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

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Supporting Information

Content **Page No.**

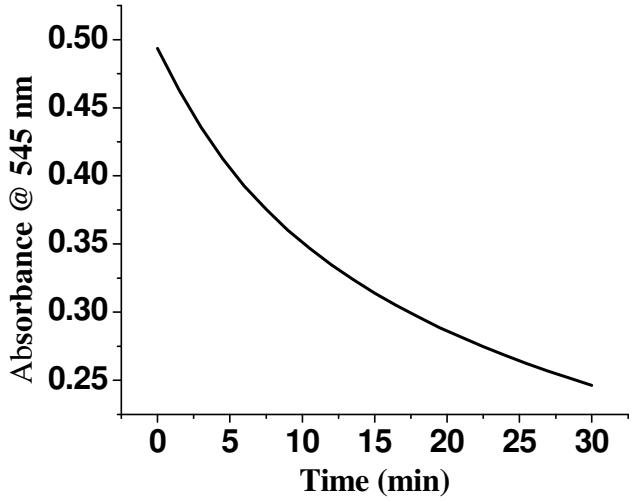

Figure SF1: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm in the presence of benzaldehyde [29 mM]. [Sm(II)] = 1.37 Mm

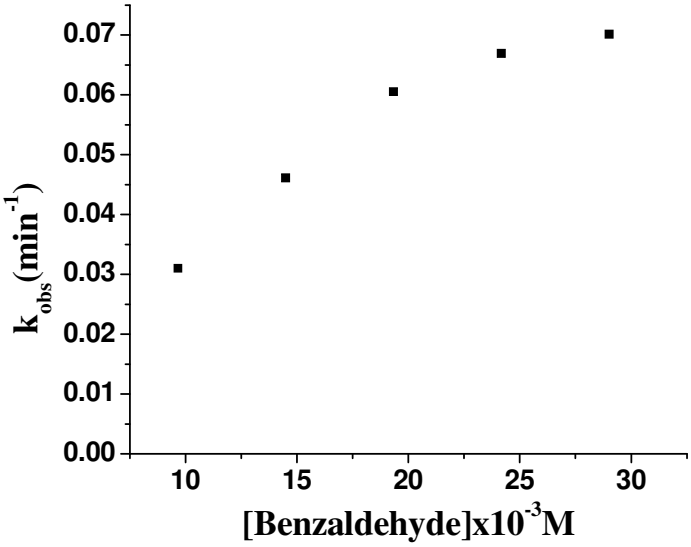

Figure SF2: Observed rate constant vs concentration plot for Sm[15-crown-5]$_2$I$_2$ -benzaldehyde system. Rate constant = (5.08±.21) M^{-1} s^{-1}.

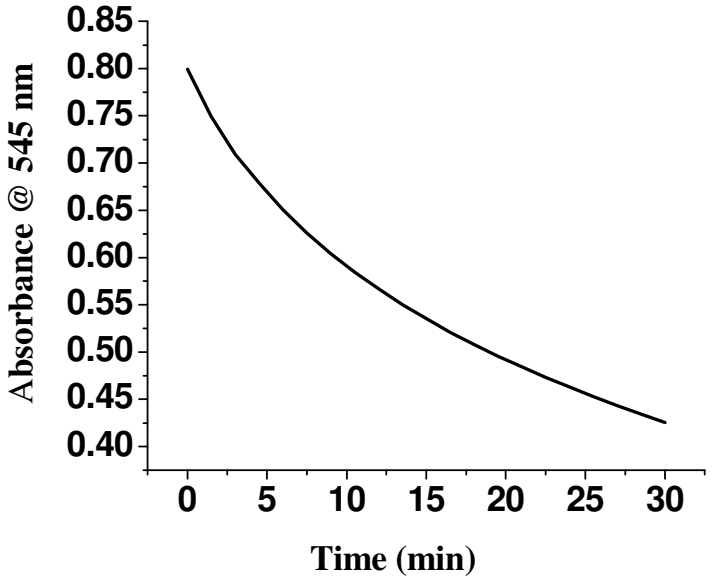

Figure SF3: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm in the presence of benzophenone [29 mM]. [Sm(II)] = 1.37 mM

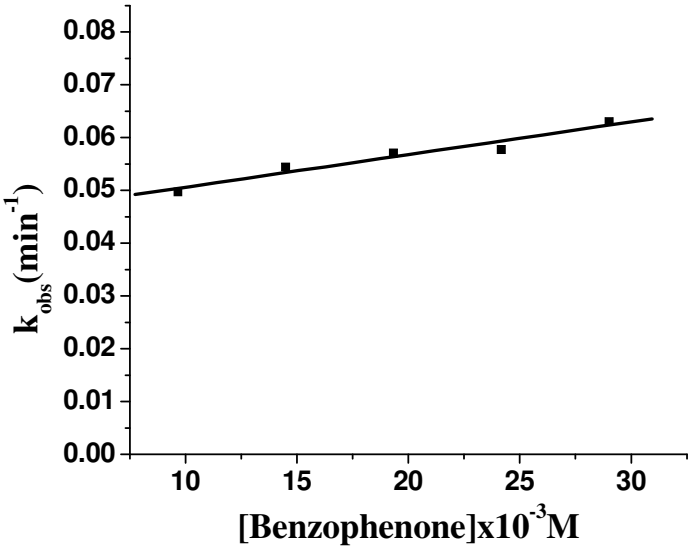

Figure SF4: Observed rate constant vs concentration plot for Sm[15-crown-5]$_2$I$_2$ -benzophenone system. Rate constant = (1.03±.02) M^{-1} s^{-1}.

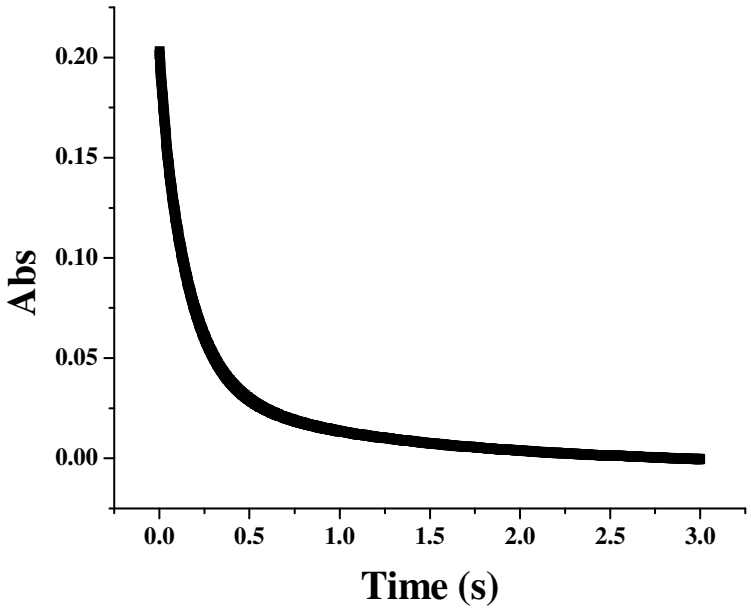

Figure SF5: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm in the presence of nitrobenzene [75 mM]. [Sm(II)] = 5 mM.

