Photophysical characterization of a highly luminescent divalent-europium-containing azacryptate

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Experimental procedures

Commercially available chemicals were of reagent-grade purity or better and were used without further purification unless otherwise noted. DriSolv anhydrous solvents were degassed under reduced pressure prior to use in the glovebox. Azacryptands 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (**1**)[1–2] and 4,7,13,16,21,24-hexamethyl-1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (**2**)[3] were prepared following published procedures.

UV–visible absorption measurements were performed using a Shimadzu UVmini-1240 spectrophotometer. Excitation and emission data were collected using a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer. Excitation and emission spectra were acquired with a 1 nm excitation slit width, 0.5 nm emission slit width, and 1 nm interval. Emission spectra were collected with an excitation wavelength of 359 nm, and excitation spectra were collected with an emission wavelength of 447 nm. The concentration of Eu for calculation of molar absorptivity was determined using energy-dispersive X-ray fluorescence (EDXF) spectroscopy at the Lumigen Instrument Center in the Department of Chemistry at Wayne State University. Elemental analyses (C, H, and N) were performed by Midwest Microlabs (Indianapolis, IN).

Synthesis of Eu1I$_2$

In a dry glovebox (O$_2$ and H$_2$O excluded) under an atmosphere of N$_2$, a solution of **1** (29 mg, 0.078 mmol) in tetrahydrofuran (1.5 mL) was added to a solution of EuI$_2$ (30 mg, 0.074 mmol) in tetrahydrofuran (1.5 mL), and a yellow precipitate immediately formed. The precipitate was washed with tetrahydrofuran (3 × 1 mL) and dried under reduced pressure to yield a yellow solid. Anal. Calcd for C$_{18}$H$_{42}$N$_8$EuI$_2$: C, 27.85; H 5.45; N, 14.43. Found: C, 28.85; H 5.93; N, 14.61. All values are given as percentages. Crystals for X-ray analysis were grown by slow evaporation of a solution of Eu**1**I$_2$ in methanol.

Synthesis of Eu2I$_2$

In a dry glovebox under an atmosphere of N$_2$, a solution of **2** (131.0 mg, 0.2811 mmol) in tetrahydrofuran (8 mL) was added to a solution of EuI$_2$ (101.5 mg, 0.2501 mmol) in tetrahydrofuran (8 mL), and a pale-yellow precipitate immediately formed. The precipitate was washed with tetrahydrofuran (3 × 9 mL) and dried under reduced pressure to yield 211 mg (98%) of a pale-yellow solid. Anal. Calcd for C$_{24}$H$_{54}$N$_8$EuI$_2$: C, 33.50; H 6.33; N, 13.02. Found: C, 33.77; H 6.13; N, 12.71. All values are given as percentages. Crystals for X-ray analysis were grown by vapor diffusion of tetrahydrofuran into a solution of Eu**2**I$_2$ in methanol.

Crystallographic data for Eu1I$_2$

X-ray intensity data were measured for a single crystal of Eu**1**I$_2$. The total exposure time was 16.10 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 128327 reflections to a maximum θ angle of 36.32° (0.60 Å resolution), of which 12756 reflections were independent (average redundancy 10.060, completeness = 100.0%, R$_{int}$ = 3.89%) and 12570 (98.54%) were greater than 2σ(F^2). The final cell constants are based upon the refinement of the XYZ-centroids of 9761 reflections above 20 σ(I) with 5.170° < 2θ < 92.15°. Data were corrected for absorption effects using the multi-scan method. The ratio of minimum to maximum apparent transmission was 0.442. The final anisotropic full-matrix least-squares refinement on F^2 with 286 variables converged at R1 = 1.79%, for the observed data and wR2 = 4.70% for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 1.097 e$^-$/Å^3 and the largest hole was –1.073 e$^-$/Å^3 with a root-mean-square deviation of 0.111 e$^-$/Å^3. The crystallographic data can be found in the Cambridge structural database under CCDC #1826977. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Table S1 Crystallographic properties of Eu**1**I$_2$:

