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Enhanced Emission of Nd^{3+} in Liquid Systems: Formation of Symmetrical Rigid Shells of Tightly Solvated DMSO Molecules and Weakly Coordinated Low-Vibrational β-Diketonato Ligands

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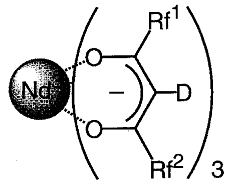
Coordination structures of neodymium(III) complexes with some β-diketones were investigated in terms of their correlations with emission efficiency in deuterated dimethylsulfoxide (DMSO-d_6). The analysis of UV-vis spectra, ^{13}C NMR, electrospray mass spectrometry (ES-MS) spectra, XANES and EXAFS analysis of tris(hexafluoroacetylacetonato)neodymium(III) complex, [Nd(hfa-H)$_3$(H$_2$O)$_2$], and tris[bis(perfluorooctanoyl)methanato]neodymium(III), [Nd(pom-H)$_3$], in DMSO indicated that the deuterated tris(hexafluoroacetylacetonato)neodymium(III), Nd(hfa-D)$_3$, and deuterated tris[bis(perfluorooctanoyl)methanato]neodymium(III), Nd(pom-D)$_3$, in DMSO-d_6 should have a symmetrical, rigid and bulky shell composed of six inner-coordinating DMSO molecules and three weakly coordinating hfa-D and pom-D molecules. The improvement in the emission efficiency of the neodymium complexes with the low vibrational and weakly coordinating β-diketonates in DMSO-d_6 was ascribed to their symmetrical rigid coordination structures, which should suppress radiationless transition via vibrational excitation and energy migration in the fluid system.

Improvement of the emission efficiency of some lanthanide metal ions has attracted attention for possible use in a scale-tunable high-power fluid laser system.$^{1)}$ In particular, the development of a fluid Nd^{3+} medium is a high priority for the production of high-power laser systems for inertial-confinement fusion experiments.$^{2)}$ Two important considerations for fluid Nd^{3+} systems are the suppression of radiationless quenching via vibrational excitation of surrounding molecules$^{3)}$ and suppression of the dipole–dipole energy transfer quenching$^{4)}$ between Nd^{3+} in fluid systems. Recently, we were able to suppress radiationless quenching in fluid Nd^{3+} systems to some extent by complexing Nd^{3+} with β-diketonato ligands composed only of low vibrational C–D and C–F bonds. The neodymium complex with deuterated hexafluoroacethylacetates (hfa-D) (see Fig. 1a) showed photoemission in anhydrous deuterated organic solvents.$^{5)}$ Moreover, dipole–dipole energy transfer quenching was successfully suppressed in a fluid system by using a novel neodymium complex with deuterated bis(perfluorooctanoyl)methanates (pom-D) (Fig. 1b).$^{6)}$ In addition, we found that the emission of Nd(hfa-D)$_3$ was sensitive to solvent, and that anhydrous DMSO-d_6 induced the most effective emission of Nd(hfa-D)$_3$.$^{7)}$

Generally, spectroscopic characteristics of Nd^{3+} are influenced by the coordination structures of the surrounding shell because the introduction of different electrostatic fields to the surrounding shell of Nd^{3+} leads to the change of the selectivity in electronic transition between the f-orbitals. Van Vleck, Judd, and Ofelt proved mathematically the effects of the coordination structures of lanthanide ions on their electronic transition.$^{8)}$ With regard to the coordination and solvation of lanthanide trivalent ions, Bünzli and his co-workers$^{9,10)}$ reported that such complexes and solvates are dominated by strong ion–dipole interactions, and that the number and arrangement of the ligand and solvent molecules in the coordination sphere are the result of interaction between electrostatic and steric factors. Moreover, Beeby and Faulkner have recently reported about the enhanced emission of Nd(NO$_3$)$_3$ in DMSO-d_6.$^{11)}$ There observations suggest that it is important to understand the coordination sphere of the Nd^{3+} site in DMSO-d_6.$^{7)}$

In this study, we report correlation between spectroscopic properties of Nd^{3+} complexes in solutions and the structures of their coordination spheres. Judd–Ofelt analysis in liquid media was attempted to estimate the symmetry of the coordination structure around Nd^{3+} in some solvents. Solvent shell structures of Nd^{3+} were characterized by XANES and EXAFS measurements, ^{13}C NMR analysis, and electrospray



a: $Nd(hfa\text{-}D)_3$
$Rf^1, Rf^2 = CF_3$

b: $Nd(pom\text{-}D)_3$
$Rf^1, Rf^2 = CF_2CF_2CF_2CF_2CF_2CF_2CF_3$

c: $Nd(tfa\text{-}D)_3$
$Rf^1 = CF_3, Rf^2 = CH_3$

d: $Nd(acac\text{-}D)_3$
$Rf^1, Rf^2 = CH_3$

Fig. 1. Chemical structure of the tris(β-diketonato)-neodymium(III) complexes examined.

mass (ES-MS) spectra analysis. Based on the structural analysis and the characterization of spectroscopic properties, we conclude that Nd^{3+} in the systems of the $Nd(hfa\text{-}D)_3$ and $Nd(pom\text{-}D)_3$ in DMSO is coordinated by a rigid double-shell formation composed of six inner-coordinating DMSO molecules and outer weakly-coordinating ligands[12] of respective hfa-D and pom-D molecules.[12] Such structural information of the surrounding shell of the luminescent Nd^{3+} presents a novel aspect for development of luminescent materials in fluid media.

Experimental

Materials. Tris(trifluoroacetylacetonato)neodymium(III) trihydrates, $[Nd(tfa\text{-}H)_3(H_2O)_3]$, and tris(acetylacetonato)neodymium(III) dihydrates ($[Nd(acac\text{-}H)_3(H_2O)_2]$), were prepared in the similar way as previously reported for tris(hexafluoroacetylacetonato)neodymium(III) dihydrates ($[Nd(hfa\text{-}H)_3(H_2O)_2]$) and deuterated tris[bis(perfluorooctanoyl)methanato]neodymium(III), $[Nd(pom\text{-}D)_3]$.[5,6] Other chemicals were obtained and used as described previously.[7]

Deuterated complexes were prepared by the keto-enol tautomerism of the nondeutrated Nd^{3+} complexes in CD_3OD (concn 0.05 M, 1 M = 1 mol dm^{-3}). Deuteration was monitored by ^{1}H NMR and more than 90% deuteration of the complexes were confirmed after their solutions were permitted to stand for at least 6 h. Evaporation of each solvent let a slightly purple residue. The solutions (0.05 M) of the Nd^{3+} complex was prepared by dissolving each deuterated Nd^{3+} complex in 1 ml of a deuterated solvent under 10^{-3} torr (1 Torr = 133.322 Pa) and then transferred to a quartz cell for optical measurements under anhydrous conditions.

