Solvoluminescence of Cerium(III) Thiocyanate Complex

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Dedication ((optional))

Abstract: A cerium(III) thiocyanate complex shows bright blue emission at *ca.* 450 nm in acetonitrile whose quantum yield reaches more than 40% at 298 K. Non-coordinating solvents such as acetonitrile give blue emission whereas oxygen-coordinating and nitrogen-coordinating solvents afford near UV and green emissions, respectively.

Cerium is a lanthanide element and an earth-abundant metal whose reserve is more than that of copper in the earth's crust.[1] Among the lanthanide elements, Ce(III) ion shows unique emission properties based on the electric-dipole-allowed 4f–5d and the spin-allowed doublet–doublet transitions. In contrast to the fact that the well-known Eu(III) and Tb(III) ions show their specific emission colours based on the parity-forbidden 4f–4f transitions,[2] the emission colour of Ce(III) ion is tunable from UV to red by changing the host material in inorganic crystals because the 5d orbital, which is sensitive to the surrounding environment, relates to the emission from the Ce(III) ion;[3] *e.g.* Ce(III) ion doped in $Y_3Al_5O_{12}$ shows yellow emission at 536 nm while Ce(III) ion doped in Li_2SrSiO_4 shows blue emission at 442 nm.[3c] A large variety of emission colours have been achieved, whereas the mechanism by which the host material affects the 4f–5d transition is not yet fully understood.[3a]

The molecular Ce(III) complexes, which can dissolve in organic solvents and sublime, have great potential in applications as the emitter in organic light-emitting diodes (OLED)[4,5] and the photosensitizer in homogeneous photoredox catalysis[6,7] due to the characteristic emission features of the Ce(III) ion. However, in contrast to the large number of reports for Ce(III)-doped solid-state phosphors, there are a limited number of reports for the luminescent molecular Ce(III) complexes.[4-18] Su and co-workers reported that the Ce(III) complexes encapsulated with two polybenzimidazole tripodal ligands show bright sky-blue emissions in ethanol at 298 K, and the Ce(III) complex is air-stable.[5] Schelter and co-workers reported that the Ce(III) complexes containing the disilazane and/or guanidine ligands show intense emissions with various colours from blue to yellow in toluene, while the Ce(III) complexes were handled under an inert atmosphere (N_2).[6,7,18] They further demonstrated that the emission quantum yield of tris(guanidinate) complexes correlates with the steric demand of the ligand backbone substituents in C_3 symmetry.[18]

A thiocyanate ion (SCN^-) coordinates a metal ion by either nitrogen or sulfur atoms, which depends on the hardness of the metal ion. The crystal structure of heptakis(thiocyanate)-coordinated Ce(III) complex, $[Ce(SCN)_7(H_2O)]^{4-}$, was elucidated to show the ligation of SCN^- through the nitrogen atom, reflecting the hard acidity of the Ce(III) ion.[19] The luminescence of the Ce(III) ion in a KSCN crystal was reported as solid-state material to show blue emission whose maximum intensity was observed on use of *ca.* 50 equiv of KSCN against Ce(III) ion.[20] In this report, we found that addition of $^nBu_4NSCN$ to an acetonitrile solution containing $Ce(OTf)_3$ formed a stable $Ce(SCN)_3(CH_3CN)_{x-m}$ complex that showed a bright blue emission at room temperature, whose emission quantum yield reached more than 40%. In addition, we found that coordinating solvents significantly changed the emission peak of the cerium(III) thiocyanate complex, whereas non-coordinating solvents hardly affected the emission.

