

Synthesis of Novel Pseudo-Fréchet-Type Dendrons and Their Fluorescent Enhancement to Eu^{3+} Ion

Dongmei Xu, Xiaohong Liu, Haijie Chen, Lili Qian, Keda Zhang

Key Laboratory of Organic Synthesis of Jiangsu Province, Chemical Engineering and Materials Science, College of Chemistry, Soochow University, Suzhou 215123, People's Republic of China

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ABSTRACT: Novel pseudo-Fréchet-type dendrons with 1,3,5-triazine structure G1.0(NOT) and G2.0(NOT) were synthesized under mild conditions by cyanuric chloride, β -naphthol, and 3,5-dihydroxybenzyl alcohol with the yields of 96.3 and 85.6%. The structure of the dendrons was characterized by elementary analysis, IR spectrum, $^1\text{H-NMR}$, and FAB-MS. The dendrons had good thermo stability and solubility. They could partially transfer their absorbed energy to Eu^{3+} ion in tetrahydrofuran/acetone solutions. When the

concentration of G1.0(NOT), G2.0(NOT), and Eu^{3+} ion was 5×10^{-4} mol/L, G1.0(NOT) could enhance the fluorescent intensity of Eu^{3+} ion at 613 nm by 4.2-fold, whereas G2.0(NOT) could enhance the fluorescent intensity of Eu^{3+} ion at 465 and 613 nm by 18.6- and 11.7-fold, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3184–3189, 2009

Key words: cyanuric chloride; pseudo-Fréchet-type dendrons; Eu^{3+} ion; fluorescence; energy-transfer

INTRODUCTION

A dendrimer molecule is uniquely suited to arrange multiple peripheral chromophores around a single core unit. An array of terminal donor chromophores can absorb the incident light and transfer their energy by through-space Förster energy transfer to an acceptor unit located at the core or focal point of the dendrimer, which can be luminescent organic molecules, metal ions, and quantum dots.^{1,2} This kind of energy-transfer system has potential applications in photovoltaic systems, light amplification, light emitting diodes, and fluorescent probes.^{3,4} Fréchet-type polyether is one of the most famous dendrimers, which has been used in versatile application studies.⁵ In particular, it was applied to the design of a varied array of energy-harvesting and light emitting.⁶ Hahn et al.⁷ attached eight dansyl- and eight 2nd Fréchet dendrons with naphthalene-

terminated groups to the second generation poly(propylene amine) dendrimer and hosted eosin. They found that in such a host-guest system the encapsulated dye molecule collected electronic energy from all of the 64 chromophoric units of the dendrimer with high efficiency. Kawa and Fréchet^{8,9} assembled Fréchet-type dendrons around a single lanthanide ion (Er^{3+} , Eu^{3+} , Tb^{3+}) serving as a core to improve the luminescence properties of the lanthanide metals and reduced the normally troublesome high rate of self-quenching of the emission from lanthanide ions, which are extremely attractive for use in fiber-optic amplifiers and other optoelectronic devices. Vicinelli et al.¹⁰ reported the luminescent properties of the systems of poly(amido-amine), poly(propylene imine), Fréchet-type polyether terminated with different functional groups combined with lanthanide ions like Er^{3+} ion.

Benefiting from its excellent luminescent properties in aqueous and organic solutions and the high sensitivity of its fluorescence to environment such as ligand and solvent, Eu^{3+} ions is a typical kind of metal ions used as fluorescent probes. Energy transfer between dendrimers and Eu^{3+} ions will enhance the fluorescent intensity of Eu^{3+} ions and sensitize the Eu^{3+} ions fluorescent probe.^{11,12}

Dendrimers are usually prepared step by step, commonly, with protection-deprotection or deactivation-reactivation steps. In the synthesis of Fréchet dendrons, the growth steps, and the functional group-reactivation steps must be carried out alternately.¹³ The reactivation steps not only complicated the synthetic procedures but also increased the

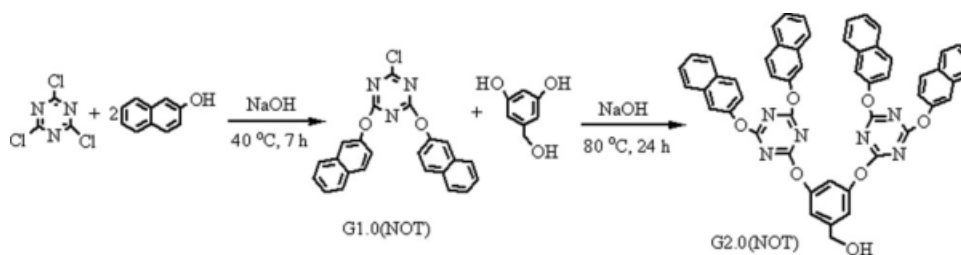
Correspondence to: D. Xu (xdm.sd@163.com).