Optical Measurements. Transmittance spectra were obtained using a monochromator (JASCO, PS-H150) and a photomultiplier (Hamamatsu Photonics, C659B). Scan rate and time constants are 180 nm min^{-1} and 100 mV s^{-1}, respectively. Emission spectra were measured by a Ge detector, and then were normalized so that the emission intensities of peak emission wavelength (λ_p: $^4F_{3/2}-^4I_{11/2}$) were set for a value of 100. Quantum yields were measured as reported previously.[7] Lifetime of emission was determined using a Q switch Nd : YAG laser (Spectra-Physics, Quanta-Ray PCR-2, 20 Hz), and Si photodiode (Hamamatsu Photonics, S3759, time response $\leq$ 1 ns). Each sample was excited by the second harmonic (532 nm) of fundamental nanosecond pulse. Emission from the sample was filtered by low-cut optical filters (Hoya, R66 and R68) placed in front of the detector. The response of the photo diode was monitored by a digital oscilloscope (Iwatsu, TS-8422, 400 MHz) synchronized to single-pulse excitation. The *Judd–Ofelt parameters* Ω_λ were determined by a least-squares fitting of the calculated oscillator strength to the absorption line strength.[13)#]

XANES and EXAFS Measurements. An aqueous neodymium perchlorate solution was prepared by dissolving neodymium oxide in aqueous perchloric acid and then adding distilled water as necessary. The concentration of the sample solution was adjusted to be R (H_2O or deuterated solvent/Nd^{3+} complex molar ratio) = 28.[14] A slight excess of perchloric acid (2%) was added to prevent the hydrolysis of neodymium perchlorate. X-Ray absorption spectra at the Nd L_{III}-edges (6208 eV) of the Nd compounds were measured in the transmission mode at the BL-6B station of the Photon Factory at the National Laboratory for High Energy Physics. Broad band synchrotron radiation from a storage ring operated at 2.5 GeV with a maximum store current of 345 mA was monochromatized by a set of two Si(III) crystals. Liquid samples were sealed in a cell of polyethylene film. A Teflon® (polytetrafluoroethylene) spacer with a suitable thickness was used to obtain an appropriate dege jump. X-Ray absorption near-edged structure (XANES) spectra were measured by scanning X-ray energy with an integration time of 1 s in the region from 6178 to 6278 eV (301 points). For extended X-ray absorption fine structure (EXAFS) spectra, the integration time was set to 2, 2, and 4 s in the region of 5902—6195 eV (48 points), 6195—6230 eV (110 points), and 6230—6704 eV (271 points), respectively. EXAFS data were analyzed as previously reported.[15]

Electrospray Mass Spectrometry. The electrospray mass spectrometry was measured according to the procedure described in the previous papers.[16] Two samples for ES-MS analysis were prepared as follows. The complex $[Nd(hfa\text{-}H)_3(H_2O)_2]$ was dissolved in DMSO or DMSO-d_6 (GR grade, Wako Chemical) and the solution was concentrated to some extent using a rotary evaporator under reduced pressure. The resulting residue was dissolved in commercial acetone (GR grade, Wako Chemical Co.) and used for analysis. The complex $[Nd(hfa\text{-}H)_3(H_2O)_2]$ was also analyzed in a similar manner after dissolving in acetonitrile (GR grade, Wako Chemical Co.). The sample concentration was < 0.1 mM.

In the calculation the tensor parameter U^λ of Nd^{3+} are given by,

$$U_2 = \begin{vmatrix} 0.0680 \\ 0.9710 \\ 0.0010 \\ 0.0010 \\ 0.0100 \\ 0.0000 \end{vmatrix}, \quad U_4 = \begin{vmatrix} 0.2219 \\ 0.5897 \\ 0.0094 \\ 0.0448 \\ 0.2431 \\ 0.2296 \end{vmatrix}, \quad U_6 = \begin{vmatrix} 0.1274 \\ 0.0663 \\ 0.0398 \\ 0.6582 \\ 0.5148 \\ 0.0563 \end{vmatrix}.$$

Each wavelength of procession parameters is defined 490—540 nm, 550—610 nm, 670—700 nm, 715—775 nm, 775—845 nm, and 845—915 nm, respectively.

Results and Discussion

(a) Emission Characteristics of Nd^{3+} Complexes in Deuterated Solvents. Table 1 shows characteristic of the emission due to the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition of neodymium complexes with some β-diketonates, deuterated hexafluoroacethylacetonate (hfa-D), deuterated bis(perfluorooctanoyl)-methanate (pom-D). The emissions of each complex were measured after deuteration of methyne proton of each β-diketonato in the complexes (see Experimental Section). Full width at half-maximum (fwhm) of the emission, quantum yields, lifetime, and the emission rate are also shown in Table 1.

Complexes with hfa-D and pom-D showed enhanced emission in DMSO-d_6, as reported previously.[7] The emission intensity of Nd(pom-D)$_3$ with a longer lifetime (14.5 μs) was more than twice that of Nd(hfa-D)$_3$. In the system of Nd(pom-D)$_3$, the introduction of long perfluorinated alkyl chains should effectively suppress radiationless quenching via cross relaxation and excitation migration as well as vibrational excitation, as reported previously.[6] Interestingly, neodymium complexes with tfa-D (Fig. 1c) or acac-D (Fig. 1d) in DMSO-d_6 showed grater emission than Nd(hfa-D)$_3$ in acetone-d_6, although they are composed of C–H bonds with a higher vibrational frequency that may cause radiationless quenching via vibrational excitation. In general, emission quantum yields and lifetime are closely related to each other. Larger quantum yields of Nd^{3+} reflect a more stable excited state, leading to a long lifetime of the emission. It is interesting to note that the emission rates in DMSO-d_6 were smaller that those in methanol-d_4, acetone-d_6, THF-d_8, and DMF-d_7. The aspect of the emission rate offers only information about optical selection for electric or magnetic dipole transition.[17] The smaller emission rate indicates that the magnetic dipole transition become dominant with the decreased electric dipole transition. Thus, the decreased electric dipole transition in DMSO-d_6 suggests that the symmetric field of Nd(hfa-D)$_3$ in DMSO-d_6 should be increased, being distinct from those in other solvents.

