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Antenna-functionalized dendritic β-diketonates and europium complexes: synthetic approaches to generation growth

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Abstract—Six dendritic β-diketonates and their corresponding europium complexes were synthesized. These dendritic β-diketonate ligands consist of dibenzoylmethane cores, Fréchet-type poly(aryl ether) dendrons, and the carbazole-grafted peripheral functional groups. The designs of dendrimers are on the basis of high light-harvesting capability and dendron functionalization in virtue of the high extinction coefficient and carrier-injection adjustment of carbazole units. Different approaches to generation growth were utilized: the first generation europium complexes through etheral connectivity were developed via convergent synthetic approach; the second and third generation dendrons through esteral connectivity were developed by a hyperbranch core approach containing the advantages of convergent and divergent approaches. Their chemical structures were well characterized. Preliminary results show that the dendron-functionalized carbazole units not only tune the carrier-transporting capability, but also exhibit strong light-harvesting potential, resulting in a strong intense emission from the central Eu(III) ion via sensitization.

1. Introduction

Due to the extreme narrow-width emission band, europium complexes have attracted considerable interest for the design of laser materials,[1] organic light-emitting diodes,[2–5] and fluorescent probes.[6–9] However, the luminescence efficiency is suffered from the low extinction coefficient and non-radiative deactivation of Eu(III) ion.[10–13] Up to now, little work was concerned about modifying the light harvesting of β-diketonate ligand except the pursuit of novel second ligands.[3,14–17]

Dendrimers have attracted much interest because of their unique structures and properties.[18–22] The globular shape of dendrimers provides a large surface area that can be decorated with chromophores,[23–25] resulting in a large absorption cross section and efficient capture of photons. Another interesting properties of dendritic molecules are the site-isolation effect of dendrons to create a micro-environment to prevent the intermolecular interaction and avoid self-quenching effect.[11]

On the basis of our earlier work,[26,27] here we report a series of novel carbazole-terminated dendritic β-diketonates and their corresponding Eu(III) complexes developed through diverse approaches (see Scheme 1). The dendritic β-diketonates consist of dibenzoylmethane cores, Fréchet-type poly (aryl ether) dendrons, and carbazole (CZ) peripheral functional groups. Once they were chelated with Eu(III) ions, such dendritic ligands were expected to create encapsulating cages, thus reducing the self-quenching process and environmental influence. In virtue of high extinction coefficient of the terminated carbazole units, more photons could be efficiently harvested and then transferred to the focal ion.

Due to the acceptable yield of Claisen condensation, convergent synthetic approach was utilized to achieve the first generation europium complexes. The second and third generation dendrons were synthesized via hypercore synthetic approach[28] to circumvent the weak reactivity of senior generation esters. These complexes ranging from the first generation to the third generation are denoted by $[x\text{Caz-G}_y]_3$-Eu, where [*x*Caz] refers to the number of carbazole units incorporated into dendron and [G_y] denotes the generation number (y=1, 2, 3).

2. Results and discussion

2.1. β-Diketonate as core

In order to obtain different generations of dendritic β-diketonates, it is necessary to synthesize the branched

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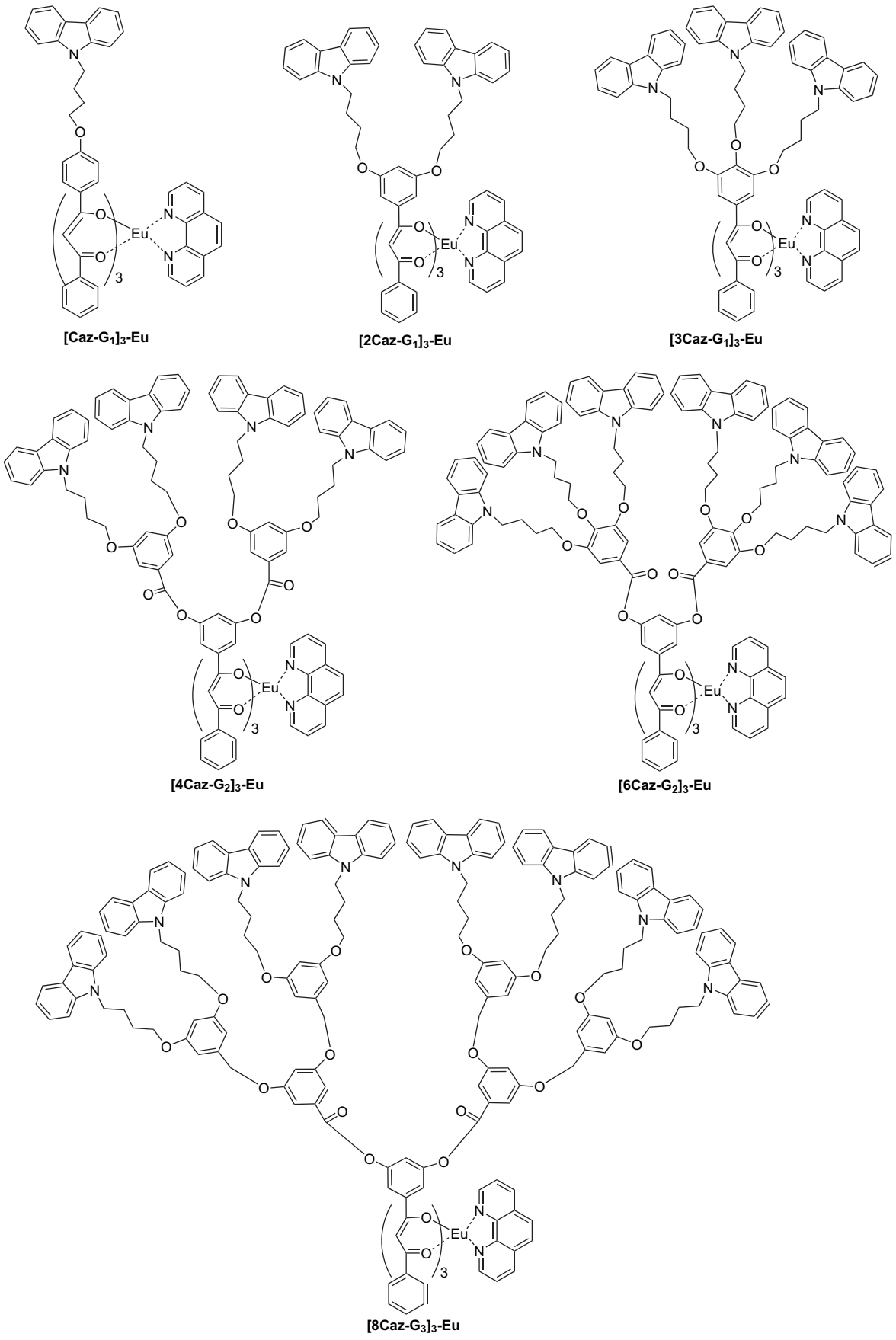
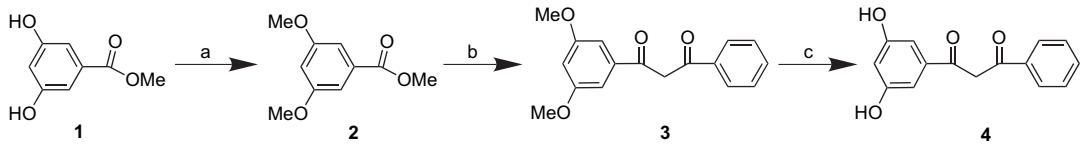


Scheme 1. Chemical structures of six target dendritic europium complexes.



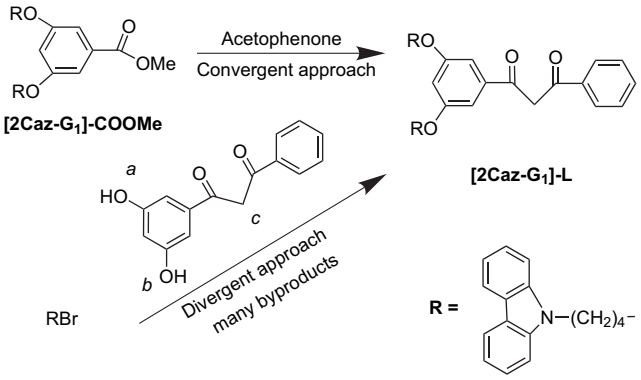
Scheme 2. Divergent synthesis of focal β-diketonate **4**. Reagents and conditions: (a) CH_3I, acetone, K_2CO_3, reflux, 48 h, 92%; (b) NaH, acetophenone, THF, 60 °C, 72 h, 22%; (c) BBr_3, CH_2Cl_2, −78 °C for 0.5 h, then rt, overnight, 84%.

dibenzoylmethane derivatives. Phenolate **4** (Scheme 2) is an ideal intermediate with two phenolic hydroxyl groups on which convergent carboxylate dendrons can be incorporated to form a higher generation derivatives. As shown in Scheme 2, phenolate **4** was synthesized via three steps with good overall yield, that was, O-alkylation of methyl 3,5-dihydroxybenzoate (**1**) with methyl iodide, Claisen condensation between methyl 3,5-dimethoxybenzoate (**2**) and acetophenone, and finally the methyl deprotection by BBr_3.

2.2. The first generation dendron via convergent approach

There are two basic approaches to construct dendrimers: the divergent approach and convergent approach.[29] The synthesis of first generation (**8**) was very straightforward without any group protection and deprotection via convergent approach with acceptable yield. In Scheme 3, the alkylation of phenol group of ethyl 4-hydroxybenzoate (**5**) with 9-(4-bromobutyl)-9*H*-carbazole underwent smoothly in the presence of anhydrous potassium carbonate and 18-crown-6 in acetone under reflux. Then, the resulting intermediate **6** reacted with acetophenone via Claisen condensation in the presence of sodium hydride to give **7**, followed by chelating with europium ion.

In the synthesis of first generation dendrons (**11a** and **11b**), Claisen condensation became the crucial step and was accompanied with many side reactions, such as aldol condensation and hydrolysis. Once the steric hindrance of the ester (**10a** and **10b**) was increased, the resulting yield of Claisen condensation dropped dramatically. Therefore, we attempted to synthesize the first generation derivatives in two paths to optimize the reaction procedures. Taking the synthesis of [2Caz-G_1]-L as an example shown in Scheme 4, the first approach was convergent one in which [2Caz-G_1]-COOMe was coupled with acetophenone in an acceptable yield. In contrast, treatment of 9-(4-bromobutyl)-9*H*-carbazole with phenolate **4** via the divergent way yielded several byproducts owning to three active sites (a, b, and c indicated in Scheme 4), which was a time-consuming work to determine and purify the target ligands.

