Coordination Polymers

Deutsche Ausgabe: DOI: 10.1002/ange.201606371
Internationale Ausgabe: DOI: 10.1002/anie.201606371

Luminescent Europium(III) Coordination Zippers Linked with Thiophene-Based Bridges

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

***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 (ca. 80%) due to their asymmetrical and low-vibrational coordination structures around Eu^{III} ions. Furthermore, the characteristic alternative orientation of substituents also contributes to the dramatically high ligand-to-metal energy transfer efficiencies of up to 80% in the 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 ($\varepsilon < 10\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), 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:

$$\Phi_{\mathrm{total}} = \Phi_{\mathrm{ff}}\eta_{\mathrm{sens}} = \frac{k_{\mathrm{r}}}{k_{\mathrm{r}} + k_{\mathrm{nr}}}\eta_{\mathrm{sens}} \quad (1)$$

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] 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 ($\Phi_{\mathrm{ff}} \approx 70\%$) 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} coordi-

---

[*] Y. Hirai
Graduate School of Chemical Sciences and Engineering
Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Sapporo, Hokkaido, 060-8628 (Japan)
Dr. T. Nakanishi, Dr. Y. Kitagawa, Dr. K. Fushimi, Dr. T. Seki,
Prof. Dr. H. Ito, Prof. Dr. Y. Hasegawa
Faculty of Engineering, Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Sapporo, Hokkaido, 060–8628 (Japan)
E-mail: hasegaway@eng.hokudai.ac.jp

Supporting information for this article can be found under:
http://dx.doi.org/10.1002/anie.201606371.

nation polymers with a characteristic ILCT band can be constructed by a zig-zag chained polymer, or coordination zipper.

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, the 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.

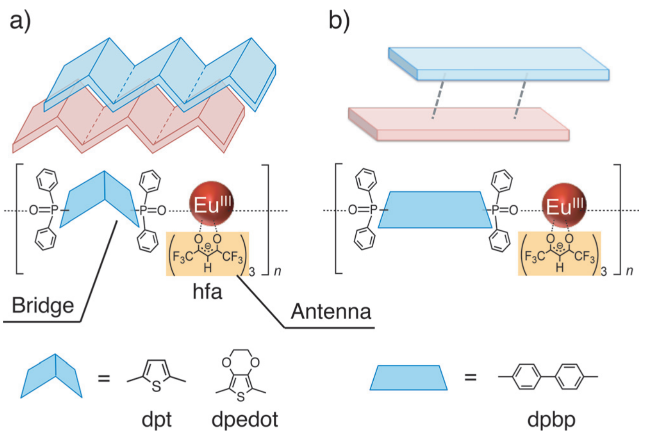

Figure 1. Diagram of a) Eu^{III} coordination zippers with thiophene-based bridges and b) Eu^{III} coordination polymer with biphenylne bridge.

Thiophene-based bridging ligands, dpt and dpedot (Figure 1 a), 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 1 b). 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 an 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 spectrometry, and elemental analysis (Supporting Information, Scheme S1, Figure S1).

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

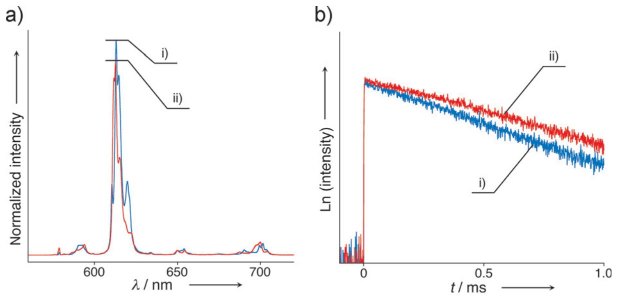

Figure 2. a) Emission spectra excited at 380 nm and b) emission decay profiles excited at 355 nm for i) $[Eu(hfa)_3(dpt)]_n$ (blue line) and ii) $[Eu(hfa)_3(dpedot)]_n$ (red line) in solid state.

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] $\lambda_{ex} = 380$ nm. [b] $\lambda_{ex} = 465$ nm, equation 2–4 (see the Supporting Information). [c] $\lambda_{ex} = 355$ nm. [d] Reference [9].

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 (ca. 60 %) due to high η_{sens}.

