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Polyaryl Ether Dendrimer with a 4-Phenylacetyl-5-pyrazolone-based Terbium(III) Complex as Core: Synthesis and Photopysical Properties

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A series of novel dendritic β-diketone ligands, 1-phenyl-3-[G-*n*]-4-phenylacetyl-5-pyrazolone ($n = 0$–3, G stands for polyaryl ether), were synthesized by introducing Fréchet-type dendritic branches. The corresponding Tb^{3+}-cored dendritic complexes were characterized by X-ray crystallography, elemental analysis, ESI mass spectra, and FT-IR spectra. These dendritic complexes, prepared from aqueous solution, exhibit high stability. Interestingly, the study of photophysical properties shows that the luminescence quantum yields of the dendritic Tb-complexes increase from 0.1 to 2.26% with an increase of the dendritic generation from 0 to 3. Importantly, an “energy-reservoir effect” was observed in the dendritic system using the method based on the resonance energy transfer from these complexes to rhodamine 6G. With the increase of the dendritic generation, the metal-centered luminescence quantum yield was almost the same, and the energy transfer (ϕ_{transfer}) from the ligand to Tb^{3+} increased. Further measurements of the triplet state and oxygen quenching of these dendritic complexes verify that this enhancement of the energy transfer (ϕ_{transfer}) is attributed to both an “antenna effect” and a “shell effect”.

Introduction

Because luminescent lanthanide complexes display unusual photophysical properties (long luminescence lifetime, very sharp emission band, and a large Stokes shift),[1] rare earth complexes, especially terbium(III) and europium(III) complexes, as photoluminescent materials, have attracted attention not only for academic interest but also for their potential applications, such as bioassays,[2] chemosensors,[3] electroluminescent devices, and laser systems.[4−9] Generally, the Eu(III) and Tb(III) ions show very weak absorption in the visible region of the spectrum and often require the application of strongly absorbing “antennae” for light harvesting to obtain efficient photoluminescence. Among them, the β-diketone ligand is one kind of the important antennae for the Eu(III) and Tb(III) ions.[4−6]

Dendrimers are monodisperse macromolecules with a special treelike molecular architecture synthesized with precisely tuned structural components, the core, branches,

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and surface terminal groups, to have particular chemical and physical properties.[10,11] Recently, the dendrimer as a light-harvesting material has received particular attention,[11] and some photoresponsive dendrimers which are a combination of a metal cation-binding subunit (such as Tb^{3+}, Eu^{3+}, Ru^{2+}, and Cu^{+}) and an efficient ultraviolet light-harvesting dendron have been reported.[12] The development of strategies for the synthesis of dendrimers based on novel cores, especially, luminescent lanthanide complexes and branches, continues to be one of the important aspects of dendrimer chemistry. At present, some Tb^{3+}-cored dendrimer complexes have been reported previously.[12a−d] Fréchet and co-workers found that the dendritic shell could achieve site isolation of the Ln^{3+} cation and maximize their luminescent characteristics.[12a,c] Simth et al. studied the effect of Lewis acids on dendritic lanthanide complexes.[13] However, for the weak noncovalent ionic interaction of the dendritic carboxylyate subunit with the Ln^{3+} cation and the dynamic equilibrium between the dendrons and self-assembled dendrimers, these dendritic lanthanide complexes should be obtained under anhydrous and high-temperature conditions.

In our previous papers, we reported 4-acyl-5-pyrazolone-based ligands with different substituents which could be used as sensitizers for the terbium(III) and europium(III) ions.[7,8] For example, the terbium complexes based on 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone[7] and 1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolone[7] can emit characteristic Tb(III) luminescence with a high quantum yield. In a continuation of with our investigations on the lanthanide complexes, a facile synthetic routine of poly(aryl ether) dendritic ligands LG-*n* ($n = 0-3$) (see Scheme 1), based on the 4-phenylacethyl-5-pyrazolone group, was reported herein, and a series of novel dendrimer complexes $Tb(LG\text{-}n)_3$ ($n = 0-3$) (see Scheme 1) were synthesized by combining the Tb^{3+}-cored complexes with the Fréchet-type polylbenzyl ether dendrons. The dendrimers were characterized successfully by elemental analysis, ESI mass spectra, and FT-IR spectra, and the low-generation dendrimers $Tb(LG\text{-}0)_3$ and $Tb(LG\text{-}1)_3$ have been characterized by X-ray crystallography. Moreover, the photophysical properties, including the ligand-sensitized Tb^{3+} emission behavior, have been investigated.

Results and Discussion

Synthesis and Characterization of the Dendrimer Complexes $Tb(LG\text{-}n)_3$ ($n = 0-3$). The dendritic ligands 1-phenyl-3-[G−*n*]-4-phenyl-5-pyrazolones were prepared using benzyl ether-type dendrons [G−*n*]-X ($n = 1-3$) as building blocks, where [G−*n*]-X refers to dedrons with *n* as the generation numbers and X as the functional group located at the focal point, according to Scheme 2 and were characterized by NMR spectra. Dendritic benzylic bromides of the first ($n = 1$) and second ($n = 2$) generations were prepared according to the general procedure developed by Hawer and Fréchet.[14] Subsequent modification of [G−*n*]-Br with 3,5-dihydrobenzyl ketone, potassium carbonate, and [18]-crown-6 in acetone gave dendritic ketones with rather good yields. Then, the dendritic ketones were converted to the corresponding β-diketone esters using the Claisen condensation method.[15] In the presence of 2 equiv of NaH and diethyl carborate in anhydrous THF, the reaction proceeded efficiently when the mixture was heated at 70 °C for 6−8 h, producing the corresponding β-diketone esters in high yields (>90%).

Generally, small molecular 5-pyrazolones were synthesized by using β-diketone esters and hydrazines under room temperature.[16] However, no product was obtained by the condensation of the dendritic β-diketone esters with hydrazine at room temperature. It seems that the steric hindrance and electron-richness of the benzyl ether-type dendron substitution seriously retarded the progress of the reaction. Hence, it was necessary to increase the reaction temperature and prolong the reaction time; the pyrazolone dendrons were obtained successfully in refluxing xylene under the protection of N_2 in 2 days. After the mixture was cooled, the raw product was separated and recrystallized from $CHCl_3$ to give the purified product in a yield of ∼50%. The acylpyrazolones, accessible from pyrazolone via the method of Jensen (heating with $RCOCl/Ca(OH)_2$, $Ba(OH)_2$ in THF),[17] were transformed into the corresponding ligands 1-phenyl-3-[G-*n*]-4-phenylacetyl-5-pyrazolone. However, because of the steric hindrance, the higher generation ligands were obtained with lower yields: the yield of the third generation product, LG-3, was only 12%.

These compounds were well characterized by spectroscopic data. For the conversion of the enol form into ketone form β-diketone ligands, no obvious ^1H NMR signals were observed for the hydrogen atoms of the pyrazolone ring. The ^1H NMR signals of methylene hydrogen atoms of the phenylacetyl were shifted from 3.78 to 3.68 and 3.60 ppm for the first and second generation ligands, respectively. However, no obvious shift was observed for the third generation ligand (LG-3). With the increase of the dendron

