

# Effect of Crown Ethers on the Ground and Excited State Reactivity of Samarium Diiodide in Acetonitrile

*Sandeepan Maity,<sup>‡</sup> Kimberly Choquette,<sup>§</sup> Robert A. Flowers II<sup>\*,§</sup>, Edamana Prasad<sup>\*,‡</sup>*

<sup>§</sup> Department of Chemistry, Lehigh University, Bethlehem, PA 1805, USA

<sup>‡</sup> Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

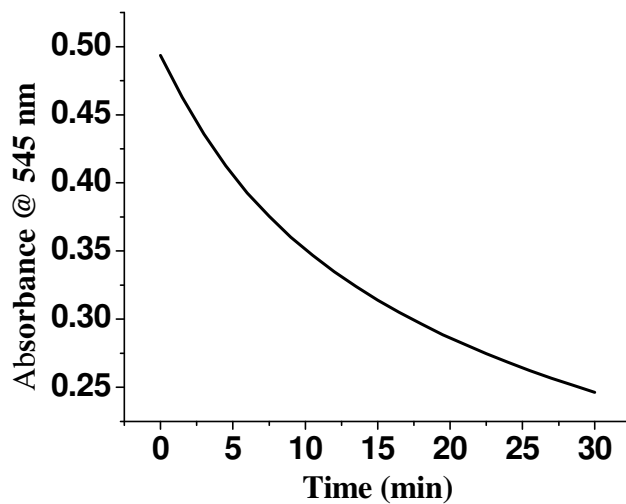
E-mail: [rof2@lehigh.edu](mailto:rof2@lehigh.edu) and [pre@iitm.ac.in](mailto:pre@iitm.ac.in)

## Supporting Information

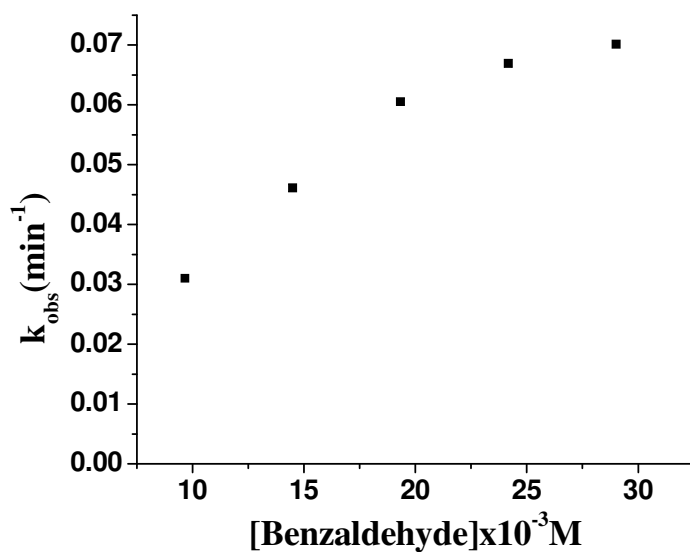
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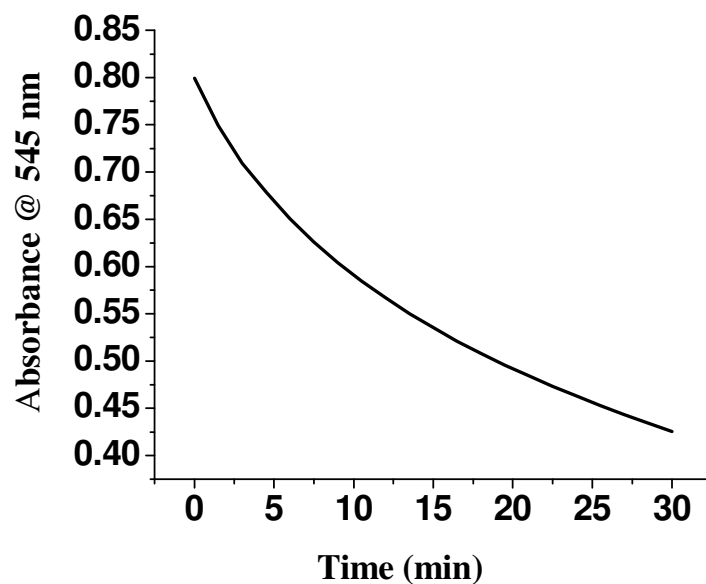
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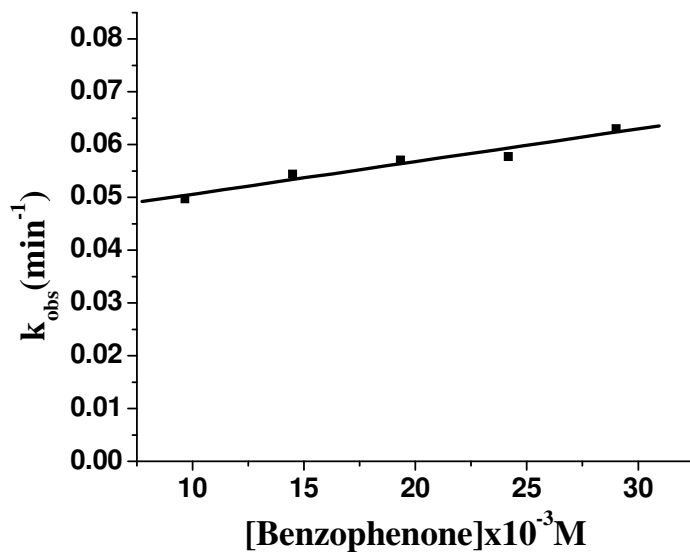
**Figure SF1:** Absorbance decay of  $\text{Sm}[\text{15-crown-5}]_2\text{I}_2$  at 545 nm in the presence of benzaldehyde [29 mM].  $[\text{Sm}(\text{II})] = 1.37 \text{ Mm}$



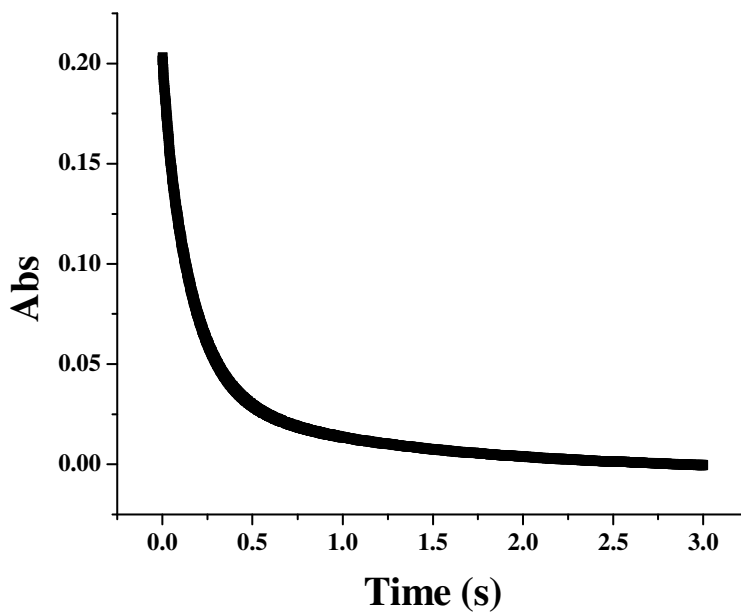
**Figure SF2:** Observed rate constant vs concentration plot for  $\text{Sm}[\text{15-crown-5}]_2\text{I}_2$  -benzaldehyde system. Rate constant =  $(5.08 \pm 0.21) \text{ M}^{-1} \text{ s}^{-1}$ .



