

XAFS studies of Tb or Eu cored dendrimer complexes with various properties of luminescence

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We studied the extended X-ray absorption fine structure (EXAFS) of Tb or Eu L₃-edge of Tb(III) or Eu(III)-cored complexes of different luminescence to which different poly(benzyl ether) dendrons coordinated. The complexes were prepared via a ligand exchange reaction of dendritic carboxylic acid and acetate. Results show that (a) the Eu complex of the first generation of the 3,4- or 3,5-dibenzoyloxyphenyl type had a coordination structure different from that of the 2,4-dibenzoyloxyphenyl type; (b) the Eu complex of the first generation of 3,5-dinaphthylmethoxyphenyl type had a Eu-O coordination number higher than the total number of oxygen atoms in the carboxylate groups; (c) the Tb complex of the bulky fourth generation had a Tb-O coordination number higher than that of the first generation. These results show that the different poly(benzyl ether) dendrons cause the different coordination, which might differently influence the luminescence properties of the complexes.

Keywords: XAFS; dendrimer; Tb; Eu; luminescence.

1. Introduction

The application of photoluminescence properties of lanthanide (III) complexes to optical tools and bioassay is an important subject. Therefore, their photoluminescence behavior has been studied extensively in recent decades (Gelade & De schryver, 1984; Murru et al., 1993; Steemers et al., 1995; Webber, 1990; Darwent et al., 1993; Sabbatini et al., 1994; Magennis et al., 1999; Kawa & Fréchet, 1998; Gust et al., 1993; Mwalupindi et al., 1991). Tb(III) and Eu(III) complexes to which Fréchet type poly(benzyl ether) dendrons shown in Fig. 1 lower coordinated exhibited high intensity fluorescence when these were exposed to ultraviolet light (Kawa & Fréchet, 1998). The Tb and Eu complexes with different poly(benzyl ether) dendrons exhibited different intensity fluorescence. It was clear that the effect of poly(benzyl ether) dendrons on photoluminescence was mainly an antenna effect

(Magennis et al., 1999) of collecting light and transferring its energy to the lanthanide. However, the structure of coordination connecting the lanthanide and the light absorber, namely, dendrons was not clear. To clarify the structure, we studied the extended X-ray absorption fine structure (EXAFS) of Tb or Eu K-edge of the amorphous complexes.

2. Experiment and analysis

We prepared the Tb(III) or Eu(III)-cored dendrimer complexes (Fig. 1) from corresponding anhydrous terbium or europium triacetate (1 equiv.) and the dendron ligand (3 equiv.) bearing a carboxyl group at the focal point via a ligand exchange reaction in a solvent of chlorobenzene at temperature of reflux (Kawa & Fréchet, 1998). Thus, the three dendrons are probably assembled as carboxylate ligands surrounding the lanthanide core. In this study, we designated the benzyloxy groups whose generation number *n* was G-*n*. The complex [G-*n*-xy]₃-Ln is a Tb or Eu complex having three G-*n* dendrons where phenyl group is bonded at *x* and *y* positions by two benzyloxy groups.

We measured Tb and Eu L₃-edge absorption spectra of the dendrimer complexes at room temperature using the X-ray absorption fine structure (XAFS) facilities of BL-12C line in the Photon Factory at High Energy Accelerator Research Organization (Tsukuba,

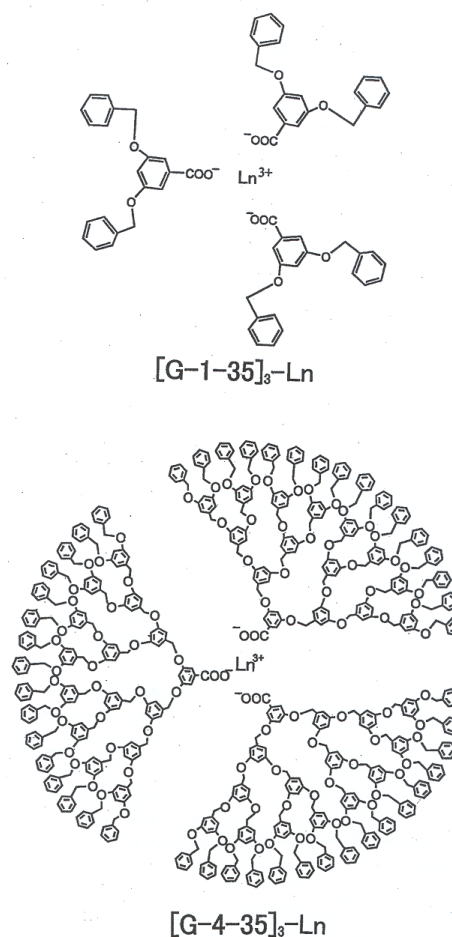


Figure 1

Schematic of typical dendrimer complexes of Tb or Eu.

