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Aqueous Eu^{II}-Containing Complex with Bright Yellow Luminescence

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Supporting Information

ABSTRACT: Eu^{II}-containing materials have unique luminescence, redox, and magnetic properties that have potential applications in optoelectronics, sensors, and imaging. Here, we report the synthesis and characterization of Eu^{II}-containing aza-222 cryptate that displays yellow luminescence and a quantum yield of 26% in aqueous media. The crystal structure reveals a staggered hula-hoop geometry. Both solid-state and solution-phase data are presented that indicate that the high quantum yield is a result of the absence of OH oscillators in the inner sphere of the complex. We expect that Eu^{II}-containing aza-222 cryptate is a step toward Eu^{II}-containing luminescent materials that can be used in a variety of applications including biological imaging.

Luminescent materials with high quantum yields are important for imaging applications and optoelectronic materials,[1] and the luminescence properties of Eu^{II}-containing materials make them desirable choices for use in these applications.[2] Although the emission of Eu^{II} in the solid state is relatively strong (quantum yields of 25−92%),[2c,d,3] in aqueous solutions, weak emissions (quantum yields of ∼0.1%) are observed due to quenching of the excited state of Eu^{II} by OH oscillators.[4] This quenching limits the usefulness of Eu^{II}-based luminescence in aqueous systems.[4c,5] Additionally, materials that emit yellow light are desirable in the lighting and imaging fields.[2c] Reported Eu^{II}-containing complexes in aqueous media absorb in the UV and emit in the blue region (380−530 nm) of the electromagnetic spectrum.[4c] These complexes mainly include crown ethers and cryptand-based ligands, and the quantum yields of these complexes are low (≤0.1%).[4c] Here, we report a Eu^{II}-containing aza-222 cryptate that displays bright yellow emission (500−700 nm) in aqueous solution.

In our pursuit of oxidatively stable Eu^{II}-containing complexes for use as contrast agents for magnetic resonance imaging,[6] we synthesized Eu^{II}-containing aza-222 cryptate, **1** (Figure 1), with the thought that the nitrogen donors and cavity size would be a good match for Eu^{II}, resulting in an oxidatively stable complex. Complex **1** has a high oxidative stability (0.13 ± 0.05 V vs Ag/AgCl), and interestingly, we noticed that aqueous solutions of **1** were yellow and highly luminescent (Figure 2).

To characterize the luminescence properties of **1**, we acquired excitation and emission spectra in an aqueous medium (Figure 2). The excitation of **1** occurs at 380−520 nm (λ_{ex}^{max} = 415 nm) resulting in a broad yellow emission (500−700 nm,

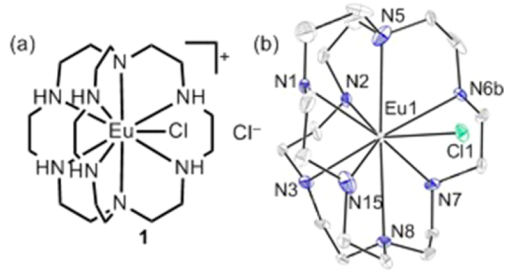

Figure 1. (a) Eu^{II}-containing aza-222 cryptate **1** and (b) the crystal structure of **1**. Thermal ellipsoids are drawn at the 50% probability. Hydrogen atoms, the noncoordinated Cl^- counterion, and a molecule of methanol are not shown in the structure for clarity. *R*-factor = 0.0543. Resolution = 0.54 Å.

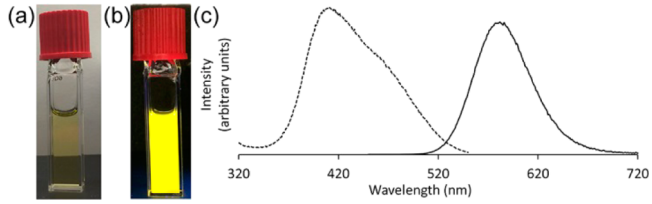

Figure 2. Pictures of 1 (5.0 mM) in 4 mL cuvettes in a pH 12.0 solution of KOH (a) in ambient light and (b) under a hand-held UV lamp (254−400 nm). (c) Excitation (---) and emission (—) spectra of **1** (0.50 mM) in a pH 12.0 solution of KOH.