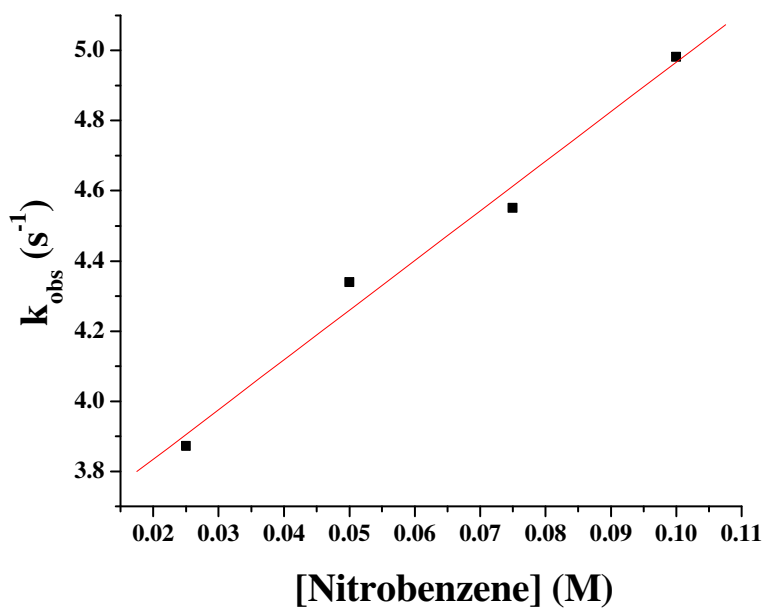
**Figure SF3:** Absorbance decay of  $\text{Sm[15-crown-5]}_2\text{I}_2$  at 545 nm in the presence of benzophenone [29 mM].  $[\text{Sm(II)}] = 1.37 \text{ mM}$



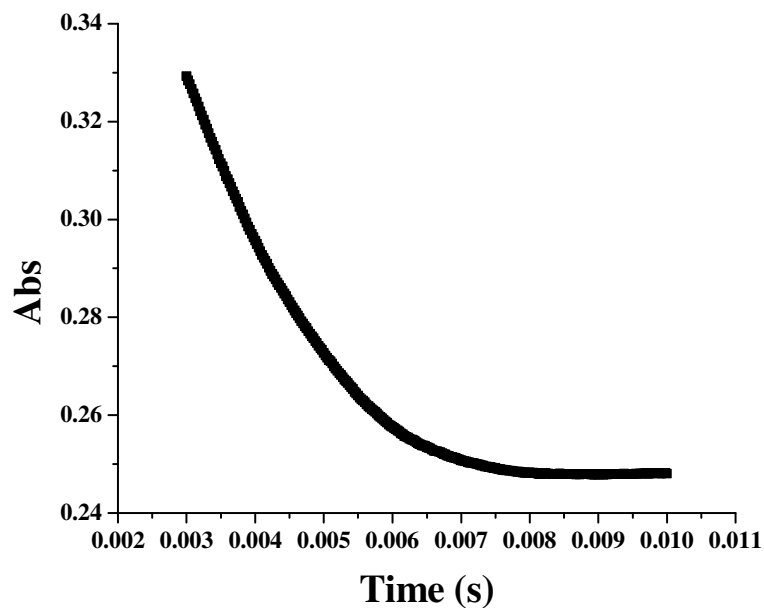
**Figure SF4:** Observed rate constant vs concentration plot for  $\text{Sm[15-crown-5]}_2\text{I}_2$ -benzophenone system. Rate constant =  $(1.03 \pm 0.02) \text{ M}^{-1} \text{ s}^{-1}$ .



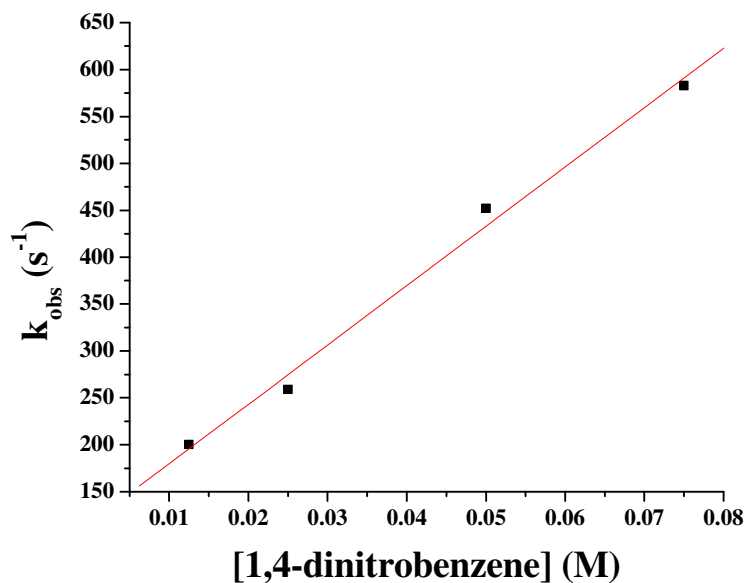
**Figure SF5:** Absorbance decay of  $\text{Sm}[15\text{-crown-5}]_2\text{I}_2$  at 545 nm in the presence of nitrobenzene [75 mM].  $[\text{Sm}(\text{II})] = 5 \text{ mM}$ .



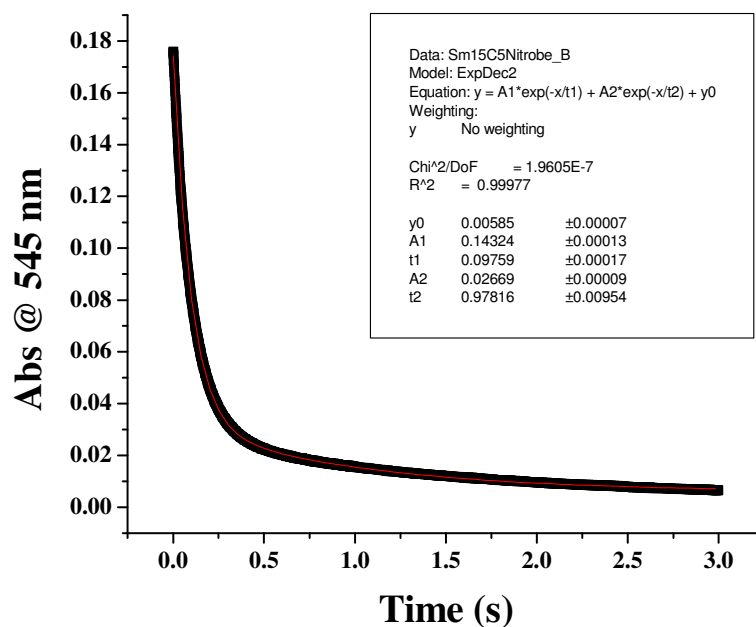
**Figure SF6:** Observed rate constant vs concentration plot for  $\text{Sm}[15\text{-crown-5}]_2\text{I}_2$  -nitrobenzene system.  $[\text{Sm}(15\text{-crown-5})_2\text{I}_2] = 5 \text{ mM}$ ;  $[\text{Nitrobenzene}] = 25\text{-}100 \text{ mM}$ . Rate constant  $14.2 \pm 1.4 \text{ M}^{-1}\text{s}^{-1}$ .



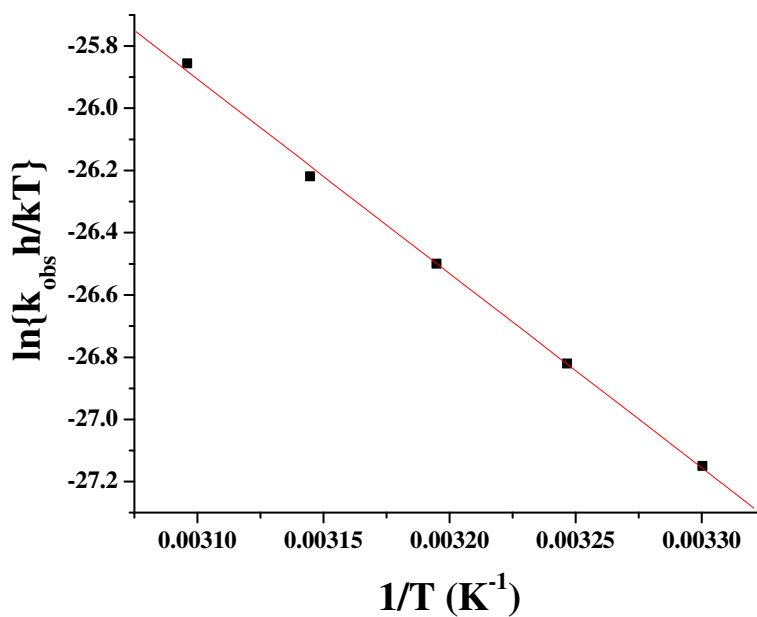
**Figure SF7:** Absorbance decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 545 nm in the presence of 1,4-dinitrobenzene [50 mM]. [Sm(II)] = 5 mM.



