Supporting Information

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Contents:

X-ray crystallography.

Table S1. Crystallographic, data collection, and refinement details for the two structures.

Complex	**3**	**5•(MeCN)$_{1.5}$•(H$_2$O)$_{0.5}$**
Empirical formula	$C_{41}H_{40}CrF_9N_6O_9S_3$	$C_{38}H_{27}CrF_9N_{7.5}O_{9.5}S_3$
Formula weight	1079.97	1059.85
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a/Å	19.81110(10)	10.32310(8)
b/Å	19.25680(10)	13.17947(11)
c/Å	12.00480(10)	19.03913(12)
α/°	90	104.3938(6)
β/°	105.8810(10)	93.7452(6)
γ/°	90	113.0060(8)
Volume / Å^3	4405.01(5)	2270.79(3)
Z	4	2
ρ $_{calc}$ / g.cm^{-3}	1.628	1.550
μ/mm^{-1}	4.375	4.255

***F*(000)**	2212.0	1073.0
Crystal size/mm^3	0.14 × 0.1 × 0.08	0.523 × 0.163 × 0.150
Data/restraints/parameters	9527/0/628	9717/92/656
Goodness-of-fit on F^2	1.079	1.033
Final *R* indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0337$, $wR_2 = 0.0888$	$R_1 = 0.0717$, $wR_2 = 0.2048$
Final *R* indexes [all data]	$R_1 = 0.0354$, $wR_2 = 0.0900$	$R_1 = 0.0726$, $wR_2 = 0.2057$
Largest diff. peak/hole / e Å^{-3}	0.41/-0.55	1.54/-0.68

Normalized Emission Spectra

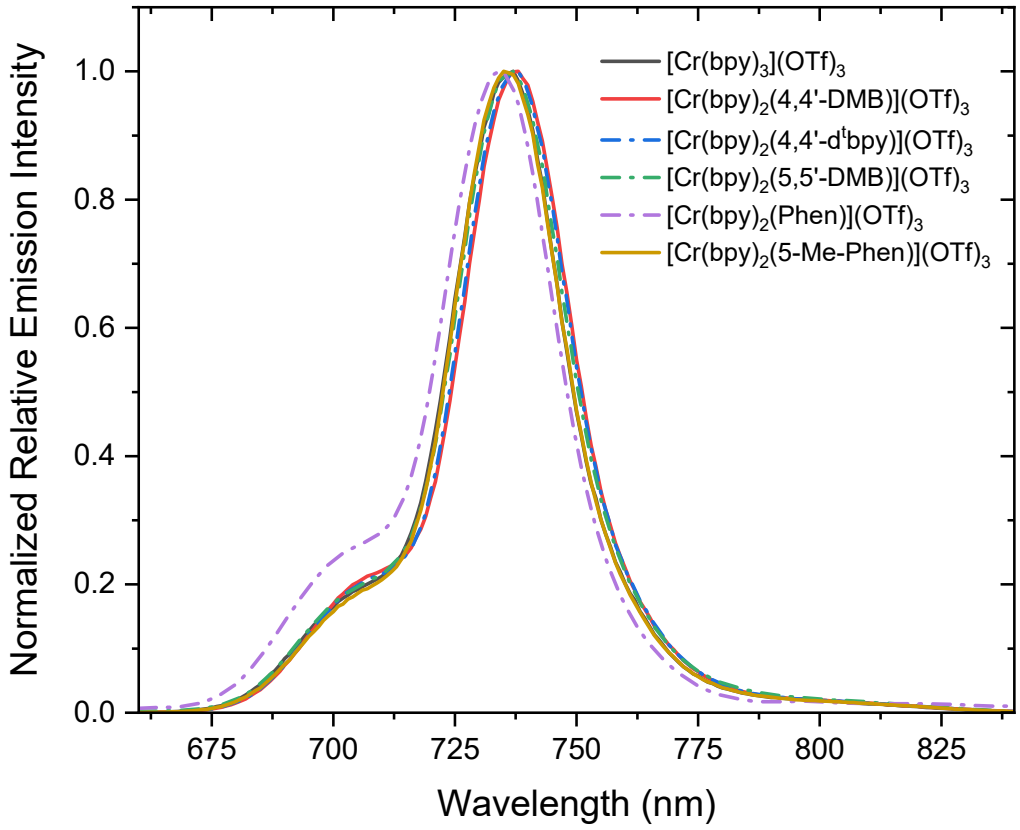

Figure S1. Normalized emission spectra for Cr(III) complexes in 1 M HCl(aq) following excitation at 320 nm.