It is well-known that UV-vis spectra are very sensitive to the symmetry of crystal or ligand fields. An important characteristic in the spectra of neodymium complexes or solvates is a Stark splitting of the absorption peak around λ = 850—870 nm, which is attributed to the transition $^4I_{9/2}\rightarrow{}^4F_{3/4}$ (Fig. 2).[18] The splitting energy at the transition level ($^4I_{9/2}\rightarrow{}^4F_{3/2}$) was determined for Nd(hfa-D)$_3$ systems and some other neodymium β-diketonato complexes in DMSO-d_6 (Table 2). For Nd(hfa-D)$_3$ systems, the $^4F_{3/2}$ level splits slightly into two levels in methanol-d_4, acetone-

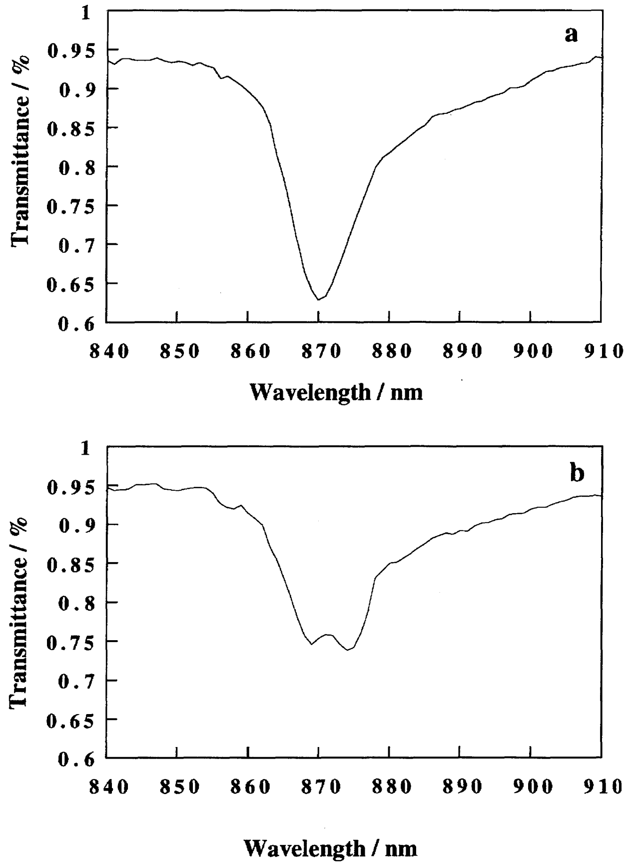


Fig. 2. Stark splitting of $^4F_{3/2}$ level of Nd(hfa-D)$_3$ in a) DMSO-d_6 and b) acetone-d_6.

Table 1. Characteristics of the Emission due to the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ Transition of Nd^{3+} Complexes in Deuterated Solvents

Complex	Solvent	λ_{max}	fwhm	Φ[a)]	Lifetime[b)]	Emission rate[c)]
		nm	nm	%	μs	10^3 s^{-1}
Nd(hfa-D)$_3$ [d)]	Methanol-d_4	1063	33.3	ca. 0.1	0.7	—
	Acetone-d_6	1055	32.9	0.2 (0.4)	1.7	2.3
	THF-d_8	1059	32.0	0.3 (0.5)	2.3	2.1
	DMF-d_7	1059	30.6	0.3 (0.6)	2.9	2.1
	DMSO-d_6	1063	31.2	0.6 (1.1)	6.3	1.7
Nd(tfa-D)$_3$ [e)]	DMSO-d_6	1057	34.0	0.6 (1.1)	5.7	2.1
Nd(acac-D)$_3$ [e)]	DMSO-d_6	1058	34.0	0.4 (0.8)	3.3	2.4
Nd(pom-D)$_3$ [e)]	Methanol-d_4	1049	30.0	0.3 (0.7)	1.6	4.4
	DMSO-d_6	1049	25	1.5 (3.2)	14.5	2.2

a) Excitation at 585 nm. Values of Φ present the quantum yield of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition. Values in parentheses are the total quantum yield ($^4F_{3/2}\rightarrow{}^4I_{9/2}$, $^4F_{3/2}\rightarrow{}^4I_{11/2}$, and $^4F_{3/2}\rightarrow{}^4I_{13/2}$). b) Excitation at 532 nm. c) Emission rates were calculated by total quantum yield/lifetime. d) Ref. 7. Concentration was 0.1 mol m^{-3}. e) Concentration was 0.05 mol m^{-3}.

Table 2. Characteristics of Stark Splitting at the Transition Level $^4F_{3/2}$ and Judd–Ofelt Parameters of Nd^{3+} Complex in Varaious Solvents

Complex[a)]	Solvent	λ_{max} of $^4F_{3/2}$	Splitting energy	Ω_2 parameters
		nm	cm^{-1}	10^{-20} cm^2
$Nd(hfa\text{-}D)_3$	Methanol-d_4	864.9, 969.8	66	14.8
	Acetone-d_6	864.9, 871.5	87	16.3
	THF-d_8	864.4, 871.9	100	17.5
	DMF-d_7	867.2, 870.0	37	—
	DMSO-d_6	869.4	0	9.2
$Nd(tfa\text{-}D)_3$	DMSO-d_6	867.1, 874.5	98	19.1
$Nd(acac\text{-}D)_3$	DMSO-d_6	867.1, 873.2	81	22.2
$Nd(pom\text{-}D)_3$	Methanol-d_4	868.1	0	2.2
	DMSO-d_6	868.6	0	1.4

a) The concentration of Nd^{3+} complexes in liquid media was 0.05 mol m^{-3}.

d_6, THF-d_8, and DMF- d_7 (Fig. 2b). These splittings may be due to a decrease in the symmetry of the coordination structure induced by competitive solvation. In DMSO-d_6, however, no splitting was observed (Fig. 2a). The same was true for $Nd(pom\text{-}D)_3$. On the other hand, other neodymium complexes with stronger coordinating β-diketonato ligands, i.e., tfa-D and acac-D, showed the Stark splitting in DMSO-d_6. These facts suggest that DMSO molecules coordinate symmetrically to Nd^{3+} only in the complexes with weakly coordinating hfa-D and pom-D.