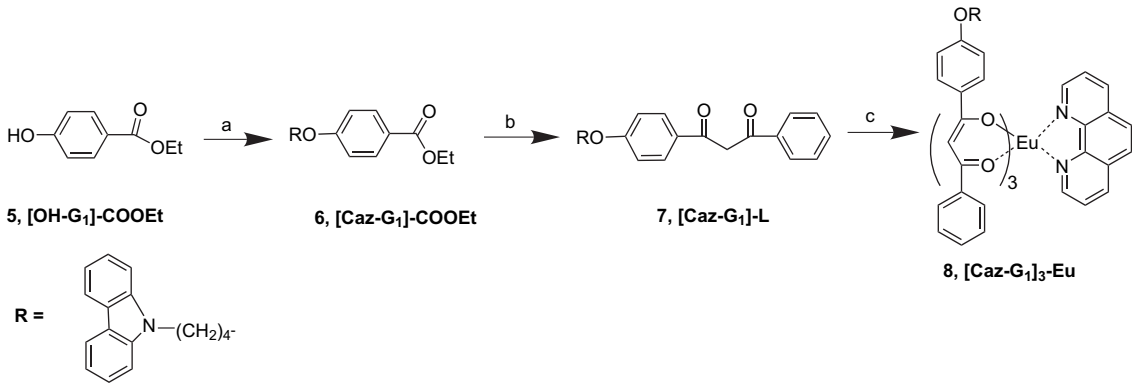


Scheme 4. Procedure for designing the first generation dendritic ligand [2Caz-G_1]-L.

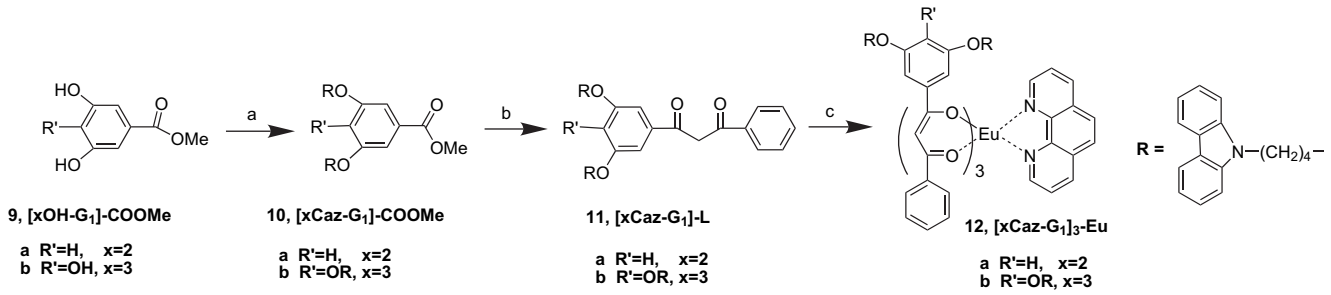
Dendritic europium complexes with the first generation dendron of AB_2 and AB_3 type were synthesized in convergent approach, which were identical to that of AB type **7** (Scheme 5). Furthermore, since β-diketonates **11a** and **11b** have green-yellowish fluorescence, the reaction can be monitored easily by TLC, and the target β-diketonates were separated smoothly by column chromatography.

2.3. The second and third generation dendrons via hypercore approach

Although the convergent approach seemed to be very helpful during the syntheses of the first generation dendrons, many unexpected problems took place during the preparation of



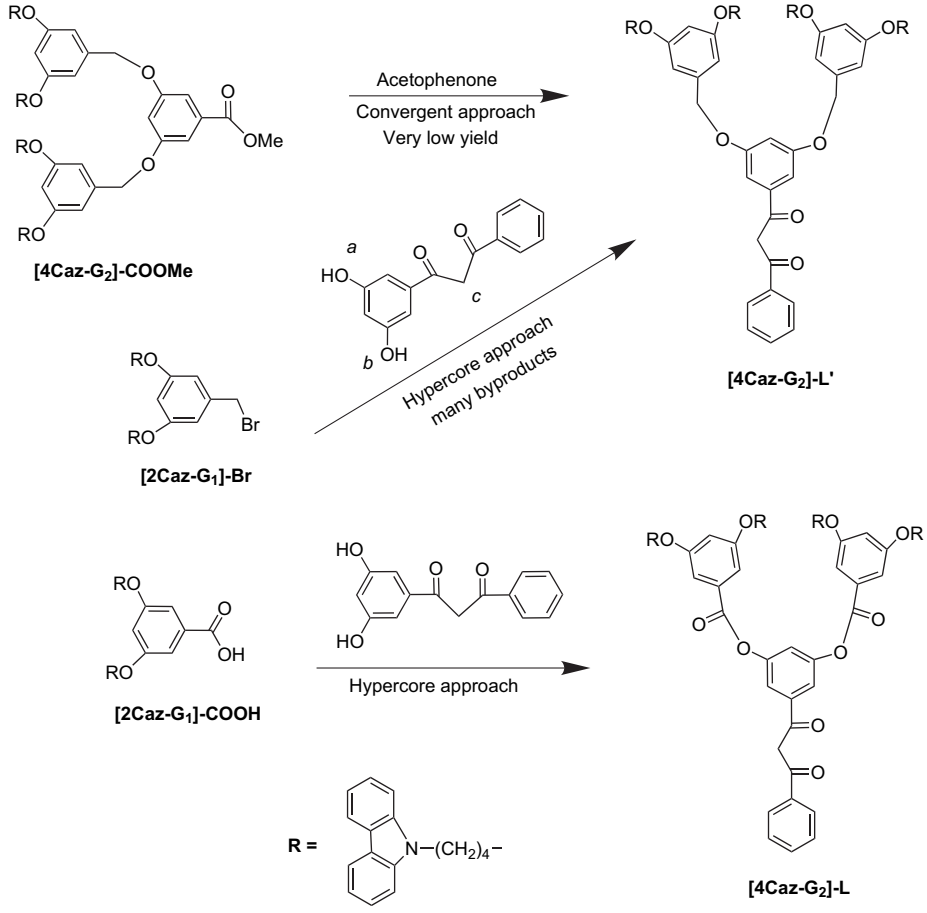
Scheme 3. Convergent synthesis of the first generation complex [Caz-G_1]$_3$-Eu. Reagents and conditions: (a) 9-(4-bromobutyl)-9*H*-carbazole, acetone, K_2CO_3, reflux, 56 h, 66%; (b) NaH, acetophenone, THF, 60 °C, 90 h, 16%; (c) $EuCl_3 \cdot 6H_2O$, phenanthroline·H_2O, NaOH, THF, ethanol, 60 °C, 4 h, 76%.



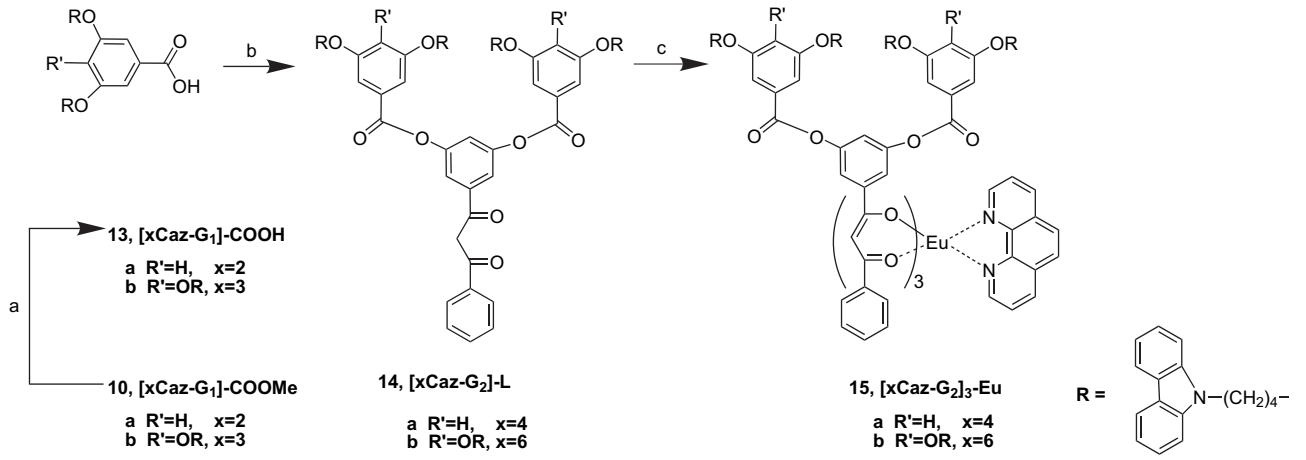
Scheme 5. Convergent synthesis of the first generation dendrimer. Reagents and conditions: (a) 9-(4-bromobutyl)-9*H*-carbazole, acetone, K_2CO_3, reflux, 56 h, 70–90%; (b) NaH, acetophenone, THF, 60 °C, 90 h, 19–30%; (c) $EuCl_3 \cdot 6H_2O$, phenanthroline·H_2O, NaOH, THF, ethanol, 60 °C, 4 h, 45–75%.

the second generation dendrons. When the generation of corresponding methyl benzoxylate [4Caz-G_2]-COOMe was increased, Claisen condensation between the ester and acetophenone became very difficult, and little corresponding ligand [4Caz-G_2]-L′ was obtained (Scheme 6).

To solve the problem, a hypercore (hyperbranch core) synthetic approach[28] containing the advantages of convergent and divergent approaches was introduced. It involved the pre-assembly of oligomeric species, which could then be linked together to give dendrimers in a short route and high yields. In our design, phenolate **4** containing two reactive phenolic hydroxyl groups at its extremity was utilized for divergent growth by attaching other preformed dendritic wedges through their single focal point reactive group. As shown in Scheme 6, we firstly attempted to use ether bond as the dendritic wedge bridge between [2Caz-G_1]-Br with **4**, but the yields were unacceptable with many byproducts, which were similar to the aforementioned O-alkylation in Scheme 4. Fortunately, the esterification could be preceded smoothly with the assistance of dicyclohexylcarbodiimide (DCC) at room temperature with a fairly good yield when esteral connectivity was chosen as the dendritic wedge. As a case shown in Scheme 7, the dendron propagation was started with the saponification of **10**. Then the dendritic wedge **13** containing focal carboxylic group was esterified with **4** to give the corresponding dendritic β-diketonate **14** with around 55% yield. Treatment of compound **13** with **4** could achieve the second generation dendron **14**, which was a rapid generation-growth approach with respect to



