Aqueous Eu^{II}-containing complex with bright yellow luminescence

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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. Water was purified using a PURELAB Ultra Mk2 water purification system (ELGA). Azacryptand-1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (**2**) was prepared by following a published procedure.[1]

Samples of **1** were prepared in a wet (water allowed but no molecular oxygen) glovebox under an Ar atmosphere. Quantum yield standards (fluorescein and coumarin-153) were crystallized three times from ethanol, and their purity was checked using a high-performance liquid chromatography (HPLC) system (Shimadzu) equipped with an analytical pinnacle column (Restek International, Pinnacle DB Cyano, 5 μm, 250 mm × 4.6 mm). Analytical HPLC used a binary gradient method (pump A: water; pump B: acetonitrile; flow rate: 1 mL/min). Fluorescein eluted at 19.7 min using 0% B for 4 min, 0→25% B over 2 min, 25% B for 4 min, 25→50% B over 2 min, 50% B for 6 min, then 50→75% B over 2 min. Coumarin-153 eluted at 14.8 min using 0% B for 4 min, 0→75% B over 4 min, then 75% B for 8 min. Fluorescein and coumarin-153 were detected with a photodiode array detector by monitoring absorbance at 474 and 429 nm, respectively.

UV–vis absorbance was measured using a Shimadzu UVmini-1240 spectrophotometer. Emissions, decay rates, and integrated emissions were recorded using a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer. Variable-temperature ^{17}O-NMR measurements were performed using a Varian-500S (9.4 T) spectrometer for sample **1** and for a Sr^{II} analog of **1** (5.0 mM, 700 μL) at pH 12.0 in 0.5% ^{17}O-enriched water (Cambridge Isotope Laboratories, Inc.) at 15, 20, 30, 40, 50, 60, and 70 °C following a published procedure.[2] Job plots were obtained by measuring the integrated emission (λ_{ex} = 415 nm and λ_{em} = 580 nm) using a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer for different mole fractions (0.1–0.9) of Eu^{II} relative to **2** prepared by mixing $EuCl_2$ with **2** at ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1.

The emission intensity (λ_{ex} = 415 nm) vs pH was performed by preparing 5 samples of **1** (1.0 mM, 3.0 mL) at different pH values (8.0, 9.5, 10.0, 11.3, and 12.0) by adjusting the pH of solutions of **1** with KOH (0.05 M) or HCl (0.05 M). Emission spectra are acquired on a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer.

Decay rates were calculated from decay curves measured at 580 nm emission (λ_{ex} = 415 nm) with excitation and emission slit widths of 3 nm, initial delay of 0.01 ms, maximum delay of 0.2 ms, and an increment of 0.0025 ms. Samples of **1** at pH 12.0 and 9.5 were prepared by dissolving **1** (8.8 mg) in water (2.0 mL) and adjusting the pH with aqueous solutions of KOH (0.05 M) or aqueous solutions of HCl (0.05 M). Samples of **1** for decay-rate analysis were prepared by withdrawing a 100 μL from the stock solutions and diluting to 3.0 mL with aqueous solutions of KOH (pH 12.0 and 9.5). The pH values were measured using Hanna checker portable pH meter at ambient temperature, and the solutions were transferred to air-tight quartz cuvettes under an Ar atmosphere.

Molar conductivity was calculated from three independently prepared solutions of **1** (1.0 mM, 15.0 mL) measured at pH 10.0 under an Ar atmosphere and ambient temperature using an Omega CDH 280 portable conductivity meter that was calibrated with aqueous KCl (0.01 M, 1.413 mS/cm). Results are reported as mean ± standard error.

