DOI: 10.1002/ejoc.200600583

# The Synthesis of Dendritic β-Diketonato Ligands and Their Europium Complexes

Bao-Lin Li,[a,b] Zi-Tong Liu,[a,b] Guo-Jun Deng,[a] and Qing-Hua Fan*[a]

**Keywords:** β-Diketonato ligands / Dendrimers / Europium / Luminescence

Two kinds of dendritic β-diketonato ligands (**1a**,**1b** and **2a**–**2c**) which contain a dibenzoylmethane (dbm) core and poly(aryl ether) dendron, have been synthesized by a convergent strategy. The attachment point of the dendron to dbm is found to play an important role in the preparation of europium(III) complexes. Reaction of the β-diketonato ligands **2a**–**2c**, which bear a dendron substituted on the phenyl group of dbm, with $EuCl_3 \cdot 6H_2O$ gives the first- to third-generation dendritic europium(III) complexes in good yields, while europium(III) complexes could not be formed with β-diketonato ligands **1a** and **1b**, which have dendrons attached to the 2-position of dbm. The resulting dendritic europium(III) complexes were characterized by elemental analysis and MALDI-TOF mass spectrometry, and further confirmed by luminescence measurements. Incorporation of 1,10-phenanthroline as the second ligand in these dendritic (β-diketonato)europium(III) complexes gives new dendritic europium(III) complexes with enhanced luminescence intensity.

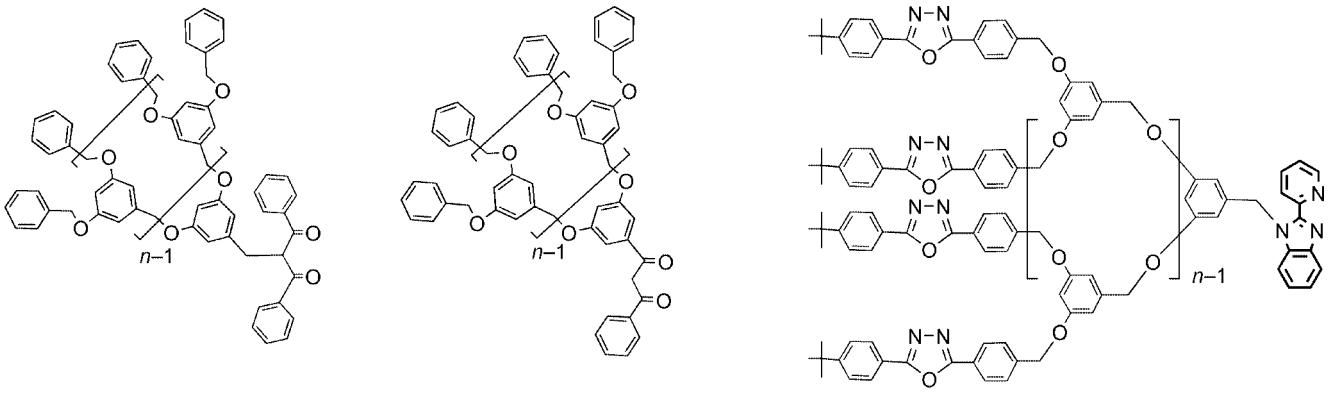

## Introduction

Trivalent lanthanide ions are known for their unique luminescence properties, such as their 100% theoretical quantum efficiency and narrow-width emission bands.[1] However, lanthanide ions often suffer from quite low luminescence intensity owing to their low extinction coefficients and the easy formation of lanthanide clusters, which cause the self-quenching of lanthanide ions. Although the formation of lanthanide complexes through rational design of the ligands could increase the luminescence intensity significantly,[1,2] in most cases their electroluminescence (EL) performance is not satisfactory. Dendrimers are highly branched molecules that are composed of a core, dendrons, and surface groups and have well-defined structures and a three-dimensional geometry.[3] Dendritic structures have been incorporated into different molecular materials to increase their luminescence efficiency.[4,5] Recently, Kawa and co-workers reported the first lanthanide-cored dendrimers obtained by self-assembly between lanthanide ions and a polyether dendron with a carboxy group at the focal point.[6] They found that the luminescence intensity of the lanthanide ions was enhanced due to the site isolation imparted by the dendrons, which decreases their rate of self-quenching. Inspired by this work, and as part of our continuing efforts on the synthesis of organometallic dendrimers,[7] we report here the synthesis of a new kind of europium complexes employing dendritic β-diketonato ligands.

(β-Diketonato)lanthanide complexes are well-known molecular luminescent materials.[1,8,9] Over the past several years, considerable efforts have been devoted to the modification of β-diketonato ligands[9a–9e] and the pursuit of novel second ligands.[9f–9h] Most recently, a remarkable EL breakthrough obtained from the terbium complex [Tb(eb-pmp)$_3$-tppo] [eb-pmp = 4-(2-ethylbutanoyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one; tppo = triphenylphosphane oxide] was reported.[9h] However, there has been little work on the design and synthesis of well-defined polymeric[10,11] or dendritic (β-diketonato)lanthanide complexes.[6,12,13] During our study on the synthesis of dendritic (β-diketonato)-lanthanide complexes, Tian and co-workers reported the synthesis of a first-generation poly(aryl ether) dendritic β-diketonate and antenna-functionalized dendritic β-diketonates, and their europium complexes.[13] These reports caused us to present our own results in this area. Thus, we describe herein the synthesis of two new kinds of dendritic β-diketonato ligands (**1a**,**1b** and **2b**,**2c**) and a new series of dendritic 2-(2-pyridyl)benzimidazoles (**3a**–**3c**) by a convergent strategy and their applications in the preparation of europium(III) complexes (Scheme 1).

[a] Beijing National Laboratory for Molecular Sciences, Center for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080, P. R. China
E-mail: fanqh@iccas.ac.cn
[b] Graduate School of the Chinese Academy of Sciences,
Beijing 100080, P. R. China.
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.




2-G$_n$dbm **1a**: $n$ = 1, **1b**: $n$ = 2 1-G$_n$dbm **2a**: $n$ = 1, **2b**: $n$ = 2, **2c**: $n$ = 3 oxdG$_n$pbm **3b**: $n$ = 2, **3c**: $n$ = 3

Scheme 1. Chemical structures of the three kinds of dendritic ligands.

## Results and Discussion

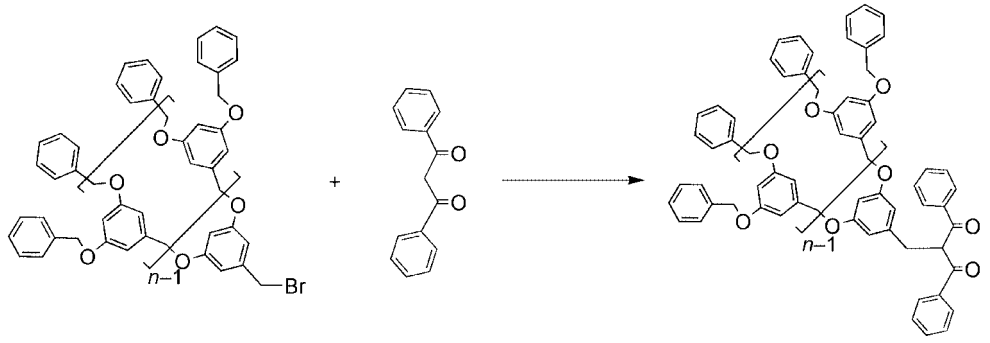
For the synthesis of dendritic β-diketonato-containing europium(III) complexes, dendritic wedges can be attached onto either the β-diketonato ligand or the second ligand. In our study, dibenzoylmethane (dbm) and 2-(2-pyridyl)benzimidazole (pbm) were chosen as the first and the second ligand, respectively, due to the following factors: (1) dbm and its derivatives exhibit relatively high PL and EL efficiencies in europium complexes; (2) dbm is easily synthesized or modified according to well-established methodologies; and (3) pbm is one of the most commonly used second ligands and can be easily modified by an *N*-alkylation reaction.

