



Title	Luminescent Europium(III) Coordination Zippers Linked with Thiophene-Based Bridges
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# Luminescent Eu<sup>III</sup> coordination zippers linked with thiophene-based bridges

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**Abstract:** Novel Eu<sup>III</sup> coordination polymers [Eu(hfa)<sub>3</sub>(dpt)]<sub>n</sub> (dpt: 2,5-bis(diphenylphosphoryl)thiophene) and [Eu(hfa)<sub>3</sub>(dpedot)]<sub>n</sub> (dpedot: 2,5-bis(diphenylphosphoryl)ethylenedioxythiophene) with hydrogen-bonded zipper structures are reported. The coordination polymers are composed of Eu<sup>III</sup> ions, hexafluoroacetylacetonato ligands, and thiophene-based phosphine oxide bridges. The zig-zag orientation of single polymer chains induced the formation of densely packed coordination structures with multiple intermolecular interactions, resulting in thermal stability above 300°C. They exhibit a high intrinsic emission quantum yield (~80%) due to their asymmetrical and low-vibrational coordination structures around Eu<sup>III</sup> ions. In addition, the characteristic alternative orientation of substituents also contributes to the dramatically high ligand-to-metal energy transfer efficiencies of up to 80% in solid state.

The development of luminescent molecular materials with high quantum efficiencies is required for applications in bioassays, light-emitting devices, and chemical and physical sensors.<sup>[1]</sup> There have been many reports on luminescent organic and coordination compounds. Swager and co-workers developed amplifying fluorescent conjugated polymers for biological and chemical sensors such as highly explosive trinitrotoluene in seawater.<sup>[2]</sup> Adachi et al. demonstrated very high phosphorescence efficiency of Ir<sup>III</sup> coordination compounds in organic light-emitting devices.<sup>[3]</sup>

Among these materials, lanthanide coordination compounds are promising candidates for pure and strong luminophores due to their versatile photophysical properties derived from the 4f-4f transitions in lanthanide (Ln<sup>III</sup>) ions.<sup>[4]</sup> Ln<sup>III</sup> ions, however, show small absorption coefficients ( $\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$ ), and various organic chromophores such as  $\beta$ -diketonates and pyridine-based ligands have been developed to sensitize the luminescence of Ln<sup>III</sup> ions.<sup>[5]</sup> These organic compounds with  $\pi$  conjugation systems are referred to as light-harvesting antenna ligands. The overall emission quantum yields of Ln<sup>III</sup> compounds are described as

$$\Phi_{\text{total}} = \Phi_{\text{ff}} \times \eta_{\text{sens}} = \frac{k_r}{k_r + k_{\text{nr}}} \times \eta_{\text{sens}} \cdots (1)$$

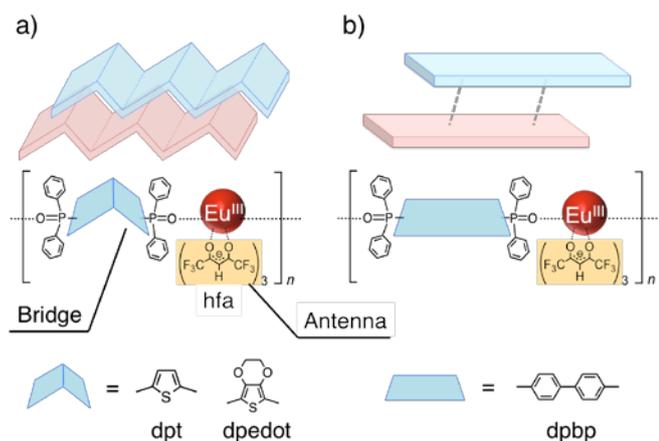
where  $\Phi_{\text{ff}}$  is Ln<sup>III</sup>-centered emission quantum yield,  $\eta_{\text{sens}}$  is efficiency of the sensitization process, and  $k_r$  and  $k_{\text{nr}}$  are radiative and nonradiative rate constants, respectively.

