Measurement of the Dissociation of Eu$^{II}$-Containing Cryptates Using Murexide

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Supporting Information

ABSTRACT: The dissociation rates of five Eu$^{II}$-containing cryptates in water were measured using UV−visible spectros-copy and murexide at pH 6.5, 7, 7.5, 8, and 9. Murexide was used as a coordinating dye for Eu$^{II}$. The results for a known cryptate were within experimental error of the value obtained using other methods and enabled the measurement of other cryptates. This validation of the use of murexide to study the dissociation of Eu$^{II}$-containing cryptates enables its use with other complexes of Eu$^{II}$.

INTRODUCTION

Eu$^{II}$-containing complexes have potential uses in catalysis,¹ luminescence applications,⁴ and redox-responsive magnetic resonance imaging,⁴,⁵ because of their redox, optical, and magnetic properties. In many applications, kinetic inertness is a key parameter for the design of ligands. However, there are a limited number of reports describing measurement of the rates of dissociation of Eu$^{II}$-containing complexes.⁵−⁷ Part of the reason for the limited number of studies is that many of the methods used to measure the dissociation rates of metal complexes are not conveniently compatible with Eu$^{II}$-containing complexes; consequently, there is a need for new methods to measure the kinetic parameters of Eu$^{II}$-containing complexes.

Techniques commonly used to measure the dissociation rates of metal chelates include NMR-based methods,⁸ electrochemical techniques,⁵ relaxometric methods,⁹ and spectrophotometric methods (luminescence¹⁰ and UV−visible spectroscopy).¹¹,¹² Direct NMR-based methods are not suitable for kinetic measurements of Eu$^{II}$-containing complexes due to NMR line broadening. Electrochemical techniques have been used to study the dissociation rates of some Eu$^{II}$-containing cryptates,⁵,⁶ but these methods require high concentrations (>10 mM) of samples, rendering this technique impractical in many cases. Relaxometric methods can be influenced by the presence of different counterions. Furthermore, luminescence spectroscopy is not always useful because not all Eu$^{II}$-containing complexes are luminescent and solvents, like water, often quench luminescence. Among the techniques mentioned above, UV−visible spectroscopy is the most widely used;¹² however, the overlap of the UV−visible absorption spectra of Eu$^{II}$-containing cryptates with uncomplexed Eu$^{II}$ can limit the usefulness of UV−visible spectroscopy with respect to monitoring their dissociation. Therefore, metallochromic indicators can be useful in measuring the dissociation rates that are otherwise difficult to study. These indicators provide an optical response to changes in the concentration of complexed and uncomplexed metal ions.

Murexide (Figure 1) has been used as an indicator to monitor the formation and dissociation of alkali and alkaline-earth cryptates.¹³,¹⁴ Furthermore, trivalent lanthanide and transition-metal ions are known to coordinate with murexide.¹⁴,¹⁵ Solutions of murexide are deep purple and turn to orange upon coordination with metal ions, even in dilute (~0.2 mM) conditions. Because murexide binds to Sr$^{II}$ and Ca$^{II}$ and because Eu$^{II}$ is intermediate in size between these two ions,¹⁶ we hypothesized that murexide would respond to uncomplexed Eu$^{II}$ similarly to how it responds to alkaline-earth metals, enabling kinetic and thermodynamic quantities, including dissociation rates that are of interest for many applications of Eu$^{II}$-containing complexes, to be calculated from the amount of uncomplexed Eu$^{II}$. Herein, we describe

Figure 1. Structure of murexide.

Special Issue: Innovative f-Element Chelating Strategies

Received: December 26, 2018
Published: February 19, 2019
testing of the use of murexide to measure the dissociation rates of Eu\(^{III}\)-containing cryptates.

