Intramolecular Excited Energy Transfer from Phenanthroline Fluorophore to Pr(III) in a Metal Complex

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From the measurement of the picosecond time-resolved luminescence spectra of a Pr(III) complex with phenanthroline in the solid state, an intramolecular energy-transfer mechanism from the ligand to the center metal has been discussed. The rate constant of the energy transfer can be estimated as $3.3 \times 10^9\ s^{-1}$, and it is necessary the excited triplet state of the ligand and a singlet of the metal ion to pass the energy transfer.

Many sorts of lanthanoide (Ln) compounds have been synthesized recently for the application to functional materials. In cases of the metal complex with Ln(III), the Eu(III)–ligand complex is known to be very useful from the viewpoint of the high luminescence quantum yields or the visible luminescence of Eu(III) (ca. 620 nm assigned to the $^5D_0 \rightarrow {}^2F_2$ transition). In order to obtain highly effective and brighter f–f emission from Ln(III), it is important to design the active organic ligand in the complex.[1] It is known that Pr(III) has no strong luminescence in the visible region, although it has many split f levels, e.g. ^3P_J, $^1I_6$, $^1D_2$, etc.[2] To specify the f level of Pr(III) from which the emission occurs, it is important to clarify the mechanism of the excitation energy transfer and the energy flow path from the ligand to the center metal ion. It is known that phenanthroline (phen) is an effective fluorophore in a stable metal–ligand complex. In this paper, the intramolecular energy transfer between the ligand and Pr(III) in a coordination complex, i.e., the mechanism of the excitation intramolecular energy transfer of Pr(III) complexes is discussed on the basis of the picosecond time-resolved luminescence spectra.

Pr(III) complex with phen (referred to as $[Pr(phen)(DMF)_2(NO_3)_3]$) was prepared by stirring a mixed ethanol solution of $Pr(NO_3)_3 \cdot 6H_2O$ and phen for 24 h, and recrystallized from DMF solution. The crystal data of this complex was deposited on the Cambridge Crystallographic Data Centre as $[Pr(phen)(DMF)_2(NO_3)_3]$ (CCDC-236438). Electronic absorption and luminescence spectra were measured by Shimadzu UV3101 and Hitachi F3010, respectively. The time-resolved spectra were measured by using a single-photon timing apparatus with an instrumental response function of 30-ps FWHM,[3] and the excitation laser of 10-ps pulsewidth at 280 nm (Coherent, Mira 900 and Innova 300).

Luminescence and electronic absorption spectra of $[Pr(phen)(DMF)_2(NO_3)_3]$ in the solid state are shown in Figure 1 with the band assignment. This complex shows the π–π^* absorption band around 285 nm (35,000 cm^{-1}), and the f–f transitions in the wavelength region of 400–1000 nm (25,000–10,000 cm^{-1}). As described later, the electronic band existence of the $^1I_6$ state of Pr(III) is important. To evaluate the band position of the $^1I_6$ transition, the absorption bands around 23,000–20,000 cm^{-1} were analyzed into components

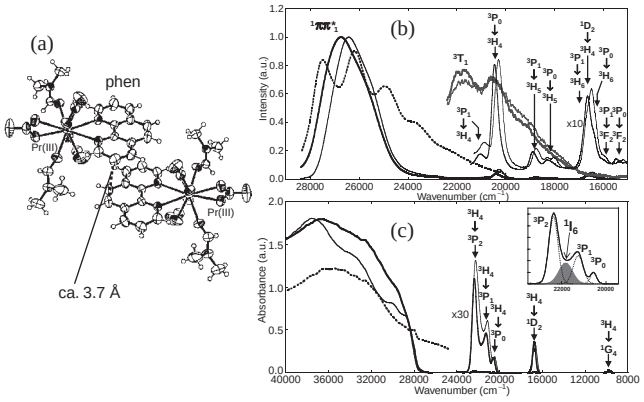

Figure 1. ORTEP drawing of a dimer of $[Pr(phen)(DMF)_2(NO_3)_3]$ (a), and luminescence (b) and electronic absorption (c) spectra of $[Pr(phen)(DMF)_2(NO_3)_3]$, $[Pr(phen)_2(NO_3)_3]$, and phen in the solid state at 300 K (phosphorescence spectra obtained at 77 K). The bold, thin, and dotted line show spectra of $[Pr(phen)(DMF)_2(NO_3)_3]$, $[Pr(phen)_2(NO_3)_3]$, and phen, respectively in (b) and (c). Inset in (c) shows Gaussian profile of the electronic absorption bands of $[Pr(phen)(DMF)_2(NO_3)_3]$.