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. 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, a π–π* transition band of hfa was observed at around 300 nm. In the solid state, both polymers exhibited large π–π* absorption bands at 330 nm and sharp and small absorptions 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.

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

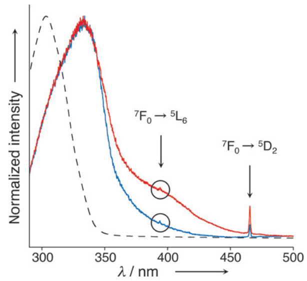

Figure 3. An absorption spectrum in methanol (10^{-5} M for monomer, black dashed line) and a diffuse reflectance spectra of [Eu(hfa)$_3$(dpt)]$_n$ (blue solid line) and [Eu(hfa)$_3$(dpedot)]$_n$ (red solid line) in solid state.

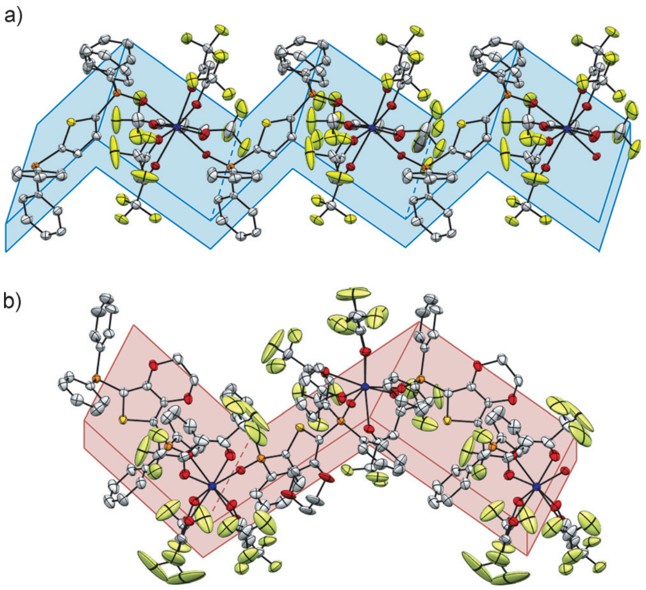

Figure 4. ORTEP drawings (ellipsoids set at 50% probability) of a) [Eu(hfa)$_3$(dpt)]$_n$ and b) [Eu(hfa)$_3$(dpedot)]$_n$.[17]

the coordination geometry around Eu^{III} ions based on the crystal data. 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 the 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 ($S_{8\text{-SAP}} = 8.84$, $S_{8\text{-TDH}} = 9.21$).

Next, we focused on the orientations and interactions of polymer chains (Supporting Information, Figure S5). The coordination zipper [Eu(hfa)$_3$(dpt)]$_n$ showed highly ordered and densely packed structure with multiple intra- and intermolecular 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 (Supporting Information, Table S4), which would induce the formation of ILCT states.

TG-DTA analyses were performed to determine the thermal stability of coordination zippers (Supporting Information, 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.

In conclusion, 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.

Along with the conventional molecular design of ligand fields around Ln^{III} ions, we have 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 the solid state, which can be employed in highly emissive and stable materials for displays and lighting.

Acknowledgements

We appreciate RIGAKU Co., Application Laboratories, and Frontier Chemistry Center Akira Suzuki "Laboratories for Future Creation" Project. This work was partly supported by Grants-in-Aid for Scientific Research on Innovative Areas of

"New Polymeric Materials Based on Element-Blocks (no. 2401)" (no. 24102012) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Keywords: coordination polymers · energy transfer · europium · luminescence · thermal stability

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 12059–12062
Angew. Chem. **2016**, *128*, 12238–12241

[1] a) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539–541; b) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99–117; c) E. G. Moore, A. P. S. Samuel, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 542–552; d) S. V. Eliseeva, J. C. G. Bunzli, *Chem. Soc. Rev.* **2010**, *39*, 189–227; e) M. Schäferling, *Angew. Chem. Int. Ed.* **2012**, *51*, 3532–3554; *Angew. Chem.* **2012**, *124*, 3590–3614; f) J. F. Callan, A. P. de Silva, D. C. Magri, *Tetrahedron* **2005**, *61*, 8551–8588; g) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566.

[2] S. W. Thomas, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339–1386.