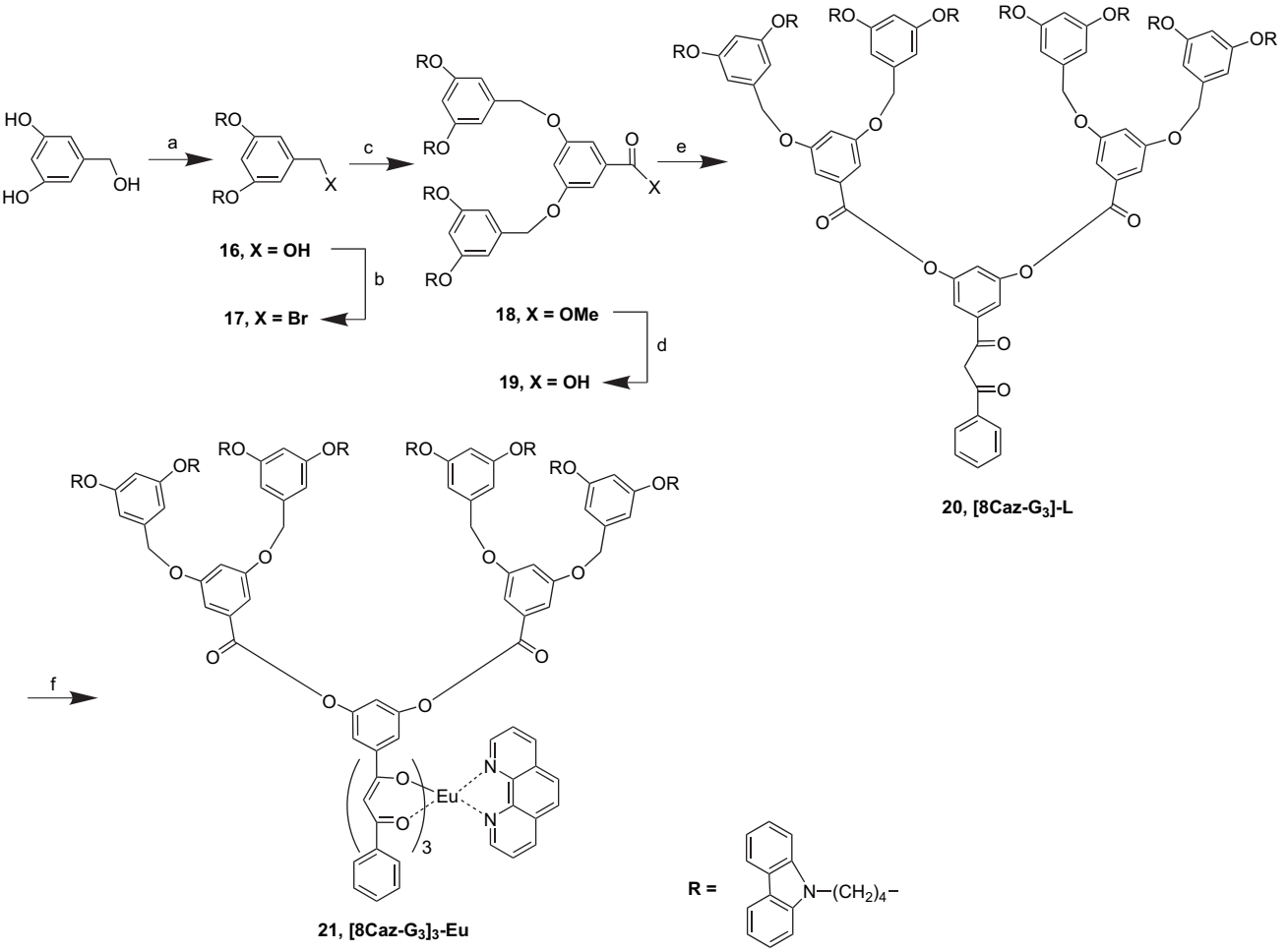
Scheme 6. Procedure for designing the second dendritic ligands.



Scheme 7. Hypercore synthesis of the second dendritic complexes. Reagents and conditions: (a) NaOH, THF, H_2O, reflux, 8 h, ~93%; (b) **4**, DCC, DPTS, CH_2Cl_2, rt, 24 h, ~55%; (c) $EuCl_3 \cdot 6H_2O$, phenanthroline·H_2O, triethylamine, THF, ethanol, 60 °C, 4 h, ~80%.

the convergent synthesis from the reaction of [4Caz-G_2]-COOMe and acetophenone.

The third generation dendrimer was also obtained via hypercore approach with multiple steps consisting O-alkylation, bromo-substitution, hydrolysis, and esterification. Two simple synthetic transformations were used for synthesizing dendrons: (1) selective alkylation of phenolic hydroxyl groups, and (2) conversion of a benzylic alcohol to a benzylic bromide to generate a reactive focal moiety (Scheme 8). Herein, O-alkylation was the repetitive steps for the synthesis of higher generation of Fréchet-type poly(aryl ether)



Scheme 8. Hypercore synthesis of the third dendritic complexes. Reagents and conditions: (a) 9-(4-bromobutyl)-9*H*-carbazole, acetone, K_2CO_3, reflux, 56 h, 83%; (b) PPh_3, CBr_4, CH_2Cl_2, rt, 5 h, 92%; (c) methyl 3,5-dihydroxyl benzoate, 18-crown-6, acetone, K_2CO_3, reflux, 56 h, 81%; (d) NaOH, THF, H_2O, reflux, 5 h, 93%; (e) **4**, DCC, DPTS, CH_2Cl_2, rt, 24 h, 17%; (f) $EuCl_3 \cdot 6H_2O$, phenanthroline·H_2O, triethylamine, THF, ethanol, 60 °C, 4 h, 87%.

dendrons. The O-alkylation of 9-(4-bromobutyl)-9*H*-carbazole and 3,5-dihydroxyl benzyl alcohol afforded the first generation of benzyl alcohol **16**, which was facile to be purified via recrystallization. Then the corresponding dendritic benzyl bromide **17** was prepared by the combinatorial bromination reagents of PPh_3 and CBr_4, followed by phenolic alkylation of methyl 3,5-dihydroxyl benzoate to yield the second generation of methyl benzoate **18**. Treatment of product **19** with **4** in the presence of DCC/DPTS gave the third generation of desirable dendritic ligand **20**. The third generation dendrimer of Eu(III) complex **21** was finally obtained by the treatment of the corresponding ligand with $EuCl_3 \cdot 6H_2O$ in the mixing solvents of ethanol and THF kept in oil bath at 60 °C. The coordination was easily observed by instantaneous color change of the reaction mixture upon addition of Eu(III) salt.

2.4. Structure characterization

All dendrimers were recrystallized from acetone for several times. Further purification of the obtained Eu(III) coordinated dendrimers by silica gel column chromatography failed, only yielding the corresponding starting dendrons. This might be the result of ligand exchange reaction between the coordinated dendrimers and surface silanol groups (Si–OH) of silica gel, resulting in the adsorption of Eu(III) onto the silica gel.[11] Dendritic β-diketonates and their europium complexes were well characterized. In order to assign functional groups in detail, the IR spectra of [2Caz-G_1]-L and [2Caz-G_1]$_3$-Eu are illustrated in Figure 1. The ligand [2Caz-G_1]-L (Fig. 1a) has a broad vibration band at 3300–3600 cm^{-1} assigned to hydroxyl group of enol form of β-diketonates, which almost disappeared after the coordination with Eu(III) (complex [2Caz-G_1]$_3$-Eu, Fig. 1b). A single peak at 3051 cm^{-1} and a doublet at about 2855 and 2930 cm^{-1} are corresponding to the C–H stretching vibration of aryl ring and alkyl chain. The C=O and C=C stretching vibrations of ligand in the complex [2Caz-G_1]$_3$-Eu (Fig. 1b) appear at about 1551 and 1592 cm^{-1}, respectively, whereas these vibrations in ligand [2Caz-G_1]-L (Fig. 1a) are at 1600 cm^{-1}. The ring vibration of the second ligand, 1,10-phenanthroline, usually observed at 1610 cm^{-1}, is difficult to be distinguished due to the overlapping with the vibration peak of double bond. Another peak at 1340 cm^{-1} is attributed to the stretching vibration of C–N bond.[5,30] Two spectra both contain two sharp and strong absorption peaks at 726 and 747 cm^{-1}, associated with the characteristic absorption of the carbazole moieties. All demonstrate a successful coordination between [2Caz-G_1]-L and Eu(III) ion.

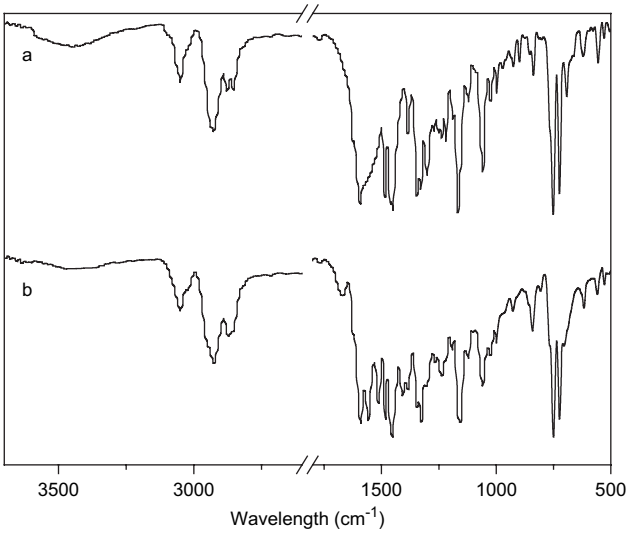


Figure 1. IR spectra of [2Caz-G_1]-L (a) and [2Caz-G_1]$_3$-Eu (b).

To date, most europium complexes haven't been characterized by ^{1}H NMR spectrum due to the Eu(III) paramagnetism.[3,17,31,32] Although NMR signals for the second- and third-generation Eu(III) dendrimers are too complicated and broad, ^{1}H NMR spectra of dendritic ligands and their first generation europium complexes provide useful information and solid evidences for Eu(III) coordination. As a result of the ring current effect between phenanthroline and β-diketonate, the proton chemical shifts of ligands in the complexes have a dramatic change with respect to that of corresponding free ligands. For Eu(III) complexes, protons of phenanthroline are deshielded while protons linking to β-diketonates are shielded. As a typical example, the ^{1}H NMR spectra of [2Caz-G_1]-L and [2Caz-G_1]$_3$-Eu are shown in Figure 2. Owing to the ligand of [2Caz-G_1]-L existing in enol form,[13,33] each of the protons (H_h, H_i, and H_j) in [2Caz-G_1]-L is characteristic of single peak. Comparing with the assignment of the proton signals of [2Caz-G_1]-COOMe, the chemical shift of H_g in [2Caz-G_1]-L is shifted downfield to 7.97 ppm due to the adjacent electron-withdrawing effect of carbonyl group, indicating that the form of enol-1 is more favorable as shown in Scheme 9. Thermodynamically, the conjugation state of enol-1 is more stable than that of enol-2. Upon coordination with Eu(III) ion, ^{1}H NMR spectrum of [2Caz-G_1]$_3$-Eu becomes complicated. Due to [2Caz-G_1]-L existing in anionic form, the protons of the focal β-diketonate in the complex are shielded so that dramatic changes are observed for the chemical shifts of H_e, H_f, H_g, H_h, H_i, and H_j, which are shifted from 7.55, 7.49, 7.97, 6.75, 7.04, and 6.53 ppm to approximately 7.53, 7.26, 7.40, 6.00, 6.61, and 5.67 ppm, respectively. In contrast, due to the deshield effect, H_a, H_b, H_c, and H_d signals of phenanthroline ligand appear at the downfield of 10.71, 7.97, 10.42, and 8.53 ppm.