Chemical Formula	C$_{18}$H$_{48}$N$_8$EuI$_2$
Formula Weight	782.40
Temperature	100 K
Wavelength	0.71073 Å
Crystal System	orthorhombic
Space Group	$Pca2_1$
Unit Cell Dimensions	a = 15.770(2) Å
	b = 12.1249(19) Å
	c = 13.749(2) Å
	α = 90°
	β = 90°
	γ = 90°
Volume	2628.9(7) Å^3
Z	4
Density (calculated)	1.977 g cm^{-3}
Absorption Coefficient	4.755 mm^{-1}
F(000)	1524

Crystallographic data for Eu2I$_2$

Data were collected on a Bruker Apex-II Kappa geometry diffractometer using Mo Kα radiation. Spectral collection was performed with a charge coupled device and the temperature of the crystal was maintained at 100 K using an Oxford Cryostream low-temperature device. An initial solution was found using the method of intrinsic phasing via ShelXT[4] and further refined by the method of least squares using ShelXL[5] interfaced with OLEX2 and ShelXle.[6]

The Eu^{II}-containing complex crystallized in the space group $P2_13$ with four dicationic units of [Eu**2**]$^{2+}$, eight outer-sphere iodide anions, and four outer-sphere molecules of methanol in the unit cell. All non-hydrogen atoms were refined anisotropically. The ethylene unit of C0 and C1 was found to have two positions: one with 68% occupancy and the other with 32% occupancy. Absolute stereochemistry for this structure was not assigned. The crystallographic data can be found in the Cambridge structural database under CCDC #1826978. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Author response to PLAT410_ALERT_2_A: This alert concerns a short H . . . H contact distance between H3B and H00M of PART 1. Residual electron density around the ethylene unit of C3 and C00C alludes to possible unmodeled disorder, although acceptable positions could not be found. Therefore, proton H3B was left as is.

Table S2 Crystallographic properties of Eu**2**I$_2$:

Chemical Formula	$C_{25}H_{57}EuI_2N_8O$
Formula Weight	891.54
Temperature	100 K
Wavelength	0.71073 Å
Crystal System	cubic
Space Group	$P2_13$
Unit Cell Dimensions	a = 14.9671(10) Å
	b = 14.9671(10) Å
	c = 14.9671(10) Å
	$\alpha = 90^o$
	$\beta = 90^o$
	$\gamma = 90^o$
Volume	3352.8(7) Å^3
Z	4
Density (calculated)	1.766 g cm^{-3}
Absorption Coefficient	3.743 mm^{-1}
F(000)	1760.0

Calculation of quantum yield

The photoluminescence quantum yield of Eu**2**I$_2$ (starting from isolated complex) was determined using a Fluorolog 3–222 fluorometer with an 80 mm integrating sphere (Horiba Scientific). Four samples of optical densities 0.009, 0.02, 0.028, and 0.048 were prepared using methanol as the solvent and loaded in 10 mm quartz cuvettes (Thor Labs). Cuvettes were sealed with a Teflon cap under an atmosphere of nitrogen. A xenon lamp was employed as the excitation source. The excitation wavelength was set to 355 nm, and the fluorescence emission was collected between 405 and 530 nm in right-angle geometry. A photomultiplier tube (R928) was used as the detector. Emission spectra were corrected for lamp-power fluctuations, detector sensitivity, and integrating-sphere response. Additionally, self-absorption and secondary fluorescence corrections were included following a reported procedure.[7] Quantum yields were computed using a four-curve analysis. The resulting average quantum yield was 47% with a standard error of 3%.