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Scheme 1 Synthesis of G1.0(NOT) and G2.0(NOT)

synthetic cost and produced pollution. Preparation dendrimers without protection–deprotection or deactivation–reactivation steps is greatly desirable.

The reactivity of the cyanuric chloride nucleus offers interesting possibilities for derivatization in successive nucleophilic substitution steps. The groups of Chouai and Simanek¹⁴ and Kaifer and coworkers¹⁵ have reported nice examples of this stepwise chemistry and prepared novel dendrimers, respectively.

In this article, novel pseudo-Fréchet-type dendrons were synthesized by directly reaction of cyanuric chloride, β -naphthol, and 3,5-dihydroxybenzyl alcohol (DHA) without functional group-reactivation steps, and the dendrons were used as donors in the energy-transfer systems.

EXPERIMENTAL

Materials

3,5-dihydroxybenzyl alcohol (DHA) was the product of Fluka, cyanuric chloride, β -naphthol, tetrahydro-

furan (THF), acetone, dehydrated alcohol (EtOH), ethyl acetate, 1,4-dioxane, dichloromethane, petroleum ether, *N,N*-dimethylformamide, NaOH, Eu_2O_3 were purchased from the Third Reagent Company of Shanghai (China). The solvents were used after distillation; the others were used without purification.

Measurements

Infrared (IR) spectra were carried out with a Magna-550 Fourier-transform infrared spectrometer (Nicolet Co.). Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on an INOVA 400 MHz using CDCl_3 as a solvent (Varian Co.). Elemental analysis was carried out with a Shimadzu EA-1110 CHNSO (Carlo-Erba Co., Italia). FAB-MS were recorded on an VG Masslab Trio-2000 (VG MasslabInc., UK), TGA analysis was done on a SDT 2960 simultaneous DSC–TGA instrument (TA Company) using nitrogen as the purge gas.

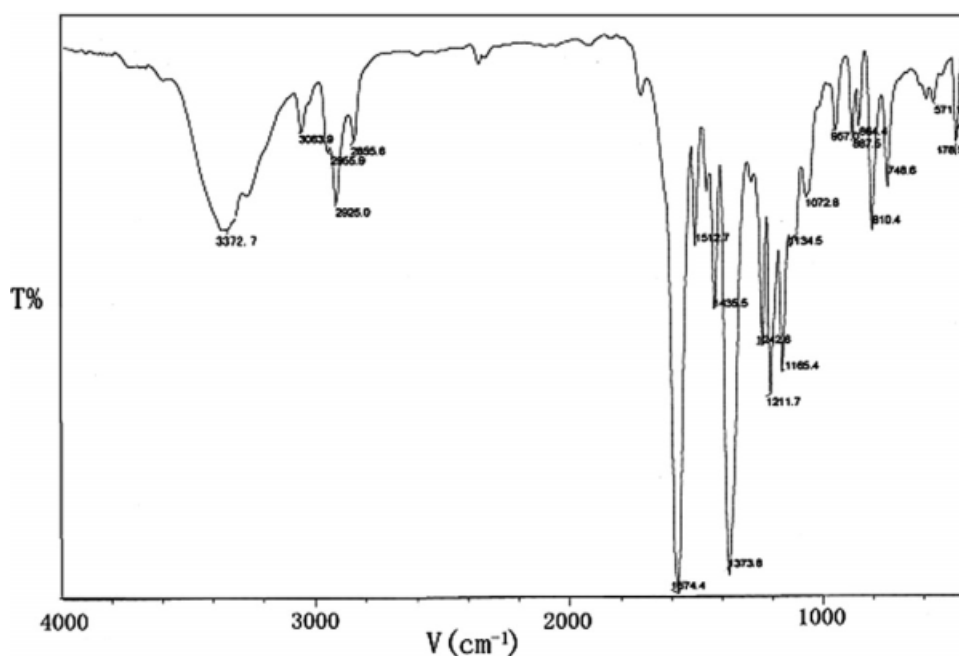


Figure 1 The FTIR spectrum of G2.0(NOT).