With the dendron-generation growth, ^{1}H NMR signals become more complicated and difficult to discern structures. To assess more clearly the identity of chemical structures, further characterization has been performed by MALDI-TOF mass spectroscopy. This technique provides macromolecular mass determinations for intact molecular ions of nonvolatile species, and is particularly useful for structural characterization of high molecular weight dendrimers. MALDI-TOF results of the ligand dendrons and their corresponding europium complex dendrimers are shown in Section 4. Some signals observed are either potassium or sodium adducts of the molecular ions, depending on the matrix used. The MALDI-TOF spectra of the second- and third-generation β-diketonate ligands are shown in Figure 3. The MALDI-TOF spectra of the europium dendrimers for the first- and second-generation derivatives are presented in Figure 4. These peaks occurred at *m*/*z* values consistently within 0.2% of the theoretical values. Thus, the MALDI-TOF data provided additional support for the identity of these dendrimers.

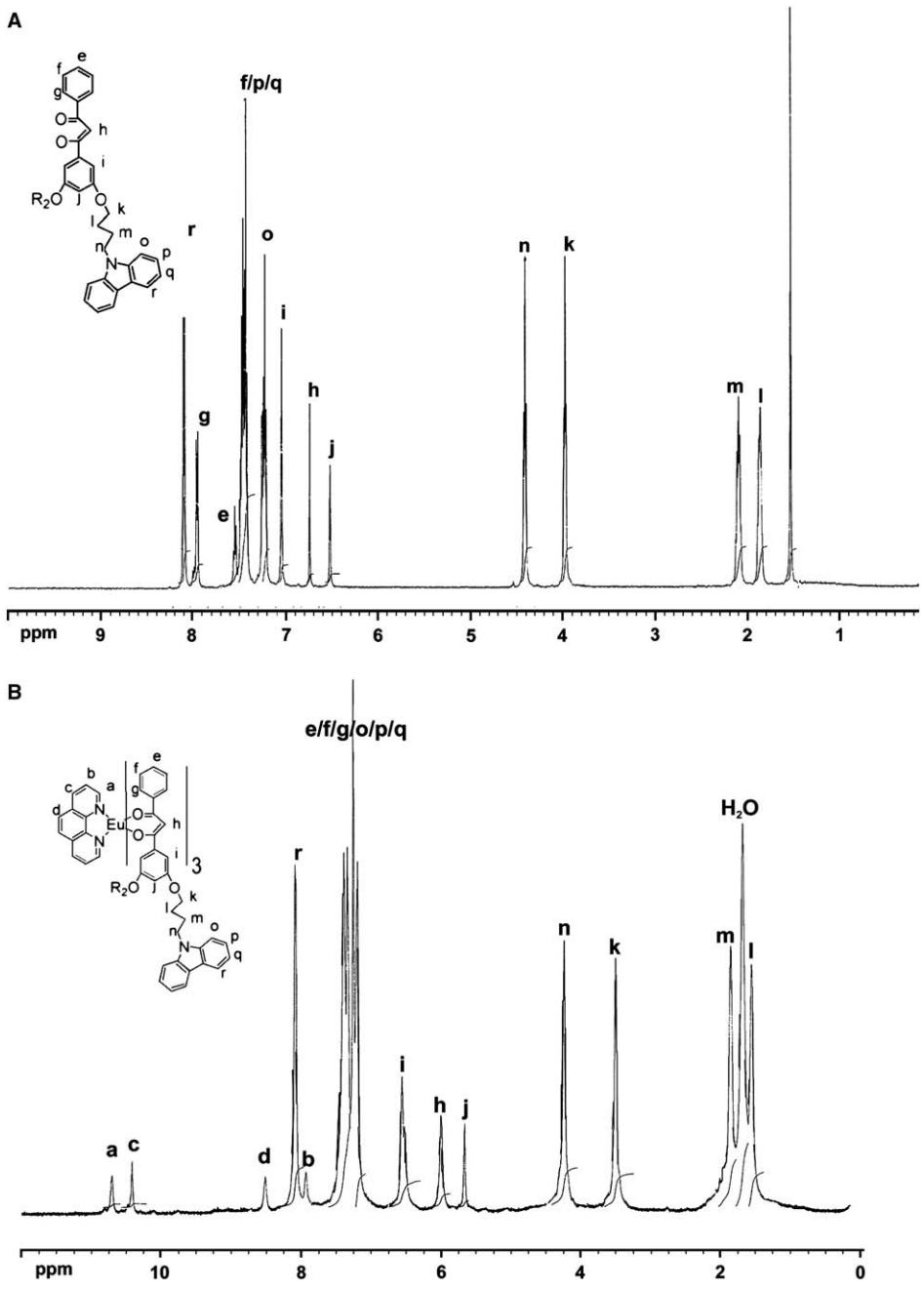
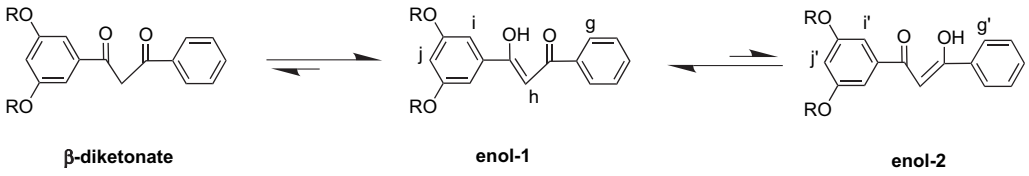


Figure 2. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of (A) $[2Caz\text{-}G_1]_3$-L and (B) $[2Caz\text{-}G_1]_3$-Eu.



Scheme 9. Tautomers of $[2Caz\text{-}G_1]$-L. Note: NMR spectra suggest that the form of enol-1 is more favorable.

2.5. Light-harvesting effect of the peripheral carbazole units in europium complexes

Generally, because the central Eu(III) ion shows little or no absorption in the visible light region, the luminescence of lanthanide complexes is critically dependent on the energy transfer from 'light-harvesting antenna' ligand (donor) to central lanthanide ion. Excitation mechanism of the central metal ion also differs widely from that of organic fluorescent compounds. For Eu(III) complexes with π-conjugated ligands such as β-diketonate, Eu(III) ions are excited via intramolecular energy transfer from the triplet excited states of

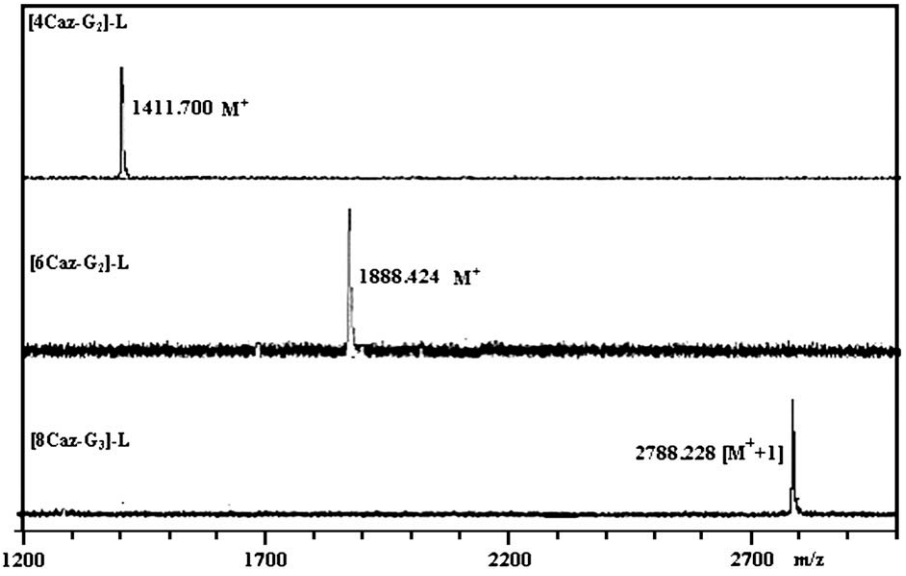


Figure 3. MALDI-TOF mass spectra of [4Caz-G_2]-L, [6Caz-G_2]-L, and [8Caz-G_3]-L.

the ligands.[2] To improve the energy transfer to Eu(III) ions, the triplet states of ligands must be closely matched to or slightly above the emitting resonance levels of center Eu(III) ions.

When excited at the absorption wavelength of the grafted carbazole units, all dendritic europium complexes in CH_2Cl_2 or solid film emit a characteristic sharp luminescence peak at 615 nm with four shoulders ascribed to

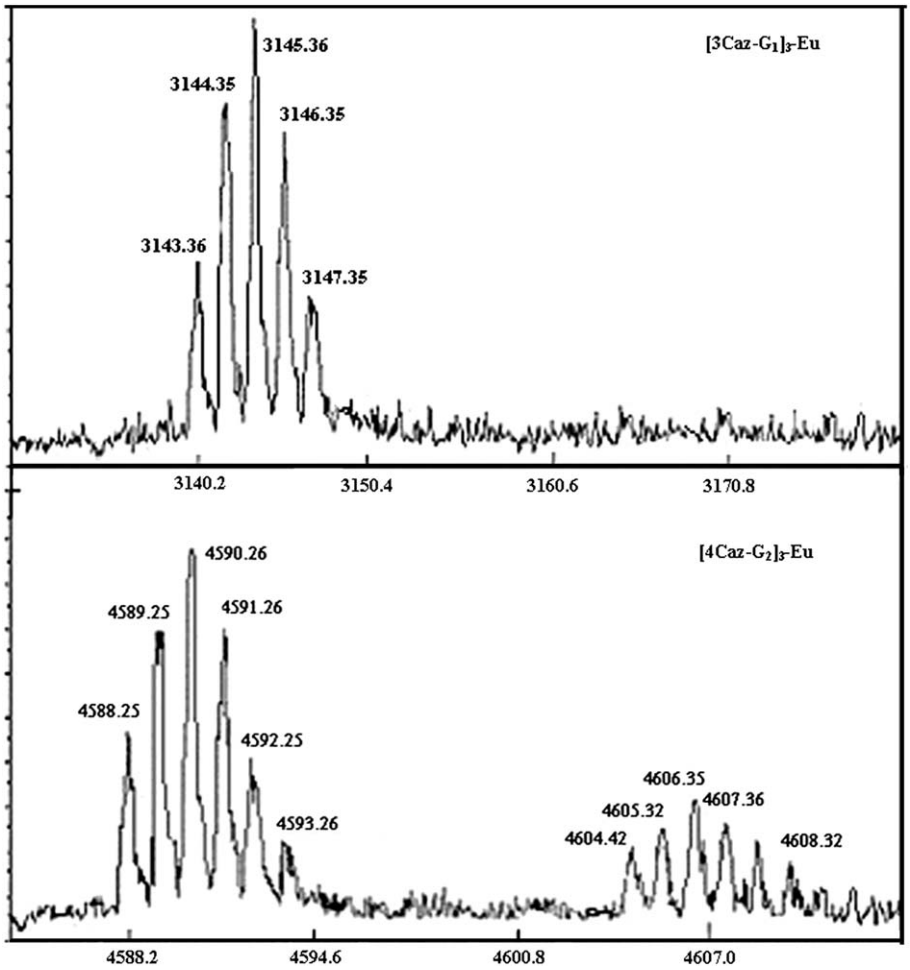


Figure 4. MALDI-TOF mass spectra of [3Caz-G_1]$_3$-Eu ([M^+]), top) and [4Caz-G_2]$_3$-Eu ([M^++Na], [M^++K], bottom).

transitions between 4f states of Eu(III) ion. All five peaks at 586, 591, 615, 651, and 702 nm are corresponding to Eu(III) characteristic transitions ($^5D_0 \rightarrow {}^7F_j$, j=0–4).

