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Lanthanide Luminescence

Solvation-Controlled Luminescence of Sm^{II} Complexes**

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The effect of additives and solvents on the reactivity of samarium diiodide (SmI_2) has been widely investigated during the past two decades.[1] Numerous additives ranging from simple organic substrates to inorganic metal salts have been utilized to enhance the rate and diastereoselectivity of SmI_2-mediated reactions.[2] A variety of solvents such as tetrahydrofuran (THF), dimethoxyethane, tetrahydropyran, and acetonitrile have also been explored as suitable reaction media for SmI_2 reductions.[3,4] Additives and solvents that contain suitable functional groups can coordinate to samarium and as a result alter the mechanism of many reactions.[4] The relative propensity for coordination between competing additives and solvents can potentially alter the stability and reactivity of Sm^{II}. Here, we demonstrate how controlling the coordination sphere of SmI_2 through changes in solvation induces remarkable changes in property both in the ground and excited states. The data described herein show two important features: 1) Changes in solvation of SmI_2 can significantly alter the interaction between a ligand and Sm^{II}, and 2) addition of the appropriate crown ether to SmI_2 in acetonitrile not only stabilizes the ground state reductant but also generates a highly luminescent complex. The method described herein provides an alternative approach to luminescent materials utilizing the unique properties of Sm^{II} complexes.

Salts of Sm^{II} generated in crystal lattices of Ca or Sr exhibit luminescence lifetimes on the order of microseconds to milliseconds, whereas Sm^{II} in THF solution shows luminescence lifetimes in the nanosecond regime.[5] The electronic transitions responsible for luminescence in the solid and solution states have been identified as $4f^55d^1$ to $4f^6$.[5] Luminescence quenching of Sm^{II} compounds in solution is a function of the frequency of solvent collision and is inversely related to the affinity of solvent for the metal. These findings lead to the reasonable hypothesis that providing a chelating ligand for SmI_2 in a solvent incapable of displacing it would significantly enhance the luminescence properties of Sm^{II} by 1) encapsulating the metal through a strong metal–ligand interaction and 2) decreasing the frequency of solvent collision in the absence of the ligand.

The fact that Sm^{II} salts are highly oxophilic suggests that crown ethers should be suitable chelating additives for Sm^{II} for the purpose described above, and examination of the literature shows a number of reports of complex formation between Sm^{II} salts and crown ethers.[5b,6] The addition of [15]crown-5 (15-C-5) and [18]crown-6 (18-C-6) to SmI_2 in THF led to precipitation. However, when a solution of SmI_2 in acetonitrile was treated with 15-C-5 or 18-C-6, two different types of soluble complexes were generated.

Addition of two or more equivalents of 15-C-5 to a solution of SmI_2 in acetonitrile resulted in an immediate color change from muddy green to bright red, consistent with the UV/Vis spectral changes depicted in Figure 1. Addition of one or more equivalents of 18-C-6 produced a bright green color and a less significant hypsochromic shift compared to that observed with the addition of 15-C-5 (Figure 1). The strong interaction between both crown ethers and Sm^{II} is evident by the large blue shifts in the absorption peak of SmI_2 in acetonitrile.

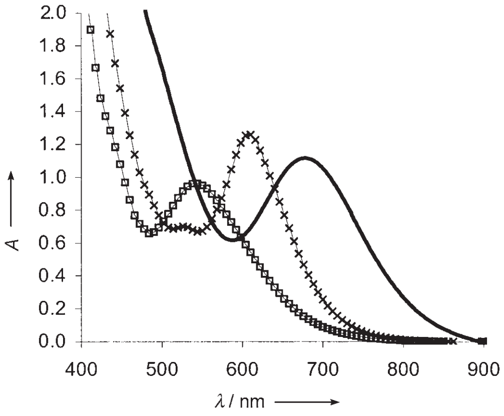

Figure 1. UV/Vis spectra of 2 mM SmI_2 (——) in acetonitrile in the presence of 4 mM 15-C-5 (□) and 3.5 mM 18-C-6 (×).