## RESULTS AND DISCUSSION

To study the interaction of Eu\(^{III}\) with murexide in aqueous solution, we acquired UV–visible spectra of murexide in the presence and absence of Eu\(^{III}\). These spectra show that the absorption maximum of murexide shifts from 525 to 485 nm upon the addition of EuCl\(_2\) (Figure 2). Further, the difference in the maximum absorption shifted slightly to shorter wavelengths with increasing amounts of Eu\(^{III}\). This type of spectral shift in murexide toward shorter wavelengths upon interaction with metal ions has been observed for alkaline-earth metal–murexide interactions,\(^{18}\) transition metal–murexide interactions,\(^{19}\) and lanthanide–murexide interactions.\(^{14}\)

In addition to a shift in the wavelength, the absorption intensity decreased with increasing concentration of Eu\(^{III}\) (Figure 2), and the solutions became colorless upon reaching Eu\(^{III}\)-to-murexide ratios of 1:1 or greater. To confirm that the color change was due to the reduction of murexide by Eu\(^{III}\), we performed a control experiment that involved the oxidation of Eu\(^{II}\) to Eu\(^{III}\). A mixture of EuCl\(_2\) (10 mM, 60 \(\mu\)L, 1 equiv) and murexide (10 mM, 60 \(\mu\)L, 1 equiv) in a 2-amino-2-(hydroxymethyl)propane-1,3-diol buffer (100 mM, pH 7) was colorless when opened to air to oxidize Eu\(^{II}\) to Eu\(^{III}\). The color of the sample changed to orange in less than 2 min. To confirm that this color change was due to the interaction of Eu\(^{III}\) with murexide, we mixed EuCl\(_2\)-6H\(_2\)O and murexide in a 1:1 stoichiometry and observed the same color change as that with the Eu\(^{III}\) sample that was exposed to air. These results indicate that the interaction of Eu\(^{III}\) with murexide caused the orange color and that murexide was not degraded to a noticeable amount by Eu\(^{III}\). Additionally, when Eu\(^{III}\) was mixed with murexide in water, there was no significant change (ANOVA single factor analysis; 95% confidence interval) in the absorbance as a function of time, indicating that the system reached equilibrium within minutes of mixing Eu\(^{III}\) with murexide and was stable for at least 50 min (Figure S2).

After characterizing the spectroscopic changes to murexide upon interaction with Eu\(^{III}\), we validated the use of murexide to measure the dissociation rates by measuring the dissociation rates of two reported complexes, Eu1Cl\(_2\) and Eu2Cl\(_2\) (Figure 3).\(^{6}\)

To measure the dissociation rate of Eu1Cl\(_2\), we selected conditions (0.5 M Me\(_4\)NClO\(_4\)) similar to those used to determine a first-order rate constant with electrochemistry.\(^{5}\)

To match the pH conditions used in the electrochemistry study, we adjusted the pH to 7 using 2-amino-2-(hydroxymethyl)propane-1,3-diol. We measured the change in the absorption at 485 nm as a function of time. The measured absorption values were used to calculate the concentrations of Eu\(^{III}\) using a calibration curve, and a linear relationship between the natural log of the cryptate concentration and time indicated that the dissociation is first-order with respect to Eu1Cl\(_2\) (Figure 4), consistent with the report using electrochemistry.\(^{6}\)

\[\text{Results and Discussion} \]

To measure the dissociation rates of Eu1Cl\(_2\) and Eu2Cl\(_2\) in aqueous solutions of murexide with EuCl\(_2\) in water (pH 7); [murexide] = 0.2 mM, [EuCl\(_2\)] = 0 (bold ---), 0.1 (---), 0.12 (----), 0.15 (-----), 0.16 (----), and 0.18 mM (---).

