



Title	Luminescent Europium(III) Coordination Zippers Linked with Thiophene-Based Bridges
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Luminescent Eu^{III} coordination zippers linked with thiophene-based bridges

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Abstract: Novel Eu^{III} coordination polymers [Eu(hfa)₃(dpt)]_n (dpt: 2,5-bis(diphenylphosphoryl)thiophene) and [Eu(hfa)₃(dpdot)]_n (dpdot: 2,5-bis(diphenylphosphoryl)ethylenedioxythiophene) with hydrogen-bonded zipper structures are reported. The coordination polymers are composed of Eu^{III} 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^{III} 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.^[1] 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.^[2] Adachi et al. demonstrated very high phosphorescence efficiency of Ir^{III} coordination compounds in organic light-emitting devices.^[3]

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^{III}) ions.^[4] Ln^{III} ions, however, show small absorption coefficients ($\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$), and various organic chromophores such as β -diketonates and pyridine-based ligands have been developed to sensitize the luminescence of Ln^{III} ions.^[5] These organic compounds with π conjugation systems are referred to as light-harvesting antenna ligands. The overall emission quantum yields of Ln^{III} 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 Φ_{ff} is Ln^{III}-centered emission quantum yield, η_{sens} is efficiency of the sensitization process, and k_r and k_{nr} are radiative and nonradiative rate constants, respectively.

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

The antenna and bridging ligands in Ln^{III} coordination polymers dominate their photophysical and thermodynamic properties. Bünzli and co-workers reported that Eu^{III} coordination polymers with low-vibrational frequency hfa and carboxylic bridging ligands showed very large Φ_{ff} .^[8] We previously reported that Ln^{III} 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.^[9] The intermolecular networks are fabricated through noncovalent interactions such as aromatic CH/ π and CH/F hydrogen bonds. However, their η_{sens} are estimated to be approximately 50%. Ln^{III} coordination polymers with high η_{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^{III} 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^{III} complexes.^[10] 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.^[11] Our group has also demonstrated effective photosensitized luminescence of Eu^{III} coordination polymers through the ILCT band.^[12] The formation of an ILCT band should affect the efficiency of energy transfer from ligands to Ln^{III} 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^{III} coordination polymers with a characteristic ILCT band can be constructed by a zig-zag chained polymer, "coordination zipper."

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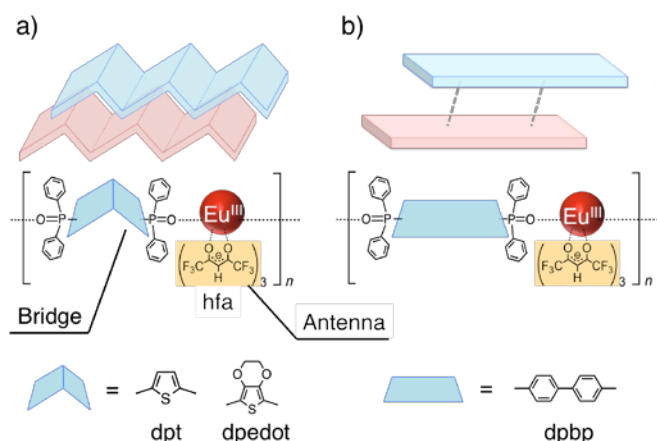


Figure 1. Schematic diagram of a) Eu^{III} coordination zippers with thiophene-based bridges and b) Eu^{III} coordination polymer with biphenylene bridge.

In this study, a zig-zag Eu^{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 dpdot (Figure 1a), were synthesized by α -substitution reaction of thiophene derivatives. Intermolecular CH/F and CH/ π interactions were introduced through bridging ligands and antenna ligands. We also prepared an Eu^{III} coordination polymer with a linear-typed bridge ($[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$ [9], 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 Eu^{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, dpdot, and corresponding coordination zippers $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dpdot})]_n$ were prepared and identified by IR, mass spectroscopy, and elemental analyses (Scheme S1, Figure S1).

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

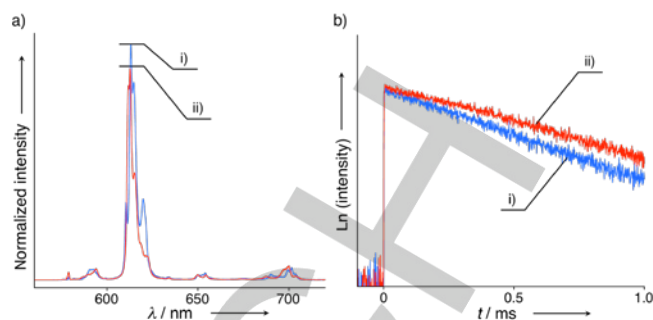


Figure 2. a) Emission spectra excited at 380 nm and b) emission decay profiles excited at 355 nm for i) $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$ (blue line) and ii) $[\text{Eu}(\text{hfa})_3(\text{dpdot})]_n$ (red line) in solid state.

