


Fig. 1. Formulas of the dendrimer and of the reference monofluorescein compound.



Scheme 1. Synthesis of G3.

32H, CH_2=), 5.70–5.90 (m, 16H, CH_2=C*H*CH_2–), 7.30–7.35 (m, 3H, Ph(o,p)), 7.40–7.50 (m, 2H, Ph(m)).

2.2. Synthesis of peripherally aminated carbosilane dendrimer (G3-NH_2)

The synthesis of amino-terminated carbosilane dendrimer according to Ref. [13] is described in Scheme 2. The amino groups of the allylamine were protected by trimethylsilyl groups, and the hydrosilylation reaction was employed in order to link the aminopropyl groups to the parent dendrimer.

IR (cm^{-1}): 3292 (m, –CH_2NH_2), 3075 (s, C=C), 2913 (m), 2868 (m), 1629 (s, –CH_2NH_2), 1414 (m), 1252 (s, Si–$(CH_3)_3$), 1056 (m, Si–O–Si), 892 (s), 838 (m), 794 (m).

^{1}H NMR (ppm): −0.20–0.1 (m, 36H, Si*CH_3*), 0.40–0.70 (m, 24H, Si*CH_2*CH_2), 1.20–1.60 (m, 26H, SiCH_2*CH_2*CH_2Si, Si *CH_2*CH=CH_2, *NH_2*), 2.50–2.70 (m, 4H, NH_2*CH_2*–), 4.60–5.00 (m, 8H, *CH_2*=), 5.50–6.00 (m, 4H, CH_2=C*H*CH_2–).

2.3. Synthesis of carbosilane dendrimer with peripheral fluorescein units and the model solution

The reaction is described in Scheme 3. 0.008 g of G3-NH_2 and 0.01 g fluorescein isothiocyanate (FITC) were added into methanol, and the total volume was 50 ml. The solution was stirred 24 h at room temperature. Then the solution was diluted to 100 ml to keep the concentration of the fluorescein being 2.57×10^{-4} M. At the same time, the model solution was