Notably, with respect to carbazole, the emission of peripheral donor carbazole unit in the system of the synthesized europium dendrimers is almost completely quenched under the direct excitation of 331 nm (curve c, Fig. 5). As can be seen in Figure 5 (curves a and b), the luminescence of carbazole units is overlapped with the absorption of [3Caz-G_1]$_3$-Eu to a certain extent, thus an efficient Förster-resonance energy transfer in the complex system can take place from the singlet excited state of the grafted carbazole to the singlet excited state of β-diketonate ligand, and followed by the intersystem crossing to the excited triplet state of β-diketonate, where it is finally transferred to the central Eu(III) ion. The efficient energy transfer is further confirmed by the excitation spectrum of [3Caz-G_1]$_3$-Eu (Fig. 6), indicating that the peripheral carbazole units in such complexes can exhibit efficient light-harvesting potential. Thus, it is possible to obtain a strong intense emission from the central Eu(III) when excited via sensitization from a large light-harvesting antenna. Moreover, the site isolation of dendrons can also be favorable to enhance luminance. For comparing the relative luminescence quantum yields, we normalized the spectra of the absorption peak at β-diketonate region (360 nm), and compared the relative intensity of luminescence. As a result of the carbazole light harvesting and the site isolation of dendrons, in comparison with the luminescence intensity of reference complex Eu(BPPD)$_3$Phen[26] in solid film excited at 331 nm (carbazole absorption maximum), the relative luminescence quantum yields of [Caz-G_1]$_3$-Eu, [2Caz-G_1]$_3$-Eu, and [3Caz-G_1]$_3$-Eu are 3.3, 7.9, and 4.5 folds, respectively. It should be noted that the luminescence of [3Caz-G_1]$_3$-Eu containing three carbazole units is unexpectedly weaker than that of [2Caz-G_1]$_3$-Eu containing two carbazole units, which might be attributed to the spatial hindrance of three neighboring carbazole units incorporated into one side of ligand and leading to a less effective energy transfer between carbazole and β-diketonate. The detailed studies of energy transfer, luminescence dynamics, and photo-physical properties with these dendrimers are now undergoing, and will be reported elsewhere. Notably,

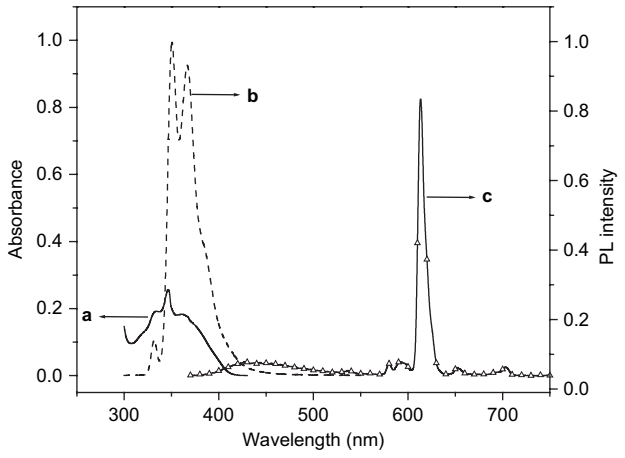


Figure 5. Absorption spectrum of [3Caz-G_1]$_3$-Eu in CH_2Cl_2 (2.0×10^{-5} mol L^{-1}, curve a), and PL spectra excited at 331 nm in CH_2Cl_2 (2.0×10^{-5} mol L^{-1}) of carbazole (curve b) and [3Caz-G_1]$_3$-Eu (curve c).

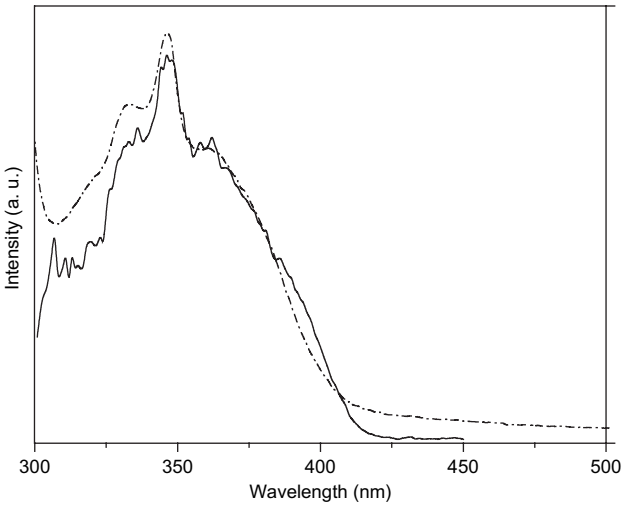


Figure 6. Absorption spectrum (solid line) and excitation spectrum (dash dot line) of [3Caz-G_1]$_3$-Eu monitored at 615 nm. The excitation spectrum is normalized at the absorption peak at β-diketonate region (360 nm). All measurements are in CH_2Cl_2 (1.2×10^{-6} mol L^{-1}).

preliminary results show that white light electroluminescence (CIE: 0.333, 0.348) using a complex [3Caz-G_1]$_3$-Eu can be achieved,[27] indicating that modifying ligands can not only tune the carrier-transporting properties of complexes, but also provide a useful clue to use electroplex or exciplex to realize a broad or even white electroluminescence.

3. Conclusions

Several dendritic β-diketonates and corresponding europium complexes were designed and synthesized based on the following consideration: (1) high light-harvesting capability and efficient energy transfer to the focal ion in virtue of high extinction coefficient of the terminated carbazole units, (2) dendron functionalization to incorporate carbazole units to realize the carrier-injection adjustment, and (3) avoiding core luminescence quenching by the means of the dendron to enhance core luminescence. Their dendritic β-diketonate ligands consist dibenzoylmethane cores, Fréchet-type poly (aryl ether) dendrons, and the grafted carbazole (CZ) peripheral functional groups. Due to the acceptable yield of Claisen condensation, convergent synthetic approach through etheral connectivity was utilized to achieve the first generation europium complexes. For the second and third generation dendrons, a hyperbranch core synthetic approach containing the advantages of convergent and divergent approaches was introduced. Preliminary results showed that the peripheral carbazole units in such complexes can not only tune the carrier-transporting capability, but also exhibit strong light-harvesting potential, thus resulting in a strong intense emission from the central Eu(III) via the sensitization.

4. Experimental

4.1. General

THF was dried from metal sodium. Sodium hydride was purchased from *J&K*, kept in a vacuum drier at room

temperature. $EuCl_3 \cdot 6H_2O$ (99.9%) and carbazole were obtained from Aldrich. Acetophenone from Aldrich was dried with $MgSO_4$ and redistilled prior to usage. All other starting materials and reagents were of analytic purity without treatment. Melting points were measured on X4 Micro-melting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on a Brucker AM-500 spectrometer. TMS was used as internal reference for all the compounds. MS were recorded on FAB or MALDI-TOF mass spectroscopy. IR spectra of thin films on KBr plates were recorded on a Nexus 470 FTIR spectrometer. Elemental analyses were obtained on a Perkin–Elmer 240C elemental analyzer.

4.1.1. Synthesis of methyl 3,5-dimethoxybenzoate ([2Me-G_1]-COOMe, 2). To a 100 mL flask were added methyl iodide (9.0 g, 63.4 mmol), methyl 3,5-dihydroxybenzoate (5.0 g, 29.5 mmol), potassium carbonate (8.6 g, 62.3 mmol), and anhydrous acetone (60 mL). The mixture was heated at reflux and stirred vigorously under argon for 48 h. Then it was allowed to cool and evaporate to dryness under reduced pressure. The residue was washed with water. After filtration and recrystallization, pink crystals were obtained (5.3 g), yield 92%. Mp: 55–57 °C. ^1H NMR (500 MHz, $CDCl_3$): δ ppm, 3.82 (s, 6H, $-OCH_3$), 3.89 (s, 3H, $-OCH_3$), 6.54 (s, 1H, Ph–H), 7.14 (s, 2H, Ph–H). MS (FAB): *m/z* 197.1 [M^++1], 196.1 [M^+] (100%).

4.1.2. 1-(3,5-Dimethoxyphenyl)-3-phenylpropane-1,3-dione ([2Me-G_1]-L, 3). To a dry flask containing a solution of acetophenone (1.2 g, 10.2 mmol) and **2** (2.0 g, 10.2 mmol) in THF (60 mL) was added quickly 60% sodium hydride (0.4 g, 10.0 mmol). The reaction mixture was heated under argon at 60 °C for 72 h. The solution was then acidified with dilute HCl and extracted with CH_2Cl_2. After removal of solvent, the pure product was obtained (0.63 g) as a yellow solid over a silica gel column (CH_2Cl_2/CCl_4, 1:5/v:v), yield 21.7%. Mp: 62–63 °C. ^1H NMR (500 MHz, $CDCl_3$): δ ppm, 3.83 (s, 6H, $-OCH_3$), 6.65 (t, 1H, *J*=2.0 Hz, Ph–H), 6.80 (s, 1H, =CH), 7.12 (d, 2H, *J*=2.0 Hz, Ph–H), 7.48 (t, 2H, *J*=7.4, 7.3 Hz, Ph–H), 7.55 (t, 1H, *J*=7.3 Hz, Ph–H), 7.97 (d, 2H, *J*=7.4 Hz, Ph–H); MS (FAB): *m/z* 286.1 [M^++2], 285.1 [M^++1], 284.1 [M^+] (100%).

4.1.3. 1-(3,5-Dihydroxyphenyl)-3-phenylpropane-1,3-dione ([2OH-G_1]-L, 4). To a solution of **2** (1.6 g, 5.63 mmol) in dry CH_2Cl_2 (50 mL) at −78 °C was slowly syringed BBr_3 (1.6 mL), and after stirring at −78 °C for 0.5 h, the solution was allowed to warm to room temperature and left overnight. A dilute solution of NaOH (1 mol L^{-1}, 5 mL) was then added at 0 °C. The mixture was extracted with ethyl acetate to remove the unreacted reagent and the remaining aqueous solution was neutralized with hydrochloric acid (2 mol L^{-1}). Large amount of yellow solid was precipitated and filtered. The crude product was purified by chromatography on silica gel (CH_2Cl_2/acetone, 10:1/v:v). The total yield was 84% (1.3 g). ^1H NMR (500 MHz, $CDCl_3$): δ ppm, 6.60 (s, 1H, Ph–H), 6.78 (s, 1H, =CH), 7.10 (s, 2H, Ph–H), 7.48 (t, 2H, *J*=7.4, 7.8 Hz, Ph–H), 7.55 (t, 1H, *J*=7.3 Hz, Ph–H), 7.97 (d, 2H, *J*=7.1 Hz, Ph–H). MS (FAB): *m/z* 257 [M^++1], 256 [M^+] (100%), 255 [M^+-1], 239 [M^+-OH].

