Modification of the luminescence spectra of chloro(tetrapyridylcyclotetramine)europium complexes by fine tuning of the Eu–Cl distance with outer-sphere counterions in the solid state, in a polymer matrix and in solution†‡

Atsushi Wada,[a] Masayuki Watanabe,[b] Yoshinori Yamanoi[a] and Hiroshi Nishihara*[a]

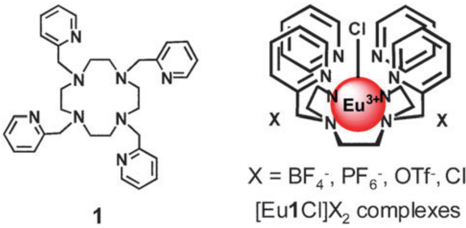
Received (in Cambridge, UK) 2nd November 2007, Accepted 18th January 2008
First published as an Advance Article on the web 6th February 2008
DOI: 10.1039/b716987f

Controlling the coordination environments and the luminescence properties of Eu^{3+} complexes with outer-sphere counterions was achieved in the solid state, in a polymer matrix and in solution.

Eu^{3+} complexes have attracted considerable interest because of their fascinating luminescence properties (high color purity and long lifetimes) and their potential application to luminescence devices (luminescent probes and biological sensors).[1] To improve the luminescence of the Eu^{3+} complexes, numerous studies have attempted to design ligands containing a transition band with large ε, which could populate the excited states of the Eu^{3+} ion and also encapsulate it to protect against the coordination of water molecules that would quench the luminescence.[2] More recent studies have attempted to improve the luminescence by controlling the coordination environments according to the Judd–Ofelt theory, which states that the luminescence is affected by the coordination environments around the Eu^{3+} ion.[3] Moreover, it is very compelling that the improvement was observed not only in the solid state but also in a polymer matrix and in solution, because Eu^{3+} complexes have been used in a wide range of applications, such as optoelectronic devices in the solid state, chemical and biological sensor sheets in a polymer matrix, and molecular imaging in solution.[4] However, to our knowledge, there has been no study in which the improvements were realized irrespective of the material state of the Eu^{3+} complexes. In this work, we have succeeded in gaining fine control over the coordination environments of Eu^{3+} complexes. We accomplished this by using an octadentate tetrapyridylcyclotetramine ligand, 1,4,7,10-tetrakis(2′-pyridylmethyl)-1,4,7,10-tetraazacyclododecane (**1**), which allowed us to realize a large variation in the luminescence properties by changing only the counterions in the outer sphere (Scheme 1). It should be noted that, although there have been several reports in which the luminescence properties were changed by counterions,[5] there has been no investigation into the effect of the counterions in the outer, rather than the inner sphere. In the present study, the strong effect of changing the counterions was not restricted to the solid state but also appeared in a polymer matrix and even in solution. The relationship between the coordination environments depending on the counterions and the luminescence was clarified based on the molecular structure.

The synthesis of a Eu^{3+} complex of **1**, [Eu**1**Cl](OTf)$_2$ (OTf = CF_3SO_3), was reported previously.[3e] [Eu**1**Cl]Cl$_2$ was obtained by the reaction of $EuCl_3{\cdot}6H_2O$ with one equivalent of **1** in MeOH. [Eu**1**Cl](BF_4)$_2$ and [Eu**1**Cl](PF_6)$_2$ were synthesized by mixing [Eu**1**Cl]Cl$_2$ with two equivalents of $AgBF_4$ and $AgPF_6$, respectively, in MeOH.

