

Supporting Information

Sn(IV) Schiff Base Complexes: a New Class of Triplet Photosensitizer for Photoredox Reactions

Tod A. Grusenmeyer^A; Albert W. King^B; Joel T. Mague^A; Jeffrey J. Rack^B; Russell H. Schmehl^A

^ADepartment of Chemistry, Tulane University, New Orleans, Louisiana 70118, United States

^BDepartment of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, United States

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A. ^1H NMR Data

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It is important to note that Sn has three spin $\frac{1}{2}$ isotopes: ^{119}Sn with a relative abundance of 8.7%, ^{117}Sn with a relative abundance of 7.1%, and ^{115}Sn with a relative abundance of 0.53% (coupling often not observed). The ortho-protons of the tin bound phenyl ring and the imine proton of the various NNO ligands couple with ^{119}Sn and ^{117}Sn . In all of the complexes, the imine singlet is shifted significantly downfield ($>8.7\text{ppm}$) and the tin bound phenyl is found as a doublet at $\sim 8.30\text{ ppm}$ and a three proton multiplet at $\sim 7.60\text{ppm}$. The splitting of the doublet resonance is clear in the NMR spectrum of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$ with coupling peaks at 8.11 ppm and on the downfield edge of the 8.39ppm resonance. A COSY spectrum was also collected for the $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$ complex. The proton at 9.90ppm does not couple to any other protons. The resonance at 8.33ppm is coupled only to the multiplet at 7.62ppm. The quinoline ring has two sets of three protons that should couple in a dtd fashion. One set contains the resonances at 8.49 (d), 8.05 (t), and 8.17 (d) ppm. The other contains the resonances at 8.55 (d), 7.84 (t), and 8.85 (d) ppm. The 2-hydroxynaphthaldehyde ring contains the coupling of the doublets at 8.08 and 7.01 ppm and the set of resonances at 7.87 (d), 7.48(t), 7.69 (t), and 8.46 (d) ppm. It is worth noting that ^1H resonances from the 8-aminoquinoline moiety are identifiable in the other complexes of the series. For instance, a doublet occurs in all spectra in the 8.50-8.40ppm range with a characteristic coupling constant of 4.2Hz.

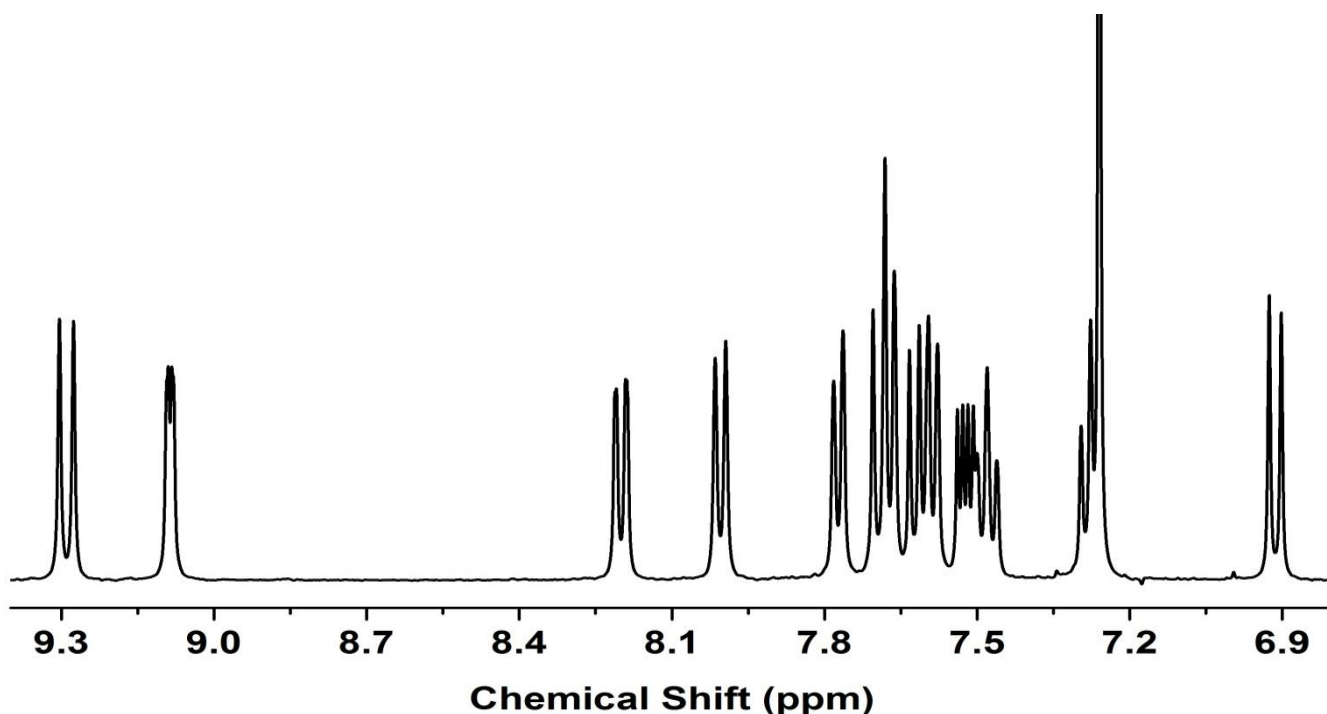


Figure S1. ^1H NMR spectrum of HLnap in d-chloroform. The spectra have been edited to show only ^1H resonances resulting from the ligand. The ^1H NMR spectrum of this complex also contains residual CH_3CN , H_2O , and n-hexane.

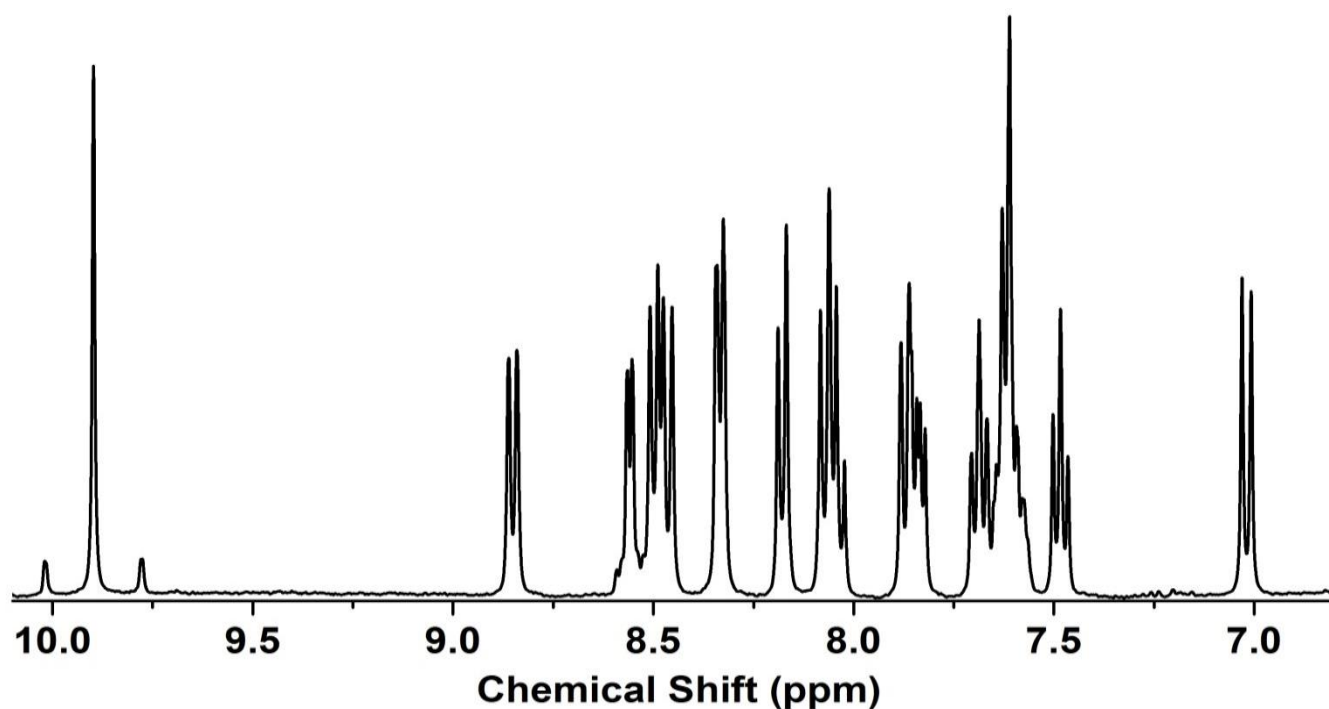


Figure S2. ^1H NMR spectrum of $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$ in d_3 -acetonitrile. The spectra have been edited to show only ^1H resonances resulting from the tin complex. The ^1H NMR spectrum of this complex also contains residual CH_3CN , H_2O , and n -hexane.

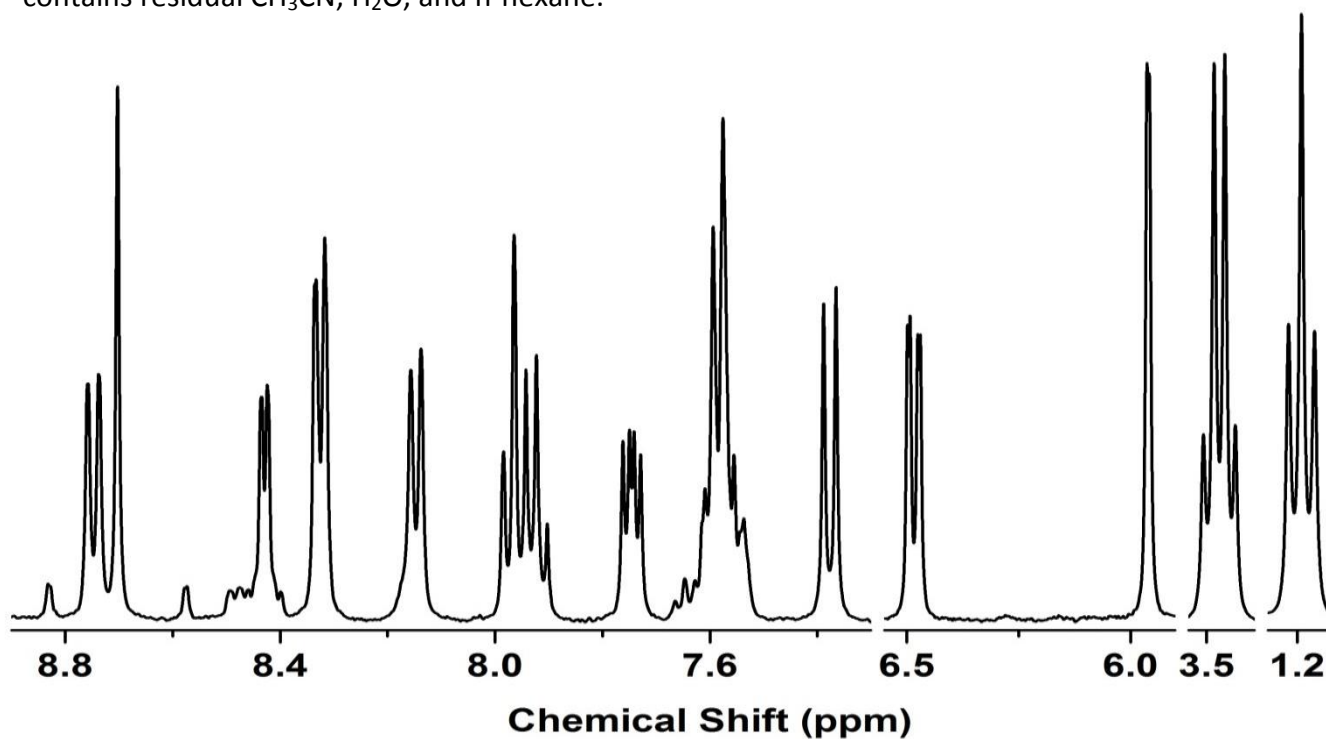


Figure S3. ^1H NMR spectrum $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$ in d_3 -acetonitrile. The spectra have been edited to show only ^1H resonances resulting from the tin complex. The ^1H NMR spectrum of this complex also contains residual CH_3CN , H_2O , and n -hexane.

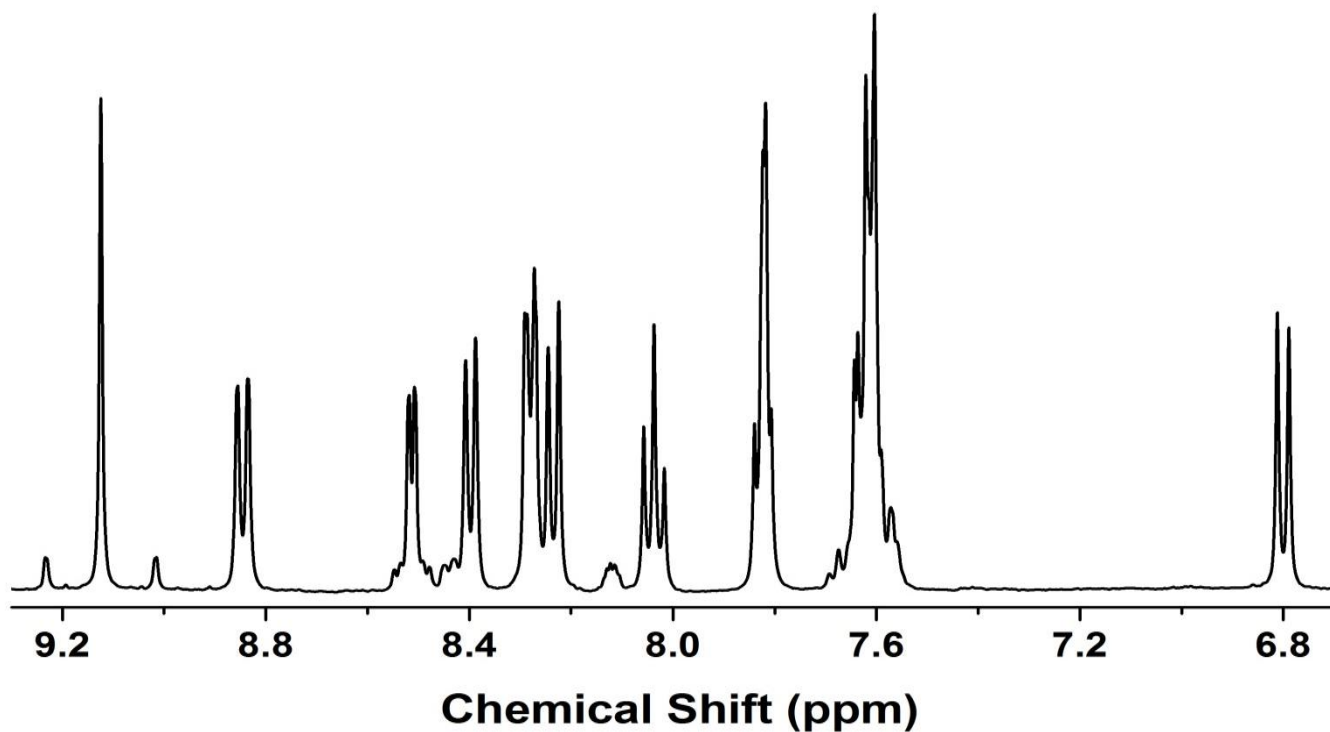


Figure S4. ^1H NMR spectrum of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$ in d_3 -acetonitrile. The spectra have been edited to show only ^1H resonances resulting from the tin complex. The ^1H NMR spectrum of this complex also contains residual CH_3CN , H_2O , n -hexane

