Photophysical Properties of Quaternary Lanthanide Molecular Functional Complex Systems

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According to the molecular fragment principle, a series of twelve quaternary luminescent lanthanide complex molecular systems were assembled. Their compositions were determined using elemental analyses and infrared spectra: $Ln(inic)_3(L) \cdot H_2O$, where Ln = Sm, Eu, Tb, Dy; Hinic = pyridine-4-carboxylic acid; L = *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, 2-pyrrolidone. The photophysical properties of these functional molecular systems were studied using ultraviolet-visible absorption spectra, fluorescence excitation and emission, and phosphorescence spectra. It was found that the conjugated Hinic acts as the main energy donor and luminescence sensitizer for the suitable energy match and effective energy transfer to the luminescent Ln^{3+} ions. Amide molecules (L) were used only as the assistant structural ligands to influence the luminescence. Especially the luminescent property of terbium species is the strongest for the optimum energy transfer between the triplet of Hinic and Tb^{3+}. The luminescence intensities of europium and dysprosium species were weaker than those of Tb^{3+} ones and the samarium species were the least for that there exist some internal energy levels of $^6F_{11/2}$, $^6F_{9/2}, \ldots, ^6H_{11/2}$ between the first excited state $^4G_{5/2}$ and the ground state $^6H_{9/2}$ for Sm^{3+} ion, so the nonradiative energy transfer processes dissipate the energy greatly.

The photophysical properties of lanthanide coordination compounds with organic ligands have been the hot subject of much interest because these functional complex systems can be used as active centres of luminescent materials [1—3] or the structural and functional probes for chemical or biological macromolecule systems [4—6]. A variety of research works were reported on the energy transfer and luminescence of lanthanide complexes with β-diketones, aromatic carboxylic acids, and some macrocyclic compounds which have good energy match and are suitable for the luminescence of lanthanide ions [7—10]. The energy match and intramolecular energy transfer mechanism of binary and ternary lanthanide complexes with aromatic carboxylic acids and 1,10-phenanthroline have been studied in detail [11—14]. Recently, according to the molecular fragment principle, our work has focused on the assembly luminescence polybasic lanthanide molecular systems with different ligands which play different role. In the context, using conjugated carboxylic acid (pyridine-4-carboxylic acid) as the energy donor and luminescence sensitizer of lanthanide ions and amide molecules as the second or the third assistant structural ligand, a series of twelve quaternary lanthanide (Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}) complex systems were assembled. The corresponding photophysical properties were discussed.

The compositions of the complex systems were confirmed by elemental analyses, which are shown in Table 1, where Hinic = pyridine-4-carboxylic acid (isonicotinic acid), DMF = *N*,*N*-dimethylformamide, DMA = *N*,*N*-dimethylacetamide, pyro = 2-pyrrolidone.

All the IR spectra of these molecular systems show the similar features (Table 2). For $Tb(inic)_3(DMF) \cdot H_2O$ systems, the characteristic absorption bands of C═O ($\tilde{\nu}$ = 1716.6 cm^{-1}) and C—O ($\tilde{\nu}$ = 1414.4 cm^{-1}) belonging to the free ligands (Hinic) disappear, while the characteristic absorption peaks of carboxylic group $—COO^-$ appear (*i.e.* $\tilde{\nu}$ = 1424.9 cm^{-1}, 1548.1 cm^{-1}), which suggests that the oxygen atom of Hinic carboxylate group is coordinated with Ln^{3+}. The C—O stretching vibration frequency of amide group shifts from high frequency ($\tilde{\nu}$ = 1676 cm^{-1}) for free DMF to low frequency of $\tilde{\nu}$ = 1606.5 cm^{-1} for complexes, indicating that DMF participates in the coordination with Tb^{3+}. For $Tb(inic)_3(DMA) \cdot H_2O$ system, the absorption peaks of Hinic carboxylate groups show the similar feature as those of $Tb(inic)_3(DMF) \cdot H_2O$. The C—O stretching vibration frequency of amide of DMA shifts from high frequency ($\tilde{\nu}$ = 1675 cm^{-1}) for free DMA to low frequency of $\tilde{\nu}$ = 1600.0 cm^{-1} for