Ln<sup>III</sup> coordination compounds with high  $\Phi_{\text{ff}}$  have been successfully synthesized by introducing asymmetric coordination structures, resulting in a large  $k_r$  value.<sup>[6]</sup> In order to improve thermal and photophysical properties of Ln<sup>III</sup> compounds for optical applications, Ln<sup>III</sup> coordination polymers with rigid multi-dimensional networks have been developed over the past two decades.<sup>[7]</sup> The rigid coordination structures can also contribute to strong emission by suppressing a non-emissive process ( $k_{\text{nr}}$ ) associated with vibrational relaxation.

The antenna and bridging ligands in Ln<sup>III</sup> coordination polymers dominate their photophysical and thermodynamic properties. Bünzli and co-workers reported that Eu<sup>III</sup> coordination polymers with low-vibrational frequency hfa and carboxylic bridging ligands showed very large  $\Phi_{\text{ff}}$ .<sup>[8]</sup> We previously reported that Ln<sup>III</sup> coordination polymers with hfa ligands and bidentate phosphine oxide bridges exhibit thermal stability at temperatures above 300°C and high emission quantum efficiency ( $\Phi_{\text{ff}} \sim 70\%$ ) induced by a low-vibrational coordination environment.<sup>[9]</sup> The intermolecular networks are fabricated through noncovalent interactions such as aromatic CH/ $\pi$  and CH/F hydrogen bonds. However, their  $\eta_{\text{sens}}$  are estimated to be approximately 50%. Ln<sup>III</sup> coordination polymers with high  $\eta_{\text{sens}}$  are required for ideal optical devices.

Here we focus on specific intra-ligand charge transfer (ILCT) states via charge redistribution of the hfa ligands in Ln<sup>III</sup> coordination polymers for enhancement of the energy transfer efficiency. ILCT states are found under the specific packing structures and are known to contribute to the photosensitized emission process in Ln<sup>III</sup> complexes.<sup>[10]</sup> Eliseeva and co-workers recently reported that the formation of low-lying ILCT states contributes to the improvement of ligand-to-metal energy transfer efficiency.<sup>[11]</sup> Our group has also demonstrated effective photosensitized luminescence of Eu<sup>III</sup> coordination polymers through the ILCT band.<sup>[12]</sup> The formation of an ILCT band should affect the efficiency of energy transfer from ligands to Ln<sup>III</sup> ions in solid systems. A dense and tight coordination structure in crystal units may induce the formation of ILCT states, leading to high emission quantum yields. We consider that luminescent Ln<sup>III</sup> coordination polymers with a characteristic ILCT band can be constructed by a zig-zag chained polymer, "coordination zipper."

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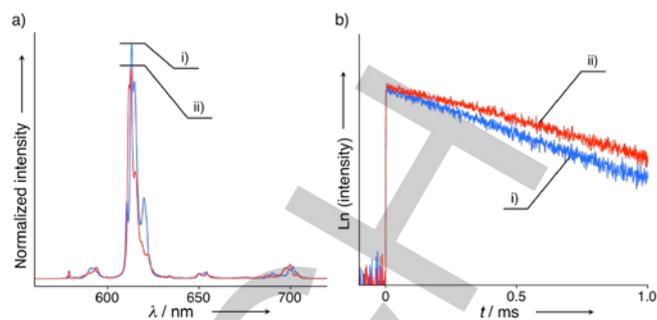
**Figure 1.** Schematic diagram of a)  $\text{Eu}^{\text{III}}$  coordination zippers with thiophene-based bridges and b)  $\text{Eu}^{\text{III}}$  coordination polymer with biphenylne bridge.