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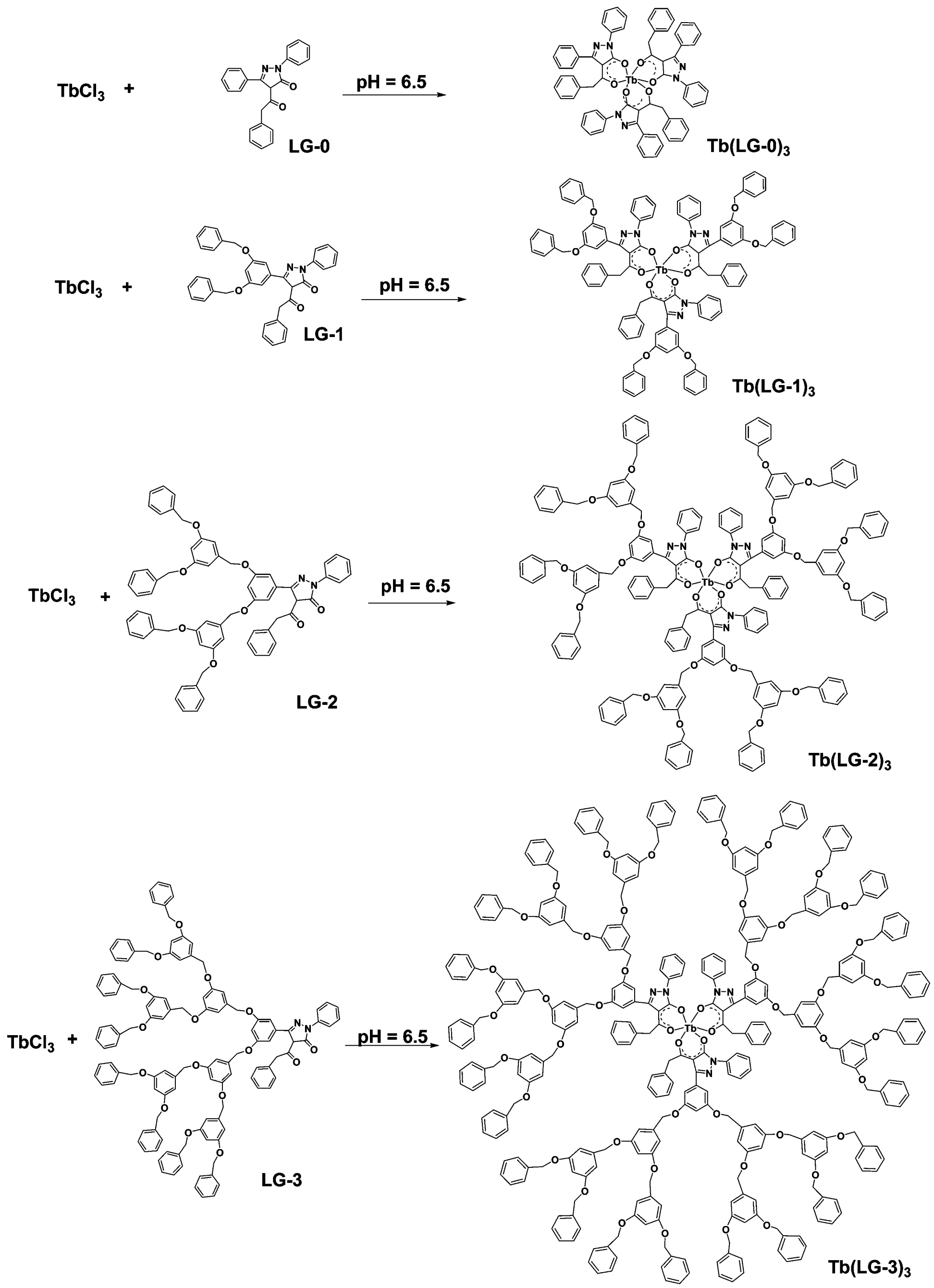
Scheme 1. Chemical Structures and the Synthetic Routine of Tb(LG-*n*)$_3$ ($n = 0-3$)

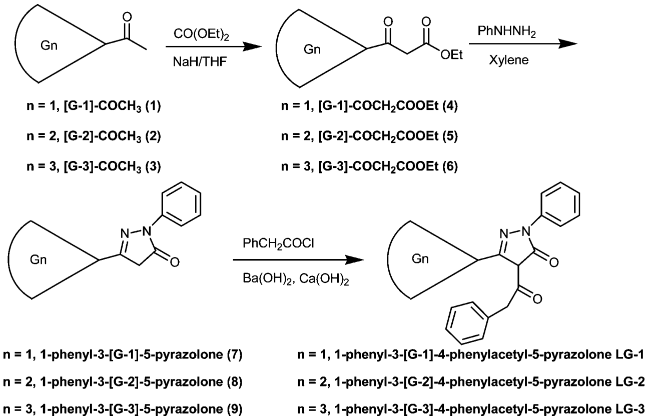


generation, ^{1}H NMR and ^{13}C NMR signals become more complicated, and it is difficult to discern the structure of the ligand LG-3. To assess more clearly the identity of the chemical structure, further characterization has been performed by matrix-assisted laser desorption ionization time-of flight (MALDI-TOF) mass spectroscopy. The MALDI-TOF MS of each dendron showed the molecular ion peaks [$M + Na^+$, $M + K^+$, or $M + Ag^+$].

The complexes were then obtained in an EtOH/H_2O solution from $TbCl_3$, and the corresponding dendritic ligands (1:3 mole ratio) at pH of 6.5. They all have good solubility in some common organic solvents such as chloroform, toluene, and acetone. However, compared with the ligands, the solubility of the corresponding complexes was decreased. To confirm the formation of the terbium(III) complex, all Tb^{3+}-cored dendrimer complexes were characterized by FT-IR spectra, elemental analysis, and ESI mass spectra.

Figure 1 shows the FT-IR spectra for the second generation pyrazolone-based ligand (LG-2) and the corresponding complex Tb(LG-2)$_3$. The free pyrazolone ligand LG-2 exhibited two types of strong C═O bond stretching vibrations at 1633 and 1596 cm^{-1}, respectively. The former peak was assigned to the $\nu_{C=O}$ vibration at the 5-position of the pyrazolone ring. The coordination of the terbium ion to the oxygen atom of the carbonyl group weakened the C═O band. The latter peak was attributed to the acyl carbonyl group which has some single-bond characteristic because of the keto−enol tautomerization of the β-diketone group. However, after coordination of the terbium ion, the two bands of the pyrazolone dendron disappeared, and a new band at 1594

Scheme 2. Synthetic Routine of Dendritic Ligands LG-n ($n = 0-3$)



cm^{-1} was observed. This indicates that the ligand was coordinated with the terbium ion, and the new band was strengthened by equalization of a single double-bond length upon complexation. Similar phenomena were observed for the comparison of the other pyrazolone-based ligand dendrons with their corresponding Tb complexes.

Mass spectrometry was used to provide further characterization of the dendritic Tb complexes Tb(LG-n)$_3$ (n = 0−2). In the previous reports, none of mass spectrometry characterization was achieved for the dendritic lanthanide complexes because of their fragile nature, resulting from the weak noncovalent ionic interaction of the dendritic carboxylate ligands with the Ln^{3+} cation. Our electrospray mass spectrum (ESI) gave a molecular ion peak corresponding to the mass of the three pyrazolone ligands coordinating to one terbium ion [3(LG-n−H)$^-$ + Tb^{3+} + H^+] without a neutral small molecule. The values of the molecular ion peak for Tb(LG-0)$_3$, Tb(LG-1)$_3$, and Tb(LG-2)$_3$ were m/z 1219.9 (M + H^+), 1856.9 (M + H^+), and 3126.9 (M + H^+), respectively. The molecular ion peak of Tb(LG-3)$_3$ could not be observed because the limit of our electrospray detector was <4000 (m/z). These facts suggest that the 4-acyl-5-pyrazolone ligands showed strong coordination ability to the terbium ion, and their complexes could be characterized as readily as covalent molecules.

Crystal Structure Characterization of Tb(LG-0)$_3$(EtOH)(H_2O) and Tb(LG-1)$_3$(H_2O)$_2$. The solid-state structures of Tb(LG-0)$_3$(EtOH)(H_2O) and Tb(LG-1)$_3$(H_2O)$_2$ were determined by the X-ray diffraction study. The ORTEP diagrams for the asymmetric unit of Tb(LG-0)$_3$(EtOH)(H_2O) and Tb(LG-1)$_3$(H_2O)$_2$ are shown in Figures 2 and 3, respectively. Details of the crystal data and parameters for Tb(LG-0)$_3$(EtOH)(H_2O) and Tb(LG-1)$_3$(H_2O)$_2$ are given in Table 1. Selected bond lengths and bond angles for Tb(LG-0)$_3$(EtOH)(H_2O) and Tb(LG-1)$_3$(H_2O)$_2$ are listed in Table 2. Both of the complexes crystallizes in triclinic space group $P\bar{1}$, and the coordination geometry of the metal center is described as a dodecahedron.

