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Luminescence of Novel Neodymium Sulfonylaminate Complexes in Organic Media**

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Nobuaki Nakashima, and Shozo Yanagida*

Neodymium(III)-containing solids are the most popular luminescent materials for application in laser systems.[1] Inorganic Nd^{III} compounds such as oxides, fluorides, phosphates, and their mixed matrices were investigated for the capability of high power laser radiation by controlling the Nd^{III} density in matrices. The construction of strongly luminescent Nd^{III} materials in organic media would be desirable for developing applications in novel organic Nd^{III} devices, such as organic liquid lasers, optical-fiber polymers, organic electroluminescent devices, and near-IR immunoassays.[2] However, the energy gap theory shows that the presence of C–H or O–H bonds in the vicinity of Nd^{III} leads to effective radiationless transitions by vibrational excitation of C–H or O–H bonds, and this results in negligible emission quantum yields.[3] Suppression of such vibrational excitation in the Nd^{III} system requires deuteration of C–H and O–H bonds or replacement of C–H bonds with C–F bonds in ligating molecules, and the use of deuterated solvents with low vibrational frequencies. By using these strategies, various researchers recently observed effective emission in certain organic/Nd^{III} systems.[4] However, an emission quantum yield on the order of 10^{-5} was never observed in solvents that contain H atoms. Here we report on the luminescence of novel Nd^{III} complexes and the first observation of enhanced luminescence of Nd^{III} in a solvent of high vibrational frequency, namely, undeuterated acetone, by using bis(perfluoroalkylsulfonyl)aminates as bulky ligands with low vibrational frequencies.

Bis(perfluorooctylsulfonyl)amine (posH) was synthesized by treating the corresponding perfluorooctylsulfonylamine with perfluorooctylsulfonyl fluoride in the presence of triethylamine (TEA) as base in THF, followed by acidification with 10% aqueous H_2SO_4. $[Nd(pos)_3]$ was prepared by treating posH with neodymium oxide in water. For comparison, we prepared $[Nd(pbs)_3]$ (pbs = bis-perfluorobutylsulfo-

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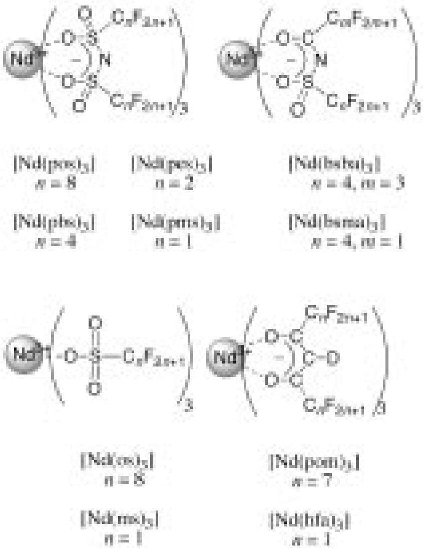
nylaminate), [Nd(pes)$_3$] (pes = bis-perfluoroethylsulfonylaminate), [Nd(pms)$_3$] (pms = bis-perfluoromethylsulfonylaminate), [Nd(bsba)$_3$] (bsba = *N*-perfluorobutylsulfonylperfluorobutylaminate),[5] [Nd(bsma)$_3$] (bsma = *N*-trifluoromethylsulfonylperfluorobutylaminate),[5] [Nd(os)$_3$] (os = perfluorooctylsulfonate) and [Nd(ms)$_3$] (ms = perfluoromethylsulfonate) by similar methods. [Nd(pom)$_3$] (pom = bis(perfluorooctanoyl)-[D]methanato) and [Nd(hfa)$_3$] (hfa = hexafluoro[3-D]acetylacetonato) were prepared according to the procedure described elsewhere.[4a–c] All the Nd^{III} complexes (see Scheme 1) were characterized by ^{1}H (when the compound contains hydrogen atoms), ^{19}F, and ^{13}C NMR spectroscopy; IR spectroscopy; elemental analysis; and differential scanning calorimetry (DSC). Water of crystallization was determined by elemental analysis and DSC (Table 1).