To estimate the strength of the crystal field in the liquid systems, we calculated the parameters Ω_2 of Nd^{3+} in the present systems, which are derived from the Judd–Ofelt theory (Table 2). Reisfeld and Jørgensen have shown that Ω_2 is quite sensitive to the metal ion surroundings.[19)] Relationship between the calculated Ω_2 and the inner coordination sphere of Nd^{3+} in various matrices can be discussed in terms of coordination structures affecting the emission. Symmetric crystal fields of the lanthanide ion leads to significant decrease in values of the parameter Ω_2 because of domination of magnetic dipole transition along with decrease of electric dipole transition.[17)] It is well-known that Nd^{3+} in water has symmetrically coordinated water molecules, whose systems give a small Ω_2 value.[9,17)] On the other hand, its value increases dramatically when anionic ligands such as acetonitrile, DMF and tributylphosphate are bonded in the organic solvents. The same was true for the $Nd(hfa\text{-}D)_3$ in most organic liquid media. The inner coordination sphere of $Nd(hfa\text{-}D)_3$ in the liquid media should be in equilibrium with three HFA ligands and solvent molecules or two water molecule, which leads to the unsymmetrical inner coordination of Nd^{3+}. Thus, the relatively large Ω_2 values reflect the unsymmetrical inner coordination sphere of Nd^{3+}. Interestingly, the Ω_2 parameters of the $Nd(hfa\text{-}D)_3$ and $Nd(pom\text{-}D)_3$ gave smaller values in DMSO-d_6. This facts support the conclusion that the surrounding environment of Nd^{3+} should tend to be more symmetric, when compared with those in methanol-d_4, acetone-d_6, THF-d_6 and DMF-d_7. In this case, one can say that the odd crystal field components in the systems of $Nd(hfa\text{-}D)_3$ and $Nd(pom\text{-}D)_3$ in DMSO-d_6 are much smaller than those in he other solvents, i.e., the contribution of electric dipole radiation becomes weaker in these systems, and the optical transition in dominated by the magnetic dipole transition which is forbidden by the Laporte selection rule. This rationale also explains why the emission of the systems has a longer lifetime, in other words, why the emission rate of Nd^{3+} in DMSO-d_6 would become slower than those in other solvents.

(b) In-situ Structure Analysis of Nd^{3+} in Liquid Systems. b-1) NMR Spectroscopy. In our previous paper, the weaker coordination of hfa-H in $Nd(hfa\text{-}H)_3$ in DMSO-d_6 was confirmed by a relatively small difference in the ^{13}C and ^{19}F NMR chemical shifts in DMSO-d_6.[7)] Upon further careful examination of the ^{13}C NMR spectrum of the $Nd(hfa\text{-}H)_3$ system in DMSO-d_6, a novel signal was observed at 64.4 ppm (see signal 4 in Fig. 3a). The characteristic ^{13}C NMR spectrum suggests that the exchange of DMSO molecules is very slow on the NMR time-scale, supporting the tight inner coordination of DMSO molecules in the $Nd(hfa\text{-}H)_3$ system. The $Nd(hfa\text{-}H)_3$/DMSO-d_6 system was concentrated under reduced pressure and the ^{13}C NMR spectrum of the residue was measured in acetone-d_6.## A similar signal was observed (Fig. 3b), and the intensity of signal 4 in both Figs. 3a and 3b was confirmed to be very low (ca. 4/5 and 1/3 of the expected intensity, respectively), because it should arise from 12 carbon atoms if 6 DMSO were coordinated. The intensity of ^{13}C NMR signals is generally affected by the mobility of the molecules.[20)] Decreased signal intensity may be rationalized as due to restriction of movement of the coordinated DMSO by the outer-coordinating hfa-H ligands. In acetone-d_6, rapid exchange of the Nd^{3+}-coordinated DMSO with acetone-d_6 may also contribute to the decreased intensity of the signal 4 in Fig. 3b. This interpretation was supported by the observation of the Stark splitting in acetone and by ES-MS analysis in the presence of acetone (see next section).

b-2) Electrospray Mass Spectroscopy. Electrospray mass spectrometry (ES-MS) is a powerful tool for measuring the molecular masses of nonvolatile, thermally unstable compounds.[16)] Residues obtained from $Nd(hfa\text{-}H)_3$ in DMSO or in DMSO-d_6 were dissolved in acetone and analyzed by ES-MS (Fig. 4). The signals with

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The composition of the isolated residuce could not be determined because it was oily.

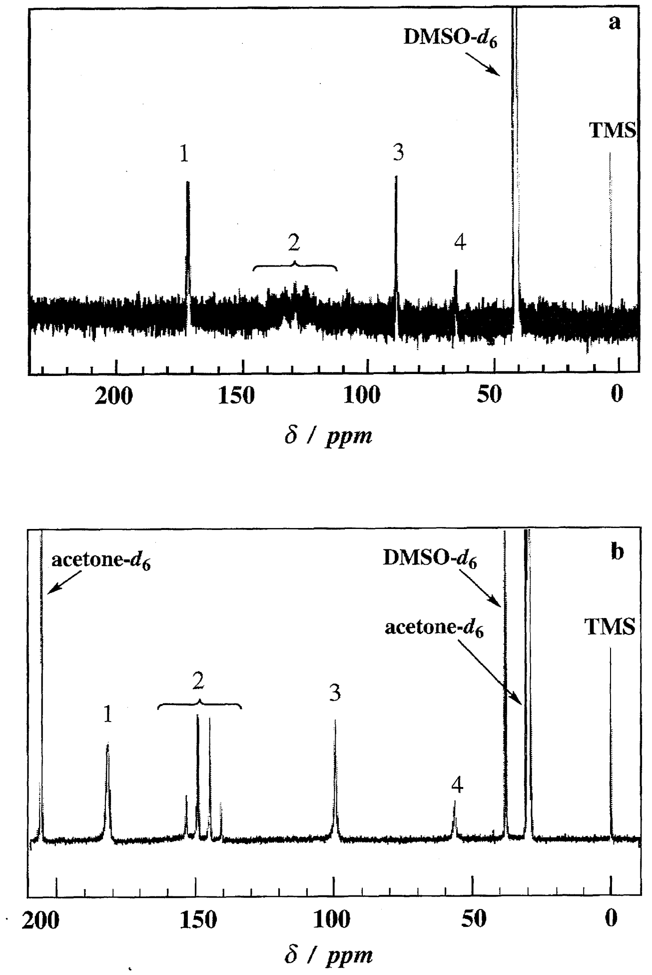


Fig. 3. ^{13}C NMR spectra of a) $Nd(hfa\text{-}H)_3$ in DMSO-d_6 and b) $Nd(hfa\text{-}H)_3(DMSO)_n$ in acetone-d_6. Signals 1, 2, and 3 were assigned to carbonyl carbon (>C=O), trifluoromethyl carbon ($-CF_3$), and methyne carbon (–CH–), respectively. Signal 4 was assigned to the deuterated methyl groups ($-CD_3$) of the tightly coordinated DMSO-d_6.

mass-numbers of 712, 790, 868, 945, and 1024 were assigned to $[Nd(DMSO)_2(hfa\text{-}H)_2]^+$, $[Nd(DMSO)_3(hfa\text{-}H)_2]^+$, $[Nd(DMSO)_4(hfa\text{-}H)_2]^+$, $[Nd(DMSO)_5(hfa\text{-}H)_2]^+$, and $[Nd(DMSO)_6(hfa\text{-}H)_2]^+$, respectively (Figs. 4a and 4b). Acetone-coordinated ions were also observed at mass-numbers of 750, 830, 906, and 984, which were assigned to $[Nd(DMSO)_1(acetone)_2(hfa\text{-}H)_2]^+$, $[Nd(DMSO)_2(acetone)_2(hfa\text{-}H)_2]^+$, $[Nd(DMSO)_3(acetone)_2(hfa\text{-}H)_2]^+$, and $[Nd(DMSO)_4(acetone)_2(hfa\text{-}H)_2]^+$, respectively. The assignment was made by comparing the observed isotope distribution with the calculated one (Fig. 4a), insert). Measurement of a $Nd(hfa\text{-}H)_3$/DMSO-d_6 sample gave signals that were increased by 6 in the mass numbers, which supported the validity of the above assignment.

