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13. ABSTRACT (Maximum 200 words) The structural and photophysical properties of a series of dendritic lanthanide complexes of increasing size are reported. Theoretical calculations indicate that a meridional geometry is lower in energy and more likely than a facial geometry. ¹ H NMR T ₁ relaxation times of terminal methoxy groups indicate that the ligands exist in two environments consistent with a meridional isomer. Photophysical studies confirm <i>tris</i> chelation of the lanthanide, and indicate that each dendrimer exists as a single isomer of high asymmetry at the core. These dendrimers were shown to be photon harvesting arrays. Detailed photophysical studies showed that these complexes were <i>tris</i> -chelated and asymmetrical at the lanthanide first coordination sphere. The total energy transfer process (A→B→C) was deconvoluted into two parts: the phenyl rings of the dendrons to the β-diketonate (A→B), and the latter moiety to the lanthanide core (B→C). The A→B process possessed a light-harvesting effect (<i>i.e.</i> , an antenna effect), and the B→C process showed a site isolation effect. From a detailed study of the dendrimers' photophysical properties, the contribution of each effect is shown to display a complex dependence on the size of the dendrimer.				
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Part I: Structural Studies

Introduction

Over the past ten years there has been much interest in mimicking light-harvesting processes seen in nature.¹⁻⁵ For example, Xu and Moore demonstrated the use of polyphenylacetylene monodendrons to transfer absorbed energy to perylene.¹ Jiang and Aida used energy transfer in dendrimers to facilitate infrared light induced *cis-trans* isomerization of an azobenzene core.² Vogtle and Balzani surrounded a [Ru(bpy)₃]²⁺ core with second generation dendrons containing naphthyl peripheral moieties.³ Kawa and Fréchet encapsulated lanthanide ions with carboxylate-focused poly(aryl ether) dendrons for potential use in optical signal amplification.⁴ In this study, we report the synthesis and photophysical properties of a series of dendritic β -diketonate europium complexes. These complexes possess a complex generational dependence on europium emission. Molecular modeling and NMR and absorption spectroscopies are employed to explain this phenomenon.

Trivalent lanthanide complexes are used in many applications such as luminescent probes,⁵ lasers,^{6,7} and organic light emitting diodes.⁸⁻¹⁰ Unlike organic dyes and organic polymers, which have broad fluorescence or phosphorescence bands, lanthanides have narrow emission bands (<10 nm full width at half maximum).¹¹ The sharp inter-*f* orbital emission bands of lanthanides are attributed to overlying 5s and 5p orbitals effectively shielding the 4f orbitals from the external vibrational perturbations. Other consequences of this shielding are long excited-state lifetimes (ranging from hundreds of microseconds to seconds) and fixed emission energies. These attributes allow luminescent lanthanide-containing materials to be used in a variety of applications that require such distinct optical properties.

One drawback of using uncoordinated lanthanides in optical and photonic applications is that the high photon flux of lasers is required to excite lanthanides due to their small extinction coefficients ($\sim 1\text{-}10\text{ M}^{-1}\text{cm}^{-1}$).¹² The most common way to circumvent this limitation is to use ligands capable of sensitizing the lanthanide. Provided that spatial and energetic considerations of sensitization are met, energy transfer efficiencies in these organolanthanide coordination compounds can be very high. Absorption characteristics of such complexes are dominated by the organic ligands, while emission characteristics are dominated by the lanthanide. A benefit of this is that the organic ligands are amenable to chemical modification to meet auxiliary requirements for a given application without detriment to the photophysical properties of the complex.

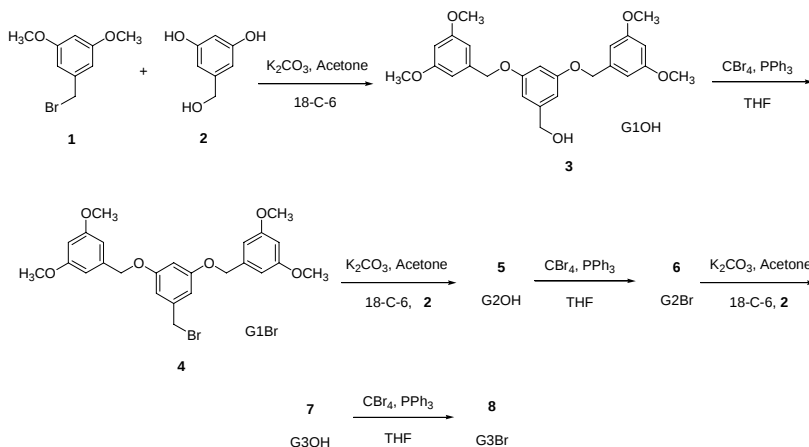
One versatile class of organolanthanide coordination complexes is the lanthanide β -diketonates. While these complexes have been known since the pioneering investigations of such materials, only recently have dendritic lanthanide β -diketonates been prepared. Dalton and coworkers have synthesized and used first-generation dendrimers containing core europium(III) β -diketonate moieties as the emitting species in OLED devices.¹³ We report here the syntheses and structural properties of a series of luminescent lanthanide-cored dendrimers by chelating dendritic β -diketonate ligands to trivalent europium. The ligands are modified benzoyltrifluoroacetate (BTFA) moieties with increasing generations of poly(benzyl aryl ether) attachments. The dendrons are similar to those used by Kawa and Fréchet⁵ in their construction of lanthanide-cored dendritic carboxylates, however, the use of β -diketonates as the coordinating moieties produces markedly different structural and photophysical behavior of our series of dendrimers. Furthermore, the terminal phenyl rings in the dendrons possess methoxy groups which enable a detailed investigation of the dendrimer structure. Such knowledge is instrumental in explaining the complex photophysical properties of these dendrimers.

General Procedure for the Preparation of the Lanthanide Complexes. The lanthanide complexes were synthesized by the conventional method.¹⁴ Three equivalents of the dendritic β -diketone (typically 150 mg) were dissolved in 10 mL of anhydrous ethanol or anhydrous THF. The β -diketone was deprotonated by the addition of three equivalents of a 1.0 M sodium ethoxide solution. One equivalent of anhydrous lanthanide(III) chloride dissolved in 10 mL of anhydrous ethanol or THF was added to the reaction. After stirring for 30 minutes, NaCl was filtered off and the filtrate was evaporated.

Results and Discussion

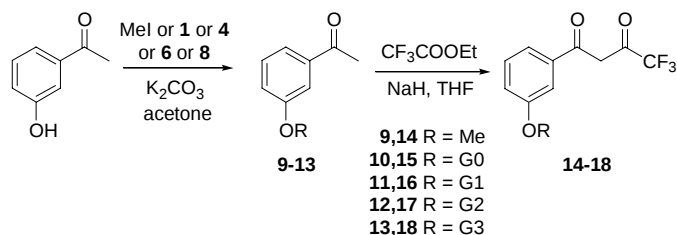
Synthesis and Characterization. The dendritic β -diketone ligands are generated in three steps as shown in Schemes 1 and 2. The poly(aryl ether) dendrons are prepared using the general synthetic route developed by Hawker and Fréchet.¹⁵ To start, the coupling of two equivalents of benzyl bromide **1** with one equivalent of 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate give a first generation dendron (**3**, G1OH) with a benzyl alcohol moiety at its focus. Alcohol **3** is then brominated with carbon tetrabromide to produce the first generation benzyl bromide (**4**, G1Br). Two equivalents of benzyl bromide **4** are then coupled to one equivalent of 3,5-dihydroxybenzyl alcohol to obtain the second generation benzyl alcohol (**5**, G2OH). The sequence is continued to give the third generation dendron (**7**, G3OH) as shown in Scheme 1. All of the dendrons that are produced by this method are obtained in yields of greater than 87% for each step.

Scheme 1.



The next step in the syntheses of the β -diketone ligands involves the coupling of the series of benzyl bromides with 3'-hydroxyacetophenone in the presence of potassium carbonate to obtain the acetophenone-focused monodendrons as shown in Scheme 2. The syntheses of the dendritic β -diketone ligands are accomplished by a Claisen condensation between the acetophenone-focused monodendrons and ethyl trifluoroacetate. All isolated yields of the acetophenone-focused monodendrons and β -diketone ligands are above 70%.

Scheme 2.



The lanthanide complexes are made by deprotonating three equivalents of the ligands with sodium ethoxide, and adding one equivalent of an anhydrous lanthanide(III) chloride. All isolated yields of these complexes are above 50%. The lanthanide complexes synthesized and studied are shown in Figure 1.

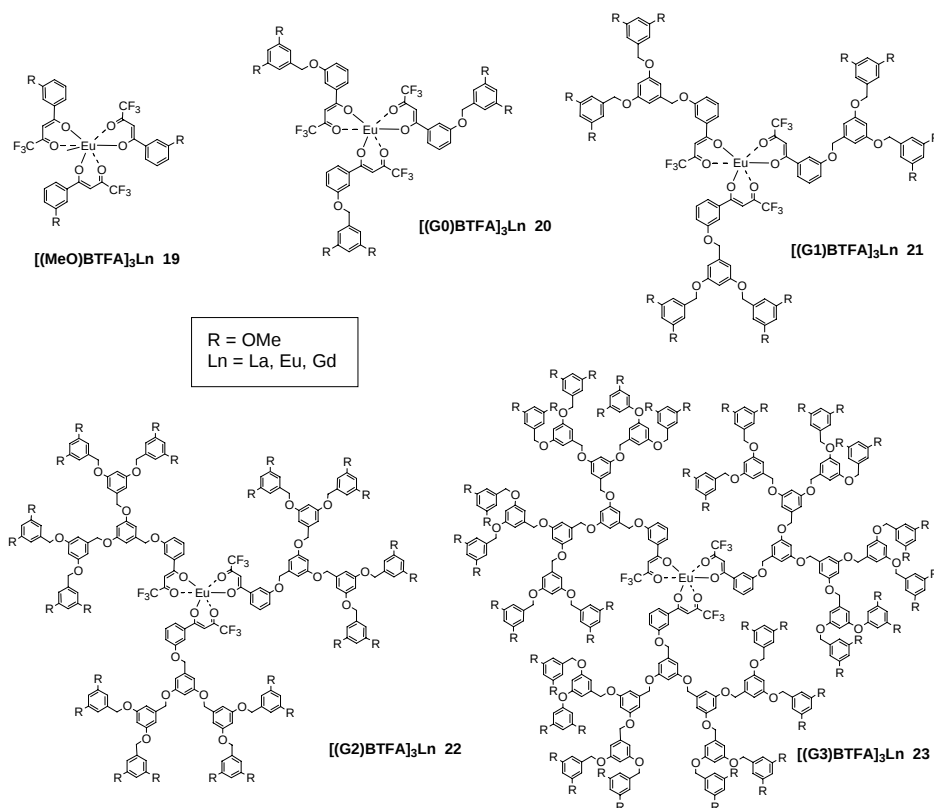


Figure 1. Structures of the dendritic europium coordination complexes (R = OMe).