Scheme 1. Neodymium(III) complexes investigated in this study.

Samples for measurements of the luminescence of Nd^{III} in organic media were prepared under deoxygenated conditions because oxygen molecules can affect the transition luminescence of f orbitals.[4e] Solutions (0.05 M) of the Nd^{III} complexes were prepared in 1 mL of a solvent under 10^{-3} torr and then transferred to a quartz cell for optical measurements.[4c] Solutions in quartz cells (optical path length 10 mm) were excited at 585 nm ($^4I_{9/2} \rightarrow {}^2G_{7/2}$) with a spectromator (JASCO, SS-25). A Ge detector was used to detect emission in the near-infrared region (band path 4 mm). The spectra presented here were corrected for detector sensitivity and lamp intensity. The emission quantum yields were determined by standard procedures with an integrating sphere and quartz cells (optical path length 1 mm).[4c] Emission lifetimes were determined by using a Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PCR-2) and a Si photodiode (Hamamatsu Photonics S3759). Samples were excited by the second harmonic (532 nm) of the fundamental nanosecond pulse. The emission from the sample was measured by using low-cut optical filters (HOYA, R66 and R68) that were placed in front of the detector. Quenching of the excited state by dioxygen was investigated by introducing oxygen gas (99 %, 760 torr) into the [Nd(pos)$_3$]/[D$_6$]acetone and [Nd(pms)$_3$]/[D$_6$]acetone systems.

The emission quantum yields of the Nd^{III} complexes in [D$_6$]DMSO, [D$_6$]acetone, and undeuterated acetone are listed in Table 1. [Nd(pos)$_3$], [Nd(pbs)$_3$], and [Nd(bsba)$_3$] produced emissions with respectable quantum efficiency in undeuterated acetone, whereas the emission of other complexes was not observable in undeuterated acetone under the same instrumental conditions. The emission spectrum of [Nd(pos)$_3$] in undeuterated acetone had the typical shape of an Nd^{III} emission with a branching ratio in the three transitions similar to that observed for [Nd(hfa)$_3$] in [D$_6$]DMSO (Figure 1).[4c] The quantum yield was 3.0 ± 0.5 %. This is the first observation of the effective emission of the Nd^{III} complex in an organic solvent with C–H bonds.

The quantum efficiency of [Nd(pos)$_3$] in acetone was comparable to those in [D$_6$]acetone and [D$_6$]DMSO. However, the emission efficiency of other complexes was affected by solvent, and the quantum yield in [D$_6$]acetone was much lower (≤ 1.2 %). These results indicate that the Nd^{III} ion in [Nd(pos)$_3$] is shielded due to the strong coordination of pos,

Table 1. Emission quantum yields and lifetimes of Nd^{III} complexes in organic media.

Complex	nH$_2$O	Chain length	Emission quantum yields [%]			Lifetime [µs]
			[D$_6$]DMSO	[D$_6$]acetone	acetone	[D$_6$]acetone
[Nd(pos)$_3$]	0	$n = 8$	3.3	3.2	3.0	13 (12)[a]
[Nd(pbs)$_3$]	0	$n = 4$	3.3	2.5	0.8	2.0
[Nd(pes)$_3$]	2	$n = 2$	3.3	1.0	< 0.01	–
[Nd(pms)$_3$]	2	$n = 1$	3.3	0.8	< 0.01	–
[Nd(bsba)$_3$]	0	$n = 4, m = 3$	3.3	1.1	0.8	2.0
[Nd(bsma)$_3$]	2	$n = 4, m = 1$	3.3	0.8	< 0.01	1.9
[Nd(os)$_3$]	6	$n = 8$	3.3	1.2	< 0.01	2.0
[Nd(ms)$_3$]	6	$n = 1$	3.3	1.1	< 0.01	4.0
[Nd(pom)$_3$]	0	$n = 7$	3.2[b]	0.8[c]	< 0.01	–
[Nd(hfa)$_3$]	2	$n = 1$	1.1	0.3	< 0.01	1.7
[Nd(NO$_3$)$_3$]	6	$n = 0$	3.3	< 0.01	< 0.01	< 0.1