In this study, a zig-zag  $\text{Eu}^{\text{III}}$  coordination polymer with high intrinsic emission quantum yields (> 75%), high energy transfer efficiency (80%) and thermal stability up to 320°C was successfully constructed (Figure 1). We used hexafluoroacetylacetonate (hfa) for ideal antenna ligands, and we designed novel thiophene-based bridging ligands for a close-packed coordination system. The novel packing system, “coordination zipper,” should induce more dense coordination structures for higher efficiencies of ligand-to-metal energy transfer due to the ILCT between antenna ligands. Thiophene derivatives were selected as ideal bridging ligands because of their aromaticity for rigidity, bite-angles and hetero S atom for a large dipole moment. Polar thiophene bridging ligands are expected to lead to a characteristic alternative orientation in polymer chains.

Thiophene-based bridging ligands, dpt and dpedot (Figure 1a), were synthesized by  $\alpha$ -substitution reaction of thiophene derivatives. Intermolecular CH/F and CH/ $\pi$  interactions were introduced through bridging ligands and antenna ligands. We also prepared an  $\text{Eu}^{\text{III}}$  coordination polymer with a linear-typed bridge ( $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$ ), Figure 1b). Their photophysical properties were estimated by UV/Vis absorption, emission, and excitation spectra. Thermal stability is discussed on the basis of results of TG-DTA analyses and single crystal X-ray analyses.  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  is one of the most emissive  $\text{Eu}^{\text{III}}$  coordination polymers with energy transfer efficiency of 80% and thermal stability above 300°C. The strategy of constructing “coordination zippers” has the potential for breaking new ground in highly luminescent and stable molecular materials.

The novel bridging ligands dpt, dpedot, and corresponding coordination zippers  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  and  $[\text{Eu}(\text{hfa})_3(\text{dpedot})]_n$  were prepared and identified by IR, mass spectroscopy, and elemental analyses (Scheme S1, Figure S1).

Steady-state emission spectra of the  $\text{Eu}^{\text{III}}$  coordination polymers in solid state are shown in Figure 2 and S2. The coordination zippers exhibit bright red luminescence.



**Figure 2.** a) Emission spectra excited at 380 nm and b) emission decay profiles excited at 355 nm for i)  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  (blue line) and ii)  $[\text{Eu}(\text{hfa})_3(\text{dpdp})]_n$  (red line) in solid state.

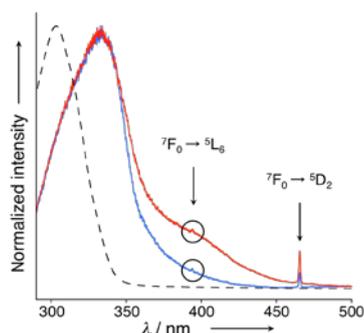
The photophysical parameters are summarized in Table 1. The  $\Phi_{\text{f}}$  values for both polymers were estimated to be as high as that of the previous coordination polymer  $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$ , indicating a low-vibrational coordination structure. The larger  $k_{\text{r}}$  values also indicate that the coordination geometries around  $\text{Eu}^{\text{III}}$  ions are greatly distorted. The most remarkable point is that both polymers exhibited large  $\Phi_{\text{total}}$  values (~ 60%) due to high  $\eta_{\text{sens}}$ .

**Table 1.** Photophysical parameters for  $\text{Eu}^{\text{III}}$  coordination polymers  $[\text{Eu}(\text{hfa})_3(\text{X})]_n$  in solid state.

X	$\Phi_{\text{tot}}$ / % <sup>[a]</sup>	$\Phi_{\text{f}}$ / % <sup>[b]</sup>	$\eta_{\text{sens}}$ / % <sup>[a]</sup>	$\tau_{\text{obs}}$ / ms <sup>[c]</sup>	$k_{\text{r}}$ / s <sup>-1</sup> <sup>[b]</sup>	$k_{\text{nr}}$ / s <sup>-1</sup> <sup>[b]</sup>
dpt	60	75	80	0.75	$1.0 \times 10^3$	$3.3 \times 10^2$
dpedot	56	85	66	0.93	$9.1 \times 10^2$	$1.6 \times 10^2$
dpbp <sup>[d]</sup>	29	72	40	0.85	$8.5 \times 10^2$	$3.2 \times 10^2$