The acetophenone-focused monodendrons and β -diketone ligands are characterized by ^1H , ^{13}C , and ^{19}F NMR, mass spectrometry and elemental analysis. All data are in agreement with proposed structures. For the lanthanide complexes, MALDI-TOF mass spectrometry and fast atom bombardment mass spectrometry (FAB-MS) yield complex spectra with signals corresponding to the mass of the ligands. This problem is not unexpected because inconclusive analysis with mass spectrometry had been seen in the literature with similar dendritic compounds.⁵ In contrast, elemental analysis proves quite useful. The data are in good agreement with calculated values. With this elemental analysis data and photophysical data that will be discussed later, we are able to confirm that complete *tris* chelation has occurred.

Molecular modeling and calculations of structures. As mentioned earlier, one disadvantage of the lanthanides is their low extinction coefficients and effective absorptivities. This is due to the low oscillator strengths associated with forbidden inter-*f* orbital transitions involved in their excitation. The magnitude of these oscillator strengths, and hence the lanthanides' absorptivities, can be increased by creating an asymmetric ligand field around the lanthanide.¹⁶ In such cases, the selection rules governing the transition probabilities of the lanthanides are slightly relaxed, making them more allowed. In designing organolanthanide coordination complexes, this is achieved by using a mixed ligand system, in which the coordinating atoms are dissimilar in electrostatic potential (*i.e.* the strengths of the various coordinative interactions are not all identical). In our dendrimers, this is achieved by using asymmetric β -diketonate-based ligands.

A consequence of having asymmetric coordinating moieties at the foci of the dendrons is that assembly of three such ligands around a lanthanide ion produces octahedral complexes that are themselves asymmetric. Using three asymmetric bidentate ligands to form octahedral coordination complexes there can be two geometric isomers: facial and meridional. As shown in Figure 2, the facial isomer has two of the three alpha attachments (denoted by **X**) in the equatorial plane, and the meridional isomer has all three alpha attachments in the equatorial plane.

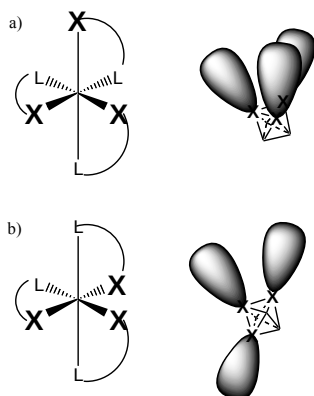


Figure 2. Schematic representation of the geometric isomers of octahedral complexes and positions of dendritic bulk (represented by the shaded lobes) where a) is the facial isomer and b) is the meridional isomer.

In order to determine the most probable isomer for the core moieties of these dendrimers, restricted Hartree-Fock geometry optimizations have been performed for both isomers of $[(\text{MeO})\text{BTFA}]_3\text{La}$. The meridional isomer is 55.0 kcal/mol lower in energy than the facial isomer, indicating that the meridional isomer is the more stable isomer.

Consideration of steric interactions among the dendritic portions of the complexes in both isomers also suggests that the meridional isomer is preferred. In the facial isomer, all three dendritic benzoyl moieties are located at the alpha positions. This places the bulk of all three dendrons in close proximity, leading to a high degree of steric crowding. On the other hand, the meridional isomer has one of the ligands “flipped over,” which places the bulk of one dendron on the opposite side of the complex, thereby minimizing steric interactions among the ligands. This latter arrangement thus favors the meridional isomer. Crystals cannot be grown from these dendritic compounds, which prevents direct observation of their structures. However, computational methods and ^1H NMR pulse relaxation measurements provide insight into the structures of these dendrimers.

The lowest-energy extended conformation of the G0, G1, G2, and G3 dendrimers are shown in Figure 3. The asymmetric placement of the ligands, characterized by a “two-up, one-down” motif, is clearly seen. For the sake of convenience we designate the upper left, upper right, and bottom ligands of each structure in Figure 3 as ligands 1, 2, and 3, respectively. As shown in the figure, ligands 1 and 2 are close together, while ligand 3 is relatively isolated. Due to the spatial location of these ligands, one may expect that as the dendrimer increases in size, ligands 1 and 2 would experience steric congestion more rapidly than ligand 3. It is interesting to note that as the dendrimer increases in size, the core $(\text{BTFA})_3\text{Eu}$ moiety becomes increasingly encapsulated in the interior of the dendrimer. Despite the asymmetric shape at the core, the dendrimer adopts a more spherical overall shape as the number of generations increase, in accord with the globular transition phenomenon observed for dendrimers.¹⁷

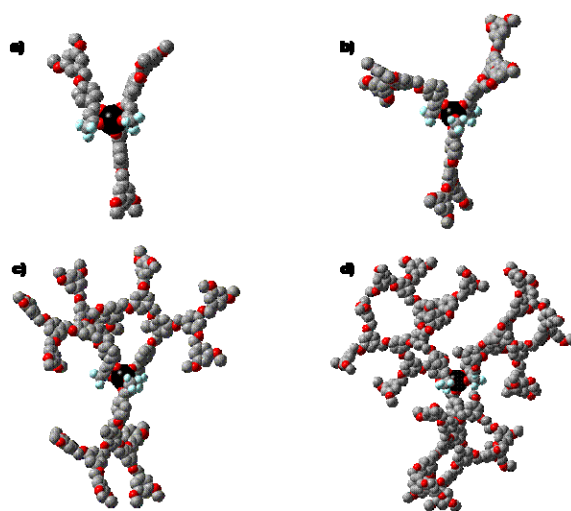


Figure 3. Calculated structures of the lowest-energy extended conformation of the dendritic europium complexes, where a) is [(G0)BTFA]₃Eu, b) is [(G1)BTFA]₃Eu, c) is [(G2)BTFA]₃Eu, d) is [(G3)BTFA]₃Eu. The hydrogen atoms have been omitted for clarity.

It is well known that as a dendrimer increases in size, steric interactions among its branch and peripheral units control structural features such as the spatial distribution of its end-groups, its radial density profile, and its overall shape.¹⁸ Considering the coordinative nature of the core moieties of our dendrimers, it is of particular interest to determine any generational dependence on the structure and symmetry of the core moieties. Figure 4 shows the O-Eu bond lengths for each of the benzoyl- (denoted as “dendron side”) and acetonyl-type (denoted as “CF₃ side”) coordinated oxygens for each ligand of the G0, G1, G2, and G3 dendrimers. The O-Eu bond lengths are in the range of 2.292 - 2.373 Å, with an average of 2.329 Å. This is consistent with experimental O-Ln bond lengths obtained from X-ray crystallographic data of related lanthanide β -diketonate complexes.¹⁹ Bond lengths for the acetonyl O-Eu bonds are on average 0.071 Å shorter than that of the benzoyl O-Eu bonds. The shorter bond lengths of the acetonyl O-Eu bonds suggest that these bonds are more ionic in character, while the benzoyl O-Eu bonds are more dative in nature. The locations of the ionic and dative bonds have been seen in similar BTFA-containing europium complexes.²⁰

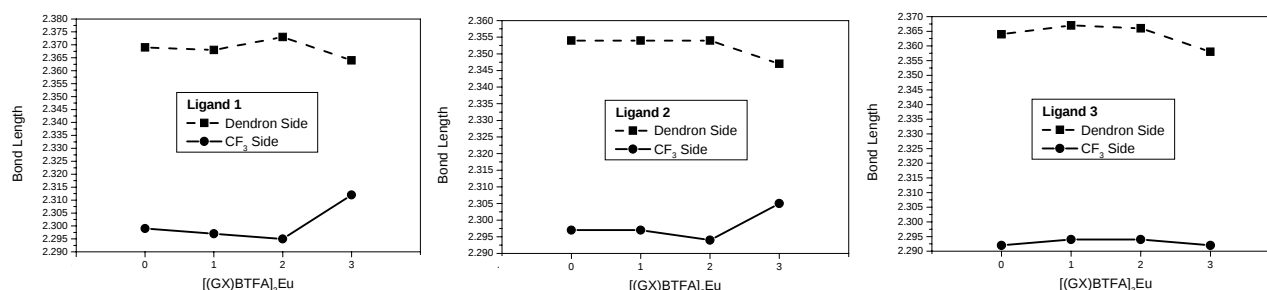


Figure 4. Calculated Ln-O distances (Å) for each of the ligands in the dendritic β -diketonates. Ligands 1, 2, and 3 refer to the left, right, and bottom ligands in each of the structures in Figure 3. The values on the x-axis denote the generation of the dendrimer (*i.e.* X of [G(X)BTFA]₃Eu).

It can be seen from these plots that the various O-Eu bond distances remain relatively unchanged upon increasing the dendrimer size from G0 to G1 to G2. In the G3 complex, however, the benzoyl O-Eu bonds for all three ligands shorten slightly, by an average of 0.006 Å. The acetonyl O-Eu bond ligand 3 remains unchanged, while that of ligands 1 and 2 lengthen by 0.011 Å and 0.017 Å, respectively. These observations are consistent with the previously discussed expectation that as the dendrimer generation increases, more steric congestion in ligands 1 and 2 than in ligand 3 should perturb the former ligands, and hence their interactions with the lanthanide ion to a greater degree than for ligand 3.

¹H-NMR pulse relaxation studies. Further insight into the structure of these dendrimers is obtained by determining the spatial location of methoxy groups at the terminal positions of the dendrons. While the spatial distribution of terminal moieties of dendrimers is presently a subject of debate, it is generally believed that flexible dendrimers possess a nonuniform radial distribution of end groups throughout the internal space of the dendrimer, as well as at its periphery.^{19,21} ¹H NMR pulse relaxation time (*T*₁) measurements have been used to study steric congestion and conformational mobility of dendrimer end groups. It has been shown in dendrimers containing benzyl aryl ether type dendrons (similar to ours) that as terminal methoxy groups became less mobile, their *T*₁ values decrease.²² Because the paramagnetic nature of the europium ions in our dendrimers prevent acquisition of adequate NMR data

(spectra were nearly featureless, and peaks were broad and weak), ^1H NMR pulse relaxation studies have been performed on analogous dendrimers containing the nonparamagnetic lanthanum ion. The use of lanthanum keeps the dendrimer in a chemical and physical environment as close to that of europium as possible, while allowing for NMR data to be obtained.