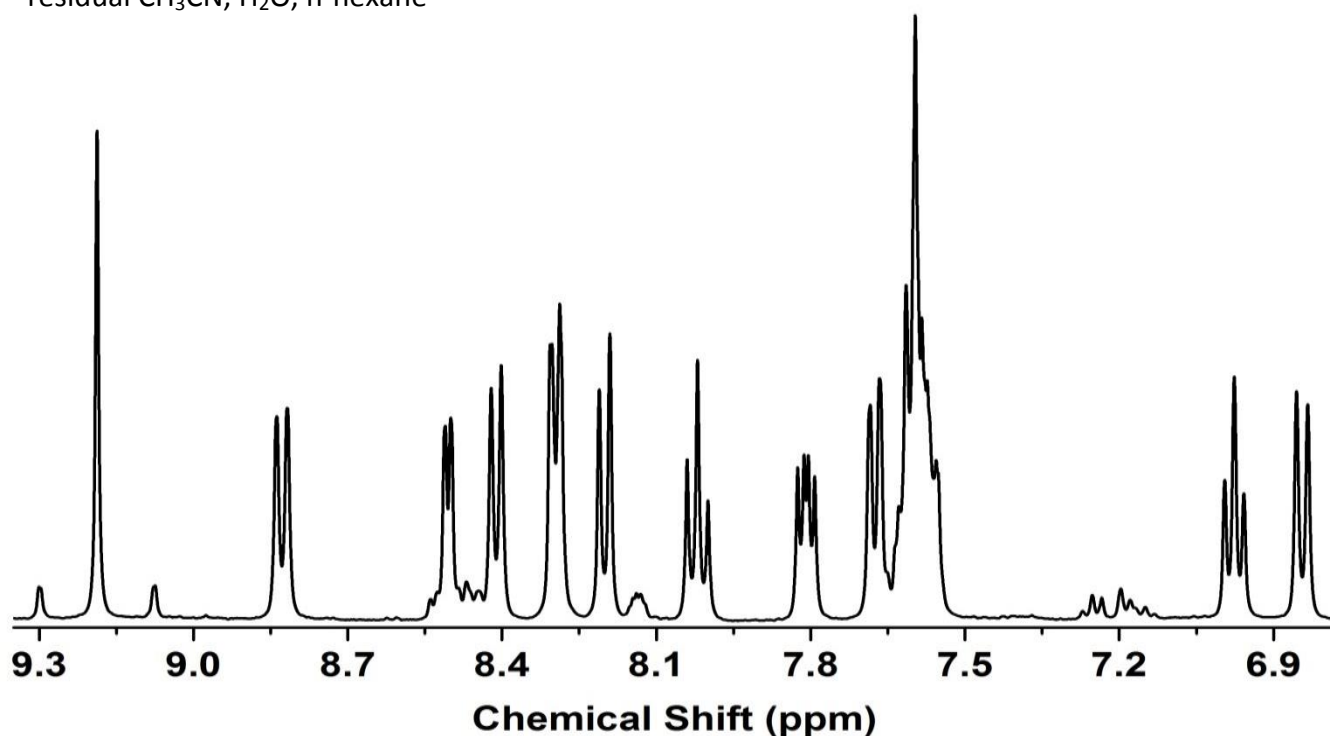


Figure S5. ^1H NMR spectrum of $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$ in d_3 -acetonitrile. The spectra have been edited to show only ^1H resonances resulting from the tin complex. The ^1H NMR spectrum of this complex also contains residual CH_3CN , H_2O , n -hexane, and toluene. The ^1H resonances of the residual toluene appear as the multiplet centered at 7.2 ppm in the spectrum above.

B. Cyclic Voltammetry

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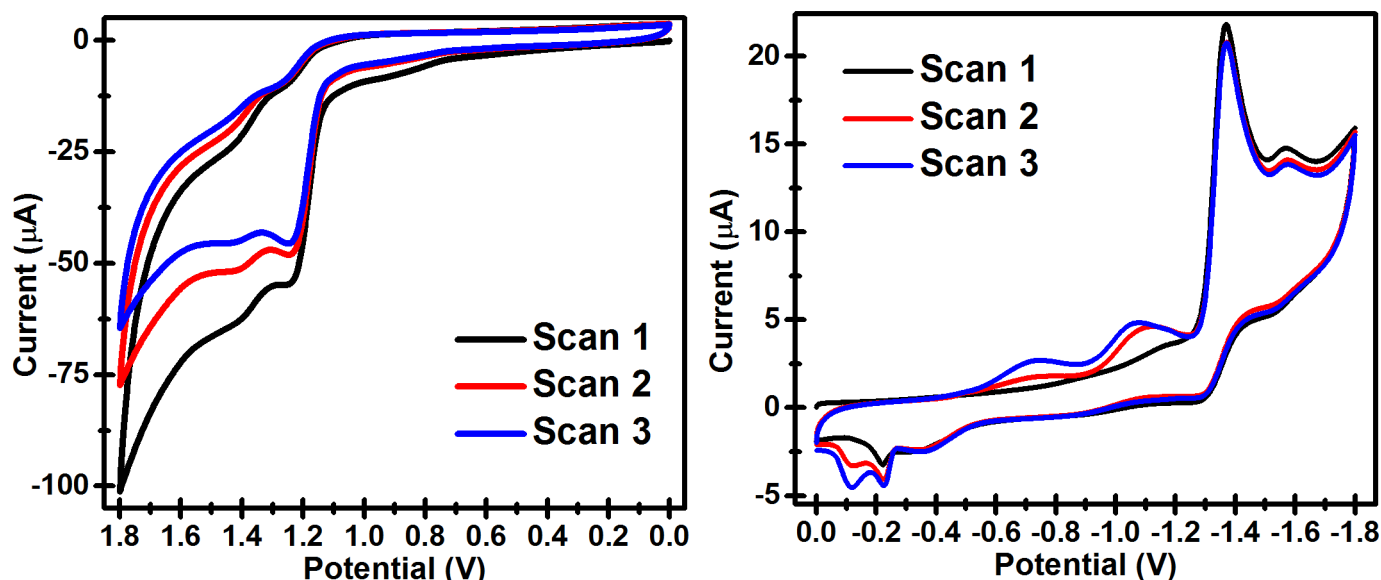


Figure S6. Cyclic voltammograms of $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$ in acetonitrile. Left: Anodic scan. Right: Cathodic scan. Three successive scans are shown in each figure. The voltammograms were collected in solutions containing 0.1M $[\text{nBu}_4\text{N}][\text{PF}_6]$, and were bubble degassed with argon for 10 minutes prior to collection. The presented sweep segments were collected at a scan rate of 100 mV/s. Working electrode: glassy-carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgPF₆ in acetonitrile.

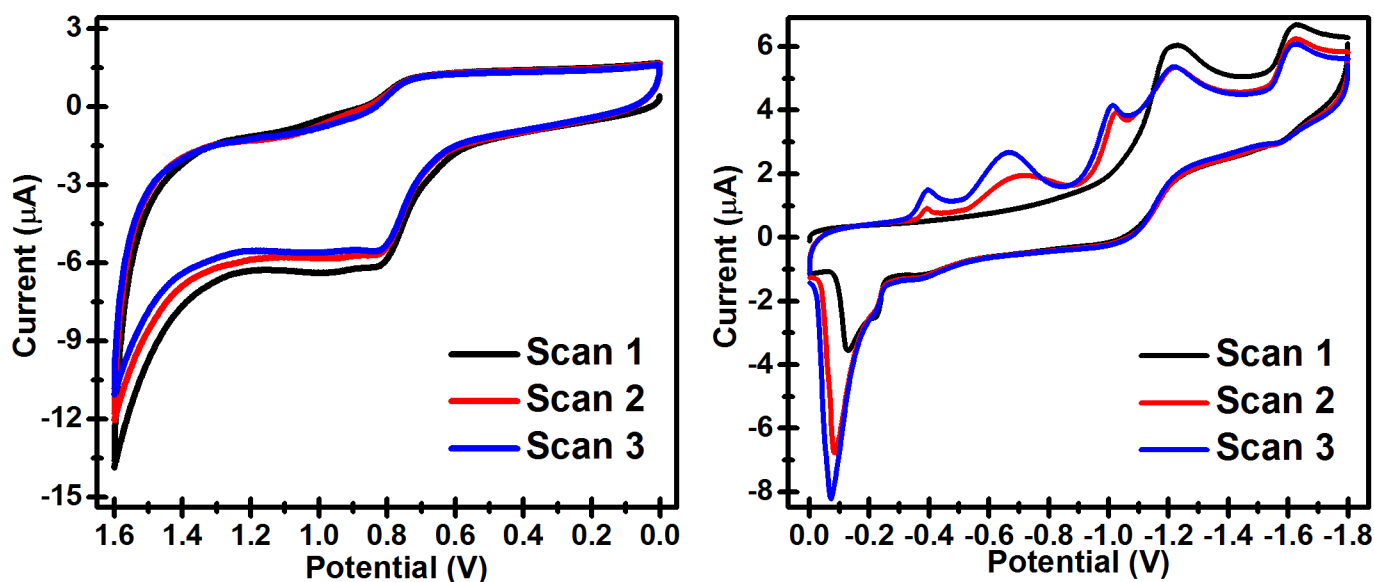


Figure S7. Cyclic voltammograms of $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$ in acetonitrile. Left: Anodic scan. Right: Cathodic scan. Three successive scans are shown in each figure. The voltammograms were collected in solutions containing 0.1M $[\text{nBu}_4\text{N}][\text{PF}_6]$, and were bubble degassed with argon for 10 minutes prior to collection. The presented sweep segments were collected at a scan rate of 100 mV/s. Working electrode: glassy-carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgPF₆ in acetonitrile.

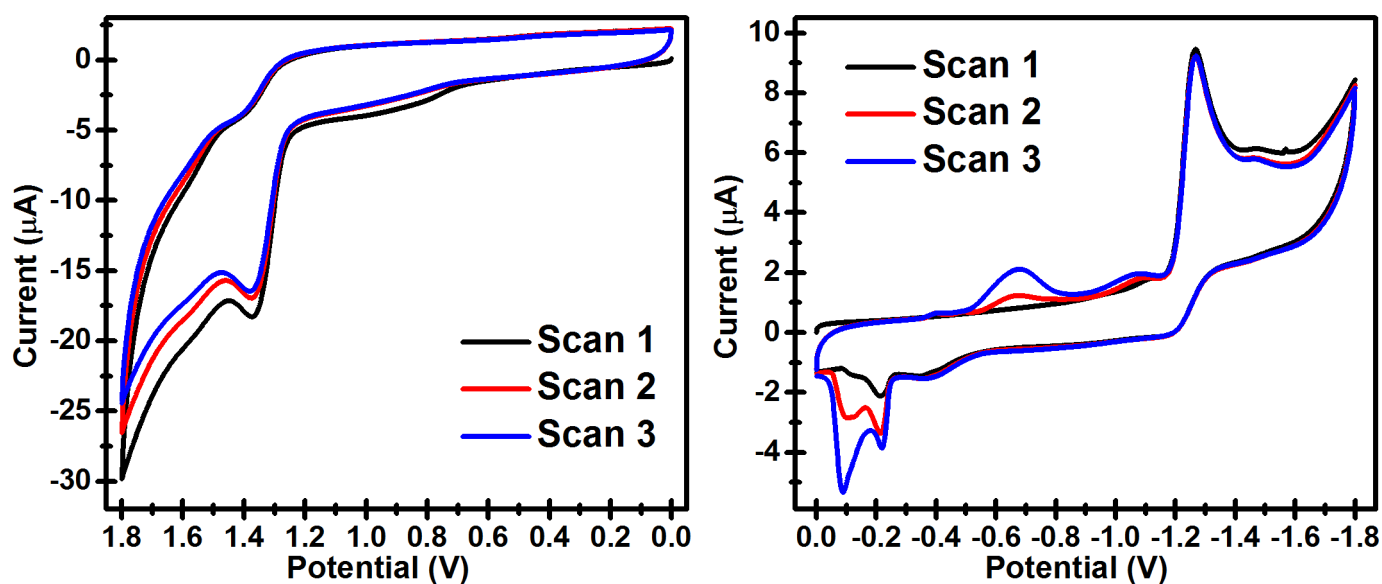


Figure S8. Cyclic voltammograms of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$ in acetonitrile. Left: Anodic scan. Right: Cathodic scan. Three successive scans are shown in each figure. The voltammograms were collected in solutions containing 0.1M $[\text{nBu}_4\text{N}][\text{PF}_6]$, and were bubble degassed with argon for 10 minutes prior to collection. The presented sweep segments were collected at a scan rate of 100 mV/s. Working electrode: glassy-carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgPF₆ in acetonitrile.