**Figure SF8:** Observed rate constant vs concentration plot for Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> -1,4-dinitrobenzene system. [Sm(15-crown-5)<sub>2</sub>I<sub>2</sub>] = 5 mM; [1,4-Nitrobenzene] = 125-750 mM. Rate constant  $6329.6 \pm 390.5 \text{ M}^{-1}\text{s}^{-1}$ .

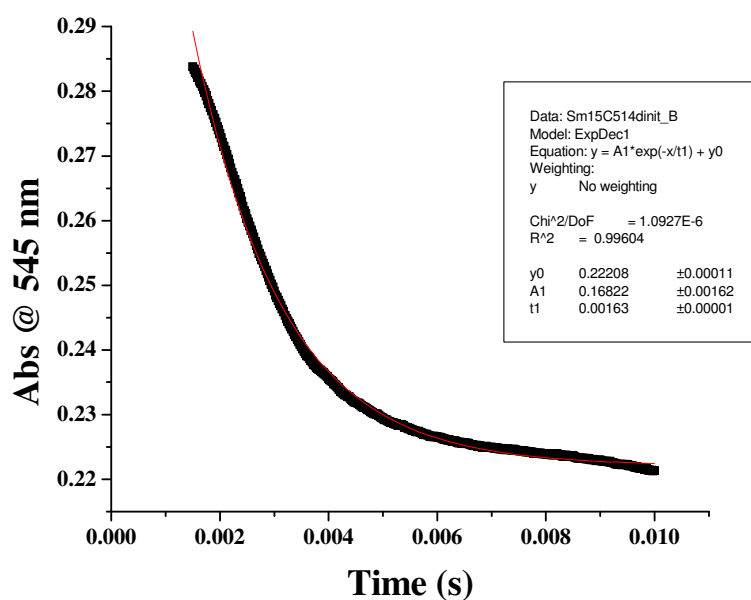


**Figure SF9:** Absorbance decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 545 nm at 30°C in the presence of nitrobenzene [50 mM]. [Sm(II)] = 5 mM.

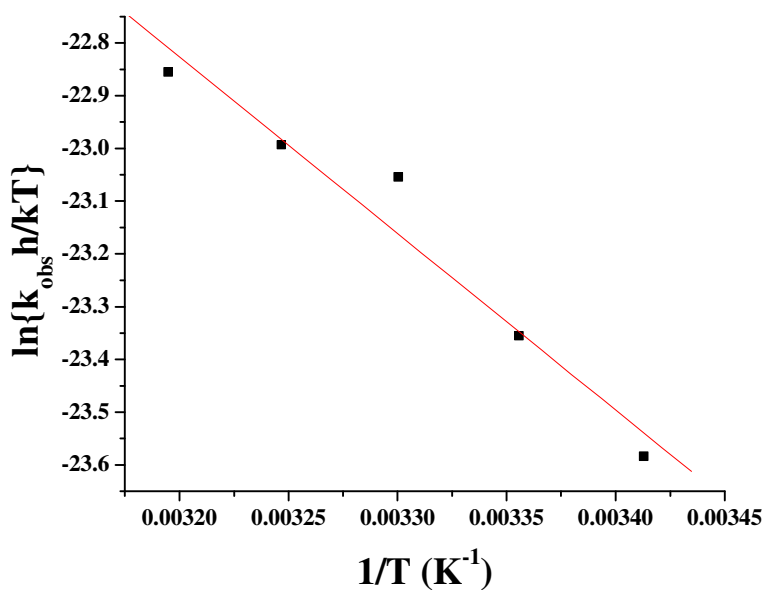


**Figure SF10:** Eyring plot for Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> -nitrobenzene system over a temperature range of 30-50°C. [Sm(15-crown-5)<sub>2</sub>I<sub>2</sub>] = 5 mM; [Nitrobenzene] = 50 mM.  $y = -6243.42x - 6.5519$

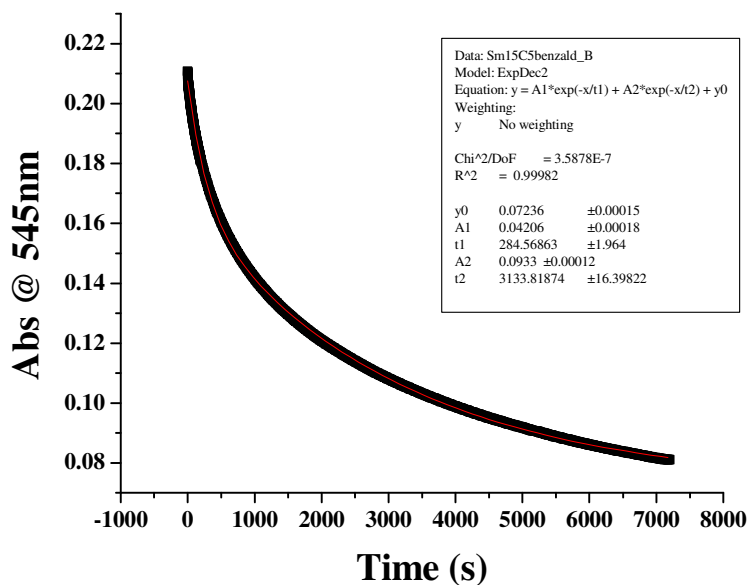




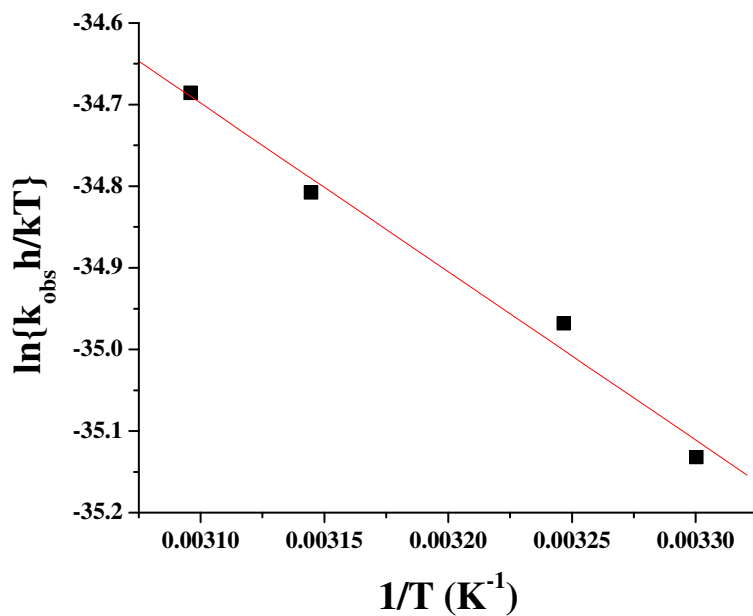
**Figure SF11:** Absorbance decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 545 nm at 30°C in the presence of 1,4-dinitrobenzene [50 mM]. [Sm(II)] = 5 mM.