λ_{em}^{max} = 580 nm). The broad excitation and emission spectra are likely due to Laporte allowed f−d transitions between ground ($4f^7$) and excited ($4f^6 5d^1$) states, and this assignment is supported by the molar extinction coefficient (3.0×10^3 M^{-1} cm^{-1}) that is in the range of f−d transitions and not charge transfers.[4b] The yellow emission of complex **1**, relative to blue emitting Eu^{II}-containing complexes,[4c] is likely due to the relatively strong-field amine donors compared to ether donors in cryptands and crown ethers.[7] Similar shifts in excitation and emission spectra have been observed for Eu^{II} in the solid state,[2c] but not in aqueous solutions. Further, besides not displaying yellow emission in aqueous media, Eu^{II} containing complexes are usually weak emitters at ambient temperature because of quenching from inner sphere OH oscillators.[4] However, despite being in an aqueous solution, complex **1** displays bright yellow luminescence. To quantify the

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luminescence of **1**, we measured its quantum yield (26%). This value is, to the best of our knowledge, the highest quantum yield reported for a Eu^{II}-containing complex in aqueous media.

We suspected that the luminescence of **1** would be influenced by pH because of the amines on the ligand. To explore the influence of pH on luminescence, we acquired emission spectra at pH 12.0, 11.3, 10.0, 9.5, and 8.0 (Figure 3a).

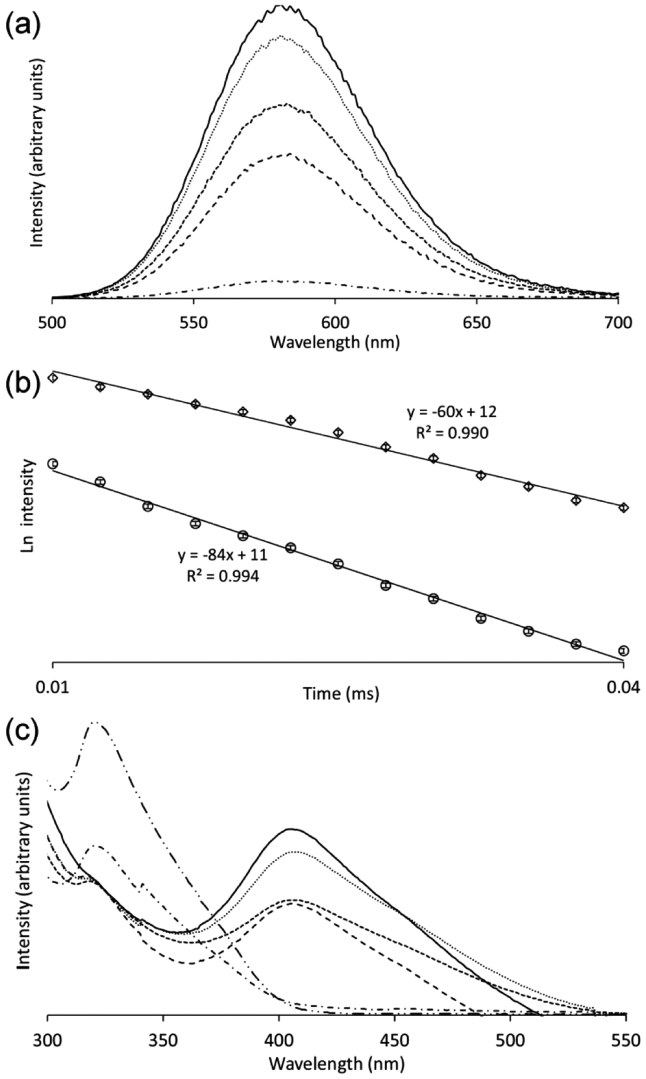

Figure 3. (a) Emission spectra (λ_{ex} = 415 nm) of **1** at pH 12.0 (——), 11.3 (··), 10.0 (--), 9.5 (— —), and 8.0 (— · —). (b) Plots of the natural log of luminescence intensity vs time at pH 12.0 in H_2O (◇) and at pH 9.5 in H_2O (○) (λ_{em} = 580 nm, λ_{ex} = 415 nm). Lines are the linear best fit, and the decay rates were derived as the slopes of the lines; (c) absorption spectra of **1** at pH 12.0 (——), 11.3 (··), 10.0 (--), 9.5 (— —), and 8.0 (— · —) and $EuCl_2$ (—— ·· ——) at pH 8.0. Error bars indicate the standard error of the mean of three independently prepared samples.