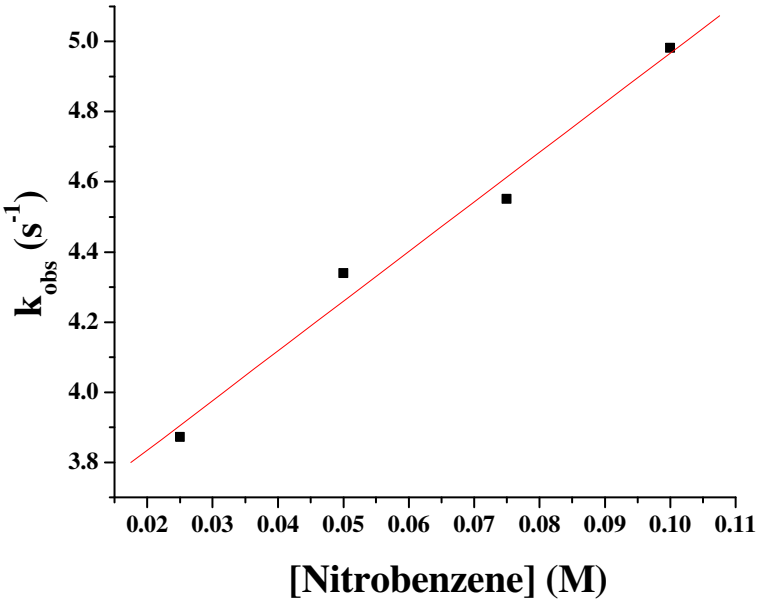

Figure SF6: Observed rate constant vs concentration plot for Sm[15-crown-5]$_2$I$_2$ -nitrobenzene system. [Sm(15-crown-5)$_2$I$_2$] = 5 mM; [Nitrobenzene] = 25-100 mM. Rate constant 14.2 ± 1.4 M^{-1}s^{-1}.

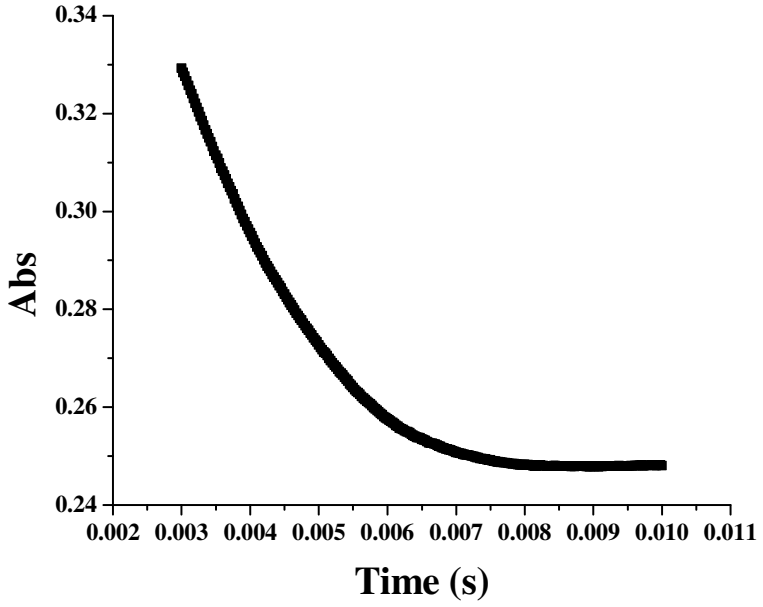

Figure SF7: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm in the presence of 1,4-dinitrobenzene [50 mM]. [Sm(II)] = 5 mM.

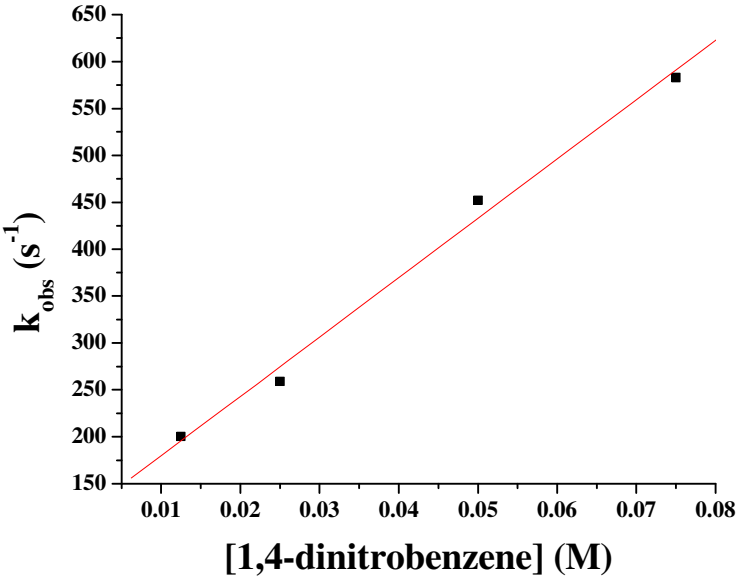

Figure SF8: Observed rate constant vs concentration plot for Sm[15-crown-5]$_2$I$_2$ -1,4-dinitrobenzene system. [Sm(15-crown-5)$_2$I$_2$] = 5 mM; [1,4-Nitrobenzene] = 125-750 mM. Rate constant 6329.6 ± 390.5 M^{-1}s^{-1}.

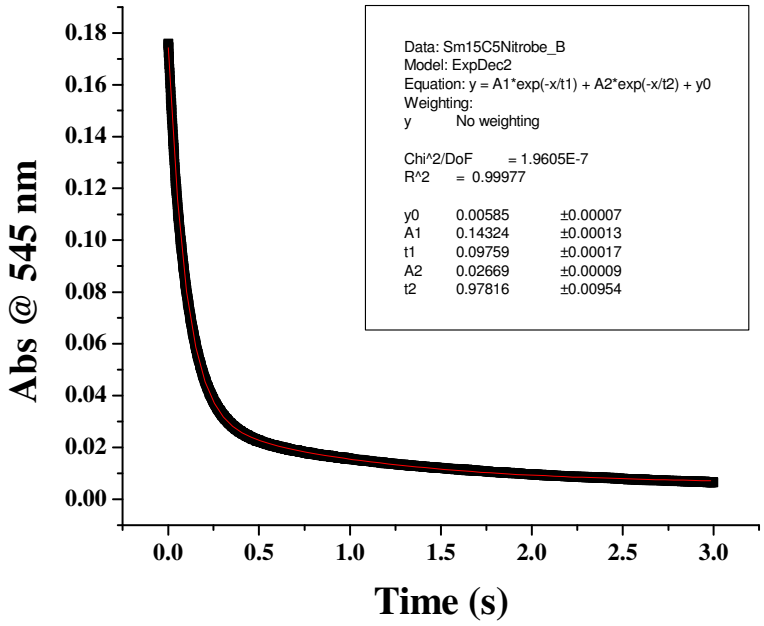

Figure SF9: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm at 30°C in the presence of nitrobenzene [50 mM]. [Sm(II)] = 5 mM.

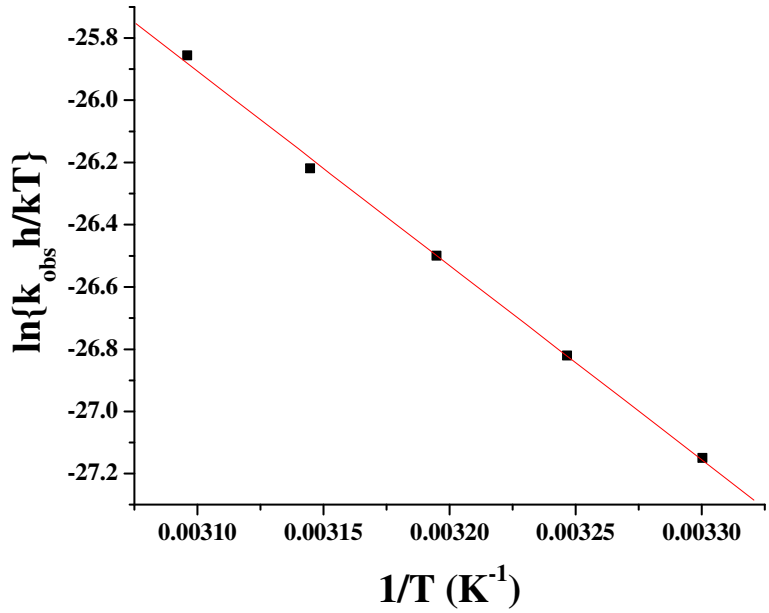

Figure SF10: Eyring plot for Sm[15-crown-5]$_2$I$_2$ -nitrobenzene system over a temperature range of 30-50°C. [Sm(15-crown-5)$_2$I$_2$] = 5 mM; [Nitrobenzene] = 50 mM. y = -6243.42x -6.5519

