Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Modification of the Luminescence Spectra of Chloro(tetrapyridylcyclotetramine)europium Complexes by Fine Tuning of the Eu-Cl Distance with the Outer-sphere Counterions in the Solid State, in a Polymer Matrix, and in Solution

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Table S1[a] Crystallographic Data for [Eu**1**Cl]$(BF_4)_2$, [Eu**1**Cl]$(PF_6)_2$, [Eu**1**Cl]$(OTf)_2$, and [Eu**1**Cl]Cl_2.

	[Eu**1**Cl]$(BF_4)_2$	[Eu**1**Cl]$(PF_6)_2$	[Eu**1**Cl]$(OTf)_2$	[Eu**1**Cl]Cl_2
formula	$C_{32}H_{40}B_2ClEuF_8N_8$	$C_{32}H_{40}ClEuF_{12}N_8P_2$	$C_{34}H_{40}ClEuF_6N_8O_6S_2$	$C_{128}H_{160}Cl_{12}Eu_4N_{32}$ $(4(C_{32}H_{40}Cl_3EuN_8))$
mol wt	897.7	1014.1	1022.3	3180.2
crystal system	orthorhombic	orthorhombic	orthorhombic	cubic
space group	$I2_12_12_1$	$P22_12_1$	$P22_12_1$	$F432$
a, Å	10.836(2)	7.8902(5)	8.346(2)	47.958(5)
b, Å	16.259(4)	11.1217(7)	11.116(3)	47.958(5)
c, Å	20.307(5)	20.804(2)	21.206(5)	47.958(5)
α, deg	90	90	90	90
β, deg	90	90	90	90
γ, deg	90	90	90	90
V, Å^3	3577.7(1)	1825.6(2)	1967.4(8)	110302(20)
Z	4	2	2	24
No. reflns. collected	14547	14755	15578	220444
No. indep. reflns. (R_{int})	4108 (0.048)	4186 (0.0487)	4455 (0.0356)	10581 (0.0888)
No. reflns used [$I > 2\sigma(I)$]	4108	4186	4455	10581
GOF	1.121	1.085	1.106	1.167
$R_1{}^a$	0.060	0.059	0.055	0.096
$wR_2{}^b$	0.151	0.153	0.136	0.272
Flack parameter	0.50(3)	0.32(3)	0.47 (3)	0.02(3)

$^aR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (observed reflections). $^bwR_2 = [\sum w(|F_o{}^2|-|F_c{}^2|)^2 / \sum w|F_o{}^2|^2]^{1/2}$ (observed reflections).

Table S2 Selected Bond Lengths (Å), Angles (deg), Dihedral Angles (deg) for [Eu**1**Cl](BF_4)$_2$, [Eu**1**Cl](PF_6)$_2$, [Eu**1**Cl](OTf)$_2$, and [Eu**1**Cl]Cl_2.

