First Observation of Photosensitized Luminescence of Nd^{3+} in Organic Solution

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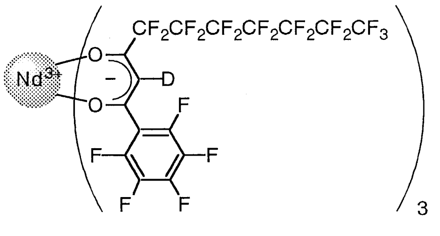
Photosensitized luminescence of Nd^{3+} in solution was successfully observed for the first time by coordinating the metal cation with deuterated 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-1-pentafluorophenyl-1,3-decanedione as a ligand with a low vibrational chromophore.

Nd^{3+}-containing systems have been regarded as the most popular luminescent materials for application of the laser systems, and then we have aimed at developing luminescent materials consisting of Nd^{3+} complexes in liquid organic media. In general, effective luminescence of Nd^{3+} was regarded almost impossible in organic solvent, because the emitting level of Nd^{3+} is susceptible to the radiationless transition via vibrational excitation of liquid matrix molecules, and the excitation migration induced by collision between Nd^{3+} is unavoidable in liquid matrix. Radiationless energy transfer via vibrational excitation was suppressed and energy transfer through cross relaxation and excitation migration at diffusion collision in liquid systems was prevented when Nd^{3+} was coordinated in deuterated solvents with deuterated hexafluoroacetylacetone as a low vibrational ligand,[1,2] or deuterated diperfluorooctanoyl-methane as a bulky β-diketone ligand,[3] leading to the successful observations of luminescence of the Nd^{3+} complex in liquid system. On the other hand, the absorption of Nd^{3+} due to electronic transition in its *f*-orbitals is very week because the electronic transition in the *f*-orbitals is forbidden by the selection rule. The very low absorptivity of Nd^{3+} also contributes to weak luminescence from the emitting level of Nd^{3+} (the $^4F_{3/2}$ state). In order to increase population of the excited state, we have now successfully designed a new β-diketone with a chromophore. This paper concerns photosensitization to achieve drastic enhancement of the Nd^{3+} luminescence.



Scheme 1.

We have synthesized a new β-diketone, 4,4,5,5,6,6,7,7,8,8,-9,9,10,10,10-pentadecafluoro-1-pentafluorophenyl-1,3-decanedione (H(PDD-H)) as a ligand containing a chromophore in their structure and successfully observed the photosensitized luminescence of Nd^{3+} by deuteration of the Nd^{3+} complex with H(PDD-H) (Scheme 1). The deuterated ligand molecule possesses low vibrational C–F and C–D bonds and a pentafluorophenyl group as a chromophore. It is known that when fluorinated aromatic rings are excited, the singlet excited state undergoes intersystem crossing to give the triplet state.[4] Therefore, the chromophore is considered to play a role as a photosensitizer via energy transfer based on the resonance between the lowest triplet levels and the excited levels of Nd^{3+}.[5]

The ligand H(PDD-H) was synthesized according to the reported method.[6] The Nd^{3+} complex, $Nd(PDD\text{-}H)_3$, was synthesized by reacting H(PDD-H) with neodymium nitrate hexahydrate and a catalytic amount of aqueous ammonia solution in a mixture of ether and water, and purified by recrystallization from a solution of ether and hexane.[7] The deuterated complex, $Nd(PDD\text{-}D)_3$, was obtained by treatment with excess methanol-d_4 under vacuum (0.1 Pa). Acetone-d_6 and methanol-d_4 solution of this complex were manipulated under vacuum (0.1 Pa) and subjected to optical measurements. Optical path length of the cell for absorption and emission measurements was 10 mm.