To further characterize the impact of addition of crown ethers to SmI_2 in CH_3CN, cyclic voltammetry (CV) studies were carried out by preparing samples containing increasing ratios of either 15-C-5 or 18-C-6 and SmI_2 in CH_3CN and recording a cyclic voltammogram for each sample. In the absence of additive, a quasi-reversible voltammogram was obtained with an estimated $E_{1/2}$ value of (-1.28 ± 0.05) V versus a saturated $Ag/AgNO_3$ electrode. While addition of 18-C-6 to SmI_2 in CH_3CN containing electrolyte showed the green color change as described above, there was little

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difference in the measured potential compared to SmI_2 alone within experimental error. Surprisingly, addition of 15-C-5 led to a substantial change in the redox properties. The cyclic voltammograms of SmI_2, and SmI_2 containing two and four equivalents of 15-C-5, are shown in Figure 2. The sample containing two equivalents of 15-C-5 shows the presence of two redox active species. One species provides an $E_{1/2}$ value of (-1.32 ± 0.05) V likely corresponding to uncomplexed SmI_2, and another appears at (-1.00 ± 0.05) V. Addition of four equivalents of 15-C-5 provides a voltammogram with an estimated $E_{1/2} = (-1.00 \pm 0.05)$ V. The addition of 15-C-5 to SmI_2 in CH_3CN clearly produces a more stable complex. Results from other studies show that two equivalents of 15-C-5 are sufficient to produce the complex (see below), hence it is likely that the high concentration of electrolyte necessary for successful electrochemical studies may inhibit coordination of the crown ether to some extent.

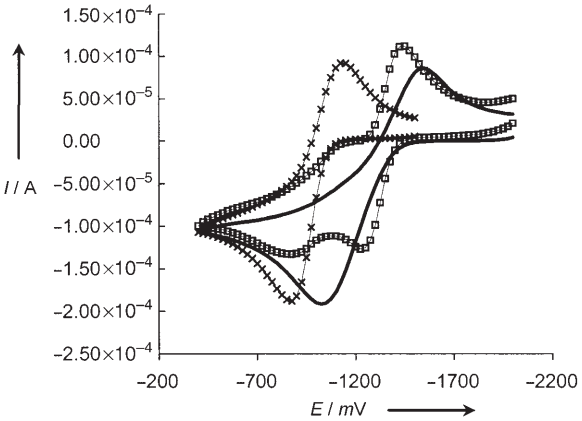

Figure 2. Cyclic voltammograms of 15 mM SmI_2 (——) in CH_3CN in the presence of 2 mM 15-C-5 (□) and 4 mM 15-C-5 (×).

To determine whether the ligands have a sufficiently high affinity necessary to suppress interaction with solvent, thermodynamic parameters for complex formation were determined by employing isothermal titration calorimetry (ITC) measurements. Addition of successive 5-μL aliquots of 15-C-5 (0.20 M) to SmI_2 (10 mM) in acetonitrile at 298 K revealed the formation of a 2:1 complex. This stoichiometry is consistent with the X-ray crystal structure of $[Sm(15\text{-}C\text{-}5)_2](ClO_4)_2$ reported recently by Starynowicz.[6a] The association constants for formation were found to be $(2.0 \pm 0.3) \times 10^5\,\text{M}^{-1}$ and $(3.7 \pm 0.9) \times 10^4\,\text{M}^{-1}$, respectively, and show that the interaction between Sm^{II} and 15-C-5 is quite strong in acetonitrile. Examination of the structure reported by Starynowicz suggests that the solution complex can be represented by $[Sm(15\text{-}C\text{-}5)_2]I_2$ as the metal cannot accommodate two 15-C-5 ligands without displacement of iodide to the outer sphere. To date, we have been unable to isolate X-ray quality crystals to verify this hypothesis. Identical ITC experiments performed on the SmI_2–18-C-6 system revealed a fractional stoichiometric ratio of 1:1.5 (see Supporting Information), whereas the reported X-ray crystal structure of $[Sm(ClO_4)_2(18\text{-}C\text{-}6)]$ reveals a 1:1 stoichiometric ratio in the solid state. Results based on ITC are consistent with one 18-C-6 moiety strongly attached to the metal with an association constant of $(2.8 \pm 0.6) \times 10^4\,\text{M}^{-1}$.