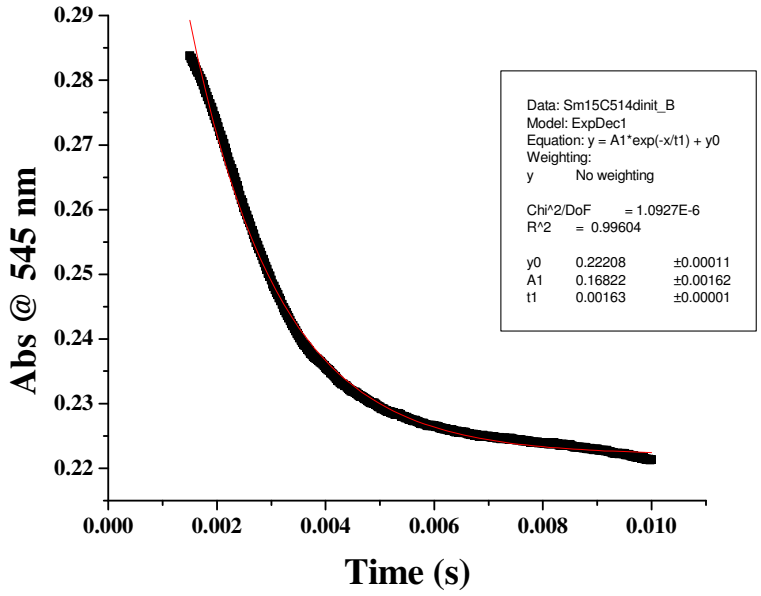

Figure SF11: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm at 30°C in the presence of 1,4-dinitrobenzene [50 mM]. [Sm(II)] = 5 mM.

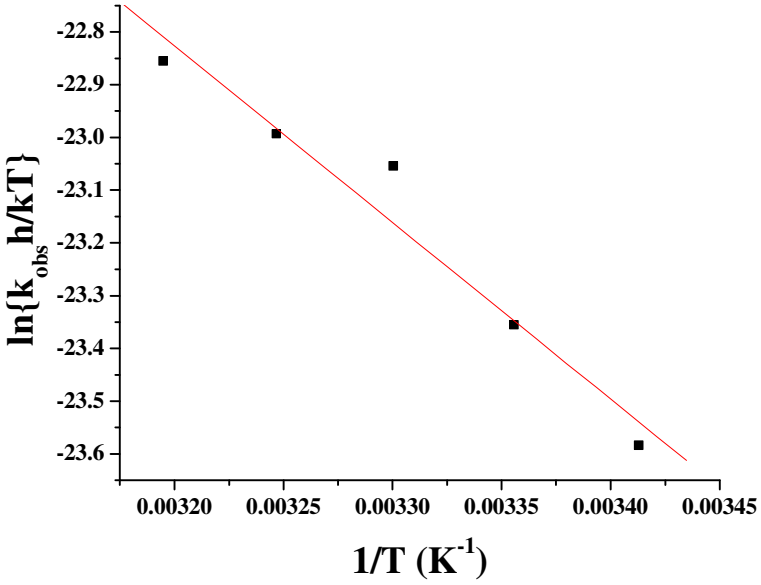

Figure SF12: Eyring plot for Sm[15-crown-5]$_2$I$_2$ -1,4-dinitrobenzene system over a temperature range of 30-50°C. [Sm(15-crown-5)$_2$I$_2$] = 5 mM; [1,4-dinitrobenzene] = 50 mM. y = -3349.77x – 12.11

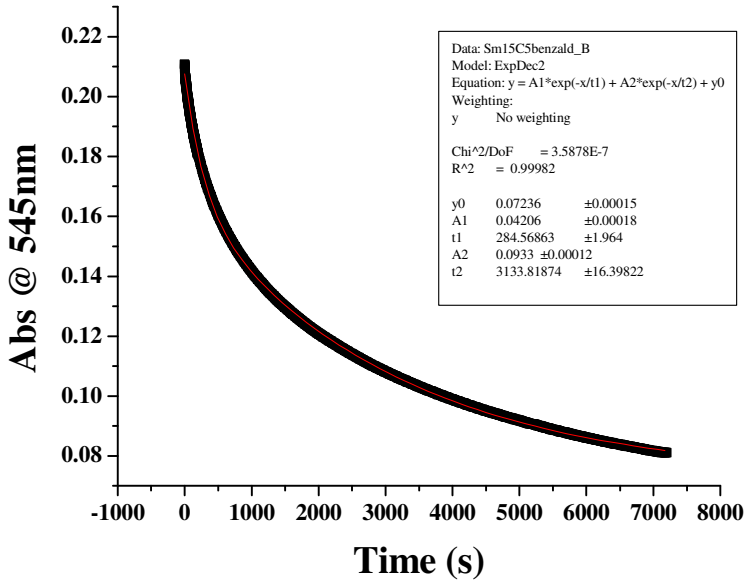

Figure SF13: Absorbance decay of Sm[15-crown-5]$_2$I$_2$ at 545 nm at 30°C in the presence of benzaldehyde [50 mM]. [Sm(II)] = 5 mM.

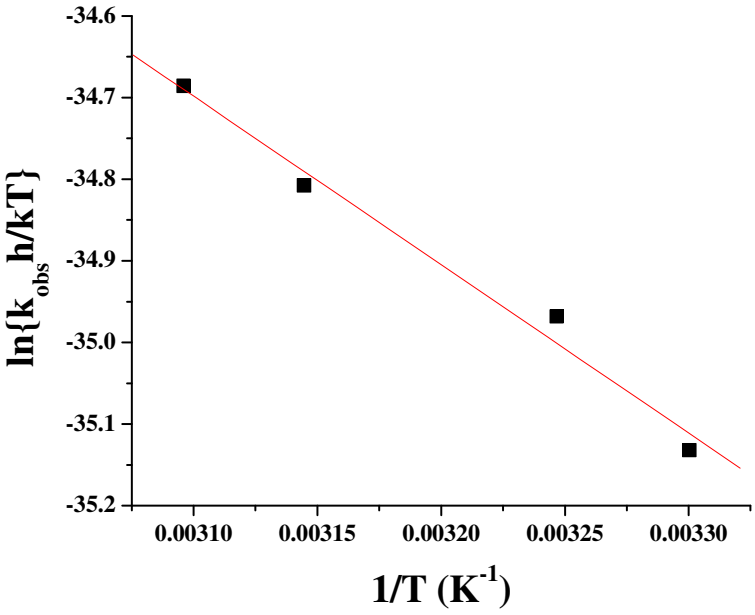

Figure SF14: Eyring plot for Sm[15-crown-5]$_2$I$_2$ -benzaldehyde system over a temperature range of 30-50°C. [Sm(15-crown-5)$_2$I$_2$] = 5 mM; [benzaldehyde] = 50 mM. y = -2062.5x – 28.3.