In Tb(LG-0)$_3$(EtOH)(H_2O), there are eight O atoms coordinated to Tb^{3+}, six of which come from three β-diketones (O1, O2, O3, O4, O5, O6), and the others (O7 and O8) come from one ethanol molecule and one water molecule, respectively. The average distance of Tb−O is 2.368 Å (2.300(4)−2.455(5) Å), which is smaller than the sum of the radi of Tb^{3+} (0.98 Å, eight coordinated) and O^{2-} (1.42 Å), and the bond angles of O−Tb−O are 70.99(16)−146.87(16)°. The bond lengths between the oxygen and carbon atoms of the β-diketonato anions are almost unified (1.259(7), 1.272(7), 1.265(7), 1.241(7), 1.251(8), and 1.258(8) Å corresponding to C(7)−O(1), C(16)−O(2), C(30)−O(3), C(39)−O(4), C(53)−O(5), and C(62)−O(6), respectively), implying that strong conjugation exists in the chelate rings.

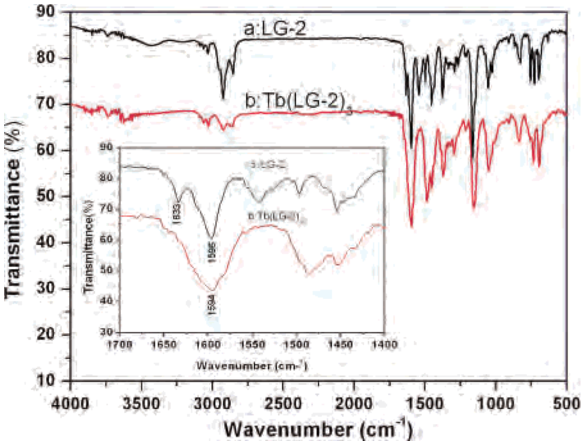


Figure 1. The FT-IR spectra for the dendritic LG-2 (a) and Tb(LG-2)$_3$ (b). The inset shows an expanded view of the FT-IR spectra for LG-2 and Tb(LG-2)$_3$ in the range of 1400−1700 cm^{-1}.

Similarly, in Tb(LG-1)$_3$(H_2O)$_2$, there are eight O atoms coordinated to Tb^{3+}, six of which come from three β-diketones (O1, O2, O3, O4, O5, O6) and two of which (O7 and O8) are from two water molecules. The average bond length between the terbium ion and the pyrazolone oxygen atom is 2.349 Å, which is slightly shorter than that between Tb^{3+} and the oxygen atom of water (2.452 Å). This may be the result of the negative charge of the pyrazolone oxygen, which could be more strongly coordinated to the terbium ion because of the electrostatic effect. The average C═C bond distance of the enol anion in the complex is 1.418 Å, and the C−C single bond distance is 1.54 Å, reflecting a certain amount of electron delocalization upon complexation.

UV−vis Spectra. The UV−vis absorption spectra of the dendritic ligands (LG-0, LG-1, LG-2, and LG-3) and their corresponding Tb(III) complexes are shown in Figure 4. The electronic spectra of the ligands LG-0, LG-1, LG-2, and LG-3 display the maximum absorption wavelengths at 257, 259, 259, and 275 nm, respectively, which are attributed to the singlet−singlet $\pi-\pi^*$ enol absorption of β-diketonates. Similarly, the maximum absorption bands peak at 264, 261, 274, and 275 nm for complexes Tb(LG-0)$_3$, Tb(LG-1)$_3$, Tb(LG-2)$_3$, and Tb(LG-3)$_3$, respectively. Compared with the spectra of LG-0, LG-1, LG-2, and LG-3, the first absorption bands of the corresponding terbium complexes are all red-shifted slightly, which is a consequence of the enlargement of the conjugate structure of ligands after the coordination to the terbium ion. The shapes of the absorption spectra of the terbium complexes in CH_3CN are similar to those of the corresponding ligands, indicating that the coordination of the terbium ion does not significantly influence the energy of the singlet state of the β-diketone ligands. The molar

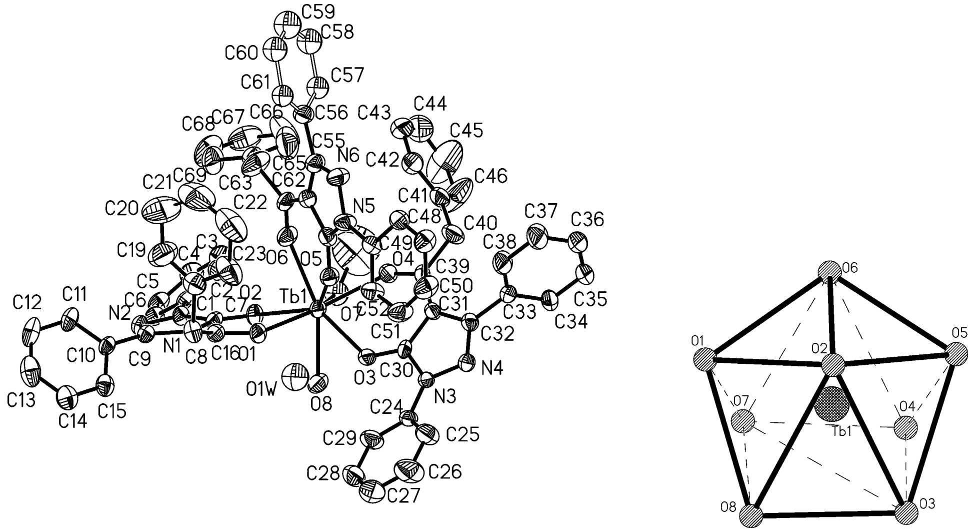


Figure 2. ORTEP diagram of $Tb(LG\text{-}0)_3(EtOH)(H_2O)$ with thermal ellipsoids drawn at the 30% probability level and the H atoms are removed for clarity.

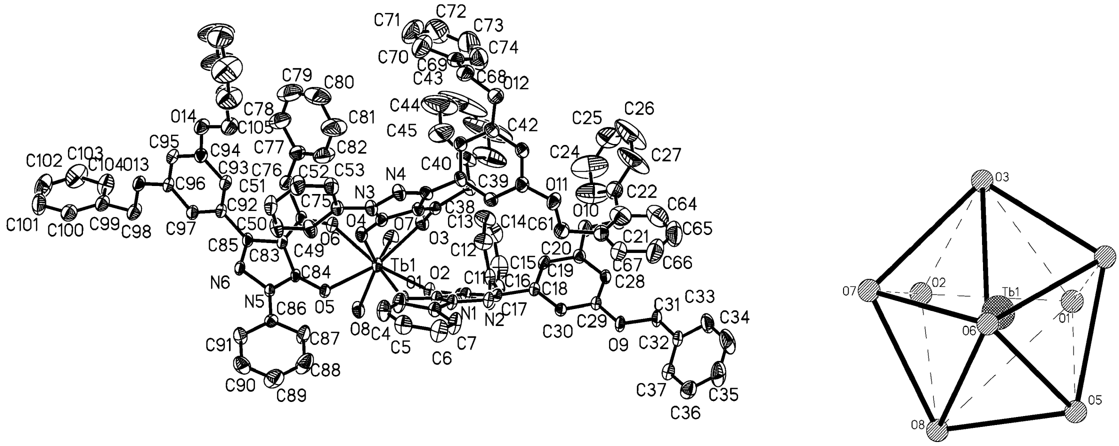


Figure 3. ORTEP diagram of $Tb(LG\text{-}1)_3(H_2O)_2$ with thermal ellipsoids drawn at the 30% probability level and the H atoms are removed for clarity.