We observed that luminescence intensity decreased with decreasing pH. Further, the yellow emission was almost completely missing at pH 8. The observed decrease in intensity with decreasing pH is likely due to protonation of the metal-bound secondary amines ($pK_a \approx 13-14$)[8] of the ligand giving rise to NH oscillators that quench the luminescence of Eu^{II}. We suspect that NH oscillators quench the excited state of complex **1** for two reasons: (1) NH oscillators quench the excited state energies of Eu^{III}, and Eu^{III} and yellow-emitting Eu^{II}-containing complexes have similar excited state energies;[2,4,9] and (2) similar oscillators to NH (OH and BH) quench the excited state energy of both Eu^{II} and Eu^{III}.[2,4,9] Furthermore, protonation of too many of the amines of the ligand could also facilitate demetalation, which would lead to a decrease in emission intensity.

To test for the presence of NH oscillators, we acquired luminescence-decay rate data at pH 9.5 and 12.0 in H_2O (Figure 3b). The gradients of the plots of Ln intensity vs time yielded the decay rates. The decay rates obtained from the plots are 60 and 84 ms^{-1} at pH 12.0 and 9.5, respectively. These results suggest that more amines are protonated at pH 9.5 than at 12.0 because more NH oscillators would increase the decay rate. To test for the demetalation of Eu^{II} at lower pH values, we acquired the absorption spectra of **1** at pH 12.0, 11.3, 10.0, 9.5, and 8.0 (Figure 3c). As the pH was decreased, the intensity of the peak at 415 nm decreased, while a peak at 320 nm increased in intensity. The new peak at 320 nm aligned with the peak from uncomplexed $EuCl_2$ suggesting the occurrence of demetalation at lower pH values. Although no absorption at 415 nm was observed at pH 8, there is likely a small amount of complex **1** present at this pH based on the emission spectrum (Figure 3a) and the relative sensitivities of fluorometric methods and absorption spectroscopy.[10] Based on these data, the decrease in emission intensity of **1** with decreasing pH is likely a combination of quenching from protonated amines and demetalation, with quenching appearing to dominate above pH 9.5.

To relate the luminescence behavior of **1** to its structure, we studied the coordination environment of **1** in the solid state and in solution. The crystal structure of **1** shows that Eu^{II} is coordinated to all eight nitrogens of the ligand and to a chloride ion in a distorted staggered hula-hoop geometry (Figure 1).[11] The feet of the structure comprise N2 and N3, and the remaining nitrogen atoms compose the hoop. There is also a noncoordinated chloride counterion and a molecule of methanol in the unit cell (not shown for clarity). Importantly, the crystal structure shows no inner sphere solvent molecules; therefore, if the solid-state structure is indicative of solution behavior, then the bright luminescence of **1** is likely a result of the absence of inner-sphere, solvent-based OH oscillators. If protonated, the NH oscillators of the ligand are capable of quenching the excited state of Eu^{II}, and the geometry around the secondary amines coordinated to Eu^{II} and combustion analysis of **1** suggest that the amines are protonated in the solid state; however, the solution measurements (Figure 3) suggest that these NH oscillators are not as prevalent at high pH values relative to lower pH values. Consequently, NH oscillators appear to not be contributing as much to the quenching of the excited state of Eu^{II} at high pH values relative to lower pH values.

To determine the relationship between the solid- and solution-phase behaviors of **1**, we characterized the coordination environment of **1** in aqueous media using the continuous variation method (Job plot), variable-temperature ^{17}O NMR spectroscopy, and conductivity measurements.