An acetonitrile solution containing only $Ce(OTf)_3$ hardly showed visible-light emission on excitation at 365 nm using a UV lamp (Handy UV Lamp, AS ONE, SLUV-6). Herein, in acetonitrile, $Ce(OTf)_3$ is expected to have a solvate form represented as $[Ce(CH_3CN)_x](OTf)_3$.[21] When thiocyanate ion (KSCN) was added to the solution, a strong blue emission was observed. To confirm the emitting species, we carried out titration experiments using $^nBu_4NSCN$, which is readily soluble in acetonitrile. Figure 1a shows the UV–vis absorption spectral change, in which the addition of SCN^- causes the appearance of a new absorption band at 340 nm. The absorbance at 340 nm significantly increases during the addition of 1 to *ca.* 3 equiv of SCN^- and continues to increase slightly by adding more than *ca.* 3 equiv of SCN^-. On the addition of *ca.* 5 equiv of SCN^- the absorption coefficient of the new peak at 340 nm becomes *ca.* 800 M^{-1} cm^{-1}, which is the same order ($\varepsilon \approx 10^2$ M^{-1} cm^{-1}) as
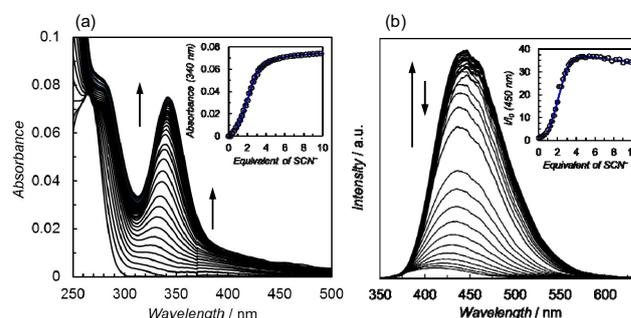
Figure 1. (a) UV-vis absorption spectral change by the addition of $^nBu_4NSCN$ to $Ce(OTf)_3$ (8.5×10^{-5} M) in acetonitrile at 298 K. The inset shows a titration plot of the absorbance change at 340 nm and the theoretical curve (solid line). (b) Appearance of the emission (λ_{ex} = 330 nm) by the addition of $^nBu_4NSCN$ to $Ce(OTf)_3$ (8.5×10^{-5} M) in acetonitrile at 298 K. The inset shows a titration plot of the emission intensity ratio against the initial intensity (I_0) at 450 nm before the addition of $^nBu_4NSCN$ and the theoretical curve (solid line). Theoretical curves for both the UV-vis absorption and emission spectra were drawn using $K_1 = 3.0\times10^6$ M^{-1}, $K_2 = 3.5\times10^5$ M^{-1}, $K_3 = 5.0\times10^4$ M^{-1}, $K_4 = 4.0\times10^2$ M^{-1}.

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those of the absorption bands corresponding to the 4f → 5d transition in the previous reports.[5,6,18] Figure 1b shows the emission spectral change excited at 330 nm. The emission at *ca.* 450 nm dramatically increases during the addition of 1 to *ca.* 5 equiv of SCN− and starts to decrease slightly after the addition of *ca.* 5 equiv of SCN−. Herein, the titration of *n*Bu$_4$NSCN to a La(OTf)$_3$ solution instead of Ce(OTf)$_3$ caused no visible-light emission, indicating that the emission is a characteristic behaviour of the Ce(III) ion. In addition, the formation of the cerium(III) thiocyanate complex was confirmed with IR and ^{13}C NMR spectra (Figure S1 and S2 in the Supporting Information).[22, 23]