Table 1. Crystal Data Collection and Structure Refinement

	$Tb(LG\text{-}0)_3(EtOH)(H_2O)$	$Tb(LG\text{-}1)_3(H_2O)_2$
empirical formula	$C_{71}H_{59}N_6O_{8.50}Tb$	$C_{111}H_{99}N_6O_{15}Tb$
fw	1291.16	1915.88
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
cryst size	0.50 × 0.40 × 0.20	0.15 × 0.10 × 0.08
a (Å)	11.995(2)	13.3740(12)
b (Å)	15.612(3)	17.2653(15)
c (Å)	16.549(3)	21.2036(18)
α (deg)	86.96(3)	92.8360(10)
β (deg)	77.81(3)	105.2690(10)
γ (deg)	84.53(3)	91.1850(10)
V (Å^3)	3013.6(10)	4714.5(7)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.423	1.350
μ (mm^{-1})	1.238	0.821
F(000)	1 320	1 984
R1 [$I > 2\sigma(I)$]	0.0593	0.0441
wR2 [$I > 2\sigma(I)$]	0.1229	0.1092
R1 (all data)	0.1081	0.0683
wR2 (all data)	0.1412	0.1269
GOF	1.042	1.048

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $Tb(LG\text{-}0)_3(EtOH)(H_2O)$ and $Tb(LG\text{-}1)_3(H_2O)_2$

	$Tb(LG-0)_3(EtOH)(H_2O)$		
Tb(1)−O(3)	2.300(4)	Tb(1)−O(6)	2.350(5)
Tb(1)−O(5)	2.331(5)	Tb(1)−O(2)	2.356(5)
Tb(1)−O(1)	2.362(4)	Tb(1)−O(4)	2.363(4)
Tb(1)−O(7)	2.428(6)	Tb(1)−O(8)	2.455(5)
C(7)−O(1)	1.259(7)	C(53)−O(5)	1.251(8)
C(16)−O(2)	1.272(7)	C(62)−O(6)	1.258(8)
C(30)−O(3)	1.265(7)	C(39)−O(4)	1.241(7)
O(3)−Tb(1)−O(6)	146.87(16)	O(3)−Tb(1)−O(5)	75.95(15)
O(1)−Tb(1)−O(8)	70.99(16)		
	$Tb(LG-0)_3(EtOH)(H_2O)$		
Tb(1)−O(1)	2.301(3)	Tb(1)−O(3)	2.362(3)
Tb(1)−O(5)	2.324(3)	Tb(1)−O(6)	2.368(3)
Tb(1)−O(4)	2.357(3)	Tb(1)−O(2)	2.378(3)
Tb(1)−O(8)	2.411(3)	C(1)−O(1)	1.277(4)
Tb(1)−O(7)	2.492(3)	C(9)−O(2)	1.264(4)
C(47)−C(46)	1.431(6)	C(1)−C(8)	1.422(5)
C(8)−C(9)	1.412(5)	C(75)−O(6)	1.253(5)
C(38)−O(3)	1.263(5)	C(47)−O(4)	1.258(5)
C(84)−O(5)	1.270(4)	C(46)−C(38)	1.406(6)
C(75)−C(83)	1.412(6)	C(83)−C(84)	1.423(5)

absorption coefficients (ϵ) of ligands LG-0, LG-1, LG-2, and LG-3 are calculated to be 2.8 × 10^4 (257), 2.8 × 10^4 (259), 2.6 × 10^4 (259), and 3.4 × 10^4 L mol^{-1} cm^{-1} (275 nm), respectively, revealing that these dendritic ligands have a strong ability to absorb light. Similarly, the determined molar absorption coefficients (ϵ) of the terbium complexes Tb(LG-0)$_3$, Tb(LG-1)$_3$, Tb(LG-2)$_3$, and Tb(LG-3)$_3$ are 7.8 × 10^4 (264), 7.6 × 10^4 (261), 8.4 × 10^4 (274), and 1.0 × 10^5 L mol^{-1} cm^{-1} (275 nm), respectively, which are about three

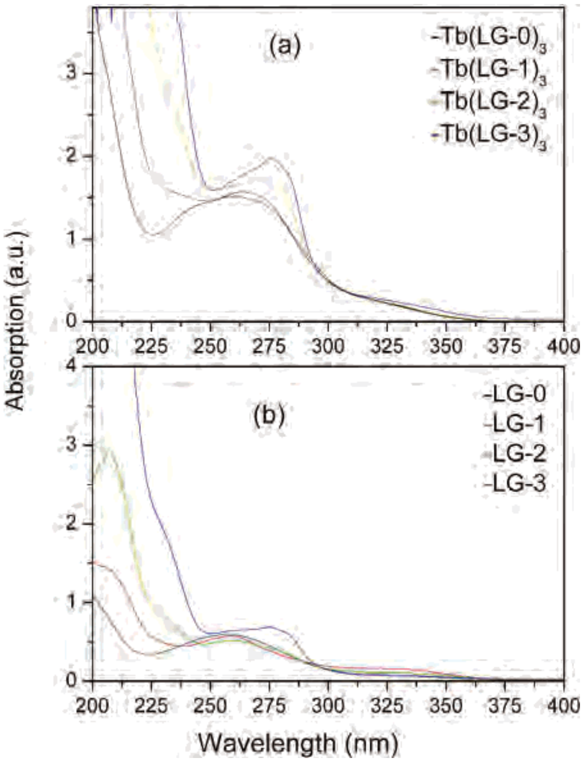


Figure 4. Absorption spectra of the dendritic Tb(III) complexes (a) and the corresponding ligands (b) in CH_3CN solution ($c = 2.0 \times 10^{-5}$ M).

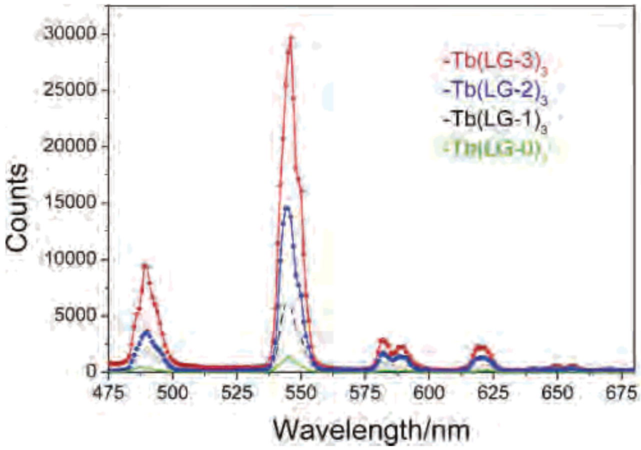


Figure 5. The luminescence spectra of Tb[LG-*n*]$_3$ ($n = 1-3$) in CH_3CN solution ($c = 2.0 \times 10^{-5}$ M).

times that of the corresponding ligand, indicating the presence of three ligands per terbium complex molecule.

Photoluminescent Properties of the Terbium Complexes. Figure 5 shows the photoluminescence spectra of the dendritic terbium complexes Tb(LG-*n*)$_3$ ($n = 0-3$) in CH_3CN solution. These terbium complexes produced typical Tb(III) emission bands at ~490, 545, 585, and 620 nm corresponding to the deactivation of the excited state $^5D_4$ to the ground states ^7F_J ($J = 3$, 4, 5, and 6) when the Tb(LG-*n*)$_3$ complexes ($n = 0-3$) were excited at 290 nm (see Figure 5). The emission band at 545 nm ($^5D_4$-$^7F_5$) was the strongest among the five bands.