Cyclic Voltammetry

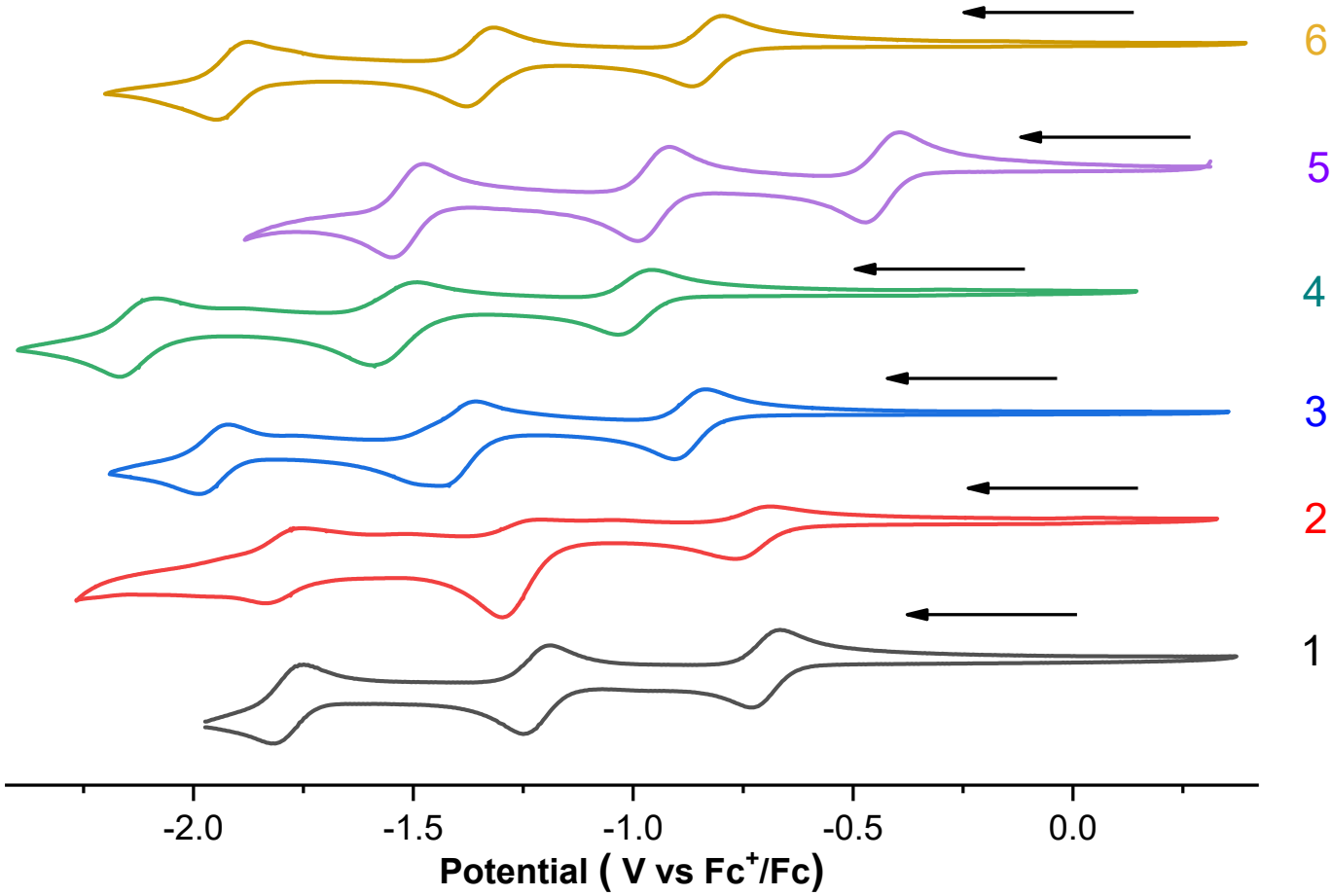

Figure S2. Comparison of cyclic voltammograms for all Cr(III) polypyridyl complexes in 0.1M $[nBu_4N][PF_6]$ acetonitrile solution. Arrows indicate the starting point and direction for each voltammogram.