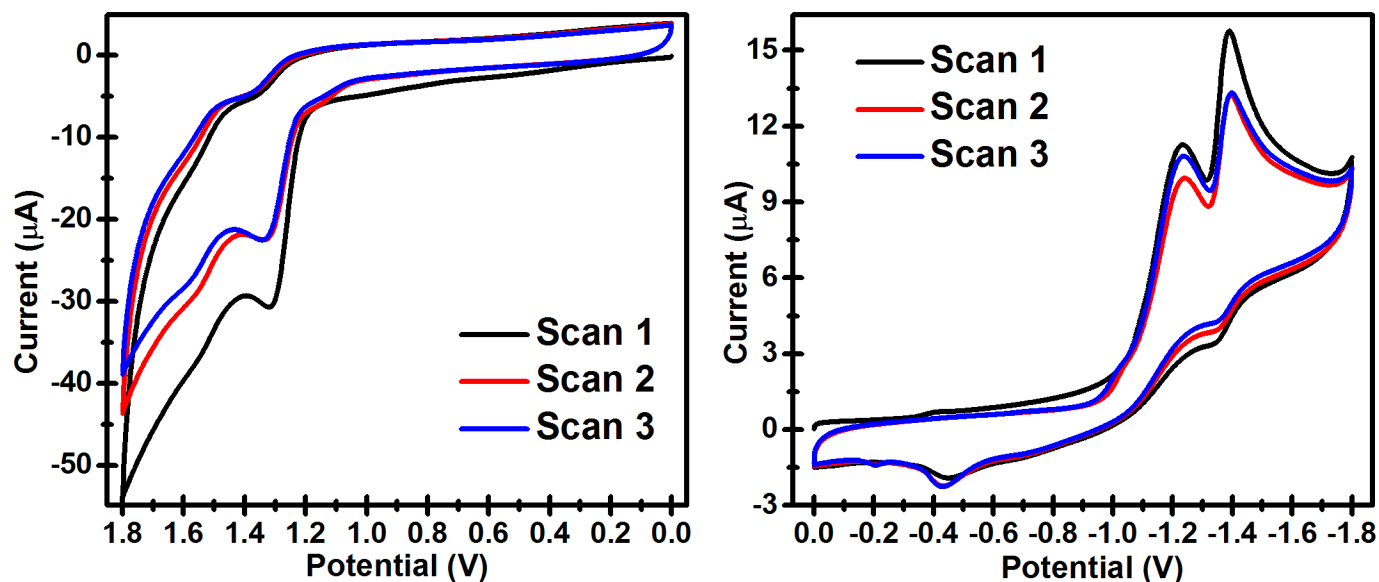


Figure S9. Cyclic voltammograms of $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$ in acetonitrile. Left: Anodic scan. Right: Cathodic scan. Three successive scans are shown in each figure. The voltammograms were collected in solutions containing 0.1M $[\text{nBu}_4\text{N}][\text{PF}_6]$, and were bubble degassed with argon for 10 minutes prior to collection. The presented sweep segments were collected at a scan rate of 100 mV/s. Working electrode: glassy-carbon. Counter electrode: Pt wire. Reference electrode: Ag/AgPF₆ in acetonitrile.

C. Room Temperature Luminescence

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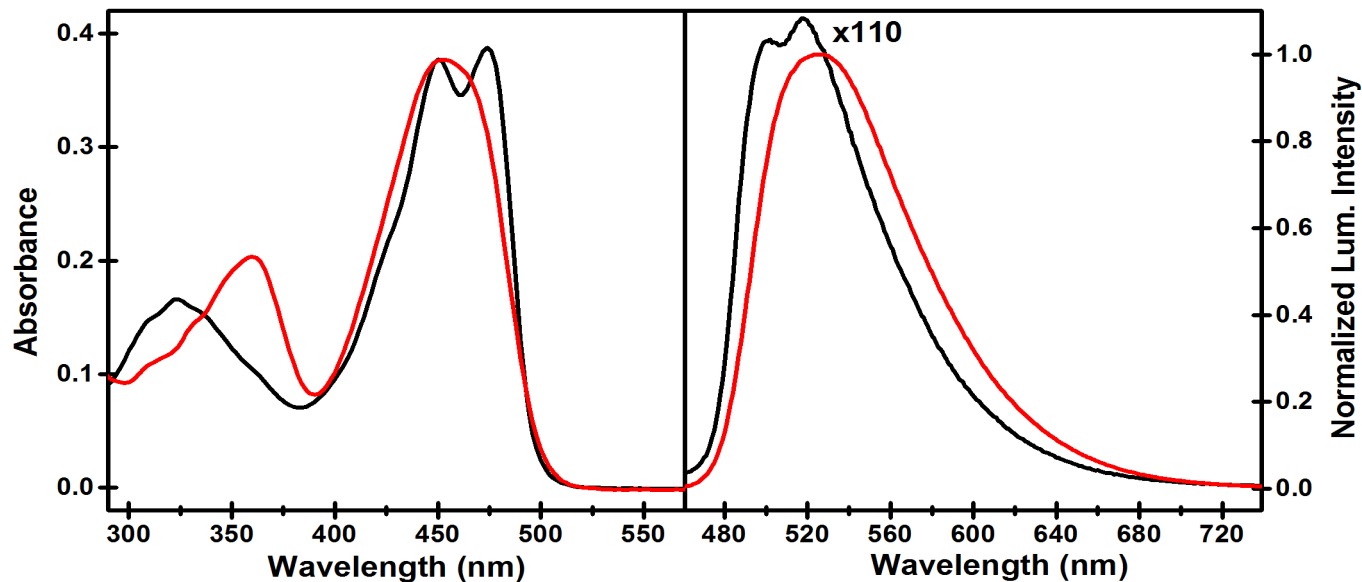


Figure S10. Left: Absorbance matched samples of HLnep (—) and [PhSn(Lnap)Cl₂] (—) in acetonitrile. Right: Normalized luminescence spectra of HLnep (—) and [PhSn(Lnap)Cl₂] (—) collected from the absorbance spectra presented on the left. Note: The luminescence of the Lnap ligand is displayed at 110x amplification.

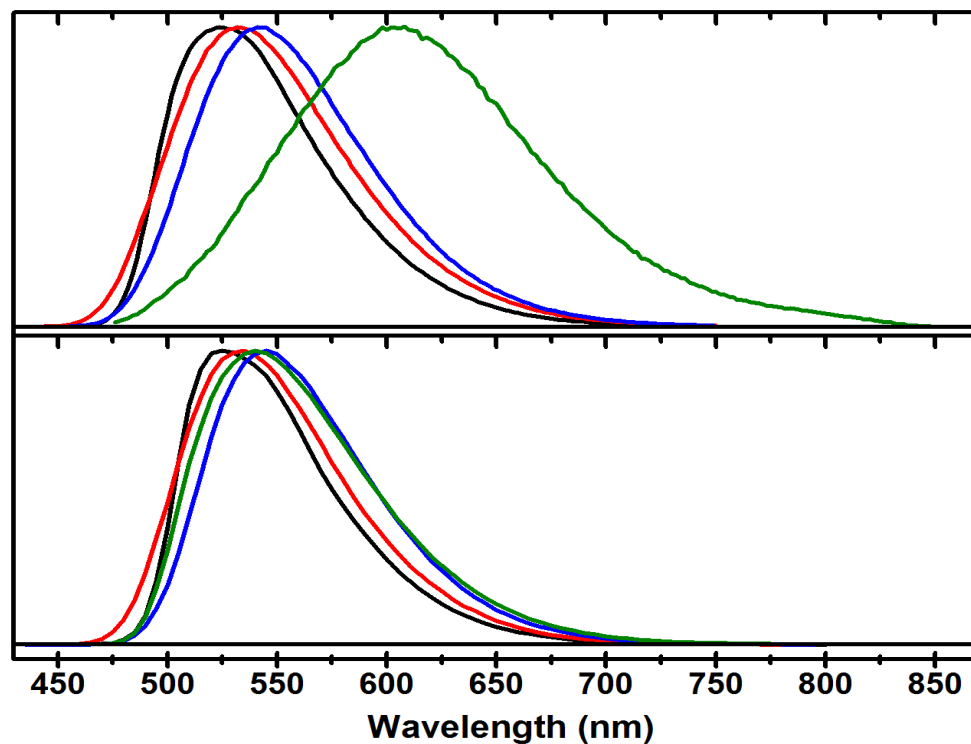


Figure S11. Normalized luminescence spectra of [PhSn(Lnap)Cl₂] (—), [PhSn(Lsal)Cl₂] (—), [PhSn(LBr)Cl₂] (—), and [PhSn(Ldea)Cl₂] (—). Top: Spectra collected in acetonitrile. Bottom: Spectra collected in chloroform.

D. Nanosecond Transient Absorption

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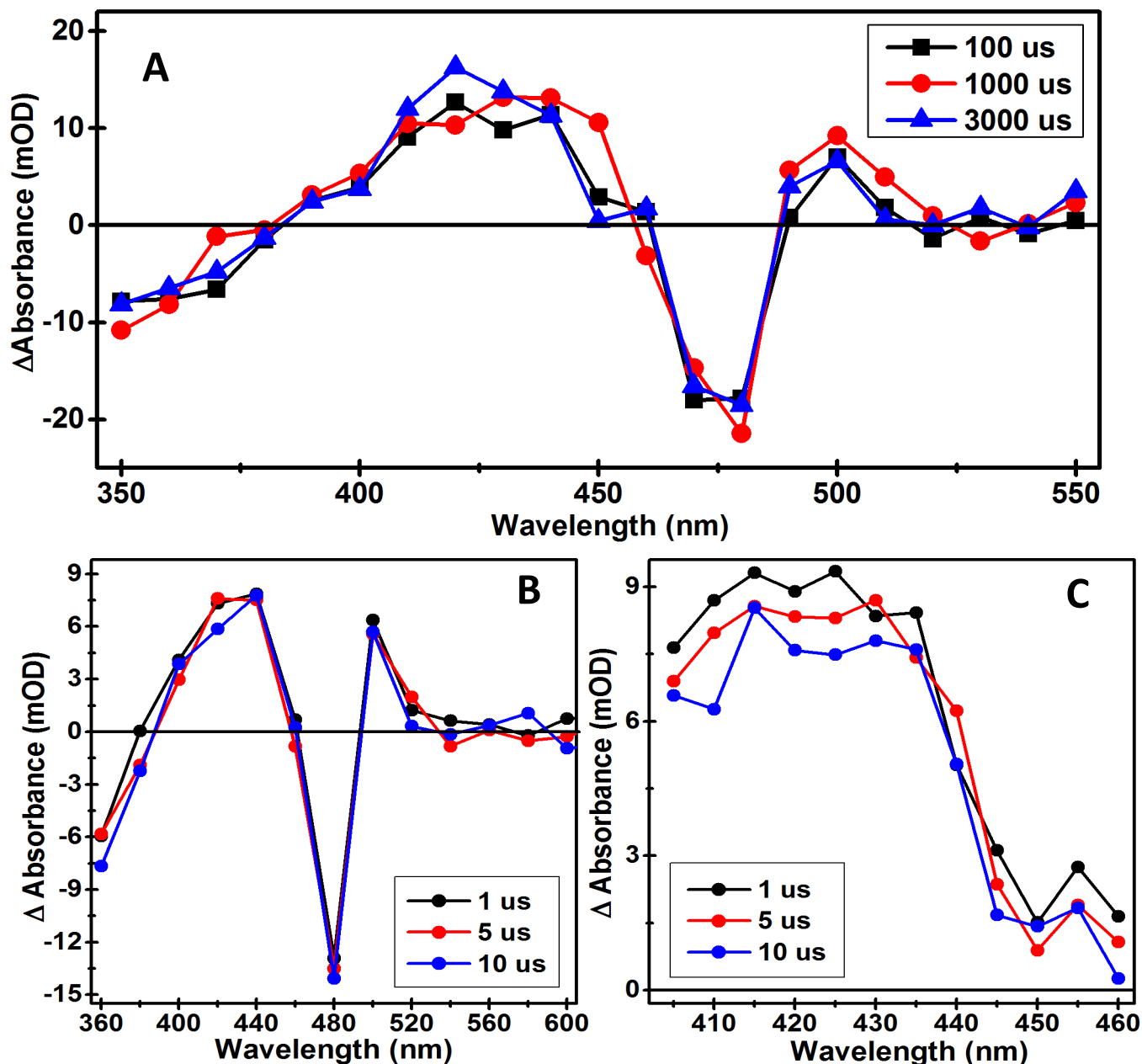


Figure S12. (A) Nanosecond transient absorption spectrum of an deoxygenated solution of HLnap in acetonitrile. (B) Nanosecond transient absorption spectrum of HLnap in a 1mM deoxygenated solution of MPTZ in acetonitrile. Note: MPTZ cation radical is not observed in the TA spectrum. (C) Nanosecond transient absorption spectrum of HLnap in a 8.9mM deoxygenated solution of 9-bromoanthracene in acetonitrile. C focuses on the region of the TA spectrum where absorption from triplet sensitized 9-bromoanthracene occurs. Note: Absorption from triplet sensitized 9-bromoanthracene is not observed in the TA spectrum.

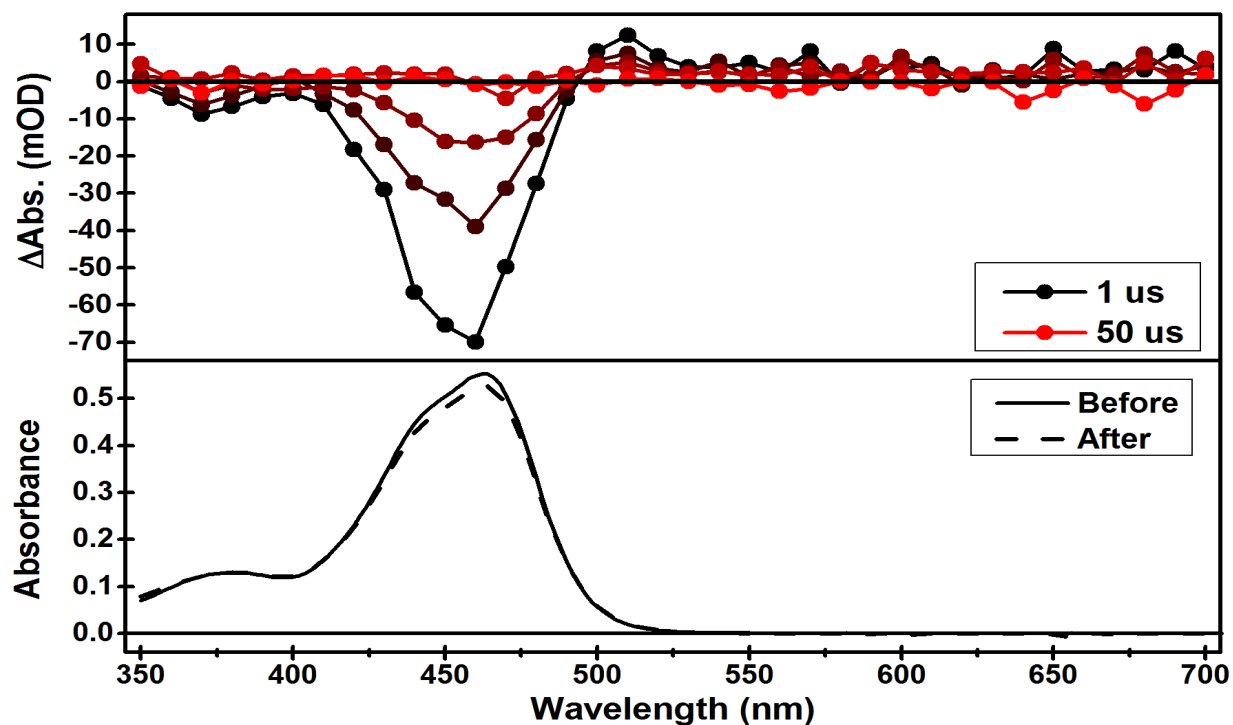


Figure S13. (Top) Nanosecond Transient Absorption Spectrum of $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$ in acetonitrile. (Bottom) Ground state absorption spectrum of $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$ (—) before and (---) after collection of the TA spectrum.

