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 $[Eu(hfa)_3(dpedot)]_n$ (dpedot: 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 (ε < 10 M^{-1} 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

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

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 (Φ_{ff} ~ 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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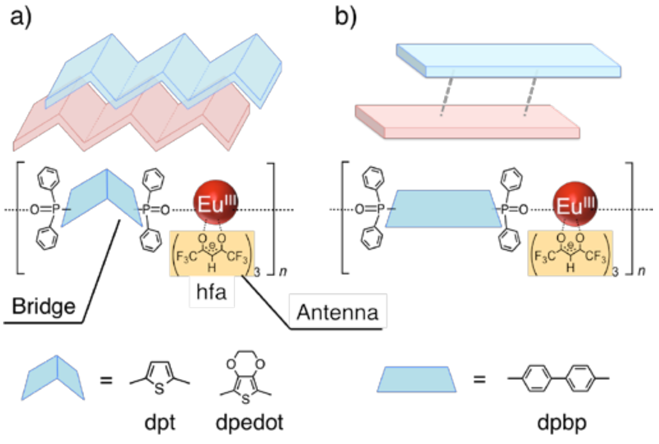

Figure 1. Schematic diagram of a) Eu^{III} coordination zippers with thiophene-based bridges and b) Eu^{III} coordination polymer with biphenylne bridge.

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 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 Eu^{III} coordination polymer with a linear-typed bridge ([Eu(hfa)$_3$(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. [Eu(hfa)$_3$(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, dpedot, and corresponding coordination zippers [Eu(hfa)$_3$(dpt)]$_n$ and [Eu(hfa)$_3$(dpedot)]$_n$ 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.

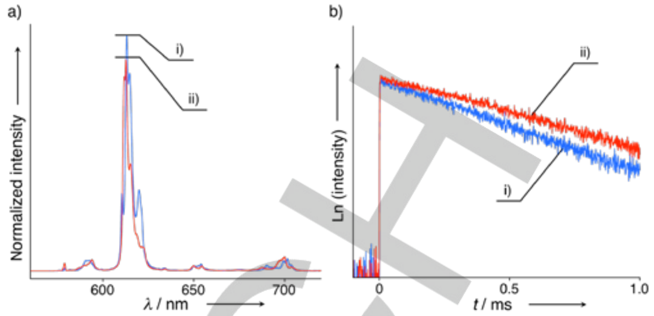

Figure 2. a) Emission spectra excited at 380 nm and b) emission decay profiles excited at 355 nm for i) [Eu(hfa)$_3$(dpt)]$_n$ (blue line) and ii) [Eu(hfa)$_3$(dpedot)]$_n$ (red line) in solid state.

The photophysical parameters are summarized in Table 1. The Φ_{ff} 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 Eu^{III} ions are greatly distorted. The most remarkable point is that both polymers exhibited large Φ_{total} values (~ 60%) due to high η_{sens}.

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

X	Φ_{tot} / % [a]	Φ_{ff} / % [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
dpedot	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] λ_{ex} = 380 nm. [b] λ_{ex} = 465 nm, equation 2-4 (see supporting information). [c] λ_{ex} = 355 nm. [d] Reference [9].

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 $^7F_0$-$^5L_6$ and $^7F_0$-$^5D_2$ 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.

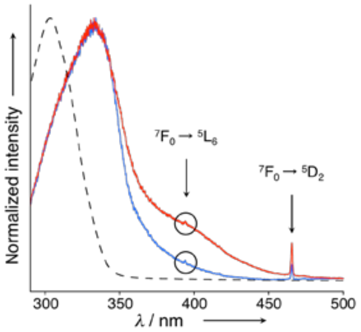

Figure 3. An absorption spectrum in methanol (10^{-5} M for monomer, black dashed line) and a diffuse reflectance spectra of [Eu(hfa)$_3$(dpt)]$_n$ (blue solid line) and [Eu(hfa)$_3$(dpedot)]$_n$ (red solid line) in solid state.

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 distorsion 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 [Eu(hfa)$_3$(dpedot)]$_n$, 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).

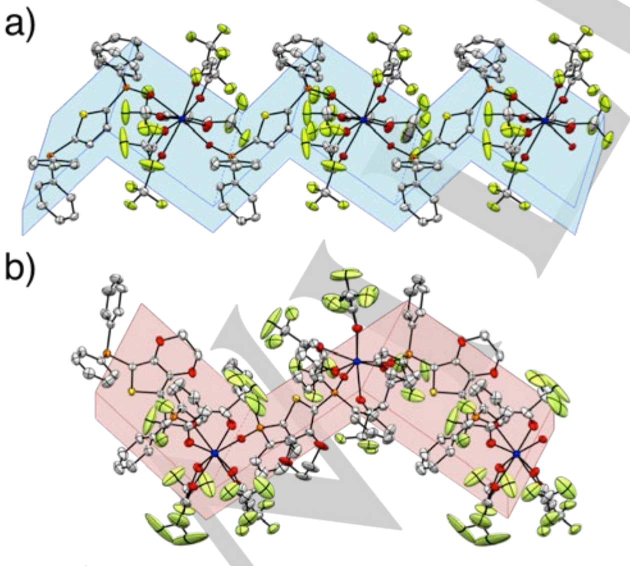

Figure 4. ORTEP drawings (showing 50% probability displacement ellipsoids) of a) [Eu(hfa)$_3$(dpt)]$_n$ and b) [Eu(hfa)$_3$(dpedot)]$_n$.

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/π interactions were also found. In the case of [Eu(hfa)$_3$(dpedot)]$_n$, intramolecular π/π 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/π 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 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 [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 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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Layout 1:

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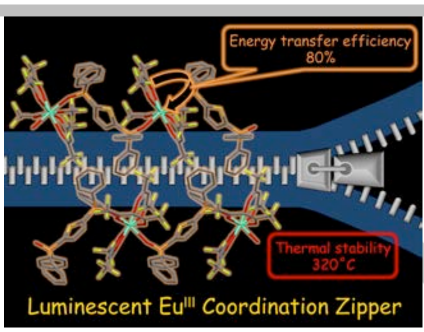

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