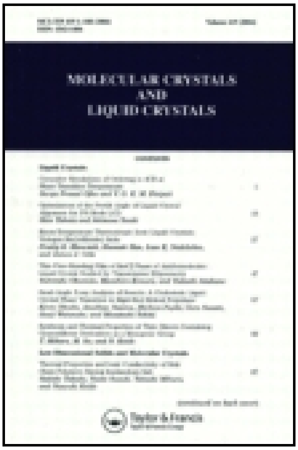

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Synthesis and Properties of Europium Complex of Polybenzimidazole Containing N-Eu Bond

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NaH promoted deprotonation of the NH groups in poly(benzimidazole)s, $[\text{-Im-}C_6H_4\text{-}]_n$ (**1a**) (Im: 5,5'-dibenzimidazole-2,2'-diyl) and $[\{\text{-Im-}(CH_2)_{11}O(CH_2)_{11}\text{-}\}_{0.98}\{\text{-Im-}(CH_2)_{10}\}_{0.02}\text{-}]_n$ (**1b**) followed by addition of 4 equiv. of $EuCl_3$ gave new soluble Eu complexes of poly(benzimidazole)s (**2a** and **2b**) having N-Eu bonds in 66 and 42% yields, respectively. The Eu polymer complexes **2a** and **2b** have two molecules of Cl and DMSO as ligands, which was revealed from IR and ^{1}H NMR spectra and elemental analysis. Energy transfer from the benzimidazole group in polymer main chain to the Eu(III) metal was occurred upon irradiation with UV light in the solid state. This resulted in light emission from both the polymer chain and the Eu(III) center, although the Eu(III) itself could not be excited by irradiation with the UV light.

Keywords: Europium complex; Polybenzimidazole; Energy transfer

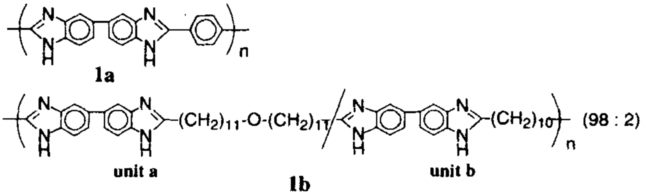
INTRODUCTION

Lanthanoid polymer complexes have been much attentioned due to their showing unique photoluminescence properties and catalyses.[1] Most lanthanoid polymer complexes have been prepared by the reaction of the lanthanoid metal with a bidentate ligand introduced in the polymer chain.[1b,1f,1g] Recently polycondensation using a lanthanoid complex monomer has been reported to afford a lanthanoid polymer complex.[2] Properties of the lanthanoid-polymer complexes strongly depend on structure and properties of the starting polymer material.

Polybenzimidazoles exhibit high thermal stabilities and chemical resistance[3] and have reactive NH groups which are expected to react with the lanthanoid to form stable metal complexes. Europium (Eu)-polymer complexes have been widely studied among the lanthanoid-polymer complexes, because Eu complexes show unique catalyses and prominent luminescence properties.[4] Substitution reaction of the NH hydrogen of polybenzimidazole with Eu would provide a novel Eu complex of polybenzimidazole. Here we report the first preparation of such Eu complexes of polybenzimidazoles and physical properties of the polymer complexes.

RESULTS AND DISCUSSION

Polybenzimidazoles used as starting materials in this study are shown in Chart 1. Poly(alkylenebenzimidazole) (**1b**) which contains **unit a** and **b** in a 98:2 ratio was synthesized by Ru-complex-catalyzed polycondensation of 3,3'-diaminobenzidine with 1,12-dodecanediol.[5]



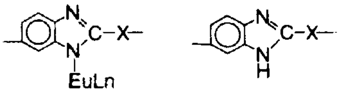
1a

1b

CHART 1 Polybenzimidazoles used in this study.

Reactions of **1a** and **1b** with sodium hydride in DMSO caused deprotonation of the imidazole NH group to give deep red solutions of polyanions. Subsequent treatment of the polyanions with $EuCl_3$ in a 1:4 molar ratio caused N-Eu bond formation to afford polymer complexes (**2a** and **2b**) as off-white solids in 66 and 42% yields, respectively.