	[Eu**1**Cl](BF_4)$_2$	[Eu**1**Cl](PF_6)$_2$	[Eu**1**Cl](OTf)$_2$	[Eu**1**Cl]Cl_2
Eu-N1(pyridine)	2.542(7)	2.578(7)	2.626(6)	2.60(1)
Eu-N2(pyridine)	2.588(7)	2.540(7)	2.596(6)	2.60(1)
Eu-N3(pyridine)	2.542(7)	2.578(7)	2.626(6)	2.56(1)
Eu-N4(pyridine)	2.588(7)	2.540(7)	2.596(6)	2.59(1)
Eu-N5(amine)	2.645(8)	2.703(6)	2.652(6)	2.67(1)
Eu-N6(amine)	2.663(8)	2.675(6)	2.627(6)	2.67(1)
Eu-N7(amine)	2.645(8)	2.703(6)	2.652(6)	2.67(1)
Eu-N8(amine)	2.663(8)	2.675(6)	2.627(6)	2.63(1)
Eu-Cl	2.153(5)	2.212(5)	2.725(2)	2.763(3)
N1(pyridine)-Eu-N2(pyridine)	84.7(2)	83.5(3)	82.5(2)	86.3(3)
N2(pyridine)-Eu-N3(pyridine)	85.3(2)	87.1(3)	86.7(2)	84.0(3)
N3(pyridine)-Eu-N4(pyridine)	84.7(2)	83.5(3)	82.5(2)	86.0(3)
N4(pyridine)-Eu-N1(pyridine)	85.3(2)	87.1(3)	86.7(2)	85.0(3)
N5(amine)-Eu-N6(amine)	68.0(3)	68.0(3)	68.3(5)	68.6(3)
N6(amine)-Eu-N7(amine)	69.1(3)	67.0(3)	67.7(4)	67.3(3)
N7(amine)-Eu-N8(amine)	68.0(3)	68.0(3)	68.3(5)	67.5(4)
N8(amine)-Eu-N5(amine)	69.1(3)	67.0(3)	67.7(4)	67.8(3)
N1(pyridine)-Eu-Cl	72.6(2)	73.6(2)	72.3(1)	72.8(2)
N2(pyridine)-Eu-Cl	73.1(2)	73.1(2)	72.0(2)	73.0(2)
N3(pyridine)-Eu-Cl	72.6(2)	73.6(2)	72.3(1)	73.9(2)
N4(pyridine)-Eu-Cl	73.1(2)	73.1(2)	72.0(2)	73.9(3)
(N1, N2, N3, N4), (N5, N6, N7, N8)	0	0	0	0

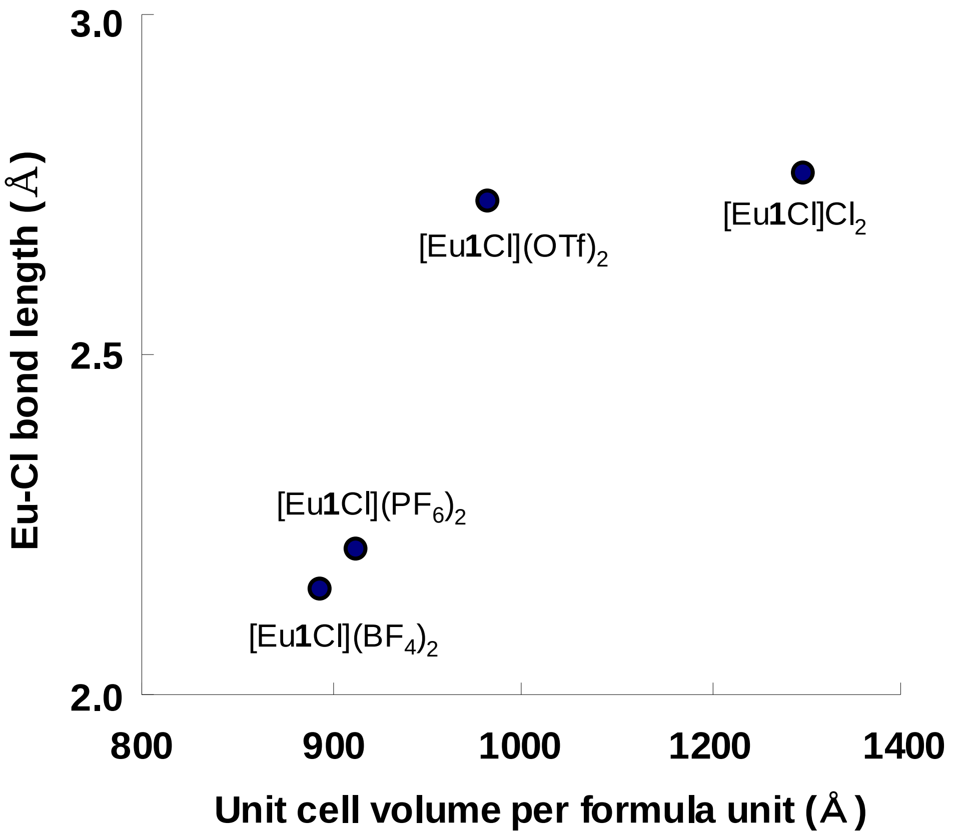

Fig. S1 The relationship between the Eu-Cl bond length (Å) and the cell volume per formula unit for [Eu**1**Cl](BF_4)$_2$, [Eu**1**Cl](PF_6)$_2$, [Eu**1**Cl](OTf)$_2$, and [Eu**1**Cl]Cl_2.