by using the Gaussian profile (Inset in Figure 1c). The result demonstrated a new band with a peak at 458.6 nm (21,805 cm^{-1}) which was assigned as the $^1I_6$ transition. A fluorescence band of $[Pr(phen)(DMF)_2(NO_3)_3]$ appears around 370 nm (27,000 cm^{-1}) due to the π–π^*_1 transition of phen, and at 77 K a phosphorescence band appears around 456 nm (21,900 cm^{-1}) due to the $T_1 \rightarrow S_0$ transition of the ligand. In the case of another Pr(III) complex with two phen ligand $[Pr(phen)_2(NO_3)_3]$,[4] each f–f band position differs clearly from that in $[Pr(phen)(DMF)_2(NO_3)_3]$, suggesting that the ligand field efforts to the internal transition metal ion, Pr(III). The π–π^*_1 fluorescence of $[Pr(phen)(DMF)_2(NO_3)_3]$ is broader than that of $[Pr(phen)_2(NO_3)_3]$, meaning that the phen moiety of $[Pr(phen)(DMF)_2(NO_3)_3]$ may interact to another molecule strongly in the solid state, and show an excimer-like luminescence. The single crystal X-ray analysis data of $[Pr(phen)(DMF)_2(NO_3)_3]$ also suggests that two neighboring phen moieties interact each other in the van der Waals distance (Figure 1a). In the wavelength region longer than the π–π^*_1 transition, $[Pr(phen)(DMF)_2(NO_3)_3]$ shows f–f luminescence bands of Pr(III) at 475.2 (21,044), 489.1 (20,444), 529.4 (18,889), 546.8 (18,289), 593 (16,863), 601.1 (16,637), 615 (16,264), 623 (16,053), and 647.1 nm (15,454 cm^{-1}), which can be assigned to the $^3P_1 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_5$, $^3P_1 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$, $^3P_1 \rightarrow {}^3F_2$, and $^3P_0 \rightarrow {}^3F_2$ transitions, respectively. It is important to note that the peak position of the $T_1 \rightarrow S_0$ band locates close to that of the $^1I_6$ band.

Figure 2 shows picosecond time-resolved luminescence spectra of $[Pr(phen)(DMF)_2(NO_3)_3]$ in the solid state at 77 K,

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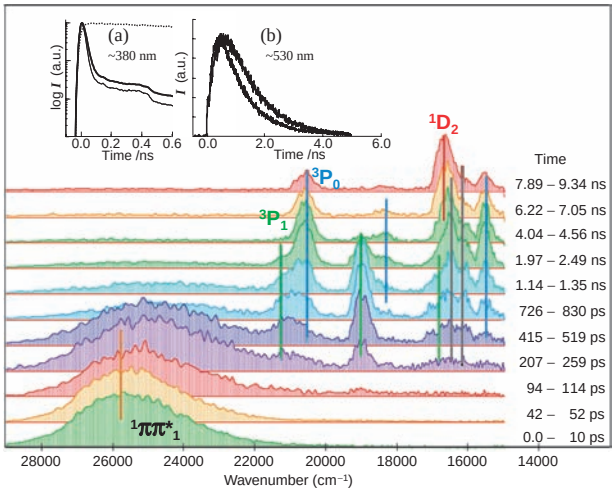

Figure 2. Picosecond time-resolved luminescence spectra of [Pr(phen)-$(DMF)_2(NO_3)_3$] at 77 K in the solid state, and decay curves of the π–$\pi^*{}_1$ (a) and the $^3P_1 \rightarrow {}^3H_4$ (b) luminescence band (inset: the bold, thin, and dotted line shows the curve of [Pr(phen)$(DMF)_2(NO_3)_3$], [Pr$(phen)_2$-$(NO_3)_3$], and phen, respectively). The offset at 0.4 ns in (a) is due to the apparatus.