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Table 1. The Compositions of Quaternary Lanthanide Complex Systems

Complex systems	w_i(found)/%				w_i(calc.)/%			
	C	H	N	Ln	C	H	N	Ln
$Eu(inic)_3(DMF) \cdot H_2O$	41.39	3.18	9.01	25.16	41.73	3.50	9.19	24.94
$Tb(inic)_3(DMF) \cdot H_2O$	40.55	3.17	8.89	25.95	40.93	3.43	9.09	25.78
$Sm(inic)_3(DMF) \cdot H_2O$	41.26	3.17	9.04	24.58	41.50	3.48	9.21	24.74
$Dy(inic)_3(DMF) \cdot H_2O$	40.27	3.20	8.82	26.53	40.69	3.41	9.03	26.21
$Eu(inic)_3(DMA) \cdot H_2O$	41.99	3.41	8.85	24.09	42.38	3.72	9.03	24.38
$Tb(inic)_3(DMA) \cdot H_2O$	41.74	3.45	8.61	25.01	41.92	3.68	8.88	25.21
$Sm(inic)_3(DMA) \cdot H_2O$	42.72	3.44	8.84	24.44	42.49	3.73	9.01	24.19
$Dy(inic)_3(DMA) \cdot H_2O$	41.55	3.38	9.00	25.38	41.68	3.66	8.83	25.63
$Eu(inic)_3(pyro) \cdot H_2O$	42.70	3.22	9.15	24.32	42.52	3.41	9.01	24.46
$Tb(inic)_3(pyro) \cdot H_2O$	42.31	3.19	9.12	25.03	42.05	3.37	8.91	25.29
$Sm(inic)_3(pyro) \cdot H_2O$	42.47	3.16	8.91	24.11	42.63	3.42	9.03	24.26
$Dy(inic)_3(pyro) \cdot H_2O$	41.65	3.21	8.71	25.47	41.82	3.35	8.86	25.71

Table 2. The IR Absorption Bands of the Studied Molecular Systems

Complex systems	$\tilde{\nu}(\nu_s(COO^-))/cm^{-1}$	$\tilde{\nu}(\nu_{as}(COO^-))/cm^{-1}$	$\tilde{\nu}(\nu_s$(C—O of DMF)$)/cm^{-1}$	$\tilde{\nu}(\nu(H_2O))/cm^{-1}$
$Eu(inic)_3(DMF) \cdot H_2O$	1411.9	1548.1	1606.5	3423, 1607
$Tb(inic)_3(DMF) \cdot H_2O$	1411.9	1548.1	1606.5	3423, 1607
$Sm(inic)_3(DMF) \cdot H_2O$	1411.9	1548.1	1593.5	3423, 1613
$Dy(inic)_3(DMF) \cdot H_2O$	1424.9	1548.1	1600.0	3423, 1613
$Eu(inic)_3(DMA) \cdot H_2O$	1418.4	1554.6	1600.0	3417, 1607
$Tb(inic)_3(DMA) \cdot H_2O$	1424.9	1554.6	1600.0	3417, 1607
$Sm(inic)_3(DMA) \cdot H_2O$	1411.9	1554.6	1600.0	3417, 1607
$Dy(inic)_3(DMA) \cdot H_2O$	1424.9	1554.6	1600.0	3417, 1607
$Eu(inic)_3(pyro) \cdot H_2O$	1418.4	1554.6	1593.5	3410, 1607
$Tb(inic)_3(pyro) \cdot H_2O$	1424.9	1554.6	1600.0	3410, 1607
$Sm(inic)_3(pyro) \cdot H_2O$	1418.4	1554.6	1593.5	3410, 1607
$Dy(inic)_3(pyro) \cdot H_2O$	1418.4	1554.6	1593.5	3410, 1607