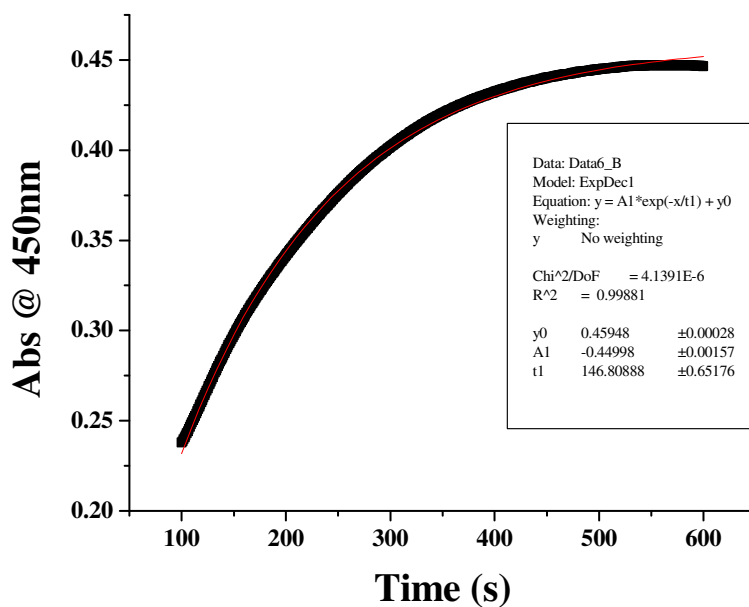
**Figure SF12:** Eyring plot for Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> -1,4-dinitrobenzene system over a temperature range of 30-50°C. [Sm(15-crown-5)<sub>2</sub>I<sub>2</sub>] = 5 mM; [1,4-dinitrobenzene] = 50 mM.  $y = -3349.77x - 12.11$



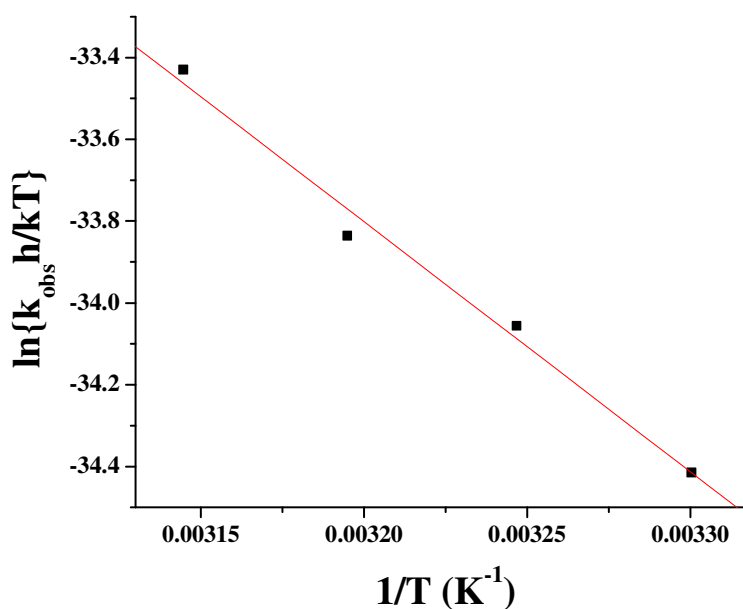
**Figure SF13:** Absorbance decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 545 nm at 30°C in the presence of benzaldehyde [50 mM]. [Sm(II)] = 5 mM.



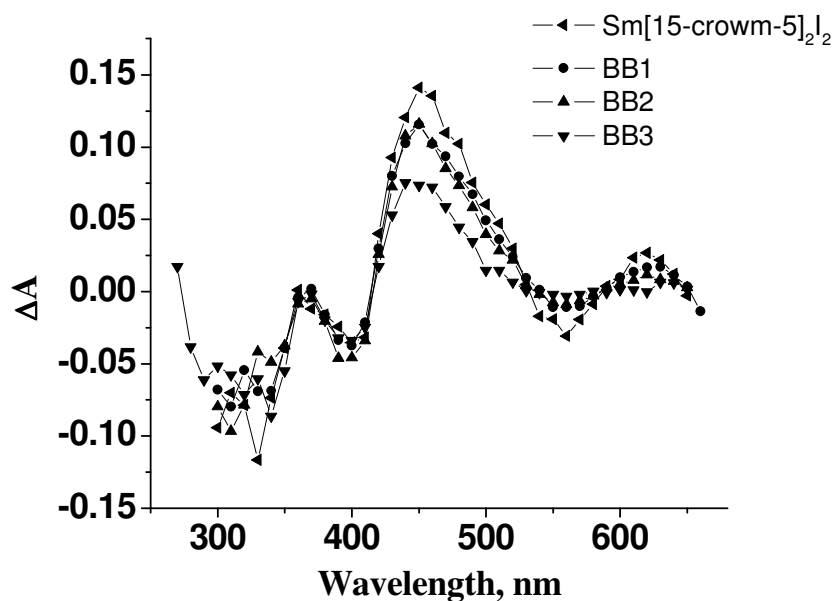
**Figure SF14:** Eyring plot for Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> -benzaldehyde system over a temperature range of 30-50°C. [Sm(15-crown-5)<sub>2</sub>I<sub>2</sub>] = 5 mM; [benzaldehyde] = 50 mM.  $y = -2062.5x - 28.3$ .



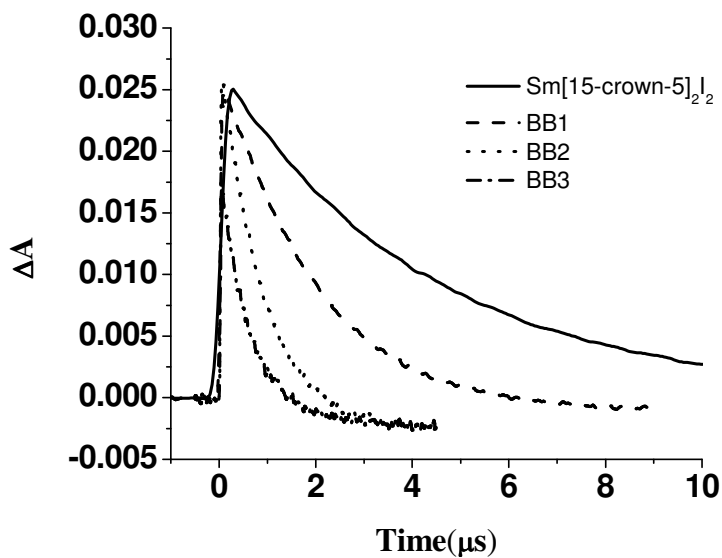
**Figure SF15:** Absorbance growth of precipitation formed through Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> reduction of benzyl bromide at 450 nm at 30°C. Benzyl bromide = [50 mM]. [Sm(II)] = 5 mM.



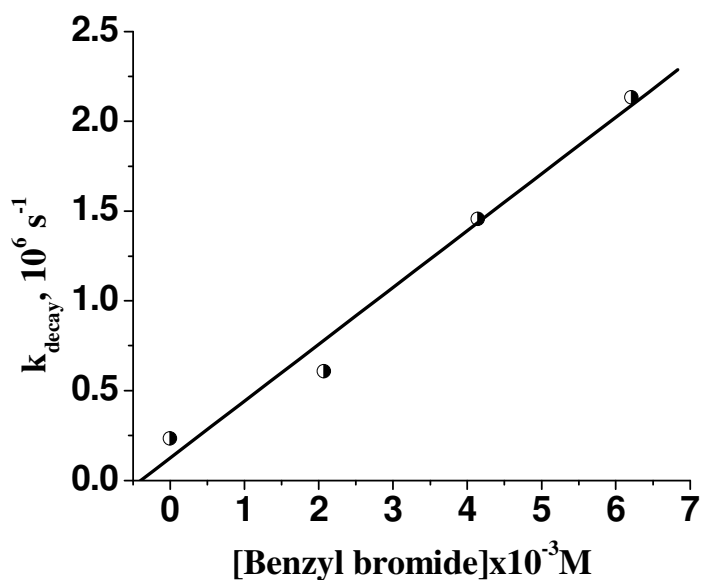
**Figure SF16:** Eyring plot for Sm[15-crown-5]<sub>2</sub>I<sub>2</sub>–benzyl bromide system over a temperature range of 30–50°C. [Sm(15-crown-5)<sub>2</sub>I<sub>2</sub>] = 5 mM; [benzyl bromide] = 50 mM.  $y = -6113.9x - 14.24$ .