### Synthesis and Characterization of the Dendritic Ligands

#### *Dendritic Dibenzoylmethane Ligands*

Firstly, attachment of the dendron to the 2-position of dbm was proposed according to the synthetic route outlined in Scheme 2. Fréchet's polyether dendritic bromides were readily prepared according to published procedures.[14] Alkylation of dbm with the corresponding dendritic bromides was carried out in the presence of NaH as a base to give the dendritic ligands **1a** and **1b** in moderate yields. Both ligands were characterized by $^1$H and $^{13}$C NMR spectroscopy, high-resolution FT-ICR mass spectrometry, and elemental analysis. All results were consistent with the structures proposed.

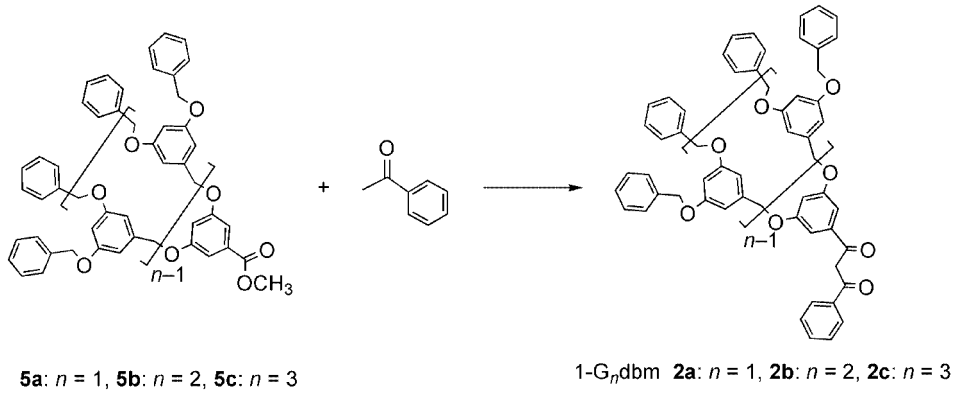
We also synthesized a series of dendritic dbm derivatives by attaching the polyether dendrons to the phenyl group of dbm. The synthetic route is shown in Scheme 3. Fréchet's dendrons with a carboxyl ester at the focal point were first synthesized according to the same procedures described above. Claisen condensation of the resulting dendritic ester with acetophenone in the presence of NaH successfully provided the desired dendritic ligands **2a**–**2c**. We found that the yield decreased slightly with increasing generation of the dendrons. The characterization of the dendrimers prepared was successfully carried out by $^1$H and $^{13}$C NMR spectroscopy, mass spectrometry, and elemental analysis. All these dendrimers show well-resolved $^1$H NMR spectra consistent with their structures.




**4a**: $n$ = 1, **4b**: $n$ = 2 2-G$_n$dbm **1a**: $n$ = 1, **1b**: $n$ = 2

Scheme 2. Reagents and conditions: NaH, thf, reflux 24 h.




**5a**: $n$ = 1, **5b**: $n$ = 2, **5c**: $n$ = 3

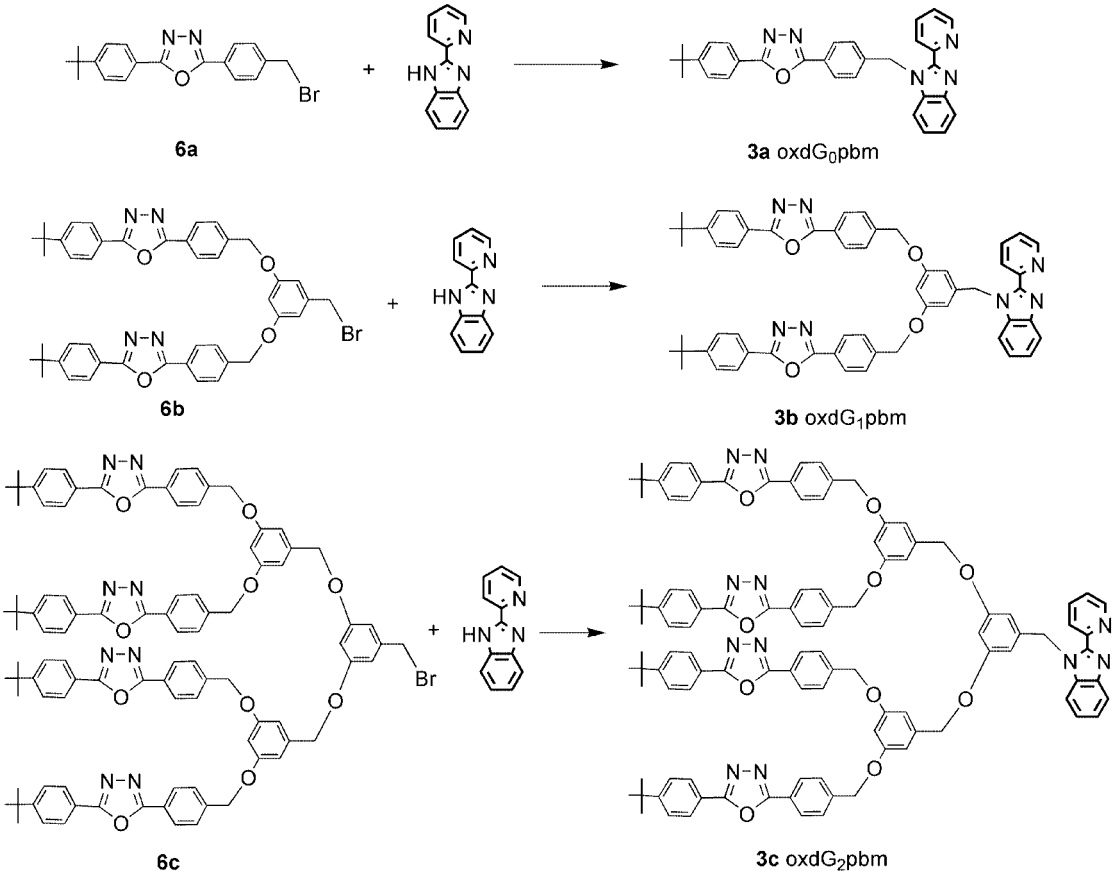
1-G$_n$dbm **2a**: $n$ = 1, **2b**: $n$ = 2, **2c**: $n$ = 3

Scheme 3. Reagents and conditions: NaH, thf, reflux 24 h.

### *Dendritic 2-(2-Pyridyl)benzimidazole Ligands*

An alternative way to improve the luminescence efficiency of the lanthanide complexes is to introduce a second ligand because it can not only saturate the coordination number of the lanthanide cation but also improve the volatility, stability, and electron-transport properties of the complexes.[1] In addition, the low electroluminescence efficiency of lanthanide complexes is due to their poor ability to transport charge carriers, especially electrons. In order to resolve this problem, modifications of 2-(2-pyridyl)benzimidazole as the second ligand with oxadiazole-functionalized groups have been reported.[9g] However, lanthanide complexes with a dendritic second ligand have not been reported to date. Therefore, with the aim of combining the advantages of both the dendrimer and functionalized oxadiazole groups, we designed and synthesized a series of dendritic 2-(2-pyridyl)benzimidazole ligands peripherally functionalized with these groups.