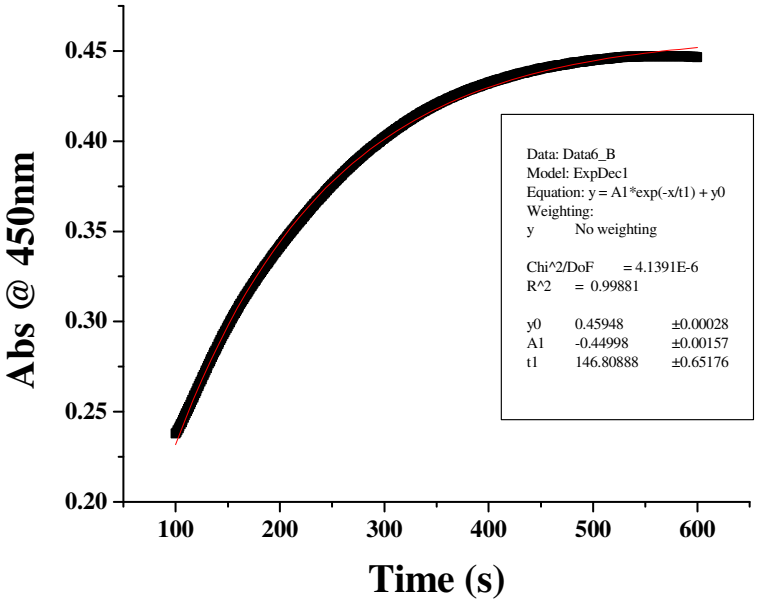

Figure SF15: Absorbance growth of precipitation formed through Sm[15-crown-5]$_2$I$_2$ reduction of benzyl bromide at 450 nm at 30°C. Benzyl bromide = [50 mM]. [Sm(II)] = 5 mM.

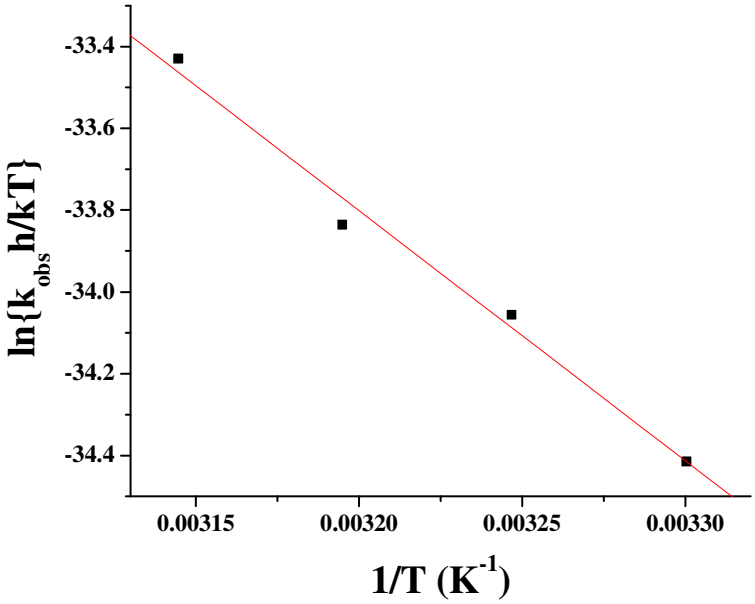

Figure SF16: Eyring plot for Sm[15-crown-5]$_2$I$_2$ –benzyl bromide system over a temperature range of 30-50°C. [Sm(15-crown-5)$_2$I$_2$] = 5 mM; [benzyl bromide] = 50 mM. y = -6113.9x – 14.24.

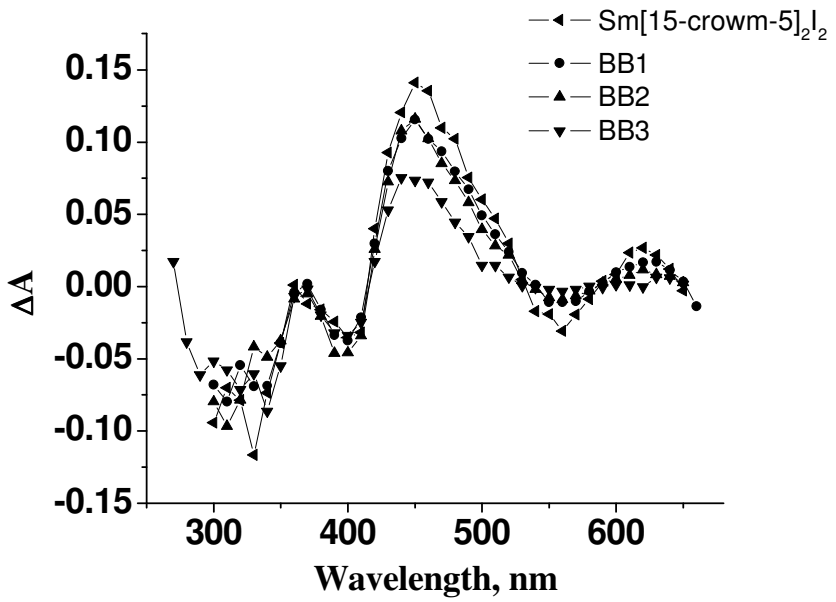

Figure SF17: Transient absorption spectra of Sm[15-crown-5]2I2 in the presence of benzyl bromide. BB= [Benzyl bromide] = 0 mM (◀), 2.07 mM [BB1] = 2.07 mM (●) and 4.14 mM [BB2] = 4.14 mM (▲) and 6.21 mM [BB3] = 6.21 mM (▼). [SmI_2] = 1.76 mM.

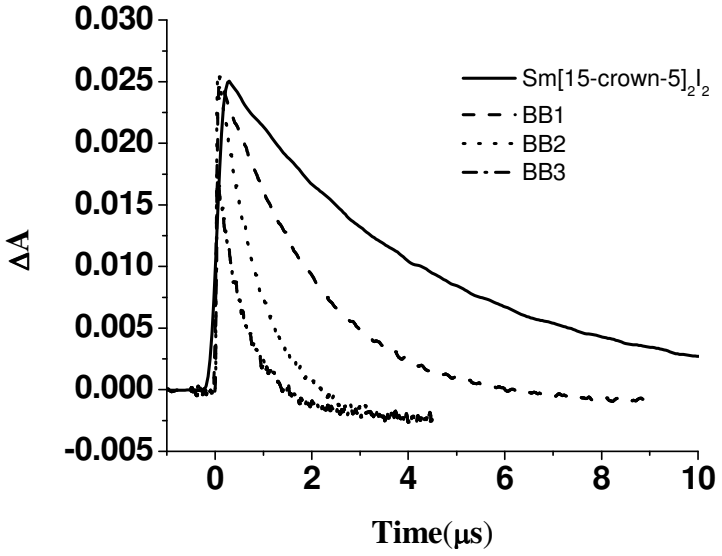

Figure SF18: Excited decay of Sm[15-crown-5]$_2I_2$ at 450 nm with increasing amount of benzyl brmide. BB=[Benzyl brmide] = 0 mM (solid), 2.07 mM [BB1] = 2.07 mM (dash), 4.14 mM [BB2] = 4.14 mM (dot) and 6.21 mM [BB3] = 6.21 mM (dash dot). [SmI_2] = 1.76 mM.

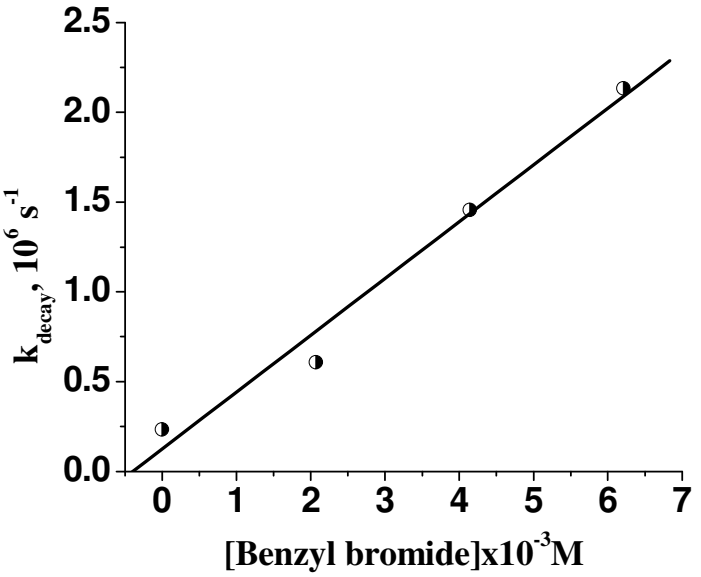

Figure SF19: Observed rate constant of excited state decay of Sm[15-crown-5]$_2$I$_2$ at 450 nm vs concentration of benzyl bromide plot.