To further examine the impact of addition of crown ether to SmI_2 in CH_3CN and provide added structural insight on the complexes in solution, a series of ^{1}H and ^{13}C NMR titration experiments were carried out by successive addition of either 15-C-5 or 18-C-6 to SmI_2 in CD_3CN. Uncoordinated 15-C-5 in CD_3CN has a ^{1}H NMR chemical shift of $\delta = 3.56$ ppm. Addition of up to two equivalents of 15-C-5 to 5 mM SmI_2 leads to a substantial change in the chemical shift with two equivalent broad signals at $\delta = 4.17$ and 2.36 ppm consistent with coordination to a paramagnetic ion. Upon further addition of 15-C-5 in excess of two equivalents, a chemical shift consistent with uncomplexed 15-C-5 begins to appear. Although ^{1}H NMR data were not reported for $[Sm(15\text{-}C\text{-}5)_2](ClO_4)_2$, the two sets of non-equivalent protons observed for the SmI_2–15-C-5 complex are consistent with a structure comparable to that reported by Starynowicz,[6a] as a similar symmetrical sandwich structure would be expected to have two sets of protons in different environments. In the ^{13}C NMR spectrum, the peak for uncomplexed 15-C-5 appears at $\delta = 71.1$ ppm and addition of the crown ether to SmI_2 shows the presence of a signal at $\delta = 94.2$ ppm. Upon further addition of 15-C-5 in excess of two equivalents, a chemical shift consistent with uncomplexed 15-C-5 begins to appear. Results consistent with coordination of 18-C-6 to SmI_2 and stoichiometries matching those suggested in previous experiments were observed as well (see Supporting Information).

Although both complexes were stable at room temperature in an inert atmosphere, the complex formed between SmI_2 and 15-C-5 was found to be unusually stable. For instance, exposure of SmI_2 in CH_3CN to the atmosphere results in nearly immediate oxidation of Sm^{II}. Conversely, when SmI_2–15-C-5 complex is exposed to air, the color dissipates slowly over a 24 h period. To examine the stability of the complex formed between SmI_2 and 15-C-5, the observed rate constant for the reduction of acetophenone by the complex in acetonitrile under pseudo-first-order conditions was examined at 25 °C and found to be $(0.50 \pm 0.01) \times 10^{-4}\,\text{s}^{-1}$. Acetophenone is reduced five orders of magnitude faster by SmI_2 alone.[7] The observed rate constant is on the same order of magnitude as the natural decay of SmI_2 under these experimental conditions and indicates that enhanced stability is provided in acetonitrile through crown complexation.

On the basis of these results, the combination of SmI_2 and 15-C-5 is expected to fulfill the requirements necessary for limiting solvent quenching of luminescence as the complex is likely to be sterically encumbered and the crown ether has a high affinity for the Sm^{II} ion. To test this supposition, the luminescence properties of SmI_2, SmI_2 in the presence of two or more equivalents of 15-C-5, and SmI_2 in the presence of one or more equivalents of 18-C-6, in acetonitrile were examined. Although SmI_2 in THF emits at 750 nm, complete loss of luminescence was observed in CH_3CN. While the solution of SmI_2 in acetonitrile is non-luminescent, the complex formed upon the addition of two or more equivalents of 15-C-5 to a solution of SmI_2 in acetonitrile resulted in a