complexes, indicating that DMA is coordinated with Tb^{3+}. For $Tb(inic)_3(pyro) \cdot H_2O$ system, the absorption peaks of Hinic carboxlate groups show the similar feature as those of $Tb(inic)_3(DMF) \cdot H_2O$. The C—O stretching vibration frequency of amide of pyro shifts from high frequency ($\tilde{\nu} = 1676$ cm^{-1}) for free pyro to low frequency of $\tilde{\nu} = 1603.5$ cm^{-1} for complexes, indicating that DMF is coordinated with Ln^{3+}. Besides this, there exist some apparent bands at about $\tilde{\nu} =$ 3423 cm^{-1} and $\tilde{\nu} =$ 1613 (1607) cm^{-1}, respectively, which are attributed to be the vibration stretching band and in-plane bending band of H_2O molecules. The absorption bands corresponding to the in-plane swing vibration of coordinated H_2O molecule have not been observed in the range of $\tilde{\nu} =$ 585—605 cm^{-1}, which verifies that the water molecule has not coordinated to lanthanide ion and belongs to crystal water [15].

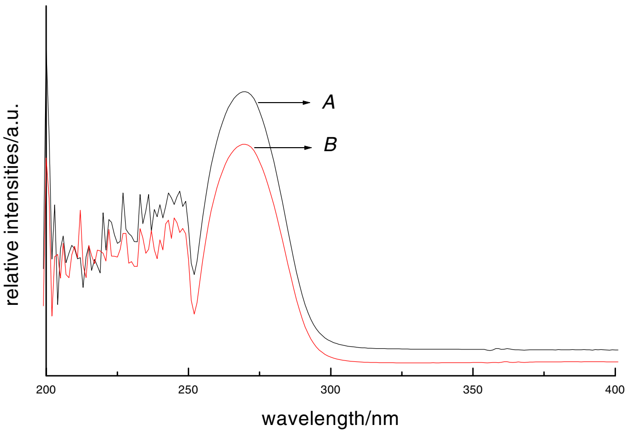

Fig. 1. Ultraviolet absorption spectrum of $Eu(inic)_3(DMF) \cdot H_2O$ (*A*) and $Tb(inic)_3(pyro) \cdot H_2O$ (*B*).

Fig. 1 shows the ultraviolet absorption spectrum for $Eu(inic)_3(DMF) \cdot H_2O$ (*A*) and $Tb(inic)_3(pyro) \cdot H_2O$ (*B*), respectively. The two absorption spectra are both similar at about 270 nm except for a little distinction of absorbance for different complex systems, which is attributed to the characteristic absorption of Hinic ligand. The results indicate that Hinic is the main energy donor and luminescence sensitizer of Eu^{3+} (or Tb^{3+}) ion. Other ultraviolet absorption spectra show the similar feature.

The excitation spectra of these complex systems show that they have no effective absorption in long-wavelength ultraviolet region of 300—400 nm. Fig. 2 gives the excitation spectrum of $Eu(inic)_3(DMF) \cdot$

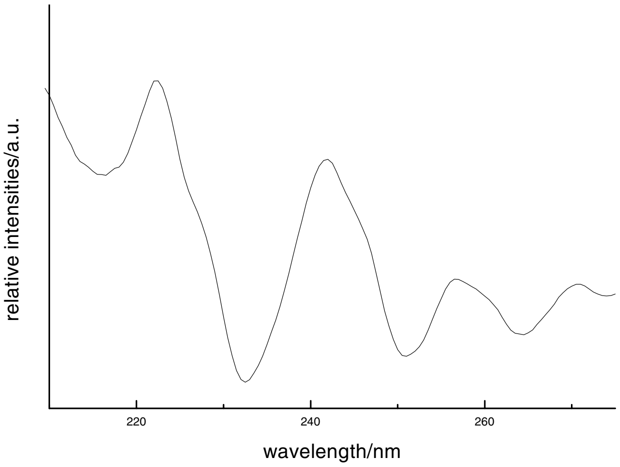

Fig. 2. Excitation spectrum of the Eu(inic)$_3$(DMF) · H_2O complex (λ_{ex} = 545 nm).

