Luminescent Eu\textsuperscript{III} coordination zippers linked with thiophene-based bridges

Yuichi Hirai, Takayuki Nakanishi, Yuichi Kitagawa, Koji Fushimi, Tomohiro Seki, Hajime Ito, Yasuchika Hasegawa

Abstract: Novel Eu\textsuperscript{III} coordination polymers [Eu(hfa)\textsubscript{3}(dpt)], (dpt: 2,5-bis(diphenylphosphoryl)thiophene) and [Eu(hfa)\textsubscript{3}(dpedot)], (doped: 2,5-bis(diphenylphosphoryl)ethylenedioxythiophene) with hydrogen-bonded zipper structures are reported. The coordination polymers are composed of Eu\textsuperscript{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\textsuperscript{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 biosensors, 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\textsuperscript{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\textsuperscript{III}) ions.\[4\] Ln\textsuperscript{III} 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\textsuperscript{III} ions.\[5\] These organic compounds with \(\pi\) conjugation systems are referred to as light-harvesting antenna ligands. The overall emission quantum yields of Ln\textsuperscript{III} compounds are described as

\[
\Phi_{\text{overall}} = \Phi_{\text{ff}} \times \eta_{\text{sens}} = \frac{k_r}{k_r + k_{nr}} \times \eta_{\text{sens}} \quad \text{(1)}
\]

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

Ln\textsuperscript{III} coordination compounds with high \(\Phi_{\text{ff}}\) 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\textsuperscript{III} compounds for optical applications, Ln\textsuperscript{III} coordination polymers with rigid multidimensional 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\textsuperscript{III} coordination polymers dominate their photophysical and thermodynamic properties. Bünzli and co-workers reported that Eu\textsuperscript{III} coordination polymers with low-vibrational frequency hfa and carboxylic bridging ligands showed very large \(\Phi_{\text{ff}}\).\[8\] We previously reported that Ln\textsuperscript{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/\pi and CH/F hydrogen bonds. However, their \(\eta_{\text{sens}}\) are estimated to be approximately 50%. Ln\textsuperscript{III} 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\textsuperscript{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\textsuperscript{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\textsuperscript{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\textsuperscript{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\textsuperscript{III} coordination polymers with a characteristic ILCT band can be constructed by a zig-zag chained polymer, "coordination zipper."
In this study, a zig-zag EuIII 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 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 EuIII coordination polymer with a linear-typed bridge ([Eu(hfa)3(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. [Eu(hfa)3(dpt)], is one of the most emissive EuIII 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 photophysical parameters are summarized in Table 1. The Φ_e values for both polymers were estimated to be as high as that of the previous coordination polymer [Eu(hfa)3(dpbp)]_n, indicating a low-vibrational coordination structure. The larger k_r values also indicate that the coordination geometries around EuIII ions are greatly distorted. The most remarkable point is that both polymers exhibited large Φ_total values (~ 60%) due to high η_sens.

<table>
<thead>
<tr>
<th>X</th>
<th>Φ_ex / %</th>
<th>Φ_τ / %</th>
<th>η_sens / %</th>
<th>τ_obs / ms</th>
<th>k_r / s^-1</th>
<th>k_nr / s^-1</th>
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<tr>
<td>dpt</td>
<td>60</td>
<td>75</td>
<td>80</td>
<td>0.75</td>
<td>1.0 × 10^3</td>
<td>3.3 × 10^2</td>
</tr>
<tr>
<td>dpedot</td>
<td>56</td>
<td>65</td>
<td>66</td>
<td>0.93</td>
<td>9.1 × 10^2</td>
<td>1.6 × 10^2</td>
</tr>
<tr>
<td>dpbp</td>
<td>29</td>
<td>72</td>
<td>40</td>
<td>0.85</td>
<td>8.5 × 10^2</td>
<td>3.2 × 10^2</td>
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The η_sens of [Eu(hfa)3(dpt)]_n and that of [Eu(hfa)3(dpedot)]_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 7F0-5L6 and 7F0-5D2 transition of EuIII 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.

Table 1. Photophysical parameters for EuIII coordination polymers [Eu(hfa)3(X)]_n, 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 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 $S$ was calculated (see supporting information). When assuming 8-SAP structure for [Eu(hfa)$_3$(dpt)]$_n$, 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 [Eu(hfa)$_3$(dpt)]$_n$ can be defined as distorted 8-SAP structure because of the close $S$ values ($S_{8\text{-SAP}} = 8.84$, $S_{8\text{-TDH}} = 9.21$).

Next, we focused on the orientations and interactions of polymer chains (Figure S5). The coordination zipper [Eu(hfa)$_3$(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 [Eu(hfa)$_3$(dpedot)]$_n$, intramolecular $\pi$/$\pi$ interactions were observed, and the number of intermolecular CH/F interactions was much smaller than that for [Eu(hfa)$_3$(dpt)]$_n$. The binding energies of CH/F and CH/$\pi$ interactions are generally known to be 10-30 and 2-10 kJ mol$^{-1}$, respectively.$^{[14]}$ Thus, [Eu(hfa)$_3$(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 [Eu(hfa)$_3$(dpt)]$_n$ is estimated to be 322°C due to the multiple intermolecular CH/F interactions. The coordination zipper [Eu(hfa)$_3$(dpedot)]$_n$ 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 ([Eu(hfa)$_3$(dpbp)]$_n$, $D = 0.0005$), coordination zippers have large $D$ values (1.1664 for [Eu(hfa)$_3$(dpt)]$_n$ and 4.2992 for [Eu(hfa)$_3$(dpedot)]$_n$, 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 $\Phi_F$. 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 $\Phi_F$ 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 [Eu(hfa)$_3$(dpt)]$_n$ and [Eu(hfa)$_3$(dpedot)]$_n$ 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 luminescence 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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Luminescent Eu\textsuperscript{III} coordination polymers with high energy transfer efficiency (80\%) and thermal stability up to 320\(^\circ\)C were successfully fabricated by introducing densely packed “coordination zipper” structure.

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