4.1.4. Ethyl 4-[4-(9*H*-carbazol-9-yl)butoxy]benzoate ([Caz-G_1]-COOEt, 6). A mixture of 9-(4-bromobutyl)-9*H*-carbazole (2.00 g, 6.62 mmol), **5** (1.43 g, 8.61 mmol), potassium carbonate (1.30 g, 9.42 mmol), and 18-crown-6 (0.13 g, 4.72 mmol) in anhydrous acetone (60 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was washed with water and a large amount of precipitate appeared followed by filtration. After recrystallization, a white needle-like crystal was obtained (1.71 g), yield 66%. Mp: 80–82 °C. ^1H NMR (500 MHz, $CDCl_3$): δ ppm, 1.37 (t, 3H, *J*=6.2 Hz, $-CH_3$), 1.87–1.91 (m, 2H, $-CH_2$), 2.10–2.14 (m, 2H, $-CH_2$), 3.98 (t, 2H, *J*=6.2 Hz, $-OCH_2$), 4.32 (t, 2H, *J*=6.0 Hz, $-OCH_2$), 4.40 (t, 2H, *J*=7.0 Hz, $-NCH_2$), 6.84 (d, 2H, *J*=8.8 Hz, Ph–H), 7.23 (t, 2H, *J*=7.0, 8.2 Hz, Ph–H), 7.43 (d, 2H, *J*=8.1 Hz, Ph–H), 7.47 (t, 2H, *J*=7.2, 8.3 Hz, Ph–H), 7.96 (d, 2H, *J*=8.8 Hz, Ph–H), 8.10 (d, 2H, *J*=7.6 Hz, Ph–H). MS (FAB): *m/z* 389.2 [M^++2], 388.2 [M^++1], 387.2 [M^+] (100%). Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.28; H, 6.32; N, 3.75.

4.1.5. 1-[4-[4-(9*H*-Carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione ([Caz-G_1]-L, 7). To a dry flask containing a solution of acetophenone (0.37 g, 3.08 mmol) and **6** (1.20 g, 3.09 mmol) in THF (60 mL) was added quickly 60% sodium hydride (0.30 g, 7.5 mmol). The reaction mixture was heated under argon at 60 °C for 90 h. The solution was then acidified with dilute HCl and extracted with CH_2Cl_2. After solvent removal, the solid residue was separated over a silica gel column (CH_2Cl_2/CCl_4, 1:2/v:v) and a light yellow solid was obtained (0.23 g), yield 16.2%. Mp: 159–162 °C. ^1H NMR (500 MHz, $CDCl_3$): δ ppm, 1.89–1.92 (m, 2H, CH_2), 2.11–2.15 (m, 2H, CH_2), 4.01 (t, 2H, *J*=6.1 Hz, $-OCH_2$), 4.43 (t, 2H, *J*=7.0 Hz, $-NCH_2$), 6.79 (s, 1H, =CH), 6.91 (d, 2H, *J*=5.2 Hz, Ph–H), 7.25 (d, 2H, *J*=6.5 Hz, Ph–H), 7.42 (d, 2H, *J*=8.1 Hz, Ph–H), 7.44–7.50 (m, 4H, Ph–H), 7.53 (t, 1H, *J*=1.4, 1.2 Hz, Ph–H), 7.93–7.97 (m, 4H, Ph–H), 8.11 (d, 2H, *J*=7.6 Hz, Ph–H). MS (FAB): *m/z* 463 [M^++2], 462 [M^++1], 461 [M^+]. Anal. Calcd for $C_{31}H_{27}NO_3$: C, 80.67; H, 5.90; N, 3.03. Found: C, 80.38; H, 5.69; N, 3.13.

4.1.6. Tris[1-[4-[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione](1,10-phenanthroline) europium (III) ([Caz-G_1]$_3$-Eu, 8). To a solution of **7** (120 mg, 0.26 mmol) and 1,10-phenanthroline monohydrate (18 mg, 90.9 μmol) in THF (10 mL), aqueous NaOH (1 mol L^{-1}, 0.2 mL) was syringed dropwise, followed by aqueous $EuCl_3$ hexahydrate (31.7 mg, 87.4 μmol). Under the protection of argon, the mixture was stirred at 60 °C for 4 h and then cooled. The product was collected by filtration and washed with deionized water twice before crystallization with acetone and vacuum drying (112 mg), yield 75.5%. Mp: 110–113 °C. ^1H NMR (500 MHz, $CDCl_3$): δ ppm, 1.72 (br, 6H, CH_2), 2.17 (br, 6H, CH_2), 3.77 (br, 6H, $-OCH_2$), 4.35 (br, 6H, $-NCH_2$), 5.59 (br, 6H, =CH, Ph–H), 5.95 (br, 6H, Ph–H), 6.20 (br, 6H, Ph–H), 6.61–6.78 (m, 12H, Ph–H), 7.26–7.46 (m, 15H, Ph–H), 8.11 (br, 9H, Ph–H), 8.97 (br, 2H, phenanthroline–H), 9.90 (br, 2H, phenanthroline–H), 10.64 (br, 2H, phenanthroline–H), 11.01 (br, 2H, phenanthroline–H). MS (FAB): *m/z* 1752.6 [M^++K], 1736.7 [M^++Na], 1714 [M^+] (100%). Anal. Calcd for

$C_{105}H_{86}EuN_5O_9$: C, 73.59; H, 5.06; N, 4.09. Found: C, 73.21; H, 4.69; N, 4.38.

4.1.7. Methyl 3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzoate ([2Caz-G$_1$]-COOMe, 10a). A mixture of 9-(4-bromobutyl)-9*H*-carbazole (3.00 g, 9.93 mmol), **9a** (0.78 g, 4.64 mmol), potassium carbonate (1.82 g, 13.1 mmol), and 18-crown-6 (0.13 g, 4.7 mmol) in anhydrous acetone (100 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was washed with water and a large amount of precipitate appeared followed by filtration. After recrystallization with ethanol, a white powder was obtained (2.5 g), yield 88.3%. Mp: 124–127 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.82–1.87 (m, 4H, CH_2), 2.05–2.11 (m, 4H, CH_2), 3.88 (s, 3H, –OCH_3), 3.94 (t, 4H, J=6.1 Hz, –OCH_2), 4.39 (t, 4H, J=7.0 Hz, –NCH_2), 6.54 (s, 1H, Ph–H), 7.14 (s, 2H, Ph–H), 7.23 (t, 4H, J=7.2, 7.4 Hz, Ph–H), 7.42 (d, 4H, J=8.1 Hz, Ph–H), 7.46 (t, 4H, J=7.4 Hz, 7.8 Hz, Ph–H), 8.10 (d, 4H, J=7.8 Hz, Ph–H). MALDI-TOF MS (FAB): *m/z* 612.5 [M$^+$+2], 611.5 [M$^+$+1], 610.5 [M$^+$] (100%). Anal. Calcd for $C_{40}H_{38}N_2O_4$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.40; H, 6.00; N, 4.82.

4.1.8. 1-[3,5-Bis[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione ([2Caz-G$_1$]-L, 11a). To a dry flask containing a solution of acetophenone (0.39 g, 3.3 mmol) and **10a** (2.00 g, 3.28 mmol) in THF (80 mL) was added quickly 60% sodium hydride (0.20 g, 5.0 mmol). The reaction mixture was heated under argon at 60 °C for 90 h. The solution was then acidified with dilute HCl and extracted with CH_2Cl_2. After solvent removal, the solid residue was separated over a silica gel column (CH_2Cl_2/CCl_4, 1:5/v:v) and a light yellow solid was obtained (0.43 g), yield 19.0%. Mp: 57–59 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.88–1.91 (m, 4H, CH_2), 2.06–2.10 (m, 4H, CH_2), 3.98 (t, 4H, J=6.1 Hz, –OCH_2), 4.41 (t, 4H, J=7.0 Hz, –NCH_2), 6.53 (s, 1H, Ph–H), 6.75 (s, 1H, =CH), 7.04 (s, 2H, Ph–H), 7.25 (t, 4H, J=7.2 Hz, Ph–H), 7.42–7.51 (m, 10H, Ph–H), 7.55 (t, 1H, J=7.2, 7.0 Hz, Ph–H), 7.97 (d, 2H, J=7.6 Hz, Ph–H), 8.11 (d, 4H, J=7.7 Hz, Ph–H). ^{13}C NMR ($CDCl_3$): δ ppm, 26.5, 27.6, 43.4, 68.5, 94.0, 106.0, 106.4, 109.3, 119.6, 121.1, 123.6, 126.4, 127.8, 129.3, 133.1, 136.0, 138.4, 141.1, 160.9, 185.9, 186.6. MS (FAB): *m/z* 700 [M$^+$+2], 699 [M$^+$+1], 698 [M$^+$]. Anal. Calcd for $C_{47}H_{42}N_2O_4$: C, 80.78; H, 6.06; N, 4.01. Found: C, 80.50; H, 5.85; N, 4.23.

4.1.9. Tris[1-[3,5-bis[4-(9*H*-carbazol-9-yl)butyloxy]-phenyl]-3-phenylpropane-1,3-dione](1,10-phenanthroline) europium (III) ([2Caz-G$_1$]$_3$-Eu, 12a). To a solution of **11a** (0.10 g, 0.14 mmol) and 1,10-phenanthroline monohydrate (11.3 mg, 57.2 μmol) in THF (10 mL), aqueous NaOH (1 mol L^{-1}, 0.20 mL) was syringed dropwise followed by aqueous $EuCl_3$ hexahydrate (17.5 mg, 48.2 μmol). Under the protection of argon, the mixture was stirred at 60 °C for 4 h and then cooled. The product was collected by filtration and washed with deionized water twice before crystallization with acetone and vacuum drying (57 mg), yield 49%. Mp: 89–92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.56 (br, 12H, CH_2), 1.86 (br, 12H, CH_2), 3.51 (br, 12H, CH_2), 4.24 (br, 12H, CH_2), 5.67 (br, 3H, =CH), 6.00 (br, 6H, Ph–H), 6.61–6.78 (m, 9H, Ph–H), 7.26–7.45 (m, 12H, Ph–H), 7.40–7.76 (m, 30H, Ph–H), 7.97 (br, 2H, phenanthroline–H), 8.10 (br, 15H, Ph–H), 8.53 (br, 2H, phenanthroline–H), 10.42 (br, 2H, phenanthroline–H), 10.71 (br, 2H, phenanthroline–H); MALDI-TOF MS *m/z*: 2425 [M$^+$]. Anal. Calcd for $C_{153}H_{131}EuN_8O_{12}$: C, 75.76; H, 5.44; N, 4.62. Found: C, 75.28; H, 5.07; N, 4.85.