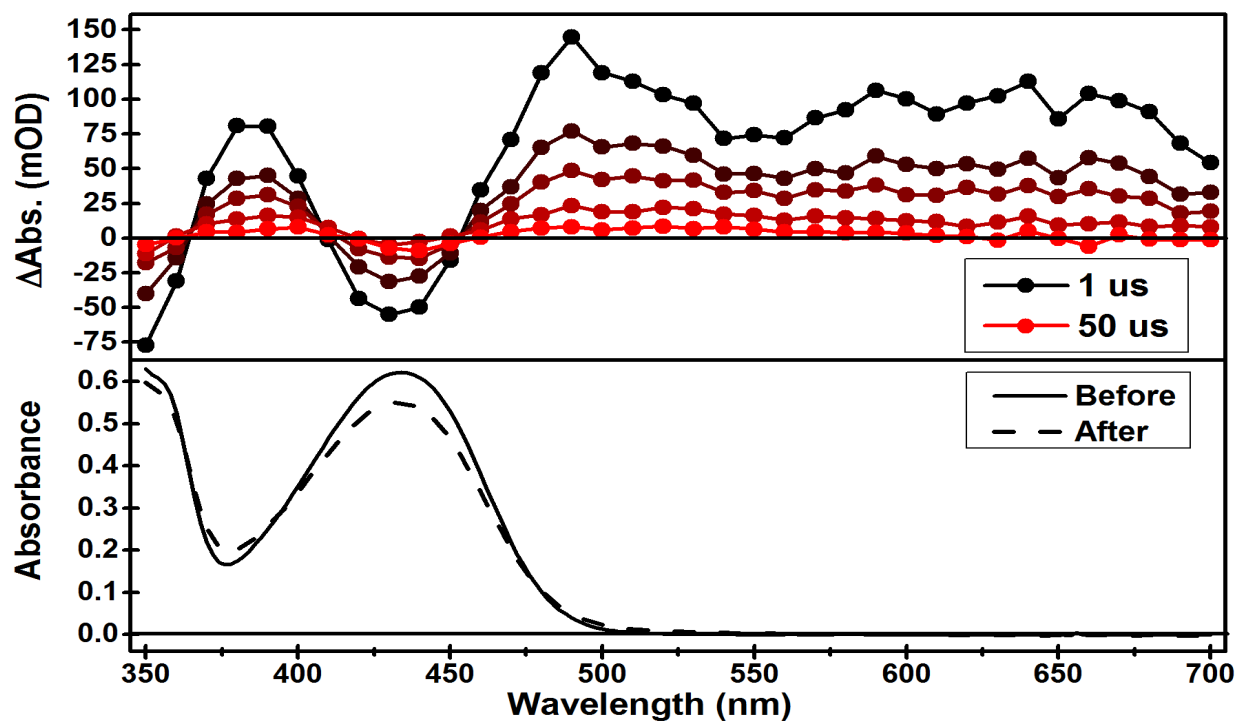


Figure S14. (Top) Nanosecond Transient Absorption Spectrum of $[\text{PhSn}(\text{NNObrsal})\text{Cl}_2]$ in acetonitrile. (Bottom) Ground state absorption spectrum of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$ (—) before and (---) after collection of the TA spectrum.

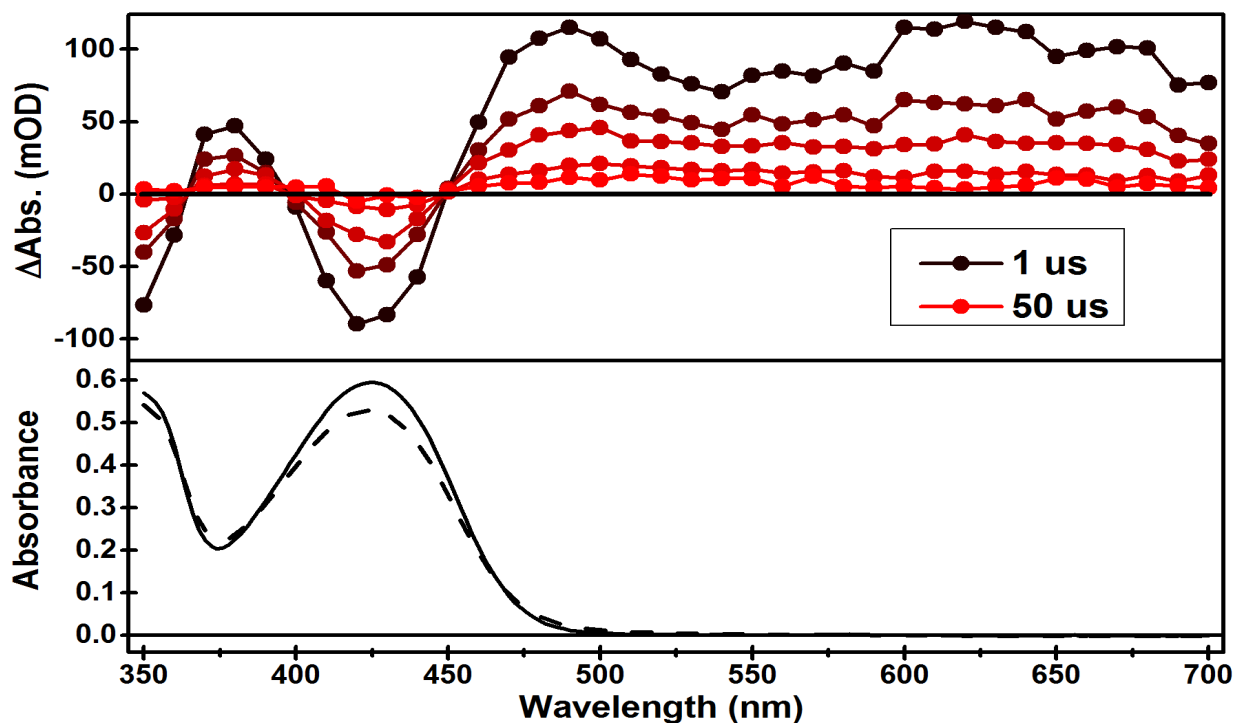


Figure S15. (Top) Nanosecond Transient Absorption Spectrum of $[\text{PhSn(Lsal)Cl}_2]$ in acetonitrile. (Bottom) Ground state absorption spectrum of $[\text{PhSn(Lsal)Cl}_2]$ (—) before and (- -) after collection of the TA spectrum.

E. Ultrafast Transient Absorption [\(return to contents\)](#)

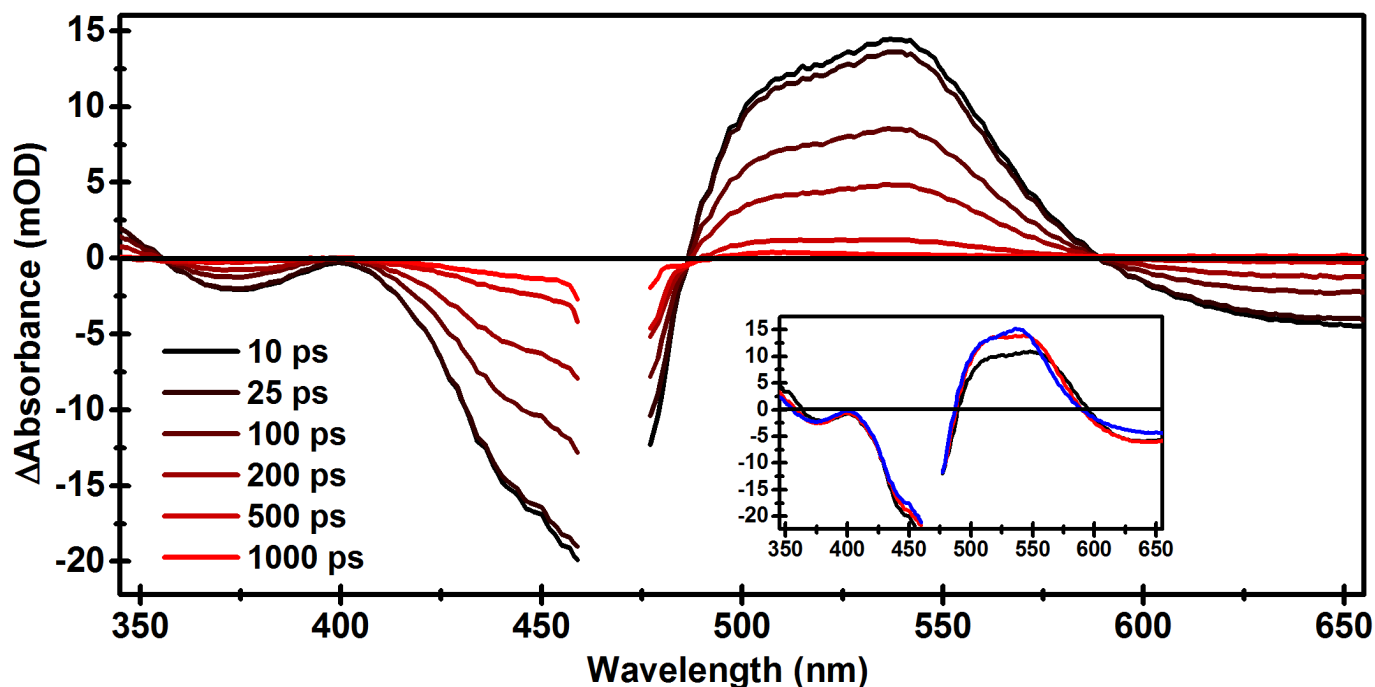


Figure S16. Ultrafast transient absorption spectrum of $[\text{PhSn(Ldea)Cl}_2]$ in acetonitrile. Inset: Early time traces 0.500 ps (—), 1 ps (—), and 5 ps (—). Evidence of the laser pulse has been omitted for clarity.

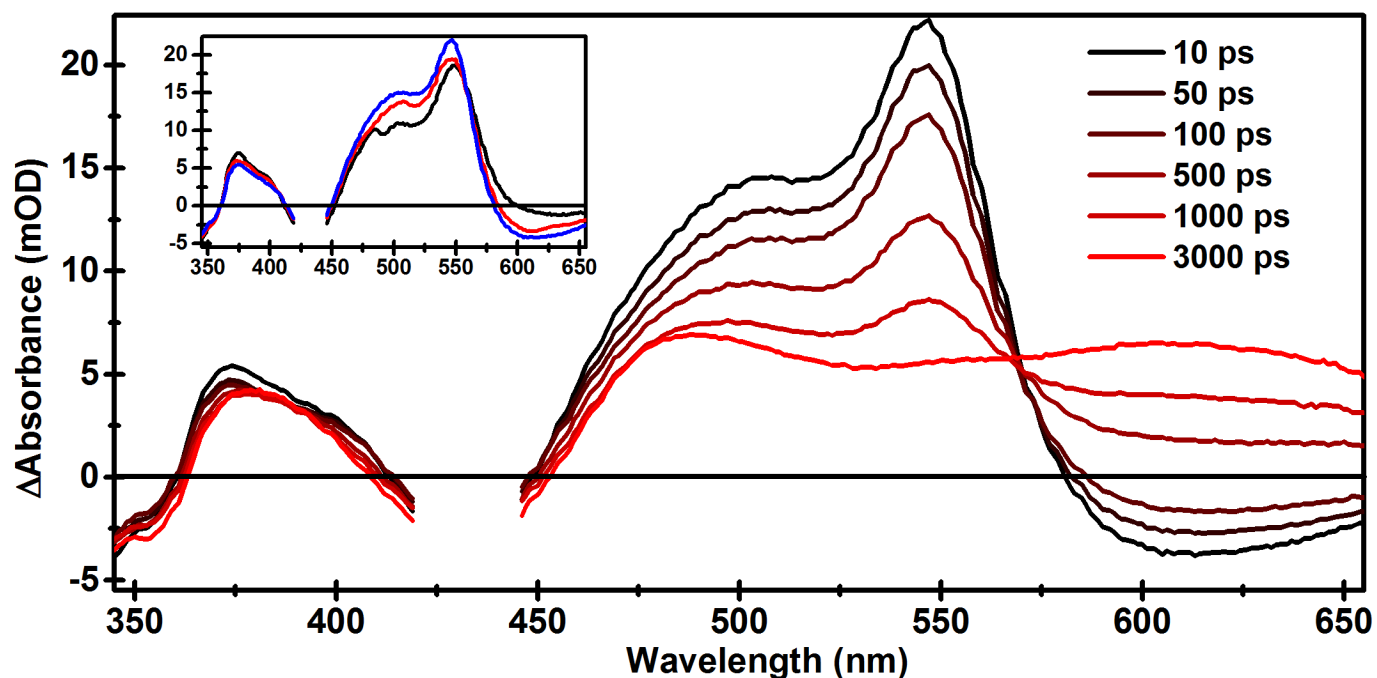


Figure S17. Ultrafast transient absorption spectrum of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$ in acetonitrile. Inset: Early time traces 0.500 ps (—), 1 ps (—), and 5 ps (—). Evidence of the laser pulse has been omitted for clarity.