[a] The value in parentheses is the lifetime in undeuterated acetone. [b] The [Nd(hfa)$_3$]/DMSO system should have a symmetrical, rigid, and bulky shell composed of six inner-coordinating DMSO molecules and three weakly outer-coordinating hfa molecules.[4h] The smaller quantum yield of [Nd(hfa)$_3$] in [D$_6$]DMSO is thought to be due to vibrational excitation from Nd^{III} to outer-coordinating C=O sites of hfa. The coordination structure of [Nd(pom)$_3$] in [D$_6$]DMSO is similar to that of [Nd(hfa)$_3$] in DMSO; however, the quantum yield of Nd(pom)$_3$ in [D$_6$]DMSO was 3.2 % due to prevention of energy migration.[4b] [c] [Nd(pom)$_3$] was insoluble in [D$_6$]acetone. The quantum yield of [Nd(pom)$_3$] in [D$_6$]acetone was estimated by using the quantum yield of [Nd(poa)$_3$] (poa = tris(perfluorooctanoyl)acetic acid).[4g].

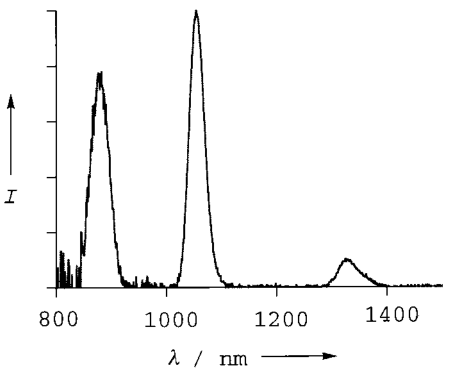


Figure 1. Emission spectrum of 0.05 M [Nd(pos)$_3$] in undeuterated acetone (880 nm: $^4F_{3/2} \rightarrow {}^4I_{9/2}$, 1054 nm: $^4F_{3/2} \rightarrow {}^4I_{11/2}$, 1325 nm: $^4F_{3/2} \rightarrow {}^4I_{13/2}$). Excitation at 585 nm. The unsymmetrical shape of the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition is due to Stark splitting of the crystal field.

and acetone molecules appear to be unable to interact with the Nd^{III} ion. The Ω_2 parameter of the Judd–Ofelt analysis was 0.09×10^{-20} cm^2 in undeuterated acetone. This result suggests that the geometrical structure of [Nd(pos)$_3$] in undeuterated acetone is symmetrical and free of coordinated solvent. To evaluate the stronger coordination of pos relative to pom, MO calculations were performed on [Nd(pos)$_3$] and [Nd(pom)$_3$] with the CAChe system (MM2/PM3). The electron density on the O atoms of the sulfonylaminate was −0.74, much more negative than those of pem (−0.29), water (−0.33), and acetone (−0.28). This supports the much stronger interaction of Nd^{III} with bis(perfluoroalkylsulfonyl)aminates than with β-diketonates.[6]

The Nd^{III} complexes possessing two long-chain perfluoroalkyl groups are always free of water of crystallization according to DSC analysis. Weakly coordinating acetone and water molecules cannot be incorporated into the coordination sphere of Nd^{III} when it is covered by bulky perfluoroalkyl groups. The emission of the complexes of bis-sulfonylaminates is superior to those of the complexes of ligands with carbonyl groups ([Nd(bsba)$_3$] and [Nd(pom)$_3$]). These facts can be rationalized by Frank–Condon factor (FC) calculations on the coordinating groups. Sulfonyl groups have lower FC values ($FC_{S-O} = 0.0031$) than ligands having carbonyl groups ($FC_{C-O} = 0.015$).[7]