4.1.10. Methyl 3,4,5-tris[4-(9*H*-carbazol-9-yl)butoxy]-benzoate ([3Caz-G$_1$]-COOMe, 10b). A mixture of 9-(4-bromobutyl)-9*H*-carbazole (3.00 g, 9.93 mmol), methyl 3,4,5-trihydroxy benzoate (0.60 g, 3.31 mmol), potassium carbonate (1.51 g, 10.9 mmol), and 18-crown-6 (0.13 g, 4.7 mmol) in anhydrous acetone (60 mL) was stirred vigorously, and refluxed for 56 h under the protection of nitrogen. After cooling, solvents under reduced pressure were removed, the resulting solid was filtrated, and recrystallized from ethanol to give a white needle-like crystal (2.13 g), yield 75%. Mp: 86–88 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 1.55–1.60 (m, 2H, –CH_2), 1.72–1.75 (m, 4H, –CH_2), 1.92–1.98 (m, 6H, –CH_2), 3.84–3.88 (m, 5H, –OCH_3, –CH_2), 3.91 (t, 4H, J=6.1 Hz, –CH_2), 4.10 (t, 2H, J=7.1 Hz, –CH_2), 4.21 (t, 4H, J=7.0 Hz, –CH_2), 7.17 (s, 2H, Ph–H), 7.19–7.21 (m, 6H, Ph–H), 7.24 (t, 2H, J=1.3, 7.2 Hz, Ph–H), 7.29 (d, 4H, J=8.2 Hz, Ph–H), 7.36–7.42 (m, 6H, Ph–H), 8.05 (d, 2H, J=7.7 Hz, Ph–H), 8.06 (d, 4H, J=5.0 Hz, Ph–H). MALDI-TOF MS (FAB): *m/z* 847.9 [M$^+$+1], 846.9 [M$^+$]. Anal. Calcd for $C_{56}H_{53}N_3O_5$: C, 79.31; H, 6.30; N, 4.95. Found: C, 79.08; H, 6.11; N, 5.20.

4.1.11. 1-[3,4,5-Tris[4-(9*H*-carbazol-9-yl)butoxy]phenyl]-3-phenylpropane-1,3-dione ([3Caz-G$_1$]-L, 11b). To a dry flask containing a solution of acetophenone (0.21 g, 1.76 mmol) and **10b** (1.50 g, 1.76 mmol) in THF (60 mL) was added quickly 60% sodium hydride (0.10 g, 2.5 mmol). The reaction mixture was heated at 60 °C for 90 h under argon. The solution was then acidified with dilute HCl, and extracted with CH_2Cl_2. After solvent removal, the solid residue was purified via a silica gel column (CH_2Cl_2/CCl_4, 1:2/v:v), a light yellow oil was obtained (0.49 g), yield 29.7%. Mp: 71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.60–1.65 (m, 2H, –CH_2), 1.74–1.78 (m, 4H, –CH_2), 1.94–2.03 (m, 6H, –CH_2), 3.88 (t, 2H, J=6.1 Hz, –CH_2), 3.94 (t, 4H, J=7.2 Hz, –CH_2), 4.12 (t, 2H, J=6.1 Hz, –CH_2), 4.22 (t, 4H, J=7.1 Hz, –CH_2), 6.65 (s, 1H, =CH), 7.08 (s, 2H, Ph–H), 7.17–7.21 (m, 6H, Ph–H), 7.25–7.28 (m, 2H, Ph–H), 7.30 (d, 4H, J=8.2 Hz, Ph–H), 7.37–7.41 (m, 6H, Ph–H), 7.47 (t, 2H, J=7.8, 7.5 Hz, Ph–H), 7.54 (t, 1H, J=7.8, 7.7 Hz), 7.92 (d, 2H, J=7.2 Hz), 8.07 (t, 6H, J=7.6, 6.8 Hz, Ph–H). MS (FAB): *m/z* 974.4 [M$^+$+K], 958.4 [M$^+$+Na]. Anal. Calcd for $C_{63}H_{57}N_3O_5$: C, 80.83; H, 6.14; N, 4.49. Found: C, 80.58; H, 5.87; N, 4.70.

4.1.12. Tris[1-[3,4,5-tris[4-(9*H*-carbazol-9-yl)butoxy]-phenyl]-3-phenyl-propane-1,3-dione](1,10-phenanthroline) europium (III) ([3Caz-G$_1$]$_3$-Eu, 12b). To a solution of **11b** (226 mg, 240 μmol) and 1,10-phenanthroline monohydrate (16 mg, 81 μmol) in THF (10 mL), aqueous NaOH (mol L^{-1}, 0.38 mL) was syringed dropwise, followed by aqueous $EuCl_3 \cdot 6H_2O$ (29.4 mg, 80 mmol). The mixture was stirred at 60 °C for 4 h under the protection of nitrogen. After cooling, the product was filtrated, washed with deionized water, and recrystallized from acetone to give light

yellow powder (180 mg), yield 71.6%. Mp: 84–87 °C. MALDI-TOF MS *m/z*: 3143.6 [M^+]. Anal. Calcd for $C_{201}H_{176}EuN_{11}O_{15}$: C, 76.94; H, 5.65; N, 4.91. Found: C, 76.58; H, 5.28; N, 5.16.

4.1.13. 3,5-Bis[4-(9*H*-carbazol-9-yl)butoxy]benzoic acid ([2Caz-G$_1$]-COOH, 13a). To a solution of **12a** (3.0 g, 4.92 mmol) in THF (60 mL) was added NaOH (0.4 g, 10 mmol) aqueous solution (20 mL) and the solution was heated to reflux with stirring for 8 h. When the solution was cooled to room temperature, it was poured into dilute HCl solution. The precipitate was filtrated and dried to get a white solid (2.7 g) in 93% yield. Mp: 179–181 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.72–1.76 (m, 4H, CH_2), 2.10–2.15 (m, 4H, CH_2), 3.90 (t, 4H, J=6.0 Hz, –OCH_2), 4.40 (t, 4H, J=7.0 Hz, –NCH_2), 6.54 (s, 1H, Ph–H), 7.17 (s, 2H, Ph–H), 7.22 (t, 4H, J=6.9 Hz, Ph–H), 7.38–7.50 (m, 8H, Ph–H), 8.10 (d, 4H, J=7.4 Hz, Ph–H). MALDI-TOF MS (FAB): *m/z* 597.2 [M^++1], 596.2 [M^+] (100%), 595.2 [M^+−1]. Anal. Calcd for $C_{39}H_{36}N_2O_4$: C, 78.50; H, 6.08; N, 4.69. Found: C, 78.23; H, 5.80; N, 4.83.

4.1.14. 1-[3,5-Bis[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy] benzoyloxy]phenyl]-3-phenylpropane-1,3-dione ([4Caz-G2]-L, 14a). To a solution of **13a** (0.28 g, 0.47 mmol), **4** (55 mg, 0.21 mmol) in dry CH_2Cl_2 (50 mL) was added 4-(dimethylamino)-pyridinium *p*-toluenesulphonate (DPTS) (25 mg, 0.08 mmol). The mixture was stirred at 25 °C for 15 min under nitrogen atmosphere. Dicyclohexylcarbodiimide (DCC) (0.10 g, 0.48 mmol) was then added and stirred at room temperature for 24 h. The reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. Pure product was obtained (0.16 g) via column chromatograph eluting with initially CH_2Cl_2 and then a mixture of CH_2Cl_2/acetone (4:1). The yield was 55%. Mp: 62–64 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.89 (m, 8H, CH_2), 2.11–2.15 (m, 8H, CH_2), 3.99 (t, 8H, J=6.1 Hz, –OCH_2), 4.41 (t, 8H, J=7.1 Hz, –NCH_2), 6.61 (s, 2H, Ph–H), 6.84 (s, 1H, =CH), 7.21 (t, 8H, J=7.4, 7.2 Hz, Ph–H), 7.26 (d, 4H, J=5.7 Hz, Ph–H), 7.34 (s, 1H, Ph–H), 7.41 (t, 8H, J=8.0, 7.8 Hz, Ph–H), 7.44 (d, 8H, J=7.5 Hz), 7.46 (t, 2H, J=8.0, 8.2 Hz, Ph–H), 7.56 (t, 1H, J=7.4, 7.9 Hz, Ph–H), 7.74 (d, 2H, J=2.0 Hz, Ph–H), 7.98 (d, 2H, J=7.8 Hz, Ph–H), 8.10 (d, 8H, J=7.7 Hz, Ph–H). MALDI-TOF MS *m/z*: 1412.7 [M^+], 1411.7 [M^+−1]. Anal. Calcd for $C_{93}H_{80}N_4O_{10}$: C, 79.01; H, 5.70; N, 3.96. Found: C, 78.75; H, 5.56; N, 4.23.

4.1.15. Tris[1-[3,5-bis[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]-benzoyloxy]phenyl]-3-phenylpropane-1,3-dione](1,10-phenanthroline) europium (III) ([4Caz-G$_2$]$_3$-Eu, 15a). To a solution of **14a** (0.15 g, 106 μmol) and 1,10-phenanthroline monohydrate (7.1 mg, 35.8 μmol) in THF (10 mL), triethylamine (0.10 mL) was syringed dropwise, followed by a solution of $EuCl_3$ hexahydrate (12.9 mg, 35.3 μmol) in ethanol (4 mL). After injection of argon repeatedly, the mixture was stirred at 60 °C for 4 h and then cooled. The product was collected by filtration and washed with deionized water twice before crystallization with acetone and vacuum drying (0.12 g), yield 74.4%. Mp: 60–62 °C. MALDI-TOF MS *m/z*: 4590.3 [M^++Na], 4606.4 [M^++K]. Anal. Calcd for $C_{291}H_{245}EuN_{14}O_{30}$: C, 76.48; H, 5.40; N, 4.29. Found: C, 76.09; H, 5.13; N, 4.50.

4.1.16. 3,4,5-Tris[4-(9*H*-carbazol-9-yl)butoxy]benzoic acid ([3Caz-G$_1$]-COOH, 13b). Similar to **13a** to get white solid in 95% yield. Mp: 85–86 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.58–1.62 (m, 2H, CH_2), 1.76–1.81 (m, 4H, CH_2), 1.97–2.02 (m, 6H, CH_2), 3.88 (t, 2H, J=6.0 Hz, –OCH_2), 3.92 (t, 4H, J=6.0 Hz, –OCH_2), 4.13 (t, 2H, J=7.2 Hz, –NCH_2), 4.22 (t, 4H, J=7.0, 7.0 Hz, –NCH_2), 7.20–7.22 (m, 8H, Ph–H), 7.23–7.25 (m, 2H, Ph–H), 7.29 (d, 4H, J=8.1 Hz, Ph–H), 7.39–7.44 (m, 6H, Ph–H), 8.08–8.12 (m, 6H, Ph–H). MALDI-TOF MS (FAB): *m/z* 835.4 [M^++1], 834.4 [M^+], 833.4 [M^+−1]. Anal. Calcd for $C_{55}H_{51}N_3O_5$: C, 79.21; H, 6.16; N, 5.04. Found: C, 79.04; H, 6.01; N, 5.20.