The relaxation times of the terminal methoxy protons for the various lanthanum-cored dendrimers are given in Table 1. $[(\text{G0})\text{BTFA}]_3\text{La}$ possesses a significantly larger relaxation time than the other three complexes. The G0 ligand is the smallest in size; therefore its T_1 value was expected to be the highest among the complexes, because steric congestion would not have been present to any significant degree. However, in $[(\text{G1})\text{BTFA}]_3\text{La}$, $[(\text{G2})\text{BTFA}]_3\text{La}$, and $[(\text{G3})\text{BTFA}]_3\text{La}$, the relaxation times decrease as the generations of the dendrimers increase. This suggests that conformational mobility of the methoxy groups is hindered as the dendrons increase in size, a result in accord with previous studies.²³ In addition to this decrease in T_1 values, there are two distinguishable methoxy proton signals for the G2 and G3 dendrimers, indicating that there are methoxy protons in two different chemical environments. These two signals integrate to a 2:1 ratio. Four possible explanations for these observations are that 1) the methoxy groups on ligands 1 and 2 are inherently different than those on ligand 3, considering the asymmetry of the ligand orientation around the lanthanide ion; 2) some of the terminal moieties are located at the periphery of the dendrimer, while others are folded into the interior of the dendrimer; 3) ligand dissociation occurs for the G2 and G3 dendrimers (perhaps due to severe steric congestion), in which one ligand dissociates from the lanthanide ion; or 4) the methoxy protons become distinguishable only when the degree of steric congestion in ligands 1 and 2 exceeds that of ligand 3. The first explanation cannot be correct, because the NMR spectra of the G0 and G1 dendrimers show that only one type of methoxy group is present in each of these compounds. We discount the second explanation on the basis of the 2:1 ratio observed for the intensities of the methoxy signals. It would be expected that the greater degree of steric congestion in the G3 dendrimer would force more terminal moieties into its interior, and the ratio would change accordingly. While it may simply be a coincidence that this ratio is 2:1, it is unlikely that both the G2 and G3 dendrimers would have the same ratio. We also discount the third explanation, because the degree of steric interactions required for ligand dissociation is unlikely for third-generation benzyl phenyl ether dendrimers, and ligand dissociation would require disrupting both the bidentate coordination and ion-pair interactions between the ligand and lanthanide ion. Any ligand dissociation would leave the ions unpaired, and so would not occur. Photophysical behavior of these complexes, which is discussed in the next section, also discredits this third explanation. Only the fourth explanation is in accord with the NMR spectra, T_1 values and trends, and photophysical data. These data suggest that as the generation of the dendrimer increases, so does the steric congestion within the ligands. Considering the asymmetry of the core moiety, the degree of crowding in ligands 1 and 2 increases faster than in ligand 3, resulting in the generation of two chemically distinct methoxy groups. This supports the 2:1 integration ratio of the NMR signals, differentiating the methoxy groups on ligands 1 and 2 from those on ligand 3. This interpretation also is consistent with these dendrimers being the meridional isomers, in which only two ligands are in similar chemical environments. If these dendrimers are the facial isomer, all three ligands would be equivalent, yielding only one chemical shift distinct methoxy signal. It is interesting to note that the greatest disparity in relaxation times for a given dendrimer size is found for G2, suggesting that the G3 dendrimer possesses sufficient steric congestion in all three ligands to make the methoxy groups more similar in chemical environment, in contrast to the G2 dendrimer.

Table 1. T_1 Relaxation Times of Peripheral Methoxy Groups.

La^{+3} complex	T_1 (sec)
G0	1.69
G1	1.36
G2	1.35
	1.31
G3	1.32
	1.31

Photophysical investigations related to molecular structure. When each dendrimer is excited at 280 nm, corresponding to the absorption maxima of the phenyl rings in the dendrons, intense emission is observed from the europium. Such sensitized emission confirms *tris* chelation of the lanthanide. When one equivalent of ligand **18** is added to $[(\text{G2})\text{BTFA}]_2\text{EuCl}$, a marked increase in europium emission is observed, as shown in Figure 5. The increase in emission is disproportionate with the increase in number of phenyl rings added. This is attributed to the site isolation effect, and confirms the *tris* chelation of the europium. When additional amounts of ligand were added, there are no further increases in europium emission, indicating that all of the $[(\text{G2})\text{BTFA}]_2\text{EuCl}$ has been chelated. Detailed investigation of these emission spectra provides further insight into the structure of these dendrimers.

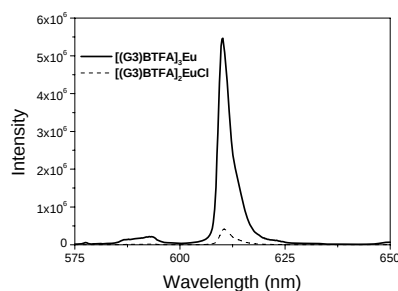


Figure 5. Comparison of emission spectra of *bis*-diketonate complex and the *tris*-diketonate complex (10^{-6} M in acetonitrile, $\lambda_{ex} = 280$ nm). Both spectra were obtained under identical conditions.

As discussed earlier, theoretical calculations indicate that the lowest energy geometric isomers of the dendritic β -diketonate lanthanide complexes are inherently asymmetric. The degrees of asymmetry and other information are ascertained by examining the transitions in the complexes' luminescence emission spectra. A typical Eu^{3+} spectrum consists of five transition bands, as shown in Figure 6. Each transition corresponds to decays from the same lowest excited state to different lower lying states of Eu^{+3} .

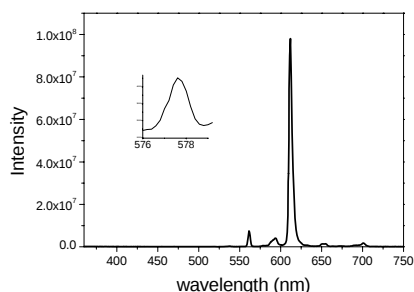


Figure 6. Sensitized emission spectrum of $[(\text{G2})\text{BTFA}]_3\text{Eu}$ in spectroscopic grade acetonitrile (1.0×10^{-6} M) at 298K. Excitation was performed at 280 nm, corresponding to the absorption maximum of the dendrons.

The radiative transitions of trivalent europium consists mainly of weak magnetic and induced electric dipole transitions.²⁴ The former transition, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition at 578 nm, is characteristically weak, and displays no ligand field splitting due to the nondegeneracy of the $^7\text{F}_0$ state. Thus, the presence of multiple species would be indicated by multiple peaks near 578 nm. As seen from Figure 6 (inset) and Figure 7, all five complexes show a similar single peak at 578 nm. This indicates that for each dendrimer only one luminescent Eu^{+3} species is present in solution.

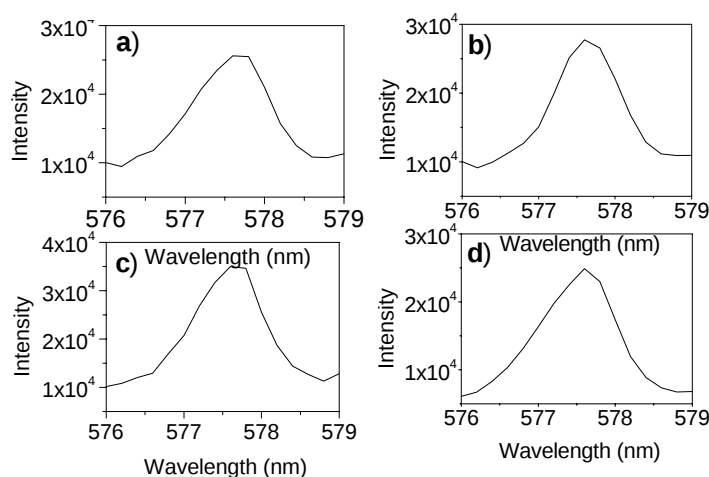


Figure 7. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition for each of a) $[(\text{OMe})\text{BTFA}]_3\text{Eu}$, b) $[(\text{G0})\text{BTFA}]_3\text{Eu}$, c) $[(\text{G1})\text{BTFA}]_3\text{Eu}$, and d) $[(\text{G3})\text{BTFA}]_3\text{Eu}$ at 1.0×10^{-6} M in acetonitrile. $\lambda_{ex} = 280$ nm. The spectrum of $[(\text{G2})\text{BTFA}]_3\text{Eu}$ is shown in the inset of the previous figure.

From Judd-Ofelt theory, magnetic dipole transitions are independent of the chemical environment while the electric dipole transitions are heavily influenced.¹⁷ The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is a magnetic dipole transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, which is always the strongest in intensity, is an induced electric dipole transition. In our complexes, this transition is extremely sensitive to changes in the environment of the first coordination sphere of Eu^{+3} , where as the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is not. Because of this

difference, the degree of asymmetry at the Eu^{+3} core can be determined by calculating the ratio of the intensities between 612 nm and 593 nm (I_{7F2}/I_{7F1}). Uncoordinated and symmetrical compounds have values close to three, while asymmetrical compounds would have values larger than three.¹⁷ These ratios for our dendrimers are summarized in Table 2.

Table 2. Symmetry Data of Dendritic Lanthanide β -Diketonates and Related Dendrimers.

Complex	I_{7F2}/I_{7F1}	I_{7F2}/I_{7F1}
	In Acetonitrile	In Toluene
[(OMe)BTFA] ₃ Eu	24.5	15.7
[(G0)BTFA] ₃ Eu	24.3	15.7
[(G1)BTFA] ₃ Eu	24.4	15.3
[(G2)BTFA] ₃ Eu	23.7	15.2
[(G3)BTFA] ₃ Eu	23.4	14.9
[G-1] ₃ -Eu*	–	3.4
[G-3] ₃ -Eu*	–	4.5
[G-4] ₃ -Eu*	–	4.9

* calculated from data in reference 5.

In comparing these complexes with similar dendritic lanthanide complexes prepared by Kawa and Fréchet (shown as the last three entries in Table 2),⁵ which have each of three similar ligands attached to the lanthanide by a carboxylate group, our complexes are significantly more asymmetric with respect to the lanthanide's first coordination sphere. This is expected due to the ligating moieties used in the present work, which are asymmetric themselves. However, the magnitudes of the ratios observed are surprising. To our knowledge, the ratios for the dendrimers in acetonitrile are the highest known, indicating that these dendrimers may be the most asymmetric organoeuropium coordination compounds prepared to date.¹¹ It is interesting to note that solvent (acetonitrile or toluene) plays a large role in the nature of the first coordination sphere, presumably due to differences in steric congestion of the ligands caused by differences in their solvation. The asymmetry ratios also discredit the third explanation given earlier for the methoxy proton relaxation data obtained. Considering the still high asymmetry ratios obtained for the G2 and G3 dendrimers, it is unlikely that dissociation of any ligands occurs in these compounds. This is further substantiated by the increasing intensities of emission upon going from G1 to G2 to G3, which is expected from the increase in potential energy donors (*i.e.* phenyl rings) and the preservation of site isolation afforded by *tris* chelation. When one equivalent of a ligand **13** (similar to ligand **18**, but incapable of chelation) is added to a solution of [(G3)BTFA]₂EuCl, no increase in emission intensity or lifetime is observed over that for [(G3)BTFA]₂EuCl alone. This suggests that a dissociated ligand does not act as a sensitizer. Since no reduction of intensity is observed upon increasing the dendrimer size, it is unlikely that ligand dissociation to produce a chemically different methoxy group is responsible for the two proton relaxation times observed for each of the G2 and G3 dendrimers, in accord with our previous assertions.