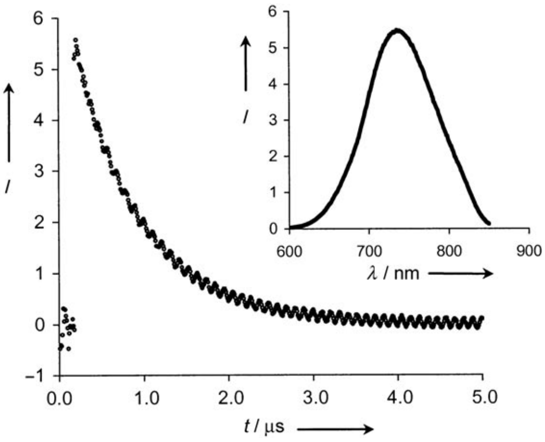

Figure 3. Excited-state decay of $[Sm(15\text{-}C\text{-}5)_2]I_2$ in acetonitrile. $[SmI_2] = 5$ mM; $[15\text{-}C\text{-}5] = 10$ mM. A single-exponential fitting of the decay provided a lifetime (τ) value of (0.80 ± 0.01) µs. The inset shows the steady-state emission spectrum.

strong luminescent material with $\lambda_{max} = 723$ nm and a quantum yield of 0.30 ± 0.01 (inset, Figure 3). The quantum yield value was found to be sixty-times higher than that for SmI_2 in THF. As expected, the emission quantum yield of SmI_2 in the presence of 18-C-6 is significantly lower at $(4.0 \pm 0.2) \times 10^{-4}$ than that of the SmI_2–15-C-5 complex. The excitation spectrum of the SmI_2–15-C-5 complex is similar to the absorption spectrum except for the UV region, where the intensity of the emission is very weak. This behavior is characteristic for Sm^{II}-based complexes and arises from poor intersystem-crossing efficiency upon excitation in the UV region.[8] The ligand-induced luminescence of SmI_2 in CH_3CN could be a result of the change in either the oscillatory strength of the transitions ($4f^6$ to $4f^5 5d^1$) or the frequency of solvent collision. The possibility of the former is ruled out based on the comparable values of molar extinction coefficients of SmI_2 and the two crown complexes.

Next, the effect of crown ethers on the excited-state lifetime of SmI_2 was investigated. Previous studies have shown that the excited-state lifetime of SmI_2 in THF is in the nanosecond domain.[5c,8] The measured excited-state lifetime of the SmI_2–15-C-5 complex in acetonitrile exhibited a value of (0.80 ± 0.01) µs (Figure 3). The excited-state lifetime of the SmI_2–18-C-6 complex was found to be (0.02 ± 0.01) µs. Table 1 summarizes the photophysical properties of both Sm–crown complexes in acetonitrile measured at room temperature. While longer excited-state lifetimes have been reported for Sm^{II} in the solid state,[5] the value for SmI_2–15-C-5 complex is the longest excited-state lifetime reported for a Sm^{II} complex in solution.

Table 1: Photophysical parameters of SmI_2, $[Sm(15\text{-}C\text{-}5)_2]I_2$, and $[Sm(18\text{-}C\text{-}6)]I_2$ in acetonitrile.

System	λ_{max}^{Abs} [nm]	λ_{max}^{Em} [nm]	τ [µs][a]	ϕ[b]
SmI_2	685	–	–	0
$[Sm(15\text{-}C\text{-}5)_2]I_2$	540	723	0.80 ± 0.01	0.30 ± 0.01
$[Sm(18\text{-}C\text{-}6)]I_2$	606	712	0.02 ± 0.01	$(4.0 \pm 0.2) \times 10^{-4}$

[a] The excited-state lifetime (τ) of Sm complexes in acetonitrile was measured utilizing a nanosecond laser flash photolysis setup. [b] In emission quantum yield (ϕ) measurements, the reference used was sulfobenzindocyanine dye (Cy 5.5 *N*-hydroxysuccinimide ester).