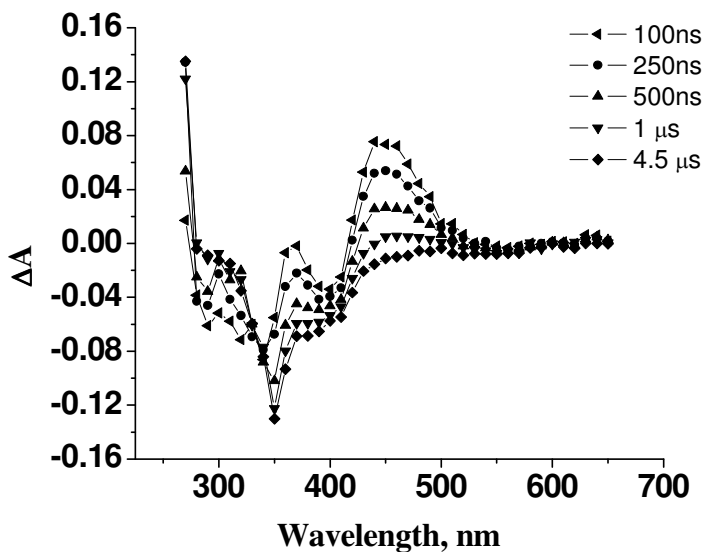
**Figure SF17:** Transient absorption spectra of  $\text{Sm}[\text{15-crown-5}]_2\text{I}_2$  in the presence of benzyl bromide.  $\text{BB} = [\text{Benzyl bromide}] = 0 \text{ mM}$  ( $\blacktriangleleft$ ),  $2.07 \text{ mM}$  [ $\text{BB1}$ ] =  $2.07 \text{ mM}$  ( $\bullet$ ) and  $4.14 \text{ mM}$  [ $\text{BB2}$ ] =  $4.14 \text{ mM}$  ( $\blacktriangle$ ) and  $6.21 \text{ mM}$  [ $\text{BB3}$ ] =  $6.21 \text{ mM}$  ( $\blacktriangledown$ ).  $[\text{SmI}_2] = 1.76 \text{ mM}$ .



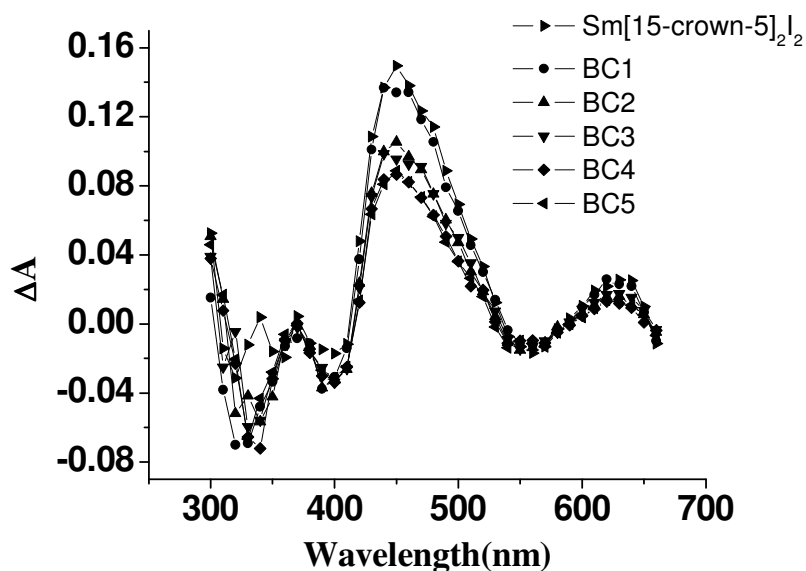
**Figure SF18:** Excited decay of  $\text{Sm}[\text{15-crown-5}]_2\text{I}_2$  at  $450 \text{ nm}$  with increasing amount of benzyl bromide.  $\text{BB} = [\text{Benzyl bromide}] = 0 \text{ mM}$  (solid),  $2.07 \text{ mM}$  [ $\text{BB1}$ ] =  $2.07 \text{ mM}$  (dash),  $4.14 \text{ mM}$  [ $\text{BB2}$ ] =  $4.14 \text{ mM}$  (dot) and  $6.21 \text{ mM}$  [ $\text{BB3}$ ] =  $6.21 \text{ mM}$  (dash dot).  $[\text{SmI}_2] = 1.76 \text{ mM}$ .



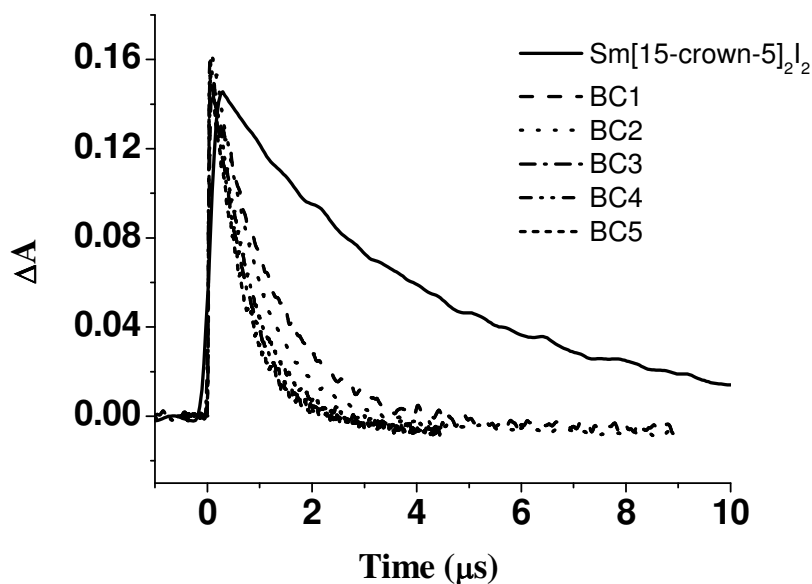
**Figure SF19:** Observed rate constant of excited state decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 450 nm vs concentration of benzyl bromide plot.



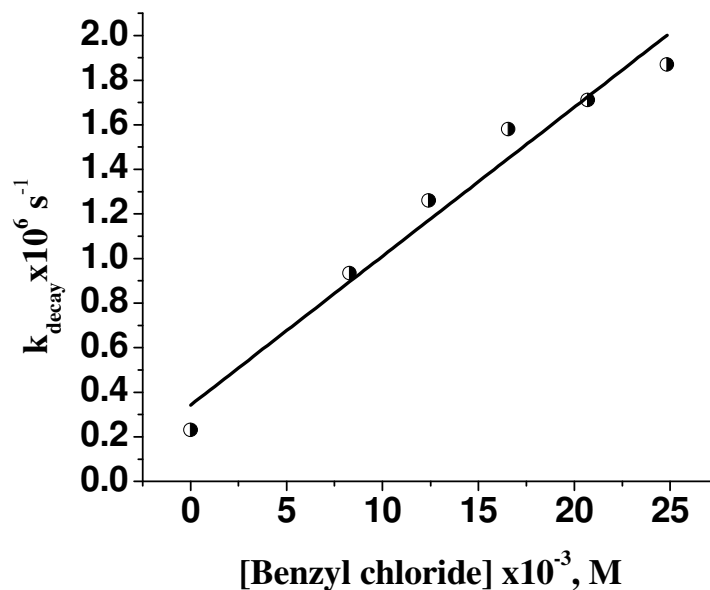
**Figure SF20:** Transient absorption spectra of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of benzyl bromide at 100 ns(◄); 250 ns (●); 500 ns (▲), 1 μs (▼) and 4.5 μs (◆) after the laser pulse. [Benzyl bromide]: 6.21 mM and [SmI<sub>2</sub>]: 1.76 mM.