A series of Nd^{III} complexes of bis(perfluoroalkylsulfonyl)aminate ligands gave the order of the quantum yields of [Nd(pos)$_3$] > [Nd(pbs)$_3$] > [Nd(pes)$_3$] > [Nd(pms)$_3$] in [D$_6$]acetone, and this indicates that the introduction of long-chain perfluoroalkyl groups is important for enhanced emission. We already reported that [Nd(pom)$_3$] emits in fluid systems more efficiently than [Nd(hfa)$_3$] due to suppression of cross relaxation as nonradiative energy transfer by maintaining the distance between the two Nd^{III} ions at the limit of diffusional collision.[3b] This should also hold for [Nd(pos)$_3$]. In contrast, the quantum yield of [Nd(os)$_3$] (1.2%) is comparable to that of [Nd(ms)$_3$] (1.1%). The monodentate ligand, os, results in an Nd^{III} coordination sphere covered by three perfluorooctyl groups, which are not sufficient to prevent the incorporation of acetone molecules and energy migration leading to cross relaxation in fluid systems.

Emission lifetimes of the Nd^{III} complexes in [D$_6$]acetone are listed in Table 1. The lifetime of [Nd(pos)$_3$] is much longer than those of other Nd^{III} complexes. However, the lifetimes were not proportional to the quantum yields. These results may be ascribed to the effect of geometrical parameters of the coordination environment of the Nd^{III} ion on the emission rate.[4h] The emission lifetime of [Nd(pos)$_3$] in undeutrated acetone was comparable with that in [D$_6$]acetone (Table 1). Interestingly, the emission in [D$_6$]acetone was not quenched by oxygen, although the singlet oygen emission can be observed in the case of [Nd(pms)$_3$] under the same conditions.[4e]

All the complexes except [Nd(hfa)$_3$] gave the same quantum efficiency in [D$_6$]DMSO as [Nd(NO$_3$)$_3$]. This appears to be attributable to predominant coordination of [D$_6$]DMSO to Nd^{III}. We previously reported that strongly coordinating DMSO molecules can penetrate into the inner coordiation sphere of [Nd(hfa)$_3$] in DMSO to give a twelve-coordinate complex with three DMSO and three hfa ligands.[4h] The predominant coordination of [D$_6$]DMSO molecules in the inner sphere of the Nd^{III} complexes may explain the uniform emission quantum efficiency (see footnote to Table 1).

In summary, to maintain the effective emission of Nd^{III} in a matrix of high vibrational frequency, the coordination sphere of Nd^{III} should consist of strongly coordinating, bulky ligands with low vibrational frequencies, that is, there are three criteria for luminescence: 1) suppression of vibrational excitation, 2) prevention of nonradiative cross relaxation at diffusional collision, and 3) suppression of solvent incorporation in the emitting Nd^{III} complex.

Experimental Section

posH: white crystal. ^{19}F NMR(270 MHz, [D$_6$]acetone, 25 °C, hexafluorobenzene): δ = −79.51 (t, 6F, CF$_3$), −111.59 (d, 4F, CF$_2$), −118.43 (s, 4F, CF$_2$), −120.10 (m, 12F, C$_3$F$_6$), −121.06 (s, 4F, CF$_2$), −124.59 (s, 4F, CF$_2$); IR (KBr): $\tilde{\nu}$ = 1373, 1237, 1206, 1151 cm^{-1}; elemental analysis calcd for $C_{16}H_1O_4S_2N_1F_{34}$: C 19.58, H 0.10, N 1.43; found: C 18.54, H 0.20, N 1.50. pbsH was also prepared and identified by the same methods. pesH, pmsH, os and ms were obtained from Fluka Chemika.