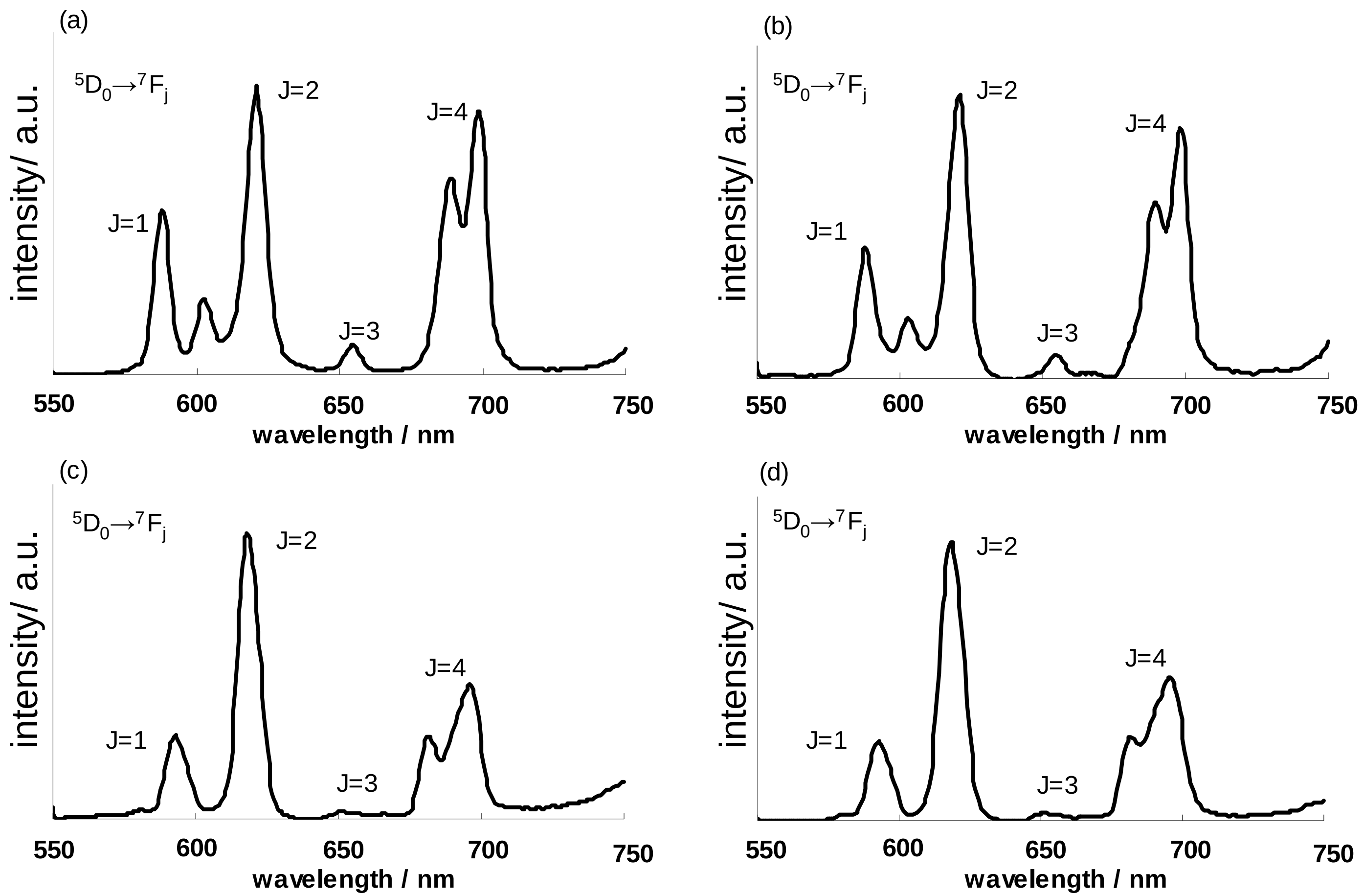

Fig. S2 Emission spectra of [Eu**1**Cl]$(BF_4)_2$ (a), [Eu**1**Cl]$(PF_6)_2$ (b), [Eu**1**Cl]$(OTf)_2$ (c), and [Eu**1**Cl]Cl_2 (d) in PVC film.

