Solvation Controlled Luminescence of Samarium(II) Complexes

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Abstract

Changes in solvation of samarium diiodide (SmI_2) can significantly alter the interaction between a ligand and metal. Addition of the appropriate "crown ether" to SmI_2 in acetonitrile not only stabilizes the ground state complex but also generates a highly luminescent complex. The advantage of direct excitation of lanthanide(II) complexes includes elimination of different deactivation pathways as well as the multi-step syntheses involved in preparing "antenna" ligands necessary for producing luminescent lanthanide(III) complexes.

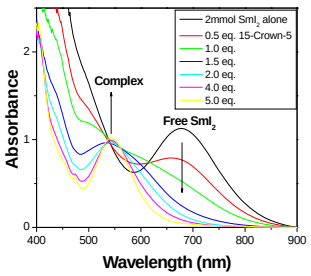
Hypothesis

♦ Providing a chelating ligand for SmI_2 in a solvent incapable of displacing it significantly enhances the luminescent properties of Sm(II) by: **1.)** *encapsulating the metal through a strong metal-ligand interaction* and **2)** *decreasing the frequency of solvent collision.*

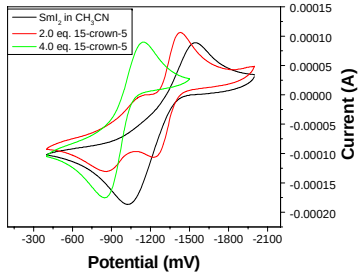
Experimental Approach

♦ ***UV-visible Spectroscopy*** was used to show that a well defined complex was formed upon the addition of 2 equiv. of 15-crown-5 to SmI_2. A visible color change from ***muddy green*** to ***bright red*** was also observed during complex formation.

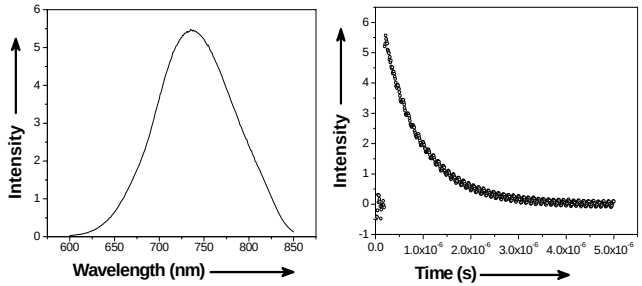
♦ ***Cyclic Voltammetry*** was used to measure the oxidation (loss of an electron) for the $Sm(15\text{-crown-}5)_2$ complex. ***The addition of 15-crown-5 to SmI_2 in acetonitrile clearly produces a more stable and less reactive complex.***



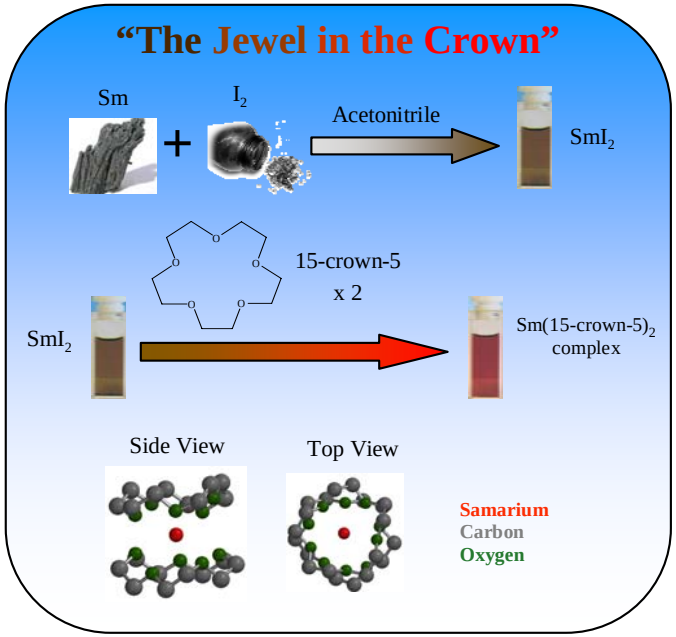
UV-visible Spectrum



Cyclic Voltammogram



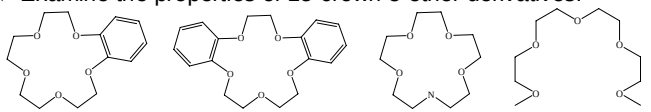
Emission Spectrum **Luminescence Lifetime**



♦ A ***luminescence lifetime*** experiment was performed to examine the stability of the excited state of the $Sm(15\text{-crown-}5)_2$ complex. ***The excited state lifetime (τ) of 0.80 ±0.01μs for the $Sm(15\text{-C-}5)_2$ complex is the longest excited state lifetime reported for a Sm(II) complex in solution.*** The emission spectrum and excited state lifetime for the $Sm(15\text{-crown-}5)_2$ complex is shown below.

Current and Future Work

♦ Examine the properties of 15-crown-5 ether derivatives.



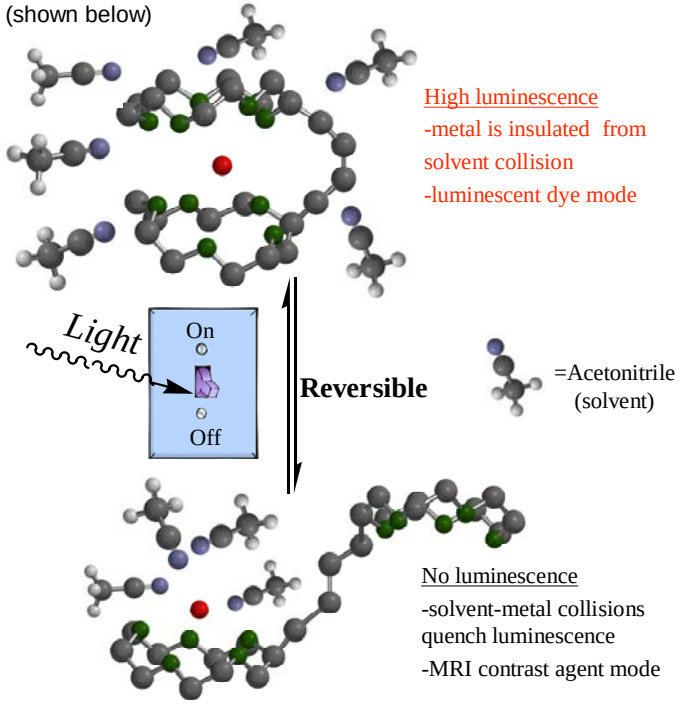
♦ How will increased steric bulk effect the ligand-metal interaction and luminescent lifetime of the complex?

♦ Do other lanthanide (II) metals such as europium or ytterbium exhibit fluorescence under similar conditions?

Potential Applications

♦ Long wavelength (>520nm) light emitting dyes (fluorescent probes) for biological imaging and assays

♦ Dual Mode Agent- MRI contrast agent or luminescent dye (shown below)



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