4.1.17. 1-[3,5-Bis[3,4,5-tri[4-(9*H*-carbazol-9-yl)butoxy]-benzoyloxy]phenyl]-3-phenylpropane-1,3-dione ([6Caz-G$_2$]-L, 14b). Similar to **14a** to get light yellow solid in 60% yield. Mp: 93–95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.55–1.61 (m, 4H, CH_2), 1.69–1.74 (m, 8H, CH_2), 1.89–1.98 (m, 12H, CH_2), 3.88 (t, 4H, J=6.1, 6.2 Hz, CH_2), 3.91 (t, 8H, J=6.1 Hz, CH_2), 4.10 (t, 4H, J=7.0 Hz, CH_2), 4.21 (t, 8H, J=7.1 Hz, CH_2), 6.80 (s, 1H, =CH), 7.16–7.21 (m, 13H, Ph–H), 7.25–7.31 (m, 10H, Ph–H), 7.30 (d, 8H, J=6.6 Hz, Ph–H), 7.37 (t, 12H, J=7.1, 7.4 Hz, Ph–H), 7.46 (t, 2H, J=7.5, 8.1 Hz, Ph–H), 7.62 (t, 1H, J=7.4, 7.7 Hz, Ph–H), 7.85 (d, 2H, J=7.7 Hz, Ph–H), 8.04 (d, 8H, J=5.3 Hz, Ph–H), 8.07 (d, 4H, J=7.8 Hz, Ph–H). ^{13}C NMR ($CDCl_3$): δ ppm, 25.6, 25.7, 27.0, 27.8, 42.5, 68.8, 72.9, 93.4, 108.6, 118.0, 118.8, 119.7, 120.4, 122.8, 123.4, 125.6, 127.3, 128.7, 132.8, 135.1, 137.9, 140.3, 142.8, 151.6, 152.6, 164.2, 183.4, 186.2. MALDI-TOF MS *m/z*: 1890.4 [M^++2], 1889.4 [M^++1], 1888.4 [M^+], 1887.4 [M^+−1]. Anal. Calcd for $C_{125}H_{110}N_6O_{12}$: C, 79.51; H, 5.87; N, 4.45. Found: C, 79.33; H, 5.68; N, 4.68.

4.1.18. Tris[1-[3,5-bis[3,4,5-tri[4-(9*H*-carbazol-9-yl)butoxy]-benzoyloxy]phenyl]-3-phenylpropane-1,3-dione](1,10-phenanthroline) europium (III) ([6Caz-G$_2$]$_3$-Eu, 15b). Similar to **15a** to get light yellow solid in 85% yield. Mp: 83–85 °C. MALDI-TOF MS *m/z*: 5989.2 [M^+−4]. Anal. Calcd for $C_{387}H_{335}EuN_{20}O_{36}$: C, 77.55; H, 5.63; N, 4.67. Found: C, 77.16; H, 5.36; N, 4.96.

4.1.19. 3,5-Bis[4-(9*H*-carbazol-9-yl)butoxy]benzyl alcohol ([2Caz-G$_1$]-OH, 16). A mixture of 9-(4-bromobutyl)-9*H*-carbazole (4.40 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.00 g, 7.1 mmol), potassium carbonate (3.40 g, 60 mmol), and 18-crown-6 (0.38 g, 1.42 mmol) in anhydrous acetone (50 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and water, and the aqueous layer was extracted with CH_2Cl_2 (40 mL×3). The combined extracts were dried with anhydrous $MgSO_4$ and evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **16** as pale yellow crystalline solid (3.5 g, yield 83%). Mp: 118–120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.83–1.88 (m, 4H, CH_2), 2.14–2.19 (m, 4H, CH_2), 3.85 (t, 4H, J=6.1 Hz, –OCH_2), 4.37 (t, 4H, J=7.1 Hz, –NCH_2), 4.71 (s, 2H, –CH_2OH), 6.25 (s, 1H, Ph–H), 6.54 (s, 2H, Ph–H), 7.21 (t, 4H, J=6.8, 1.0 Hz, Ph–H), 7.42 (d, 4H, J=8.0 Hz, Ph–H), 7.48 (t, 4H, J=7.9, 1.0 Hz, Ph–H), 8.23 (d, 4H,

J=7.8 Hz, Ph–H). MS (FAB): m/z 597.7 [M^++1], 596.6 [M^+] (100%).

4.1.20. 3,5-Bis[4-(9*H*-carbazol-9-yl)butoxy]benzyl bromide ([2Caz-G$_1$]-Br, 17). A mixture of compound **16** (1.00 g, 1.68 mmol), CBr_4 (0.57 g, 1.72 mmol) in dry CH_2Cl_2 (20 mL) was cooled to 0 °C. Triphenylphosphine (0.48 g, 1.72 mmol) was then slowly added and stirred for 5 h. After removal of CH_2Cl_2, the product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to give pale yellow powder (1.02 g), yield 92.1%. Mp: 163–164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.83–1.87 (m, 4H, CH_2), 2.15–2.19 (m, 4H, CH_2), 3.85 (t, 4H, J=6.1 Hz, –OCH_2), 4.22 (s, 2H, –CH_2Br), 4.37 (t, 4H, J=7.1 Hz, –NCH_2), 6.30 (s, 1H, Ph–H), 6.45 (s, 2H, Ph–H), 7.22 (t, 4H, J=7.3 Hz, Ph–H), 7.4 (d, 4H, J=8.0 Hz, Ph–H), 7.48 (t, 4H, J=7.8 Hz, 1.0 Hz, Ph–H), 8.21 (d, 4H, J=7.8 Hz, Ph–H). MS (FAB): m/z 659.6 [M+2]$^+$, 657.6 [M^+] (100%), 579.8 [M^+−Br]. Anal. Calcd for $C_{39}H_{37}BrN_2O_2$: C, 72.55; H, 5.78; N, 4.34. Found: C, 72.32; H, 5.62; N, 4.53.

4.1.21. Methyl 3,5-bis[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzyloxy]benzoate ([4Caz-G$_2$]-COOMe, 18). A mixture of **17** (3.00 g, 4.64 mmol), methyl 3,5-dihydroxybenzoate (0.40 g, 2.38 mmol), potassium carbonate (1.00 g, 7.25 mmol), and 18-crown-6 (0.13 g, 4.7 mmol) in anhydrous acetone (100 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was washed with water and a large amount of precipitate appeared followed by filtration. After column chromatography on silica gel using CH_2Cl_2 as eluent, a white powder was obtained (2.5 g), yield 81%. Mp: 75–77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.89–1.93 (m, 8H, CH_2), 2.05–2.09 (m, 8H, CH_2), 3.88 (s, 3H, –OCH_3), 3.99 (t, 8H, J=6.0 Hz, –OCH_2), 4.37 (t, 8H, J=7.1 Hz, –NCH_2), 4.92 (s, 4H, –OCH_2Br), 6.25 (s, 2H, Ph–H), 6.40 (s, 5H, Ph–H), 6.51 (s, 2H, Ph–H), 7.23 (t, 8H, J=7.8, 1.0 Hz, Ph–H), 7.42 (d, 8H, J=8.1 Hz, Ph–H), 7.46 (t, 8H, J=7.9, 1.0 Hz, Ph–H), 8.20 (d, 8H, J=7.8 Hz, Ph–H). Anal. Calcd for $C_{86}H_{80}N_4O_8$: C, 79.60; H, 6.21; N, 4.32. Found: C, 79.42; H, 6.02; N, 4.25.

4.1.22. 3,5-Bis[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzyloxy]benzoic acid ([4Caz-G$_2$]-COOH, 19). To a solution of **18** (1.27 g, 0.985 mmol) in THF (30 mL) was once added sodium hydroxide aqueous solution (0.20 g, 10 mL). The solution was heated to reflux for 5 h prior to concentration. The residue was washed with water and filtered. The crude product was column chromatographed eluting with initially dichloromethane and then with chloroform/ethanol (25:1) to give **19**, and it was further purified by recrystallization from ethanol as a white solid (1.10 g) in 93% yield. Mp: 94–96 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.80–1.84 (m, 8H, CH_2), 2.06–2.11 (m, 8H, CH_2), 3.90 (t, 8H, J=6.0 Hz, –OCH_2), 4.40 (t, 8H, J=7.0 Hz, –NCH_2), 4.92 (s, 4H, –OCH_2), 6.32 (s, 2H, Ph–H), 6.50 (s, 4H, Ph–H), 6.75 (s, 1H, Ph–H), 7.20 (t, 8H, J=7.1 Hz, Ph–H), 7.25 (s, 2H, Ph–H), 7.30–7.50 (m, 16H, Ph–H), 8.12 (d, 8H, J=7.6 Hz, Ph–H). MALDI-TOF MS m/z: 1282.8 [M^+]. Anal. Calcd for $C_{85}H_{78}N_4O_8$: C, 79.54; H, 6.13; N, 4.36. Found: C, 79.30; H, 5.95; N, 4.53.

4.1.23. 1-[3,5-Bis[3,5-bis[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzyloxy]benzoyloxy]phenyl]-3-phenyl propane-1,3-dione ([8Caz-G$_3$]-L, 20). To a solution of **19** (0.60 g, 0.47 mmol), **4** (55 mg, 0.22 mmol) in dry dichloromethane (50 mL) was added 4-(dimethylamino)-pyridinium p-toluenesulphonate (DPTS) (50 mg, 0.17 mmol). The contents were stirred at 25 °C for 15 min under nitrogen atmosphere. Dicyclohexylcarbodiimide (DCC) (0.20 g, 0.97 mmol) was then added and stirring continued at room temperature for 24 h, during this time a precipitate of dicyclohexyl urea appeared. The reaction mixture filtered and the filtrate evaporated to dryness under reduced pressure, pure product (0.15 g) was obtained via column chromatograph eluting with initially CH_2Cl_2 and then a mixture of CH_2Cl_2/acetone (4:1), yield 17%. Mp: 68–70 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm, 1.89–1.95 (m, 16H, CH_2), 2.05–2.13 (m, 16H, CH_2), 3.99 (t, 16H, J=6.2 Hz, –OCH_2), 4.37 (t, 16H, J=7.2 Hz, –NCH_2), 4.98 (s, 8H, –OCH_2), 5.30 (s, 1H, Ph–H), 6.32 (s, 4H, Ph–H), 6.51 (s, 8H, Ph–H), 6.73 (s, 1H, Ph–H), 6.78 (s, 1H, Ph–H), 6.83 (s, 1H, ═CH), 7.19 (t, 16H, J=7.3 Hz, Ph–H), 7.38–7.48 (m, 40H, Ph–H), 7.54 (t×d, 1H, J=7.8 Hz, 1.2 Hz, Ph–H), 7.95 (d, 2H, J=7.6 Hz, Ph–H), 8.07 (d, 16H, J=7.8 Hz, Ph–H). MALDI-TOF MS m/z: 2788.2 [M^++1]. Anal. Calcd for $C_{185}H_{164}N_8O_{18}$: C, 79.72; H, 5.93; N, 4.02. Found: C, 79.32; H, 5.75; N, 4.35.

4.1.24. Tris[1-[3,5-bis[3,5-bis[3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzyloxy]benzoyloxy]phenyl]-3-phenylpropane-1,3-dione](1,10-phenanthroline) europium (III) ([8Caz-G$_3$]$_3$-Eu, 21). Similar to **15** in yield 87.4%. Mp: 81–82 °C. MALDI-TOF MS m/z: 8722.2 [M^++Na]. Anal. Calcd for $C_{567}H_{497}EuN_{26}O_{54}$: C, 78.36; H, 5.76; N, 4.19. Found: C, 77.95; H, 5.44; N, 4.31.

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