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Preparation of luminescent lanthanide polymers by ring-opening metathesis polymerization

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ABSTRACT

Polymeric lanthanide complexes have been synthesized through ring-opening metathesis polymerization of monomeric lanthanide complexes of pyridine dicarboxylates that contain a norbornene group. The lanthanide monomer complexes, Eu(III) and Tb(III) complexes, have three norbornene groups that allow three-dimensional polymeric networking, and the corresponding polymers of Eu(III), Tb(III), and their equimolar complexes are highly luminescent with intense emission bands in the characteristic visible region.

Fluorescent metal–organic frameworks based on trivalent lanthanides have received considerable interest due to their remarkable optical and magnetic properties such as characteristic sharp emission, long excited-state luminescence lifetimes of up to milliseconds, and a large Stokes' shift of >200 nm. Such luminescent materials have great potential for applications to optical glasses and lasers, telecommunications, lighting and displays, magnetic materials, hard-disk drives, security inks and counterfeiting tags, catalysis, bioscience, and medicine.[1–8] The lanthanide ions, however, usually absorb weakly due to the spin- and parity-forbidden nature of f–f transitions. Accordingly, the well-established 'antenna effect' has been used to obtain intense characteristic emissions of lanthanide ions, where the energy transfer occurs from the triplet excited states of an antenna molecule (organic ligand) to the metal center coordinated to the organic ligand.[9–15]

There are several special lanthanide-based metal organic frameworks containing dinuclear Eu(III) complexes, which display high luminescence due to the direct excitation at the f–f transitions (394 nm).[16–18] Also, a number of delocalized π-electron systems that contain a didentate ligand such as carboxylates,[19–22] phosphonates,[23,24] and sulfonates[25–28] have been explored over the years to construct lanthanide-based metal organic frameworks with bright luminescence. Among them, the β-diketonates and aromatic carboxylates have been frequently used as ligand with desirable antenna effect through the energy transfer from the ligand to Ln^{3+} ions.[29–37] A few lanthanide complexes based on a flexible aromatic carboxylic ligand also showed high luminescence.[38–40]

Polymeric lanthanide materials have also attracted much attention for their flexibility in fabricating them into optoelectronic devices.[41–49] Mostly, the polymers have been synthesized through a coordination process between a lanthanum ion and a bidirectional ligand[47,48] or by incorporating lanthanum ions or lanthanum-doped luminescent complexes into polymeric matrixes.[41–46] Holliday and co-workers first reported europium-containing conducting metallopolymers, where the polymers were formed through an electrochemical polymerization process.[49] These lanthanide polymeric matrices showed good thermal stability, excellent mechanical properties, bright luminescent properties, good transparency, impact resistance, low temperature processability, and dyeability. Most of the polymeric luminophores, however, usually showed severe concentration-induced self-quenching due to occurrence of ionic aggregates even at low lanthanide ion contents. Also, sometimes elucidation of luminescent properties was difficult because of a complex microenvironment of lanthanide ions in the polymeric matrices. On the other hand, most of the reported lanthanide metal-containing polymers were prepared by direct incorporation of lanthanide ions or lanthanide complexes into polymeric ligands, where the solubility of most lanthanide ions or complexes in polymer systems was poor, which

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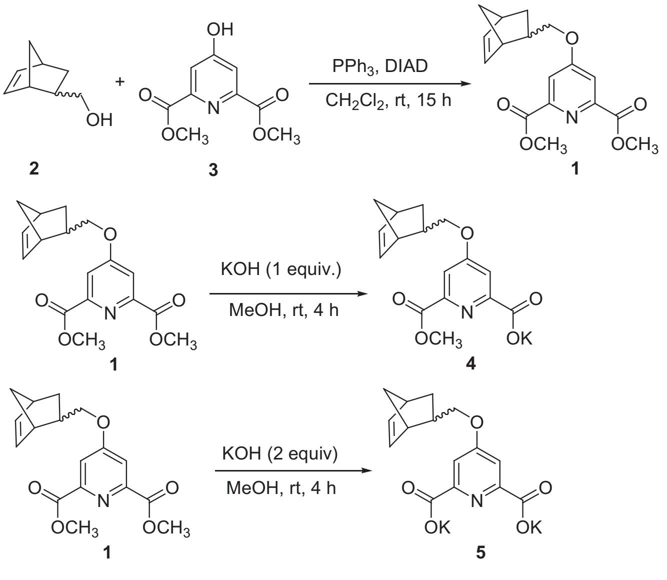
caused complexity in making uniform thin films or solid polymeric materials with high contents of lanthanide ions.

Here, we report synthesis of polymeric lanthanide complexes through the ruthenium catalyzed ring opening metathesis polymerization (ROMP), which has proven to be powerful for the preparation of functional polymers. We aimed at the generation of homogenous lanthanide polymers with three dimensional networking. To this end, we chose chelidamic acid as an antenna ligand, on which a norbornene group at the 4-position of the pyridine ring was introduced for ROMP. We demonstrate that synthesis of lanthanide polymer complexes through ROMP is an efficient approach to construct homogenous lanthanide-doped polymeric networks with a flexibility of formulating a ‘mixed’ lanthanide polymer complex. To the best of our knowledge, this is a rare example of lanthanide based luminescent polymers prepared through ROMP.

