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# Fluorescence Quenching in $\{Ln[Fe(CN)_6]\cdot nH_2O\}_x$ (Ln=Eu(III) or Tb(III))

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**Synopsis.** Fluorescent properties of cyanide-bridged Ln(III)-Fe(III) complex assemblies, $\{Ln[Fe(CN)_6]\cdot nH_2O\}_x$ ($n$=4 for Ln=Eu; $n$=5 for Ln=Tb), have been investigated in solid state in comparison with those of the 1 : 1 mixtures of $K_3[Fe(CN)_6]$ and $LnCl_3\cdot 6H_2O$ (Ln=Eu, Tb). Fluorescence of Eu(III) and Tb(III) is almost completely quenched in the complexes but little quenched in the mixtures.

Investigations on the effect of the co-existing metal ions or metal complexes upon the fluorescence of rare earth ions will give basic and useful informations for the development of fluorescent materials, since the metal complexes reported so far are beyond enumeration and show a great variety of characteristic colors of the respective complexes. However, there are few such studies:[1,2] Berner et al.[1] reported that the fluorescence of Tb(III) is enhanced when two of the four Ca(II) in proteolytic enzyme, thermolysin, are replaced by Tb(III), whereas decreases by further replacement of Zn(II) bound at the active site of the enzyme by Co(II). Higashiyama and Adachi[2] found that the emission intensity of Eu(II) in the Eu(II)-poly(methacrylate containing 15-crown-5 structure) complex increases by the co-existence of Zn(II) and luminescence lifetime gets much longer. Recently, we investigated the effect of copper(II) and nickel(II) complexes [M(saltn)] (M=Cu, Ni) of *N,N'*-disalicylidene-1,3-propanediamine ($H_2$saltn) upon the fluorescence of Eu(III).[3] The fluorescence of Eu(III) decreased markedly by the addition of [M(saltn)] and this is presumed to be due to the formation of M-Eu heteronuclear species bridged by the phenolic oxygen atoms of the ligand saltn$^{2-}$. In the present work we have investigated the fluorescent properties of Eu(III) and Tb(III) in complex assemblies $\{Ln[Fe(CN)_6]\cdot nH_2O\}_x$ (Ln=Eu, Tb), which are known to have the three-dimensional network structure constructed by Fe(III)-CN-Ln(III) linkages,[4] in order to examine further the fluorescence quenching affected by adjacent d-transition metal ions.

## Experimental

**Syntheses.** Potassium hexacyanoferrate(III) was obtained commercially and recrystallized from hot water. The complex assemblies, $\{Ln[Fe(CN)_6]\cdot nH_2O\}_x$ (Ln=Eu, Tb), were synthesized as follows: An aqueous solution (10 cm$^3$) of the corresponding rare earth nitrate hexahydrate (10 mmol) was added to an aqueous solution (8 cm$^3$) of $K_3[Fe(CN)_6]$ (10 mmol) under stirring at room temperature. After stirring for 5 min, reddish orange microcrystals were collected by suction filtration, washed successively with water, methanol and diethyl ether, and dried in the open air. Yields were 80 and 90% for Eu-Fe and Tb-Fe complexes, respectively.

Found for Eu-Fe complex: C, 16.35; H, 1.95; N, 18.95; Eu, 34.25; Fe, 12.80%. Calcd for $Eu[Fe(CN)_6]\cdot 4H_2O$ ($C_6H_8N_6O_4EuFe$): C, 16.53; H, 1.85; N, 19.28; Eu, 34.86; Fe, 12.81%. Found for Tb-Fe complex: C, 15.71; H, 1.96; N, 18.57; Tb, 34.65; Fe, 12.43%. Calcd for $Tb[Fe(CN)_6]\cdot 5H_2O$ ($C_6H_{10}N_6O_5FeTb$): C, 15.63; H, 2.19; N, 18.23; Tb, 34.48; Fe, 12.12%.

**Measurements.** Elemental analyses of C, H, and N were carried out at the Service Center of Elemental Analysis, Kyushu University. Metal contents were determined by EDTA titration after the mixed oxides obtained by the ignition of complex assemblies at about 850 °C in air were

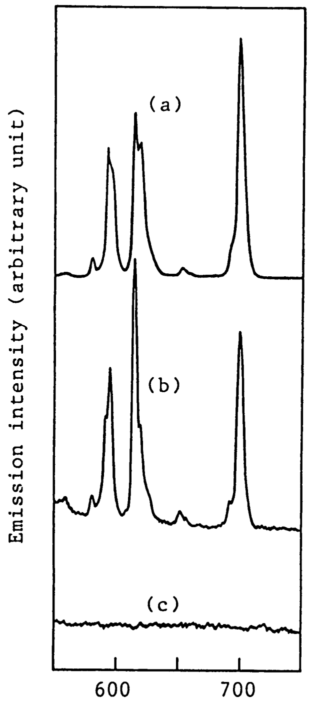

Fig. 1. Fluorescence spectra of $EuCl_3\cdot 6H_2O$ (a), (1 : 1) mixture of $EuCl_3\cdot 6H_2O$ and $K_3[Fe(CN)_6]$ (b), and $\{Eu[Fe(CN)_6]\cdot 4H_2O\}_x$ (c) in solid state. Exciting wavelength is 394 nm. Slit widths (nm) of (excitation and emission sides) are (2 and 2). Ordinate scales are ×8 for (a), ×512 for (b), and ×1024 for (c). Filters, UV-35 and V-Y47, are used for excitation and emission sides, respectively.

dissolved in dilute nitric acid. Infrared spectra were measured on KBr disks with a JASCO IR-G Spectrometer. Fluorescence spectra were measured on solid samples with a Shimadzu RF-540 Fluorospectrophotometer.