The association constants of SCN− to Ce(III) ion, which are estimated from both the UV–vis absorption and emission spectra, decrease by one order of magnitude when each coordination of SCN− proceeds up to 3 equiv. The association constant (K_4) of SCN− to the electrically neutral Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$ is two orders of magnitude smaller than the value of K_3. The stability constant for the Ce(III) complex with three SCN− ($\beta_{13} = K_1 \cdot K_2 \cdot K_3$) is determined to be 5.3×10^{16} M^{-3} and the electrically neutral Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$ complex is very stable even in polar acetonitrile. Figure 2 shows the distribution of Ce(III) species based on the association constants. The distribution of Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$ reaches the highest point when *ca.* 5 equiv of SCN− is added. The emission intensity also reaches the maximum at *ca.* 5 equiv of SCN− in Figure 1b (inset), which is well correlated to the distribution of Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$. These results suggest that the bright blue emission mainly comes from the electrically neutral Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$ complex. Judging from the fitting analysis for the emission, [Ce(SCN)(CH$_3$CN)$_{x−j}$]$^{2+}$ hardly show emission by exciting at 330 nm whereas [Ce(SCN)$_2$(CH$_3$CN)$_{x−k}$]$^+$ and [Ce(SCN)$_4$(CH$_3$CN)$_{x−n}$]$^−$ also show the emissions at *ca.* 450 nm whose intensities are respectively 38% and <10% of that of Ce(SCN)$_3$ (See Experimental Section in the Supporting Information). The emission quantum yield of the solution containing *ca.* 5 equiv of SCN−, in which *ca.* 84% of the total amount of Ce(III) ion forms Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$, was calculated with reference to 9,10-diphenylanthracene in cyclohexane (Φ_f = 97%) to be 40% at 298 K. The acetonitrile solution retains the ability to emit for at least several days at
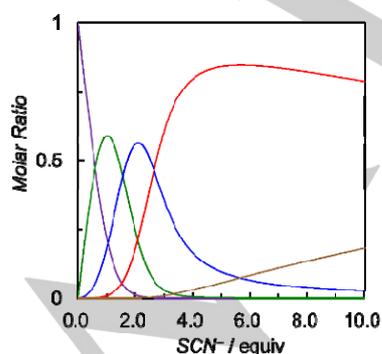
Figure 2. Distribution of Ce(III) species by addition of SCN− in acetonitrile by using K_1 = 3.0×10^6 M^{-1}, K_2 = 3.5×10^5 M^{-1}, K_3 = 5.0×10^4 M^{-1}, K_4 = 4.0×10^2 M^{-1}, and [Ce^{3+}]$_{total}$ = 8.5×10^{-5} M: [Ce(CH$_3$CN)$_x$]$^{3+}$ (purple), [Ce(SCN)(CH$_3$CN)$_{x−j}$]$^{2+}$ (green), [Ce(SCN)$_2$(CH$_3$CN)$_{x−k}$]$^+$ (blue), Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$ (red), [Ce(SCN)$_4$(CH$_3$CN)$_{x−n}$]$^−$ (brown).
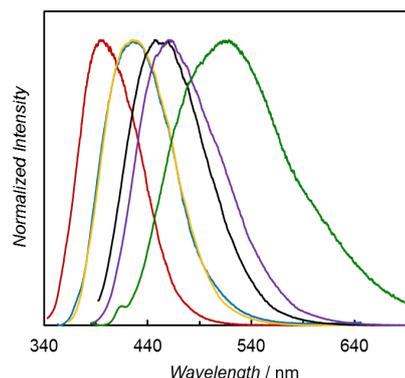
Figure 3. Emission spectra of the Ce(III) complex, composed of Ce(OTf)$_3$ and *n*Bu$_4$NSCN (1:3 molar ratio), in the representative solvents; methanol (red, λ_{ex} = 267 nm), chloroform (cyan, λ_{ex} = 333 nm), tetrahydrofuran (yellow, λ_{ex} = 343 nm), acetonitrile (black, λ_{ex} = 365 nm), toluene (purple, λ_{ex} = 365 nm), and pyridine (green, λ_{ex} = 365 nm).

room temperature in air, indicating that the cerium(III) thiocyanate complex is stable under ambient conditions. It is considered that the bright blue emission comes from the 4f–5d transitions of Ce(III) ion because the emission band can be fitted with two Gaussian peaks whose peak difference is 1600 cm^{-1}, which is close to the characteristic splitting of the two Ce(III) 4f levels ($^2F_{5/2}$ and $^2F_{7/2}$) caused by spin–orbit interaction (Figure S3 in the Supporting Information).[5,7]

Time-resolved emission decays of the acetonitrile solutions containing Ce(OTf)$_3$ and *n*Bu$_4$NSCN (1:3 and 1:9 molar ratios) were collected at 450 nm upon excitation of 346 nm (Figure S4 in the Supporting Information). The time profiles featured two decay components with 9 ns (12%) and 30 ns (88%) for 1:3 molar ratio and 15 ns (23%) and 29 ns (77%) for 1:9 molar ratio, respectively. These lifetimes are comparable with the reported time ranges of luminescent Ce(III) complexes.[5-7] By comparing between the amplitudes of the components and the molar fractions of the excited species which are calculated from Figure 2 and the absorption coefficients of each Ce(III) complex (See the Supporting Information), the lifetime components of 9 ns, 29-30 ns and 15 ns could be assignable to [Ce(SCN)$_2$(CH$_3$CN)$_{x−k}$]$^+$, Ce(SCN)$_3$(CH$_3$CN)$_{x−m}$, and [Ce(SCN)$_4$(CH$_3$CN)$_{x−n}$]$^−$, respectively.