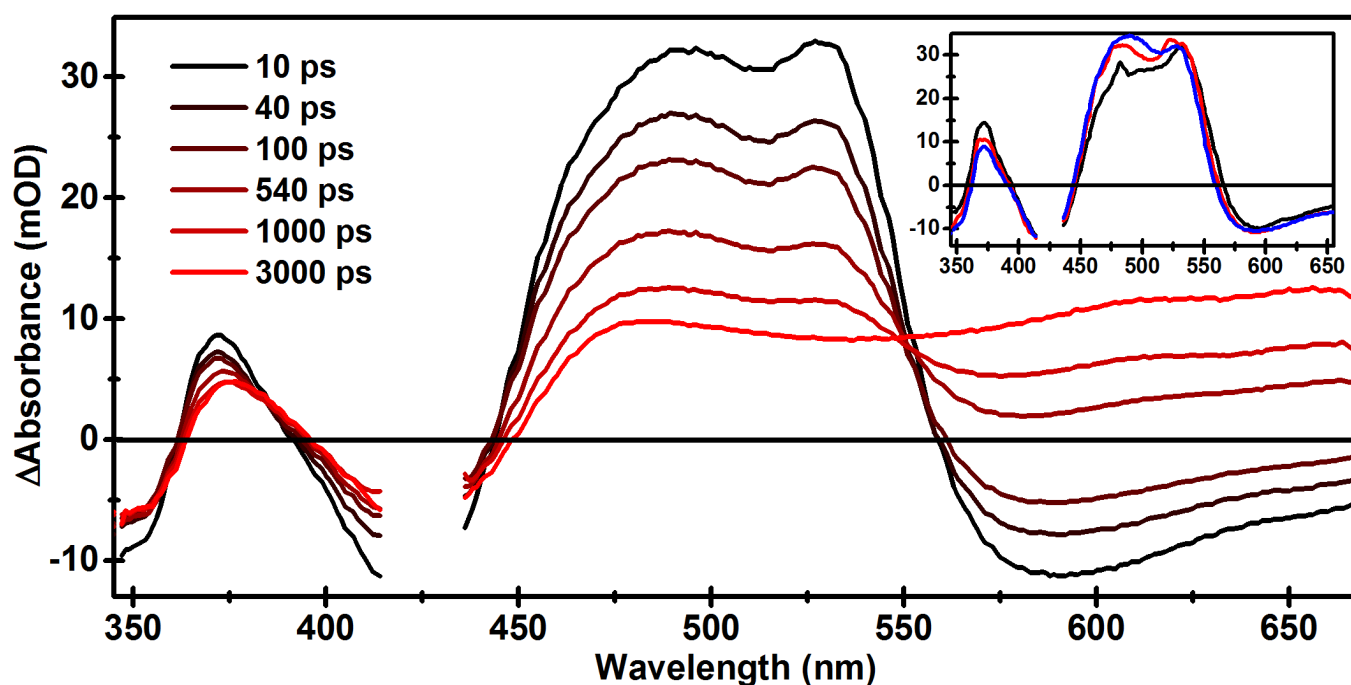
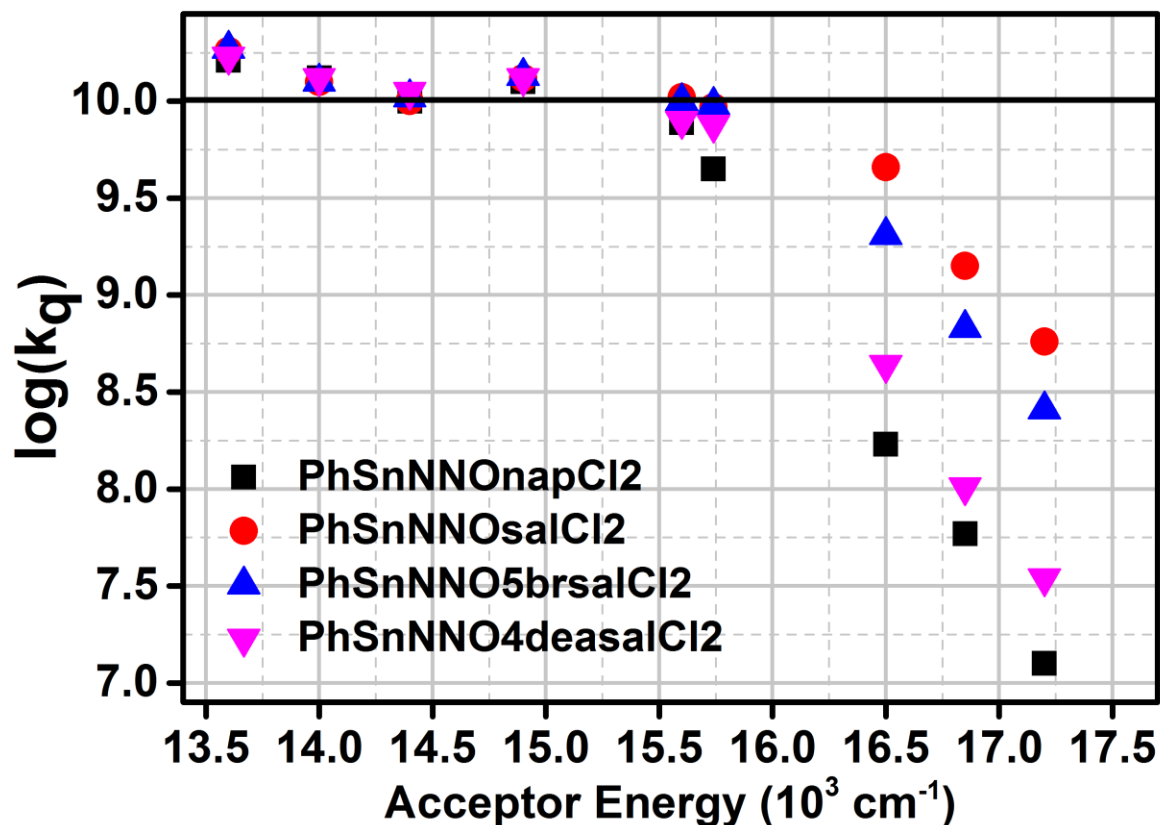


Figure S18. Ultrafast transient absorption spectrum of $[\text{PhSn}(\text{Lsa})\text{Cl}_2]$ in acetonitrile. Inset: Early time traces 0.500 ps (—), 1 ps (—), and 5 ps (—). Evidence of the laser pulse has been omitted for clarity.

F. Saltiel Plot

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Triplet Energy (cm^{-1})	Quencher
13600	Azulene
14000	9,10-dibromoanthracene
14400	9-bromoanthracene
14900	Anthracene
15600	Phenazine
15740	Acridine
16500	Benz[a]anthrone
16850	Pyrene
17200	stilbene
17600	9-fluorenone

Figure S19. (Top) Energy transfer quenching analysis of each chromophore with a series of triplet energy acceptors. (Bottom) List of the energy acceptors used to collect the data.

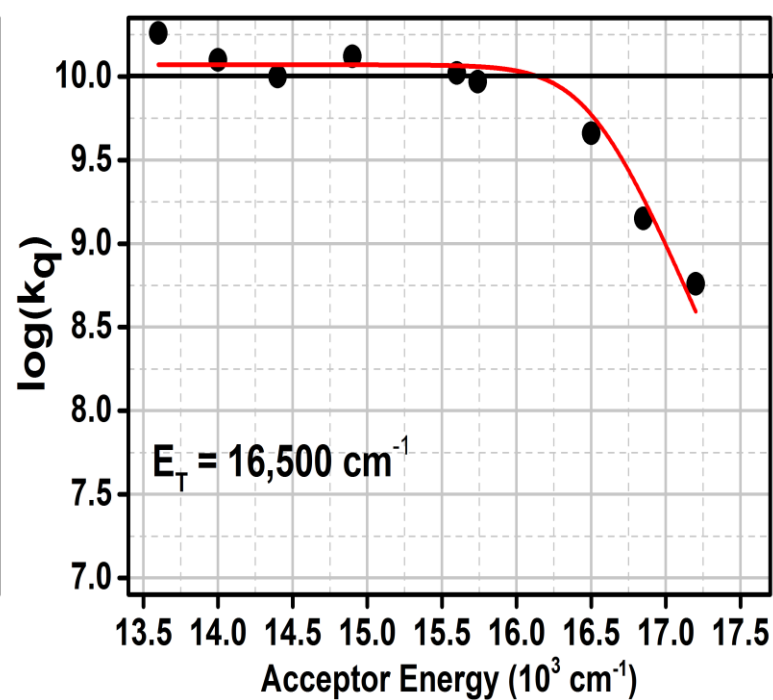
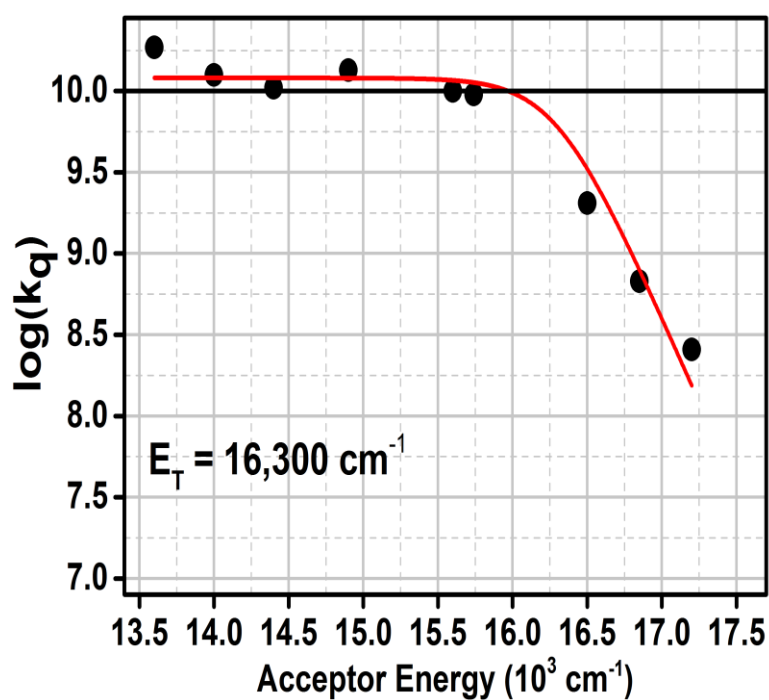
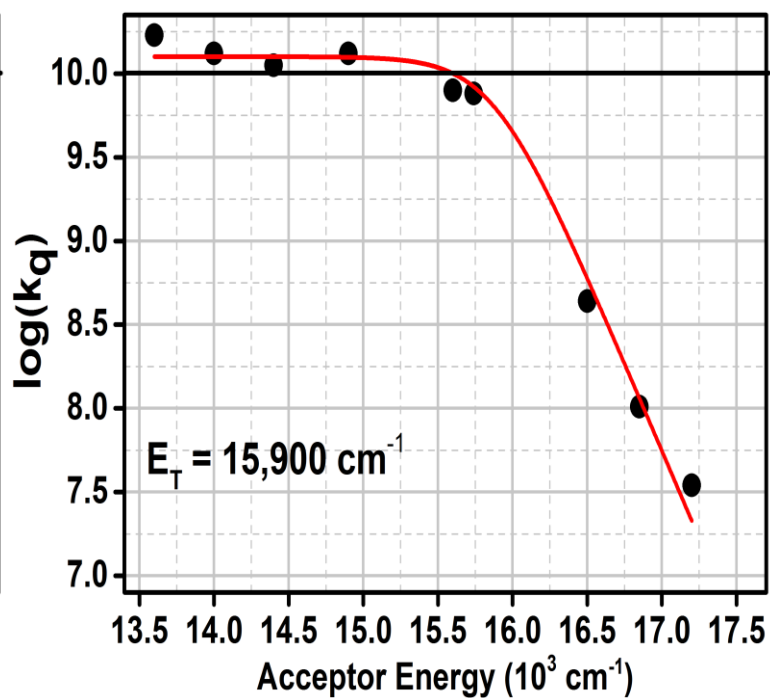
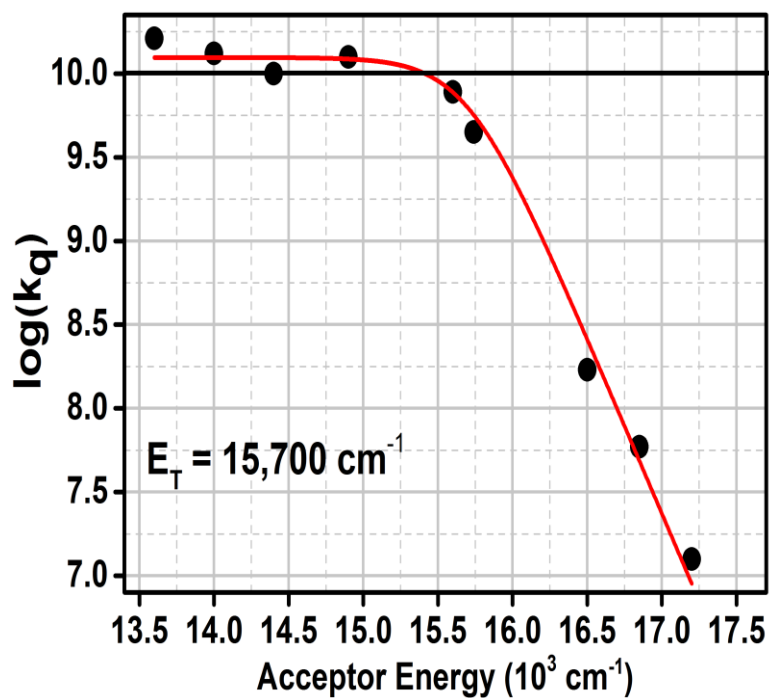


Figure S20. Fits of the individual quenching curves for (A) $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$, (B) $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$, (C) $[\text{PhSn}(\text{LBr})\text{Cl}_2]$, (D) $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$. The donor energy obtained from the data fit is presented in each image.

G. ORTEP representations

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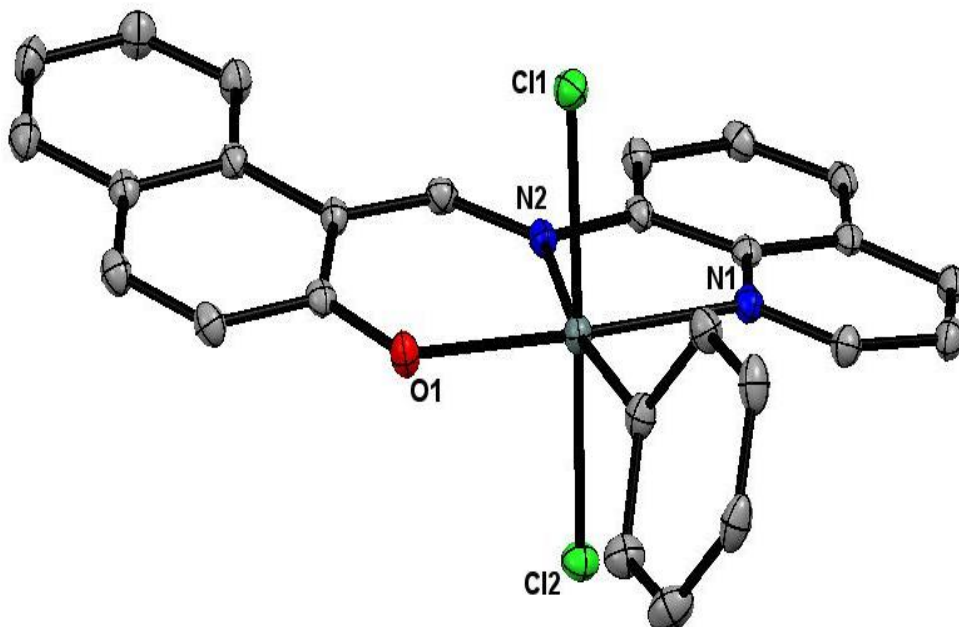


Figure S21. ORTEP Representation of [PhSn(Lnap)Cl₂]. Thermal Ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity.