Conclusion. A series of dendritic β -diketonate lanthanide complexes have been synthesized and their structural properties studied. Molecular modeling and theoretical calculations indicate that each of these dendrimers exist as the meridional isomer. Ln-O bond lengths suggest that some lengthening occurs in the third-generation dendrimer, in order to relieve the stress brought about by steric hindrance. ¹H NMR T₁ relaxation times of the terminal methoxy groups indicate a relatively open interior of the dendrimers. The same data indicate that there are two different types of ligands in a 2:1 ratio, in accord with the complexes being meridional isomers. Photophysical studies support *tris* chelation of the lanthanide, meridional isomer arrangement of the ligands, and high asymmetry at the first coordination sphere of each of the complexes prepared. The structural features of these dendrimers have a significant effect on the complex photophysical properties of these dendrimer complexes, which is discussed in a separate paper.²⁵

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Part II: Photophysical and Energy Transfer Properties

Introduction

Natural photon-harvesting systems are often composed of sequentially assembled subunits consisting of light-harvesting moieties, known as chromophores, which absorb one or more photons and transport the absorbed energy in a particular direction within the system. An example of one such system is phycobilisome,¹ the light-harvesting array in blue-green algae. These complexes are essentially stacks of light-absorbing chromophores radiating from a central point. They consist of an external shell complex (light-harvesting complex, LH2), an interior shell complex (light-harvesting complex, LH1), and the central core.² The chromophores are positioned along each stack with the higher-energy absorbers (LH2) at the outside of the array and those of lower energy (LH1) closer to the locus of the array. This arrangement produces an energy gradient for the excitation energy to be transferred from the outer high-energy sites to the lower energy ones at the locus.

Over the past ten years there has been much interest in mimicking the light-harvesting ability seen in nature.³⁻⁷ Xu and Moore demonstrated the use of polyphenylacetylene monodendrons to transfer absorbed energy to perylene.⁴ Jiang and Aida used energy transfer in dendrimers to facilitate infrared light induced *cis-trans* isomerization of an azobenzene core.⁵ Vögtle and Balzani

surrounded a $[\text{Ru}(\text{bpy})_3]^{2+}$ core with second generation dendrons containing naphthyl peripheral moieties.⁶ Kawa and Fréchet encapsulated lanthanide ions with carboxylate-focused poly(aryl ether) dendrons for use in possible optical signal amplification.⁷

Over the past thirty years, trivalent lanthanide complexes have been used in many applications such as luminescent probes,⁸ lasers,^{9,10} and organic light emitting diodes (OLEDs).¹¹⁻¹³ Unlike organic dyes and polymers, whose fluorescence or phosphorescence bands are typically broad, lanthanides have narrow width emission bands (<10 nm full width at half maximum).¹⁴ The sharp emission bands of lanthanides can be attributed to the effective shielding of the 4f orbitals from vibrational forces by the overlying 5s and 5p orbitals.

As luminescent species, one advantage of organolanthanide complexes over transition metal complexes is that their excitation and emission mechanisms are independent from one another. Direct excitation of a lanthanide ion can be achieved only with the use of lasers because of the small extinction coefficients of lanthanides (on the order of $1\text{--}10\text{ M}^{-1}\text{cm}^{-1}$).¹⁵ However, by using ligands that can be excited very easily through less energetic means, and non-radiatively transferring the energy to the lanthanide, the latter can be easily excited. Because of this separation of absorption and emission, one can tailor organolanthanide coordination complexes to have absorption properties characteristic of the ligands, while retaining the inherent emission properties of the lanthanide ion. This may be advantageous in some areas of biophotonics and information technology, where flexibility of absorption, and therefore excitation, is desired, but the emissive characteristics are invariant to chemical modification or chemical environment of the lumophore. Examples of such areas include multi-channel luminescence assays that require the use of different colors of narrow-bandwidth emissive lumophores that are excitable at the same wavelength, and in optical amplifier devices that require luminescent species that do not change their emission wavelength as the chemical environment changes.

While β -diketonates have long been used as ligands for trivalent lanthanide ions, only recently have dendritic lanthanide β -diketonates been prepared. Dalton¹⁶ and coworkers have investigated first-generation dendrimers in OLED devices. Here we report the syntheses and photophysics of a series of photon-harvesting lanthanide complexes by chelating dendritic β -diketonate ligands to trivalent europium, as shown in Figure 1. The ligands are modified 3-benzoyl-1,1,1-trifluoroacetate (BTFA) units with increasing generations of poly(aryl ether) dendrons.

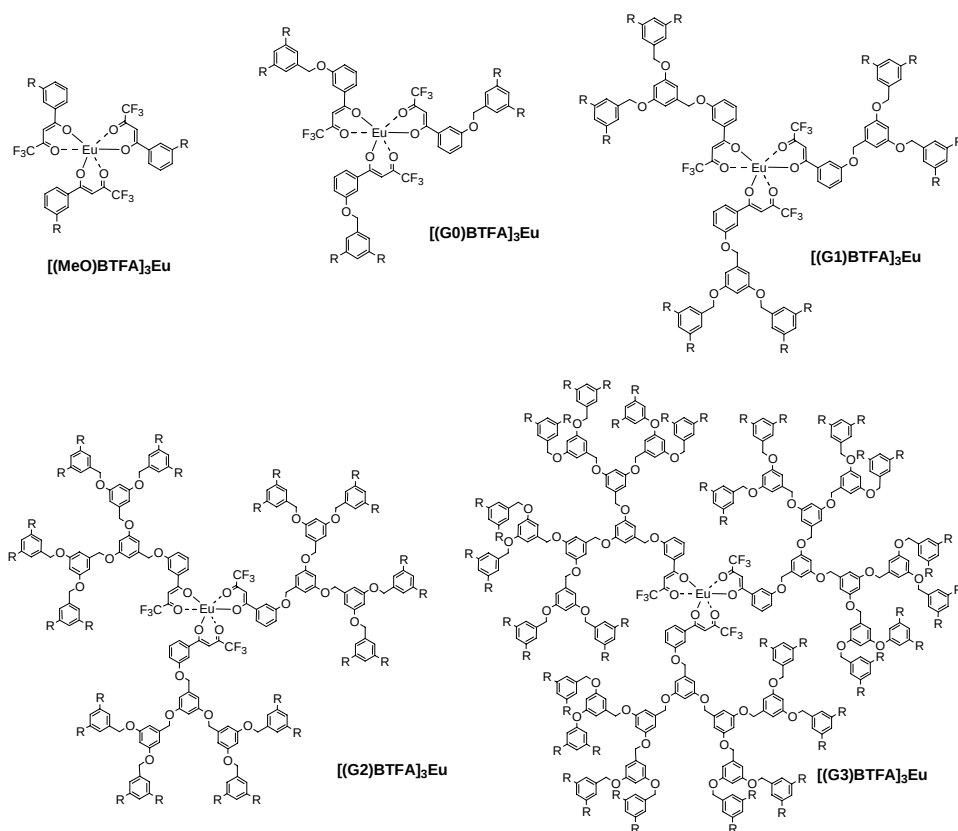


Figure 1. The structures of the *tris* europium complexes, where R = OMe.

Experimental Section

Materials. The synthetic procedures and characterization of the ligands and complexes not shown below are reported elsewhere.¹⁷

Photophysical studies. Steady-state emission and excitation spectra were recorded using a Jobin-Yvon Fluorolog-3 spectrofluorometer model FL3-21 with a 450 W xenon lamp source, double grating excitation monochromator, single grating emission monochromator, and a room temperature R928 PMT as detector. Plots were generated using GRAMSTM and DataMaxTM software. Lifetime studies were carried out using the Fluorolog-Tau3 system and DataMax lifetime software that was based on acquisition of frequency-domain lifetime measurements. Phosphorescence studies were carried out with a SPEX 1934D3 phosphorimeter using a

xenon flash lamp in connection with the Fluorolog-Tau3 model FL3-21 system. Absorbance spectra were generated using an OLIS modified Cary 14 UV/VIS/NIR spectrophotometer equipped with deuterium and tungsten lamps for the UV and Vis/NIR regions. Quantum yields were measured in chloroform relative to quinine sulfate (1N H₂SO₄) ($\Phi_s = 0.546$) as per the method described previously.¹⁸

Results and Discussion

A series of dendrimers have been prepared in which the benzyl phenyl ether dendrons increase in size, up to the third generation. The hierarchical ordering of the electroactive subunits in these dendrimers are patterned after natural light harvesters that have been mentioned previously. Each dendrimer consists of three parts, as shown in Figure 2: a layer of high-energy phenyl moieties (A), in which the size of the layer increases throughout the series of dendrimers prepared; a layer of intermediate energy β -diketonates (B), in which the size of the B layer remains constant throughout the series of dendrimers; and the low-energy trivalent lanthanide core (C), which also remains constant in size throughout the series of dendrimers.

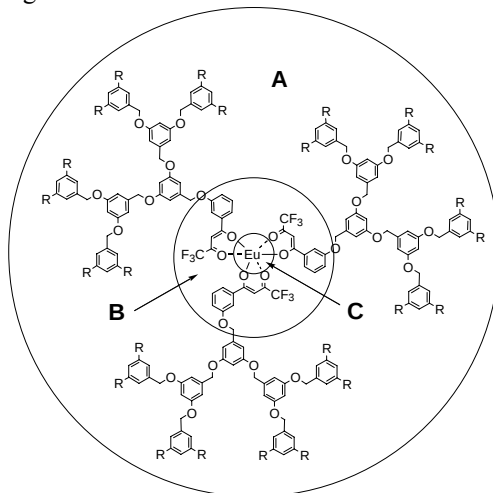


Figure 2. [(G2)BTFA]₃Eu, showing the designations of shells A, B, and C. R = OMe.

When the phenyl rings are excited, emission is observed from the lanthanide ion at the core. The energy transfer pathway for these dendritic complexes is denoted as (A→B→C). The simplified Jablonski diagram for this process is shown in Figure 3.