The polymer complexes **2a** and **2b** are soluble in DMF and DMSO at 80 °C similar to the corresponding starting materials. The ^1H NMR peaks of the *p*-phenylene unit of **2a** appeared at the same positions (δ 7.59 and 7.88) as those of the starting material **1a**. On the other hand, peaks assigned to hydrogens of 5,5'-dibenzimidazole-2,2'-diyl group shifted to higher magnetic field positions (δ 9.15, 8.29, and 7.93). These data indicates that introduction of Eu metal to the imidazole ring caused changes of magnetic circumstance of the dibenzimidazole group. Similar shifts of peaks were observed in the ^1H NMR spectrum of **2b**. The ^1H NMR spectra of **2a** and **2b** exhibited a peak assignable to DMSO coordinated with the Eu metal at δ 2.50. The peak ratio indicated that **2a** and **2b** contained two molecules of DMSO per Eu. An absorptions due to v(S=O) vibration was observed at about 1090 cm^{-1} in IR spectra of **2a** and **2b**. Mössbauer spectrum of **2b** shows a singlet peak at δ 0.65 mm s^{-1} which is assignable to Eu(III). The above spectroscopic and analytical data indicate that **2a** and **2b** contain the following structural units **A** and **B** in 0.31 : 0.69 and 0.27 : 0.73 ratios, respectively, as exhibited in Chart 2.



X = p-C_6H_4 (**2a**), $(CH_2)_{11}O(CH_2)_{11}$, $(CH_2)_{10}$ (**2b**)
L = 2 Cl, 2 DMSO, 2 H_2O

unit **A** unit **B**

CHART 2 Benzimidazole units in **2a** and **2b**.

It is well known that Eu complexes serve as shift reagents to cause shift of the ^{1}H NMR peaks shift to a lower magnetic field by interaction between electron orbital of Eu and lone pair orbital of a substrate. However, the NH ^{1}H NMR signal of **2a** and **2b** appears as a broad peak at the same position (δ 13.20) as that of the corresponding starting materials. These results indicate that all the Eu complexes in **2a** and **2b** are covalently bonded to the N atom of the imidazole ring.

Figure 1 depicts photoluminescence and excitation spectra of **2b** in solid state. When irradiated with UV light of 335 nm, **2b** exhibited photoluminescence not only a peak at 382 nm due to polymer main chain but also additional peaks at 581, 593, and 614 nm, which correspond to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions in Eu(III) metal, respectively.

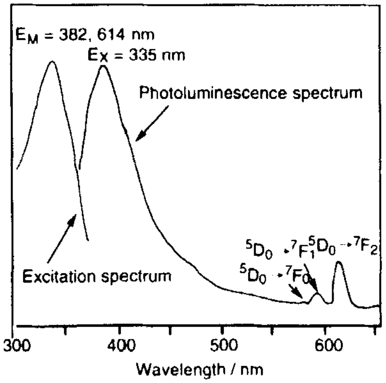


FIGURE 1 Photoluminescence (irradiated with 335 nm light) and excitation (monitored at 614 nm) spectra of **2b** in solid state.

Both the excitation spectra of **2b** obtained by monitoring with 382 and 614 nm light, respectively gave only a peak at 335 nm. Polymer complex **2a** in the solid state also gave similar results. It showed photoluminescence peak at 347 nm due to polymer main chain and photoluminescence peaks at 580, 593, and 615 nm corresponding to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions in Eu(III), respectively upon irradiation with UV light (299 nm).

$EuCl_3$ does not exhibit photoluminescence upon irradiation with the UV light (335 or 299 nm). Thus the light emission from Eu(III) is considered to arise through energy transfer from the benzimidazole ring absorbed with the UV light to the Eu metal as depicted in Chart 3. Similar energy transfer from aromatic polymer main chain to coordinated metal center has been reported for poly(2,2'-bipyridine-5,5'-diyl)-Ru complex.[6]

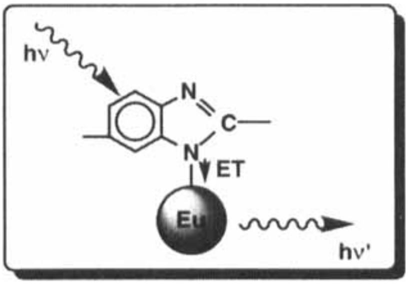


CHART 3 Energy transfer from benzimidazole ring to Eu metal.

Although **2a** and **2b** in DMSO solutions showed photoluminescence peaks at 446 and 347 nm due to the polymer chain upon irradiation with the UV light, photoluminescence peak from the Eu metal was not observed.

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