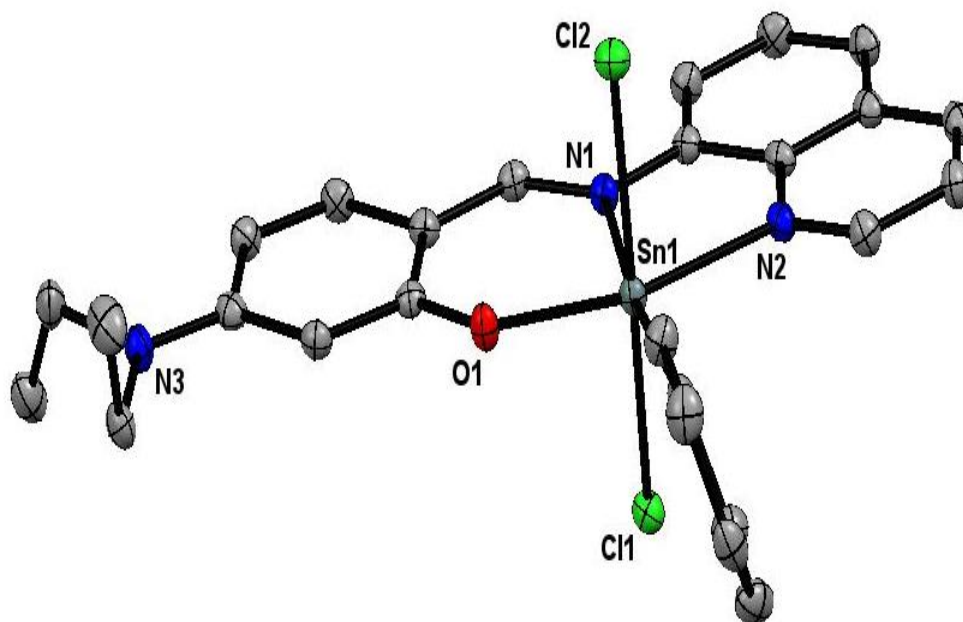


Figure S22. ORTEP Representation of [PhSn(Ldea)Cl₂]. Thermal Ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity.

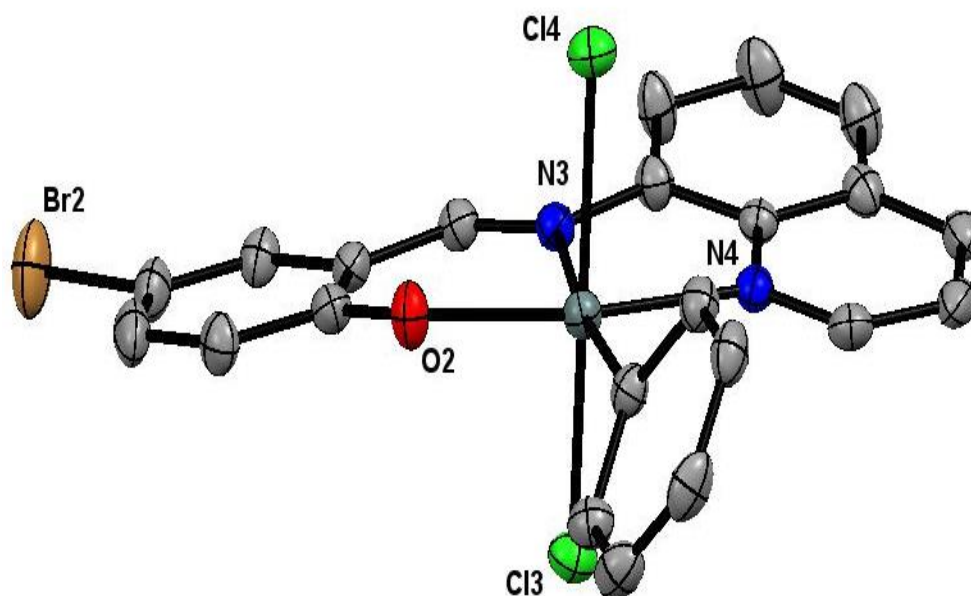


Figure S23. ORTEP Representation of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$. Thermal Ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity.

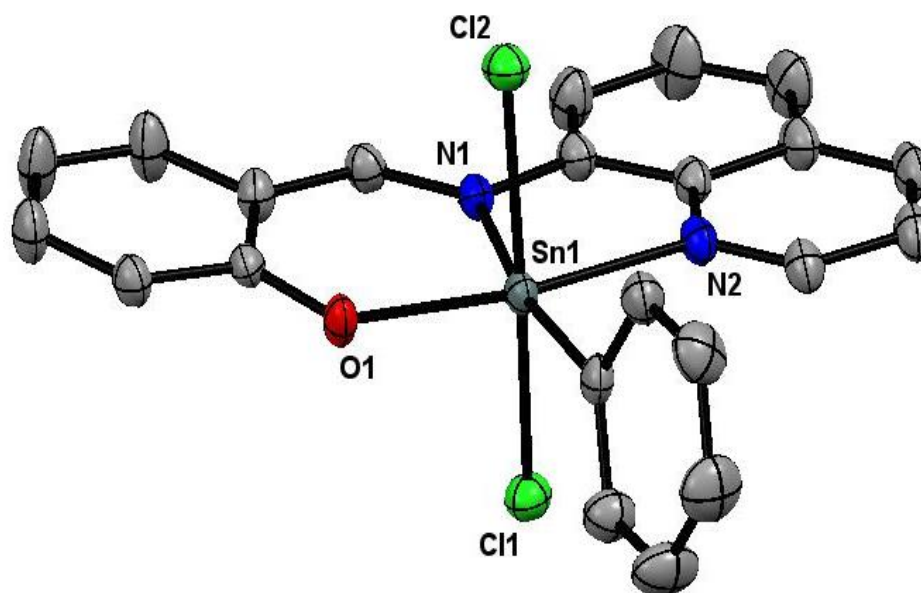


Figure S24. ORTEP Representation of $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$. Thermal Ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity.

H. Illustrations of calculated HOMO and LUMO orbitals [\(return to contents\)](#)

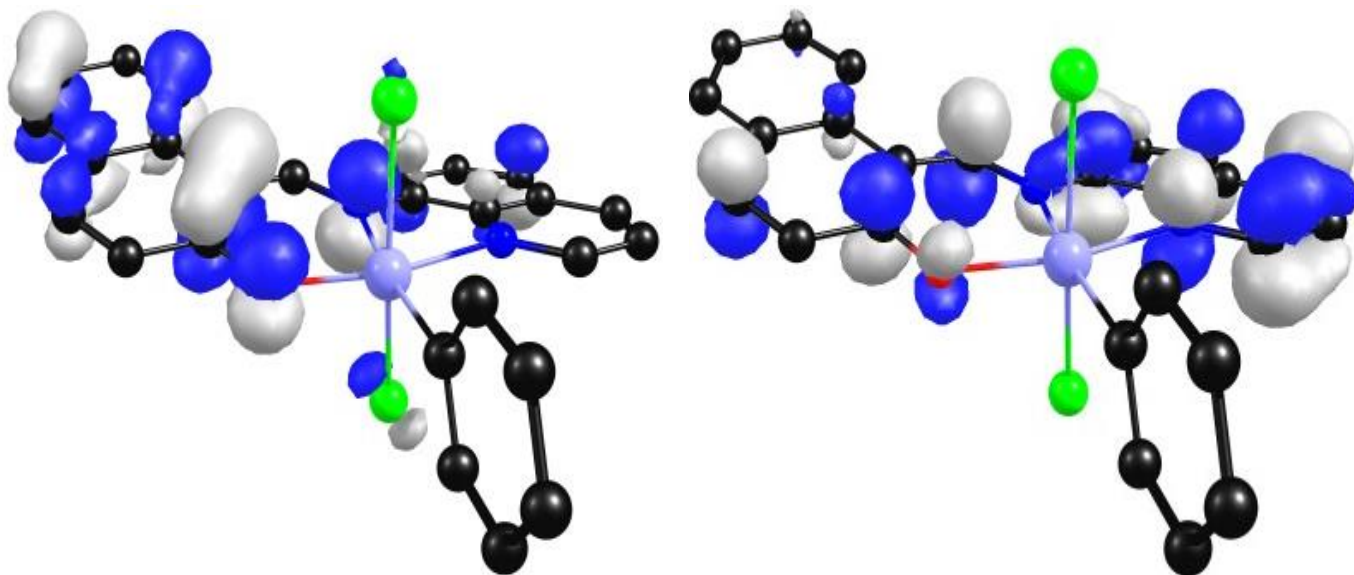


Figure S25. Illustrations of the HOMO (Left) and LUMO (Right) for B3LYP/LANL2DZ(Sn) 6-31G(d,p)(all other atoms) calculated structures of [PhSn(Lnap)Cl₂]. The depicted pair of orbitals are involved in the lowest energy allowed electronic transitions for PhSnLnapCl₂.

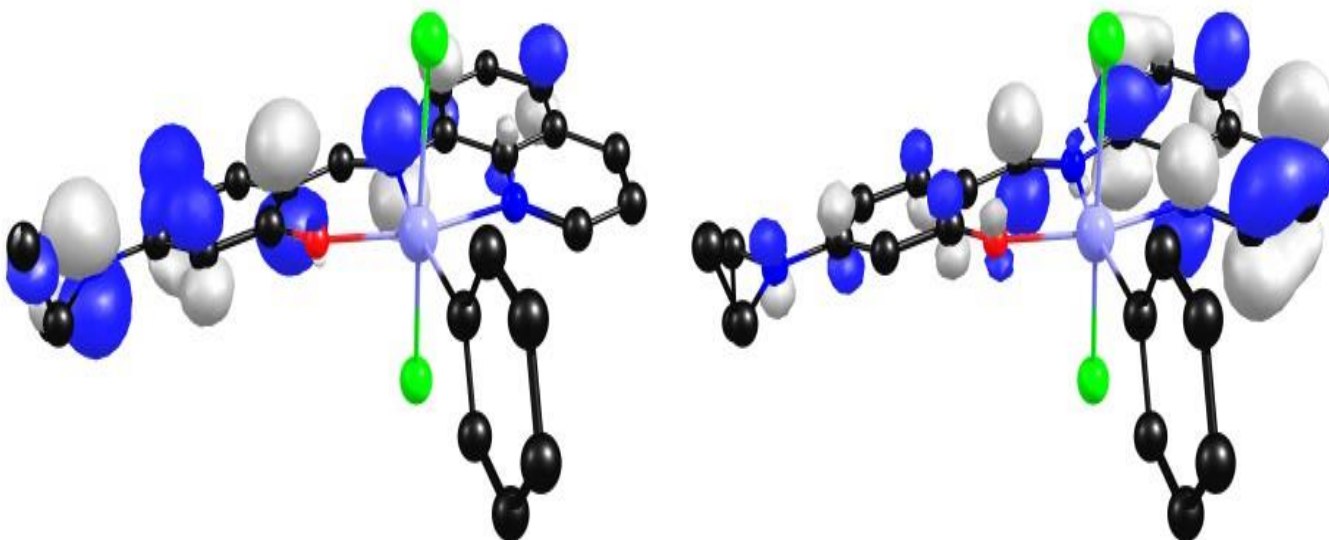


Figure S26. Illustrations of the HOMO (Left) and LUMO (Right) for B3LYP/LANL2DZ(Sn) 6-31G(d,p)(all other atoms) calculated structures of [PhSn(Ldea)Cl₂]. The depicted pair of orbitals are involved in the lowest energy allowed electronic transitions for ₁₆PhSnLdeaCl₂.

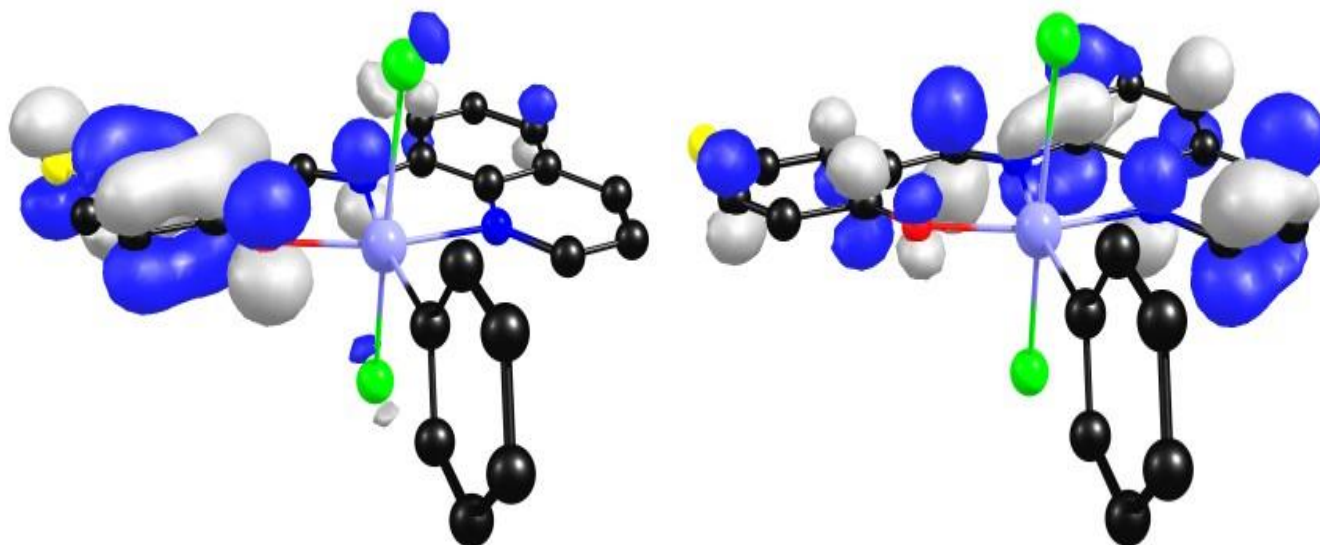


Figure S27. Illustrations of the HOMO (Left) and LUMO (Right) for B3LYP/LANL2DZ(Sn) 6-31G(d,p)(all other atoms) calculated structures of $[\text{PhSn}(\text{LBr})\text{Cl}_2]$. The depicted pair of orbitals are involved in the lowest energy allowed electronic transitions for PhSnLBrCl_2 .