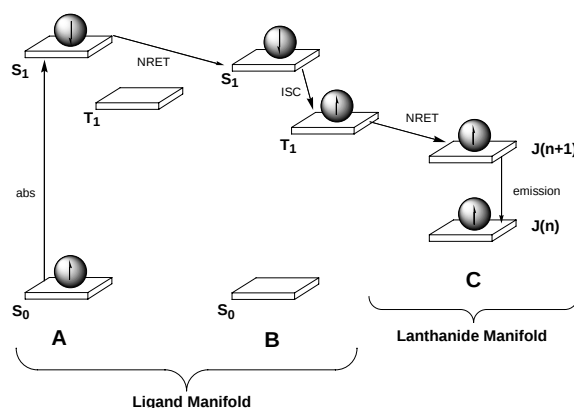


Figure 3. Energy diagram for energy transfer within these dendritic lanthanide complexes.

Excitation of a phenyl ring in a dendron promotes it from its ground singlet state (S_0) to its first excited state (S_1). By the Förster mechanism, the energy is non-radiatively transferred to the S_1 level of the β -diketonate. Because the lanthanide is directly coordinated to the β -diketonate, the lanthanide exerted a heavy atom effect on the β -diketonate.¹⁹ The heavy atom effect facilitates intersystem crossing (ISC) from a singlet state to a triplet state. Hence, once the β -diketonate is excited, the singlet state energy transfers to the T_1 state of the β -diketonate. The possibility the lanthanide exerting a heavy atom effect on the phenyl rings in the dendron and facilitating triplet-triplet energy transfer, or Dexter energy transfer, between phenyl ring and β -diketonate is unlikely, given the closeness (*i.e.*, on the order of bond lengths) necessary for both the heavy atom effect and triplet-triplet energy transfer. This spatial proximity requirement also negates the possibility of direct transfer of energy from a dendron phenyl moiety to the lanthanide. The final step of the energy transfer pathway is the non-radiative energy transfer (NRET) from the β -diketonate triplet state to the emissive J state of the lanthanide, from which emission occurs.

The absorbance spectra for the dendritic ligands display features typical for ultraviolet absorbing materials as shown in Figure 4. The peaks at 280 nm correspond to the $\pi^* \leftarrow \pi$ transition of the phenyl moieties in the dendrons, and display a monotonic increase in absorptivity as the number of phenyl rings increase from generation to generation. In other words, if the absorptivities of

the four dendritic complexes at 280 nm are normalized to the number of phenyl rings in the dendrons, the resulting values are the same for all four complexes. This indicates that each phenyl ring in each complex is able to absorb the same amount of light. Any deviation from linearity would have indicated that the transition moments of the phenyl rings could not orient themselves to coincide with the wavevector of the incident light, leading to a decrease in the effective extinction coefficient at that wavelength. Since there is no deviation, the phenyl rings can be regarded as freely-orienting chromophores despite their bond connectivity. Because each phenyl ring absorbs the same amount of light, any attenuation of lanthanide emission must be due to other characteristics of the compounds.

The bands centered at 340 nm correspond to the $\pi^* \leftarrow n$ transition of the BTFA moiety. The similar absorptivities at 340 nm of all the complexes indicate the same concentration of β -diketonates were in solution, in accord with all compounds having the same *tris*-chelated core. The excitation spectrum of each of the five dendritic complexes matched its corresponding absorption spectrum of the ligand used, indicating that the mode of sensitization of lanthanide emission occurs as discussed earlier.

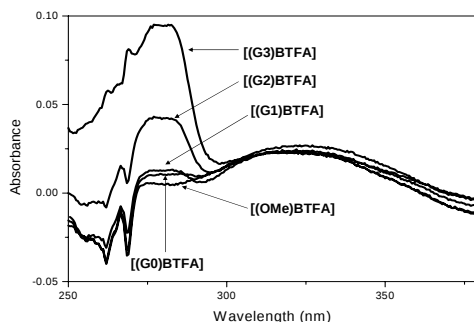


Figure 4. Absorbance spectra of 1.0×10^{-6} M solutions of the dendritic ligands in spectroscopic grade acetonitrile.

Since energy transfer from ligand to lanthanide occurs from the triplet state of the ligand, it is important to determine the triplet energies (E_T) of the ligands in the chelate environment. This is accomplished by phosphorescence spectroscopy of the gadolinium chelate (at 77 K in 2-methyltetrahydrofuran), where the phosphorescence maximum is taken as the 0-0 transition as shown in Figure 5 for [(G3)BTFA]₃Gd.

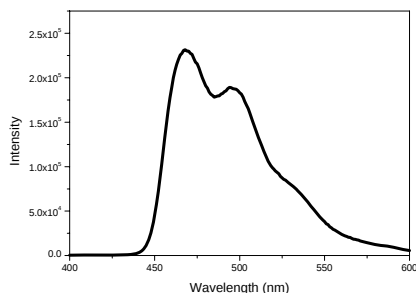


Figure 5. Phosphorescence spectrum at 77K of [(G3)BTFA]₃Gd in 2-methyltetrahydrofuran.

The lowest excited state for Gd^{3+} (6P) is located at $32,000 \text{ cm}^{-1}$. Since this state is much higher in energy than any organic ligand, the energy from the ligand can not be transferred to Gd^{3+} . Therefore, any emission of [(G3)BTFA]₃Gd and the other Gd^{3+} complexes is due only to the ligands. From the phosphorescence spectrum of [(G3)BTFA]₃Gd the E_T is determined to be $21,254 \text{ cm}^{-1}$ (2.64 eV). The other dendritic ligands have similar values as summarized in Table 1.

Table 1. Triplet energies (E_T) for the ligands, as determined from [(Gn)BTFA]₃Gd (n = generation number).

Ligand	E_T	
	(cm^{-1})	(eV)
(G3)BTFA	21,254	2.64
(G2)BTFA	21,156	2.62
(G1)BTFA	20,940	2.60
(G0)BTFA	20,851	2.59
(OMe)BTFA	19,546	2.42

When the Gd^{3+} complexes are excited at either 280 nm or 340 nm, corresponding to the dendron phenyl and BTFA absorbances, respectively, only phosphorescence from the BTFA moiety was seen. This meant that energy transfer from the dendron to the BTFA moiety was fairly efficient or the residual decay from the dendrons was non-radiative. In such systems, efficient energy transfer from energy donor to energy acceptor occurs when the E_T of the donor is approximately 2000 cm^{-1} higher than the accepting level of the acceptor.^{20,21} If the E_T is within 2000 cm^{-1} of the accepting level, then thermal back energy transfer to the donor occurs, resulting in reduced energy transfer efficiency and weak acceptor emission. The non-transferred energy is dissipated nonradiatively to the host matrix and/or radiatively as residual emission from the donor.

The energies of the lowest emitting levels for the typical visible wavelength emitting lanthanides Tb^{3+} , Sm^{3+} and Eu^{3+} are ($^5\text{D}_4 = 20,400\text{ cm}^{-1}$), ($^4\text{G}_{5/2} = 17,924\text{ cm}^{-1}$), and ($^5\text{D}_0 = 17,500\text{ cm}^{-1}$), respectively. The relevant transitions are shown in Figure 6.

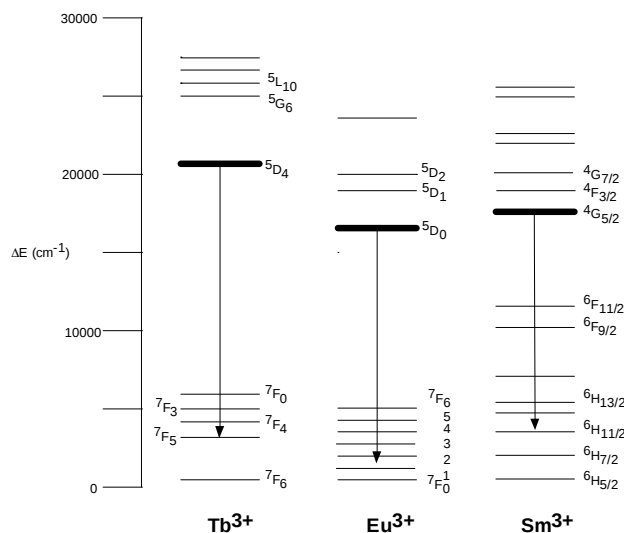


Figure 6. Energy levels of some visible emitting lanthanides, lowest emitting level is shown in bold.

Energy transfer to Tb^{3+} . As shown in Table 1, the five ligands have E_T values near $20,000\text{ cm}^{-1}$. Their differences in energies with the emitting level of Tb^{3+} (e.g., $\Delta E_T = 756\text{ cm}^{-1}$ for (G2)BTFA) make them poor choices to sensitize Tb^{3+} . For each of the ligands, back energy transfer occurs leading to considerable residual ligand emission. This is shown in Figure 7a. The spectrum consists of the characteristic sharp emission for Tb^{3+} : $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (487 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (544 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (583 nm), and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (621 nm). However, an intense, broad peak centered at 420 nm is also present, and is the emission from the ligand. If this latter emission is due to thermal back energy transfer, cooling the sample should prevent it, and result in an increase in Tb^{3+} emission. Indeed, when the sample is cooled to 77K in 2-methyltetrahydrofuran, the ligand-centered emission is absent, and the Tb^{3+} emission is much stronger, indicating that thermal back energy transfer does occur at ambient temperature.

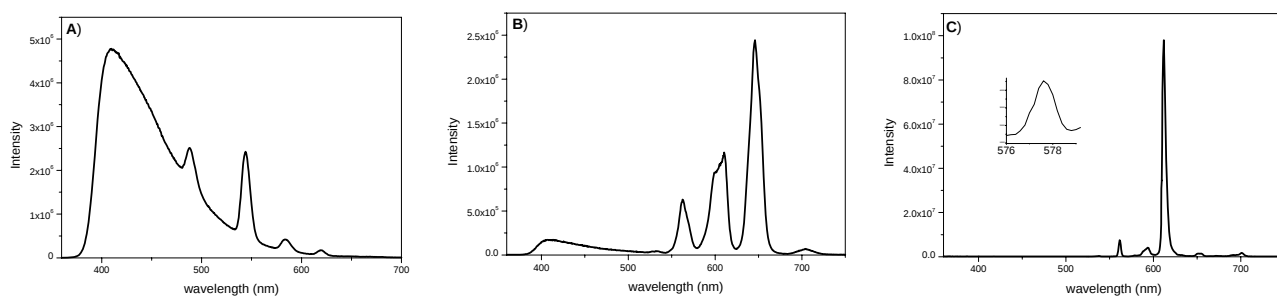


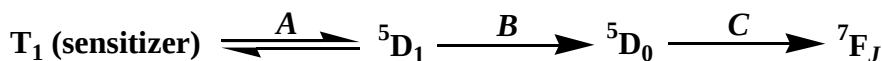
Figure 7. Emission spectra of $[(\text{G2})\text{BTFA}]_3\text{Ln}$ in spectroscopic grade acetonitrile. (a) $[(\text{G2})\text{BTFA}]_3\text{Tb}$ ($1.0 \times 10^{-6}\text{ M}$) at 298K, (b) $[(\text{G2})\text{BTFA}]_3\text{Sm}$ ($1.0 \times 10^{-6}\text{ M}$) at 298K, and (c) $[(\text{G2})\text{BTFA}]_3\text{Eu}$ ($1.0 \times 10^{-6}\text{ M}$) at 298K. Excitation was performed at 280 nm, which corresponds to the absorption maximum of the dendrons.