The photophysical parameters are summarized in Table 1. The Φ_{IT} 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_{r} values also indicate that the coordination geometries around Eu^{III} ions are greatly distorted. The most remarkable point is that both polymers exhibited large Φ_{total} values ($\sim 60\%$) due to high η_{sens} .

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

X	Φ_{tot} / % [a]	Φ_{IT} / % [b]	η_{sens} / % [a]	τ_{obs} / ms [c]	k_{r} / s^{-1} [b]	k_{nr} / s^{-1} [b]
dpt	60	75	80	0.75	1.0×10^3	3.3×10^2
dpdot	56	85	66	0.93	9.1×10^2	1.6×10^2
dpbp [d]	29	72	40	0.85	8.5×10^2	3.2×10^2

[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 η_{sens} of $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$ and that of $[\text{Eu}(\text{hfa})_3(\text{dpdot})]_n$ were estimated to be 80% and 66%. The high η_{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, π - π^* transition band of hfa was observed at around 300 nm. In solid state, both polymers exhibited large π - π^* 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 Eu^{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.

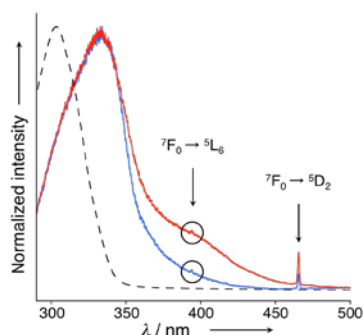


Figure 3. An absorption spectrum in methanol (10^{-5} M for monomer, black dashed line) and a diffuse reflectance spectra of $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$ (blue solid line) and $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$ (red solid line) in solid state.

The η_{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 Eu^{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 ($S_{8\text{-SAP}} = 8.84$, $S_{8\text{-TDH}} = 9.21$).

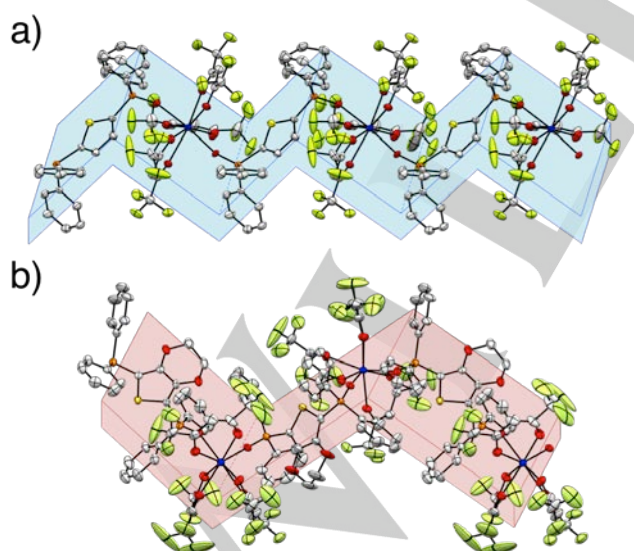


Figure 4. ORTEP drawings (showing 50% probability displacement ellipsoids) of a) $[\text{Eu}(\text{hfa})_3(\text{dpt})]_n$ and b) $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$.

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/ π interactions were also found. In the case of $[\text{Eu}(\text{hfa})_3(\text{dpedit})]_n$, intramolecular π/π 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/ π interactions are generally known to be 10–30 and 2–10 kJ mol^{-1} , respectively.^[14] 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 ($[\text{Eu}(\text{hfa})_3(\text{dpbbp})]_n$, $D = 0.0005$), 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. Eu^{III} coordination polymers with larger D values were also found to show larger Φ_{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.^[15] The effect on dipole moment of the ligand in an Ln^{III} complex has also been reported^[16], and large dipole moment of the ligands should increase 4f-4f transition probability. The enhancement of Φ_{ff} in Eu^{III} coordination zippers might be caused by the larger magnitude of the dipole moment in bridging ligands.

Highly emissive and thermally stable Eu^{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 Eu^{III} ions.

In addition to the conventional molecular design of ligand field around Ln^{III} ions, we provided guidelines for a densely packed assembly of luminescent Ln^{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

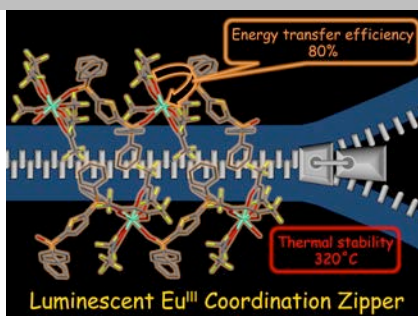
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Entry for the Table of Contents

Layout 1:

COMMUNICATION

Luminescent Eu^{III} coordination polymers with high energy transfer efficiency (80%) and thermal stability up to 320 °C were successfully fabricated by introducing densely packed "coordination zipper" structure.



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Page No. – Page No.

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