Fluorescent Property of Bulk- and Nanocrystals of Cyanide-bridged Eu(III)Co(III) Heteronuclear Coordination Polymer

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Fluorescent properties of Eu(III) in the bulk- and nanocrystals of coordination polymer, Eu[Co(CN)$_6$]•4H$_2$O, were compared with those of EuCl$_3$•6H$_2$O. Fluorescent intensity of bulk crystals was greatly enhanced on forming the coordination polymer, whereas that of nanocrystals was little affected. These results were discussed considering the coordination surroundings around Eu(III) located on the crystal surface.

Europium(III) is well known to exhibit the red fluorescence and its fluorescence enhancement has been extensively studied for the development of new photomaterials, immunoassay reagents and so on. In these studies, a large number of ligands has been designed in order that the effective energy transfer occurs from the excited ligand to the Eu(III) center. However, as to the effect of coexisting metal ions, only two reports by the separate groups are available on the decrease of fluorescent intensity.[1,2] There is no report on the effect of coexisting metal complexes, except our reports since 1991.[3] Despite of efforts to enhance the fluorescent intensity of Eu(III) by the adjacent metal complexes, our results showed only the decrease of fluorescence.

In this work, we, for the first time, found that the fluorescence of Eu(III) was enhanced in the bulk crystals of a cyanide-bridged coordination polymer, Eu[Co(CN)$_6$]•4H$_2$O, compared with that of bulk EuCl$_3$•6H$_2$O. Besides the bulk materials, much attention has been recently paid to the physicochemical properties of nanoparticles and nanocrystals which will open a door to the development of new nanomaterials. From this point of view, in the present work, we prepared the nanosized Eu[Co(CN)$_6$]•4H$_2$O crystals and investigated their fluorescent property. These results will be also reported below.

Bulk crystals of Eu[Co(CN)$_6$]•4H$_2$O, were synthesized by mixing a 10 cm^3 of an aq. EuCl$_3$ solution (1 mol dm^{-3}) with a 10 cm^3 of an aq. K$_3$[Co(CN)$_6$] solution (1 mol dm^{-3}).[4] Nanocrystals of Eu[Co(CN)$_6$]•4H$_2$O were prepared as follows: aqueous solutions (5×10^{-2} mol dm^{-3}) of EuCl$_3$ and K$_3$[Co(CN)$_6$] were prepared. 50 μL of each solution was added to 10 cm^3 of a hexane solution (5×10^{-2} mol dm^{-3}) of AOT, separately. These two clear reversed micelle solutions were mixed to give nanocrystals of Eu[Co(CN)$_6$]•4H$_2$O well dispersed in hexane.

The IR spectrum of bulk Eu[Co(CN)$_6$]•4H$_2$O showed the ν(CN) band at 2161 cm^{-1}. The corresponding band for bulk K$_3$[Co(CN)$_6$] was observed at 2129 cm^{-1}. A reversed micelle solution of K$_3$[Co(CN)$_6$] exhibited the ν(CN) at 2127 cm^{-1}. After the reaction of K$_3$[Co(CN)$_6$] and EuCl$_3$ in the reversed micelle, the band was shifted to 2159 cm^{-1}. The shift to higher frequency indicates the coordination of CN nitrogen to Eu(III)[5] and the construction of three-dimensional network structure by Co–CN–Eu linkage for both bulk- and nanocrystals.[6]

Electronic spectrum of the bulk Eu[Co(CN)$_6$]•4H$_2$O is shown in Figure 1. Ligand field bands of the Co(III) attributable to the $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions were observed at 269 and 307 nm, respectively.[7] A weak and sharp band at 394 nm is assigned to the $^7F_0 \rightarrow {}^5L_6$ transition of Eu(III). These three wavelengths were chosen as the excitation wavelengths for measurements of the fluorescence spectra. Figure 2 shows fluorescence spectra of the bulk Eu[Co(CN)$_6$]•4H$_2$O. Fluorescent bands attributable to the $^5D_0 \rightarrow {}^7F_J$ of Eu(III) were observed in the 580–700 nm region. The intensities of these bands for Eu[Co(CN)$_6$]•4H$_2$O were about twice those for EuCl$_3$•6H$_2$O when the excitation wavelength was 394 nm (Figure 2a). When 269 and 304 nm were adopted as the excitation wavelengths, the fluorescence for Eu[Co(CN)$_6$]•4H$_2$O was much more enhanced. Figure 2b shows the spectrum measured by the excitation at 307 nm. These results indicate that the energy transfer effectively occurs from the excited Co(III) to Eu(III) through the cyanide-bridges. A similar energy transfer from Cr(III) to Nd(III) was reported using Nd[Cr(CN)$_6$]•4H$_2$O.[8] However, to the best of our knowledge, such fluorescence enhancement by the adjacent metal complex is the first observation.