Energy transfer to Sm^{3+} . The energy difference between the ligands and Sm^{3+} are above 2000 cm^{-1} (e.g., $\Delta E_T = 3232\text{ cm}^{-1}$ for (G2)BTFA). Thus, these ligands are suitable for sensitizing Sm^{3+} at room temperature. The emission spectrum for $[(\text{G2})\text{BTFA}]_3\text{Sm}$ at 298 K is shown in Figure 7b, and displays the characteristic emission lines for Sm^{3+} : $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{3/2}$ (532 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (564 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (610 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (648 nm), and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ (711 nm). The weak, broad peak centered at 420 nm is residual emission from the BTFA moiety. Because this peak disappears upon cooling the sample to 77K, it is due back energy transfer. The weakness of residual emission indicates that the ΔE_T value between (G2)BTFA and Sm^{3+} is near the limit of back energy transfer at room temperature, and increasing the energy gap slightly would prevent it altogether.

Energy transfer to Eu^{3+} . The difference in triplet energy levels of the ligands and Eu^{3+} (e.g., $\Delta E_T = 3656 \text{ cm}^{-1}$ for (G2)BTFA and the $^5\text{D}_0$ state of Eu^{3+}) are higher than that for Sm^{3+} . These complexes are therefore expected to have no residual emission and be strongly luminescent at room temperature. The emission spectrum for [(G2)BTFA]₃Eu, shown in Figure 7c, was taken at 298 K. It displays the characteristic emission lines for Eu^{3+} : $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (579 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (594 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (612 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (651 nm), and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (704 nm). That no residual emission is seen from the BTFA moiety, and strong europium emission indicates efficient energy transfer, details of which are given later. Because the ^5D manifold of Eu^{3+} contains two closely-spaced emitting levels (i.e. $^5\text{D}_0$ and $^5\text{D}_1$), the exact mechanism of energy transfer from ligand to these states is often poorly understood. A detailed examination of the spectrum for [(G2)BTFA]₃Eu provides insight into the energy transfer to Eu^{3+} in these complexes.

It is generally believed that sensitization from the ligands populates both the $^5\text{D}_1$ and the $^5\text{D}_0$ states, but all the emission from Eu^{3+} emanates from the $^5\text{D}_0$ state. Watson and Stucky have argued that the $^5\text{D}_0$ state was populated by two methods: a fast direct and a slower indirect energy transfer from the $^5\text{D}_1$ state.²² However, current studies have shown that both states are emissive. van Veggel and coworkers have shown that emissions from the $^5\text{D}_1 \rightarrow ^7\text{F}_1$ transitions of trivalent europium can be deconvoluted from the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions using a pulsed laser system and streak camera.²³ Emissions from the former transitions are much lower in intensity than those from the latter transitions. Also, the $^5\text{D}_0$ state decays in the order of milliseconds, while the $^5\text{D}_1$ state decays in the order of microseconds. Recent work of de Silva *et al.*²⁴ can explain these observations. They have derived some selection rules for energy transfer from sensitizers to the emitting levels of Eu^{3+} . Via multipolar interactions (i.e., Förster-type energy transfer mechanism), energy transfer is an “allowed” process when transferring to the $^5\text{D}_4$, $^5\text{G}_6$, $^5\text{L}_6$, and $^5\text{D}_2$ states. By means of electron exchange (i.e., the Dexter energy transfer mechanism), energy transfer is an “allowed” process when transferring to the $^5\text{D}_1$ state. In all cases, energy transfer to the $^5\text{D}_0$ state was a “forbidden” process. The work of van Veggel *et al.* mentioned above justifies this derivation in noticing that no direct energy transfer occurs to the $^5\text{D}_0$ level for their complexes, but is populated indirectly through decay from the $^5\text{D}_1$ state.²³ In other words, direct energy transfer from ligand to the emitting state of Eu^{3+} is forbidden. Instead, energy is first transferred from the ligand to the $^5\text{D}_1$ state of Eu^{3+} . The excited ion then decays to the $^5\text{D}_0$ state, from which emission occurs.

This notion that energy transfer from a sensitizer to the $^5\text{D}_1$ state being favored over the $^5\text{D}_0$ state in [(G2)BTFA]₃Eu brings into question the requirement that the donor energy level should be more than 2000 cm^{-1} higher than the acceptor level of Eu^{3+} . The $^5\text{D}_1$ level of Eu^{3+} has energy of $19,270 \text{ cm}^{-1}$, which is 1770 cm^{-1} higher in energy than the $^5\text{D}_0$ level. The energy differences between the triplet levels of the BTFA moieties of our ligands and the $^5\text{D}_1$ level is around 1800 cm^{-1} . If the ligands transfer their energy to this state, then there would be a significant amount of back energy transfer and residual donor emission. However, the europium spectra of the dendrimers are devoid of such emission. The $^5\text{D}_0$ level being populated without back energy transfer can be reconciled if the rate of decay from the $^5\text{D}_1$ state to the $^5\text{D}_0$ state is faster than the rate of back energy transfer. This has indeed been found to be the case.^{25,26} The energy transfer pathway from a sensitizer to Eu^{3+} is schematically shown as:



A denotes the equilibrium energy transfer from the sensitizer to the $^5\text{D}_1$ state, *B* denoted the decay from the $^5\text{D}_1$ level to the $^5\text{D}_0$ level, and *C* denoted emissive decay from the $^5\text{D}_0$ level to the $^7\text{F}_J$ level. It has been determined both theoretically and experimentally that *A* occurs at a rate of 10^5 s^{-1} , *B* occurs at a rate of 10^6 s^{-1} , and *C* occurs at a rate 10^3 s^{-1} . Thus, the faster internal conversion between the $^5\text{D}_n$ states relative to the sensitization equilibrium rate allows the sensitizer triplet level to be closer than 2000 cm^{-1} to the $^5\text{D}_1$ level of Eu^{3+} without back energy transfer at room temperature, and so to maintain high energy transfer efficiency.

Eu^{3+} Series Comparison. Exciting each of the five dendritic Eu^{3+} complexes at 280 nm results in an emission spectrum similar to that shown in Figure 7c; the only difference among the series being the intensity of emission. When excited at 280 nm, the intensity of emission of each dendrimer is greater than the model compound [(OMe)BTFA]₃Eu, despite being of the same concentration in solution, as shown in Figure 8.

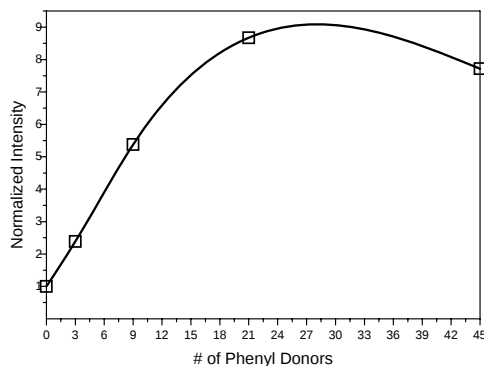


Figure 8. Graphical comparison of the intensities of the dendritic europium complexes ($1.0 \times 10^{-6} \text{ M}$) in spectroscopic grade acetonitrile at 298 K when excited at 280 nm. All spectra were normalized with respect to [(OMe)BTFA]₃Eu.

As the number of generations increase, the number of energy donors (i.e. phenyl moieties) increase. However, the emission intensity does not increase in proportion. Rather, the increase reaches a maximum with [(G2)BTFA]₃Eu being 8.6 times brighter than [(OMe)BTFA]₃Eu, but decreased for the next larger dendrimer, [(G3)BTFA]₃Eu.

Moore *et al.*⁴ noticed a decrease in emission in their larger dendrimer systems where a true energy gradient was not present. This decrease has been attributed to a geometric bias to direct the excited state energy to the dendrimer terminal moieties. In dendrimers that also possess an energetic bias to direct the excited state energy toward the core moiety, these two biases are in competition, and the actual behavior of energy migration is complex.³⁰ The energetic bias in our dendrimers is established by the relatively high energy phenyl moieties of the dendrons, the intermediate energy BTFA moieties in the interior of the dendrimer, and the lowest energy lanthanide ion at the dendrimer core. Thus, the energetic bias is in opposition to the geometric bias. Thus, the decrease in emission intensity may be explained as the geometric bias becoming a stronger factor in the energy transfer pathway upon increasing the dendrimer size from G2 to G3. However, this decrease was somewhat unexpected for the third generation dendrimer, because similar poly(aryl ether) dendritic lanthanide compounds showed no such decreases in intensity at higher generations.³¹

The quantum yields for these dendrimers follow the same trend as their intensities. However, the Eu^{3+} excited state lifetimes do not follow this trend. The quantum yields and lifetimes are summarized in Table 2. The lifetimes of the complexes increase monotonically from 0.659 ms for $[(\text{G0})\text{BTFA}]_3\text{Eu}$ to 0.802 ms for $[(\text{G3})\text{BTFA}]_3\text{Eu}$. This increase, without the roll-over seen in the trend in intensities, indicates that the ligands are protecting the core from non-radiative de-excitation mechanisms more efficiently as the dendrons increased in size. In other words, the site isolation effect of the dendrimers is preserved throughout this series of compounds. In theory, a longer lifetime should correspond to a proportionate increase in emission intensity. However, this is not seen with these complexes. Reconciliation of these photophysical data is made by considering that in the case of sensitization, the observed intensity is related to not only the quantum efficiency of acceptor emission, but also to the energy transfer efficiency from donor to acceptor. The Eu^{3+} excited state lifetimes indicate that the inherent quantum yields of the europium emission of the series increase throughout the series. This suggests that the source of the attenuation of intensity is due to decreasing energy transfer efficiencies, which is most pronounced in the third-generation dendrimer. Since the energy transfer occurs in two steps, *i.e.* (A $\rightarrow$ B) and (B $\rightarrow$ C), overall energy transfer efficiencies must be deconvoluted to these components, in order to delineate their roles in the observed photophysical behaviors of the dendrimers.