Single crystals of [Eu**1**Cl](BF_4)$_2$, [Eu**1**Cl](PF_6)$_2$, [Eu**1**Cl](OTf)$_2$ and [Eu**1**Cl]Cl$_2$ were obtained by recrystallization from acetonitrile–diethyl ether, and their structures were determined by X-ray structural analysis.[6] ORTEP drawings of the Eu^{3+} complexes are shown in Fig. 1. In all four Eu^{3+} complexes, the coordination number of the Eu(III) center was nine, with eight nitrogen atoms of **1** and one chlorine atom. Selected bond lengths for Eu^{3+} complexes are shown in Fig. 2 (further selected bond lengths, angles and dihedral angles are summarized in Table S2, ESI‡). For all [Eu**1**Cl]$^{2+}$ complexes with BF_4^-, PF_6^-, OTf^- and Cl^- as counterions, the Eu–N(pyridine) and Eu–N(amine) bond lengths were within the range of 2.540(7)–2.626(6) Å and 2.627(6)–2.703(6) Å, respectively, and the bond angles and dihedral angles showed



Scheme 1 Chemical structures of ligand **1** and [Eu**1**Cl]X$_2$ (X = BF_4^-, PF_6^-, OTf^-, Cl^-) complexes.

---

[a] Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan. E-mail: nisihara@chem.s.u-tokyo.ac.jp; Fax: (+81) 3-5841-8063; Tel: (+81) 3-5841-4346
[b] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai-mura, Ibaraki, 319-1195, Japan

† CCDC 641702 ([Eu**1**Cl]Cl$_2$), 673484 ([Eu**1**Cl](OTf)$_2$), 641703 ([Eu**1**Cl](PF_6)$_2$) and 641704 ([Eu**1**Cl](BF_4)$_2$). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716987f

‡ Electronic supplementary information (ESI) available: Crystallographic data (Table S1), selected bond lengths, angles and dihedral angles (Table S2), ESI MS data (Table S3), the relationship between the Eu–Cl bond length (Å) and the cell volume per formula unit (Fig. S1), emission spectra in PVC film (Fig. S2), and in CH_3CN (1.0×10^{-4} M) at 77 K (Fig. S3) of the Eu^{3+} complexes, UV absorption spectra of the Eu^{3+} complexes (Fig. S4) and experimental section. See DOI: 10.1039/b716987f

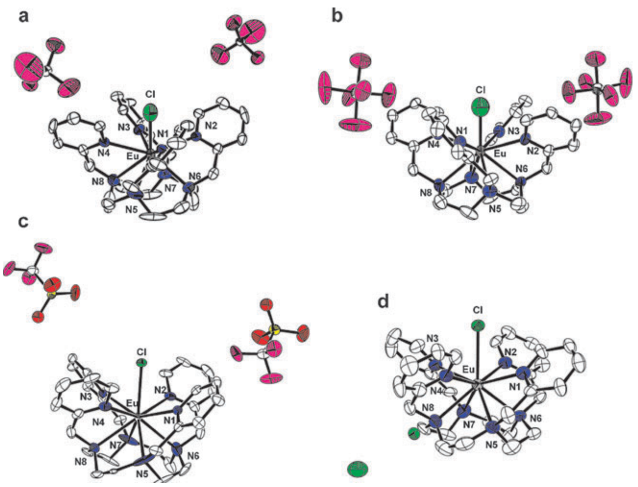


Fig. 1 ORTEP drawings of [Eu**1**Cl](BF_4)$_2$ (a), [Eu**1**Cl](PF_6)$_2$ (b), [Eu**1**Cl](OTf)$_2$ (c), and [Eu**1**Cl]Cl_2 (d) with 50% probability. H atoms have been omitted for clarity. Crystallographically, [Eu**1**Cl](BF_4)$_2$, [Eu**1**Cl](PF_6)$_2$ and [Eu**1**Cl](OTf)$_2$ have C_2 symmetry. For the purpose to compare their structures with [Eu**1**Cl]Cl_2 which has no C_2 symmetry, eight N atoms are labeled with different numbers in the figure (N1/N3, N2/N4, N5/N7 and N6/N8 in the figure are N1, N2, N3 and N4 in the CIFs, respectively).