![Figure 2. UV–visible spectra of aqueous solutions of murexide with EuCl\(_2\) in water (pH 7); [murexide] = 0.2 mM, [EuCl\(_2\)] = 0 (bold ---), 0.1 (---), 0.12 (----), 0.15 (-----), 0.16 (----), and 0.18 mM (---).](Image)

![Figure 3. Cryptands used for dissociation studies.](Image)

![Figure 4. Representative plot of ln [Eu1Cl\(_2\)] versus time.](Image)

![Table 1. Dissociation of Eu1Cl\(_2\) (0.5 mM) at 25 °C](Table)

<table>
<thead>
<tr>
<th>electrolyte (0.5 M)</th>
<th>Ba(NO(_3))(_2) (mM)</th>
<th>murexide (mM)</th>
<th>(k_{d,ob}) (\times 10^{-5}) s(^{-1})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et(_4)NClO(_4)</td>
<td>3.3</td>
<td>0</td>
<td>3.0*</td>
<td>7</td>
</tr>
<tr>
<td>Me(_4)NClO(_4)</td>
<td>0.2</td>
<td>0.2</td>
<td>3.0 ± 0.3</td>
<td>7</td>
</tr>
</tbody>
</table>

*From ref 6. Mean ± standard error of the mean of three independently prepared samples.

Additionally, the conditional dissociation rates \((k_{d,ob})\) for Eu2Cl\(_2\) were reported at different pH values in aqueous LiClO\(_4\)/HClO\(_4\) (1 M),\(\text{ where the y intercept of the linear fit of the plot of } k_{d,ob} \text{ versus } [H^+]) was used to report \(k_d\) as 1 \(\times 10^{-4}\) s\(^{-1}\).\(\text{ However, when we mixed murexide with Eu2Cl2 in LiClO4/HClO4 (1 M), the color of the murexide disappeared instantaneously at each pH value. These color-change observations were inconsistent with a } k_d \text{ value of } 1 \times 10^{-4} \text{ s}\(^{-1}\).
To explore the cause of the rapid color change, we further studied Eu2Cl₄ in the solid state and in solution. Crystal structure analysis and proton relaxation enhancement measurements revealed that Eu³⁺ complexed with ligand 2 both in the solid state and in solution. The crystal structure of Eu2Cl₄ (Figure 5) shows Eu³⁺ with a coordination number of 9 in an eclipsed hula-hoop geometry. Seven of the nine sites are occupied by the five oxygen and two nitrogen atoms of the cryptand, and two adjacent coordination sites are occupied by water molecules. In solution, the water proton relaxation rate was measured as a function of the amount of ligand 2 added to a solution of Eu²⁺. The relaxation rate decreased with the addition of 2 up to a 1:1 ligand-to-metal ratio (Figure 6), and after that point, the rate did not change (ANOVA single factor analysis; 95% confidence interval). Because ligand 2 binds to Eu³⁺ in solution and the crystal structure reveals two adjacent coordinated water molecules, we envision that, upon mixing of murexide with Eu2Cl₄, one molecule of murexide replaces the two adjacent inner-sphere water molecules, binding to [Eu2]²⁺ in a bidentate manner.

To test if murexide displaced water bound to Eu2Cl₄ in solution, we measured the change in the relaxation rate of solutions of Eu2Cl₄ as a function of the amount of murexide (Figure 7). The results show that the relaxation rate decreased as the amount of murexide increased, consistent with what would be expected if murexide replaced the bound water. The formation of a ternary complex of murexide, Eu³⁺, and 2 suggests that murexide is not suitable to measure the dissociation of Eu³⁺-containing complexes with adjacent coordination sites available for bidentate ligands.