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A Mechanistic Dichotomy Leading to a Ruthenium-Catalyzed *cis*-Addition for Stereoselective Formation of (*Z*)-Vinyl Bromides**

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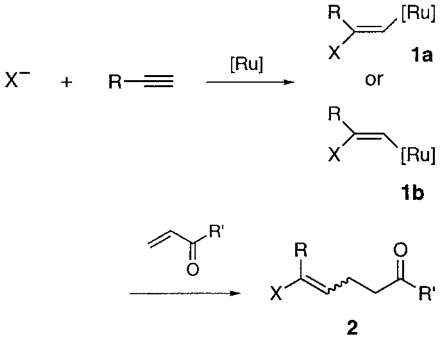
Addition reactions of alkenes and alkynes catalyzed by transition metals normally lead either to a *cis* or to a *trans* product (excluding stereorandom processes). A situation wherein both mechanistic pathways are energetically accessible with the same catalyst system has not been described. In our exploration of ruthenium-catalyzed three-component couplings, we have discovered such a mechanistic duality, which has led to the *cis*-bromoalkylation of alkynes. Vinyl bromides are extremely useful as cross-coupling partners in a variety of transition metal catalyzed processes[1] and as precursors to organolithium and related organometallic compounds. However, there are difficulties of selectivity during their preparation. Poor steroselectivity in the addition of HBr to alkynes or in the bromination–dehydrobromination processes in the case of alkenes limits the utility of these classic protocols. Olefination reactions[2] and stoichiometric bromination of carbon–metal bonds[3, 4] are the main pathways for the more selective preparation of vinyl bromides. More efficient methods, notably wherein such entities are created by simple additions,[5] become an important objective. Our earlier work demonstrated the viability of (*E*)-vinyl chloride formation via a three-component coupling,[6] presumably through a *trans*-chlororuthenation followed by olefin insertion into the metal–halide bond. The availability of a nonhalogen-bearing ruthenium complex as a useful catalyst induced us to consider the development of a stereoselective synthesis of vinyl bromides. This led to a geometrically complementary process compared to our earlier study with chloride wherein tri- and tetra-substituted (*Z*)-vinyl bromides are available by a three-component coupling.

Initial experiments using [CpRu(cod)Cl][7] (Cp = cyclopentadienyl, cod = cycloocta-1,4-diene) gave competitive vinyl chloride formation (the chloride source is the catalyst) even at high concentration of bromide salts [Eq. (1)]. The development of a bromo-alkylation reaction led us to turn to a halide-free ruthenium complex, $[CpRu(CH_3CN)_3]PF_6$,[8] as a potential catalyst [Eq. (2), MVK = methyl vinyl ketone].



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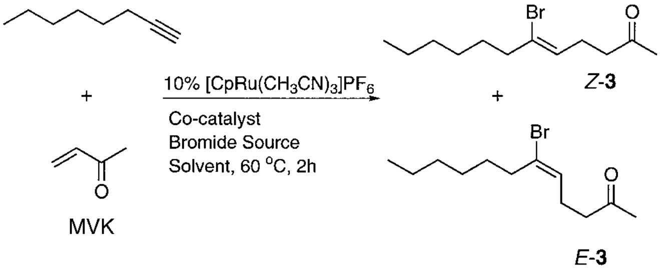

(2)

Table 1 summarizes the initial studies for optimizing cocatalyst concentration, bromide source, and solvent for these reactions. Improved yields were achieved upon switching from dimethylformamide (DMF) to an acetone/DMF mixture as solvent (entry 3 versus 2). In this mixture a more soluble bromide source, such as tetramethylammonium bromide instead of ammonium bromide, gave more of the (*Z*)-product, but in lower yields (entry 4 versus 3). In acetone alone the (*Z*)-product was formed with very high selectivity, albeit in even lower yields (entries 5 and 6). Adding DMF to acetone increased the yield but lowered the geometrical selectivity drastically (entries 7 and 8). Switching to a bromide source fully soluble in acetone, lithium bromide, gave high yields as well as high selectivities (entry 9); further, only 1.5 equivalents of the salt were necessary (entry 10). Entries 1, 11, and 12 show the vital nature of the co-catalyst for high yields as well as higher selectivities, an effect that has been observed previously.[6]

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