In order to get an information regarding the effect of size-control on the emission property, nanocrystals of Eu[Co(CN)$_6$]•4H$_2$O well dispersed in AOT/hexane solution were prepared as described above, and their fluorescence spectra were measured. Figure 3 shows the DF-STEM image of Eu[Co(CN)$_6$]•4H$_2$O nanocrystals, the sizes of which are less than 5 nm. This is the

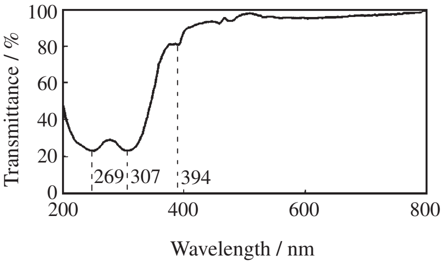

Figure 1. Reflection spectrum of Eu[Co(CN)$_6$]•4H$_2$O.

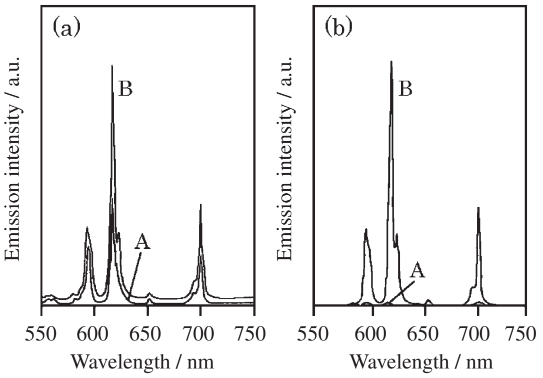

Figure 2. Fluorescence spectra of $EuCl_3 \cdot 6H_2O$ (A) and $Eu[Co(CN)_6] \cdot 4H_2O$ (B) in solid state. Excitation wavelengths are 394 nm (a) and 307 nm (b). Ordinate scales are ×8 (a) and ×2 (b).

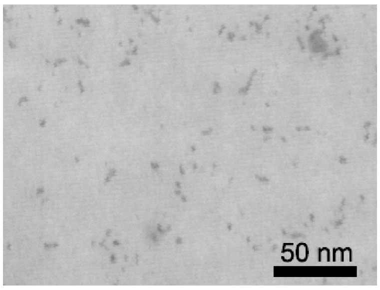

Figure 3. DF-STEM image of $Eu[Co(CN)_6] \cdot 4H_2O$ in reversed micelle solution.

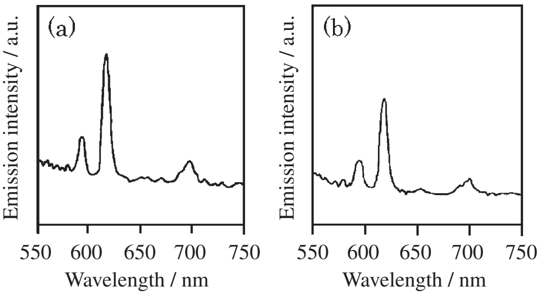

Figure 4. Fluorescence spectra of $EuCl_3 \cdot 6H_2O$ (a) and $Eu[Co(CN)_6] \cdot 4H_2O$ (b) in reversed micelle solutions. Excitation wavelength is 307 nm. Ordinate scale is ×1024.

first example of the d–f heteronuclear coordination polymer nanocrystals prepared by the reversed micelle technique. Very recently, stimulative studies were reported on nanocrystals of the d–d systems.[9–11] Fluorescence spectrum of these nanocrystals was compared with that of $EuCl_3$ in the reversed micelle solution. Typical spectra obtained by the excitation at 307 nm are given in Figure 4. Fluorescent intensity of Eu(III) was little affected by the formation of $Eu[Co(CN)_6] \cdot 4H_2O$ nanocrystals. This was also the case for the excitation at 268 nm. Such a remarkable difference between bulk- and nanocrystals can be rationalized by the coordination surroundings around Eu(III) as emission sites. According to the X-ray structural analysis, Eu(III) ions are eight-coordinated by six nitrogens from the bridging cyanides and two oxygens from water molecules.[6] As easily imagined, this structure is not taken by the Eu(III) ions located on the crystal surface, where Eu(III) ions are coordinated by less than six cyanide nitrogens. Especially, in the nanocrystals formed in the reversed micelle solution, Eu(III) ions on the surface are probably surrounded by much more than two water molecules. The increase in ratio of such surface Eu(III) ions to those inside the crystals leads to the increase of Eu(III) sites which are responsible for the radiationless energy transfer from the emmisive state, $^5D_0$ of Eu(III), to the OH vibration overtones of the coordinating water molecules. This may be one of the reasons why the fluorescence of Eu(III) in the reversed micelle solution of $EuCl_3$ is little influenced by the formation of $Eu[Co(CN)_6] \cdot 4H_2O$ nanocrystals.

In order to explain the present fluorescent behavior more clearly, investigation on the effect of crystal size is in progress. Further, various d–f heteronuclear coordination bulk crystals and their nanocrystals prepared using some kinds of surfactants are being subjected to the fluorescent measurements.

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