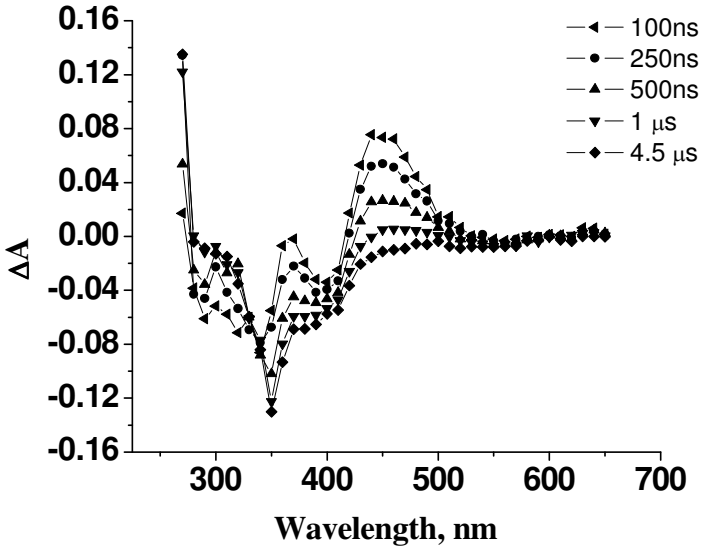

Figure SF20: Transient absorption spectra of Sm[15-crown-5]$_2$I$_2$ in the presence of benzyl bromide at 100 ns(◄); 250 ns (●); 500 ns (▲), 1 μs (▼) and 4.5 μs (♦) after the laser pulse. [Benzyl bromide]: 6.21 mM and [SmI_2]: 1.76 mM.

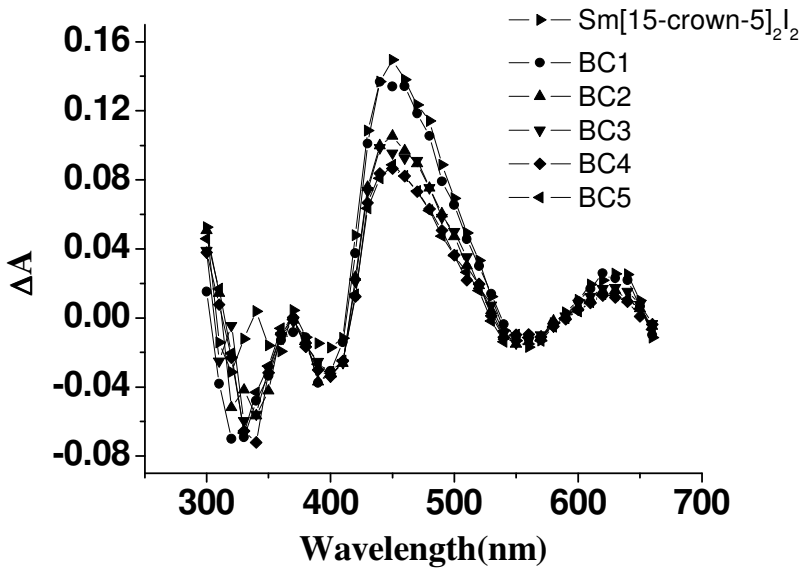

Figure SF21: Transient absorption spectra of Sm[15-crown-5]2I2 in the presence of benzyl chloride. BC= [Benzyl chloride] = 0 mM (►), [BC1] (●) and 12.42 mM [BC2] = 12.42 mM(▲), [BC3] = 16.56 mM (▼), [BC4] = 20.7 mM (♦) and 24.84 mM [BC5] = 24.84 mM (◄) [SmI_2] = 1.76 mM.

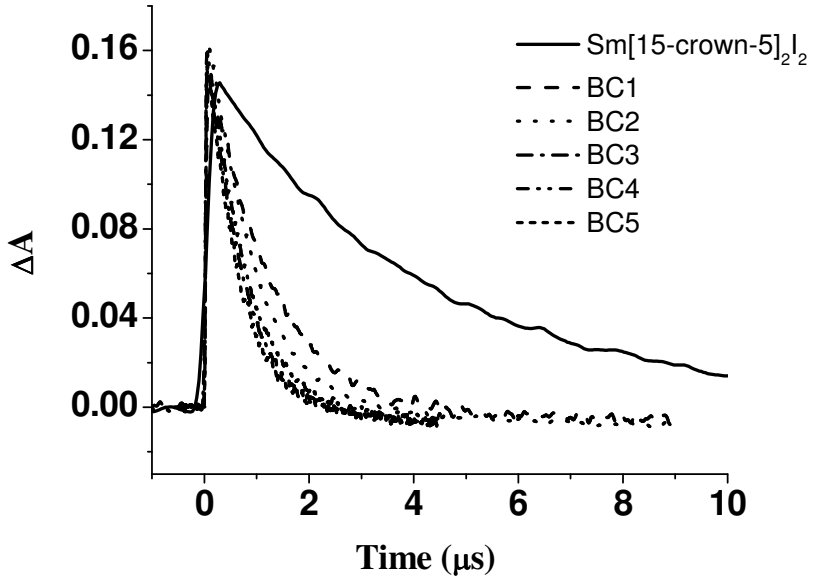

Figure SF22: Excited decay of Sm[15-crown-5]$_2I_2$ at 450 nm with increasing amount of benzyl chloride. BC = [Benzyl chloride] = 0 mM (solid), [BC1] = 8.28 mM (dash), [BC2] = 12.42 mM (dot), 16.56 mM [BC3] = 16.56 mM (dash dot), 20.7 mM [BC4] = 20.7 mM (dash dot dot) and 24.84 mM [BC5] = 24.84 mM (short dash). [SmI_2] = 1.76 mM.

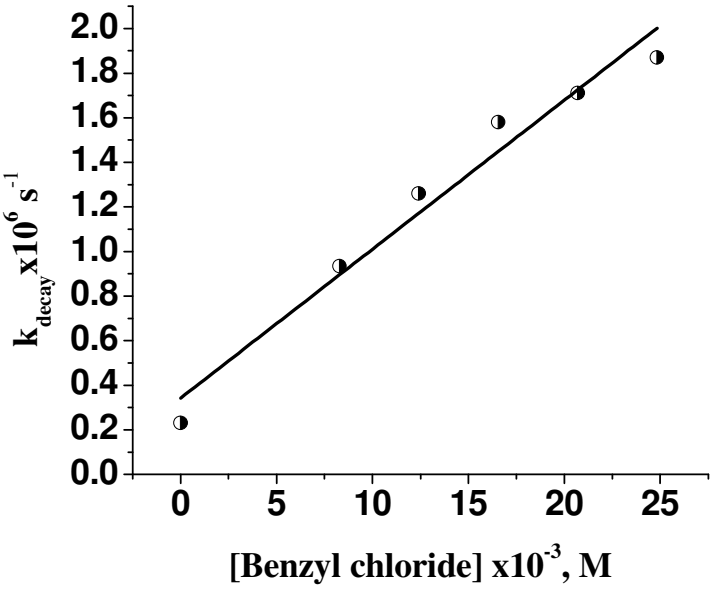

Figure SF23: Observed rate constant of excited state decay of Sm[15-crown-5]$_2$I$_2$ at 450 nm vs concentration of benzyl chloride plot.