The synthetic route is outlined in Scheme 4. We first prepared 5-[4-(bromomethyl)phenyl]-2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (**6a**) and the oxadiazole-functionalized first- and second-generation dendritic benzylic bromides **6b**




Scheme 4. Reagents and conditions: NaH, thf, reflux 24 h.

and **6c** by a convergent method according to literature procedures.[15] Coupling of 2-(2-pyridyl)benzimidazole with the corresponding dendritic benzylic bromides in the presence of NaH afforded the zeroth- to second-generation dendritic ligands **3a**–**3c**. All these dendritic ligands were fully characterized by $^1$H and $^{13}$C NMR spectroscopy, mass spectrometry, and elemental analysis.

### Synthesis and Characterization of the Europium(III) Complexes

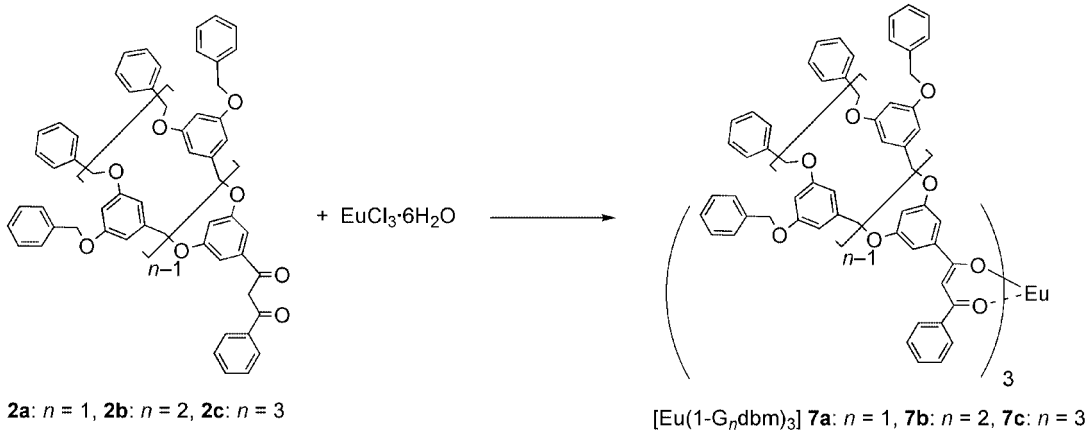
With these dendritic ligands in hand, we studied the synthesis of the dendritic europium(III) complexes with both dendritic β-diketonato ligands (**1a**,**1b** and **2a**–**2c**) according to conventional literature methods (Scheme 5).[8,9d] We found that the attachment point of the dendron plays an important role in the formation of europium(III) complexes. Thus, reaction of **2a**–**2c** with $EuCl_3{\cdot}6H_2O$ in a mixture of thf and $H_2O$ proceeded smoothly to give the first- to third-generation dendritic (β-diketonato)europium(III) complexes **7a**–**7c** in high yields. However, we failed to prepare the corresponding europium(III) complexes when using β-diketonato ligands **1a** and **1b** bearing a dendron attached to the 2-position of dbm. The sterically demanding dendritic structure substituted in the 2-position might influence the formation of europium(III) complexes. Similarly, although a dbm derivative bearing an oxadiazole group in the 2-position was synthesized recently, its lanthanide complex was not reported.[9b]

Purification of the dendritic complexes **7a**–**7c** by silica gel column chromatography failed as they were found to decompose on the column, possibly due to interaction with the surface silanol groups of the silica gel. Fortunately, the dendrimer structure facilitated the purification of these complexes by a solvent precipitation method.

Because of the paramagnetism of europium(III), the dendritic complexes could not be characterized by conventional spectroscopy techniques. For example, the $^1$H NMR spectra did not provide useful information because of the extremely broad signals. To assess more clearly the identity of chemical structures, further characterization was performed by MALDI-TOF mass spectrometry. The peaks were consistently found at *m*/*z* values within 0.1% of the theoretical values for all three [Eu(1-G$_n$dbm)$_3$] complexes **7a**–**7c**. Finally, the purity of all three dendritic complexes was confirmed by elemental analysis. The results obtained were consistent with the proposed structures. Further experimental evidence for the formation of the dendritic europium complexes was provided by luminescence measurements.

UV/Vis absorption spectra were recorded in toluene solution with a typical concentration of $1 \times 10^{-5}$ M; photoluminescence spectra were obtained from the same solution. Figure 1 shows the absorption and emission spectra of [Eu(1-G$_n$dbm)$_3$] (**7a**–**7c**). All three dendritic europium(III) complexes give similar absorption and luminescence intensities. The absorption peak located at about 354 nm is associated with the β-diketonato part of the dendritic ligands. The sharp bands in the PL spectra are due to the characteristic emission of the Eu$^{III}$ ion. The main emission peak at 612 nm corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu$^{III}$ ion. Generally, because the central Eu$^{III}$ ion itself shows little or no absorption in the Vis region, the luminescence of the europium complexes is critically dependent on the energy transfer from the π-conjugated β-diketonato ligand. Therefore, the strong luminescence observed for all three dendritic europium complexes undoubtedly confirms the formation of dendritic (β-diketonato)europium complexes. The photoluminescent quantum yields of all three europium(III) complexes were also determined to be 0.0069 (**7a**), 0.0072 (**7b**) and 0.0087 (**7c**) by an optically dilute relative method[16] using [Ru(2,2′-bipyridyl)$_3$]Cl$_2$ ($\Phi_{ref.}$ = 0.028 in aerated $H_2O$)[17] as a reference. As expected, the generation of a dendrimer has only a slight effect on the quantum yield in dilute solution.

Having successfully synthesized these dendritic β-diketonate europium complexes, we next investigated the incorporation of a second ligand into these complexes to further improve the luminescence intensity of the lanthanide complexes. In our initial study, 1,10-phenanthroline was chosen as the second ligand. Thus, reaction of [Eu(1-G$_n$dbm)$_3$] (**7a**–**7c**) with 1,10-phenanthroline in toluene was carried out successfully to furnish the first- to third-generation dendritic β-




**2a**: *n* = 1, **2b**: *n* = 2, **2c**: *n* = 3

[Eu(1-G$_n$dbm)$_3$] **7a**: *n* = 1, **7b**: *n* = 2, **7c**: *n* = 3

Scheme 5. Reagents and conditions: 1 M NaOH, thf/$H_2O$, 60 °C, 2 h.