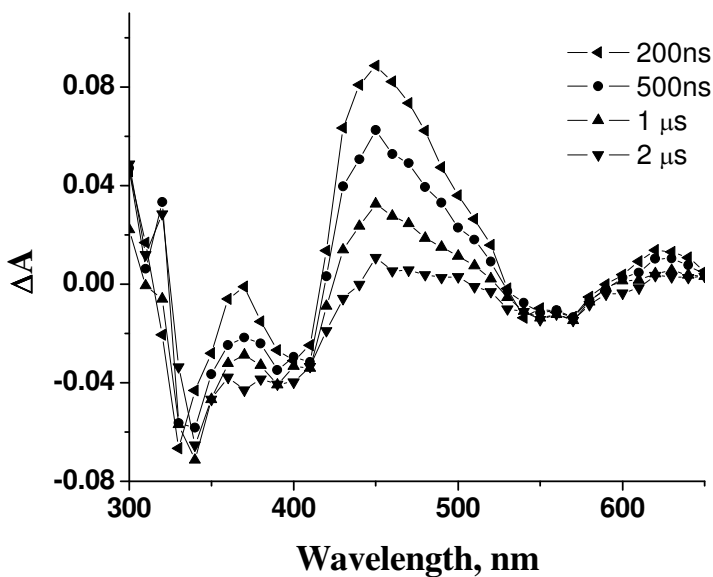
**Figure SF21:** Transient absorption spectra of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of benzyl chloride. BC= [Benzyl chloride] = 0 mM (►), [BC1] (●) and 12.42 mM [BC2] = 12.42 mM (▲), [BC3] = 16.56 mM (▼), [BC4] = 20.7 mM (◆) and 24.84 mM [BC5] = 24.84 mM (◄) [SmI<sub>2</sub>] = 1.76 mM.



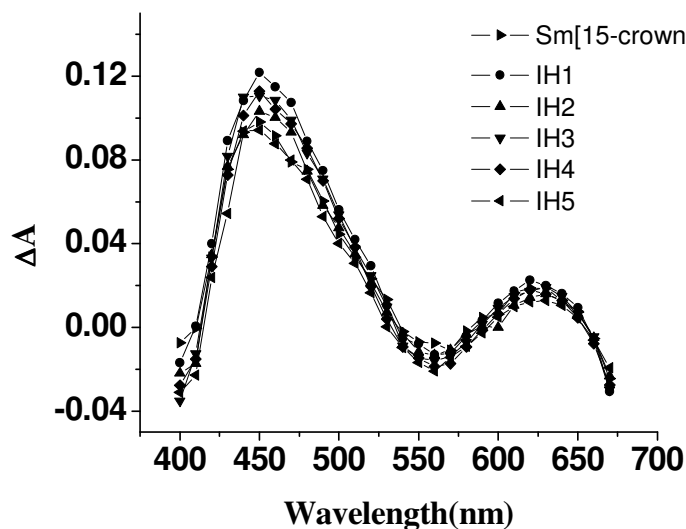
**Figure SF22:** Excited decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 450 nm with increasing amount of benzyl chloride. BC = [Benzyl chloride] = 0 mM (solid), [BC1] = 8.28 mM (dash), [BC2] = 12.42 mM (dot), 16.56 mM [BC3] = 16.56 mM (dash dot), 20.7 mM [BC4] = 20.7 mM (dash dot dot) and 24.84 mM [BC5] = 24.84 mM (short dash). [SmI<sub>2</sub>] = 1.76 mM.



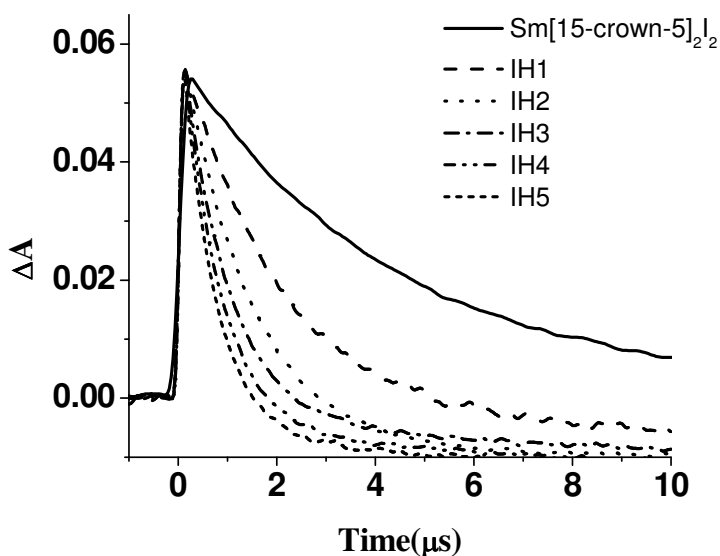
**Figure SF23:** Observed rate constant of excited state decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 450 nm vs concentration of benzyl chloride plot.



**Figure SF24:** Transient absorption spectra of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of benzyl chloride at 200 ns (◄); 500 ns (●); 1 μs (▲) and 2 μs (▼) after the laser pulse. [Benzyl chloride]: 24.84 mM and [SmI<sub>2</sub>]: 1.76 mM.

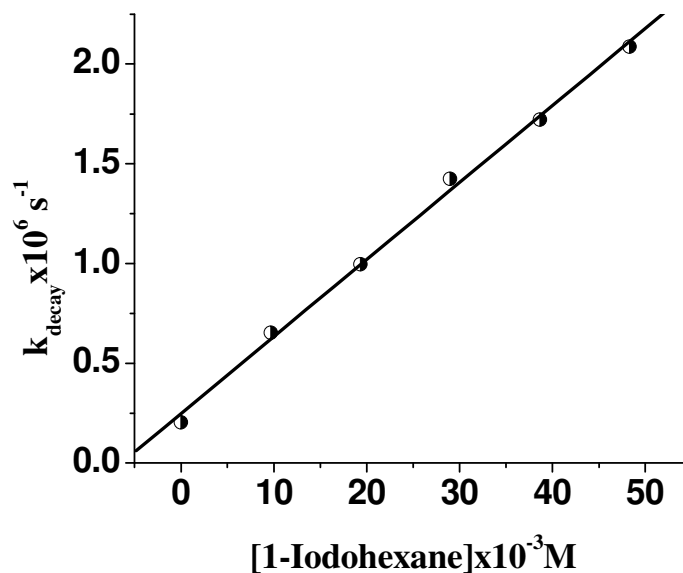


**Figure SF25:** Transient absorption spectra of  $\text{Sm[15-crown-5]}_2\text{I}_2$  in the presence of 1-Iodohehexane. IH= [1-Iodohehexane] = 0 mM ( $\blacktriangle$ ), 9.66 mM [IH1] = 9.66 mM ( $\bullet$ ) and 19.32 mM [IH2] = 19.32 mM ( $\blacktriangle$ ), [IH3] = 28.98 mM ( $\blacktriangledown$ ), 38.64 mM [IH4] = 38.64 mM ( $\blacklozenge$ ) and 48.3 mM [IH5] = 48.3 mM ( $\blacktriangleleft$ ) [ $\text{SmI}_2$ ] = 1.76 mM.

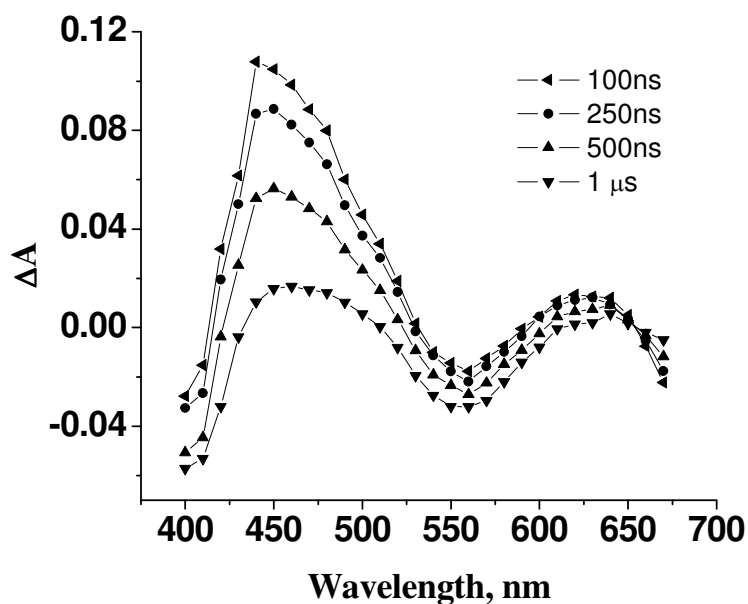


**Figure SF26:** Excited decay of  $\text{Sm[15-crown-5]}_2\text{I}_2$  at 450 nm with increasing amount of 1-Iodohehexane. IH = [1-Iodohehexane] = 0 mM (solid), 9.66 mM [IH1] = 9.66 mM (dash), [IH2] 19.32 mM (dot), 28.98 mM [IH3] = 28.98 mM (dash dot), 38.64 mM [IH4] = 38.64 mM (dash dot dot) and [IH5] = 48.3 mM (short dash). [ $\text{SmI}_2$ ] = 1.76 mM.