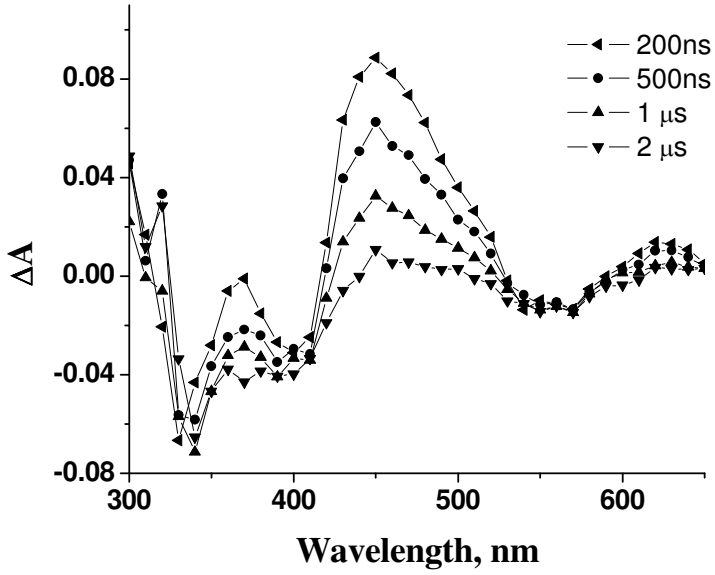

Figure SF24: Transient absorption spectra of Sm[15-crown-5]$_2$I$_2$ in the presence of benzyl chloride at 200 ns(◄); 500 ns (●); 1 μs (▲) and 2 μs (▼) after the laser pulse. [Benzyl chloride]: 24.84 mM and [SmI_2]: 1.76 mM.

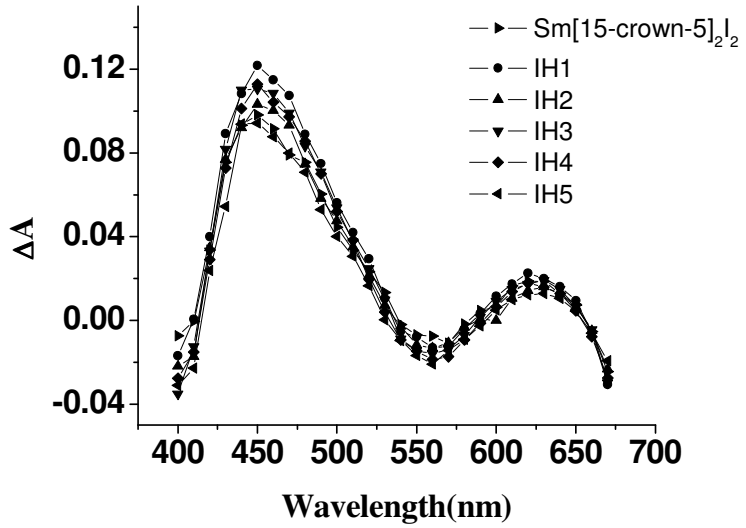

Figure SF25: Transient absorption spectra of Sm[15-crown-5]2I2 in the presence of 1-Iodohexane. IH= [1-Iodohexane] = 0 mM (►), 9.66 mM [IH1] = 9.66 mM (●) and 19.32 mM [IH2] = 19.32 mM (▲), [IH3] = 28.98 mM (▼), 38.64 mM [IH4] = 38.64 mM (♦) and 48.3 mM [IH5] = 48.3 mM (◄) [SmI_2] = 1.76 mM.

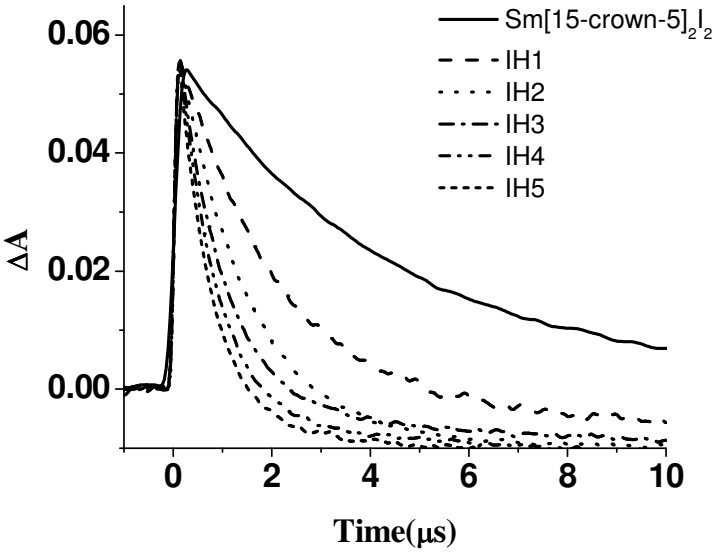

Figure SF26: Excited decay of Sm[15-crown-5]$_2I_2$ at 450 nm with increasing amount of 1-Iodohexane. IH = [1-Iodohexane] = 0 mM (solid), 9.66 mM [IH1] = 9.66 mM (dash), [IH2] 19.32 mM (dot), 28.98 mM [IH3] = 28.98 mM (dash dot), 38.64 mM [IH4] = 38.64 mM (dash dot dot) and [IH5] = 48.3 mM (short dash). [SmI_2] = 1.76 mM.

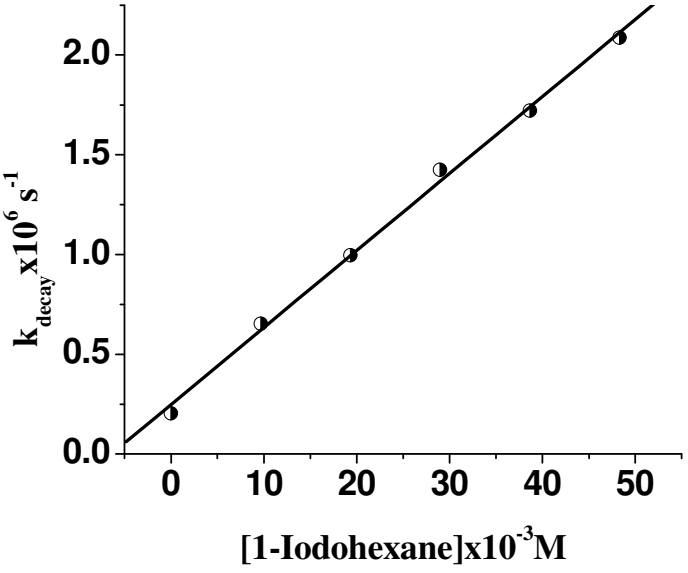

Figure SF27: Observed rate constant of excited state decay of Sm[15-crown-5]$_2$I$_2$ at 450 nm vs concentration of 1-Iodohexane plot.