The transient absorption spectra of Cr(III) complexes under study

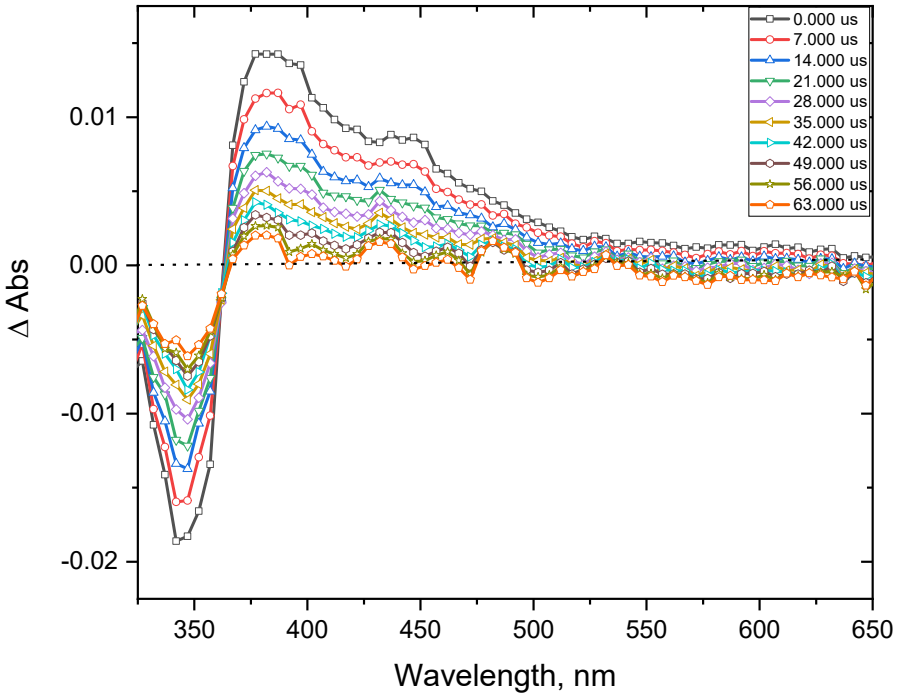

Figure S3. TA spectrum of $[Cr(bpy)_3](OTf)_3$ in air-equilibrated 1 M HCl.

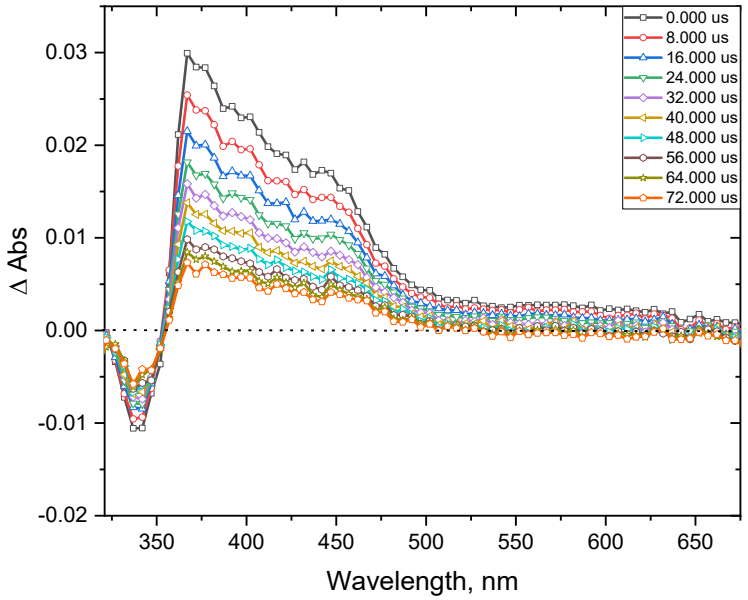

Figure S4. TA spectra of $[Cr(bpy)_2(4,4'\text{-DMB})](OTf)_3$ in air equilibrated 1 M HCl.