Solera et al. recently reported that Nd^{3+} in water has a twelve-coordinated structure on the basis of EXAFS analysis.[21] To evaluate the coordination number for the Nd^{3+} site in the HFA systems, $[Nd(hfa\text{-}H)_3(H_2O)_2]$ in acetonitrile was analyzed by means of ES-MS. We observed a series of signals at mass-numbers 556, 574, 592, 610, 628, 646, and 664, which were assigned to $[Nd(hfa\text{-}H)_2]^+$, $[Nd(hfa\text{-}H)_2(H_2O)]^+$, $[Nd(hfa\text{-}H)_2(H_2O)_2]^+$, $[Nd(hfa\text{-}H)_2(H_2O)_3]^+$, $[Nd(hfa\text{-}H)_2(H_2O)_4]^+$, $[Nd(hfa\text{-}H)_2(H_2O)_5]^+$, and $[Nd(hfa\text{-}H)_2(H_2O)_6]^+$, respectively (Fig. 4c). The parent signal was for $[Nd(hfa\text{-}H)_2(H_2O)_2]^+$, and the largest mass-number was for $[Nd(hfa\text{-}H)_2(H_2O)_6]^+$. Taking into account that neutral

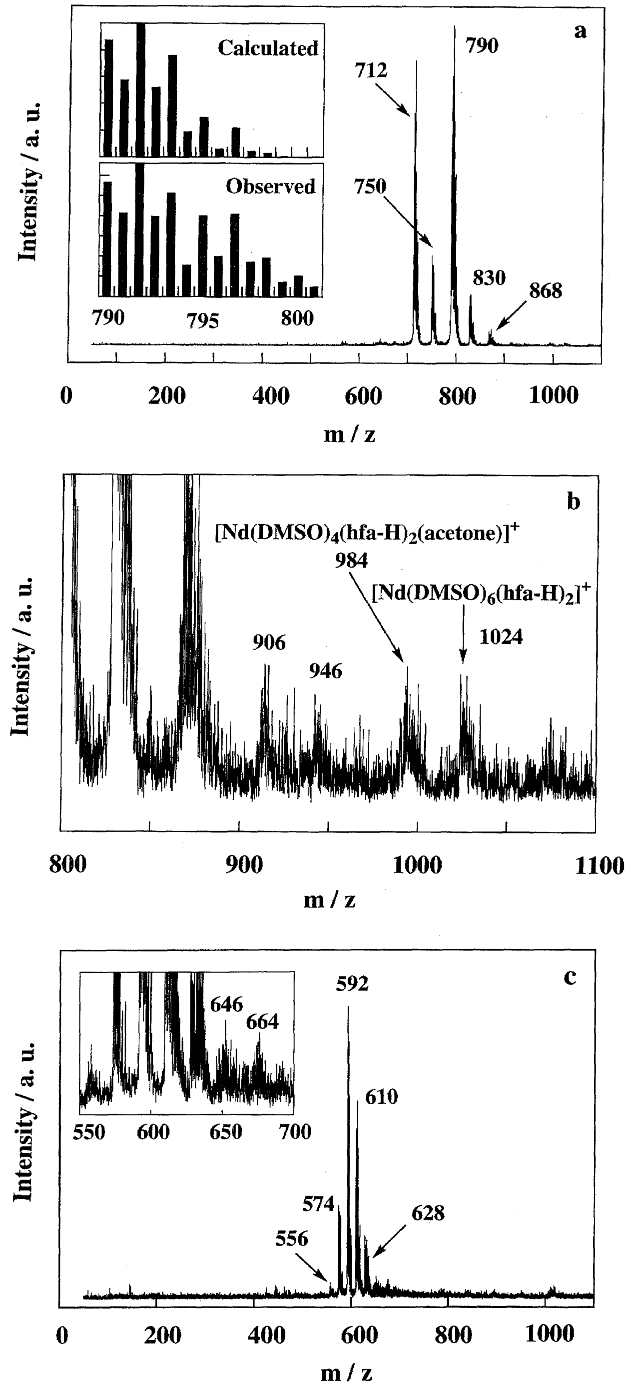


Fig. 4. Electrospray MS spectra of $[Nd(hfa\text{-}H)_3(DMSO)_n]$ in acetone (a), (b), and $Nd(hfa\text{-}H)_3$ in acetonitrile (c). The bar graphs in the insert in (a) show the calculated and observed isotope distributions for representative fragments of the complex.

species are undetectable in ES-MS measurements, Nd^{3+} may have twelve-coordination through electrostatic-charge and ion–dipole interactions in the present systems.

To compare the coordination strength of DMSO through ion–dipole interaction and that of hfa-H through electrostatic-charge interaction, we analyzed reactions of Nd(NO$_3$)$_3$ (concn 1×10^{-4} M) with respective DMSO and hfa-H (concn 5×10^{-4} M) in acetonitrile (AN). The reaction products were analyzed by ES-MS spectra, giving the parent signals attributed to [Nd(NO$_3$)$_2$(DMSO)$_3$]$^+$ (MZ$^+$ = 502) and [Nd(HFA)$_2$(AN)$_2$(H$_2$O)$_2$]$^+$ (MZ$^+$ = 676), respectively. The intensity of the former signal was four times larger than that of the latter. When DMSO (5×10^{-4} M) was added into the reaction mixture of Nd(NO$_3$)$_3$ (1×10^{-4} M) and hfa-H (5×10^{-4} M), the signal due to [Nd(hfa-H)$_2$(DMSO)$_3$]$^+$ species was observed as parent signal as in Fig. 4a, and the signals of [Nd(NO$_3$)$_2$(DMSO)$_3$]$^+$ and [Nd(hfa-H)$_2$(AN)$_2$(H$_2$O)$_2$]$^+$ disappeared completely. The signal intensity in ES-MS analysis qualitatively indicate that hfa-H is stronger ligand to Nd^{3+} than NO$_3^-$ and the formation constant of Nd^{3+} with hfa-H may be smaller than that with DMSO. The weakened coordination ability of the bidentate HFA ligand can be rationalized as due to the strong electron-withdrawing effect of trifluoromethyl groups. Recently, the weakened coordination of hfa-H was also reported in the system of Zn^{2+}.[22)]