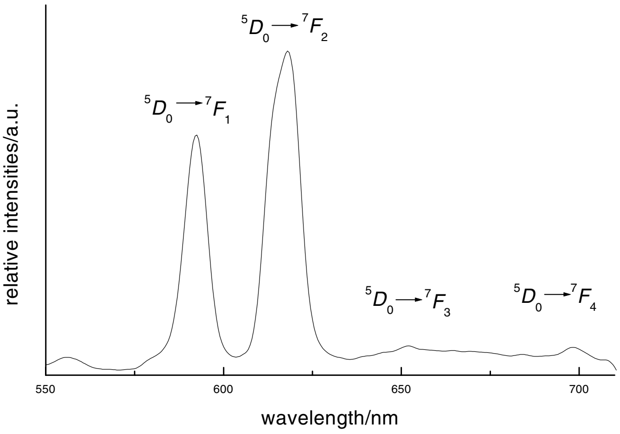

Fig. 3. Emission spectrum of the Eu(inic)$_3$(pyro) · H_2O complex (λ_{ex} = 241 nm).

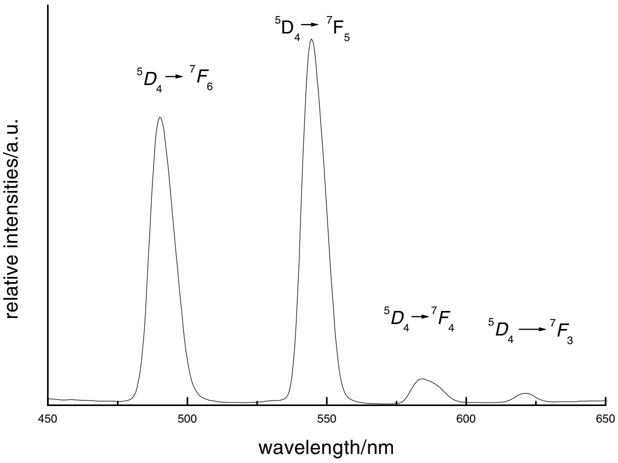

Fig. 4. Emission spectrum of the Tb(inic)$_3$(DMA) · H_2O complex (λ_{ex} = 241 nm).

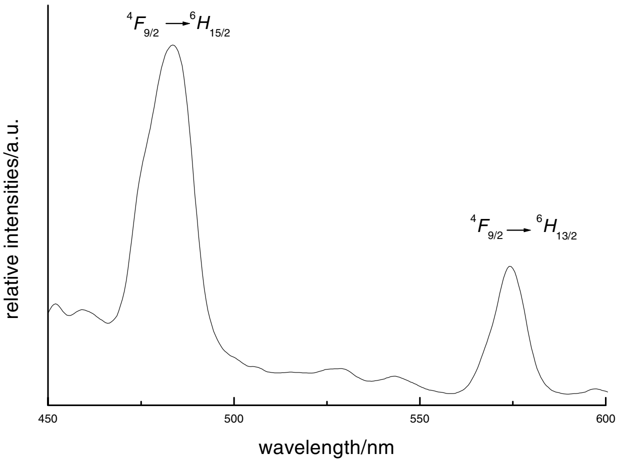

Fig. 5. Emission spectrum of the Dy(inic)$_3$(DMF) · H_2O complex (λ_{ex} = 241 nm).

H_2O. The effective energy absorption mainly takes place in the narrow ultraviolet region of 200—280 nm, and the excitation bands have about four main peaks, at 220 nm, 240 nm, 255 nm, and 270 nm, respectively. We further measured the corresponding emission spectra by selective excitation with the four different excitation wavelengths, and they show the similar emission position except for different luminescent intensities, which indicates that the four excitation bands are all the effective energy sensitizers for the luminescence of Ln ions.