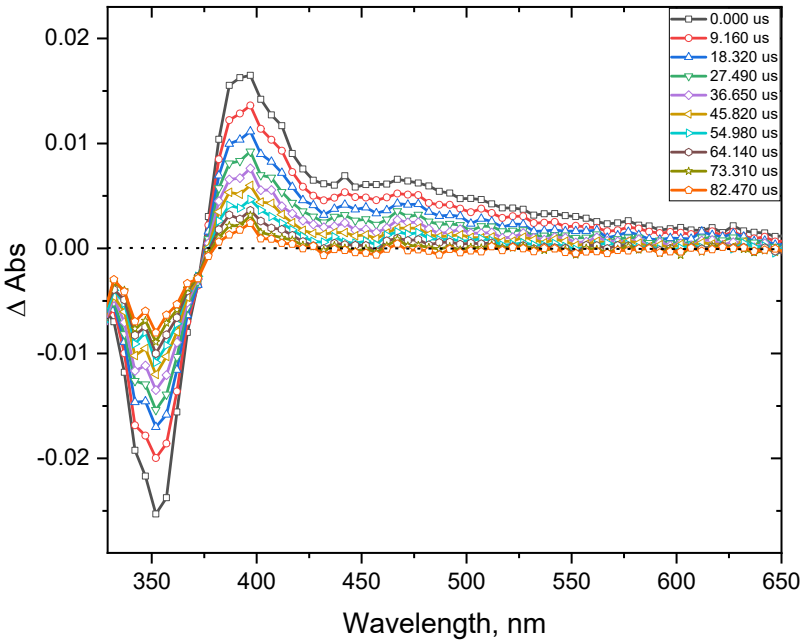

Figure S5. TA spectra of $[Cr(bpy)_2(5,5'\text{-DMB})](OTf)_3$ in air equilibrated 1 M HCl.

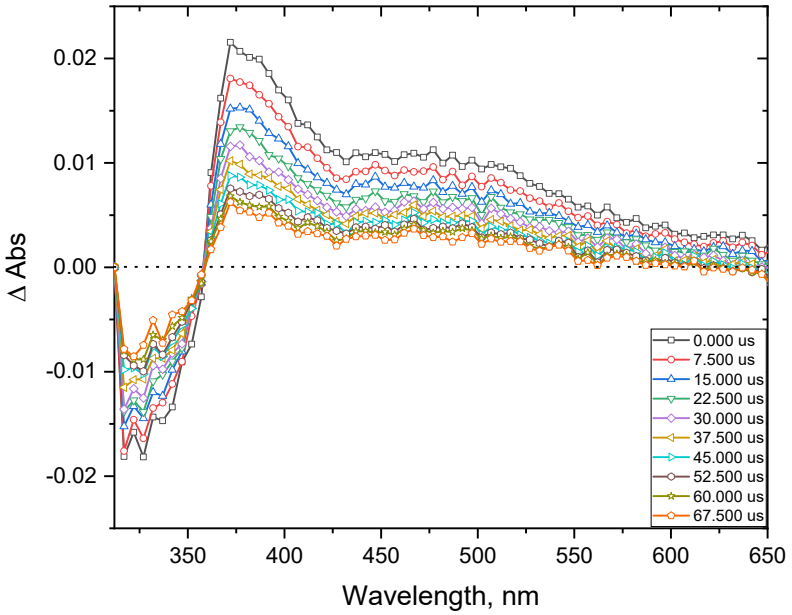

Figure S6. TA spectra of $[Cr(bpy)_2(Phen)](OTf)_3$ in air equilibrated 1 M HCl.

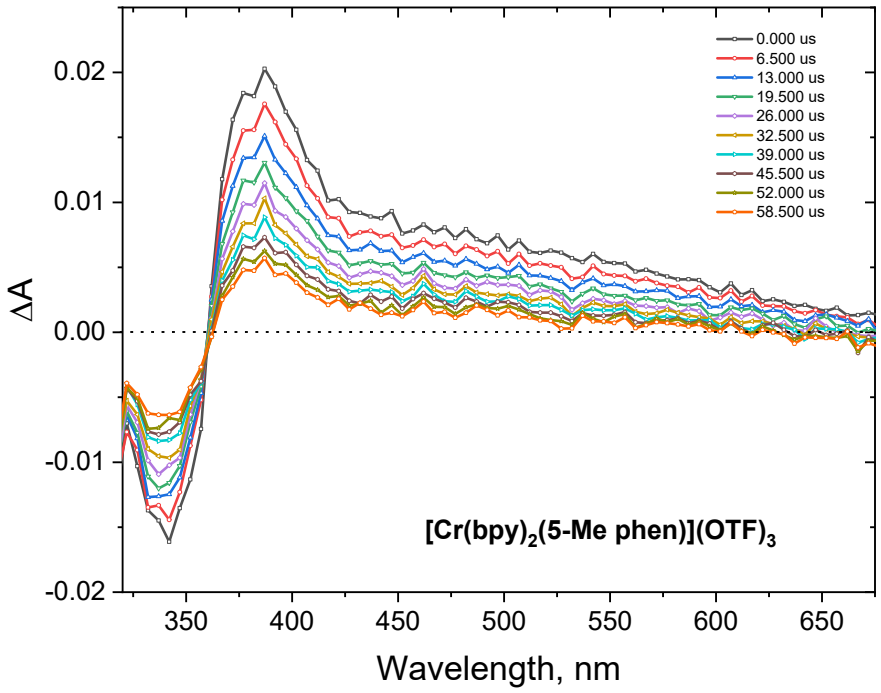

Figure S7. TA spectra of $[Cr(bpy)_2(5\text{-Me-Phen})](OTf)_3$ in air equilibrated 1 M HCl.