The data of photophysical properties for Tb(LG-*n*)$_3$ ($n = 0-3$) are shown in Table 3. The overall luminescent quantum yields (ϕ_{overall}) of these terbium complexes were measured using rhodamine 6G in ethanol (2.0×10^{-5} mol/L, $\phi_{\text{ref}} = 94\%$)[19] as a reference and were calculated according to the well-known method given as

$$\phi_{\text{overall}} = \frac{n^2 A_{\text{ref}} I}{{n_{\text{ref}}}^2 A I_{\text{ref}}} \phi_{\text{ref}}$$

Here, n, A, and I denote the refractive index of solvent, the absorbance at the excitation wavelength and the intensity of the emission spectrum, respectively. The subscript ref denotes the reference, and no subscript denotes the sample. The overall luminescent quantum yields (ϕ_{overall}) of Tb(LG-0)$_3$, Tb(LG-1)$_3$, Tb(LG-2)$_3$, and Tb(LG-3)$_3$ were calculated as ~0.10, 0.43, 1.11, and 2.26% (see Table 3), respectively, revealing that the luminescence quantum yield of Tb(LG-*n*)$_3$ increased obviously with the increase of the dendron generation. Similar phenomena were observed by Fréchet and co-workers.[12a,c]

The luminescence lifetimes (τ) were also investigated for these dendritic complexes. The measured luminescent decays of Tb(LG-*n*)$_3$ could be described by monoexponential kinetics, which suggests that only one species exists in the excited state of these complexes. Compared with the lower generation dendritic complexes, Tb(LG-0)$_3$ and Tb(LG-1)$_3$, the higher generation dendrimer complexes, Tb(LG-2)$_3$ and Tb(LG-3)$_3$, showed longer luminescence lifetimes (see Table 3). According to the above results, we can conclude that the introduction of the dendritic ligand is effective for improving the photoluminescent properties of the Tb complexes.

To elucidate the energy-transfer process of the terbium complexes, the energy levels of the relevant electronic states should be estimated. It is well known that the transition probability is proportional to the square of the dipole moment. In these dendritic terbium complexes, Tb(LG-*n*)$_3$, the negatively charged central ligands (LG-*n*) show a larger dipole moment than the neutral molecules (such as H_2O and ethanol); therefore, the sensitizer of the terbium ion in this system is 4-phenylacetyl-5-pyrazolone, not the neutral molecules (such as H_2O and ethanol). Furthermore, the singlet energy levels of LG-*n* ($n = 0-3$) were estimated to be 31 150−33 200 cm^{-1} (see Table 3) in reference to their UV−vis absorbance edge wavelengths. Meanwhile, according to the lower-wavelength emission edges of the corresponding phosphorescence spectra of Gd(LG-*n*)$_3$ ($n = 0-3$), the triplet energy levels of LG-*n* ($n = 0-3$) are measured to be ~21 050 cm^{-1} (see Table 3) and are higher than the $^5D_4$ (20 500 cm^{-1}) value of Tb^{3+}, indicating that the dendritic ligands LG-*n* ($n = 0-3$) could be used as sensitizers for Tb(III). However, their energy gaps, $\Delta E(^3\pi\pi^* - {}^5D_4)$, between ligand- and metal-centered levels are ($\Delta E \approx 550$ cm^{-1}) too low to prevent the thermally competitive back energy transfer from the Tb(III) excited state to the triplet state of LG-*n* ($n = 0-3$), which predicts that little effective energy transfer takes place from LG-*n* to Tb(III), resulting

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[18] McClenaghan, N. D.; Barigelletti, F.; Maubert, B.; Campagna, S. *Chem. Commun.* **2002**, 602.

[19] Filipescu, N.; Mushrush, G. W.; Hurt, C. R.; McAvoy, N. *Nature* **1966**, *211*, 960.

Table 3. Photophysical Data of Dendritic Complexes in CH_3CN Solution[a]

	λ_{max}^{abs} (nm)	ϵ ($\times 10^4$ L mol^{-1} cm^{-1})	S_1 (cm^{-1})	T_1 (cm^{-1})	$\phi_{overall}$ (%)	$\phi_{transfer}$ (%)	ϕ_{Tb} (%)	τ (μs)	k_{rad} (s^{-1})	k_{nr} (s^{-1})
Tb(LG-0)$_3$	264	7.8	~31 150	~21 050	0.10			2.4		
Tb(LG-1)$_3$	261	7.6	~31 550	~21 050	0.43	3.7	11.8	49.6	2379	17 782
Tb(LG-2)$_3$	274	8.4	~31 850	~21 050	1.11	9.2	13.2	404.7	326	2145
Tb(LG-3)$_3$	275	10.0	~33 200	~21 080	2.26	22.6	10.0	389.4	256	2311

[a] λ_{max}^{abs} = the maximum absorption wavelength; ϵ = molar absorption coefficient; S_1 = singlet energy level; T_1 = triplet energy level.

in a low fluorescence quantum yield (especially 0.1% of Tb(LG-0)$_3$) and a relatively short luminescence lifetime of Tb(LG-*n*)$_3$.

Generally, the sensitization pathway in luminescent terbium complexes consists of excitation of the coordinated ligands into their excited singlet states, subsequent intersystem crossing of the ligands to their triplet states, and energy transfer from the triplet state of the ligand to the ^5D_J manifold of the Tb^{3+} ion, followed by internal conversion to the emitting $^5D_4$ state, and finally the Tb^{3+} ion emition from $^5D_4$ occurs.[5,6] Therefore, the efficiency of energy transfer from the antenna to Tb^{3+} ($\phi_{transfer}$), the probability of the Tb^{3+} emission (ϕ_{Tb}), and radiative and nonradiative rates of the terbium excited state (k_{rad} and k_{nr}) are central to understanding the photophysics of the character of and energy transfer from ligand to the Tb^{3+} ion.

Early studies of the energy transfer from sensitizer to a chelated lanthanide ion were carried out using both Förster and Dexter energy-transfer mechanisms by some groups.[20] Herein, to understand the effect of the different generation dendron modification on the photoluminescent properties of the terbium complexes Tb(LG-*n*)$_3$, we investigated the efficiency of energy transfer ($\phi_{transfer}$) from the dendritic ligand to Tb^{3+} and the probability of the Tb^{3+} emission (ϕ_{Tb}) according to the method developed by Selvin et al.[21] The terbium complex was treated as a "black box", where internal processes are not explicitly considered: given that the complex absorbs a photon (i.e., the antenna is excited), the overall quantum yield ($\phi_{overall}$) of the terbium complex is a product of the energy-transfer efficiency from antenna to Tb^{3+} ($\phi_{transfer}$) multiplied by the probability of the Tb^{3+} emission (ϕ_{Tb}) once the terbium ion is excited.

The results for the diffusion-enhanced energy transfer between the dendritic complexes Tb(LG-*n*)$_3$ ($n = 1-3$) and rhodamine 6G as the energy acceptor are shown in Table 3. However, for the relatively weak fluorescent emission and short lifetime of Tb(LG-0)$_3$, we did not obtain the probability of the terbium emission (ϕ_{Tb}) and the energy-transfer efficiency ($\phi_{transfer}$) using this method. It can be seen from Table 3 that the energy-transfer efficiencies from antenna to lanthanide ($\phi_{transfer}$) were measured to be 3.7, 9.2, and 22.6% for complexes Tb(LG-1)$_3$, Tb(LG-2)$_3$, and Tb(LG-3)$_3$ (see Table 2), respectively, indicating that the energy-transfer efficiency ($\phi_{transfer}$) from the ligand to the terbium ion increased with the increasing dendron generation. We rationalized the observation as a consequence of increased antenna effect. Similarly, the probabilities of terbium emission (ϕ_{Tb}) of Tb(LG-1)$_3$, Tb(LG-2)$_3$, and Tb(LG-3)$_3$ are 11.8, 13.2, and 10.0% (see Table 3), respectively; ϕ_{Tb} is almost constant when the generation number increases. This observation (no obvious change on the metal-centered luminescence quantum yield, whereas there is an obvious change on the energy transfer from ligand to metal-centered cation) could be donated as "energy-reservoir effect".[22] Furthermore, the phenomena could be modulated by oxygen quenching. The oxygen quenching is likely more effective for the lower-generation dendrimers, Tb(LG-0)$_3$ and Tb(LG-1)$_3$, but less effective for the quenching of the higher-generation dendrimers, Tb(LG-2)$_3$ and Tb(LG-3)$_3$, which suggests that a shell effect (improved site isolation of the lanthanide center by the steric bulk of the dendritic ligands) leads to a more hindered approach of the oxygen to the higher-generation dendrimers.[18] From the above experimental result, therefore, we can conclude that the increasing luminescence quantum yield in the dendrimer complexes Tb(LG-*n*) ($n = 0-3$) with the increasing dendron generation is the result of a combination of the consequence of an antenna effect and a shell effect.