With these facts in mind, it is reasonable to assume that DMSO can displace hfa-H in an outer coordination sphere of Nd^{3+}, resulting in the twelve-coordination expansion. Accordingly, the neutral twelve-coordinated complex, [Nd(DMSO)$_6$(hfa-H)$_3$] might be in equilibrium with [Nd(DMSO)$_6$(hfa-H)$_n$]$^+$ (n = 1 or 2) in the system. However, our attempt to determine spectroscopically the binding constants of [Nd(DMSO)$_6$(hfa-H)$_1$]$^{2+}$, [Nd(DMSO)$_6$(hfa-H)$_2$]$^+$, and [Nd(DMSO)$_6$(hfa-H)$_3$] was in vain because the change in UV-vis absorption based on the forbidden f–f transitions was very small.

b-3) Nd L$_{\mathrm{III}}$-Edge XANES and EXAFS Spectroscopy. The Nd L$_{\mathrm{III}}$ XANES and EXAFS spectra were measured for [Nd(hfa-H)$_3$(H$_2$O)$_2$] in methanol-d_4, acetone-d_6, THF-d_8, DMF-d_7, and DMSO-d_6. A typical XANES spectrum is shown in Fig. 5a. The strong absorption of the L$_{\mathrm{III}}$-edge due to the 2p→5d ($^2P_{3/2}\rightarrow{}^2D_{5/2}$) transition was observed in this system. Although the absorption maxima did not depend on the choice of solvents, widening of the spectra was observed. The first derivative of each spectrum is shown in Fig. 5b. The widening was clearly in the order of methanol-d_4 <acetone-d_6 <THF-d_8 <DMF-d_7 <DMSO-d_6. Since the observed widening of the absorption in the system reflects increased interaction between the Nd^{3+} ion and oxygen atoms in the solvents, the strength of the interaction was in the order of methanol<acetone<THF<DMF<DMSO. Rao and Wong reported that an increase in L$_{\mathrm{III}}$-edge absorption in Nd oxide could be attributed to a covalent-like bonding effect due to electron donation from the $^2D_{5/2}$ orbital to the partially filled 4f orbitals of Nd^{3+}.[23)] The characteristics of the XANES spectrum of [Nd(hfa-H)$_3$(H$_2$O)$_2$] in DMSO-d_6 would support the presence of the strongest interaction between the Nd^{3+} site and the oxygen atoms of DMSO, where covalent-like bonding may form through electron donation into the f orbitals.

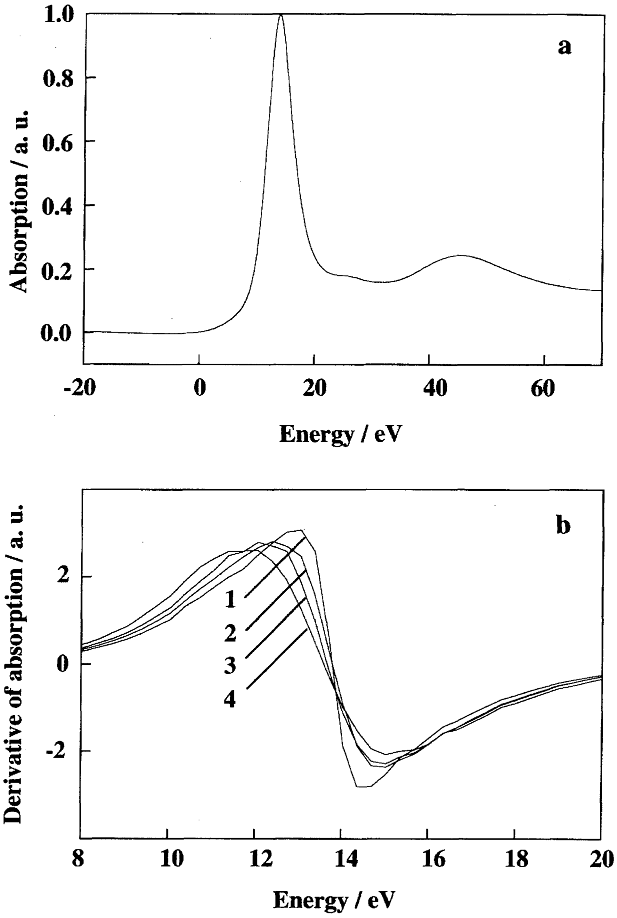


Fig. 5. L$_{\mathrm{III}}$-edge XANES spectra of Nd(hfa-H)$_3$. a) Nd(hfa-H)$_3$ in DMSO-d_6. b) first derivative of the spectra of Nd-(hfa-H)$_3$ in 1) acetone-d_6, 2) THE-d_8, 3) DMF-d_5, and 4) DMSO-d_6.

Phase-uncorrected Fourier transforms of the L$_{\mathrm{III}}$ EXAFS of [Nd(hfa-H)$_3$(H$_2$O)$_2$] in acetone-d_6 and DMSO-d_6 are shown in Fig. 6. Both spectra exhibit an intense peak around 2.0 Å, which is believed to be due to the coordinated oxygen atoms of the surrounding molecules. The structural parameters determined by EXAFS analysis in water, methanol-d_4, acetone-d_6, THF-d_8, DMF-d_7, and DMSO-d_6 are summarized in Table 3. For the [Nd(hfa-H)$_3$(H$_2$O)$_2$] crystal, the bonding distance and the coordination number of oxygen atoms were determined to be 2.49±0.01 Å and 8.0±1.4, respectively. Since three bidentate hexafluoroacetylacetonate ligands (hfa-H) coordinate to an Nd^{3+} center, oxygen atoms of HFA occupy six coordination sites of the [Nd(hfa-H)$_3$(H$_2$O)$_2$] system. Two other oxygens are undoubtedly due to water from crystallization. This eight-coordinated structure was also supported by elemental analysis and DSC analysis, as reported previously.[5)] The agreement in the coordination number supports the validity of the present EXAFS measurements. In the system of [Nd(hfa-H)$_3$(H$_2$O)$_2$] in methanol-d_4, acetone-d_6, THF-d_8, and DMF-d_7, the bonding