[3] C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2001**, *90*, 5048–5051.

[4] a) A. de Bettencourt-Dias, *Dalton Trans.* **2007**, *22*, 2229–2241; b) J. C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048–1077; c) K. Binnemans, *Chem. Rev.* **2009**, *109*, 4283–4374; d) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger, F. M. Pfeffer, *Coord. Chem. Rev.* **2006**, *250*, 3094–3117.

[5] a) G. E. Khalil, K. Lau, G. D. Phelan, B. Carlson, M. Gouterman, J. B. Callis, L. R. Dalton, *Rev. Sci. Instrum.* **2004**, *75*, 192–206; b) N. B. D. Lima, S. M. C. Goncalves, S. A. Junior, A. M. Simas, *Sci. Rep.* **2013**, *3*, 2395; c) A. de Bettencourt-Dias, P. S. Barber, S. Viswanathan, *Coord. Chem. Rev.* **2014**, *273*, 165–200; d) L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, *Coord. Chem. Rev.* **2010**, *254*, 487–505.

[6] a) K. Binnemans, R. Van Deun, C. Gorller-Walrand, S. R. Collinson, F. Martin, D. W. Bruce, C. Wickleder, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3753–3757; b) M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542–1548.

[7] a) H. B. Zhang, L. J. Zhou, J. Wei, Z. H. Li, P. Lin, S. W. Du, *J. Mater. Chem.* **2012**, *22*, 21210–21217; b) M. S. Liu, Q. Y. Yu, Y. P. Cai, C. Y. Su, X. M. Lin, X. X. Zhou, J. W. Cai, *Cryst. Growth Des.* **2008**, *8*, 4083–4091; c) J. Rocha, L. D. Carlos, F. A. A. Paz, D. Ananias, *Chem. Soc. Rev.* **2011**, *40*, 926–940.

[8] S. V. Eliseeva, D. N. Pleshkov, K. A. Lyssenko, L. S. Lepnev, J. C. G. Bunzli, N. P. Kuzminat, *Inorg. Chem.* **2010**, *49*, 9300–9311.

[9] K. Miyata, T. Ohba, A. Kobayashi, M. Kato, T. Nakanishi, K. Fushimi, Y. Hasegawa, *ChemPlusChem* **2012**, *77*, 277–280.

[10] A. D'Aleo, F. Pointillart, L. Ouahab, C. Andraud, O. Maury, *Coord. Chem. Rev.* **2012**, *256*, 1604–1620.

[11] a) S. V. Eliseeva, O. V. Kotova, F. Gumy, S. N. Semenov, V. G. Kessler, L. S. Lepnev, J. C. G. Bunzli, N. P. Kuzmina, *J. Phys. Chem. A* **2008**, *112*, 3614–3626; b) E. R. Trivedi, S. V. Eliseeva, J. Jankolovits, M. M. Olmstead, S. Petoud, V. L. Pecoraro, *J. Am. Chem. Soc.* **2014**, *136*, 1526–1534.

[12] Y. Hasegawa, R. Hieda, K. Miyata, T. Nakagawa, T. Kawai, *Eur. J. Inorg. Chem.* **2011**, 4978–4984.

[13] J. D. Xu, E. Radkov, M. Ziegler, K. N. Raymond, *Inorg. Chem.* **2000**, *39*, 4156–4164.

[14] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**.

[15] a) S. F. Mason, R. D. Peacock, B. Stewart, *Chem. Phys. Lett.* **1974**, *29*, 149–153; b) S. F. Mason, R. D. Peacock, B. Stewart, *Mol. Phys.* **1975**, *30*, 1829–1841.

[16] a) T. Nakagawa, Y. Hasegawa, T. Kawai, *J. Phys. Chem. A* **2008**, *112*, 5096–5103; b) Y. Hasegawa, N. Sato, Y. Hirai, T. Nakanishi, Y. Kitagawa, A. Kobayashi, M. Kato, T. Seki, H. Ito, K. Fushimi, *J. Phys. Chem. A* **2015**, *119*, 4825–4833.

[17] CCDC 1477386 ([Eu(hfa)$_3$(dpt)]$_n$) and 1048291 ([Eu(hfa)$_3$-(dpedot)]$_n$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Received: June 30, 2016