Conclusions

We reported the synthesis of the dendritic ligand 1-phenyl-3-(G-*n*)-4-phenylacetyl-5-pyrazolone (LG-*n*) ($n = 0-3$) and the corresponding complexes Tb(LG-*n*)$_3$. The photophysical studies indicated that the dendritic complexes in solution exhibited enhanced luminescence with increasing dendron generation. By measuring the probability of the terbium emission (ϕ_{Tb}) and the energy transfer ($\phi_{transfer}$) from the ligand to Tb^{3+} using the method based on resonance energy transfer, we found an energy-reservoir effect; that is, the energy transfer ($\phi_{transfer}$) from the ligand to Tb^{3+} increased, and the metal-centered luminescence quantum yield was almost the same when the generation increased. Moreover, the triplet-state levels of the ligands were the same, and the lower-generation dendrimers, Tb(LG-0)$_3$ and Tb(LG-1)$_3$, exhibited more effective oxygen quenching of the luminescent quantum yield than the higher-generation dendrimers, Tb(LG-2)$_3$ and Tb(LG-3)$_3$. These facts confirmed that the light-harvesting antenna effect and shell effect contribute to

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the enhanced fluorescent emission for the dendritic terbium complexes, Tb(LG-*n*)$_3$.

Experimental Section

Materials and Apparatus. Acetone, THF, xylene, and ethyl alcohol were used as purchased from Shanghai Chemical Reagent Company. 3,5-Dihydroxyacetophenone was received a gift from Zhejiang Hisoar Co., Ltd. Anhydrous acetone was obtained using anhydrous calcium chloride for 24 h before distillation. Anhydrous THF was freshly prepared by distillation over Na/benzophenone. Other reagents were purchased as reagent grade and used without further purification. Tb_4O_7 was purchased from Shanghai Yuelong Co., Ltd., and $TbCl_3 \cdot 6H_2O$ was synthesized in our lab. 1,3-Diphenyl-4-phenylacetyl-5-pyrazolone was prepared by the previous method.[23] [G-1]-Br and [G-2]-Br were synthesized according to the previous literature.[14]

The photoluminescence spectra were measured on an Edinburgh LFS920 fluorescence spectrophotometer. UV−vis absorption spectra were obtained with a Shimadzu 3000 UV−Vis−NIR spectrophotometer. NMR spectra were recorded on Mercury Plus 400NB NMR spectrometer. MALDI-TOF-MASS spectra were obtained with a SHIMADZU matrix-assisted laser desorption/ionization time-of-light mass spectrometer. ESI-MS spectra were measured on a Finnigan LCQ Deca XP Plus ion-trap mass spectrometer (San Jose, CA). The elemental analyses were performed with Vario EL III O-Element analyzer system. Fluorescence lifetimes were recorded on a single-photon-counting spectrophotometer from Edinburgh Instruments (FLS920) with microsecond pulse lamp as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments.

General Procedure for Synthesis of the Ligand LG-*n*. The ligands (LG-*n*) were synthesized according to a general procedure, as shown in Scheme 2.

General Procedure for Synthesis of G-*n*−Ketone Dendrons (1−3). [G-1]-Br, [G-2]-Br, or benzyl chloride (2.05 equiv), 3,5-dihydroxyacetophenone (1.00 equiv), potassium carbonate (2.50 equiv), and 18-crown-6 (0.20 equiv) were dissolved in anhydrous acetone. The mixture was refluxed and stirred vigorously under a nitrogen atmosphere until the bromo dendron was no longer seen on TLC (thin layer chromatography). The mixture was then evaporated to dryness under reduced pressure. The residue was partitioned between water and CH_2Cl_2, and the aqueous layer was subsequently extracted three times with CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and evaporated, and the crude product was purified as follows.

[G-1]-$COCH_3$ (**1**) was prepared form benzyl chloride and recrystallized from EtOH to give the purified product as colorless crystals. Yield: 90%. mp: 60−61°C. ^{1}H NMR ($CDCl_3$): δ 7.30−7.42 (m, 10H), 7.18 (d, $J = 2.0$ Hz, 2H), 6.79 (s, 1H), 5.03 (s, 4H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 197.89, 160.23, 139.31, 136.67, 128.94, 128.45, 127.89, 107.62, 107.09, 70.58, 27.01. MALDI-TOF Calcd for $C_{22}H_{20}O_3$: m/z 332.1. Found: m/z 439 ($M + Ag^+$).

[G-2]-$COCH_3$ (**2**) was prepared form [G-1]-Br and purified by flash column chromatography, eluted with 5:1 hexane/ethyl acetate, to give colorless crystals. Yield: 90%. mp: 139−140 °C. ^{1}H NMR ($CDCl_3$): δ 7.30−7.42 (m, 10H), 7.18 (d, $J = 2.0$ Hz, 2H), 6.79 (s, 1H), 5.03 (s, 4H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 197.89, 160.23, 139.31, 136.67, 128.94, 128.45, 127.89, 107.62, 107.09, 70.58, 27.01. MALDI-TOF Calcd for $C_{50}H_{44}O_7$: m/z 756.3. Found: m/z 865 ($M + Ag^+$).

[G-3]-$COCH_3$ (**3**) was prepared fromm [G-2]-Br and purified by flash column chromatography, eluted with 5:1 hexane/ethyl acetate, to obtain colorless crystals. Yield: 90%. ^{1}H NMR ($CDCl_3$): δ 7.36−7.49 (m, 20H), 7.25 (d, $J = 2.0$ Hz, 2H), 6.85 (s, 1H), 6.76 (s, 4H), 6.66 (s, 2H), 5.08 (s, 8H), 5.05 (s, 4H), 2.60 (s, 3H).^{13}C NMR ($CDCl_3$): δ 197.89, 160.51, 160.16, 139.35, 139.13, 137.05, 128.91, 128.35, 127.87, 107.68, 107.07, 106.73, 101.95, 70.44, 70.39, 27.06. MALDI-TOF Calcd for $C_{106}H_{92}O_{15}$: m/z 1605.7. Found: m/z 1714 ($M + Ag^+$).

General Procedure for Synthesis of G-*n*-β-diketo-ester Dendrons (4−6). NaH (2.00 equiv), diethyl carbonate (2.50 equiv), and 30 mL of anhydrous THF were placed in a three-necked flask under nitrogen. The reaction mixture was stirred, and a 20 mL anhydrous THF solution of [G-*n*]-ketone (2.00 equiv) was slowly added from the dropping funnel. Then the reaction mixture was heated at 70 °C for 6−8 h. After it was cooled, the mixture was evaporated to dryness under reduced pressure. The residue was added to 10 mL of water, neutralized by acetic acid, and extracted three times with CH_2Cl_2. The combined extract was dried (Na_2SO_4) and evaporated, and the crude product was purified.

[G-1]-$COCH_2COOEt$ (**4**) was prepared from [G-1]-$COCH_3$ (**1**) and purified by flash column chromatography, eluted with 5:1 hexane/ethyl acetate, to give a colorless viscous oil. Yield: 93%. ^{1}H NMR ($CDCl_3$): δ 7.33−7.44 (m, 10H), 7.24 (s, 1H), 7.04 (d, $J = 2.4$ Hz, 1H), 6.84 (s, 1H), 5.08 (s, 4H), 4.21 (q, $J = 14.4$ Hz, 2H), 3.93 (s, 1H), 1.26 (t, $J = 14.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 192.37, 160.30, 138.12, 136.48, 128.92, 128.47, 127.85, 107.79, 107.70, 105.48, 70.63, 61.75, 48.30, 14.35. MALDI-TOF Calcd for $C_{25}H_{24}O_5$: m/z 404.2. Found: m/z 513 ($M + Ag^+$).