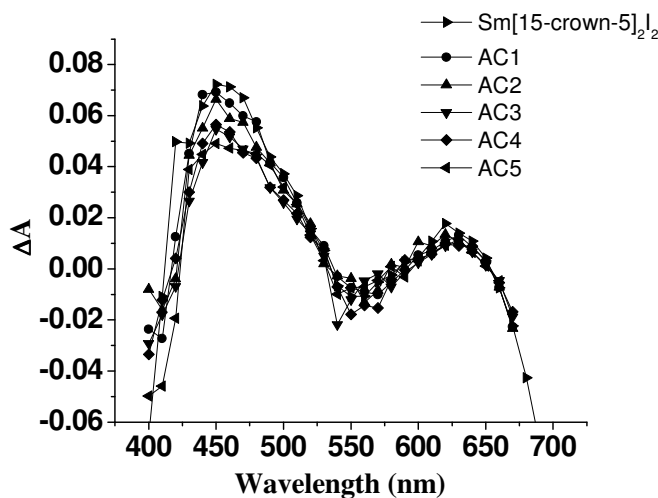




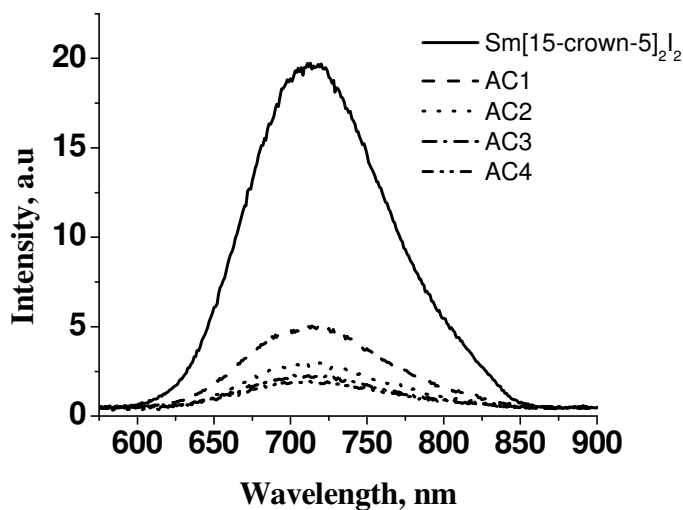
**Figure SF27:** Observed rate constant of excited state decay of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> at 450 nm vs concentration of 1-Iodohexane plot.



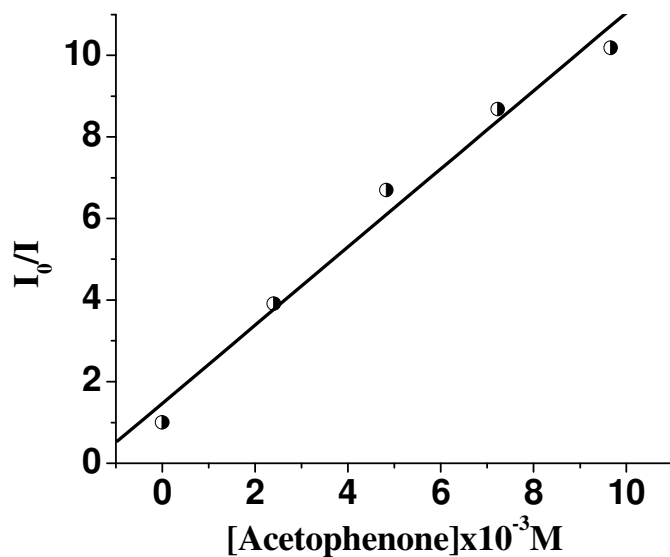
**Figure SF28:** Transient absorption spectra of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of 1-Iodohexane at 100 ns (◄); 250 ns (●); 500 ns (▲) and 1 μs (▼) after the laser pulse. [1-Iodohexane]: 48.3 mM and [SmI<sub>2</sub>]: 1.76 mM.



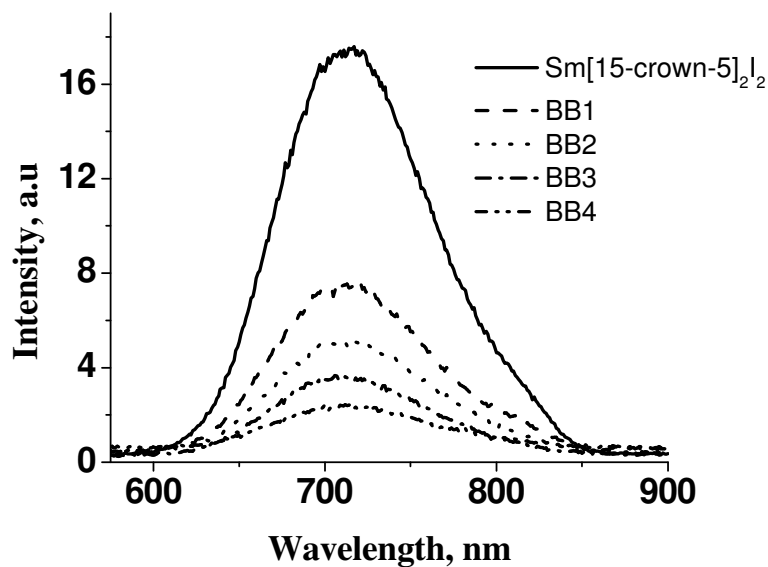
**Figure SF29:** Transient absorption spectra of  $\text{Sm}[\text{15-crown-5}]_2\text{I}_2$  in the presence of acetophenone.  $\text{AC} = [\text{Acetophenone}] = 0 \text{ mM}$  ( $\blacktriangle$ ),  $4.83 \text{ mM}$   $[\text{AC1}] = 4.83 \text{ mM}$  ( $\bullet$ ),  $[\text{AC2}] = 7.24 \text{ mM}$  ( $\blacktriangle$ ),  $[\text{AC3}] = 9.66 \text{ mM}$  ( $\blacktriangledown$ ),  $[\text{AC4}] = 12.07 \text{ mM}$  ( $\blacklozenge$ ) and  $14.49 \text{ mM}$   $[\text{AC5}] = 14.49 \text{ mM}$  ( $\blacktriangleleft$ )  $[\text{SmI}_2] = 1.76 \text{ mM}$



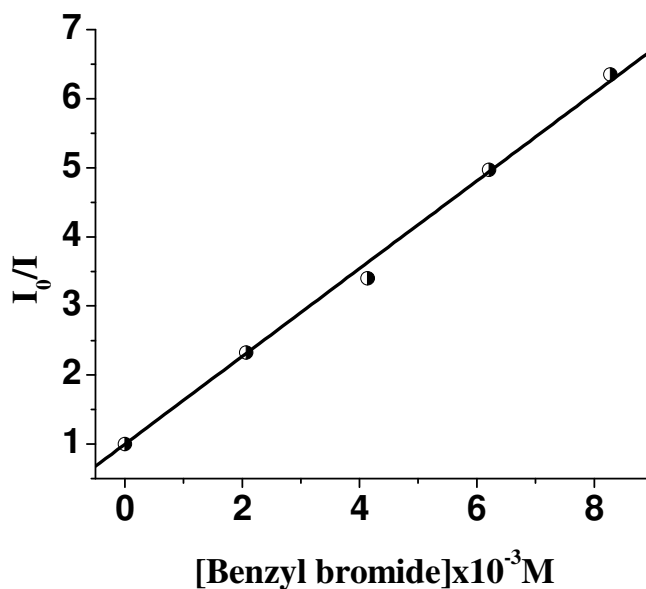
**Figure SF30:** Steady state luminescence spectra of  $\text{Sm}[\text{15-crown-5}]_2\text{I}_2$  in the presence of increasing amount of acetophenone.  $\text{AC} = [\text{Acetophenone}] = 0 \text{ mM}$  (solid),  $2.41 \text{ mM}$   $[\text{AC1}] = 2.41 \text{ mM}$  (dash),  $4.83 \text{ mM}$   $[\text{AC2}] = 4.83 \text{ mM}$  (dot),  $[\text{AC3}] = 7.23 \text{ mM}$  (dash dot) and  $[\text{AC4}] = 9.66 \text{ mM}$  (dash dot dot).  $[\text{SmI}_2] = 1.76 \text{ mM}$ .