After validation of the technique with the reported complexes, the dissociation rates of three other Eu³⁺-containing cryptates were measured with murexide. The dissociation rates for Eu³⁺ and these ligands, 3–5, have not been reported. Ligands 3 and 4 were selected because they have been studied with Eu³⁺ as potential MRI contrast agents, and ligand 5 was selected to establish the ability of murexide to differentiate small differences in the dissociation rates, expected based on the differences in the electronics of the ring among ligands 3–5. The introduction of a methyl group onto the benzo ring was expected to slightly decrease the dissociation rates because of the inductive donating effect of the methyl group. Cryptand 3 is commercially available, and the synthesis of cryptand 4 has been reported. Additionally, characterization of Eu³⁺-containing complexes of cryptands 3 and 4 has been reported. Cryptand 5 was synthesized in four steps starting from a commercially available catechol (Scheme 1). We studied the formation of Eu5Cl₄ in solution using proton relaxation enhancement (Figure 8). The relaxation rate decreased with the addition of ligand up to a ligand-to-metal ratio of 1:1, and after that point, the rate did not change. These data are consistent with the formation of a 1:1 complex in solution. After characterization, we focused on studying the kinetic dissociation of Eu³⁺-containing cryptates of cryptands 1 and 3–5.

The conditional dissociation rates of Eu³⁺-containing complexes Eu1Cl₂, Eu3Cl₂, Eu4Cl₂, and Eu5Cl₂ were measured at pH values of 6.5, 7.0, 7.5, 8.0, and 9.0 to include physiologically relevant values and to enable the collection of enough data to obtain graphs of k_d,obs versus [H⁺] to determine spontaneous dissociation rates (k_d, eq 1).

\[
k_{d,obs} = k_d + k_{H} [H^+] \tag{1}
\]

In eq 1, k_d is the spontaneous dissociation rate, and k_H is the acid-catalyzed dissociation rate. In the measurement of k_d,obs, pH values lower than 6.5 were not explored because murexide is not stable at low pH. And pH 9 was chosen as the upper limit because Eu³⁺ precipitates as hydroxide above pH 9. For the dissociation experiment, Eu³⁺-containing complexes were prepared by mixing an aqueous solution of ligand (1:1 equiv) with an aqueous solution of EuCl₃ (1:0 equiv). Dissociated Eu³⁺ interacts with murexide, as indicated in eq 2, and this interaction changes the absorption of murexide. Therefore,
the dissociation rates were measured using the change in the absorption at 485 nm [constant ionic strength (0.5 M Me₄NClO₄) at 25 ± 0.5 °C] as a function of time.

\[ \text{Eu}^{II}L \rightleftharpoons \text{Eu}^{II} + L \xrightleftharpoons[^{-xM}]{^xM} \text{Eu}^{II}M_x + L \; x = 1 - 3 \] (2)

In eq 2, L is a cryptand, M is murexide, and x is the number of murexide molecules bound to Eu²⁺. For clarity, water and counterions are not included in the equation. The dissociated Eu²⁺ ion interacts with murexide, and the interaction of Eu with murexide inhibits back-complexation of cryptand with Eu²⁺.

The validity of this experiment was supported by our data with Eu¹Cl₂ that reproduced the dissociation rate of Eu¹Cl₂, which was determined using electrochemistry. The conditional dissociation rates obtained for Eu²⁺-containing cryptates Eu¹Cl₂, Eu³Cl₂, Eu⁴Cl₂, and Eu⁵Cl₂ at five different pH values (Table 2) were used to obtain \( k_d \) values at 25 °C. The plots of \( k_{\text{obs}} \) versus [H⁺] were fit to straight lines (Figure 9), and the values of \( k_d \) were calculated as the y intercepts of the lines (Table 3). The value of \( k_d \) obtained in this way for Eu¹Cl₂ using murexide is in good agreement with the value reported from electrochemical methods (∼5 × 10⁻⁵ s⁻¹). The dissociation rate of an unsubstituted cryptate from that of a benzo-substituted cryptate, we compared the dissociation rates of Eu¹Cl₂ with Eu³Cl₂. The dissociation rate (\( k_d \)) of Eu³Cl₂ is 4.2 times faster than that of Eu¹Cl₂. This difference of the dissociation rates between Eu¹Cl₂ and Eu³Cl₂ likely arises from the structural differences between the two ligands. Previous kinetic studies with alkaline-earth-metal complexes of ligands 1 and 3−5 revealed that the introduction of a benzo group increases the dissociation rates. For example, the dissociation rate of Sr²⁺ is 3.3 times faster than that of Sr¹Cl₂ in water at 25 °C. Because of the similar charges and sizes of Eu²⁺ and Sr²⁺,