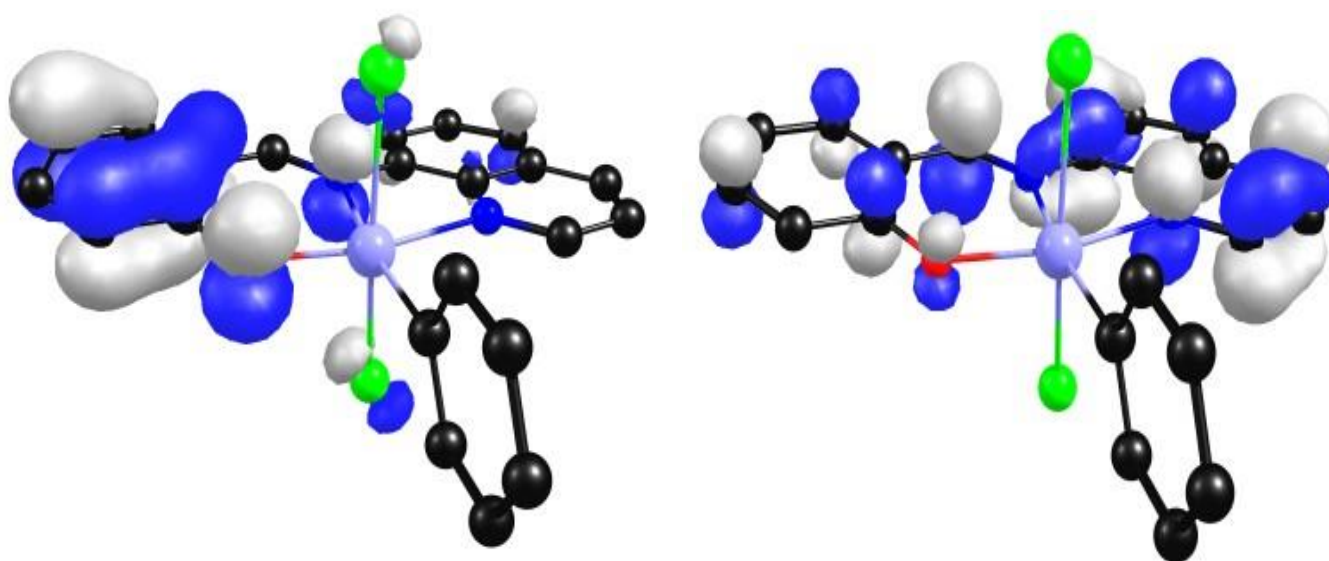


Figure S28. Illustrations of the HOMO (Left) and LUMO (Right) for B3LYP/LANL2DZ(Sn) 6-31G(d,p)(all other atoms) calculated structures of $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$. The depicted pair of orbitals are involved in the lowest energy allowed electronic transitions for PhSnLsalCl_2 .

I. Transient Absorption Decays in acetonitrile [\(return to contents\)](#)

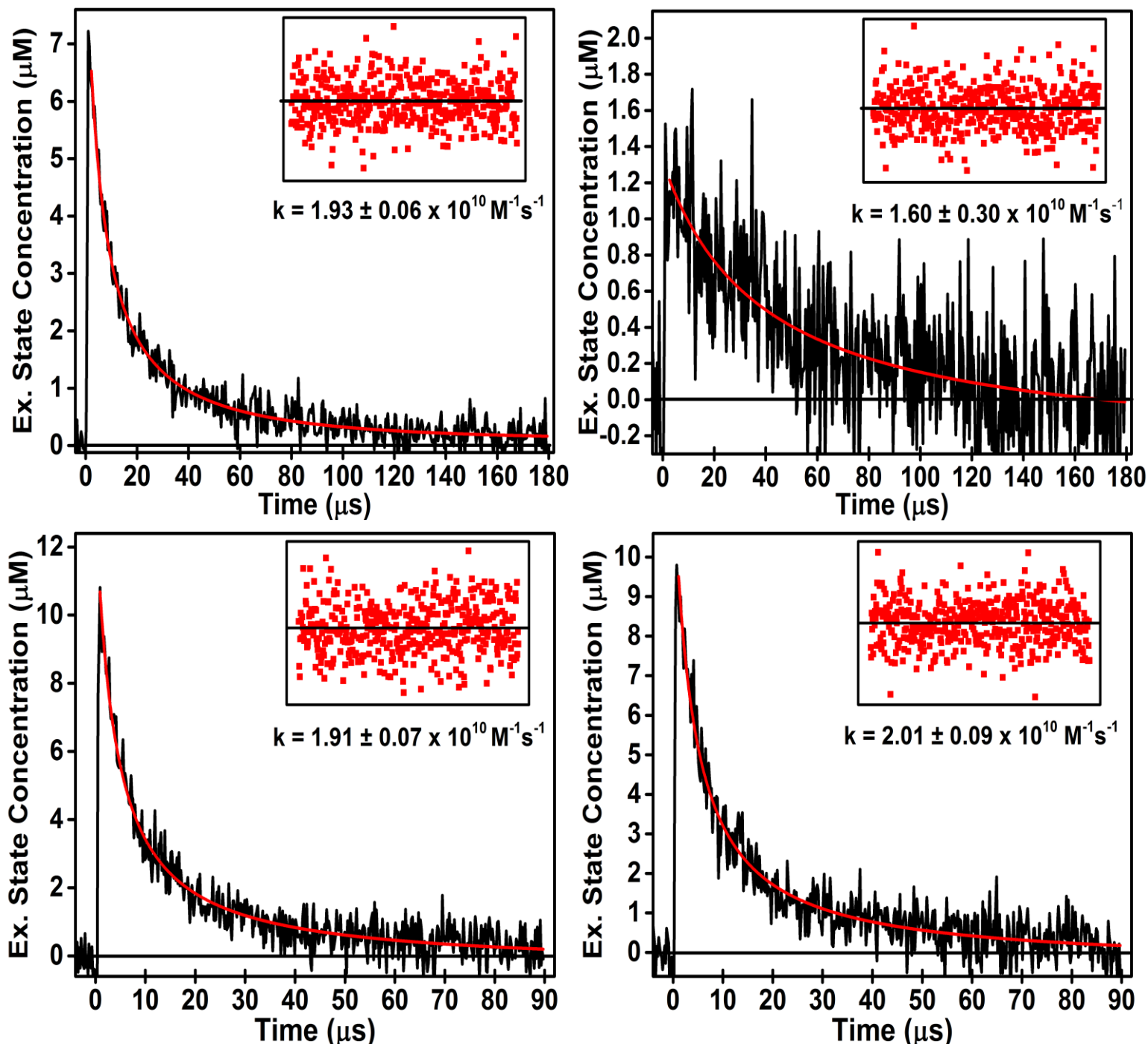


Figure S29. Transient absorption decays collected in deaerated acetonitrile: (Top Left) [PhSn(Lnap)Cl₂], (Top Right) [PhSn(Ldea)Cl₂], (Bottom Left) [PhSn(LBr)Cl₂], and (Bottom Right) [PhSn(Lsal)Cl₂]. Each curve is fit with an equal concentration second order kinetic model. The residual values for the fit are shown in the inset.

J. Transient Absorption Decays in poly(methyl methacrylate) [\(return to contents\)](#)

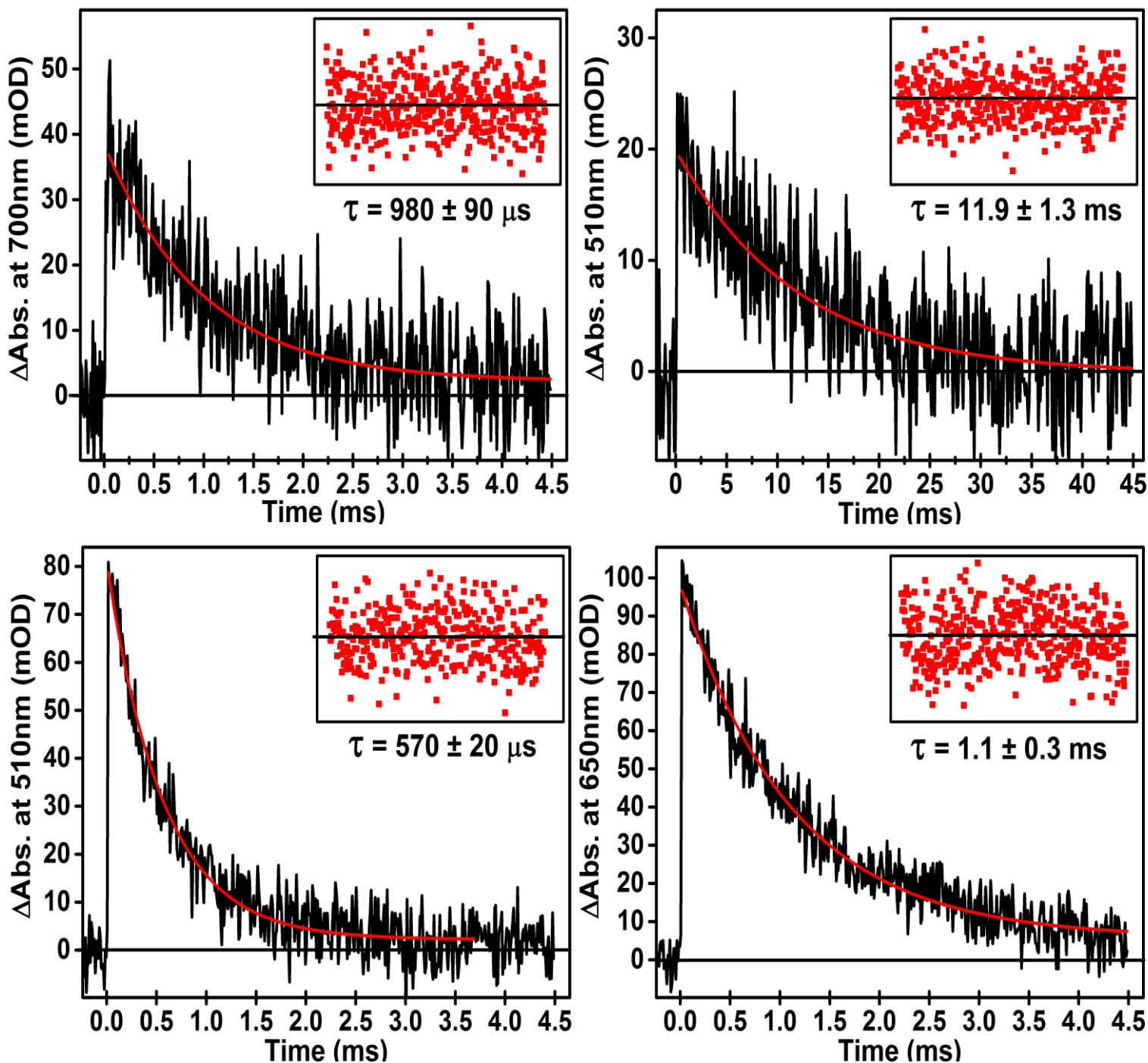


Figure S30. Transient absorption decays collected in poly(methyl methacrylate): (Top Left) $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$, (Top Right) $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$, (Bottom Left) $[\text{PhSn}(\text{LBr})\text{Cl}_2]$, and (Bottom Right) $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$. Single exponential fits are shown in red. The residual values for the single exponential fit are shown in the inset with lifetime values displayed in each image.

K. Transient Absorption Decays in acetonitrile with 1mM MPTH [\(return to contents\)](#)

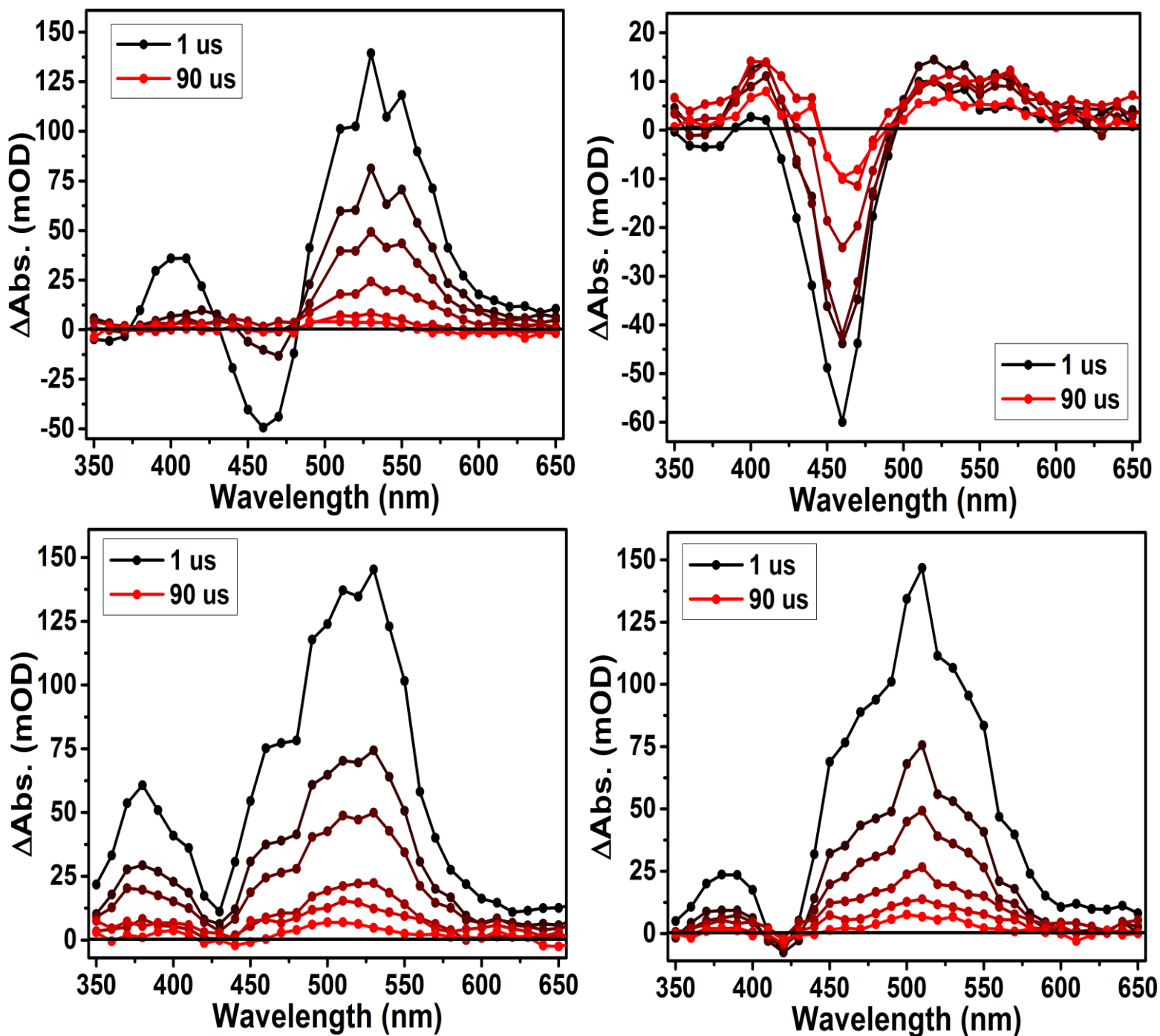


Figure S31. Transient absorption decays collected in deaerated acetonitrile in the presence of 1mM MPTH: (Top Left) $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$, (Top Right) $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$, (Bottom Left) $[\text{PhSn}(\text{LBr})\text{Cl}_2]$, and (Bottom Right) $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$.