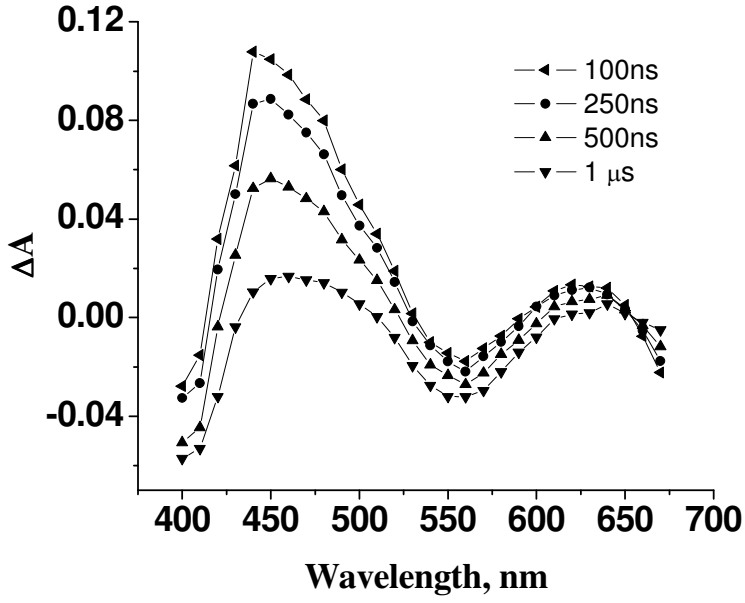

Figure SF28: Transient absorption spectra of Sm[15-crown-5]$_2$I$_2$ in the presence of 1-Iodohexane at 100 ns(◄); 250 ns (●); 500 ns (▲) and 1 μs (▼) after the laser pulse. [1-Iodohexane]: 48.3 mM and [SmI_2]: 1.76 mM.

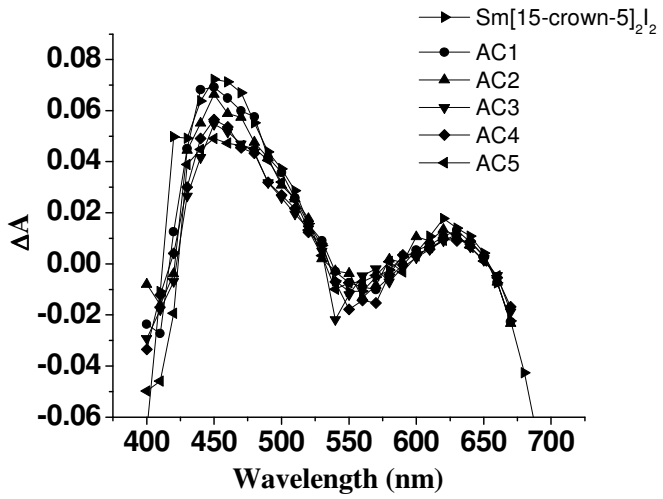

Figure SF29: Transient absorption spectra of Sm[15-crown-5]2I2 in the presence of acetophenone. AC= [Acetophenone] = 0 mM (▶), 4.83 mM [AC1] = 4.83 mM (●), [AC2] = 7.24 mM (▲), [AC3] = 9.66 mM (▼), [AC4] = 12.07 mM (♦) and 14.49 mM [AC5] = 14.49 mM (◀) [SmI_2] = 1.76 mM

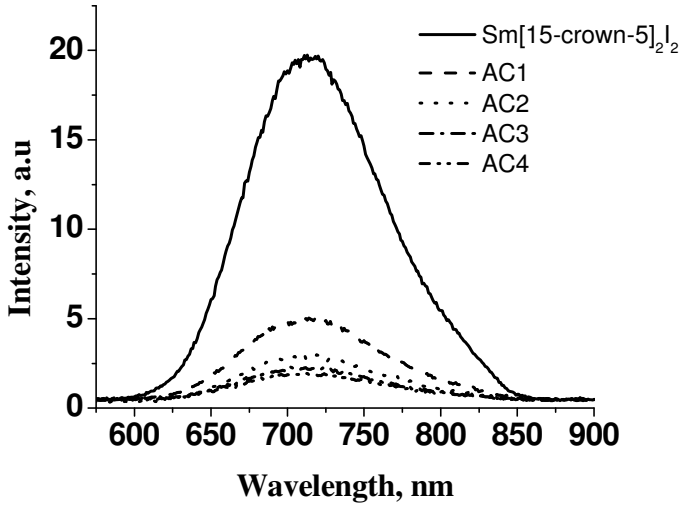

Figure SF30: Steady state luminescence spectra of Sm[15-crown-5]$_2I_2$ in the presence of increasing amount of acetophenone. AC= [Acetophenone] = 0 mM(solid), 2.41 mM [AC1] = 2.41 mM (dash), 4.83 mM [AC2] = 4.83 mM (dot), [AC3] = 7.23 mM (dash dot) and [AC4] = 9.66 mM (dash dot dot). [SmI_2] = 1.76 mM.

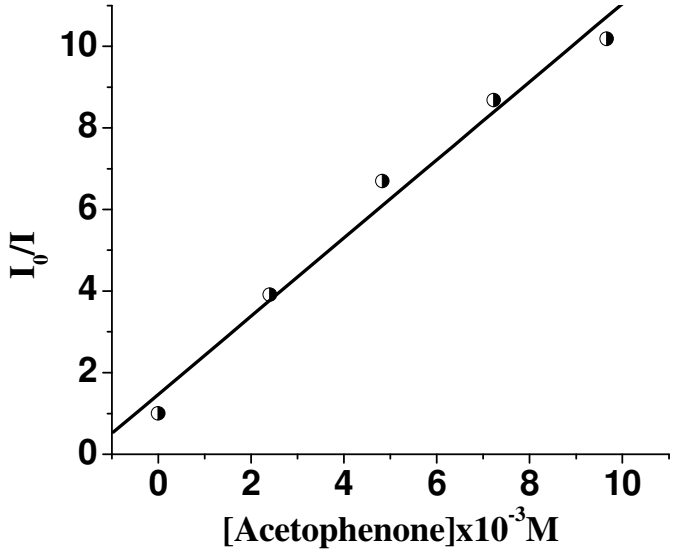

Figure SF31: Stern Volmer plot for the luminescence quenching of Sm[15-crown-]$_2$I$_2$ in the presence of Acetophenone.

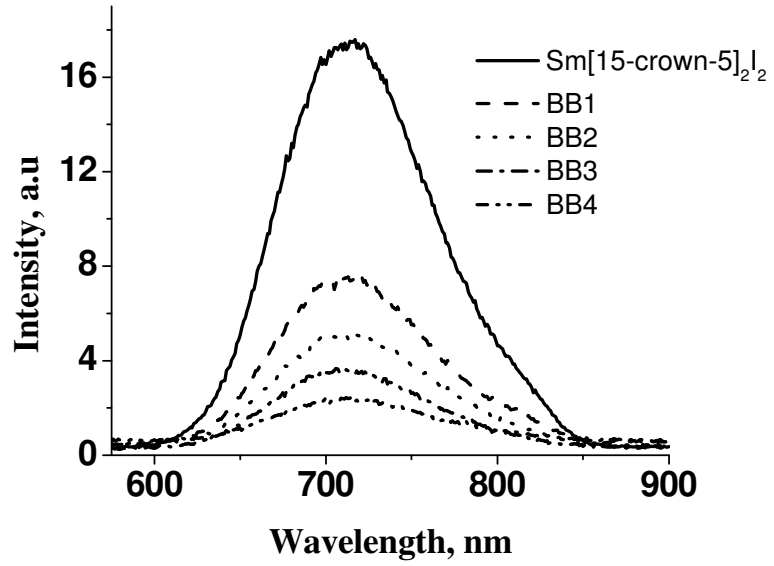

Figure SF32: Steady state luminescence spectra of Sm[15-crown-5]$_2$I$_2$ in the presence of increasing amount of benzyl bromide. BB= [Benzyl bromide] = 0 mM(solid), 2.07 mM [BB1] = 2.07 mM (dash), [BB2] = 4.14 mM (dot), [BB3] = 6.21 mM (dash dot) and 8.28 mM ([BB4] = 8.28 mM (dash dot dot). [SmI$_2$]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