<table>
<thead>
<tr>
<th>complex</th>
<th>pH 6.5</th>
<th>pH 7</th>
<th>pH 7.5</th>
<th>pH 8</th>
<th>pH 9</th>
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<tr>
<td>Eu¹Cl₂</td>
<td>1.58 ± 0.04</td>
<td>6.6 ± 0.3</td>
<td>13.4 ± 0.4</td>
<td>6.2 ± 0.2</td>
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<td>Eu³Cl₂</td>
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<tr>
<td>Eu⁴Cl₂</td>
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<td>13.4 ± 0.4</td>
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<td>13.4 ± 0.4</td>
<td>6.2 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

Values are reported as the mean ± standard error of the mean of three independently prepared samples. Ionic strength = 0.5 M.
we expected that the dissociation of EuI Cl2 and Eu3Cl2 would follow the same trend as the analogous S2I-containing complexes, and our data are in line with that expectation. The dissociation-rate studies of EuI Cl and Eu3Cl2 reveal that murexide is able to differentiate the dissociation rates between unsubstituted and benzo-substituted cryptates.

To compare functionalized benzo-substituted cryptates Eu4Cl4 and Eu5Cl4 from unfunctionalized benzo-substituted cryptate Eu3Cl3, we measured the dissociation rates of Eu4Cl4 and Eu5Cl4. The results (Table 3) show that the dissociation rate of Eu4Cl4 is 2 times faster than the dissociation rate of Eu3Cl3. The data suggest that the electron-withdrawing nature of fluorine has more influence on the dissociation rate than the π-donating ability. The inductive electron-withdrawing nature of fluorine decreases the electron-donating ability of the oxygen atoms attached to the benzo ring, consistent with more rapid dissociation, and the π-donating ability of the fluorine substituent would be expected to counteract the influence of the inductive electron-withdrawing effect. There was no difference (Student's t test; p = 0.6) between the dissociation rates of Eu3Cl3 and Eu5Cl4 (Table 3), indicating that the inductive electron-donating effect of the methyl group did not increase the electron density of the oxygen atom attached to the benzo ring enough to lead to an observable change in the dissociation rate using murexide. The difference in the dissociation rates between Eu4Cl4 and Eu5Cl4 indicates that the inductive electron-withdrawing ability of fluorine has a measurable influence on the dissociation rate relative to the inductive donating effect of a methyl group.

### CONCLUSIONS

We have described the use of UV–visible spectroscopy with murexide to study the dissociation rates of EuII-containing cryptates. The rates of dissociation of EuII-containing cryptates increase in the order of EuI Cl2 < Eu3Cl3 ≈ Eu5Cl4 < Eu4Cl4. The findings presented here demonstrate the utility of murexide in the measurement of the dissociation rates of EuII-containing cryptates, and these findings are likely to be useful in the characterization of many EuII-containing complexes.

### EXPERIMENTAL DETAILS

**General Procedures.** Commercially available chemicals were used without further purification unless otherwise stated. Water was purified using a PURELAB Ultra Mk2 water purification system (ELGA) and degassed under reduced pressure prior to use. Murexide was purchased from Sigma-Aldrich. 5,6-(4-Fluorobenzoyl)-1,10-phenanthroline was synthesized following reported procedures.4 The UV–visible absorbance was measured using a Shimadzu UVmini-1240 spectrophotometer. Samples were prepared inside a wet glovebox (water allowed, but not O2) under an atmosphere of N2. Samples were loaded into airtight cuvettes and sealed with paraffin wax prior to removal from the glovebox.

The values of the pH were measured using an Oakton pH 700 m at ambient temperature.