little differences. Conversely, the Eu–Cl bond lengths differed significantly and became longer in the order of [Eu**1**Cl](BF_4)$_2$ (2.153(5) Å) < [Eu**1**Cl](PF_6)$_2$ (2.212(5) Å) < [Eu**1**Cl](OTf)$_2$ (2.725(2) Å) < [Eu**1**Cl]Cl_2 (2.763(3) Å). This difference is due to packing effects and/or electrostatic interaction effects, because there is no chemical interaction between the metal complex cation and counterions, and the Eu–Cl bond lengths became longer in the corresponding order with increasing unit cell volume per formula unit (Fig. S1, ESI‡).[7] Briefly, [Eu**1**Cl]$^{2+}$ formed isostructures regardless of the counterions used, whereas only the Eu–Cl bond length changed depending on the counterions in the outer sphere.

The luminescence spectra of the Eu^{3+} complexes in the solid state were measured at RT. The spectra for [Eu**1**Cl](BF_4)$_2$ and [Eu**1**Cl](PF_6)$_2$ displayed characteristic sharp and intense emission bands at 590 nm ($^5D_0 \rightarrow {}^7F_1$), 621 nm ($^5D_0 \rightarrow {}^7F_2$), 655 nm ($^5D_0 \rightarrow {}^7F_3$) and 698 nm ($^5D_0 \rightarrow {}^7F_4$), and those for [Eu**1**Cl](OTf)$_2$ and [Eu**1**Cl]Cl_2 displayed these bands at 594 nm ($^5D_0 \rightarrow {}^7F_1$), 618 nm ($^5D_0 \rightarrow {}^7F_2$), 650 nm ($^5D_0 \rightarrow {}^7F_3$) and 697 nm ($^5D_0 \rightarrow {}^7F_4$) by excitation of $\pi \rightarrow \pi^*$ transitions of the pyridine moieties at 260 nm (*antenna effect*) (Fig. 3(A)).[2,8] Their spectra and colors were significantly changed by changing the counterions in the outer sphere. For the luminescence of the Eu^{3+} ions, the $^5D_0 \rightarrow {}^7F_1$ transition is magnetic-dipolar in character, and its radiative transition probability is relatively independent of the coordination environments of the Eu^{3+} ions; in contrast, the $^5D_0 \rightarrow {}^7F_2$ transition is predominantly electric-dipolar in character, and the emission intensity is very sensitive to coordination environments (hypersensitive transition).[2,3] The relative intensities (I_{rel}) of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$