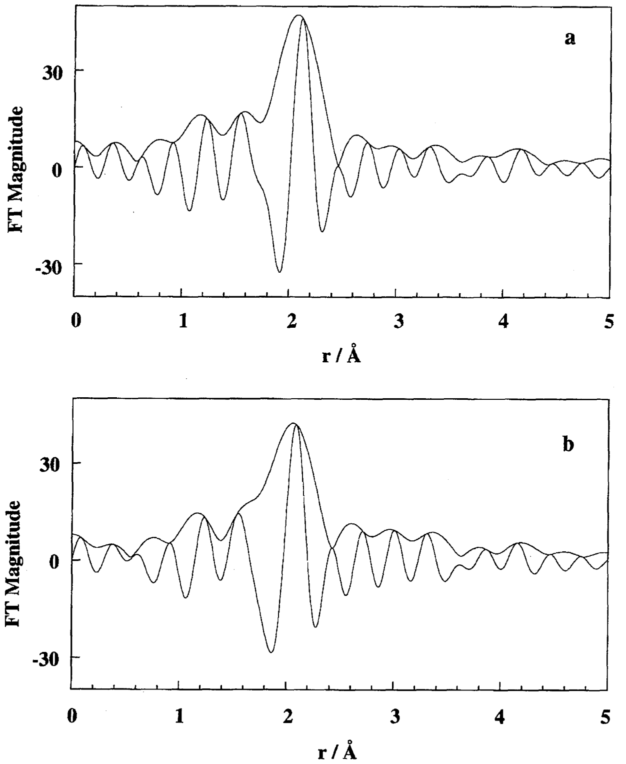


Fig. 6. Phase-uncorrected Fourier transform of $k^3\chi(k)$ of L_{III}-edge EXAFS spectra of $Nd(hfa\text{-}H)_3$ in a) acetone-d_6 and b) DMSO-d_6.

Table 3. Curve-Fitting Results for Fourier-Filtered $k^3\chi(k)$ Nd L(III)-Edge EXAFS of $Nd(ClO_4)_3$ and $Nd(HFA)_3$[a)]

Sample	r/Å[b)]	CN[c)]	σ^2/Å^2[d)]	R/%[e)]
$Nd(ClO_4)_3$				
in water	2.51	9.5	0.0976	4.9
$[Nd(hfa\text{-}H)_3(H_2O)_2]$				
crystals	2.49	8.0 (±1.4)	0.1068	9.1
$[Nd(hfa\text{-}H)_3(H_2O)_2]$				
in methanol-d_4	2.50	8.8 (±1.0)	0.0965	5.2
in acetone-d_6	2.49	9.2 (±0.9)	0.1039	4.9
in THF-d_8	2.49	8.6 (±1.2)	0.1023	7.9
in DMF-d_7	2.50	8.8 (±0.9)	0.0965	5.2
in DMSO-d_6	2.47	5.8 (±0.8)	0.0565	6.4

a) Curve-fitting was performed over a k range of 2.9—9.0 Å^{-1}. b) Atomic distance. Standard deviation: r, ±0.008 Å. c) Coordination number. Values in parentheses are standard deviations of the coordination number. d) The square of the Debye–Waller factor. e) Quality of the fit, defined as $\{\sum(k^3\chi_{\mathrm{obs}}-k^3\chi_{\mathrm{cald}})^2/\sum(k^3\chi_{\mathrm{obs}})^2\}^{1/2}$.

distance and the coordination number (CN) of the oxygen atoms were similar (r = 2.49—2.50 Å, CN = 8.6—9.2). In DMSO-d_6, however, a drastic decrease in the coordination number (CN) was observed (CN = 5.8). The quality of the fit for $[Nd(hfa\text{-}H)_3(H_2O)_2]$ in DMSO-d_6 (6.4%) proved the validity of the six-coordinated structure of $Nd(hfa\text{-}H)_3$. It should be noted that a six-coordinated hexagonal structure was observed in solid neodymium systems, such as Nd_2O_3 and NdF_3.[23)] In consideration of results from characteristic emission, the coordination structure of $[Nd(hfa\text{-}H)_3(H_2O)_2]$ in DMSO-d_6 would be similar to symmetrical Nd_2O_3.

The characteristic coordination in DMSO-d_6 was also established by the Debye–Waller factor in the EXAFS measurements. The Debye–Waller factor σ^2 in methanol-d_4, acetone-d_6, THF-d_8, and DMF-d_7 was estimated to be about 0.10 Å^2, which is on the same order as that of $Nd(ClO_4)_3$ in water. We observed a much smaller Debye–Waller factor in DMSO-d_6 (σ^2 = 0.06) than in any other solvent. Generally, the Debye–Waller factor σ has tow components, σ_{stat} and σ_{vib}, due to static disorder and thermal vibration, respectively. The component σ_{stat} reflect the magnitude of the difference in distance. Thus, the Debye–Waller factor of liquid samples is larger than that of solid crystals with a well-defined lattice structure, since a large number of structural conformations and wide bonding flexibility are present in liquid systems. The smallest Debye–Waller factor in DMSO-d_6 indicates that the deviation in coordination is smallest in this solvent. Thus, the coordination between Nd^{3+} and the six oxygen atoms should be tight due to their strong short-range interactions.

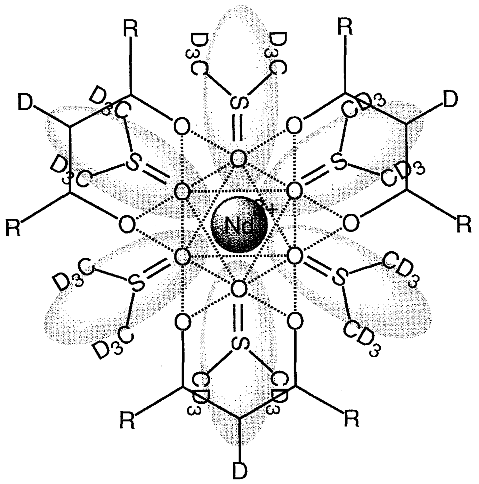
(c) Relationship between Enhanced Emission Efficiency and Formation of Symmetrical, Rigid and Bulky Shells Composed of Tightly Solvated DMSO Molecules and Weakly Coordinated Low-Vibrational β-Diketonato Ligands. It has now been clarified that DMSO-d_6 is an excellent medium for inducing photoemission of Nd^{3+} in fluid systems, especially when weakly coordinating and low vibrational hfa-D and pom-D were employed as ligands. The effect of the coordination sphere on the f-electronic transition (the emission rates, the small Judd–Oleft parameter Ω_2 and the absence of Stark splitting in the $^4I_{9/2}\rightarrow{}^4F_{3/2}$ absorption spectra) suggests that the Nd complexes with hfa-D and pom-D can dissociate from hfa-D or pom-D in DMSO, giving a symmetrical coordination sphere while keeping weak electrostatic interaction with hfa-D or pom-D.