The emission spectra were measured in detail. Figs. 3—5 give the selected emission spectra of Eu(inic)$_3$(pyro) · H_2O, Tb(inic)$_3$(DMA) · H_2O, and Dy(inic)$_3$(DMF) · H_2O, respectively. For Eu(inic)$_3$-(pyro) · H_2O complex, the emission spectra show four emission peaks under the excitation of 242 nm: at 592 nm, 618 nm, 652 nm, and 699 nm, corresponding with the characteristic emission $^5D_0 \rightarrow {}^7F_j$ transitions (j = 1, 2, 3, 4) of Eu^{3+} ion. The red luminescent intensity of $^5D_0 \rightarrow {}^7F_2$ transition is the strongest, and the emission intensity of $^5D_0 \rightarrow {}^7F_1$ transition becomes stronger for the covering of $^5D_0 \rightarrow {}^7F_0$ transition. For Tb(inic)$_3$(DMA) · H_2O complex, the emission spectra show four emission peaks under the excitation of 223 nm: at 490 nm, 544 nm, 584 nm, and 621 nm, attributed to the characteristic emission $^5D_4 \rightarrow {}^7F_j$ (j = 6, 5, 4, 3) transition of Tb^{3+} ion. The $^5D_4 \rightarrow {}^7F_5$ transition exhibits the strongest green emission, and $^5D_4 \rightarrow {}^7F_6$ transition shows the second strongest blue emission. For Dy(inic)$_3$(DMF) · H_2O complex, the luminescence spectra show two apparent emission peaks under the excitation of 238 nm: one is at 483.9 nm, the other is at 574.2 nm, which is corresponding with the characteristic emission $^4F_{9/2} \rightarrow {}^6H_j$ (j = 15/2, 13/2) transition of Dy^{3+} ion. It is worth pointing out that the blue emission intensity of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is stronger than the yellow emission of $^4F_{9/2} \rightarrow {}^6H_{13/2}$, suggesting that the Hinic is suitable for the sensitization of blue luminescence of Dy^{3+} in the $Dy(inic)_3(DMF) \cdot H_2O$ complex. Other lanthanide complex systems (Eu^{3+}, Tb^{3+}) show the similar feature.

All the samarium complex systems show no ideal luminescence spectra. Comparing the luminescence intensities of these complex systems, it can be found that the quaternary terbium complex system shows stronger luminescence than those of other lanthanide systems. The quaternary europium and dysprosium complex systems show weaker luminescence than terbium ones but stronger than samarium ones, which indicates that the triplet state energy is more suitable for the luminescence of terbium ion than europium and dysprosium ions. There exists some internal energy level ($^6F_{11/2}$, $^6F_{9/2}, \ldots, ^6H_{11/2}$, *etc.*) between the first excited state $^4G_{5/2}$ and ground state $^6H_{9/2}$ of Sm^{3+}, which causes readily some nonradiative energy transfer process to quench the excited energy of Hinic ligand. So Sm^{3+} complex systems exhibit the weakest luminescence.

EXPERIMENTAL

Polybasic Lanthanide Complex Molecular Systems

The lanthanide oxides (Eu_2O_3, Tb_4O_7, Sm_2O_3, Dy_2O_3) were converted to their nitrates by treatment with concentrated nitric acid. The quaternary lanthanide complexes were prepared by homogeneous precipitation. DMF (DMA, pyro) solutions of lanthanide nitrates were added very slowly to the DMF (DMA, pyro) solutions of Hinic, the pH values of the mixed solutions being adjusted to 6.5. Then white precipitates appeared and were filtered off, washed with DMF (DMA, pyro), dried and stored over silica gel.

Elemental analyses (C, H, N) were carried out by the Elemental Cario EL elemental analyzer. Infrared spectroscopy on KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the region of 400—4000 cm^{-1}. Ultraviolet absorption spectrum was measured with Agilent 8453 spectrophotometer. Phosphorescence spectra and fluorescence (excitation and emission) spectrum were determined with Perkin—Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

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