## Results and Discussion

In the IR spectrum of $K_3[Fe(CN)_6]$ the $\nu$(CN) vibrations are observed at 2120 and 2045 $cm^{-1}$. These vibrations for the present complexes are observed at 2150 and 2070 $cm^{-1}$, respectively, indicating the formation of Fe(III)-CN-Ln(III) linkages by cyanide-bridging.[5]

The fluorescence spectra of $\{Ln[Fe(CN)_6]\cdot nH_2O\}_x$ are given in Figs. 1 and 2. For comparison fluorescence spectra were also measured for $LnCl_3\cdot 6H_2O$ and $K_3[Fe(CN)_6]$, and are included in Figs. 1 and 2. $EuCl_3\cdot 6H_2O$ and $TbCl_3\cdot 6H_2O$ exhibit the fluorescent bands attributable to the $^5D_0\rightarrow{}^7F_J$ transitions in the 580—700 nm region and the $^5D_4\rightarrow{}^7F_J$ transitions in the 490—625 nm region, respectively. These fluorescent bands disappear almost completely in $\{Ln[Fe(CN)_6]\cdot nH_2O\}_x$, whereas apparently observed in the mixtures of $LnCl_3\cdot 6H_2O$ and $K_3[Fe(CN)_6]$. Such a fluorescence quenching was also observed when [M(saltn)] (M= Cu(II), Ni(II)) was added to a methanolic solution of $Eu(NO_3)_3\cdot 6H_2O$.[3] As the most probable quenching mechanism, we have presumed that [M(saltn)] coordinates to Eu(III) through the two phenolic oxygens of $saltn^{2-}$ and the energy transfer occurs from the excited Eu(III) to the Cu(II) or Ni(II) center through the phenolic oxygen bridges. This proposal was supported by our subsequent studies:[6,7] (i) the fluorescence of Eu(III) is significantly quenched in the binuclear Cu(II)-Eu(III) and Ni(II)-Eu(III) complexes, $[MEu(fsaen)(NO_3)(H_2O)_n]\cdot(m-n)H_2O$ (M=Cu, Ni), whereas the mononuclear Eu(III) complex, $[Eu(H_2fsaen)(NO_3)(H_2O)_n]\cdot(5-n)H_2O$, shows the intense fluorescence, where $H_4$fsaen denotes *N,N'*-bis(3-carboxysalicylidene)ethylenediamine, which can afford heterobinuclear complexes bridged by the two phenolic oxygens,[6] and (ii) the effects of the Cu(II) and Ni(II) complexes of *N,N'*-bis(3-methoxysalicylidene)ethylenediamine, which will make the formation of binuclear complex difficult by the steric hindrance of methoxy groups, upon the fluorescence quenchings of Eu(III) and Tb(III) are less compared with those of the corresponding metal complexes of *N,N'*-disalicylideneethylenediamine.[7] The results in this work also give an evidence for the quenching mechanism proposed. That is, the fluorescence quenching may be due to the energy transfer from Eu(III) or Tb(III) to Fe(III) center through the cyanide bridges.

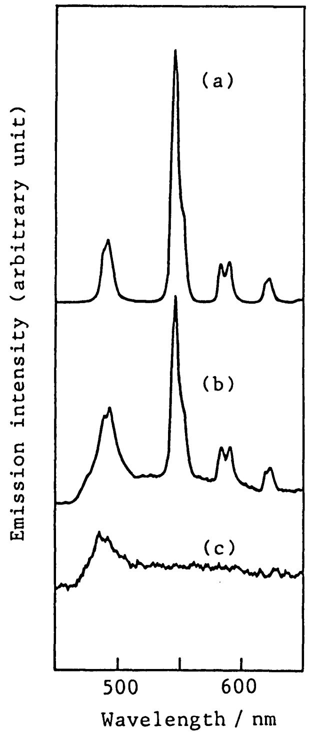

Fig. 2. Fluorescence spectra of $TbCl_3\cdot 6H_2O$ (a), (1 : 1) mixture of $TbCl_3\cdot 6H_2O$ and $K_3[Fe(CN)_6]$ (b), and $\{Tb[Fe(CN)_6]\cdot 5H_2O\}_x$ (c) in solid state. Exciting wavelength is 355 nm. Slit widths(nm) of (excitation and emission sides) are (2 and 2). Ordinate scales are ×8 for (a), ×512 for (b), and ×1024 for (c). Filters, UV-35 and V-Y47, are used for excitation and emission sides, respectively.

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