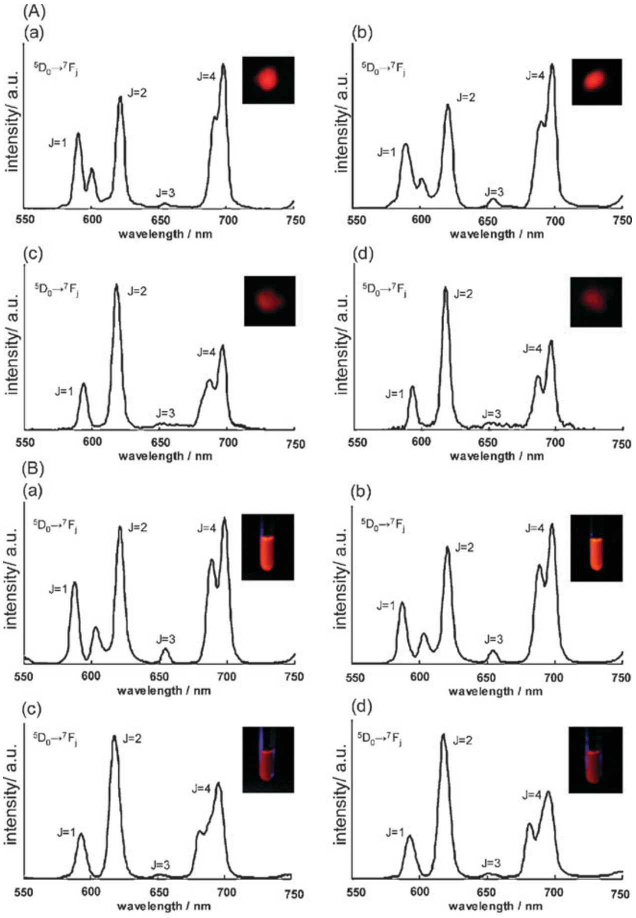


Fig. 3 (A) Emission spectra of [Eu**1**Cl](BF_4)$_2$ (a), [Eu**1**Cl](PF_6)$_2$ (b), [Eu**1**Cl](OTf)$_2$ (c) and [Eu**1**Cl]Cl_2 (d) in the solid state. (B) Emission spectra of [Eu**1**Cl](BF_4)$_2$ (a), [Eu**1**Cl](PF_6)$_2$ (b), [Eu**1**Cl](OTf)$_2$ (c) and [Eu**1**Cl]Cl_2 (d) in CH_3CN (1.0×10^{-4} M) at RT. Inset: images of the Eu^{3+} complexes under UV light (254 nm).

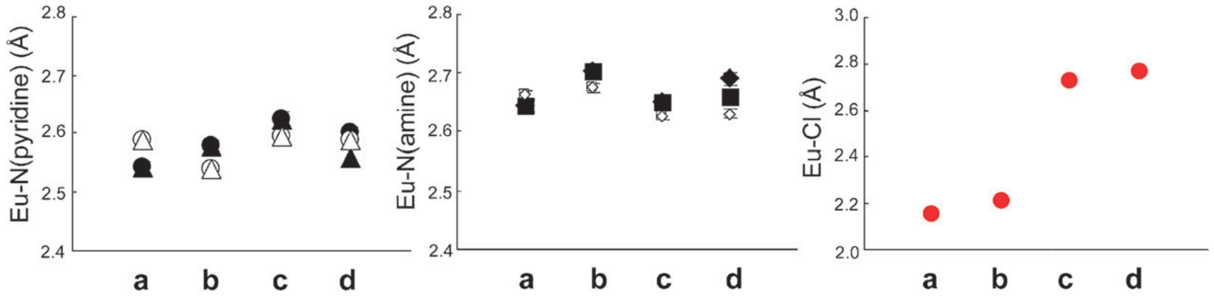


Fig. 2 Selected bond lengths (Å) for [Eu**1**Cl](BF_4)$_2$ (a), [Eu**1**Cl](PF_6)$_2$ (b), [Eu**1**Cl](OTf)$_2$ (c) and [Eu**1**Cl]Cl_2 (d): (●) Eu–N1, (○) Eu–N2, (▲) Eu–N3, (△) Eu–N4, (■) Eu–N5, (□) Eu–N6, (◆) Eu–N7, (◊) Eu–N8, (●) Eu–Cl.

Table 1 Relative intensities (I_{rel})[a] of [Eu**1**Cl]X_2 in the solid state, in a polymer matrix, and in solution at RT and 77 K, and quantum yields (Φ) of the Eu^{3+} complexes in CH_3CN at RT

	I_{rel}				
X	Solid	Polymer	CH_3CN (RT)	CH_3CN (77 K)	Φ (CH_3CN (RT))
BF_4^-	1.49	1.77	1.68	1.30	0.117
PF_6^-	1.59	2.16	1.89	1.81	0.075
OTf^-	3.14	3.43	3.12	2.37	0.024
Cl^-	3.34	3.53	3.34	2.68	0.017

[a] Relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition.

transition provide information about the coordination environments. The values of I_{rel} increased in the order of [Eu**1**Cl]$(BF_4)_2$ < Eu**1**Cl]$(PF_6)_2$ < [Eu**1**Cl](OTf)$_2$ < [Eu**1**Cl]Cl_2 (Table 1). This corresponds to the order of the Eu–Cl bond lengths described above. It is reasonable to interpret the spectral changes by the effect of the changes of the distance between the Eu^{3+} ion and the coordinating Cl^- with the counterions in the outer sphere.