Table 2. Photophysical data for Eu^{3+} complexes when excited at 280 nm.

Eu^{3+} complex	Q_{overall} Respect to QS	τ (ms) at 298K of Eu^{3+}
(OMe)BTFA	0.0584	0.637 $\pm$ 0.004
(G0)BTFA	0.0594	0.659 $\pm$ 0.002
(G1)BTFA	0.1267	0.718 $\pm$ 0.003
(G2)BTFA	0.0917	0.785 $\pm$ 0.006
(G3)BTFA	0.0432	0.802 $\pm$ 0.004
(HFA)	0.0693	

The second step of the energy transfer, *i.e.* the (B $\rightarrow$ C) process, is determined by exciting the dendrimers at a wavelength where the dendrons do not absorb (340 nm). Since the number of β -diketonate moieties is constant throughout the dendrimer series, the energy transfer efficiency should be constant. In theory, therefore, any differences in Eu^{3+} emission intensities or lifetimes are due not to changes in energy transfer efficiency, but to changes in quantum yield of emission. In other words, any trend observed in the photophysical data should coincide with the efficacy of the site isolation effect. Upon exciting the complexes at 340 nm, the Eu^{3+} emission intensities exhibit a nonlinear dependence on the generation number. This is shown in Figure 9.

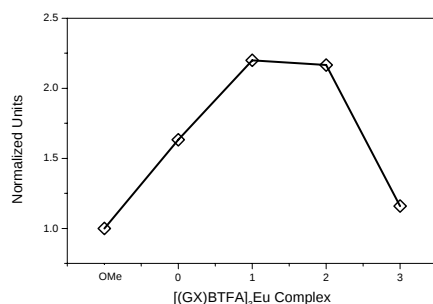


Figure 9. Graphical comparison of the intensities of the dendritic europium complexes (1.0×10^{-6} M) in spectroscopic grade acetonitrile at 298K when excited at 340 nm. All spectra are normalized relative to $[(\text{OMe})\text{BTFA}]_3\text{Eu}$.

The intensity of the G3 complex plummeted close to the value of the OMe complex. As mentioned previously, the intensities coincided with how well the dendritic shell protected the core from quenching mechanisms. At first glance, this would have indicated that the G3 complex was horrible in protecting the core; therefore, the site isolation effect was not occurring. However, looking at the lifetimes of Eu^{3+} , which were summarized in Table 2, the G3 complex had the longest lived core when excited at 340 nm. A longer

lifetime indicated that the nonradiative rate was lower than the radiative rate; hence higher emission intensity should have resulted. This would have also indicated that the dendritic shell of the G3 complex was protecting the core better than the G2 complex and the site isolation effect was intact throughout the series. If the site isolation effect was intact then the reason for the lower emission intensity for the G3 complex had to have been due to the inefficient energy transfer from the β -diketonate to the Eu^{3+} core. By using the fact that the steady-state intensity was the product of the lifetime, a constant, and the energy transfer efficiency of ($\text{B} \rightarrow \text{C}$), the contribution from the energy transfer efficiency with respect to $[(\text{OMe})\text{BTFA}]_3\text{Eu}$ can be ascertained. As shown in Figure 10, the shape of the line for the energy transfer efficiency followed closely with the intensity.

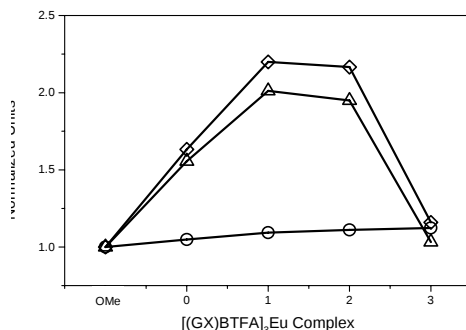


Figure 10. Graphical comparison of the intensities (diamonds), lifetimes of Eu^{3+} (circles), and energy transfer efficiencies (triangles) of the dendritic europium complexes (1.0×10^{-6} M) in spectroscopic grade acetonitrile at 298K when excited at 340 nm. All spectra were normalized with respect to $[(\text{OMe})\text{BTFA}]_3\text{Eu}$.

One possible reason for this decrease in intensity may have been due to the conformation of dendrimers with flexible branches. Many theoretical approaches such as molecular dynamics and Monte Carlo simulations found a high-density region near the core of these types of dendrimers.³²⁻³⁵ This result would have suggested that as the dendrons increased in size, the peripheral groups folded back inwards towards the core. If the peripheral phenyl rings folded back far enough to interact with the BTFA, then this could have caused quenching due to collisional deactivation of the BTFA before energy transfer to the lanthanide had occurred. This effect was analyzed through a Stern-Volmer plot.

The quencher in the present case was believed to have been the periphery of the dendrons folding back inward. For this reason 3,5-dimethoxytoluene was chosen as the quencher because it closely resembled the periphery, as shown in Figure 11.

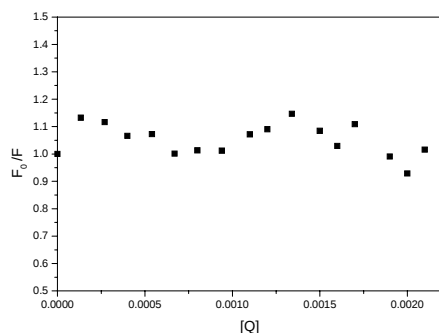


Figure 11. Stern-Volmer plot for $[(\text{OMe})\text{BTFA}]_3\text{Gd}$ and 3,5-dimethoxytoluene.

The rate at which a compound quenches another compound's fluorescence was directly proportional to the slope of the Stern-Volmer plot. A large influence should show a large positive slope. Unfortunately in the present case, the slope was zero, suggesting that the periphery may have folded back in towards the core, but it had no influence over the energy transfer problems seen in the larger complexes. This data correlated with T_1 NMR relaxation data suggesting that the peripheral methoxy groups were feeling the same steric stress or are in similar chemical environments.¹⁷

Another possible reason for the inefficient energy transfer could have been due to the ligands moving away from the lanthanide ion because the rate of energy transfer is inversely proportional to the distance of the donor and acceptor to the sixth power. From previous theoretical calculations,¹⁷ it was shown that the ligand distances were similar in the first three dendritic complexes, but in the G3 complex, there was minor lengthening of the Ln-O bonds. Although a minor stretch, it would decrease the energy transfer rate by roughly 6%. Therefore, it is believed that this was the major reason for the inefficient energy transfer between the β -diketonate and Eu^{3+} .

Now that the ($\text{B} \rightarrow \text{C}$) part was known, the magnitude of the ($\text{B} \rightarrow \text{C}$) contribution was subtracted out of the total ($\text{A} \rightarrow \text{B} \rightarrow \text{C}$) process in order to see the ($\text{A} \rightarrow \text{B}$) contribution. Any trends seen in the photophysical data for the ($\text{A} \rightarrow \text{B}$) part was directly proportional to the increase in the size of the dendrons. This was also known as the light harvesting effect, as seen in Figure 12.

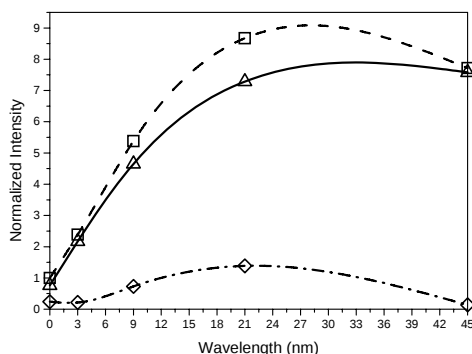


Figure 12. Graphical comparison of the intensities of the (A→B→C) process (dashed/squares), the (B→C) process (dash-dot/diamonds) and the (A→B) process (solid/triangles) of the dendritic europium complexes (1.0×10^{-6} M) in spectroscopic grade acetonitrile at 298K when excited at 340 nm. All spectra were normalized with respect to $[(\text{OMe})\text{BTFA}]_3\text{Eu}$.

As would have been expected for the (A→B) process, there was a large increase in intensity as the generations increased in size. This phenomenon had been seen in many dendritic compounds.³⁶ However, the intensity started to level out at the G2 complex and the G3 complex. As mentioned previously, dendrons, where there was no energy gradient present, became less efficient due to a geometric bias where the newly formed excitons move toward the periphery rather than the core. The efficiency of energy transfer (ϕ_{ET}) from the dendrons to the BTFA moieties was studied quantitatively by comparing absorption spectra and excitation spectra of the dendritic complexes.

This quantitative study had been used many times for compounds that exhibited singlet-singlet energy transfer.^{37,38} This experiment was valid if the lifetimes of the complexes were identical to each other. Since the presented dendritic complexes exhibited the site-isolation effect, the lifetimes of the complexes increased with generation size. In order to compensate for this effect, all excitation spectra were normalized to the same lifetime of $[(\text{OMe})\text{BTFA}]_3\text{Eu}$. Then, the excitation spectra were normalized to a region where the BTFAs absorbed the same (315 nm – 340 nm) as shown in Figure 13 for $[(\text{G3})\text{BTFA}]_3\text{Eu}$.

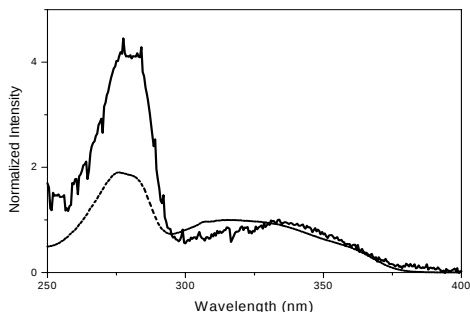


Figure 13. Absorption (solid line) and corrected excitation spectra (dotted line) of $[(\text{G3})\text{BTFA}]_3\text{Eu}$ in spectroscopic grade acetonitrile. The spectra were normalized at the BTFA absorption region.

Finally, the area of the excitation spectra in the region where the dendrons were excited (250 nm – 310 nm) was divided by the same area where the dendrons absorbed. For perfect energy transfer, i.e. $\phi_{\text{ET}} = 1$, the shape and intensity of the peaks should have been identical. As can be seen in Table 4, the ϕ_{ET} for $[(\text{G3})\text{BTFA}]_3\text{Eu}$ was 35%.

Table 4. Values of ϕ_{ET} for the Entire Series of Dendritic Eu^{3+} Complexes.