X-ray-quality crystals of Eu2Cl2 were obtained by slow evaporation in a wet glovebox. EuI Cl2 (510 mg, 0.229 mmol) and ligand 2 (88.8 mg, 0.267 mmol) were dissolved in methanol (0.8 mL) under an inert atmosphere. The resulting colorless solution was stirred for 3 h and then filtered through a 0.2 μm hydrophilic filter (Millipore-LG hydrophilic). Tetrahydrofuran vapor was diffused into the filtrate to obtain a white precipitate. The white precipitate was dissolved in acetone (0.3 mL), and the sample was allowed to slowly evaporate to yield colorless block-shaped crystals suitable for X-ray diffraction. A suitable crystal (0.20 × 0.13 × 0.08 mm3) was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2,5 the structure was solved with the SHELXT structure solution program,5 using the intrinsic-phasing solution method. The model was refined with SHELXL.6 using least-squares minimization.

**Preparation of Buffers.** Buffers for measurements at pH 7, 7.5, 8, and 9 were prepared by dissolving 2-amino-2-(hydroxymethyl)-propane-1,3-diol (12.1 g, 0.100 mol) in water (90 mL). The pH values of the solutions were adjusted to the desired pH with the addition of aqueous HCl (3 M). Additional water was added to bring the final volume of each buffer to 100.00 mL. A buffer for measurements at pH 6.5 was prepared by dissolving 3-morpholino-propane-1-sulfonic acid (21.0 g, 0.100 mol) in water (90 mL). The pH of the solution was adjusted to 6.5 with the addition of aqueous NaOH (1 M). Additional water was added to bring the final volume to 100.00 mL.

**Dimethyl 2,2′-[(4-Methyl-1,2-phenylene)bis(oxy)]diacetate (6).** A mixture of 4-methylbenzene-1,2-diol (1.00 g, 8.07 mmol, 1 equiv), acetone (50 mL), potassium carbonate (6.20 g, 40.3 mmol, 5 equiv), and methylboronic acid (10.0 mL, 106 mmol, 13.1 equiv) was heated at reflux for 8 h, cooled to ambient temperature, and filtered. The solvent was removed under reduced pressure to obtain a yellow oil. The oil was dissolved in ethyl acetate (40 mL) and washed with water (3 × 20 mL). The organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure before purification was performed using silica gel chromatography (3:1 hexanes/ethyl acetate) to yield 1.95 g (90%) of 6 as a pale-yellow oil.1H NMR (400 MHz, CDCl3): δ 2.28 (s, 3H, CH3), 3.80 (s, 3H, CH3), 4.70 (s, 2H, CH2), 4.72 (s, 2H, CH2), 6.68–6.85 (m, 3H, CH3).13C NMR (101 MHz, CDCl3): δ 21.1 (CH3), 52.4 (CH3), 66.8 (CH3), 67.2 (CH3), 116.0 (CH), 116.5 (CH2), 123.1 (CH2), 132.8, 146.0, 148.0, 169.3, 169.9. TLC: Rf = 0.18 (3:1 hexanes/ethyl acetate). HRESIMS. Calcd for C13H21O5 ([M + H]+): m/z 269.1026. Found: m/z 269.1014.

**High-resolution electrospray ionization mass spectroscopy (HRESIMS).** Spectra were obtained using an electrospray time-of-flight high-resolution Waters Micromass LCT Premier XE mass spectrometer.
obtain 0.752 g (96%) of 7 as an off-white solid. 1H NMR (400 MHz, CD2OD): δ 2.28 (s, 3H, CH3), 4.68 (s, 3H, CH3), 4.71 (s, 3H, CH3), 5.06 (brs, 2H, OH), 6.73–6.91 (m, 3H, CH). 13C NMR (101 MHz, CD2OD): δ 22.0 (CH3), 68.3 (CH3), 68.8 (CH3), 118.1 (CH), 118.6 (CH), 124.8 (CH), 134.7, 148.3, 150.4, 173.9, 174.0. HRESIMS. Calcd for C11H12O6Na ([M + Na]+): m/z 263.0532. Found: m/z 263.0536.