Elemental analysis (C, H, and N) determinations were performed by Midwest Microlab (Indianapolis). Cyclic voltametry was performed using a Pine Wavenow USB potentiostat in an electrochemical cell under an Ar atmosphere with a Ag/AgCl reference electrode, a glassy carbon working electrode, and a Pt wire auxiliary electrode. A solution (pH 9.7) of complex **1** (2.0 mM) and Et_4NClO_4 (0.1 M) in water (5.0 mL) was used for the analysis, and the potential was 0.14 V ± 0.05 V, which is the mean ± standard error of the measurements of three independently prepared samples. Inductively coupled plasma mass spectroscopy (ICP–MS) analyses were used to determine all solution concentrations and were performed with an Agilent 7700x inductively coupled plasma mass spectrometer at the Lumigen Instrument Center in the Department of Chemistry at Wayne State University. Standards of Eu were prepared by diluting commercially available standards (Eu_2O_3 in aqueous nitric acid, 5%, 1000 ppm, Alfa Aesar) with aqueous nitric acid (2%). High-resolution electrospray ionization mass spectrometry (HRESIMS) was performed using an electrospray time-of-flight high-resolution Waters Micromass LCT Premier XE mass spectrometer.

Eu^{II}-azacryptand-1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (1): To a solution of azacryptand-1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane **2** (103 mg, 0.278 mmol) and $EuCl_2$ (51.7 mg, 0.232 mmol) in methanol (3.0 mL) was added water (200 µL), and the resulting solution was stirred for 2 h under an Ar atmosphere. After 2 h, the yellow-orange solution was filtered using a 0.2 micron filter (Millex-LG hydrophilic), and into the filtrate was diffused tetrahydrofuran vapor over 3 days until yellow-green needle-like crystals formed at the bottom of the vial. The crystals were washed with diethyl ether (3 × 2 mL) and ground with a mortar and pestle prior to drying under vacuum to obtain 89.0 mg (65%) of **1** as a green powder. Anal. Calcd for $C_{18}H_{42}N_8EuCl_2 \cdot H_2O$: C, 35.36; H, 7.25; N, 18.33. Found: C, 35.13; H, 7.15; N, 17.99. All values are given as percentages. Crystals for x-ray analysis were removed prior to grinding.

Sr^{II}-azacryptand-1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (3): To a solution of azacryptand **2** (52.0 mg, 0.140 mmol) and $SrCl_2 \cdot (H_2O)_6$ (37.4 mg, 0.140 mmol) in methanol (3.0 mL) was added water (200 µL), and the resulting solution was stirred for 2 h under an Ar atmosphere. After 2 h, the colorless solution was filtered using a 0.2 micron filter (Millex-LG hydrophilic), and the solvent was removed under reduced pressure to yield a white powder that was washed with diethyl ether (3 × 2 mL) and dried under vacuum to obtain 30.0 mg (47%) of **3** as a white powder. HRESIMS (*m/z*): $[M + Cl]^+$ calcd for $C_{18}H_{42}N_8SrCl$, 493.2277; found 493.2289, Anal. Calcd for $C_{18}H_{42}N_8SrCl_2.H_2O$: C, 39.51; H, 8.11; N, 20.48. Found: C, 38.92; H, 7.78; N, 19.85. All values are given as percentages.

Calculation of Quantum Yield

Coumarin-153 was used as the quantum yield standard of which the relative quantum yield (0.58 ± 0.02) was measured against fluorescein (0.79) at λ_{ex} = 415 nm following a published procedure,[3] using a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer with excitation and emission slit widths of 0.5 nm. After calibrating coumarin-153 against fluorescein, a series of concentrations of complex **1** (0.042, 0.085, 0.12, and 0.16 mM at pH 12.0) were prepared by diluting stock solutions of **1** (5.0 mM at pH 12.0) with aqueous solutions of KOH (0.01 M). These solutions were filtered using 0.2 micron filters and were used to calculate the quantum yields by plotting integrated emission (450–700 nm) vs absorption for coumarin-153 and **1** at pH 12.0. The gradients of the plots were used to calculate the quantum yield using eq S1, where Φ_u

and Φ_s are the quantum yields of sample **1** and coumarin-153, respectively; $Grad_u$ and $Grad_s$ are the gradients of the plots of **1** and coumarin-153, respectively; and η_u and η_s are the refractive indices of the aqueous KOH (pH 12.0) solution and ethanol, respectively.[4]