The electrostatic ion–charge and ion–dipole interactions play essential role in such interactions. ^{13}C NMR, EXAFS, and XANES analyses have indicated the presence of DMSO molecules which tightly solvate the Nd^{3+} site. While DMSO has the largest donor property among the 6 solvents examined (methanol, acetone, THF, DMF, DMSO, and H_2O), hexafluoroacetylacetonate anion (hfa-H anion) can be classified as a weakly coordinating bulky ligand because it has large electron-withdrawing trifluoromethyl groups. In the ES-MS analysis, the observation of mass-numbers corresponding to $[Nd(DMSO)_n(hfa\text{-}H)_2]^+$ (n = 2, 3, 4, 5, and 6) supports that hfa-H anions should undoubtedly interact with the neodymium species, i.e., $[Nd(DMSO\text{-}d_6)_6]^{3+}$. Considering these observations with the requirement for symmetrical surroundings composed of six DMSO-d_6 and three bidentate hfa-H anions, we propose the contribution of a symmetrical rigid double shell structure for $[Nd(DMSO\text{-}d_6)_6(hfa\text{-}H)_3]$ in

DMSO-d_6 (Fig. 7).[###]

The proposed structure is consistent with the enhanced emission characteristics of neodymium complexes with weakly coordinating β-diketones in DMSO-d_6. In these systems, radiationless transition via vibrational excitation of the emission of the Nd(hfa-H)$_3$ system should be dominated by sulfonyl groups of DMSO-d_6 molecules (S=O : 1060 cm^{-1}) in the inner sphere. In other aprotic polar solvents, however, solvation should compete with coordination of the hfa-H anion, leading to the observation of a coordination number of eight to nine in EXAFS analysis. The Stark splitting and the relatively large Judd–Ofelt parameter in acetone-d_6 support the presence of an equilibrium due to the competitive solvation of acetone-d_6 and the coordination of hfa-D, which causes an unsymmetrical environment at the Nd^{3+} site in liquid systems.

Unsymmetrical coordination and solvation may be found in the neodymium complexes Nd(acac-D)$_3$ and Nd(tfa-D)$_3$ in DMSO-d_6. Their β-diketonatos may have a stronger coordination ability than the hfa-D anion, and may compete with the solvation of DMSO. In fact, the values for the Stark splitting energy of Nd(tfa-D)$_3$ and Nd(acac-D)$_3$ in DMSO-d_6 were 98 and 81 cm^{-1}, and were on the same order as that of Nd(hfa-D)$_3$ in acetone-d_6 (87 cm^{-1}).



Nd(hfa-D)$_3$
R = CF$_3$

Nd(pom-D)$_3$
R = CF$_2$(CF$_2$)$_6$F

Fig. 7. A symmetrical rigid double shell structure for [Nd(DMSO-d_6)$_6$(hfa-D)$_3$] and [Nd(DMSO-d_6)$_6$(pom-D)$_3$] in DMSO-d_6.

The coordination number of Nd^{3+} and its interaction with anions may be interpreted in terms of an equilibrium between differently coordinated species of between species with slightly different coordination properties. Thus, coordination with molecules or anions composed of high vibrational bonds such as C–H, O–H, and O–D bonds prevents radiative transition, i.e., photoemission. In particular, the presence of water molecules in such systems induces radiationless transition via vibrational excitation of O–H or O–D bonds because of preferential hydration to Nd^{3+}, leading to no emission. It is worth noting that, in the ES-MS spectrum of the DMSO-coordinated Nd(hfa-H)$_3$ system, we could not detect any hydrated intermediates, while a series of mass-numbers due to hydrated species was present in the Nd(hfa-H)$_3$(H$_2$O)$_2$ system. The strongly coordinating DMSO-d_6 molecules should repel water molecules even if water molecules are present in the inner sphere, thus contributing to the enhanced emission of Nd^{3+} in liquid systems.

In addition to the role of DMSO-d_6 in emission, weakly coordinating anions from hfa-D and pom-D should contribute to the tight solvation of DMSO-d_6 in the inner sphere. Although moderately coordinating β-diketonate anions such as acac-D and tfa-D undergo vibrational excitation of methyl groups, they are in coordination equilibrium with DMSO molecules to an appreciable extent, thus enhancing unexpectedly the emission efficiency.

We estimated the morphology of Nd(pom-H)$_3$ in DMSO by means of dynamic light scattering (DLS) because it has the most efficient emission in DMSO-d_6. At a dissociative concentration of 0.05 M, the average diameter was determined to be 4.0 nm. The proposed structure of the Nd(DMSO)$_6$(pom-H)$_3$ complex was calculated to be on the order of about 3.5 nm by a CPK model. These results are in good agreement with each other if the specific DMSO solvation at the inner layer of the particle is taken into account (Fig. 7). The effective emission of Nd(pom-D)$_3$ in DMSO-d_6 may be explained as due to the prevention of radiationless transition by the inner DMSO-d_6 sphere and the suppression of energy migration by the outer pom-D sphere. The effect of the symmetrical sphere at Nd^{3+} site on the f-electronic transition also contributes to the decrease in the emission rate in the system.

Conclusion

The results of UV-vis spectra, ^{13}C NMR, electrospray mass (ES-MS) spectra, XANES and EXAFS analysis of Nd(hfa-H)$_3$ and Nd(pom-H)$_3$ in DMSO-d_6 support the idea that DMSO-d_6 molecules coordinate tightly to the Nd^{3+} site in the Nd(hfa-D)$_3$ system in DMSO-d_6, establishing the formation of a symmetrical rigid double-shell composed of six inner-coordinating DMSO molecules and three outer-weakly-coordinating HFA molecules through ion–dipole and electrostatic ion–charge interactions. The proposed structure suggests that the strong emission of complexes with weakly coordinating hfa-D and pom-D, i.e., Nd(hfa-D or pom-D)$_3$, in DMSO-d_6 is due to the suppression of both radiationless transitions via vibrational excitation and energy migration and due to the decrease of the emission rate through the forbidden f-elec-

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[###] Recently, investigation of EXAFS at the L_{III} edges of rare earth atoms was performed for their aqueous chloride solutions at concentrations of 50 ($R = 1100$), 100 ($R = 550$), and 200 ($R = 275$) mM, and showed that the rare earth ions are always surrounded by 12 water molecules, but with a different metal–oxygen distance. The structure was proposed to have cubooctahedral symmetry.[24]

tronic transition in the emission process at the symmetrical inner sphere of the Nd^{3+} site. In conclusion, crystal-like environments composed of coordination compounds with low vibration bonding may be useful for enhancing the emission of Nd^{3+} in fluid systems. Such structural information of the surrounding shell of the luminescent Nd^{3+} presents a novel aspect for development of luminescent materials in fluid media.

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