Japan) with a ring energy of 2.5 GeV and storage current of 258-400 mA. The radiation was monochromatized by using a pair of Si(111) crystals. Harmonic rejection was achieved by detuning the primary beam to 60% of its original intensity. Spectra were recorded in the transmission mode using ionization detectors containing N_2 (I_0) and N_2/Ar (I). Fourier transform (FT) of k^3 -weighed normalized EXAFS oscillation was performed in the range of $2.5 < k < 13.3$ and $2.3 < k < 12.5 \text{ \AA}^{-1}$ for the Tb and Eu compounds, respectively. We also measured $Tb(NO_3)_3 \cdot 6H_2O$ and Eu_2O_3 of which atomic distance R and coordination number N were known. Then, we determined phase shifts and back-scattering factors, which were used in the curve fitting of spectra of all the Tb and Eu complexes. The curve fitting for each FT peak was performed in R-space. The fitness was checked by performing the k-space back-transform.

3. Results and discussion

Fig. 2 shows FT patterns of the Tb dendrimer complexes studied here. Only the first peak was evident in these patterns. The absence of a Tb-Tb shell suggests that each Tb ion is dispersed mostly in each dendrimer complex. Tb-O shell fitted the first peak. Table 1 shows the result of the curve fitting. The Tb-O coordination number in the G-4 dendrimer complex was 5.6, larger than that in the G-1 dendrimer complex, namely, 4.3. These results suggest that the coordination of three carboxylate groups to Tb is changed mainly from unidentate into bidentate type when the dendron is changed from the G-1 into the G-4. The difference in electron density in the focal carboxyl group between the G-1 and the G-4 acid dendrons is almost nothing (Kawa & Fréchet, 1998). Therefore, the difference in coordination number might be due to the difference in the size of

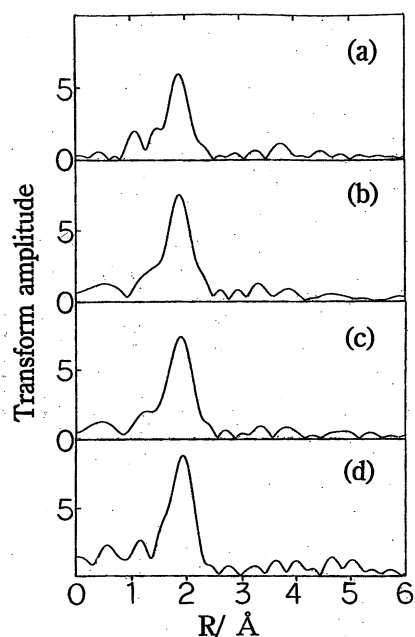


Figure 2

FT patterns of Tb compounds. (a) $Tb(OAc)_3$, (b) $[G-1-34]_3-Tb$, $[G-1-35]_3-Tb$, and (d) $[G-4-35]_3-Tb$.

Table 1

Curve fitting of the first peak in the Tb compounds by a model of Tb-O shell.

Tb compound	$Tb(OAc)_3$	$[G-1-34]_3-Tb$	$[G-1-35]_3-Tb$	$[G-4-35]_3-Tb$
Coordination number N^a	3.4(0.3)	4.3(0.3)	4.3(0.3)	5.6(0.4)
Atomic distance $R / \text{Å}^b$	2.32	2.32	2.32	2.35
Debye-Waller factor $\sigma / \text{Å}^a$	0.054	0.060	0.059	0.064
R-factor (%)	5.5	2.5	6.6	6.4

^a The estimated error is given in parentheses. We checked the errors of N and σ . First, the several samples randomly extracted from the same complexes synthesized were measured, and the experimental errors were determined. Second, the errors generated from the correlation between N and σ were also obtained by examining the deviations of N and σ calculated under different R-factors fixed (Anderson et al., 1998). In every complex the experimental error was much smaller than the error generated from the correlation, which is shown in parentheses.

^b The estimated error is 0.02 \AA . In the case of R , the experimental error was the largest in all kinds of errors. The error was estimated from the experimental error.

dendritic skeleton itself. Interestingly, our result that a larger ligand (the G-4 dendron) coordinates more is opposite to the usual phenomenon that a larger ligand coordinates less due to the steric hindrance.