Calculation of luminescence lifetime

The ambient-temperature photoluminescence decay of Eu**2**I$_2$ (starting from isolated complex) in methanol was determined using a Fluorolog 3–222 fluorometer. A 393 nm SpectraLED (Horiba Scientific) was used as the excitation source, and a photomultiplier tube (R928) was used as the detector. Luminescence decay was monitored at 448 nm in right-angle geometry. A monoexponential function was fit to the experimental decay giving a value of 1.25 μs for the lifetime, τ.
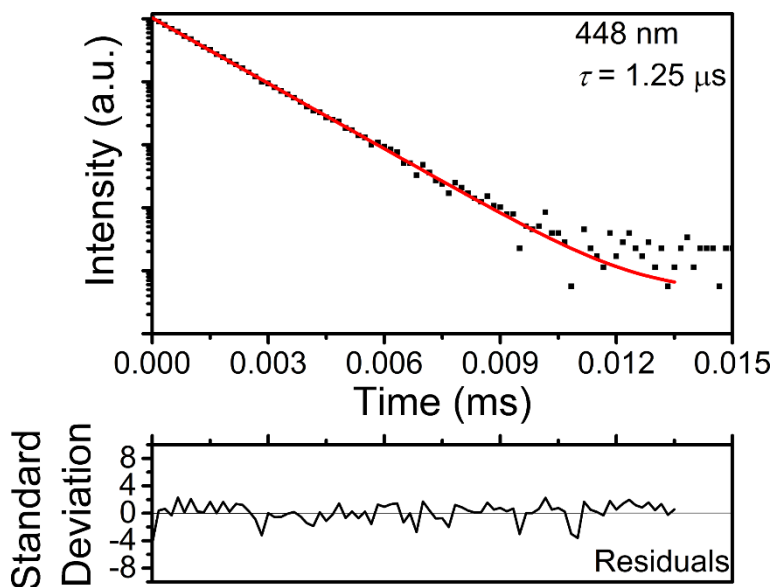

Figure S1 Ambient-temperature photoluminescence decay of Eu**2**I$_2$ at 448 nm. (Top) A fit of a monoexponential decay to the experimental data is depicted as a solid red line. (Bottom) A fit of residuals is shown. The x-axis is the same for the top and bottom plots.

Computational methods

Density functional theory (DFT) calculations, including time-dependent DFT (TD-DFT, 80 states) calculations,[8–12] were performed for [Eu**2**]$^{2+}$ starting from the crystallographic coordinates and following the same procedure as reported previously.[13] The structure for [Eu**1′**]$^{2+}$ was optimized starting from the crystallographic coordinates of [Eu**2**]$^{2+}$, replacing the methyl groups with hydrogen atoms, and limiting the step size to favor a geometry similar to [Eu**2**]$^{2+}$. All calculations employed the B3PW91 functional,[14] Stuttgardt–Dresden relativistic core potential (SDD) basis set for europium,[15–16] and the D95 basis set for the remaining elements.[17] Solvation was simulated using the SMD implicit solvation model.[18] Fluorescence of [Eu**2**]$^{2+}$ was simulated by TD-DFT after the excited-state structure corresponding to the high-oscillator-strength transition was optimized. Natural-transition-orbital calculations were performed to characterize excitations.[19] All calculations were carried out using the Gaussian 09 suite of programs,[20] and structures, spin densities, and molecular orbitals were plotted with Gaussview.[21]

Table S3 Bond lengths (Å) for [Eu**2**]$^{2+}$ from crystallographic and computational structures.
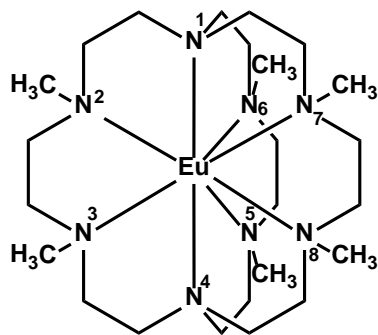
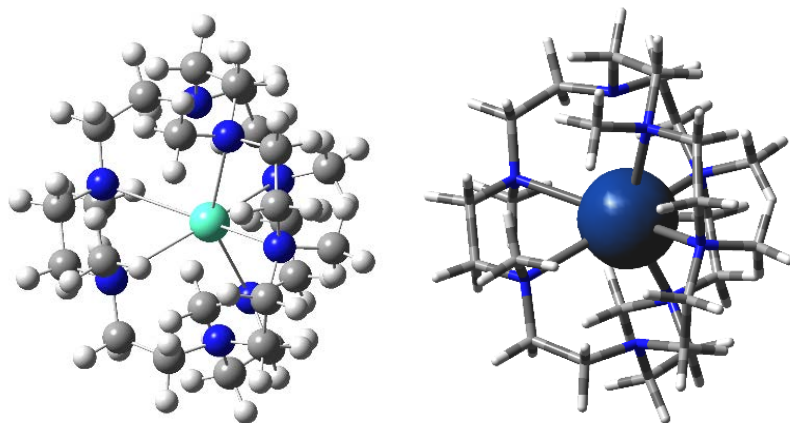| Complex [Eu2]$^{2+}$	Eu–N$_1$	Eu–N$_2$	Eu–N$_3$	Eu–N$_4$	Eu–N$_5$	Eu–N$_6$	Eu–N$_7$	Eu–N$_8$
crystallographic	2.974	2.832	2.917	2.821	2.917	2.832	2.832	2.917
calculated, ground state	3.145	2.914	2.946	3.200	3.052	3.011	2.893	2.996
calculated, excited state	2.876	2.779	2.934	3.223	2.901	3.040	2.970	3.143