Singlet Oxygen measurements in D_2O

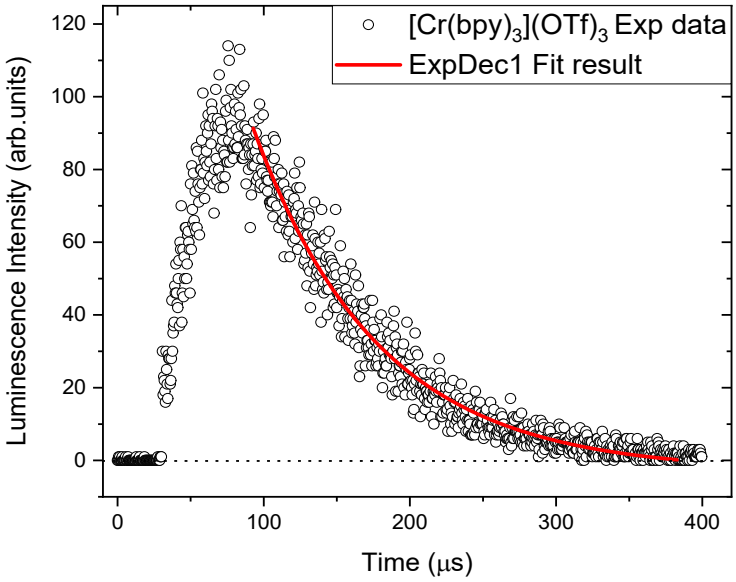

Figure S8. Decay traces of singlet oxygen phosphorescence produced by $[Cr(bpy)_3](OTf)_3$ in D_2O.

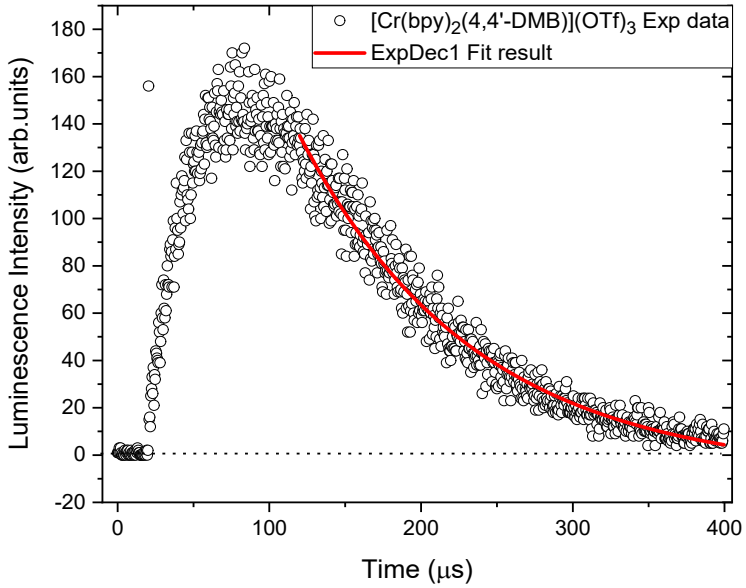

Figure S9. Decay traces of singlet oxygen phosphorescence produced by $[Cr(bpy)_2(4,4'\text{-}DMB)](OTf)_3$ in D_2O.