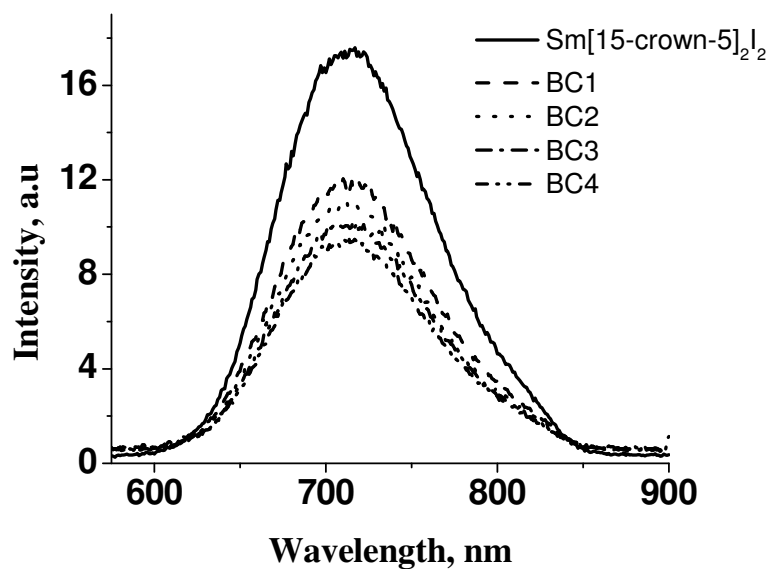
**Figure SF31:** Stern Volmer plot for the luminescence quenching of  $\text{Sm}[15\text{-crown-}5]_2\text{I}_2$  in the presence of Acetophenone.



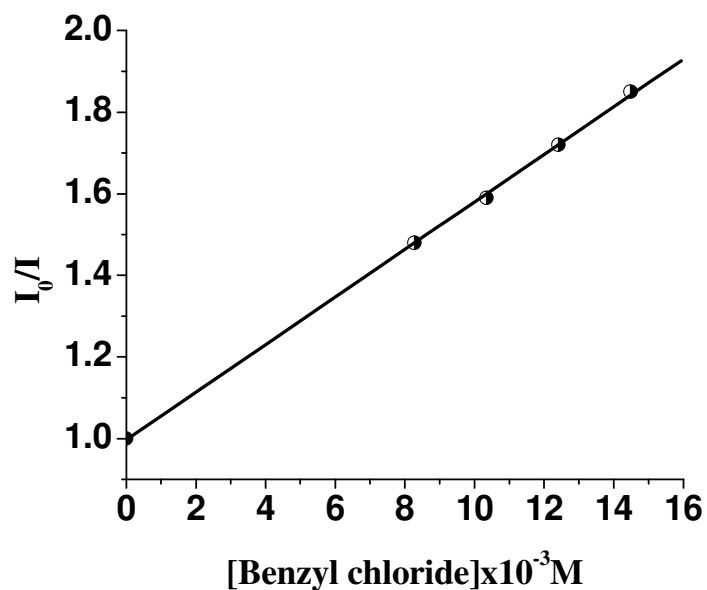
**Figure SF32:** Steady state luminescence spectra of  $\text{Sm}[15\text{-crown-}5]_2\text{I}_2$  in the presence of increasing amount of benzyl bromide. BB= [Benzyl bromide] = 0 mM(solid), 2.07 mM [BB1] = 2.07 mM (dash), [BB2] = 4.14 mM (dot), [BB3] = 6.21 mM (dash dot) and 8.28 mM ([BB4] = 8.28 mM (dash dot dot).  $[\text{SmI}_2] = 1.76 \text{ mM}$ .



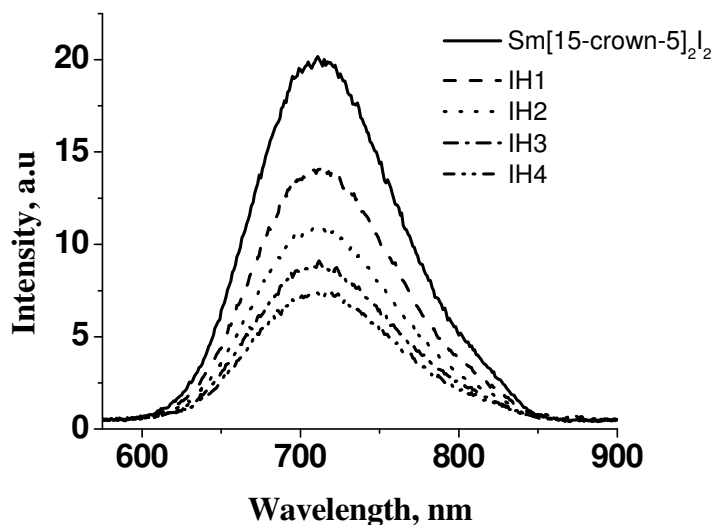
**Figure SF33:** Stern Volmer plot for the luminescence quenching of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of Benzyl bromide.



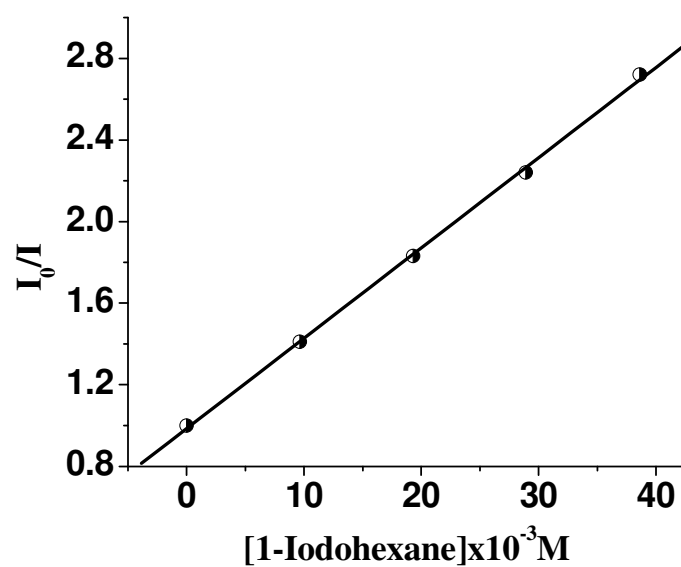
**Figure SF34:** Steady state luminescence spectra of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of increasing amount of benzyl chloride. BC= [Benzyl chloride] = 0 mM(solid), [BC1] = 8.28 mM (dash), [BC2] = 10.35 mM (dot), [BC3] = 12.45 mM (dash dot) and 14.49 mM [BC4] = 14.49 mM (dash dot dot). [SmI<sub>2</sub>] = 1.76 mM.



**Figure SF35:** Stern Volmer plot for the luminescence quenching of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of benzyl chloride.



**Figure SF36:** Steady state luminescence spectra of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of increasing amount of 1-Iodoheptane. IH= [1-Iodoheptane] = 0 mM(solid), [IH1] = 9.66 mM (dash), [IH2] = 19.32 mM (dot), [IH3] = 28.93 mM (dash dot) and [IH4] = 38.64 mM (dash dot dot). [SmI<sub>2</sub>] = 1.76 mM.



**Figure SF37:** Stern Volmer plot for the luminescence quenching of Sm[15-crown-5]<sub>2</sub>I<sub>2</sub> in the presence of 1-Iodohexane.