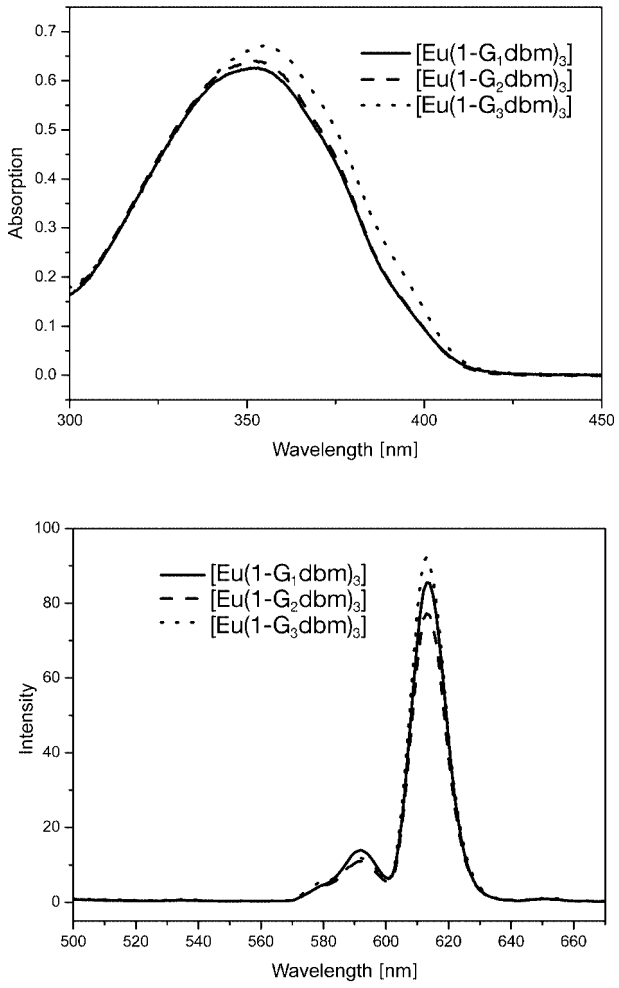



Figure 1. UV/Vis absorption and emission spectra of different generations of the dendritic europium(III) complexes [Eu(1-G$_n$dbm)$_3$] (**7a**–**7c**) ($n$ = 1, 2, 3) in toluene solution. Excitation was performed at 361 nm in the emission spectra.

diketonate europium(III) complexes [Eu(1-G$_n$dbm)$_3$(phen)] (**8a**–**8c**) in good yields (Scheme 6). All three dendritic complexes were purified by solvent precipitation and characterized by elemental analysis. Further confirmation of the chemical structures by MALDI-TOF mass spectrometry was not successful.

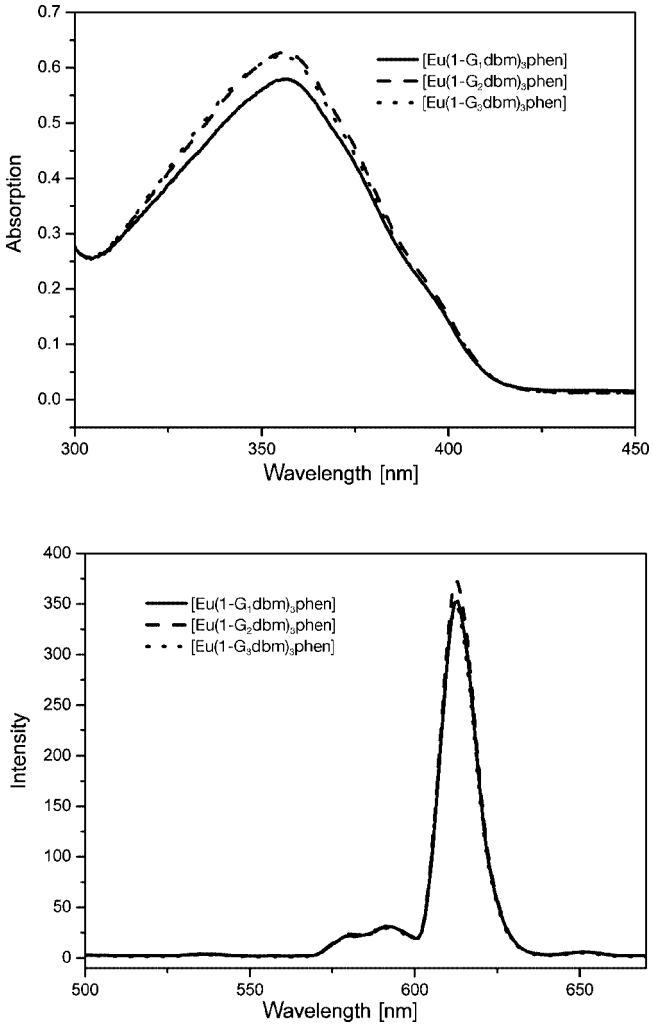
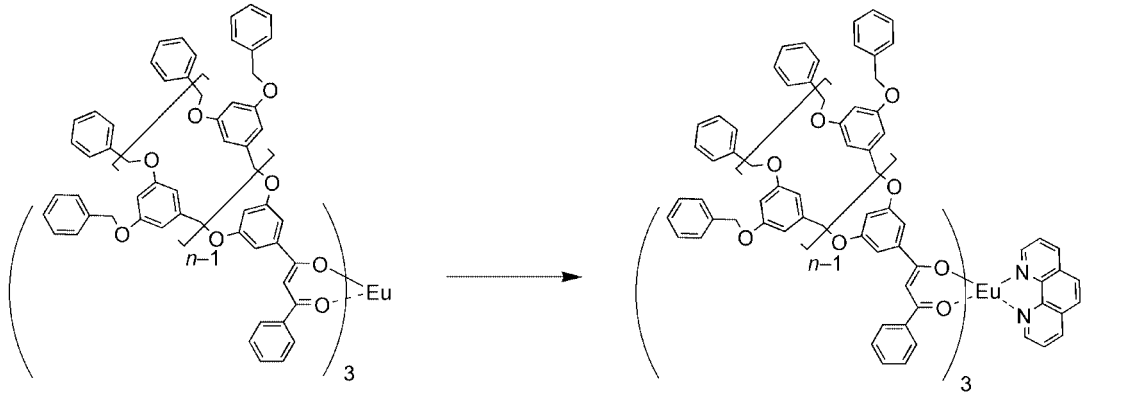



Figure 2. UV/Vis absorption spectra and emission spectra of the dendritic europium(III) complexes [Eu(1-G$_n$dbm)$_3$(phen)] (**8a**–**8c**) ($n$ = 1, 2, 3) in toluene solution. Excitation was performed at 361 nm in the emission spectra.

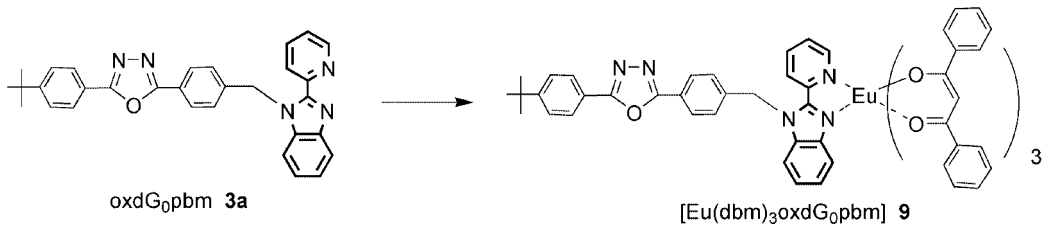



[Eu(1-G$_n$dbm)$_3$] **7a**: $n$ = 1, **7b**: $n$ = 2, **7c**: $n$ = 3

[Eu(1-G$_n$dbm)$_3$(phen)] **8a**: $n$ = 1, **8b**: $n$ = 2, **8c**: $n$ = 3

Scheme 6. Reagents and conditions: 1,10-phenanthroline, toluene, 100 °C, 2 h.




Scheme 7. Reagents and conditions: $Eu(dbm)_3 \cdot 2H_2O$, toluene, 100 °C, 2 h.