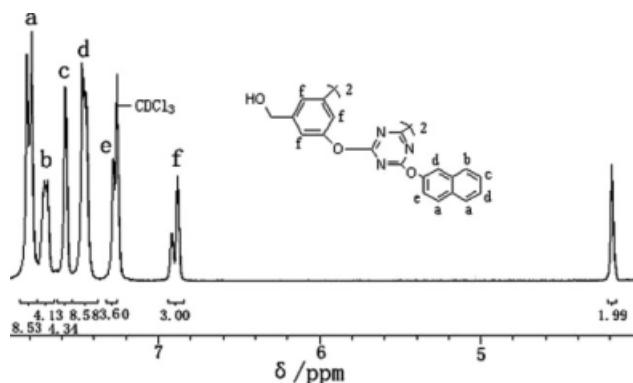


Figure 2 $^1\text{H-NMR}$ spectra of G2.0(NOT).

Synthesis of G1.0(NOT) and G2.0(NOT)

G1.0(NOT): Cyanuric chloride and β -naphthol were mixed at the stoichiometric ratio (1 : 2) in acetone/water (the volume ratio was 1 : 1) in an 100 mL three-necked flask equipped with a magnetic stirrer, sodium hydroxide was used as base (its molar ratio to cyanuric chloride was 2.1 : 1), the reaction was carried out in ice-water bath for 2 h, then at 40°C for 7 h. The mixture was filtered, and the filter cake was washed with water, dried in vacuum at room temperature to give a white solid product G1.0(NOT) (yield: 96.3%, m.p. 180–181°C).

G2.0(NOT) : G1.0(NOT), DHA, and NaOH (the molar ratio was 2.2 : 1 : 2.2) were dissolved in the mixed solvent of 1,4-dioxane and water (the volume ratio was 5 : 1) in an 100 mL three-necked

flask equipped with a magnetic stirrer. The reaction was carried out at 80°C for 24 h in a nitrogen atmosphere, then cooled down to RT. The solvent was removed under reduced pressure, and the residue was subjected to a column (silica gel), eluted with 1 : 1 (volume ratio) ethyl acetate to petroleum ether afford the target product G2.0(NOT) as a dark white solid (yield: 85.6%, m.p. 116–118°C).

The route for synthesizing G1.0(NOT) and G2.0(NOT) was shown in Scheme 1.

RESULTS AND DISCUSSION

Synthesis and characterization of G1.0(NOT) and G2.0(NOT)

Beech¹⁶ synthesized 2-chloro-4,6-di- β -naphthyloxy-1,3,5-triazine G1.0(NOT) by nucleophilic substitution reaction between cyanuric chloride and β -naphthol in water with 27% yield after recrystallization from benzene. We¹⁷ adopted acetone/water (the volume ratio was 1 : 1) mixture instead of water to raise the yield of the target product through improving the solubility of cyanuric chloride in the reaction system and reduce hydrolysis in water of the first chlorine atom in cyanuric chloride. By optimizing reaction conditions, G1.0(NOT) was obtained with 96.3%. m.p. 180–181°C. Elementary analysis: Calcd: C, 69.09%; H, 3.50%; N, 10.51%. Found: C, 69.25%; H, 3.54%; N, 10.52%. The melting point and elementary analysis data were well corresponding to that