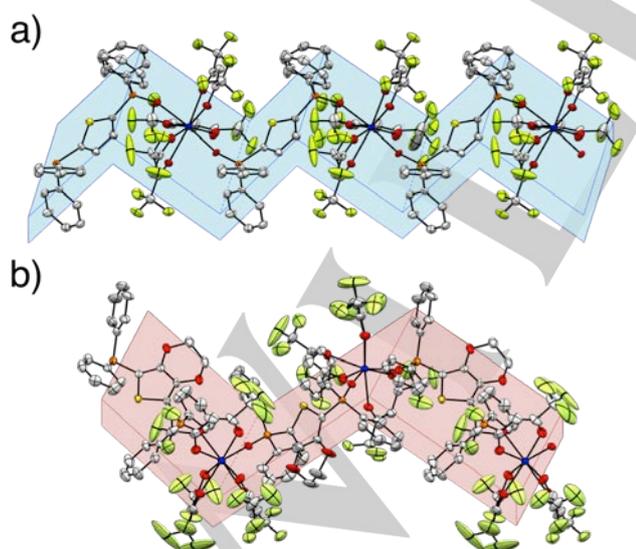
[a]  $\lambda_{\text{ex}} = 380$  nm. [b]  $\lambda_{\text{ex}} = 465$  nm, equation 2-4 (see supporting information). [c]  $\lambda_{\text{ex}} = 355$  nm. [d] Reference [9].

The  $\eta_{\text{sens}}$  of  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  and that of  $[\text{Eu}(\text{hfa})_3(\text{dpedot})]_n$  were estimated to be 80% and 66%. The high  $\eta_{\text{sens}}$  might be due to the formation of ILCT states induced by the densely packed zig-zag orientation. In order to confirm the formation of ILCT states, an absorption spectrum in methanol and diffuse reflectance spectra in solid state were measured (Figure 3). In  $10^{-5}$  M methanol solution,  $\pi$ - $\pi^*$  transition band of hfa was observed at around 300 nm. In solid state, both polymers exhibited large  $\pi$ - $\pi^*$  absorption bands at 330 nm and sharp and small absorption at 394 and 465 nm due to the  ${}^7\text{F}_0$ - ${}^5\text{L}_6$  and  ${}^7\text{F}_0$ - ${}^5\text{D}_2$  transition of  $\text{Eu}^{\text{III}}$  ions. We also found characteristic low-lying bands at around 400 nm, which might be assigned to ILCT states caused by the densely packed coordination structure.



**Figure 3.** An absorption spectrum in methanol ( $10^{-5}$  M for monomer, black dashed line) and a diffuse reflectance spectra of  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  (blue solid line) and  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$  (red solid line) in solid state.

The  $\eta_{\text{sens}}$  is considered to be linked to ILCT in solid state. Single crystals of both polymers were prepared to investigate the coordination structures. The crystal structures were determined to be typical 8-coordination with three hfa and two phosphine oxide ligands (Figure 4). First, we examined the coordination geometry around  $\text{Eu}^{\text{III}}$  ions based on the crystal data. In order to estimate the degree of distortion against 8-coordinated square-antiprismatic structure (8-SAP, point group:  $D_{4d}$ ) and 8-coordinated trigonal-dodecahedral structure (8-TDH, point group:  $D_{2d}$ ), the shape factor  $S^{[13]}$  was calculated (see supporting information). When assuming 8-SAP structure for  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$ , the  $S$  value is much smaller than that for 8-TDH ( $S_{8\text{-SAP}} = 5.13 < S_{8\text{-TDH}} = 10.6$ ), indicating that the coordination geometry is closer to 8-SAP than to 8-TDH. The geometry of  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  can be defined as distorted 8-SAP structure because of the close  $S$  values ( $S_{8\text{-SAP}} = 8.84$ ,  $S_{8\text{-TDH}} = 9.21$ ).



**Figure 4.** ORTEP drawings (showing 50% probability displacement ellipsoids) of a)  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  and b)  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$ .