Figure 2 shows the absorption and emission spectra of [Eu(1-$G_n$dbm)$_3$(phen)] (**8a**–**8c**). All three dendritic europium(III) complexes have similar absorption and luminescence intensities. Incorporation of 1,10-phenanthroline into the dendritic complexes increases the luminescence intensity about threefold. The photoluminescent quantum yields of these europium(III) complexes were determined to be 0.020 (**8a**), 0.022 (**8b**) and 0.026 (**8c**). These results also demonstrate the formation of the dendritic (β-diketonato)europium complexes with 1,10-phenanthroline as the second ligand.

Encouraged by the successful synthesis of these dendritic (β-diketonato)europium complexes, we further studied the synthesis of dendritic europium complexes by using dendritic 2-(2-pyridyl)benzimidazole derivatives as the second ligand instead of 1,10-phenanthroline (Scheme 7). Basically, incorporation of the second dendritic ligand should not only enhance the core-isolation effect imparted by the dendritic shell but also improve the carrier-transporting ability by introducing an electron-transporting oxadiazole surface group. However, we failed to prepare the dendritic europium complexes by conventional procedures. After screening several solvents and changing the ratio of the ligand oxd$G_n$pbm (**3a**–**3c**) and $Eu(dbm)_3 \cdot 2H_2O$ we were not able to obtain dendritic europium complexes, even when using the first-generation dendritic ligand oxd$G_1$pbm (**3b**). We propose that the sterically demanding dendron attached to the second ligand might result in a reduced coordination capability. This was confirmed by the following experimental evidence. When the dendritic ligands **3a**–**3c** were treated with the corresponding small molecular counterpart $Eu(dbm)_3 \cdot 2H_2O$ under conventional conditions, only the zeroth-generation europium complex [Eu(dbm)$_3$(oxd$G_0$pbm)] (**9**) was obtained. The absorption and emission spectra of **9** in toluene are shown in Figure 3.

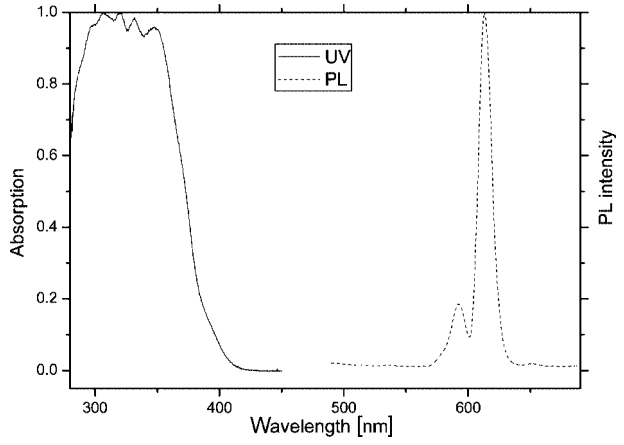



Figure 3. UV/Vis absorption and emission spectra of the europium(III) complex [Eu(dbm)$_3$(oxd$G_0$pbm)] (**9**) in toluene solution. Excitation was performed at 361 nm in the emission spectrum.

## Conclusions

We have synthesized two new kinds of dendritic β-diketonato ligands (**1a**,**1b** and **2b**,**2c**) and a new series of dendritic 2-(2-pyridyl)benzimidazole ligands (**3a**–**3c**) by a convergent strategy. The attachment point of the dendron to dbm has been found to play an important role in the preparation of europium complexes: only dendritic β-diketonato ligands bearing dendrons substituted on the phenyl group of the diketonato backbone can react with $EuCl_3 \cdot 6H_2O$ to provide the first- to third-generation dendritic $Eu^{III}$ complexes in good yields. These dendrimers were characterized by elemental analysis and MALDI-TOF mass spectrometry. Formation of the dendritic $Eu^{III}$ complexes was further confirmed by luminescence measurements. Reaction of these dendritic (β-diketonato)$Eu^{III}$ complexes with 1,10-phenanthroline as the second ligand gives new dendritic $Eu^{III}$ complexes with enhanced luminescence intensity. Generation of the dendrimer has only a slight effect on the luminescence properties of the dendritic $Eu^{III}$ complexes **7a**–**7c** and **8a**–**8c**. However, incorporation of the sterically demanding 2-(2-pyridyl)benzimidazole-cored dendrimers into (β-diketonato)$Eu^{III}$ complexes was not successful. Study of the application of these dendritic (β-diketonato)-$Eu^{III}$ complexes as electroluminescent materials is currently underway.

## Experimental Section

**General:** Toluene and thf were distilled from sodium/benzophenone under nitrogen. Trichloromethane was distilled from calcium hydride. Acetone was dried with anhydrous $K_2CO_3$. Poly(aryl ether) dendrons **4a**,**4b**, **5a**–**5c**, **6a**–**6c**[14,15] and the europium(III) complexes $Eu(dbm)_3 \cdot 2H_2O$[8] were prepared according to literature procedures. All other starting materials and reagents were obtained with analytic purity and were used without further purification, unless otherwise noted. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker WM 300 spectrometer. TMS was used as internal reference for all the compounds. Elemental analysis was performed using a Flash EA 1112 series elemental analyzer (Thermo Quest CE Instruments). High resolution mass spectra were recorded with

a Bruker APEX-II FTICR mass spectrometer. MALDI-TOF mass spectra were measured with an APEX-II spectrometer (Bruker) at an acceleration voltage of 19000 V, using α-cyano-4-hydroxycinnamic acid or 1,8,9-trihydroxyanthracene as matrix. Absorption spectra were recorded with a UV-2401 (PC) S UV/Vis recording spectrophotometer (Shimadzu) with a 10-mm quartz cell at 20 °C. PL was measured with an F-4500 (Hitachi) fluorescence spectrophotometer with a 10-mm quartz cell at 20 °C. The photoluminescence quantum yields were measured by an optically dilute relative method[16] using $[Ru(2,2'\text{-bipyridyl})_3]Cl_2$ ($\Phi$ = 0.028 in aerated $H_2O$)[17] as a reference.

**General Procedure for the Preparation of Dendritic β-Diketonato Ligands 2-G$_n$dbm (1a–1b):** A solution of dibenzoylmethane (dbm, 1 equiv.) and 60% sodium hydride (NaH, 1.2 equiv.) in anhydrous thf (5 mL) was stirred at room temperature for 0.5 h. The corresponding dendritic bromide (**4a** or **4b**; 1 equiv.) was then added, and the mixture was refluxed for 24 h. The resulting solid was filtered off, and the solvent was evaporated under reduced pressure. The residue was partitioned between water and $CH_2Cl_2$, and the aqueous layer was subsequently extracted with $CH_2Cl_2$ (3 × 10 mL). The combined extracts were dried with $Na_2SO_4$ and the solvents evaporated. The solid residue was purified by flash column chromatography as indicated below.

**2-G$_1$dbm (1a):** This compound was prepared from **4a** (0.50 g, 1.29 mmol) and purified by flash silica gel column chromatography, eluting with petroleum ether/$CH_2Cl_2$ (1:3, v/v). After precipitation from petroleum ether, a white powder was obtained (0.42 g, 62%). $^1$H NMR ($CDCl_3$, 300 Hz): $\delta$ = 3.36 (d, $J$ = 6.6 Hz, 2 H), 4.93 (s, 4 H), 5.48 (t, $J$ = 6.6 Hz, 1 H), 6.42–6.48 (m, 3 H), 7.25–7.42 (m, 14 H), 7.51–7.56 (m, 2 H), 7.86 (dd, $J_1$ = 7.2, $J_2$ = 1.4 Hz, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 35.8, 58.7, 70.1, 100.7, 108.6, 127.8, 128.2, 128.8, 129.1, 133.8, 136.2, 137.1, 141.7, 160.3, 195.7 ppm. HRMS (SIMS): calcd. for $C_{36}H_{30}O_4$ 549.2036 [M + Na]$^+$; found 549.2039. $C_{36}H_{30}O_4$ (526.62): calcd. C 82.11, H 5.74; found C 81.97, H 5.75.