and the decay curves measured at two emissive band positions, π–π^* and $^3P_1 \rightarrow {}^3H_4$. The spectral changes exhibit directly the energy-transfer pathways from phen to Pr(III). Following laser pulse excitation, first, the π–π^* fluorescence of the ligand appears at 26,000 cm^{-1}, and then decreases with time. After 100 ps, the spectrum becomes broader suggesting that the excimer band at 24,000 cm^{-1} will be grown. After 200 ps, several sharp bands appear in a longer-wavelength region, for instance, the bands assigned as $^3P_1 \rightarrow {}^3H_J$ appear. The $^3P_1 \rightarrow {}^3H_J$ bands show a series of rise and decay in a time range 180–3000 ps. Consequently the next series of the $^3P_0 \rightarrow {}^3H_J$ bands appear in a time range of 400–7000 ps, and finally the $^1D_2 \rightarrow {}^3H_4$ band is dominated after 5 ns. The decay curves of the $^1\pi$–$\pi^*{}_1$ emission of both Pr(III) complexes show much faster lifetime than that of the ligand itself (Figure 2a). The lifetime values are almost the same in the two cases. It can be seen in Figure 2b that there exists a rise component in the time profile of the $^3P_1 \rightarrow {}^3H_4$ luminescence, but that the rise time does not match the decay time of the $^1\pi$–$\pi^*{}_1$ emission. It indicates that other states do exist between the $\pi\pi^*$ and the $^3P_1$ level.

To clarify the mechanism of the excitation energy transfer from the ligand to Pr(III) quantitatively, their spin states and the spin-selective rule[5] should be taken into account for a donor–acceptor system composed of organic chromophores. In the present case, there are two possibilities for the spin state of the ligand (energy donor), the singlet or the triplet state. When the donor state is the singlet state (S_1), the energy-transfer path to the $^3H_4$ level of the split f levels on Pr(III) can be used for both energy-transfer mechanisms, the Dexter type and the Förster type.[6] Note that the spectral data show no overlap between the S_1 fluorescence band of phen and the absorption of Pr(III). Then it follows that it is difficult to assume the S_1 state to act as donor through the Förster mechanism. From the spin-selection rule, the energy acceptor state of the f orbital will exist as a singlet state, which contributes to the $^1I_6$ level. The $^1I_6$ radiation shows the rise of 300 ps and the decay of 1 ns, and the next $^3P_1$ state mostly conjugates with the $^1I_6$. According to the above theories, we can

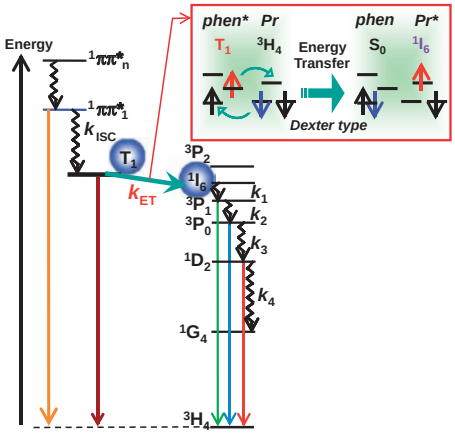

Figure 3. Grammatical representation of the excitation energy flow pathway of [Pr(phen)$(DMF)_2(NO_3)_3$] with the rate constants. Color of the arrow showing emissions corresponds to that of the band assignment in Figure 2.

explain quantitatively the excitation energy transfer on the basis of the energy-flow pathway in the Pr(III) complex as shown in Figure 3: The excitation energy on the $\pi\pi^*$ levels relax to the lowest $^1\pi\pi^*$, and trace two energy flow pathways as the π–π^* fluorescence and as the intramolecular energy transfer. The former one is originated from the ligand phen, and the latter one goes on to the $^1I_6$ state of Pr(III) via a triplet ligand state T_1, and the ff emissions and the nonradiative relaxations are derived sequentially. The rate constants of respective relaxation processes in [Pr(phen)$(DMF)_2(NO_3)_3$] have been estimated as $k_{ET} = 3.3 \times 10^9\ s^{-1}$, $k_1 = 33.3 \times 10^9\ s^{-1}$, $k_2 = 0.83 \times 10^9\ s^{-1}$, $k_3 = 0.33 \times 10^9\ s^{-1}$, or $k_4 = 0.022 \times 10^9\ s^{-1}$. These results show the energy transfer between the ligand to Pr(III) is much faster than that of intraatomic nonradiative relaxation between the $^3P_1$ and the $^3P_0$ state of Pr(III). The estimated value of energy transfer k_{ET} in [Pr(phen)$(DMF)_2(NO_3)_3$] is higher than those of other systems in Ln(III) complex.[1]

Additionally, our work will show the successful results to control the emissive f orbital by coordinating some derivatives of phen for Pr(III) complexes.[7]

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