The emission spectra of a mixture of Ce(OTf)$_3$ and *n*Bu$_4$NSCN (1:3 molar ratio) were measured in several solvents at 298 K and it was found that some solvents changed the emission from blue to near UV or green (Figure 3 and Table S1 in the Supporting Information). Herein, no visible emission was observed when either Ce(OTf)$_3$ or *n*Bu$_4$NSCN was absent (Figure S5 in the Supporting Information).[24] The excitation spectra were correlated with the emission spectra (Figure S7 in the Supporting Information). To determine the nature of the solvoluminescence, the emission peaks in the solvents were plotted against several solvent parameters, such as empirical solvent scales (donor number, π^* and $E_{T(30)}$), dielectric constant (ε) and dipolar–dipolar interaction function (($\varepsilon - 1)/(\varepsilon + 1) - (n^2 - 1)/(n^2 + 1$)) (Figures 4, S8 and S9 in the Supporting Information).[25,26]
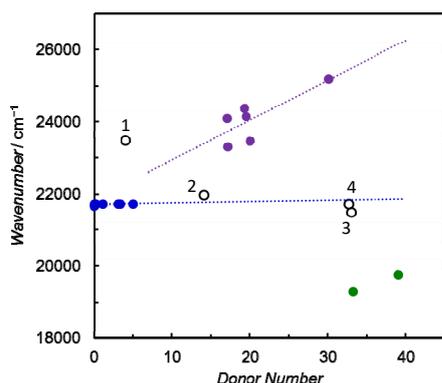
Figure 4. Plots of the emission peak against donor number in several solvents; non-coordinating solvents (blue), oxygen-coordinating solvents (purple), nitrogen-coordinating solvents (green), chloroform (1), acetonitrile (2), 2,6-dimethylpyridine (3), 2,4,6-trimethylpyridine (4).

Figure 4 shows plots of the emission peak position against donor number, in which at least three different groups can be distinguished: non-coordinating (blue circle), oxygen-coordinating (purple circle) and nitrogen-coordinating solvents (green circle). Solvents having neither oxygen nor nitrogen atoms, such as toluene and dichloromethane, are difficult to coordinate to Ce(III) ion and could be classified as non-coordinating solvents. As shown in Figures 4, S8 and S9 (blue circle), the emission peak position is independent of the solvent parameters, indicating that the non-coordinating solvent does not affect the emission of the cerium(III) thiocyanate complex. A deviation from the series of the non-coordinating solvents is observed for chloroform (Figure 4 (No. 1)). Because the chloroform used contains 0.3–1% ethanol as a stabilizer, the deviation would be explained by the coordination of ethanol to the Ce(III) ion. As a matter of fact, the addition of 1 vol% alcohol (methanol, 0.2 M) caused *ca.* 20–30 nm blue shift of the emission spectrum of the cerium(III) thiocyanate complex in toluene. The peak position in acetonitrile is similar to those in the non-coordinating solvents. Thus, it is considered that acetonitrile very weakly coordinates to the cerium(III) thiocyanate complex (Figure 4 (No. 2)).

It is well known that solvents having an oxygen atom, such as methanol and tetrahydrofuran, tend to coordinate strongly to lanthanide(III) ions. Oxygen-coordinating solvents change the emission into near-UV emission, in which the emission peak position is strongly shifted to shorter wavelength (larger wavenumber) by increasing the donor number of the solvent. On the other hand, the nitrogen-coordinating solvents, pyridine and 3-methylpyridine, shift the emission peak position to longer wavelength (smaller wavenumber) than those in non-coordinating solvents, giving green emission. The wavenumbers in 2,4,6-trimethylpyridine and 2,6-dimethylpyridine are similar to those in non-coordinating solvents (Figure 4 (No. 3 and 4)), indicating that steric hindrance of the methyl groups at the 2- and 6-positions of the pyridine suppresses coordination of the pyridine derivatives to the Ce(III) ion.