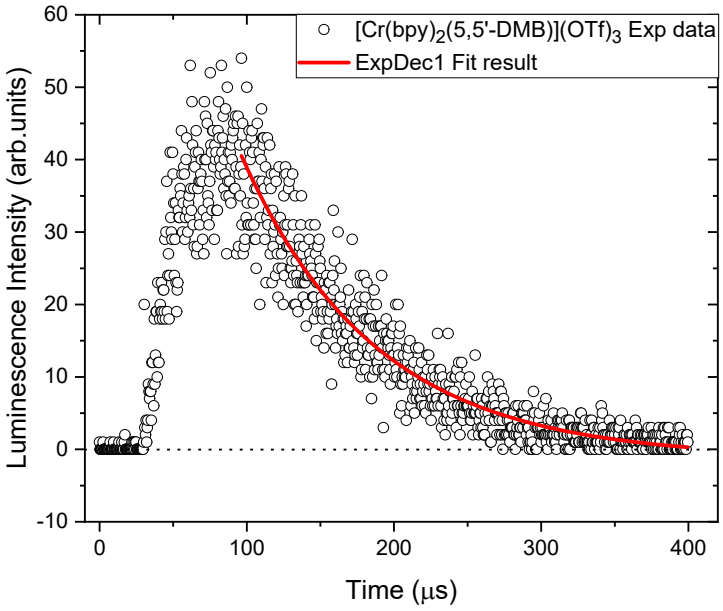

Figure S10. Decay traces of singlet oxygen phosphorescence produced by $[Cr(bpy)_2(5,5'\text{-}DMB)](OTf)_3$ in D_2O.

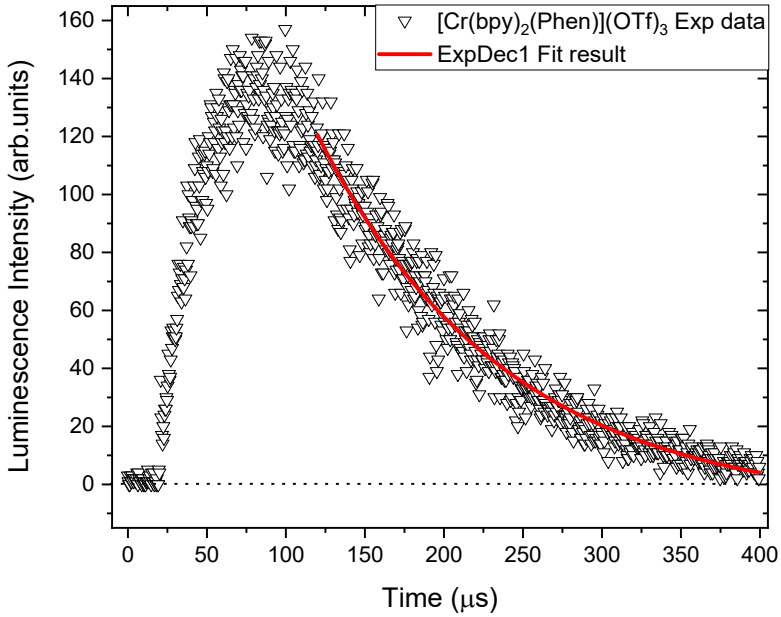

Figure S11. Decay traces of singlet oxygen phosphorescence produced by $[Cr(bpy)_2(Phen)](OTf)_3$ in D_2O.

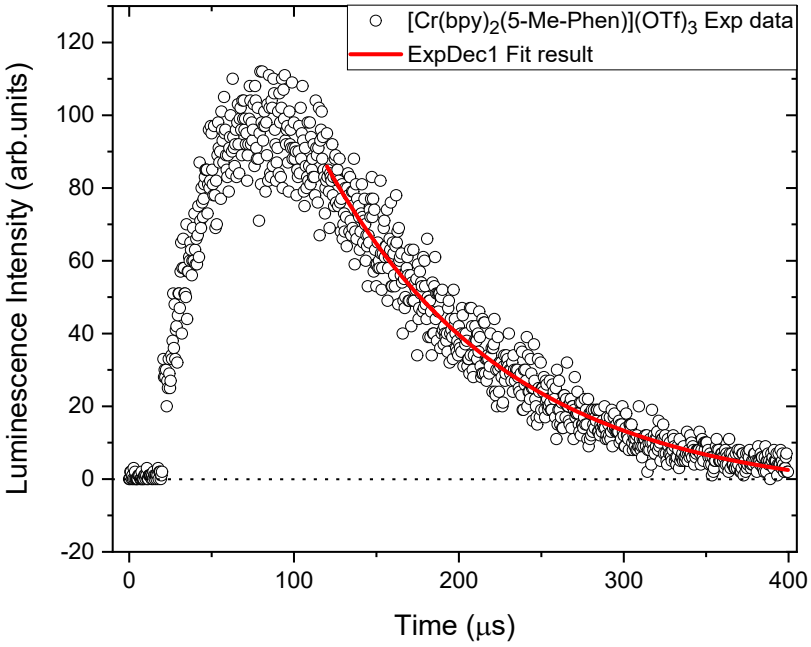

Figure S12. Decay traces of singlet oxygen phosphorescence produced by $[Cr(bpy)_2(5\text{-Me-Phen})](OTf)_3$ in D_2O.