This counterion effect on the luminescence was also observed in a polymer matrix and also in solution at RT and 77 K (Fig. 3(B) and Fig. S2 and S3, ESI‡). The Eu^{3+} complexes in poly(vinyl chloride) (PVC) film and in CH_3CN (1.0×10^{-4} M) showed that the values of I_{rel} increased in the same order, [Eu**1**Cl]$(BF_4)_2$ < [Eu**1**Cl]$(PF_6)_2$ < [Eu**1**Cl](OTf)$_2$ < [Eu**1**Cl]Cl_2. This suggests that the ion pairs existing in the polymer matrix and in solution dominate the luminescence properties to a considerable degree. This consideration is supported by the results of the ESI mass spectra of the four complexes, indicating that the ion pairs ability increases in the order, [Eu**1**Cl]$(BF_4)_2$ < [Eu**1**Cl]$(PF_6)_2$ < [Eu**1**Cl](OTf)$_2$ < [Eu**1**Cl]Cl_2 (Table S3, ESI‡).[9] The quantum yield values of the Eu^{3+} complexes in CH_3CN at RT were obtained. The values also changed significantly in the order of [Eu**1**Cl]Cl_2 < [Eu**1**Cl](OTf)$_2$ < [Eu**1**Cl]$(PF_6)_2$ < [Eu**1**Cl]$(BF_4)_2$, and the value for [Eu**1**Cl]$(BF_4)_2$ was about seven-fold larger than that for [Eu**1**Cl]Cl_2.

In conclusion, we have succeeded in obtaining fine control over the coordination environments and luminescence properties of Eu^{3+} complexes through an adjustment of the Eu–Cl bond length by changing only the counterions in the outer sphere. We have demonstrated that this counterion effect appears not only in the solid state but also in a polymer matrix and in solution. This result provides a new approach toward improving the luminescence properties of Eu^{3+} complexes irrespective of whether they are in the solid state, in a polymer matrix, or in solution.

Notes and references

1 (*a*) D. Parker, *Coord. Chem. Rev.*, 2000, **205**, 109; (*b*) J.-C. Bünzli and G. C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048; (*c*) J. Kido and Y. Okamoto, *Chem. Rev.*, 2002, **102**, 2357; (*d*) N. Weibel, L. J. Charbonnière, M. Guardigli, A. Roda and R. Ziessel, *J. Am. Chem. Soc.*, 2004, **126**, 4888; (*e*) M. Schäferling and O. Wolfbeis, *Chem.–Eur. J.*, 2007, **13**, 4342.

2 (*a*) J.-C. G. Bünzli and G. R. Choppin, *Lanthanide Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam, 1989, pp. 219–293; (*b*) N. Sabbatini, M. Guagliardi and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201; (*c*) N. Sabbatini, M. Guardigli and I. Manet, in *Handbook on the Physics and Chemistry of Rare Earth*, ed. K. A. Gschneidner, Jr. and L. Erying, Elsevier, Amsterdam, 1996, vol. 23, p. 69; (*d*) B. Alpha, R. Ballardini, V. Balzani, J.-M. Lehn, S. Perathoner and N. Sabbatini, *Photochem. Photobiol.*, 1990, **52**, 299.

3 (*a*) B. R. Judd, *Phys. Rev.*, 1962, **127**, 750; (*b*) G. S. Ofelt, *J. Chem. Phys.*, 1962, **37**, 511; (*c*) C. Görller-Warland and K. Binnemans, in *Handbook on the Physics and Chemistry of Rare Earth*, ed. K. A. Gschneidner, Jr. and L. Erying, Elsevier, Amsterdam, 1998, vol. 25, p. 101; (*d*) Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai and S. Yanagida, *J. Phys. Chem. A*, 2003, **107**, 1697; (*e*) A. Wada, M. Watanabe, Y. Yamanoi, T. Nankawa, K. Namiki, M. Yamasaki, M. Murata and H. Nishihara, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 335.