In summary, the titration experiments on the UV–vis absorption and emission demonstrated that the electrically

neutral cerium(III) thiocyanate complex, $Ce(SCN)_3(CH_3CN)_{x-m}$, exhibits bright blue emission in acetonitrile. The luminescent cerium(III) thiocyanate complex is stable at room temperature in air, allowing us to store and handle the complex under ambient conditions without special precautions. The emission is strongly affected by the coordinating solvents, giving various emission colours from near UV to green. In addition, the emission is sensitively affected by the trace amount of alcohol in chloroform, suggesting that the complex may be applied to a chemosensor for oxygen-containing materials. It is expected that the molecular Ce(III) phosphor consisting of the simple thiocyanate ligand would be a promising emitter for a wide range of applications, including OLED and photocatalysis.

Conflicts of interest

There are no conflicts to declare.

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[22] The IR spectrum of a mixture of $Ce(OTf)_3$ and $^nBu_4NSCN$ (1:3 molar ratio, 2.0×10^{-3} M of the Ce(III) ion) in acetonitrile shows a strong broad peak at 2050 cm^{-1}, which is assigned as the C=N stretching signals of the thiocyanate ligands on the Ce(III) ion. In Figure S1a, all the peaks except for thiocyanate and free water are almost completely overlapped with the sum of each spectrum of $Ce(OTf)_3$ and $^nBu_4NSCN$. Neither decrease of the thiocyanate signals (Figure S2b) nor appearance of new peaks by mixing $Ce(OTf)_3$ and $^nBu_4NSCN$ is observed, suggesting that decomposition of the cerium(III) thiocyanate complex giving a luminescent byproduct does not occur.

[23] In the ^{13}C NMR spectra, the thiocyanate carbon in a mixture of $La(OTf)_3$ and $^nBu_4NSCN$ (1:3 molar ratio, 7.0×10^{-2} M of the La(III) ion) appears at 135 ppm (Figure S2b), which is shifted by 5 ppm to lower field compared to 130 ppm for only $^nBu_4NSCN$ (Figure S2a). On the other hand, the thiocyanate carbon in a mixture of $Ce(OTf)_3$ and $^nBu_4NSCN$ (1:3 molar ratio, 7.0×10^{-2} M of the Ce(III) ion) appears at 173 ppm (Figure S2c), which is broader and significantly shifted to lower field (full width at half maximum (FWHM) = 13 Hz) compared to those of the La(III) complex and $^nBu_4NSCN$. It is thought that the broadening and large shift are caused by the paramagnetic Ce(III) ion. The thiocyanate carbon shows a single peak at 144 ppm even on using an excess amount of $^nBu_4NSCN$ (Figure S2d), indicating that exchange of the thiocyanate ligands is taking place rapidly on the NMR time scale in CD_3CN.

[24] The ^{13}C NMR of a mixture of $Ce(OTf)_3$ and $^nBu_4NSCN$ (1:3 molar ratio, 7.0×10^{-2} M of the Ce(III) ion) in [D_5]pyridine shows a peak at 163 ppm assigned as the thiocyanate carbon (Figure S6a), indicating that the thiocyanate coordinates to the Ce(III) ion in pyridine. The concentrated NMR sample shows green emission having a same spectral shape with that of a relatively dilute solution at 5.6×10^{-5} M (Figure S6b). The concentration independence implies that the green emission originated from the Ce(III) ion coordinated with three thiocyanates and several pyridines.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

A cerium(III) thiocyanate complex shows bright blue emission at ca. 450 nm in acetonitrile whose quantum yield reaches more than 40% at 298 K. The emission of the cerium(III) thiocyanate complex is affected by coordinating solvents, appearing at from the near UV region to the green colour region.
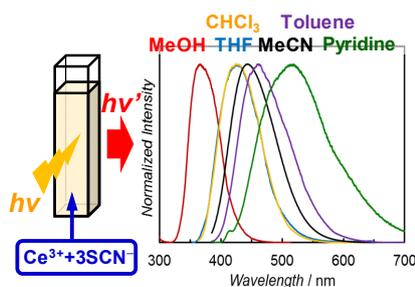
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