Figure S2 B3PW91/SDD optimized ground-state structure in SMD methanol: (left) optimized structure of [Eu**2**]$^{2+}$; (right) spin density (blue) mapped onto [Eu**2**]$^{2+}$.

268 nm (calcd)
261 nm (exptl)

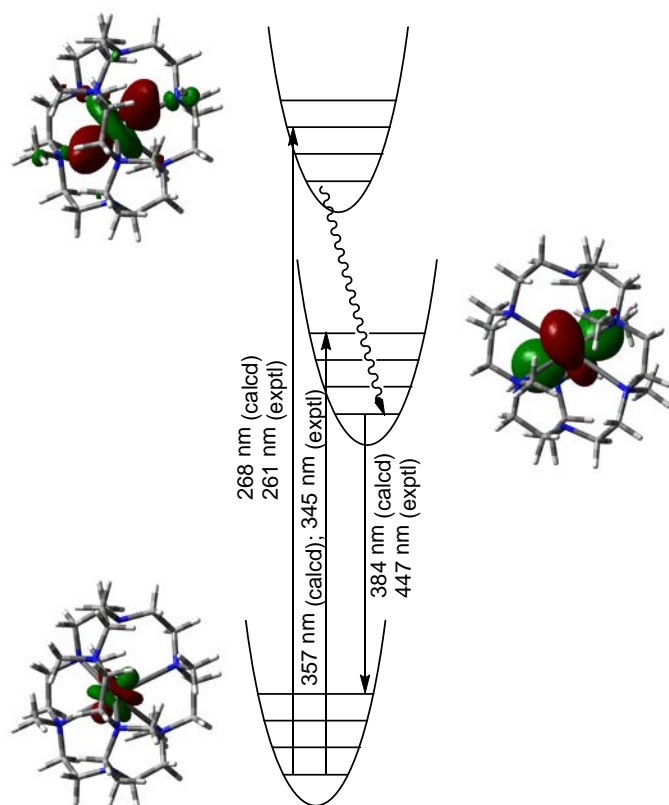357 nm (calcd); 345 nm (exptl)

384 nm (calcd)
447 nm (exptl)