5.6-(4-Methylbenzyl)-4,7,13,16,20,23-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-2,9-dione (8). To diacid 7 (0.571 g, 2.34 mmol, 1 equiv) was added thionyl chloride (10.0 mL, 0.140 mmol, 60 equiv) under an atmosphere of Ar. The mixture was heated at reflux until the mixture became a white, oily solid that was dissolved in a concentrated aqueous solution of cesium carbonate and extracted with diethyl ether (4 × 20 mL) in anhydrous toluene (40 mL) under an atmosphere of Ar. The mixture was heated at reflux until the mixture became a clear, yellow solution. The reaction mixture was concentrated under reduced pressure to obtain a yellow oil that was dissolved in anhydrous dichloromethane (7 mL in anhydrous toluene (40 mL) was prepared. Both solutions were simultaneously added dropwise over 1 h to a flask containing anhydrous toluene (300 mL) at 0 °C under an atmosphere of Ar. The resulting reaction mixture was stirred for 12 h while warming to ambient temperature. The solvent was removed under reduced pressure before purification was performed using silica gel chromatography (10:1 dichloromethane/methanol) to yield 0.590 g (54%) of 8 as a white solid. 1H NMR (400 MHz, CDCl3): δ 2.16–2.31 (m, 3H, CH3), 2.70–2.90 (m, 2H, CH2), 2.90–3.00 (m, 2H, CH2), 3.05–3.25 (m, 2H, CH2), 3.80 (m, 20H, CH), 4.57 (t, 4H, CH2), 4.89 (t, 4H, CH2), 5.55 (m, 2H, CH2), 5.06 (brs, 2H, OCH2), 6.73–6.91 (m, 3H, CH).

Dissociation Rate Measurements. Metal complexes for kinetic measurements were prepared inside a glovebox under an atmosphere of N2. Aqueous solutions of EuCl2 (0.150 mL, 10.0 mM) and ligand (1, 2.20 μL, 75.0 mM; 2, 17 μL, 95 mM; 3, 21.0 μL, 80.0 mM; 4, 21.0 μL, 78.0 mM; or 5, 16.0 μL, 102 mM) were added to water (1000 μL). The resulting solutions were stirred at ambient temperature under an inert atmosphere for 4 h before the addition of aqueous buffer (300 μL, 1.00 M) and tetramethylammonium chloride (300 μL, 5.00 M). A freshly prepared solution (36.0 μL, 25.0 mM) of murexide in water was added to the reaction mixture, and the final volume was brought to 3.00 mL with the addition of water. Samples were immediately sealed with paraffin wax, and measurements were performed outside the glovebox. Dissociation was monitored by measuring the change in the absorption with time in the range of 485–505 nm. The measured absorption values were used to calculate the concentration of europium using a calibration curve. The calibration curve was prepared by measuring the absorption of murexide (0.2 mM) in the presence of varying amounts of EuCl2 (0.01–0.18 mM). The concentrations of europium obtained from the calibration curve were used as the concentrations of Eu-containing cryptates.
(b) Bulgakov, R. G.; Elsseeva, S. M.; Galimov, D. I. Peculiarities of bright blue liquid-phase chemiluminescence of the Eu(III) ion generated at the interfaces in the systems EuX·3H2O·THF→R2→3AlH·2O2 (X = Cl, NO3 = Bu′Et and Me; n = 0, 1). J. Lumin. 2016, 172, 71–82.
(q) Bulgakov, R. G.; Elsseeva, S. M.; Galimov, D. I. The first observation of emission of electronically excited states of the divalent Eu(II) ion in the new chemiluminescent systems Eu(bu′Et)3·AlH·2O2 and Eu(bu′Et)3·AlH·2O·THF with the participation of oxygen. RSC Adv. 2015, 5, S2132–S2140.