4 (*a*) M. Morimoto, S. Kobatake and M. Irie, *J. Am. Chem. Soc.*, 2003, **125**, 11080; (*b*) Y. Wada, M. Sato and Y. Tsukahara, *Angew. Chem., Int. Ed.*, 2006, **45**, 1925; (*c*) National Research Council Committee on Polymer Science and Engineering. *Polymer Science and Engineering: the Shifting Research Frontier*, National Academy Press, Washington, DC, 1994; (*d*) G. Vereb, E. Jares-Erijman, P. R. Selvin and T. M. Jovin, *Biophys. J.*, 1998, **74**, 2210; (*e*) M. Santos, B. C. Roy, H. Golcoechea, A. D. Campiglia and S. Mallik, *J. Am. Chem. Soc.*, 2004, **126**, 10738.

5 (*a*) F. Tanaka and S. Yamashita, *Inorg. Chem.*, 1984, **23**, 2044; (*b*) M. J. Lochhead, P. R. Wamsley and K. L. Bray, *Inorg. Chem.*, 1994, **33**, 2000; (*c*) A. M. Kłonkowski, S. Lis, M. Pietraszkiewicz, Z. Hnatejko, K. Czarnobaj and M. Elbanowski, *Chem. Mater.*, 2003, **15**, 656; (*d*) E. Guillet, D. Imbert, R. Scopelliti and J.-C. G. Bünzli, *Chem. Mater.*, 2004, **16**, 4063; (*e*) L. J. Charbonnière, R. Ziessel, M. Montalti, L. Prodi, N. Zaccheroni, C. Boehme and G. Wipff, *J. Am. Chem. Soc.*, 2002, **124**, 7779.

6 Crystallographic data and refinement information of [Eu**1**Cl]Cl_2, [Eu**1**Cl](OTf)$_2$, [Eu**1**Cl]$(PF_6)_2$ and [Eu**1**Cl]$(BF_4)_2$ are given in Table S1. CCDC 641702 ([Eu**1**Cl]Cl_2), 673484 ([Eu**1**Cl](OTf)$_2$), 641703 ([Eu**1**Cl]$(PF_6)_2$) and 641704 ([Eu**1**Cl]$(BF_4)_2$) contain the supplementary crystallographic data for this paper.

7 G. J. Grant, W. Chen, A. M. Goforth, C. L. Baucom, K. Patel, P. Repovic, D. G. VanDerveer and W. T. Pennington, *Eur. J. Inorg. Chem.*, 2005, 479.

8 M. Watanabe, T. Nankawa, T. Yamada, T. Kimura, K. Namiki, M. Murata, H. Nishihara and S. Tachimori, *Inorg. Chem.*, 2003, **42**, 6977.

9 (*a*) C. Airoldi, P. L. O. Volpe and A. P. Chagas, *Polyhedron*, 1982, **1**, 49; (*b*) P. L. O. Volpe, A. P. Chagas and C. Airoldi, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1321; (*c*) T. Yutaka, M. Kurihara, K. Kubo and H. Nishihara, *Inorg. Chem.*, 2000, **39**, 3438; (*d*) T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, K. Kubo, S. Furusho, K. Matsumura, N. Tamai and H. Nishihara, *Inorg. Chem.*, 2001, **40**, 4986; (*e*) E. Leize, A. V. Dorsselare, K. Roland and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 990; (*f*) S. F. Ralph, M. M. Sheil, L. A. Hick, J. G. Rodney and A. M. Sargeson, *J. Chem. Soc., Dalton Trans.*, 1996, 2307.