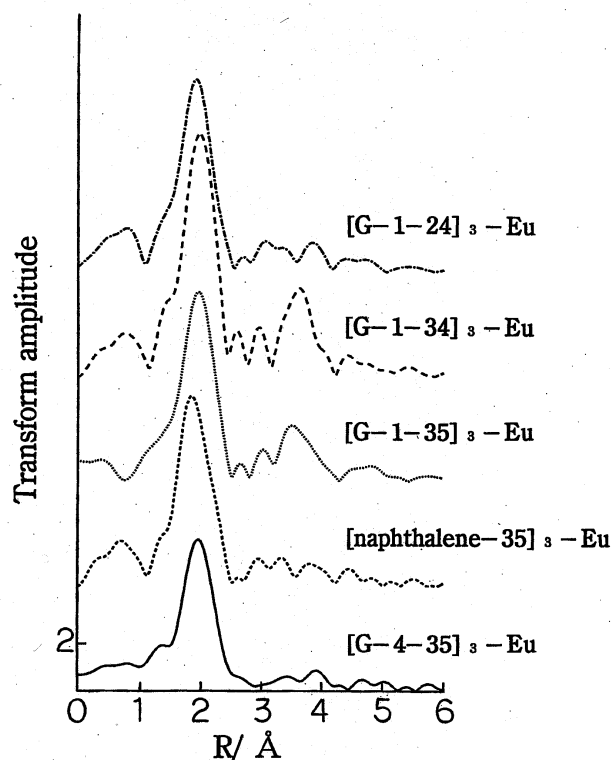


Figure 3

FT patterns of various Eu dendrimer complexes.

Table 2

Curve fitting of the first peak in the Eu dendrimer complexes by a model of Eu-O shell.

Eu compound	[G-1-24] ₃ -Eu	[G-1-34] ₃ -Eu	[G-1-35] ₃ -Eu	[naphthalene-35] ₃ -Eu	[G-4-35] ₃ -Eu
N ^a	8.9(2.2)	11.4(2.9)	8.0(2.0)	9.5(1.4)	6.3(0.9)
R / Å ^b	2.36	2.42	2.40	2.34	2.39
σ / Å ^a	0.088 (0.020)	0.081 (0.021)	0.070 (0.021)	0.092 (0.011)	0.070 (0.013)
R-factor (%)	6.5	9.0	7.2	3.2	5.1

^{a,b} The procedure and the indication of the estimated errors follow Table 1. The estimated error of R is 0.02 Å.

Fig. 3 shows FT patterns for the Eu dendrimer complexes studied here. Table 2 shows the results for the curve fitting of the first peaks in FT patterns. Eu-O shell fitted every first peak. In the G-1 complexes, the Eu-O length of [G-1-24]₃-Eu and k-space [naphthalene-35]₃-Eu was 2.36 Å and 2.34 Å, respectively, and that of [G-1-34]₃-Eu and [G-1-35]₃-Eu was 2.42 Å and 2.40 Å, respectively. The Eu-O length of the latter were about 0.06 Å longer than that of the former. In the range of 3-4 Å, [G-1-24]₃-Eu and [naphthalene-35]₃-Eu showed no second peak, whereas [G-1-34]₃-Eu and [G-1-35]₃-Eu showed such a peak. Eu-(O)-Eu shell fitted the second peaks. The peaks in the range of 0-1.0 and 4.3-6.0 Å shown in Fig. 3 were significantly changed by repeating the measurement and changing the condition of FT, suggesting that the peaks were unphysical ones or noise. The back-transform formed through the window of R= 1.0-4.3 Å was fitted by a set of Eu-O and Eu-(O)-Eu shells in [G-1-34]₃-Eu and [G-1-35]₃-Eu. Our results suggest the bridge-type coordination of one carboxylate group to two Eu ions, a type of coordination often observed in the crystalline Eu complexes by using the X-ray diffraction analysis (Shimizugawa et al., 1997; Starynowicz, 1998; Legendziewicz et al., 1998). The relatively low intensity of luminescence in [G-1-34]₃-Eu and [G-1-35]₃-Eu measured in our study is probably due to Eu aggregation. Eu aggregation might also increase the steric hindrance in coordination of the bulky dendrons, and thus weaken the strength of Eu-O bond of the two complexes, increasing the bond length.

The coordination number of Eu dendrimer complexes was large, ranging between 6 and 11. Such large coordination numbers have been reported for numerous Eu complexes (Ishida et al., 1995; Yamaguchi et al., 1988; Alpha et al., 1987). The coordination number of [naphthalene-35]₃-Eu and [G-4-35]₃-Eu, 9.5 and 6.3, respectively, is relatively precise because of the small R-factor. The Eu-O number (9) in [naphthalene-35]₃-Eu was higher than the number of oxygen atoms (6) in the three carboxylate groups, suggesting that Eu ion is exposed to the coordination of oxygen atoms other than that of the carboxylate groups belonging to the same molecule as the Eu ion, for example, the bridge-type coordination of carboxylate groups or a coordination of ether groups.

4. Conclusion

By the EXAFS analysis, we found that the different poly(benzyl ether) dendrons caused the different coordination. The Tb complex of the bulky fourth generation showed the Tb-O coordination number higher than that of the first generation. The Eu complex of the first generation of 3,4- or 3,5-dibenzoyloxyphenyl type showed a longer Eu-O length and might form Eu clusters, whereas that of 2,4-dibenzoyloxyphenyl type showed a shorter Eu-O length and showed no evidence of Eu clusters. The Eu complex of the first generation of 3,5-dinaphthylmethoxyphenyl type showed a Eu-O coordination number of about 9, which is higher than the total number of oxygen atoms in the carboxylate groups. The different luminescence properties of these complexes might be influenced by the different coordination of poly(benzyl ether) dendrons.

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