We have designed chelidamic acid derivative **1** that contains a norbornene group for ROMP. Diester **1**, ((±)-dimethyl 4-((bicyclo [2.2.1]-hept-5-en-2-yl)methoxy)-pyridine-2,6-dicarboxylate)), was readily prepared by a Mitsunobu reaction between commercially available (±)-5-norbornene-2-methyl alcohol (**2**) and the chelidamic acid dimethyl ester **3**. The methyl ester was hydrolyzed using KOH to give the corresponding mono-carboxylate ligand **4** ((±)-potassium 4-((bicycle-[2.2.1]hept-5-en-2-yl)methoxy)-6-(methoxycarbonyl)-pyridine-2-carboxylate) and the dicarboxylate ligand **5** ((±)-potassium 4-((bicyclo[2.2.1]hept-5-en-2-yl)methoxy)-pyridine-2,6-dicarboxylate) (Scheme 1).

The Eu(III) and Tb(III) complexes of the chelidamic acid ligand were then readily prepared according to the literature procedure.[50] Eu(NO$_3$)$_3$·5H$_2$O and Tb(NO$_3$)$_3$·5H$_2$O were used as the lanthanide metal source. Three equivalents of the corresponding ligand were dissolved in a mixed solution of chloroform and methanol (10:1), which was sonicated for 3–5 min at room temperature. A hazy solution was formed, which was then filtered through a Teflon filter (pore size: 0.45 μM) to remove KNO$_3$. The filtrate containing the Eu(III) or Tb(III) complex was used in the next polymerization process. Figure 1 shows the structures and fluorescence images of the Eu(III) and Tb(III) complexes (2.45 mM) prepared from the dicarboxylate ligand **5** in a mixed solvent of chloroform and methanol (10:1). The Tb(III) complex emitted bright green fluorescence, and the Eu(III) complex emitted bright red fluorescence under UV irradiation (365 nm). When a 1:1 mixture of the Eu(III) and Tb(III) sources was treated with six equivalents of dicarboxylate **5**, the resulting mixture gave orange fluorescence. This intermediate color suggests that a mixture of the Eu(III) and Tb(III) complexes was generated. Due to the paramagnetic nature of the lanthanide complexes, characterization of them by NNR was not feasible.



Scheme 1. Synthesis of chelidamic acid derivatives **1**, **4**, and **5**.

For the synthesis of three dimensional (3D) lanthanide polymers by ROMP, we chose the Grubs 2nd generation catalyst, (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro-(phenylmethylene)-(tricyclohexyl-phosphine)ruthenium.[51] We varied reaction conditions to find optimal conditions for ROMP. Thus, the polymerization reaction was monitored by changing the amounts of the monomer metal complex, and of 2-norbornene added as an additive, and of the Grubs catalyst. Also, we changed the reaction temperature, solvent, the order of reagent addition, and the dropping rate of monomer solution. The best result was obtained when a solvent system of 10/1 (v/v) ratio of CHCl$_3$/MeOH was used. While in other solvent or solvent mixture systems, ROMP was not effective. When a solution of the above Eu(III) or Tb(III) complex (0.027 mmol), 2-norbornene (10 equiv 0.27 mmol) and Grubbs 2nd generation catalyst (0.5 mol %) was stirred for 5–10 min at room temperature, the solution changed to a viscous solution. The solvent was evaporated at reduced pressure to give the polymer as film; the europium polymer (**CP-Eu**) emitted red luminescence and the terbium polymer (**CP-Tb**) emitted green luminescence, both under UV (365 nm) light. For an integrated lanthanide based polymer system containing both Eu(III) and Tb(III) ions, it took 22–24 h to complete the polymerization process. This mixed polymer, after washing several times with methanol to remove the unreacted monomer, showed orange emission under UV light (Fig. 2c). Unfortunately, the polymers have poor solubility in common organic solvents except polymer **CP-Eu**. Therefore, we used NMR to obtain information on the complexation and polymerization processes for the **CP-Eu** polymer. NMR spectra of both the europium complex **6** and its polymeric complex **CP-Eu** showed broad peaks due to the paramagnetic property of lanthanide ions, but the vinyl proton and the cyclopentane ring protons in both complexes could still be identified at 5.9–6.1 ppm (SI-Fig. S3).

FT-IR analyses showed that the carbonyl stretching vibration of the europium monomer complex **6** (at 1594 cm^{-1}) was shifted to a lower frequency in the case of the corresponding polymer (at 1591 cm^{-1}); this is typical antisymmetric and symmetric stretching vibrations of a carbonyl group. The C═C stretching vibrations of ligand **6** in the complex are broad and strong at 2967 cm^{-1}. One weak band at 498 cm^{-1} is observed due to the stretching vibration of Eu–O.[52] These results support that the formation of the coordination complex between the Eu(III) ion with ligand **5**. The typical O–H absorption at 3200–3500 cm^{-1} was detectable, indicative of the coordinated H$_2$O molecules to the complex. The FT-IR spectrum of polymeric **CP-Eu** is quite similar to that of europium monomer complex **6** (SI-Fig. S4). The C═C and C–H stretching vibrations of the aromatic ring and vinyl group in the polymer **CP-Eu** were observed at 2967 and 2863 cm^{-1}, respectively.

Luminescent properties of the lanthanide based polymers were investigated in the solid state and in solution phase at room temperature. The lanthanide based polymers, **CP-Eu**, **CP-Tb**, and **CP-Eu-Tb**, showed bright-red, green, and orange luminescence, respectively, upon irradiation using a standard 365 nm UV lamp (Fig. 2); the results indicate occurrence of the ligand-to-metal intramolecular photoinduced energy transfer. The excitation spectrum of **CP-Eu** consists of a broad band at around 275 nm, which is due to charge transfer between the ligand **5** and Eu^{3+} ions, and π–π* electron transitions of the organic bridging ligand. Ligand-to-metal energy transfer (LMET) usually provides sufficient overlap of the excited states of the ligand with the excited 4f states of the lanthanides, which makes luminescence sensitization.[53–58] The