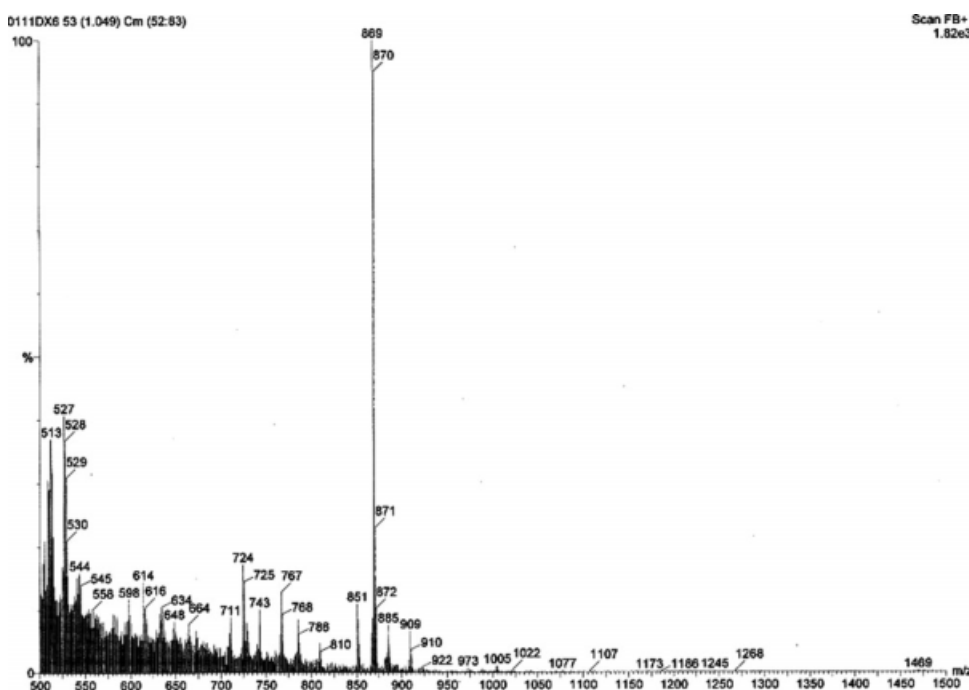


Figure 3 MS spectrum of G2.0(NOT).

TABLE I
The Solubility of G1.0(NOT) and G2.0(NOT) (20°C)

Solvents	G1.0(NOT)		G2.0(NOT)	
	Dosage of solvents (mL)	State of dissolve	Dosage of solvents (mL)	State of dissolve
Petroleum ether	101.7	–	102.1	–
Dichloromethane	3.6	+	4.1	+
THF	3.4	+	3.2	+
1,4-Dioxane	6.9	+	6.3	+
Acetone	35.7	+	31.6	+
Ethyl acetate	58.2	+	46.7	+
Dehydrated alcohol	87.7	–	84.3	+
Water	150	–	86.4	±

+: Dissolve; –: undissolve; ±: partially dissolve; G1.0(NOT), G2.0(NOT): 0.10 g.

reported by Beech, so further purification steps could be omitted. G2.0(NOT) was synthesized by nucleophilic substitution reaction between G1.0(NOT) and DHA under mild conditions. Pure product could be obtained with 85.6% yield by removal of solvents and a column separation. In the synthesis, two monomers reacted directly without protection–deprotection or deactivation–reactivation steps. The overall yield of G2.0(NOT) reached 82.4%.

The structure of G2.0(NOT) was characterized by elementary analysis, IR spectrum, ¹H-NMR and FAB-MS. Elementary analysis: Calcd: C, 73.48%; H, 3.69%; N, 9.92%. Found: C, 73.44%; H, 3.93%; N, 9.70%. It was seen that the experimental elementary analysis data was basically consistent with the theoretical ones of the target product G2.0(NOT) (C₅₃H₃₄O₇N₆).

IR spectrum of G2.0(NOT), as shown in Figure 1, could be analyzed as follows: 957–740 cm⁻¹ were peaks of CH bending vibration in aromatic rings, among which 810 cm⁻¹ belonged to triazine ring. The stretching vibration peak of ether bonds was 1165 cm⁻¹, and 1512–1211cm⁻¹ was the combination bands of the vibration of the naphthol and triazine backbone. The peaks of CH₂ stretching vibration were 2855 and 2925 cm⁻¹, 3056 cm⁻¹ was the stretching vibration peak of CH in phenyl ring, 3373 cm⁻¹ was the stretching vibration peak of OH in CH₂OH.

The chemical shifts (δ/ppm, CDCl₃) corresponding to protons in G2.0(NOT) could be found in Figure 2, which were 4.19 (2H, CH₂ in CH₂OH), 6.88–6.92 (f, 3H), 7.27–7.29 (e, 4H), 7.45–7.47 (d, 8H), 7.56–7.58 (c, 4H), 7.68–7.72 (b, 4H), 7.78–7.82 (a, 8H).