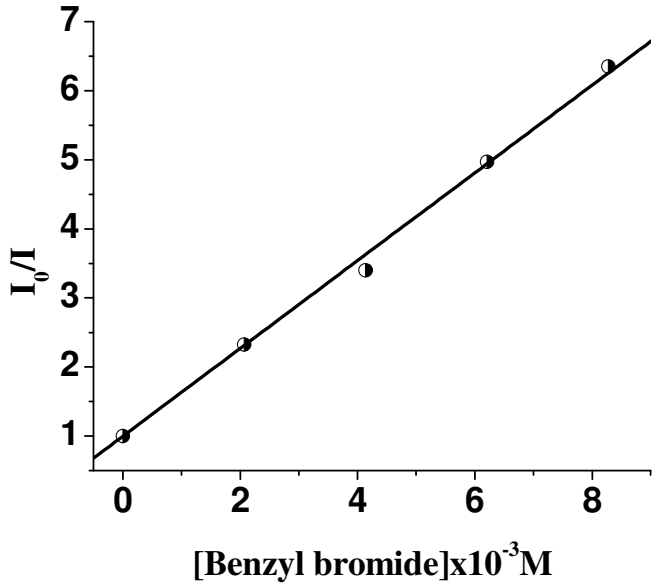

Figure SF33: Stern Volmer plot for the luminescence quenching of Sm[15-crown-5]$_2$I$_2$ in the presence of Benzyl bromide.

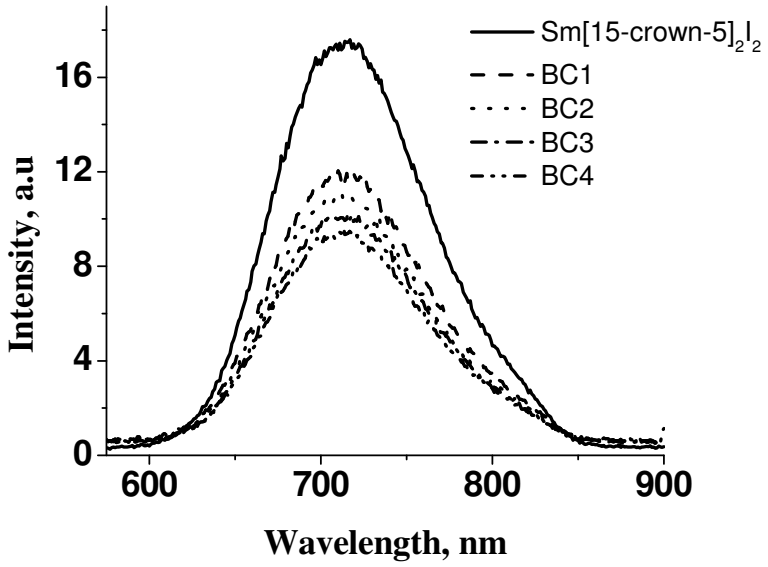

Figure SF34: Steady state luminescence spectra of Sm[15-crown-5]$_2$I$_2$ in the presence of increasing amount of benzyl chloride. BC= [Benzyl chloride] = 0 mM(solid), [BC1] = 8.28 mM (dash), [BC2] = 10.35 mM (dot), [BC3] = 12.45 mM (dash dot) and 14.49 mM [BC4] = 14.49 mM (dash dot dot). [SmI$_2$] = 1.76 mM.

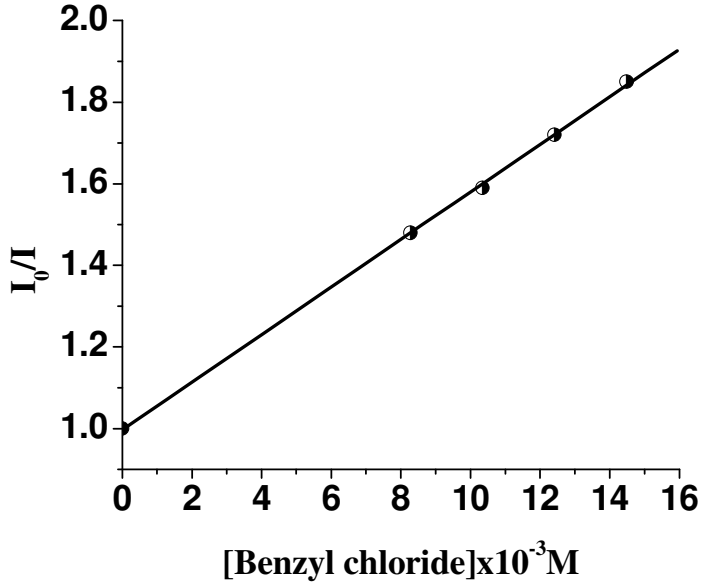

Figure SF35: Stern Volmer plot for the luminescence quenching of Sm[15-crown-5]$_2$I$_2$ in the presence of benzyl chloride.

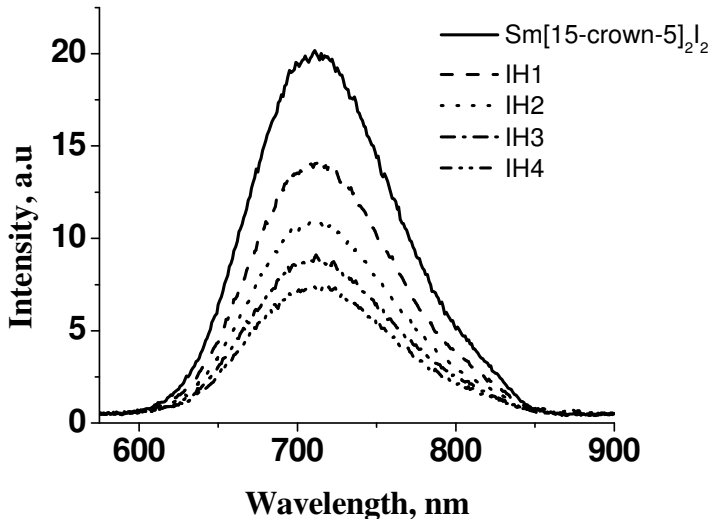

Figure SF36: Steady state luminescence spectra of Sm[15-crown-5]$_2$I$_2$ in the presence of increasing amount of 1-Iodohexane. IH= [1-Iodohexane] = 0 mM(solid), [IH1] = 9.66 mM (dash), [IH2] = 19.32 mM (dot), [IH3] = 28.93 mM (dash dot) and [IH4] = 38.64 mM (dash dot dot). [SmI$_2$] = 1.76 mM.

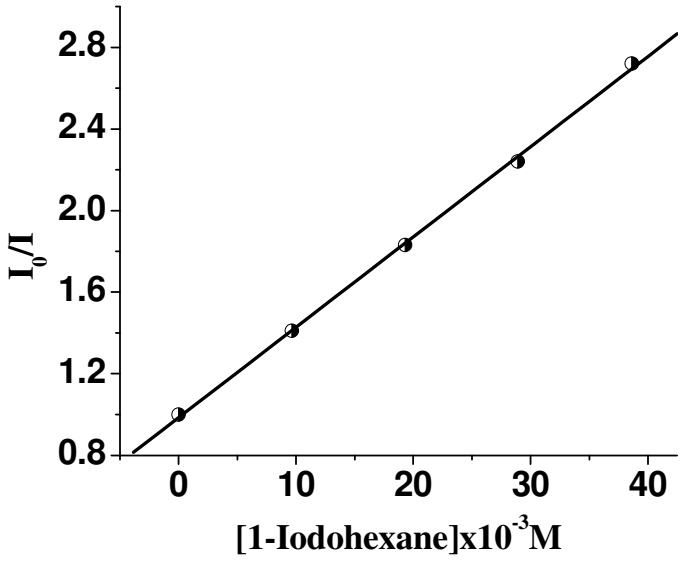

Figure SF37: Stern Volmer plot for the luminescence quenching of Sm[15-crown-5]$_2$I$_2$ in the presence of 1-Iodohexane.