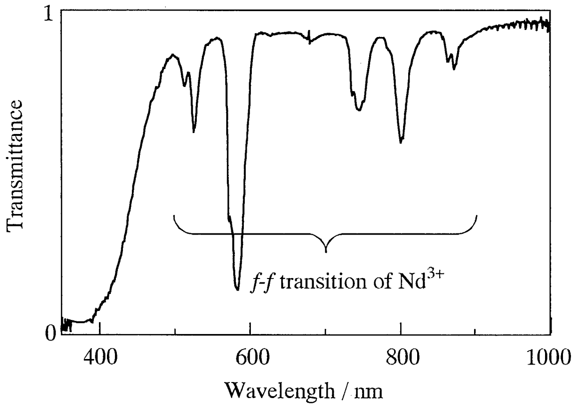


Figure 1. Transmittance spectrum of 0.05 mol dm^{-3} $Nd(PDD\text{-}D)_3$ in acetone-d_6.

Figure 1 shows the absorption spectrum of the complex. The absorption bands, λ=490-550, 550-640, 650-700, 715-775, 775-845 and 845-925 nm, were assigned to the Nd^{3+} transitions of $^4I_{9/2}$ (ground state) $\rightarrow$ $^4G_{7/2}$ + $^4G_{9/2}$ + $^2K_{13/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2}$ + $^2G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{9/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$ + $^4S_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$ + $^2H_{9/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$, respectively. The broad band observed below 480 nm was ascribed to absorption of the ligand.

Figure 2 displays photoluminescence observed for a solution of the complex in methanol-d_4 (1×10^{-3} mol dm^{-3}). When the complex was excited at λ=585 nm which corresponds to the *f-f*

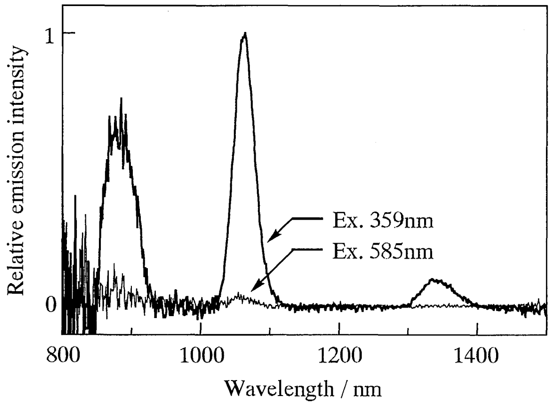


Figure 2. Emission spectra of 1x10^{-3} mol dm^{-3} Nd(PDD-D)$_3$ in methanol-d_4.

transition of Nd^{3+}, $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$, it showed extremely weak luminescence consisting of 3 bands at λ=880, 1060 and 1320 nm, which were assigned to the transitions of $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively. On the other hand, when it was irradiated by light of λ=359 nm at which the chromophore in the ligands is excited, very strong emission was observed in the same shape as above. Since Nd^{3+} has no absorption at this wavelength, this luminescence should be undoubtedly attributed to the photosensitization of Nd^{3+} by the chromophore, pentafluorophenyl group. This is the first observation of the photosensitized luminescence of Nd^{3+} in solution. It has been demonstrated that photosensitization of Nd^{3+} is a promising strategy to obtain strong emission of Nd^{3+} in solution overcoming its low absorptivity.

Energetic and coordination structure of the complex are under investigation at present.

References and Notes

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6 J. F. Engel and C. C. Chappelow, *J. Chem. Eng. Data.*, **16**, 381 (1971). ^{1}H NMR (acetone-d_6) δ 6.66 (s, C–H) and 13.78 (O–H); ^{19}F NMR (acetone-d_6, int. hexafluorobenzene δ–162.2) δ–160 (s, 2F, m-F), –148 (s, 1F, p-F), –138 (d, 2F, o-F), –124—119 (m, 12F, CF_2) and –79 (s, 3F, CF_3).

7 Blue solid. ^{1}H NMR (acetone-d_6) δ 6.00 (s, C–H) and 11.46 (O–H); ^{19}F NMR (acetone-d_6, int. hexafluorobenzene δ–162.2) δ–161 (d, 2F, m-F), –153 (d, 1F, p-F), –140 (d, 2F, o-F), –124—114 (m, 12F, CF_2) and –79.4 (d, 3F, CF_3); IR (KBr) : 3410 (O–H), 1623 (C=O), 1513 (C–H) 1243, 1211 (C–F) and 1148 (C–O).