The FAB-MS spectrum of G2.0(NOT) (Fig. 3) showed the [M+1]⁺ peak of G2.0(NOT) (m/z = 869). Elementary analysis, IR, ¹H-NMR, and MS spectra indicated that the objective product G2.0(NOT) was successfully achieved.

The solubility of G1.0(NOT) and G2.0(NOT)

G1.0(NOT) or G2.0(NOT) (0.10 g) was added to some solvents to study their solubility. The results were listed in Table I. It was showed that G1.0(NOT) and G2.0(NOT) could be dissolved in dichloromethane, tetrahydrofuran, 1,4-dioxane, acetone, and ethyl acetate. G1.0(NOT) was not soluble in petroleum ether, absolute alcohol, and water. G2.0(NOT) was not soluble in petroleum ether, it had better solubility than G1.0(NOT).

The thermo stability of G1.0(NOT) and G2.0(NOT)

The TGA curve (Fig. 4) was recorded from 20 to 600°C at the rate of 20 K/min. It was shown that G1.0(NOT) and G2.0(NOT) possessed fairly thermo stability, since they started to decompose at 260 and 290°C, respectively. G2.0(NOT) slightly lost its weight from 25 to 290°C might be caused by a small amount of absorbed water.

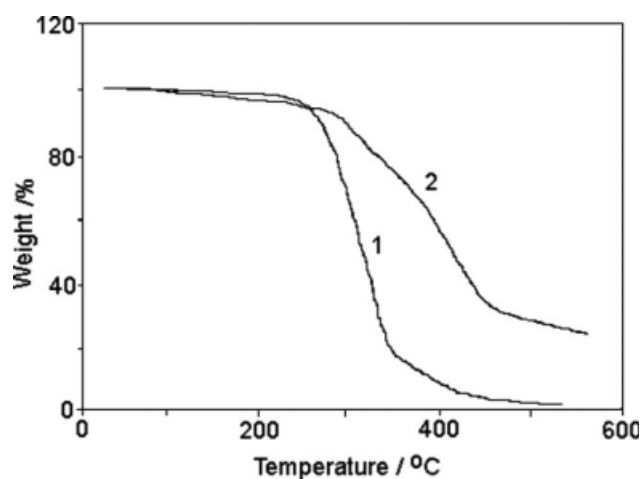


Figure 4 The TGA curves of G1.0(NOT) and G2.0(NOT) 1 : G1.0(NOT), 2: G2.0(NOT).

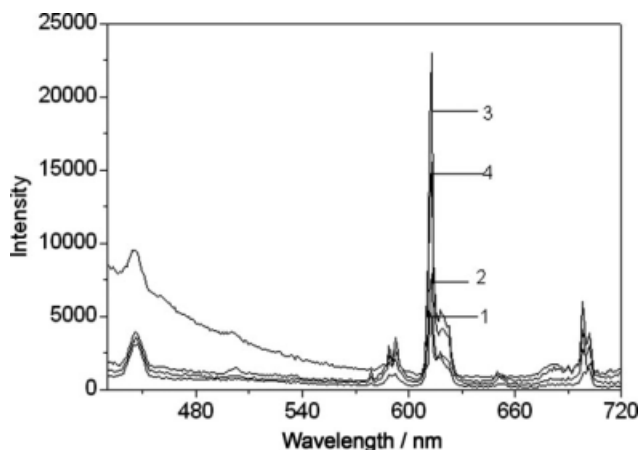


Figure 5 Fluorescent spectra of the mixture of G1.0(NOT) and Eu^{3+} : Solvent: THF/acetone (Volume 1 : 1), $\lambda_{\text{ex}} = 245$ nm. Concentration: Eu^{3+} : 5.0×10^{-4} mol/L, G1.0(NOT) = 0, 2.5, 5.0, 10.0×10^{-4} mol/L (from 1 to 4).

Energy transfer between G1.0(NOT), G2.0(NOT), and Eu^{3+} ions

Excited by the maximum absorbed wavelength of G1.0(NOT) (245 nm), the fluorescent spectra of the mixtures of G1.0(NOT) and Eu^{3+} ion in several concentrations were recorded in Figure 5. It could be seen that G1.0(NOT) could enhance the fluorescent strength of Eu^{3+} ion at 613 nm ($^5\text{D}_0$ - $^7\text{F}_2$) within the G1.0(NOT) concentration $(0.2\text{--}1.0) \times 10^{-3}$ mol/L, although the fluorescence of itself could not be observed. When the concentration of G1.0(NOT) and Eu^{3+} ion was 5×10^{-4} mol/L, G1.0(NOT) could enhance the fluorescent strength of Eu^{3+} ion at 613 nm by 4.2-fold.