[G-2]-$COCH_2COOEt$ (**5**) was prepared from [G-2]-$COCH_3$ (**2**) and purified by flash column chromatography, eluted with 5:2 hexane/ethyl acetate, to obtain yellow crystals. Yield: 92%. mp: 90−91 °C. ^{1}H NMR ($CDCl_3$): δ 7.31−7.43 (m, 20H), 7.15 (d, $J = 2.0$ Hz, 1H), 6.79 (s, 1H), 6.67 (d, $J = 2.4$ Hz, 5H), 6.59 (s, 2H), 5.04 (s, 8H), 5.01 (s, 4H), 4.21 (q, $J = 14.4$ Hz, 2H), 3.92 (s, 1H), 1.26 (t, $J = 14.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$): 192.42, 167.75, 160.51, 160.25, 139.25, 138.98, 138.17, 137.01, 128.90, 128.33, 127.85, 107.78, 106.70, 101.98, 70.47, 70.39, 61.81, 46.33, 14.43. MALDI-TOF Calcd for $C_{53}H_{48}O_9$: m/z 828.3. Found: m/z 937 ($M + Ag^+$).

[G-3]-$COCH_2COOEt$ (**6**) was prepared from [G-3]-$COCH_3$ (**3**) and purified by flash column chromatography, eluted with 5:2 hexane/ethyl acetate, to give yellow viscous oil. Yield: 92%. ^{1}H NMR ($CDCl_3$): δ 7.28−7.41 (m, 40H), 7.15 (d, $J = 2.4$ Hz, 2H), 6.81 (s, 1H), 6.65−6.67 (m, 12H), 6.55−6.57 (m, 6H), 5.01 (s, 16H), 4.98 (s, 4H), 4.96 (s, 8H), 4.18 (q, $J = 14.4$ Hz, 2H), 3.90 (s, 1H), 1.26 (t, $J = 14.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 192.40, 167.71, 160.43, 160.20, 139.47, 139.44, 138.95, 138.17, 137.03, 135.68, 128.86, 128.29, 127.85, 107.77, 106.75, 206.66, 101.98, 101.85, 70.35, 70.27, 61.77, 46.30, 45.08, 14.41. MALDI-TOF Calcd for $C_{109}H_{96}O_{17}$: m/z 1677.7. Found: m/z 1786 ($M + Ag^+$).

General Procedure for Synthesis of 1-phenyl-3-(G-*n*)-5-pyrazolone Dendrons (7−9). Dendron [G-*n*]-β-diketo ester (1.0 equiv) and hydrazine (1.0 equiv) were dissolved in xylene. The mixture was refluxed and stirred vigorously under a nitrogen atmosphere for 24 h. After the mixture was cooled, the raw product was separated and recrystallized from $CHCl_3$ to give the purified product.

1-Phenyl-3-[G-1]-5-pyrazolone (**7**) was produced as slightly yellow crystals. Yield: 60%. mp: 138−141 °C. ^{1}H NMR ($CDCl_3$): δ 7.96 (d, $J = 9.6$ Hz, 2H), 7.21−7.42 (m, 12H), 6.99−

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7.00 (m, 2H), 6.70−6.71 (m, 1H), 5.09 (s, 4H), 3.78 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 170.42, 160.44, 154.61, 138.35, 136.68, 132.90, 129.13, 128.95, 128.48, 127.91, 125.55, 119.27, 105.50, 104.38, 70.54, 39.87. MALDI-TOF Calcd for $C_{29}H_{24}N_2O_3$: *m/z* 448.2. Found: *m/z* 449. Anal. Calcd for $C_{29}H_{24}N_2O_3$: C, 77.66; H, 5.39; N, 6.25. Found: C, 77.40; H, 5.41; N, 6.25.

1-Phenyl-3-[G-2]-5-pyrazolone (**8**) was obtained as slightly yellow crystals. Yield: 55%. mp: 90−91 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.30−7.43 (m, 22H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 2H), 6.88 (d, *J* = 6.8 Hz, 2H), 6.69 (d, *J* = 2.4 Hz, 4H), 6.66 (t, *J* = 2.1 Hz, 1H), 6.59 (t, *J* = 2.4 Hz, 2H), 5.04 (s, 8H), 5.02 (s, 4H), 3.78 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 170.43, 160.49, 160.34, 154.63, 139.10, 138.33, 136.97, 132.93, 129.15, 128.31, 127.83, 125.60, 119.34, 106.72, 105.53, 104.42, 101.87, 70.37, 39.95. MALDI-TOF Calcd for $C_{57}H_{46}N_2O_7$: *m/z* 870.3. Found: *m/z* 872. Anal. Calcd for $C_{57}H_{46}$ N_2O_7: C, 78.60; H, 5.32; N, 3.22. Found: C, 78.42; H, 5.56; N, 3.32.

1-Phenyl-3-[G-3]-5-pyrazolone (**9**) was obtained as slightly yellow crystals. Yield: 50%. mp: 115−117 °C. ^{1}H NMR ($CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.28−7.42 (m, 42H), 7.19 (t, *J* = 5.6 Hz, 1H), 6.96 (s, 2H), 6.67 (s, 12H), 6.56 (s, 6H), 5.00 (s, 18H), 4.96 (s, 10H), 3.70 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 170.45, 160.44, 160.39, 154.66, 139.45, 137.01, 137.03, 132.95, 129.16, 128.87, 128.30, 127.86, 119.32, 119.32, 106.77, 106.66, 105.56, 104.30, 101.93, 101.87, 101.81, 70.33, 70.25, 39.90. MALDI-TOF Calcd for $C_{113}H_{96}N_2O_{15}$: *m/z* 1721.7. Found: *m/z* 1722 (M^+), 1744 ($M + Na^+$), 1760 ($M + K^+$). Anal. Calcd for $C_{113}H_{96}N_2O_{15}$: C, 78.82; H, 5.62; N, 1.63. Found: C, 78.53; H, 5.67; N, 1.77.

General Procedure for Synthesis of 1-Phenyl-3-(G-*n*)-4-phenylacetyl-5-pyrazolone Dendrons LG-*n* (*n* = 1−3). Dendron 1-phenyl-3-(G-*n*)-5-pyrazolone was dissolved in anhydrous THF, and then $Ca(OH)_2$ and $Ba(OH)_2$ were added. The reaction mixture was stirred, and phenylacetyl chloide/10 mL of anhydrous THF was slowly added from the dropping funnel; then the reaction mixture was heated at 80 °C for 24−48 h. After it was cooled, the mixture was added into water, neutralized by 6 mol L^{-1} HCl, and extracted three times with CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and evaporated, and the crude product was purified as follows.

1-Phenyl-3-[G-1]-4-phenylacetyl-5-pyrazolone (LG-1) was purified by flash column chromatography, eluted with 1:3 hexane/dichloromethane to give colorless crystals. mp: 120−122 °C. Yield: 30%. FT-IR (KBr disk, cm^{-1}) ν 3062(w), 3022(w), 1630(m), 11600(s), 1538(s), 1498(w), 1452(m), 1436(m), 1317(w), 1259(w), 1161(s), 1062(m), 864(w), 825(w), 756(m), 725(m), 696(m). ^{1}H NMR ($CDCl_3$): δ 7.89 (d, *J* = 6.8 Hz, 2H), 7.20−7.48 (m, 16H), 6.97 (d, *J* = 6.4 Hz, 2H), 6.76 (t, 3H), 5.04 (s, 4H), 3.68 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 196.30, 160.52, 160.24, 151.23, 137.385, 136.87, 135.06, 134.31, 129.57, 129.40, 128.93, 128.74, 128.39, 127.75, 127.29, 127.22, 121.33, 108.90, 103.77, 103.69, 70.41, 45.24. MALDI-TOF Calcd for $C_{37}H_{30}N_2O_4$: *m/z* 566.6. Found: *m/z* 567. Anal. Calcd for $C_{37}H_{30}N_2O_4$: C, 78.43; H, 5.34; N, 4.94. Found: C, 78.31; H, 5.38; N, 4.99.