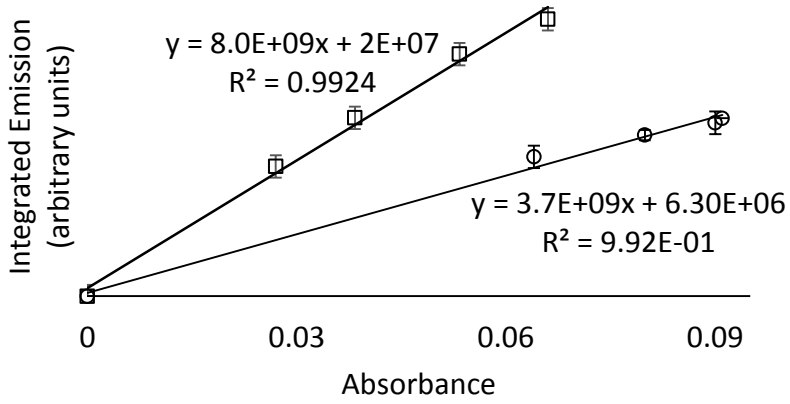


Figure S1. Integrated emission vs absorbance curves for coumarin-153 (□) in ethanol and complex **1** at pH 12.0 (○). Error bars represent the standard error of the mean of three independently prepared samples.

$$\Phi_u = \Phi_s \left(\frac{Grad_u}{Grad_s}\right)\left(\frac{\eta_u{}^2}{\eta_s{}^2}\right) \qquad \text{(S1)}$$

Φs = 0.58, $Grad_u$ = 3.7 × 10^9, $Grad_s$= 8.0 × 10^9, η_u= 1.334, η_s= 1.3611

Φ_u = 0.26 at pH 12.0

Crystallographic Data

Single X-ray crystal structure analysis was performed on a Bruker APEX-II Kappa geometry diffractometer with Mo radiation and a graphite monochromator using a Bruker charge coupled device based diffractometer equipped with an Oxford Cryostream low-temperature apparatus. The data was measured at a temperature of 100 K. The structure was solved by the direct method using the SHELXS-97 program that is part of APEX II2 and refined by the least squares method, SHELXL 2012 incorporated into ShelXle.[5] Single crystals of **1** contained one cation of **1**, one chloride counter ion, and one molecule of methanol in the asymmetric unit. The structure was solved with a resolution of 0.57 Å in space group P3c1. All non-hydrogen atoms were refined anisotropically.

Author Response to Red Alert: Plat 413 involves a solvent H atom from a methanol. The error in the calculated position of the methanol H atoms may be larger than the accuracy of the structure. However, the methanol has no relevant contribution to the conclusions in this paper. Both SHFSU01 and PLAT080 are due to disorder, possibly due to racemic twinning (Flack x parameter = 0.446), in the structure which places disordered atoms so close to one another that individual electron density positions cannot be seen. This type of disorder cannot be properly modeled. Additionally, this disorder yields a relatively large, flat potential energy minimum between adjacent positions such that each refinement cycle shifts atoms back and forth between

the adjacent atomic positions. The positions are close enough to one another to be indistinguishable, but will never reach the minimum set by SHELX regardless of the number of cycles of refinement because the atoms oscillate between their broad minima.

Table S1. Crystallographic properties of 1.

Chemical formula of **1**	$C_{19}H_{45}Cl_2EuN_8O$	
Formula weight	624.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	trigonal	
Space group	P 3 c 1	
Unit cell dimensions	a = 16.4389(6) Å	α = 90°
	b = 16.4389(6) Å	β = 90°
	c = 16.3399(8) Å	γ = 120°
Volume	3824.1(3) $Å^3$	
Z	6	
Density (calculated)	1.583 g/cm^3	
Absorption coefficient	2.695 mm^{-1}	
F(000)	1854	

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