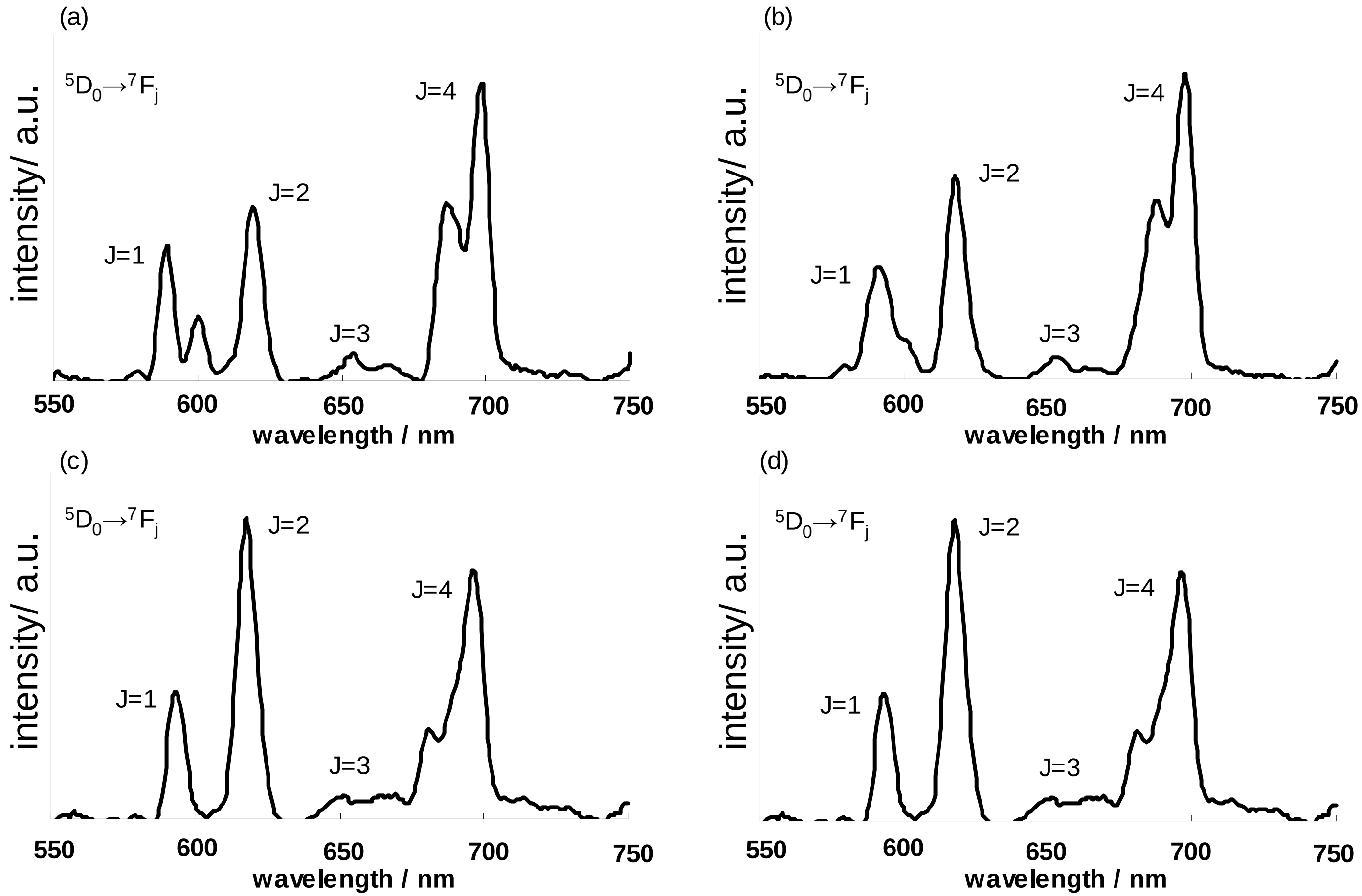

Fig. S3 Emission spectra of $[Eu\mathbf{1}Cl](BF_4)_2$ (a), $[Eu\mathbf{1}Cl](PF_6)_2$ (b), $[Eu\mathbf{1}Cl](OTf)_2$ (c), and $[Eu\mathbf{1}Cl]Cl_2$ (d) in CH_3CN (1.0×10^{-4} mol dm^{-3}) at 77 K.

Table S3 ESI MS Data of [Eu**1**Cl]$(BF_4)_2$, [Eu**1**Cl]$(PF_6)_2$, [Eu**1**Cl]$(OTf)_2$, and [Eu**1**Cl]Cl_2 in CH_3CN.

Compound	pattern	intensity
[Eu1Cl]$(BF_4)_2$	[Eu1Cl·$BF_4]^+$	[a]
	$[Eu1Cl]^{2+}$	100
[Eu1Cl]$(PF_6)_2$	[Eu1Cl·$PF_6]^+$	1
	$[Eu1Cl]^{2+}$	100
[Eu1Cl]$(OTf)_2$	$[Eu1Cl·OTF]^+$	26
	$[Eu1Cl]^{2+}$	100
[Eu1Cl]Cl_2	$[Eu1Cl·Cl]^+$	43
	$[Eu1Cl]^{2+}$	100

[a]No significant peak was observed.

Experimental section

General. ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL-400, or Bruker DRX-500 spectrometers. IR spectra and mass spectra were measured with a JASCO FT/IR-620 spectrometer and a SHIMADZU AXIMA-CFR spectrometer, respectively. Elemental analysis of the products was performed on a Yanaco MT-6 Type at the Elemental Analysis Center of the University of Tokyo. Water (>18.2 MΩ) was purified with a Millipore system. Other solvents and starting materials were purchased from Aldrich, Kanto Chemicals, or Wako Chemicals and used without further purification.