**2-G$_2$dbm (1b):** This compound was prepared from **4b** (1.50 g, 1.86 mmol) and purified by flash column chromatography, eluting with petroleum ether/$CH_2Cl_2$ (1:5, v/v). After precipitation from methanol, a white powder was obtained (0.87 g, 49%). $^1$H NMR ($CDCl_3$): $\delta$ = 3.36 (d, $J$ = 6.6 Hz, 2 H), 4.86 (s, 4 H), 5.02 (s, 8 H), 5.47 (t, $J$ = 6.6 Hz, 1 H), 6.40–6.65 (m, 9 H) 7.29–7.50 (m, 26 H), 7.86 (dd, $J_1$ = 7.2, $J_2$ = 1.4 Hz, 4 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 35.8, 58.9, 70.2, 70.3, 100.7, 101.8, 106.7, 108.6, 127.8, 128.3, 128.4, 128.8, 129.1, 133.8, 136.3, 137.1, 139.6, 141.7, 160.2, 160.4, 195.7 ppm. HRMS (SIMS): calcd. for $C_{64}H_{54}O_8$ 973.3711 [M + Na]$^+$; found 973.3692. $C_{64}H_{54}O_8$ (951.11): calcd. C 80.82, H 5.72; found C 80.75, H 5.81.

**General Procedure for the Preparation of Dendritic β-Diketonato Ligands 1-G$_n$dbm (2a–2c):** 60% Sodium hydride (NaH, 1.2 equiv.) was added to a dried flask containing a solution of acetophenone (1 equiv.) and dendritic ester (**5a**, **5b** or **5c**; 1 equiv.) in anhydrous thf. The reaction mixture was heated to reflux under nitrogen for 24 h. The solution was then acidified with dilute HCl and extracted with $CH_2Cl_2$. The combined extracts were dried with $Na_2SO_4$ and the solvents evaporated. The solid residue was purified by flash column chromatography as indicated below.

**1-G$_1$dbm (2a):** This compound was prepared from **5a** (2.18 g, 6.27 mmol) with anhydrous thf (20 mL) as the solvent, and extracted with $CH_2Cl_2$ (3 × 30 mL). The crude product was purified by flash column chromatography, eluting with petroleum ether/$CH_2Cl_2$ (1:1, v/v). Further purification by recrystallization from ethyl acetate/petroleum ether (1:5, v/v) gave **2a** as white crystals (0.93 g, 34%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 5.04 (s, 4 H), 6.70–6.74 (m, 2 H), 7.16–7.46 (m, 16 H), 7.90 (dd, $J_1$ = 7.0, $J_2$ = 1.5 Hz, 2 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 70.5, 93.6, 106.4, 106.6, 127.4, 127.8, 128.4, 128.9, 132.7, 135.5, 136.8, 138.0, 160.3, 185.3, 186.0 ppm. HRMS (SIMS): calcd. for $C_{29}H_{24}O_4$ 437.1747 [M + H]$^+$; found 437.1738. $C_{29}H_{24}O_4$ (436.50): calcd. C 79.80, H 5.54; found C 79.48, H 5.65.

**1-G$_2$dbm (2b):** This compound was prepared from **5b** (3.38 g, 4.37 mmol) with anhydrous thf (30 mL) as the solvent, and extracted with $CH_2Cl_2$ (3 × 30 mL). The crude product was purified by flash column chromatography, eluting with petroleum ether/$CH_2Cl_2$ (2:3, v/v), to give **2b** as a white powder (0.79 g, 21%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 4.98 (s, 12 H), 6.53–6.71 (m, 8 H), 7.15–7.45 (m, 26 H), 7.91 (d, $J$ = 7.1 Hz, 2 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 70.3, 93.6, 102.0, 106.4, 106.7, 127.5, 127.8, 128.1, 128.3, 128.9, 129.0, 132.8, 135.5, 137.1, 138.0, 139.3, 160.3, 160.5, 185.4, 186.0 ppm. HRMS (SIMS): calcd. for $C_{57}H_{48}O_8$ 883.3241 [M + Na]$^+$; found 883.3237. $C_{57}H_{48}O_8$ (951.11): calcd. C 79.51, H 5.62; found C 79.44, H 5.65.

**1-G$_3$dbm (2c):** This compound was prepared from **5c** (4.11 g, 2.53 mmol) with anhydrous thf (40 mL) as the solvent, and extracted with $CH_2Cl_2$ (3 × 50 mL). The crude product was purified by flash column chromatography, eluting with petroleum ether/$CH_2Cl_2$ (1:3, v/v), to give **2c** as a colourless glass (0.78 g, 18%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 4.91 (s, 8 H), 4.95 (s, 20 H), 6.51–6.71 (m, 20 H), 7.17–7.41 (m, 46 H), 7.90 (d, $J$ = 7.4 Hz, 2 H) ppm. $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ = 70.3, 93.7, 102.0, 106.5, 106.8, 127.6, 127.9, 128.2, 128.4, 129.0, 129.1, 132.9, 135.5, 136.8, 137.2, 137.6, 138.1, 139.4, 139.7, 160.4, 160.6, 185.4, 186.1 ppm. MALDI-TOF: $m/z$ = 1732.3 [M + Na]$^+$. $C_{113}H_{96}O_{16}$ (1710.0): calcd. C 79.37, H 5.66; found C 78.94, H 5.72.

**General Procedure for the Preparation of Dendritic 2-(2-Pyridyl)-benzimidazole Ligands oxdG$_n$pbm (3a–3c):** 60% Sodium hydride (NaH, 1.2 equiv.) was added quickly to a solution of 2-(2-pyridyl)-benzimidazole (pbm, 1 equiv.) in anhydrous thf or dmf. The reaction mixture was stirred under nitrogen at room temperature for 0.5 h. The corresponding dendritic bromide (**6a**, **6b** or **6c**; 1 equiv.) was then added, and the mixture was refluxed for 24 h. The resulting solid was filtered off, and the solvent was evaporated under reduced pressure. The residue was partitioned between water and $CH_2Cl_2$, and the aqueous layer was subsequently extracted with $CH_2Cl_2$ (3 × 10 mL). The combined extracts were dried with $Na_2SO_4$ and the solvents evaporated. The solid residue was purified by flash column chromatography as indicated below.

**oxdG$_0$pbm (3a):** This compound was prepared from **6a** (1.00 g, 2.69 mmol) with thf (10 mL) as solvent, and purified by flash column chromatography, eluting with $CH_2Cl_2$/$CH_3OH$ (50:1, v/v). Further purification by recrystallization from $CH_2Cl_2$/$CH_3OH$ (50:1, v/v) gave **3a** as white crystals (0.83 g, 63%). $^1$H NMR ($CDCl_3$): $\delta$ = 1.24 (s, 9 H), 6.13 (s, 2 H), 7.16–7.25 (m, 6 H), 7.41 (d, $J$ = 8.5 Hz, 2 H), 7.68–7.80 (m, 2 H), 7.90 (d, $J$ = 8.3 Hz, 4 H), 8.36 (d, $J$ = 8.3 Hz, 1 H), 8.48 (d, $J$ = 4.2 Hz, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 31.2, 35.2, 48.9, 110.6, 120.4, 121.1, 123.2, 123.9, 124.1, 124.7, 126.2, 126.8, 127.3, 127.5, 136.8, 137.1, 141.5, 142.9, 148.7, 149.9, 150.4, 155.4, 164.1, 164.7 ppm. MS (ESI): $m/z$ = 485.91 [M]$^+$. $C_{31}H_{27}N_5O$ (485.58): calcd. C 76.68, H 5.60, N 14.42; found C 76.63, H 5.62, N 14.31.