Next, we focused on the orientations and interactions of polymer chains (Figure S5). The coordination zipper  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  showed highly ordered and densely packed structure with multiple intra- and inter-molecular CH/F interactions. The intermolecular CH/ $\pi$  interactions were also found. In the case of  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$ , intramolecular  $\pi/\pi$  interactions were observed, and the number of intermolecular CH/F interactions was much smaller than that for  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$ . The binding energies of CH/F and CH/ $\pi$  interactions are generally known to be 10–30 and 2–10  $\text{kJ mol}^{-1}$ , respectively.<sup>[14]</sup> Thus,  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  is highly zipped and shows large crystal density (Table S4), which would induce the formation of ILCT states.

TG-DTA analyses were performed to determine the thermal stability of coordination zippers (Figure S6). The decomposition point of  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  is estimated to be 322°C due to the multiple intermolecular CH/F interactions. The coordination zipper  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$  exhibits relatively low decomposition temperature as compared to the alternative orientation in single polymer chains. A small drop in the thermogravimetric curve is assumed to be responsible for degradation of the dioxane ring in bridging ligands.

We also estimated the dipole moment  $D$  of the bridging ligands using DFT calculations [B3LYP 6-31G (d)] based on the CIF data. Compared to the previous compound ( $[\text{Eu}(\text{hfa})_3(\text{dpbb})]_n$ ,  $D = 0.0005$ ), coordination zippers have large  $D$  values (1.1664 for  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  and 4.2992 for  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$ , respectively). The polar character of bridging ligands resulted in a characteristic alternative orientation of inter- or intra-polymer chains.  $\text{Eu}^{\text{III}}$  coordination polymers with larger  $D$  values were also found to show larger  $\Phi_{\text{ff}}$ . Mason and co-workers proposed the “ligand polarization” theory of 4f-4f hypersensitivity, which describes the relationship between induced dipole moment and dynamic coupling in the Judd-Ofelt theory.<sup>[15]</sup> The effect on dipole moment of the ligand in an  $\text{Ln}^{\text{III}}$  complex has also been reported<sup>[16]</sup>, and large dipole moment of the ligands should increase 4f-4f transition probability. The enhancement of  $\Phi_{\text{ff}}$  in  $\text{Eu}^{\text{III}}$  coordination zippers might be caused by the larger magnitude of the dipole moment in bridging ligands.

Highly emissive and thermally stable  $\text{Eu}^{\text{III}}$  coordination polymers  $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$  and  $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$  were successfully synthesized by introducing thiophene-based bridges. They exhibit bright red luminescence with energy transfer efficiency up to 80%. The efficient ligand-to-metal energy transfer is achieved by the formation of densely packed “coordination zipper” structures induced by the polar character of bridging ligands. Incorporation of thiophene-based bridges was also found to enhance the f-f transition of  $\text{Eu}^{\text{III}}$  ions.

In addition to the conventional molecular design of ligand field around  $\text{Ln}^{\text{III}}$  ions, we provided guidelines for a densely packed assembly of luminescent  $\text{Ln}^{\text{III}}$  coordination polymers. The reported strategy of constructing a “coordination zipper” would be advantageous for efficient energy transfer and strong luminescence in solid state, which can be employed in highly emissive and stable materials for displays and lightings.

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**Keywords:** europium • luminescence • coordination polymer • energy transfer • thermal stability

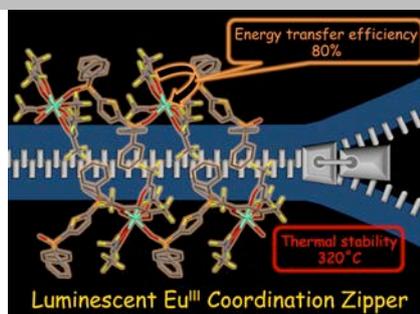
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**Entry for the Table of Contents**

Layout 1:

**COMMUNICATION**

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