Synthesis. 1,4,7,10-Tetrakis(2'-pyridylmethyl)-1,4,7,10-tetraazacyclododecane (1). 2-(Chloromethyl)pyridine hydrochloride (0.984 g, 6 mmol) in water (10 mL) was neutralized by slow addition of a 4 mol dm^{-3} NaOH aqueous solution (ca 2 mL). To this solution, 1,4,7,10-tetraazacyclododecane tetrahydrochloride (0.318 g, 1 mmol) was slowly added. The reaction mixture was stirred at room temperature for 4 days, and the pH of the mixture was maintained between 7 and 9 by periodic dropwise addition of 4 M NaOH aq. The precipitate was collected by filtration. The product was dissolved in $CHCl_3$ and washed with H_2O to removed Na^+ ions. The solvent was evaporated under a reduced pressure and dried *in vacuo*. Recrystallization from methanol/ethyl acetate gave an analytically pure compound **1** as colorless cubes (0.108 g, 20%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47 (d, J = 4.0 Hz, 4H), 7.70 (d, J = 7.3 Hz, 4H), 7.42 (t, J = 7.0 Hz, 4H), 7.09 (t, J = 5.8 Hz, 4H), 3.64 (s, 8H), 2.78 (s, 16H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.6, 149.1, 136.4, 123.1, 121.9, 62.0, 53.8. IR (KBr) 2796, 1590, 1567, 1474, 1431, 1366, 1310, 1076, 1048, 989, 755 cm^{-1}. EI-MS: *m/z* = 536 (M^+). Anal. Calcd. for $C_{32}H_{40}N_8$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.75; H, 7.50; N, 20.84.