**oxdG$_1$pbm (3b):** This compound was prepared from **6b** (0.50 g, 0.64 mmol) with thf (10 mL) as solvent, and purified by flash column chromatography, eluting with $CH_2Cl_2$/$CH_3OH$ (40:1, v/v). Further purification by precipitation from methanol gave **3b** as a white powder (0.34 g, 59%). $^1$H NMR ($CDCl_3$): $\delta$ = 1.38 (s, 18 H),

4.99 (s, 4 H), 6.10 (s, 2 H), 6.43 (s, 2 H), 6.49 (s, 1 H), 7.23–7.30 (m, 4 H), 7.45 (d, $J$ = 8.1 Hz, 4 H), 7.55 (d, $J$ = 8.4 Hz, 4 H), 7.79–7.87 (m, 2 H), 8.07 (dd, $J_1$ = 8.3, $J_2$ = 1.8 Hz, 8 H), 8.44 (d, $J$ = 8.6 Hz, 1 H), 8.54 (d, $J$ = 4.4 Hz, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 31.2, 35.2, 49.0, 69.4, 101.5, 106.3, 110.8, 120.3, 121.2, 123.0, 123.6, 123.77, 123.9, 124.7, 126.2, 126.9, 127.2, 127.7, 136.9, 140.3, 140.7, 142.8, 148.7, 149.9, 150.6, 155.5, 159.9, 164.2, 164.8 ppm. MS (ESI): $m/z$ = 898.08 $[M]^+$. $C_{57}H_{51}N_7O_4$ (898.06): calcd. C 76.23, H 5.72, N 10.92; found C 76.16, H 5.77, N 10.72.

**oxdG$_2$pbm (3c):** This compound was prepared from **6c** (0.45 g, 0.28 mmol) with dmf (10 mL) as solvent, and purified by flash column chromatography, eluting with $CH_2Cl_2$/$CH_3OH$ (20:1, v/v). Further purification by precipitation from methanol gave **3c** as a white powder (0.25 g, 52%). $^1$H NMR ($CDCl_3$): $\delta$ = 1.37 (s, 36 H), 4.86 (s, 4 H), 5.09 (s, 8 H), 6.08 (s, 2 H), 6.43 (s, 3 H), 6.58 (q, $J$ = 2.1 Hz, 6 H), 7.26 (s, 4 H), 7.53–7.57 (m, 16 H), 7.77–7.85 (m, 2 H), 8.05 (d, $J$ = 8.5 Hz, 8 H), 8.13 (d, $J$ = 8.3 Hz, 8 H), 8.40 (d, $J$ = 8.1 Hz, 1 H), 8.55 (d, $J$ = 4.9 Hz, 1 H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 31.2, 35.2, 49.1, 69.5, 69.8, 101.0, 101.8, 106.4, 106.5, 110.9, 120.22, 121.1, 123.0, 123.7, 123.7, 124.0, 124.8, 126.2, 126.9, 127.2, 127.9, 136.9, 137.0, 139.5, 140.1, 140.7, 142.8, 148.7, 149.9, 150.5, 155.5, 159.9, 160.0, 164.2, 164.8 ppm. MALDI-TOF: $m/z$ = 1723.0 $[M]^+$, 1745.9 $[M + Na]^+$, 1762.2 $[M + K]^+$. $C_{109}H_{99}N_{11}O_{10}$ (1723.0): calcd. C 75.98, H 5.79, N 8.94; found C 75.95, H 6.05, N 8.54.

**General Procedure for the Preparation of the Dendritic Eu$^{III}$ Complexes [Eu(1-G$_n$dbm)$_3$] (7a–7c):** A 1 M aqueous NaOH (3 equiv.) solution was added dropwise to a solution of 1-G$_n$dbm (**2a**, **2b** or **2c**; 3 equiv.) in thf, followed by aqueous $EuCl_3 \cdot 6H_2O$ (1 equiv.). The reaction mixture was stirred under nitrogen at 60 °C for 2 h. After removal of the solvent, the product was separated and purified by solvent precipitation from hexane.

**[Eu(1-G$_1$dbm)$_3$] (7a):** This compound was prepared from **2a** (1.50 g, 3.44 mmol) as a yellowish powder (1.40 g, 84%). MALDI-TOF: $m/z$ = 1482.0 $[M + Na]^+$. $C_{87}H_{69}EuO_{12}$ (1458.4): calcd. C 71.65, H 4.77; found C 71.56, H 4.87.

**[Eu(1-G$_2$dbm)$_3$] (7b):** This compound was prepared from **2b** (0.632 g, 0.735 mmol) as a yellowish powder (0.576 g, 86%). MALDI-TOF: $m/z$ = 2754.1 $[M + Na]^+$. $C_{171}H_{141}EuO_{24}$ (2731.9): calcd. C 75.18, H 5.20; found C 75.03, H 5.23.

**[Eu(G$_3$dbm)$_3$] (7c):** This compound was prepared from **2c** (0.350 g, 0.205 mmol) as a yellowish glass (0.273 g, 76%). MALDI-TOF: $m/z$ = 5301 $[M + Na]^+$. $C_{339}H_{285}EuO_{48}$ (5278.8): calcd. C 77.13, H 5.44; found C 77.33, H 5.58.

**General Procedure for the Preparation of the Dendritic Eu$^{III}$ Complexes [Eu(1-G$_n$dbm)$_3$(phen)] (8a–8c):** A solution of 1,10-phenanthroline (1.1 equiv.) and [Eu(1-G$_n$dbm)$_3$] (1 equiv.) in toluene was heated to 100 °C under nitrogen for 2 h. Ethanol was then added dropwise to precipitate the product. The resulting yellow oil was solidified by drying in vacuo.

**[Eu(1-G$_1$dbm)$_3$(phen)] (8a):** This compound was prepared from **7a** (0.294 g, 0.202 mmol) as a yellowish powder (0.294 g, 89%). $C_{99}H_{77}EuN_2O_{12}$ (1638.6): calcd. C 72.56, H 4.74, N 1.71; found C 72.19, H 4.79, N 1.83.

**[Eu(1-G$_2$dbm)$_3$(phen)] (8b):** This compound was prepared from **7b** (0.288 g, 0.084 mmol) as a yellowish powder (0.151 g, 62%). $C_{183}H_{149}EuN_2O_{24}$ (2912.10): calcd. C 75.48, H 5.16, N 0.96; found C 75.75, H 5.32, N 0.59.

**[Eu(1-G$_3$dbm)$_3$(phen)] (8c):** This compound was prepared from **7c** (0.200 g, 0.038 mmol) as a yellowish glass (0.122 g, 59%). $C_{351}H_{293}EuN_2O_{48}$ (5459.0): calcd. C 77.23, H 5.41, N 0.51; found C 77.87, H 5.50, N 0.46.