Excited by the maximum absorbed wavelength of G2.0(NOT) (337 nm), the fluorescent spectra of the

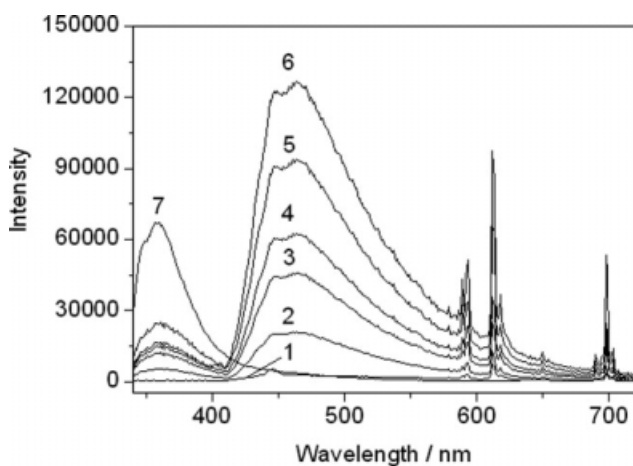


Figure 6 Fluorescent spectra of Eu^{3+} , G2.0(NOT), and G2.0(NOT)/ Eu^{3+} . Solvent: THF/acetone (Volume 1 : 1), $\lambda_{\text{ex}} = 337$ nm. (1) Eu^{3+} , (7) G2.0(NOT), concentration: 5.0×10^{-4} mol/L, from (2) to (6) Eu^{3+} : 5.0×10^{-4} mol/L, G2.0(NOT): 0.1, 0.25, 1.0, 2.5, 5.0×10^{-4} mol/L.

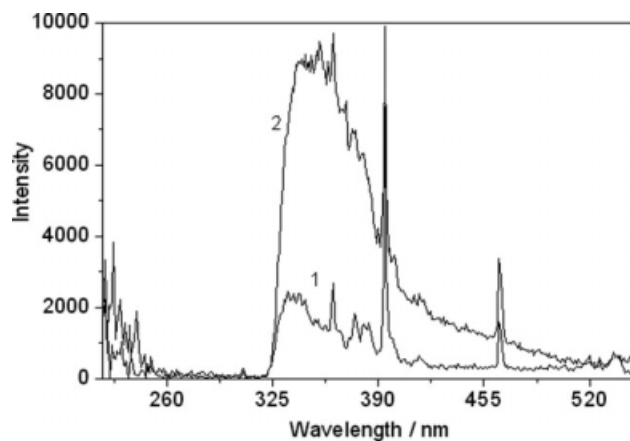


Figure 7 Excitation spectra of Eu^{3+} and Eu^{3+} /G2.0(NOT). Solvent: THF/acetone (Volume 1 : 1). (1) Eu^{3+} , concentration: 1.0×10^{-3} mol/L, (2) Eu^{3+} /G2.0(NOT), concentration: 5.0×10^{-4} mol/L.

mixtures of G2.0(NOT) and Eu^{3+} in some concentrations were recorded in Figure 6. It was showed that the fluorescence of G2.0(NOT) itself was greatly quenched, whereas the fluorescent intensity of Eu^{3+} ion at 465 nm ($^7\text{F}_0$ - $^5\text{D}_2$) and 613 nm ($^5\text{D}_0$ - $^7\text{F}_2$) was largely enhanced within the G2.0(NOT)