[Eu1Cl]Cl$_2$. Compound **1** (0.10 g, 0.19 mmol) and $EuCl_3 \cdot 6H_2O$ (0.050 g, 0.14 mmol) were dissolved in MeOH (100 mL), and the solution was refluxed for 3 days. The resulting solid product was removed by filtration. The solvent was evaporated under reduced pressure and dried *in vacuo*. Recrystallization from acetonitrile/diethyl ether gave an analytically pure compound [Eu**1**Cl]$Cl_2 \cdot 3H_2O$ (0.092 g, 80%) as white crystals. Anal. Calcd. for [Eu**1**Cl]$Cl_2 \cdot 3H_2O$ as $C_{32}H_{46}Cl_3EuN_8O_3$: C, 45.27; H, 5.46; N, 13.20. Found: C, 44.80; H, 5.75; N, 12.92.

[Eu1Cl](PF_6)$_2$. [Eu**1**Cl]$Cl_2 \cdot 3H_2O$ (0.027 g, 0.032 mmol) and Ag(PF_6) (0.017 g, 0.067 mmol) were dissolved in MeOH (50 ml). The solution was stirred for 24 h at room temperature. The resulting solid product was removed by filtration. The solvent was evaporated from the filtrate under reduced pressure, and the residue was dried *in vacuo*. Recrystallization from acetonitrile/diethyl ether gave analytically pure compound [Eu**1**Cl](PF_6)$_2$ (0.027 g, 85%) as white crystals. Anal. Calcd. for [Eu**1**Cl](PF_6)$_2$ as $C_{32}H_{40}ClEuF_{12}N_8P_2$: C, 37.90; H, 3.98; N, 11.05. Found: C, 37.82; H, 4.17; N, 11.00.

[Eu1Cl](BF_4)$_2$. [Eu**1**Cl](BF_4)$_2$ was synthesized in the same manner as [Eu**1**Cl](PF_6)$_2$ from [Eu**1**Cl]Cl_2·$3H_2O$ (0.075 g, 0.088 mmol) and Ag(BF_4) (0.036 g, 0.18 mmol). Yield: 0.068 g, 86%. Anal. Calcd. for [Eu**1**Cl](BF_4)$_2$ as $C_{32}H_{40}B_2ClEuF_8N_8$: C, 42.81; H, 4.49; N, 12.48. Found: C, 43.03; H, 4.71; N, 12.51.

X-ray Crystallography. All crystals were mounted on a loop fiber with liquid paraffin frozen under a cold stream of N_2. Reflection data were collected at 113(2) K on a Rigaku Mercury diffractometer with a CCD area detector or Rigaku VariMax Saturn with graphite monochromated Mo-Kα radiation (0.7107 Å). Reflections were corrected for Lorentz and polarization effects, and an empirical correction was applied for absorption. All the structures were solved by direct methods using SIR92 and SHELXS-97. The final cycles of full-matrix least-squares refinement on *F* were performed using the SHELXL-97. All calculations were performed using the CrystalStructure crystallographic software package of Rigaku Corporation or the WinGX program.

Luminescence Measurements. The emission spectra were recorded with a Hitachi FL-4500 spectrometer. Luminescence spectra were corrected for the instrumental function. The acetonitrile used was fluorescence-grade. Luminescence quantum yields were determined by the previous methods.[3f] The Eu^{3+} complexes in polyvinylchloride (PVC) film were prepared as follows. The solution of [Eu**1**Cl]Cl_2, [Eu**1**Cl](OTf)$_2$, [Eu**1**Cl](PF_6)$_2$, and

[Eu**1**Cl]$(BF_4)_2$ was swollen in polyvinylchloride (PVC) film, and the solvent was evaporated under reduced pressure.