Figure S3 Energy diagram depicting the excitation and emission for [Eu**2**]$^{2+}$ and the corresponding natural-transition orbitals.
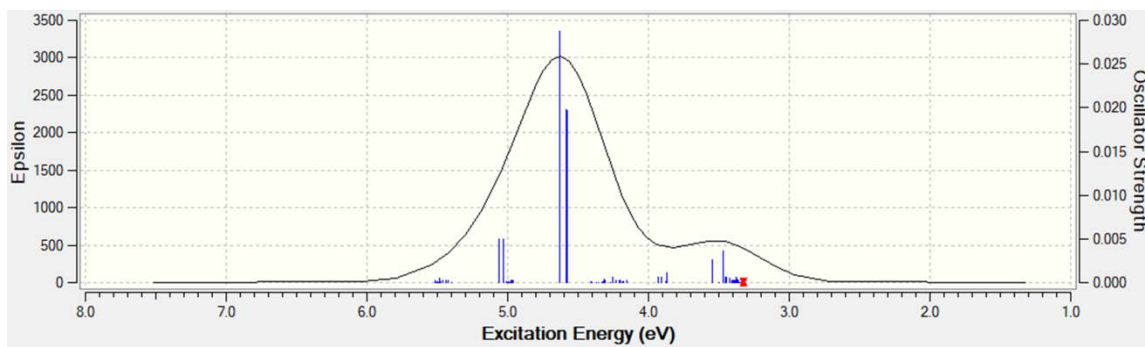
Figure S4 Spectrum depicting 80 calculated transitions of the absorption of [Eu**2**]$^{2+}$.
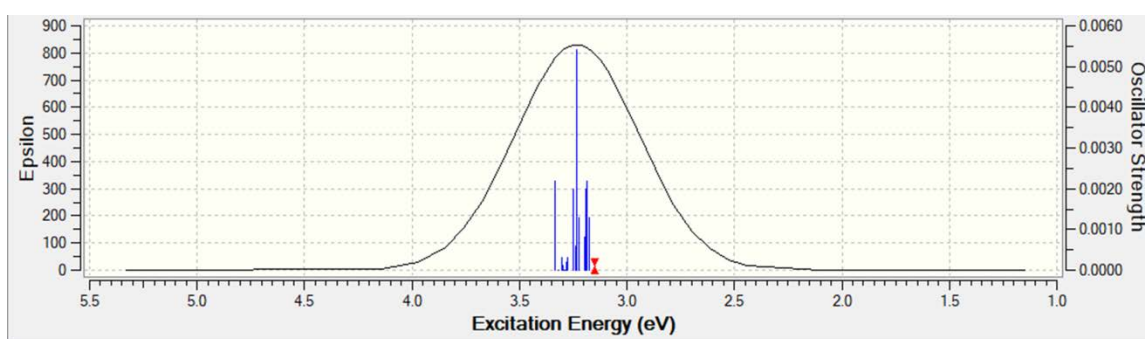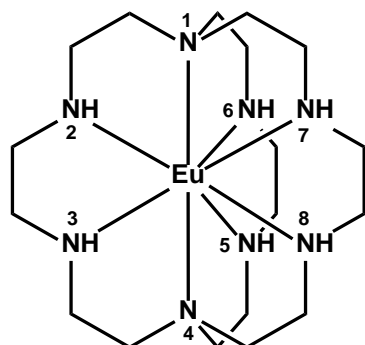

Figure S5 Spectrum depicting 80 calculated transitions of the emission of [Eu**2**]$^{2+}$.

Table S4 Bond lengths (Å) for [Eu**1′**]$^{2+}$ from ground-state computational structure.

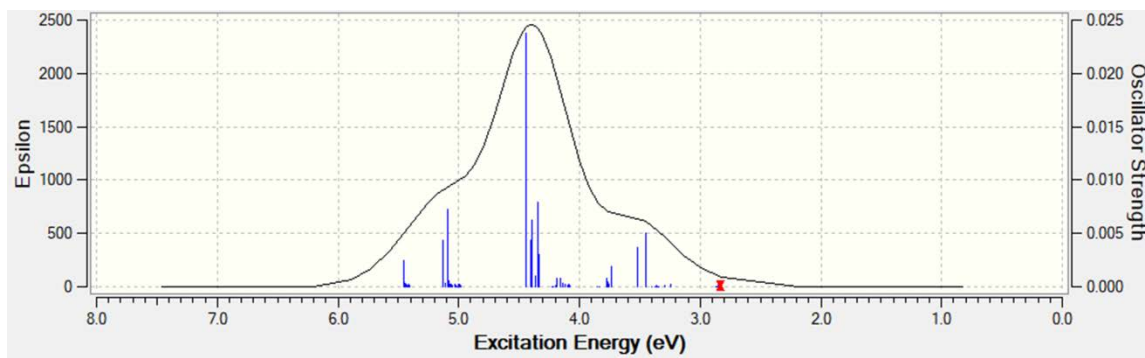| Complex [Eu**1′**]$^{2+}$	Eu–N$_1$	Eu–N$_2$	Eu–N$_3$	Eu–N$_4$	Eu–N$_5$	Eu–N$_6$	Eu–N$_7$	Eu–N$_8$
Calculated, ground state	3.207	2.826	2.917	3.424	2.895	2.824	2.831	2.872

Figure S6 Spectrum depicting 80 calculated transitions of the absorption of $[Eu\mathbf{1'}]^{2+}$.

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