A Job plot was used to determine the stoichiometry of binding between Eu^{II} and the ligand using the integrated emission at 580 nm (λ_{ex} = 415 nm) to determine if the metal-to-ligand ratio in solution matched the solid state structure. This technique can be used to determine metal-to-ligand ratios in solution by examining a property of the complex as a

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function of the mole fraction of metal.[12] Maximum complex formation occurred at a stoichiometry of 1:1 between $EuCl_2$ and aza-222 cryptand, **2** (Figure 4a). This result demonstrates

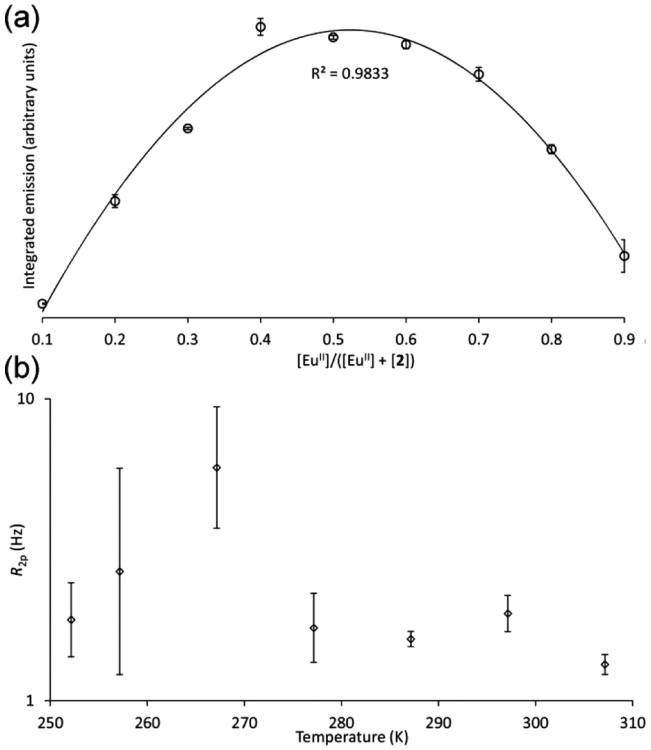

Figure 4. (a) Job plot for **1**. Data were fitted using a polynomial function. (b) Variable-temperature ^{17}O NMR data for **1** at pH 12.0. Error bars represent the standard error of the mean from three independently prepared samples for both (a) and (b).

consistency between the solid and solution structure of **1**. Despite this consistency, the Job plot analysis is inconclusive with respect to coordinated solvent molecules in solution.

Variable-temperature ^{17}O NMR spectroscopy was used to test for the presence of coordinated water in **1** in solution. This technique can be used to determine the number of exchangeable water molecules coordinated to a paramagnetic metal ion using the difference in line widths of ^{17}O peak of a paramagnetic metal complex and that of a similar diamagnetic metal complex.[6c] We measured the differences in line widths of **1** and its diamagnetic Sr^{II}-containing aza-222 cryptate analog (Sr^{II} and Eu^{II} have similar charge densities)[2a] at seven temperatures between 250 and 310 K (Figure 4b). The calculated R_{2P} (difference in line widths $\times \pi$) did not show an exponential correlation with temperature; therefore, either there are no exchangeable water molecules coordinated to the Eu^{II} center or coordinated water molecules are exchanging rapidly ($\geq 2 \times 10^{11}$ s^{-1}).[13] While ^{17}O NMR spectroscopy data support a lack of coordinated H_2O molecules in solution, the results of the experiment are inconclusive, and another technique was needed to probe the coordination environment of Eu^{II} in solution.

Molar conductivity was determined to investigate the coordination of chloride ion in solution. For **1**, molar conductivity was calculated at pH 10.0 (pH was not adjusted to 12.0 with KOH to avoid adding more ions) from the measured conductivity of **1** (137 ± 2 S mol^{-1} cm^2). The molar conductivity is within the range of 1:1 ion dissociation in water (96–150 S mol^{-1} cm^2 for 1:1 dissociation).[14] These data suggest that the chloride ion is likely coordinated to the metal center even in an aqueous basic solution because to achieve a 1:1 ion dissociation, only one cation and one anion can be present. A possible explanation for this observation is based on hard–soft acid–base theory,[15] which predicts that the relatively soft Eu^{II} ion in **1** is better matched to chloride relative to oxygen donors. The results of the conductivity measurements together with the other solution-phase studies indicate that the structure in solution is similar to the solid-phase structure.

In conclusion, we have synthesized a Eu^{II}-containing complex that displays bright yellow emission in aqueous media with a quantum yield of 26%. Solid-state and solution-phase characterization indicate 1:1 metal-to-ligand coordination and the absence of directly coordinated OH oscillators. These results demonstrate a new Eu^{II}-containing luminescent probe in an aqueous medium with high quantum yield that has the potential to be used in aqueous-based luminescence applications.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, calculation of quantum yield, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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