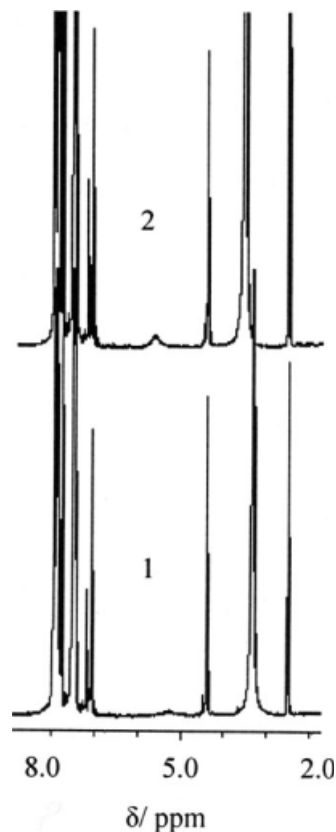


Figure 8 ^1H -NMR spectra of G2.0(NOT) and Eu^{3+} /G2.0(NOT). (1) G2.0(NOT), (2) Eu^{3+} /G2.0(NOT). Concentration: Eu^{3+} , G2.0(NOT): 10×10^{-3} mol/L.

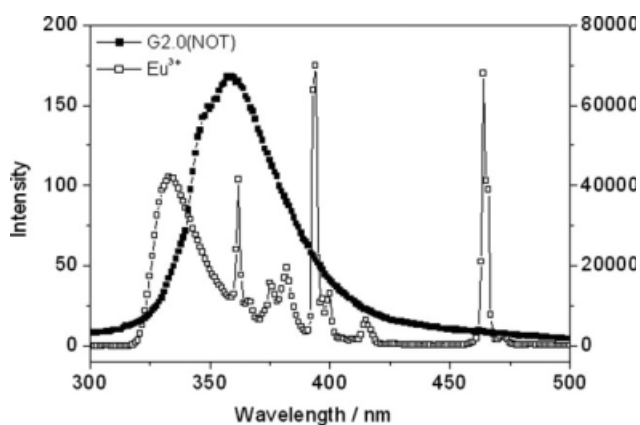


Figure 9 Excitation spectrum of Eu^{3+} and fluorescent emission spectrum of G2.0(NOT). Solvent: THF/acetone (Volume 1 : 1). Concentration: Eu^{3+} , G2.0(NOT): 1.0×10^{-3} mol/L.

concentration $(0.1\text{--}5.0) \times 10^{-4}$ mol/L. When the concentration of G2.0(NOT) and Eu^{3+} ion was 5×10^{-4} mol/L, G2.0(NOT) could enhance the fluorescent strength of Eu^{3+} ion at 465 and 613 nm by 18.6- and 11.7-fold, respectively.

It was indicated that G1.0(NOT) and G2.0(NOT) transfer the energy collected by peripheral naphthol chromophores to Eu^{3+} ion through Förster energy-transfer. The interaction between G1.0(NOT) and Eu^{3+} ion was not very clear, whereas the interaction between the hydroxyl group located at the core of G2.0(NOT) and Eu^{3+} ion could be suggested, which was indicated by the stronger excitation spectrum of Eu^{3+} /G2.0(NOT), compared with that of Eu^{3+} ions (Fig. 7),¹⁸ and the $^1\text{H-NMR}$ spectra (Fig. 8).

From Figure 8, it can be seen that the OH proton in G2.0(NOT) resonates at $\delta = 5.31$ ppm (DMSO- d_6). After added Eu^{3+} , the OH proton in G2.0(NOT) shifts downfield to 5.60 ppm, which may be caused by the interaction between dendron G2.0(NOT) and Eu^{3+} ions. At the same time, affected by Eu^{3+} , the H_2O protons from DMSO- d_6 shift from 3.34 ppm to 3.51 ppm.

The basis of Förster energy-transfer is the overlap of the emission spectrum of the donor and the excitation spectrum (or absorption spectrum) of the acceptor.¹⁹ In fact, From Figure 9, the large spectral overlap between the fluorescent emission spectrum

of G2.0(NOT) and the excitation spectrum of Eu^{3+} ion could be seen.

CONCLUSIONS

In this work, Novel pseudo-Fréchet-type dendrons G1.0(NOT) and G2.0(NOT) were synthesized under mild conditions by cyanuric chloride, β -naphthol, and DHA with 96.3 and 85.6% yields, respectively. The dendrons had good thermo stability and solubility. They could partially transfer their absorbed energy to Eu^{3+} ion in tetrahydrofuran/acetone solutions through Förster energy-transfer, and resulting in enhancement of the fluorescent intensity of Eu^{3+} ion at 613 nm by 4.2-fold [G1.0(NOT)], at 465 nm and 613 nm by 18.6-fold and 11.7-fold [G2.0(NOT)] respectively.

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