In summary, the addition of 15-C-5 to SmI_2 in acetonitrile produces a sterically encumbered complex that insulates the metal center from interaction with solvent and substrate. The decreased reactivity of the ground-state complex prevents reduction of substrates commonly reduced by SmI_2. Furthermore, solvent-induced luminescence quenching is decreased leading to a longer excited-state lifetime for the complex. From a practical point of view, these data suggest that it is possible to generate highly stable and luminescent lanthanide(II) complexes in solution through the proper choice of ligand and solvent. Distinct from lanthanide(III) complexes, the electronic excitation in Ln^{II} complexes involve quantum mechanically allowed transitions and hence direct excitation is possible to effectively populate the excited states of these complexes.[9] The advantage of direct excitation of Ln^{II} includes elimination of different deactivation pathways as well as the multistep syntheses involved in preparing "antenna" ligands necessary for producing luminescent Ln^{III} complexes.[10] The data described herein suggest that it is possible to control the luminescence properties of Sm^{II} by careful choice of solvent/additive combination. Further studies designed to understand the role of different solvent/additive combinations in stabilizing other Ln^{II} complexes as well as extension of this study with other additives are currently under investigation.

Experimental Section

Materials and General Procedures: Acetonitrile (CH_3CN) and tetrahydrofuran (THF) were purified utilizing the Solvent Purification System by Innovative Technology Inc.(Newburyport, MA). SmI_2 in acetonitrile was prepared by stirring overnight a slurry of samarium powder (0.10 g, 0.60 mmol) and iodine (0.125 g, 0.5 m mol) in acetonitrile (10 mL). The concentration of the solution was found to be 0.05 M by an iodometric titration. 15-C-5 and 18-C-6 were purchased from Aldrich and dried using standard protocols. Addition of 15-C-5 (20 µL, 0.022 g, 0.10 mmol) to a solution of SmI_2 in acetonitrile (10 mL, 5 mM) resulted in the formation of $[Sm(15\text{-}C\text{-}5)_2]I_2$ as a bright red solution. Similarly, addition of 18-C-6 (0.026 g, 0.10 mmol) to a solution of SmI_2 in acetonitrile (10 mL, 5 mM) resulted in the formation of $[Sm(18\text{-}C\text{-}6)]I_2$ as a bright green solution. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer.

UV/Vis spectroscopy experiments were performed on a Shimadzu UV-1601 UV-Visible Spectrophotometer controlled by UV Probe (version 1.11) software. Steady-state luminescence experiments were carried out using a Varian Cary Eclipse model fluorescence spectrophotometer. Luminescence lifetime studies were carried out by exciting the sample in THF at 520 nm with a Nd:YAG nanosecond laser. Measurement of the rate of reduction of acetophenone by SmI_2 in the presence of two equivalents of 15-C-5 was carried out using an SX-18 MV stopped-flow spectrophotometer (Applied Photophysics Ltd., Surrey, UK) at 25 °C.

Cyclic voltammograms for SmI_2 and the SmI_2–crown complexes in CH_3CN were measured with a BAS 100B/W MF-9063 electrochemical workstation. The working electrode was a standard glassy carbon electrode. The auxiliary electrode was a platinum wire, and the reference electrode was a saturated $Ag/AgNO_3$ electrode. The scan rate for all experiments was 100 mV s^{-1}. Tetraheptylammonium iodide and tetrabutylammonium hexafluorophosphate were employed as electrolytes, each at a concentration of 0.1 M. The concentration of Sm^{II} in each experiment was 15 mM. All solutions were prepared in a dry box and transferred to the electrochemical analyzer for analysis.

Isothermal titration calorimetry (ITC) experiments were performed employing a MicroCal Omega ITC at 25 °C. The SmI_2 solution in acetonitrile (20 mM) was placed in the calorimetric cell after providing a static Ar atmosphere over the sample, and the solutions of crown ether in acetonitrile (0.20 M) were taken in the calorimetric syringe. A 50 × 58 injection matrix was employed, with 5 μL injection lasting 10 s. The interval between each injection was 2.5 min. The enthalpies (ΔH), binding constants (K), and number of binding sites (n) were determined from the calorimetric data employing Origin TM Data Analysis Software.

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