Eu^{3+} complex	ϕ_{ET}
(G0)BTFA	99%
(G1)BTFA	99%
(G2)BTFA	93%
(G3)BTFA	35%

It was evident that the efficiency of energy transfer from dendrons to the BTFAs dramatically decreased from the G2 complex to the G3 complex, and this was the major contributor to the low emission intensity. This was easily explained because it was well

known that as dendrons increased in size, the rate of collisional or static quenching increased due to greater degrees of freedom and increased intramolecular associations within the dendrons.³⁹

Conclusions. To summarize, the lanthanide complexes containing the newly synthesized dendritic β -diketonate ligands were shown to be synthetic photon harvesting arrays, and mimicked arrays seen in nature. Photophysically, it was shown that these ligands were more appropriate for trivalent europium. With the europium spectra, these complexes were determined to be *tris*-chelated and asymmetrical in its coordination environment. With the design of these complexes, the total energy transfer process (A $\rightarrow$ B $\rightarrow$ C) was deconvoluted into two segments: the dendrons to the BTFA moiety (A $\rightarrow$ B) and the BTFA moiety to the trivalent europium core (B $\rightarrow$ C). The emission spectra from each segment displayed effects seen in dendrimers. The (A $\rightarrow$ B) process showed the light harvesting effect because the emission from europium for the most part increased directly with the increase in dendron size. The (B $\rightarrow$ C) process showed the site isolation effect because the emission from europium for the most part increased directly with how well the dendrons protected the core from the outside environment. For both processes, the energy transfer within the G3 complex was inefficient. The inefficiencies were due to the lengthening of the distance between the donor and acceptor and the geometric bias in dendrimers.

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Enclosure 2

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Enclosure 3

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The research agreement identified below is under consideration for additional funding. The contemplated funding, resulting in an extension to the performance period of the agreement, is consistent with the terms and conditions of the agreement. Before a decision can be made to provide the additional funding, the following information is needed: (i) an accounting of costs incurred to date and (ii) a projection of financial needs for the period of the agreement extension. Please complete SECTION 2, below **within 30 days of receipt of this request** and return to: U.S. Army Research Office, ATTN: (Name provided by ARO) P.O. Box 12211, Research Triangle Park, North Carolina, 27709-2211.

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Agreement Number: (Provided by ARO)
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Recipient: (Provided by ARO)
Principal Investigator: (Provided by ARO)
ARO Technical Monitor: (Provided by ARO)
ARO Technical Monitor's E-mail: (Provided by ARO)

Total Anticipated Award: (\$ Provided by ARO)
Amount Funded to Date: (\$ Provided by ARO)
Currently Funded Through: (Provided by ARO)
Planned Funding: (Provided by ARO)
Planned Extension Funding: (Provided by ARO)

Monitor's Phone #: (Provided by ARO)

SECTION 2: ACCOUNTING AND FORECASTING OR EXPENDITURES – Completed by PI

1. Expenditures (cost incurrences from date of contract/grant initiation) as of date \$100,000
2. Additional projected expenditures before (date entered by ARO): \$0
3. Total of items 1 and 2: \$100,000
4. Forecast expenditures for the proposed (number) months period of extension: \$0*
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Date: 4/12/06

Signature G.K. Surya Prakash
Principal Investigator

* The forecast cannot exceed the planned level of funding identified in SECTION 1. If the forecast expenditures differ significantly from the budget previously negotiated and included in the research agreement, a new budget must be submitted. A "significantly different" budget is defined as (i) a decrease in the planned funding level cited above or (ii) a deviation of 10% (plus or minus) to any cost element (direct labor, indirect expense, travel, etc.) included in the budget.

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___ Recommend funding in amount of \$ ___
(Comments attached)

___ Other (Explanation attached).

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Technical Monitor

Enclosure 4

FINAL PROGRESS REPORT

Papers published in peer-reviewed journals

N/A

Papers published in non-peer-reviewed journals or in conference proceedings

Case, P.J.; Harper, A.W., "Trivalent Europium Complexes Using Dendritic beta-Diketone Ligands", *Mater. Res. Symp. Proc.* 771, 65-70 (2003).

Clancy, S.O.; Padmaperuma, A.B.; Harper, A.W., "Energy transfer from polyphenylene-type polymers to a series of Coumarins and other acceptors," *Proc. SPIE* 5224, 113-120 (2003).

Clancy, S.O.; Padmaperuma, A.B.; Harper, A.W., "Energy transfer studies of polyphenylene-type polymers to a series of dyes," *Mater. Res. Symp. Proc.* 771, 71-76 (2003).

Collette, J.C.; Harper, A.W., "Properties and chemical environment effects of alkylamino styryl pyrazine two-photon fluorophores," *Proc. SPIE* 5212, 184-192 (2003).

Collette, J.C.; Harper, A.W., "Chemical environment effects on the photophysical behavior of two-photon materials," *Mater. Res. Soc. Symp. Proc.* 771, 55-60 (2003).

Padmaperuma, A.B.; Harper, A.W., "Efficient energy harvesting of conjugated polymers by direct coordination to novel low energy complexes of europium: Triplet energy harvesting by lanthanides in conjugated polymers," *Proc. SPIE* 5224, 130-137 (2003).

Padmaperuma, A.B.; Harper, A.W., "Synthesis of novel conjugated high-energy polymers with terpyridine and beta-diketonate type pendant groups to facilitate energy transfer to lanthanides," *Poly. Mater. Sci. Eng.* 89, 700-701 (2003).

Padmaperuma, A.B.; Clancy, S.O.; Harper, A.W., "Structure-property relationship of conjugated polymers: Effect of heteroaromatic rings on photophysical properties," *Poly. Mater. Sci. Eng.* 88, 514-515 (2003).

Papers presented at meetings, but not published in conference proceedings

29. Case, P. J.; Harper, A. W. "Photophysics of Europium(III) β -Diketone Complexes that Can Be Excited at Lower Energies," The Spring 2003 Materials Research Society National Meeting, San Francisco, CA, April 21-25, 2003.

- Case, P. J.; Harper, A. W., "Sensitizing Trivalent Europium Using Dendritic β -diketone Ligands," The 225th American Chemical Society National Meeting, New Orleans, LA, March 27, 2003.
- Clancy, S.O.; Padmaperuma, A.B.; Harper, A.W., "Energy transfer from polyphenylene-type polymers to a series of dyes." The Spring 2003 Materials Research Society National Meeting, San Francisco, CA, April 21-25, 2003.
- Clancy, S.O.; Padmaperuma, A.B.; Harper, A.W., "Energy transfer from polyphenylene-type polymers to a series of Coumarins and other acceptors," The 48th Annual Society of Photo-Optical Instrumentation Engineers Meeting, San Diego, CA. August 3-8, 2003.
- Collette, J.C.; Harper, A.W., "Structure-optical property relationship studies of two-photon engineered alkylamino-substituted styryl pyrazine dyes," 226th American Chemical Society National Meeting, New York, September 7-11, 2003.
- Collette, Jeremy; Harper, Aaron W., "Understanding the role of solvent on two-photon materials: Chemical environment effects on a family of new two-photon engineered alkylamino-substituted styryl pyrazine dyes," 225th American Chemical Society National Meeting, New Orleans, March 23-27, 2003.
- Padmaperuma A.B.; Harper, A.W., "Efficient energy harvesting of conjugated polymers by direct coordination to novel low energy complexes of europium: Triplet energy harvesting by lanthanides in conjugated polymers," The 48th Annual Society of Photo-Optical Instrumentation Engineers Meeting, San Diego, CA. August 3-8, 2003.
- Padmaperuma A.B.; Harper, A.W., "Photophysics of novel conjugated polymers with alternating heteroaromatic rings: syntheses and applications" The 48th Annual Society of Photo-Optical Instrumentation Engineers Meeting, San Diego, CA. August 3-8, 2003.
- Padmaperuma A.B.; Harper, A.W., "Synthesis of novel conjugated high-energy polymers with terpyridine and beta-diketonate type pendant groups to facilitate energy transfer to lanthanides," 226th American Chemical Society National Meeting, New York, September 7-11, 2003.
- A.B.; Clancy, S.O.; Harper, A.W., "Structure-property relationship of conjugated polymers: Effect of heteroaromatic rings on photophysical properties," 225th American Chemical Society National Meeting, New Orleans, March 23-27, 2003.
- Padmaperuma A.B.; Harper, A.W., "Harvesting triplet energy from conjugated polymers by europium ternary complexes: Tuning the energy of complexes to achieve higher energy-transfer efficiencies" 225th American Chemical Society National Meeting, New Orleans, March 23-27, 2003.

Nanoengineered Building Blocks for Information Technology – University of Washington, invited speaker, 11/01.

New Block Copolymers and Approaches for sub-100 nm Lithography – Beckman Young Investigator Program Anniversary Symposium, 9/01.

New Block Copolymers and Approaches for sub-100 nm Lithography – Beckman Young Investigator Symposium (invitation, poster presentation), 9/00.

Organolanthanides in Photonics – NAS Frontiers in Science Symposium (invitation, poster presentation), Irvine, CA, 9/00.

Syntheses and Applications of Organolanthanides in Photonics – joint SE/SW ACS Conference, invited speaker, New Orleans, 5/00.

“Supramolecular Interactions in Nonlinear Optical Polymers,” invited speaker, University of North Texas, Denton, TX, 4/00.

Fun with Photons: A Lighthearted Look at a Research Career,” invited speaker, University of Wisconsin – River Falls, River Falls, WI, 2/00.

“Supramolecular Interactions in Nonlinear Optical Polymers,” invited speaker, University of Wisconsin – River Falls, River Falls, WI, 2/00.

“Supramolecular Interactions in Electro-Optic Polymers,” invited speaker (and first speaker) at the 23rd Asilomar Conference on Polymers, Pacific Grove, CA, 2/00.

Manuscripts submitted, but not published

Patrick J. Case, Jeremy C. Collette, and Aaron W. Harper, “Trivalent Lanthanide Coordination Complexes Using Dendritic β -Diketonate Ligands I: Syntheses and Structural Properties,” submitted to Chemistry of Materials, 2006.

Patrick J. Case, Jeremy C. Collette, and Aaron W. Harper, “Trivalent Lanthanide Complexes Using Dendritic β -Diketonate Ligands. Part II: Photophysics and Energy Transfer” submitted to Chemistry of Materials, 2006.

List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

Asanga B. Padmaperuma (Ph.D. 2004)

Jeremy C. Collette (Ph.D. 2004)

Patrick J. Case (Ph.D. 2004)

Sean O. Clancy (Ph.D. 2005)

Michael D. Julian (Ph.D. 2005)

Cory G. Miller (Ph.D. 2004)

Bonnie E. Louridas (M.S. 2001)

Mary Ellen E. Passarelli (M.S. 2001)

Report of Inventions (by title only)

N/A