L. Transient Absorption Decays in acetonitrile with 1mM MV [\(return to contents\)](#)

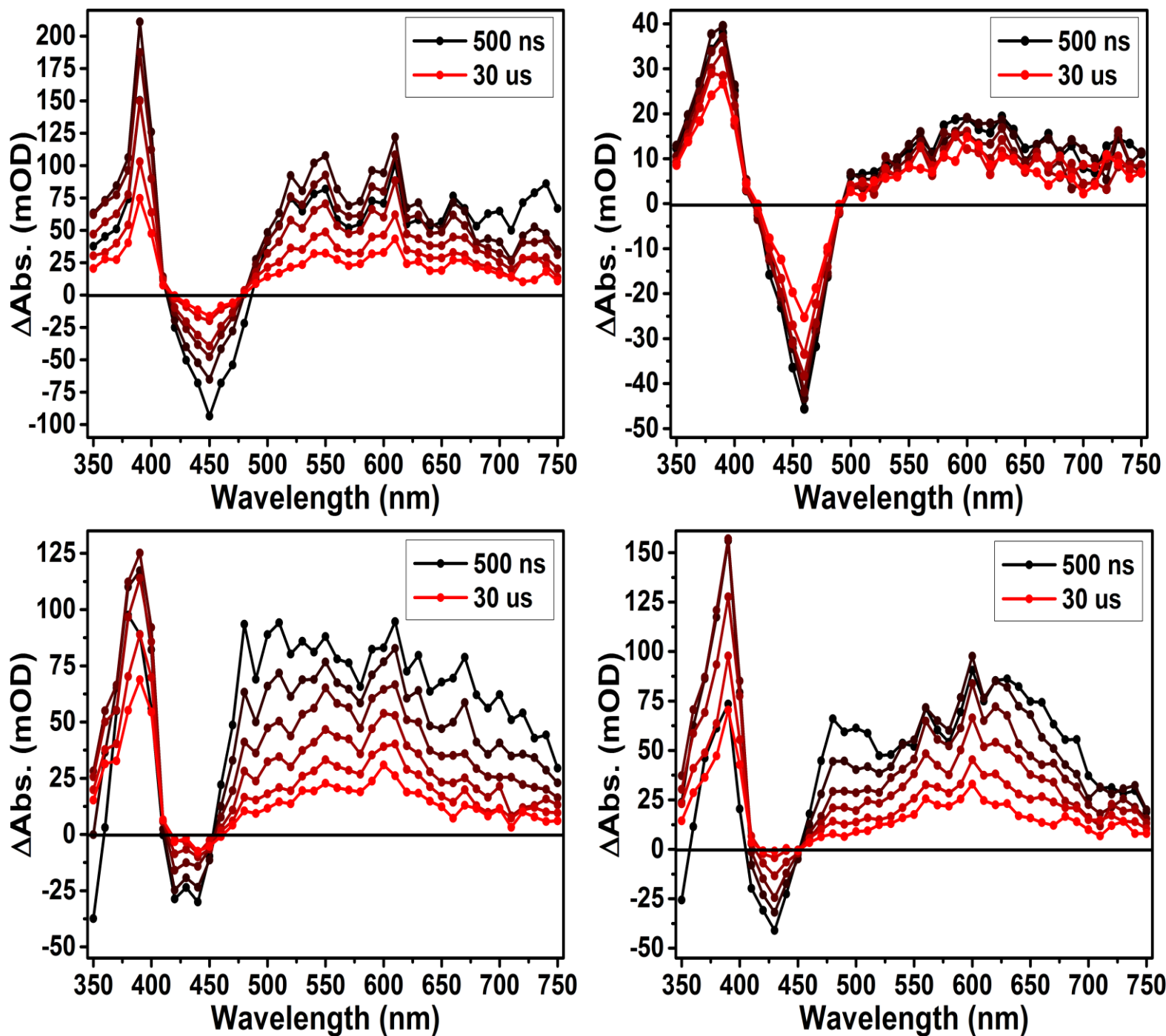


Figure S32. Transient absorption decays collected in deaerated acetonitrile in the presence of 1mM MV: (Top Left) $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$, (Top Right) $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$, (Bottom Left) $[\text{PhSn}(\text{LBr})\text{Cl}_2]$, and (Bottom Right) $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$.

M. $^1\text{O}_2$ Phosphorescence

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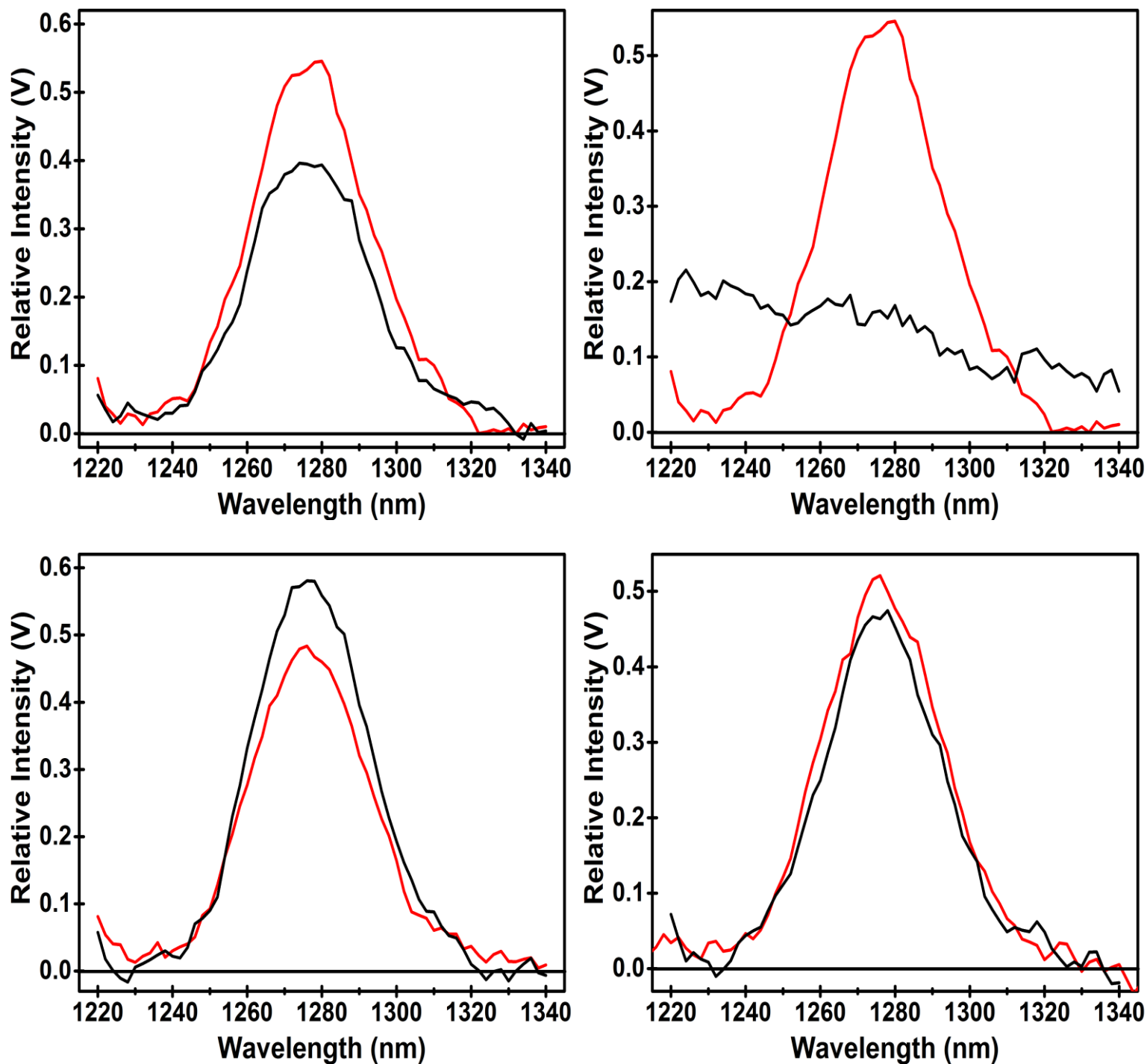


Figure S33. (Black) Sensitized $^1\text{O}_2$ phosphorescence observed in aerated acetonitrile solutions of $[\text{Ru}(\text{bpy})_3]^{2+}$. (Red) Sensitized $^1\text{O}_2$ phosphorescence observed in aerated acetonitrile solutions of (Top Left) $[\text{PhSn}(\text{Lnap})\text{Cl}_2]$, (Top Right) $[\text{PhSn}(\text{Ldea})\text{Cl}_2]$, (Bottom Left) $[\text{PhSn}(\text{LBr})\text{Cl}_2]$, and (Bottom Right) $[\text{PhSn}(\text{Lsal})\text{Cl}_2]$.

N. Time Correlated Single Photon Counting Data [\(return to contents\)](#)

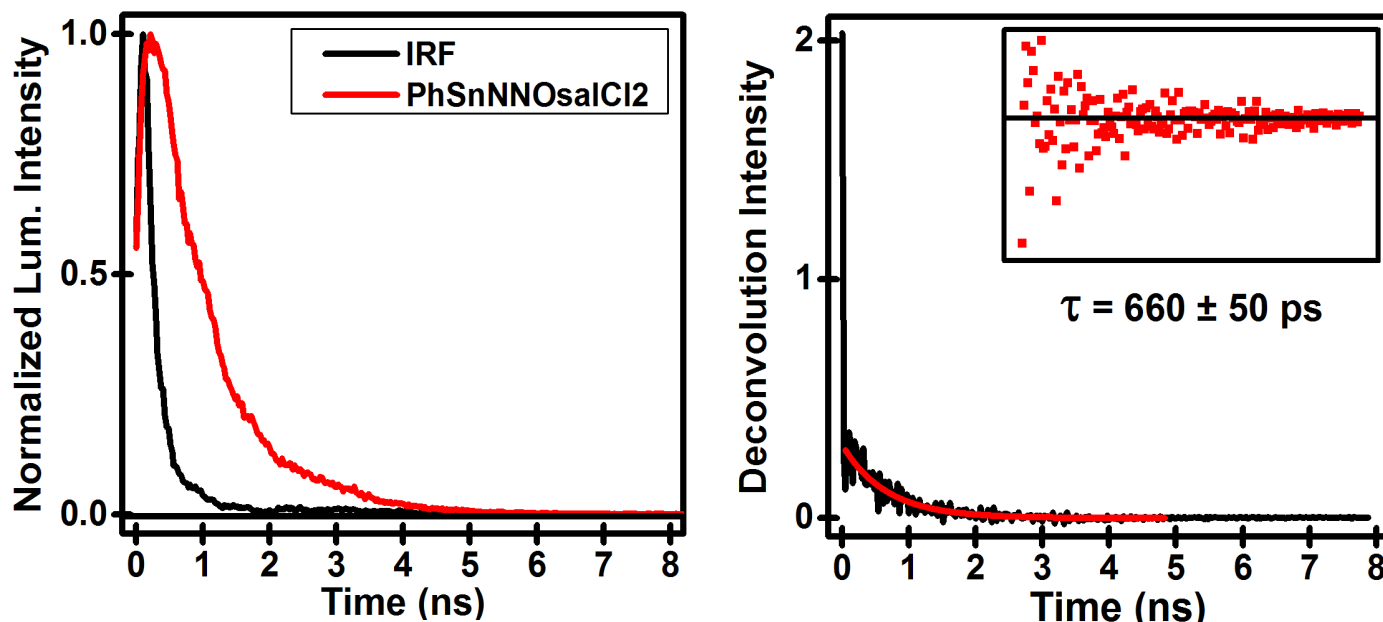


Figure S34. (Left) Depiction of the instrument response function (IRF) and the raw fluorescence decay of [PhSnLsalCl₂]. (Right) Single exponential fit of the deconvoluted TCSPC decay of [PhSnLsalCl₂] Inset: Residual values obtained from the single exponential fit.

O. Determination of Intersystem Crossing Efficiency [\(return to contents\)](#)

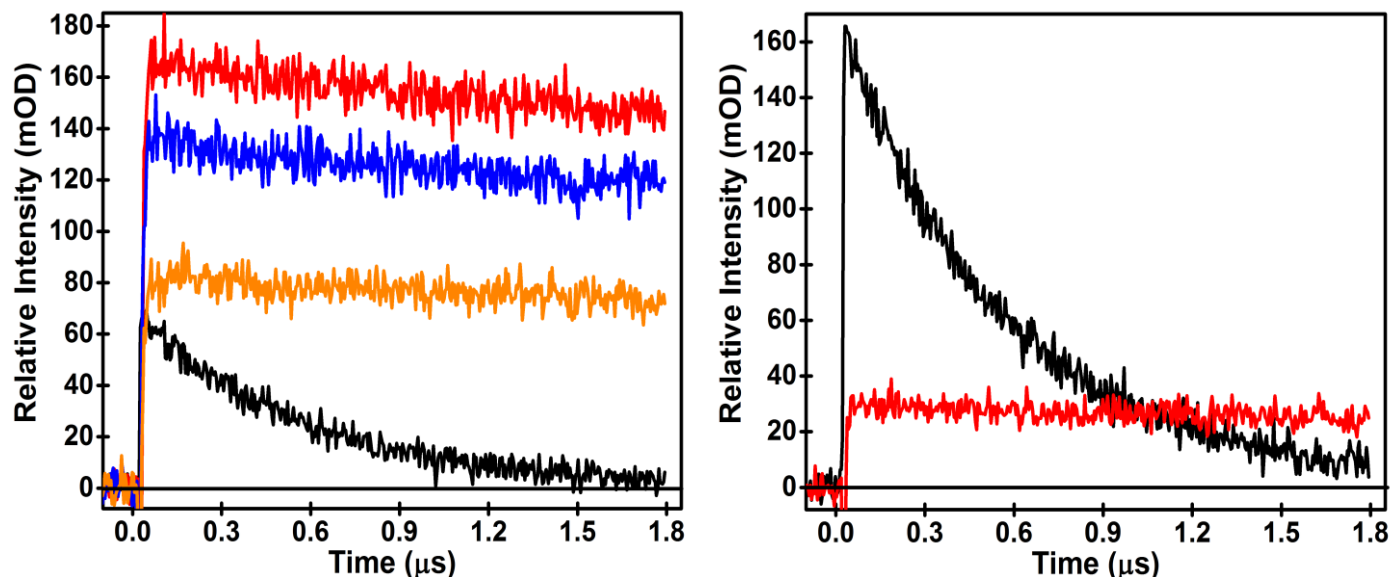


Figure S35. (Left) Transient absorption signals obtained from absorbance matched solutions ($A = 0.15$) of (black) [Ru(bpy)₃]²⁺ and (red) [PhSnLBrCl₂], (blue) [PhSnLsalCl₂], (orange) [PhSnLnapCl₂] containing 10mM anthracene in acetonitrile.. (Left) Transient absorption signals obtained from absorbance matched solutions ($A = 0.40$) of (black) [Ru(bpy)₃]²⁺ and (red) [PhSnLdeaCl₂]. [Ru(bpy)₃]²⁺ decays were collected at 370nm. [PhSnNNOCl₂] decays were collected at 420nm.