1-Phenyl-3-[G-2]-4-phenylacetyl-5-pyrazolone (LG-2) was purified by flash column chromatography, eluted with 1:4 hexane/dichloromethane, to obtain yellow crystals. mp: 170−172 °C. Yield: 25%. FT-IR (KBr disk, cm^{-1}): ν 2925(m), 2843(w), 1633(m), 1597(s), 1542(m), 1493(w), 1448(m), 1387(m), 1287(w), 1162(s), 1051(m), 827(w), 757(m), 724(m), 687(m). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.22−7.33 (m, 20H), 7.08−7.15 (m, 3H), 6.88 (d, *J* = 6.8 Hz, 2H), 6.66−6.68 (m, 3H), 6.06 (d, *J* = 2.4 Hz, 4H), 6.49 (t, *J* = 2.0 Hz, 2H), 4.93 (s, 8H), 4.90 (s, 4H), 3.60 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 196.29, 160.62, 160.53, 160.17, 151.21, 139.37, 137.42, 137.00, 135.10, 134.33, 129.62, 129.44, 128.90, 128.80, 128.34, 127.88, 127.33, 127.27, 121.34, 108.92, 106.56, 103.88, 103.69, 101.83, 70.40, 70.28, 45.24. MALDI-TOF Calcd for $C_{65}H_{53}N_2O_8$: *m/z* 989.4. Found: *m/z* 991. Anal. Calcd for $C_{65}H_{53}$ N_2O_8: C, 78.85; H, 5.40; N, 2.83. Found: C, 78.51; H, 5.57; N, 2.80.

1-Phenyl-3-[G-3]-4-phenylacetyl-5-pyrazolone (LG-3) was purified by flash column chromatography, eluted with 1:4 hexane/dichloromethane, to obtain yellow crystals. mp: 87−88 °C. Yield: 12%. FT-IR (KBr disk, cm^{-1}): ν 3025(w), 2888(w), 1634(m), 1596(s), 1540(m), 1492(m), 1449(s), 1337(s), 1287(w), 1210(w), 1160(s), 1052(s), 825(w), 757(m), 726(m), 690(m). ^{1}H NMR ($CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.26−7.44 (m, 43H), 7.13−7.20 (m, 3H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.77 (s, 3H), 6.66 (d, *J* = 2.0 Hz, 12H), 6.53−6.56 (m, 6H), 5.00 (s, 16H), 4.96 (s, 8H), 4.93 (s, 4H), 3.70 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 196.26, 160.43, 160.40, 160.17, 151.17, 139.41, 139.31, 137.38, 137.02, 135.11, 134.30, 129.58, 129.41, 128.87, 128.77, 128.29, 127.85, 127.27, 121.33, 108.91, 106.67, 106.62, 103.74, 103.67, 101.86, 70.35, 70.27, 45.28. MALDI-TOF Calcd for $C_{121}H_{102}$ N_2O_{16}: *m/z* 1839.7. Found: *m/z* 1840 (M^+), 1862 ($M + Na^+$), 1878 ($M + K^+$). Anal. Calcd for $C_{121}H_{102}$ N_2O_{16}: C, 78.98; H, 5.59; N, 1.52. Found: C, 79.19; H, 6.00; N, 1.45.

General Procedure for Synthesis of Tb-Cored Dendrimer Complexes. A solution of 1-phenyl-3-[G-*n*]-4-phenylacetyl-5-pyrazolone in THF was neutralized by NaOH aqueous solution with heating and stirring; then an aqueous solution of $TbCl_3$ (1:3 molar ratio) was added dropwise at a pH of 6.5. Water was added slowly, after the mixture had been refluxed for 6 h, and a solid was formed and filtered out. The product was washed with water. Tb-cored dendrimer complexes were obtained.

$Tb(LG\text{-}0)_3(EtOH)(H_2O)$. This compound was prepared using 1,3-diphenyl-4-phenylacetyl-5-pyrazolone (LG-0) and $TbCl_3$ and was obtained as a slightly pink solid. Yield: 85%. FT-IR (KBr disk, cm^{-1}): ν 3053(w), 3029(w), 1620(s), 1474(s), 1353(m), 1166(m), 956(s), 721(s), 664(s). ESI Calcd for $C_{69}H_{51}N_6O_6Tb$: *m/z* 1218.3. Found: *m/z* 1219.9 ($M + H^+$). Anal. Calcd for $C_{71}H_{59}N_6O_{8.50}Tb$: C, 66.04; H, 4.61; N, 6.51. Found: C, 65.78; H, 4.57; N, 6.60.

$Tb(LG\text{-}1)_3(H_2O)_2$. This compound was synthesized with 1-phenyl-3-[G-1]-4-phenylacetyl-5-pyrazolone (LG-1) and $TbCl_3$ and was obtained as a slightly pink solid. Yield: 83%. FT-IR (KBr disk, cm^{-1}): ν 3061(w), 3020(w), 1603(s), 1483(s), 1369(m), 1150(s), 1062(m), 843(m), 737(s), 679(s). ESI Calcd for $C_{111}H_{87}N_6O_{12}Tb$: *m/z* 1855.6. Found: *m/z* 1856.9 ($M + H^+$). Anal. Calcd for $C_{111}H_{99}N_6O_{15}Tb$: C, 69.58; H, 5.20; N, 4.39. Found: C, 69.83; H, 4.85; N, 4.41.

$Tb(LG\text{-}2)_3(H_2O)$. This compound was made from 1-phenyl-3-[G-2]-4-phenylacetyl-5-pyrazolone (LG-2) and $TbCl_3$ and was obtained as a yellow glass. Yield: 65%. FT-IR (KBr disk, cm^{-1}): ν 3040(w), 3020(w), 1594(s), 1488(s), 1369(m), 1290(w), 1155(s), 1052(m), 829(w), 725(m), 690(m). ESI Calcd for $C_{195}H_{156}N_6O_{24}Tb$: *m/z* 3126.0. Found: *m/z* 3126.9 ($M + H^+$). Anal. Calcd for $C_{195}H_{158}N_6O_{25}Tb$: C, 74.49; H, 5.06; N, 2.67. Found: C, 74.37; H, 5.22; N, 2.67.

$Tb(LG\text{-}3)_3$. This compound was made from 1-phenyl-3-[G-3]-4-phenylacetyl-5-pyrazolone (LG-3) and $TbCl_3$ and was obtained as a yellow glass. Yield: 40%. FT-IR (KBr disk, cm^{-1}): ν 3039(w), 3023(w), 1592(s), 1447(s), 1367(s), 1289(m), 1150(m), 1055(s), 838(w), 730(m), 690(m). Anal. Calcd for $C_{363}H_{303}N_6O_{48}Tb$: C, 76.81; H, 5.38; N, 1.48. Found: C, 77.22; H, 5.53; N, 1.43.

Structure Determination. A colorless crystal of $Tb(LG\text{-}0)_3(EtOH)(H_2O)$ was grown from a 95% ethyl alcohol solution, and a colorless crystal of $Tb(LG\text{-}1)_3(H_2O)_2$ was grown from a CH_3CN

solution at room temperature. The crystal of $Tb(LG\text{-}0)_3(EtOH)(H_2O)$ or $Tb(LG\text{-}1)_3(H_2O)_2$ was mounted on glass fiber and transferred to a Bruker SMART CCD area detector. Crystallographic measurements were carried out using a Bruker SMART CCD diffractometer, σ scan, and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the program SHELXS-97.[24] All non-hydrogen atoms were refined anisotropically except some carbon atoms (C55−C59) in $Tb(LG\text{-}0)_3(EtOH)(H_2O)$. The hydrogen atoms were calculated in ideal geometries. For the full-matrix least-squares refinements [$I > 2\sigma(I)$], the unweighted and weighted agreement factors of $R1 = \sum(F_o - F_c)/\sum F_o$ and $wR2 = [\sum w(F_o^2 - F_c^2)2/\sum wF_o^4]^{1/2}$ were used.

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Supporting Information Available: The crystal structures of $Tb(LG\text{-}0)_3(EtOH)(H_2O)$ and $Tb(LG\text{-}1)_3(H_2O)_2$. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data is available from the Cambridge Crystallographic Data Centre (CCDC 288894 and 288895 for $Tb(LG\text{-}0)_3(EtOH)(H_2O)$ and $Tb(LG\text{-}1)_3(H_2O)_2$, respectively).

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