**Preparation of the Eu$^{III}$ Complex [Eu(dbm)$_3$(oxdG$_0$pbm)] (9):** A solution of $Eu(dbm)_3 \cdot 2H_2O$ (0.109 g, 0.127 mmol) and **3a** (0.065 g, 0.133 mmol) in toluene (3 mL) was heated to 100 °C under nitrogen for 2 h. The solvent was then removed under reduced pressure in a water bath. The crude product was recrystallized from $CH_2Cl_2$/hexane (1:1, v/v) to give yellowish crystals of complex **9** (0.081 g, 49%). $C_{76}H_{60}EuN_5O_7$ (1307.28): calcd. C 69.83, H 4.63, N 5.36; found C 69.43, H 4.83, N 5.32.

**Supporting Information** (see footnote on the first page of this article): Characterization data including $^1$H and $^{13}$C NMR spectra of compounds **1a**,**b**, **2a**–**c** and **3a**–**c**, and mass spectra of compounds **1a**,**b**, **2a**–**c**, **3a**–**c**, and **7a**–**c**.

## Acknowledgments

We thank the Major State Basic Research Development Program of China (grant no. 2002CB613403) for financial support of this study.

[1] J. Kido, Y. Okamoto, *Chem. Rev.* **2002**, *102*, 2357–2368.
[2] a) M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542–1548; b) C. Yang, L. M. Fu, Y. Wang, J. P. Zhang, W. T. Wong, X. C. Ai, Y. F. Qiao, B. S. Zou, L. L. Gui, *Angew. Chem. Int. Ed.* **2004**, *43*, 5010–5013; c) A. P. Bassett, S. W. Magennis, P. B. Glover, D. J. Lewis, N. Spencer, S. Parsons, R. M. Williams, L. D. Cola, Z. Pikramenou, *J. Am. Chem. Soc.* **2004**, *126*, 9413–9424; d) P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat, L. De Cola, *Angew. Chem. Int. Ed.* **2005**, *44*, 1806–1810.
[3] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules: Concept, Synthesis and Perspectives*, Wiley-VCH, Weinheim, Germany, **1996**.
[4] a) A. Adronov, J. M. J. Fréchet, *Chem. Commun.* **2000**, 1701–1710; b) V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, *Top. Curr. Chem.* **2003**, *228*, 159–191.
[5] a) S. L. Gilat, A. Adronov, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **1999**, *38*, 1422–1427; b) S.-C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, *Adv. Mater.* **2002**, *14*, 975–979; c) N. D. McClenaghan, R. Passalacqua, F. Loiseau, S. Campagna, B. Verheyde, A. Hameurlaine, *J. Am. Chem. Soc.* **2003**, *125*, 5356–5365; d) X. Y. Cao, W. B. Zhang, J. L. Wang, X. H. Zhou, H. Lu, J. Pei, *J. Am. Chem. Soc.* **2003**, *125*, 12430–12431; e) J. P. Cross, M. Lauz, P. D. Badger, S. Petoud, *J. Am. Chem. Soc.* **2004**, *126*, 16278–16279; f) J. P. Chen, S. Y. Li, L. Zhang, B. N. Liu, Y. B. Han, G. Q. Yang, Y. Li, *J. Am. Chem. Soc.* **2005**, *127*, 2165–2171; g) J. Q. Ding, J. Gao, Y. X. Cheng, Z. Y. Xie, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Adv. Funct. Mater.* **2006**, *16*, 575–581.
[6] a) M. Kawa, J. M. J. Fréchet, *Chem. Mater.* **1998**, *10*, 286–296; b) M. Kawa, T. Takahagi, *Chem. Mater.* **2004**, *16*, 2282–2286.
[7] a) Q. H. Fan, Y. M. Chen, X. M. Chen, *Chem. Commun.* **2000**, 789–790; b) G. J. Deng, Q. H. Fan, X. M. Chen, *Chem. Commun.* **2002**, 1570–1571; c) B. Yi, Q. H. Fan, G. J. Deng, *Org. Lett.* **2004**, *6*, 1361–1364; d) G. J. Deng, G. R. Li, L. Y. Zhu, H. F. Zhou, Y. M. He, Q. H. Fan, Z. G. Shuai, *J. Mol. Catal. A* **2006**, *244*, 118–123.
[8] L. R. Melby, N. J. Rose, E. Abramson, J. C. Caris, *J. Am. Chem. Soc.* **1964**, *86*, 5117–5125.
[9] a) M. R. Robinson, M. B. O'Regan, G. C. Bazan, *Chem. Commun.* **2000**, 1645–1646; b) J. F. Wang, R. Y. Wang, J. Yang, Z. P. Zheng, M. D. Carducci, T. Cayou, N. Peyghambarian, G. E. Jabbour, *J. Am. Chem. Soc.* **2001**, *123*, 6179–6180; c) X. Z. Jiang, A. K. Y. Jen, G. D. Phelan, D. Y. Huang, T. M. Londergan, L. R. Dalton, R. A. Register, *Thin Solid Films* **2002**, *416*,

212–217; d) M. R. Robinson, J. C. Ostrowski, G. C. Bazan, M. D. McGehee, *Adv. Mater.* **2003**, *15*, 1547–1551; e) V. Marchi-Artzner, M.-J. Brienne, T. Gulik-Krzywicki, J.-C. Dedieu, J.-M. Lehn, *Chem. Eur. J.* **2004**, *10*, 2342–2350; f) L. Huang, K. Z. Wang, C. H. Huang, F. Y. Lia, Y. Y. Huang, *J. Mater. Chem.* **2001**, *11*, 790–793; g) F. S. Liang, Q. G. Zhou, Y. X. Cheng, L. X. Wang, D. G. Ma, X. B. Jing, F. S. Wang, *Chem. Mater.* **2003**, *15*, 1935–1937; h) H. Xin, F. Y. Li, M. Shi, Z. Q. Bian, C. H. Huang, *J. Am. Chem. Soc.* **2003**, *125*, 7166–7167.

[10] L. H. Wang, W. Wang, W. G. Zhang, E. T. Kang, W. Huang, *Chem. Mater.* **2000**, *12*, 2212–2218.

[11] J. Pei, X. L. Liu, W. L. Yu, Y. H. Lai, Y. H. Niu, Y. Cao, *Macromolecules* **2002**, *35*, 7274–7280.

[12] X. Jiang, A. K.-Y. Jen, G. D. Phellan, D. Huang, T. M. Londergan, L. R. Dalton, R. A. Register, *Thin Solid Films* **2002**, *416*, 212–217.

[13] a) S. F. Li, W. H. Zhu, J. F. Pan, Z. Y. Xu, H. Tian, *Huaxue Tongbao* **2004**, *67*, w86–w89 (http://www.hxtb.org, in Chinese); *Chem. Abstr.* **2005**, *142*, 366127; b) S. F. Li, G. Y. Zhong, W. H. Zhu, W. H. Li, J. F. Pan, W. Huang, H. Tian, *J. Mater. Chem.* **2005**, *15*, 3221–3228; c) S. F. Li, W. H. Zhu, Z. Y. Xu, J. F. Pan, H. Tian, *Tetrahedron* **2006**, *62*, 5035–5048.

[14] C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.

[15] a) S. J. Chung, K. S. Kim, T. C. Lin, G. S. He, J. Swiatkiewicz, P. N. Prasad, *J. Phys. Chem. B* **1999**, *103*, 10741–10745; b) C. C. Kwok, M. S. Wong, *Macromolecules* **2001**, *34*, 6821–6830.

[16] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024.

[17] K. Nakamura, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697–2705.

Received: July 9, 2006
Published Online: November 17, 2006