

Supporting information

Luminescent Lanthanide Complexes with a Pyridine-bis(Carboxamide)-Bithiophene Sensitizer Showing Wavelength-Dependent Singlet Oxygen Generation

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Table of contents

1. Experimental details	2
1.1 General information	2
1.2 Ligand synthesis	2
1.3 NMR spectroscopy of 2Tcbx	4
1.4 Mass spectrometry of 2Tcbx	5
1.5 Single crystal X-ray diffraction	6
1.6 Synthesis of lanthanide complexes	7
1.7 Mass spectrometry of the Ln^{III} complexes	8
2 Photophysical characterization	9
2.1 Absorption, excitation, and emission of 2Tcbx	11
2.2 Absorption titrations of 2Tcbx with Ln^{III} nitrates (speciation)	12
2.3 Excited state energy measurements	14
2.4 Absorption, excitation, and emission of Ln^{III} complexes in acetonitrile	15
2.5 Femtosecond pump-probe spectroscopy	16
3 References	18

1. Experimental details

1.1 General information

All commercially obtained reagents were of analytical grade and were used as received. Solvents were dried by standard methods. All synthetic steps were completed under N₂ unless otherwise specified. The stock solution of lanthanide(III) (Ln = Eu^{III}, Gd^{III}, Nd^{III}, Yb^{III} or Er^{III}) nitrate was prepared by dissolving the nitrate salt in spectroscopic grade acetonitrile. The concentration of the metal was determined by complexometric titration with EDTA (0.01 M) using xylenol orange as indicator.¹

NMR spectra were recorded on Varian 400 and 500 MHz spectrometers with chemical shifts reported (ppm) against tetramethylsilane (TMS, 0.00 ppm).

Electrospray ionization mass spectra (ESI-MS) were collected in positive ion mode on a Waters Micromass ZQ quadrupole in the low-resolution mode for the ligands and in a Agilent model G6230A in the high-resolution mode for the metal complexes with a QTOF analyzer. The samples were prepared by diluting solutions to a concentration of ~1 mg/mL with MeCN and passed through 0.2 μm microfilter.

1.2 Ligand synthesis

The ligands were synthesized using standard methods or according to modified literature procedures, as shown in Figure S1.

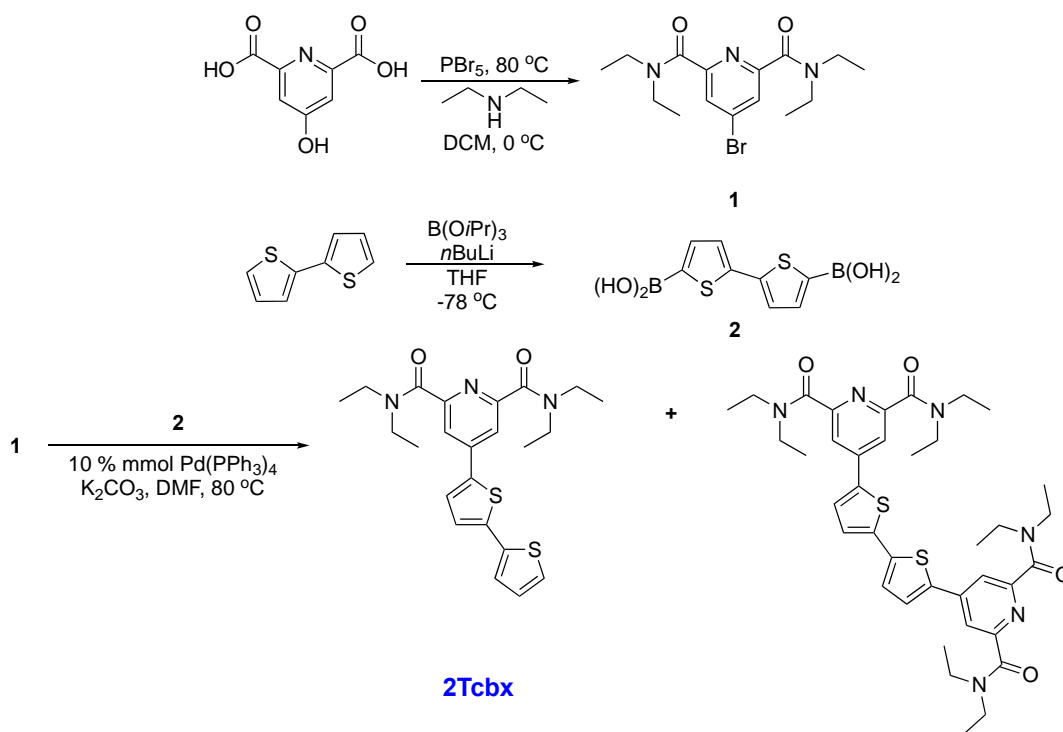


Figure S1. Syntheses of **2Tcbx**.

Synthesis of 4-bromo-N,N,N',N'-tetraethyl-2,6-pyridinedicarboxamide (1). This compound was synthesized following a published procedure.²

Synthesis of 2,2'-bithiophene-5,5'-bis(boronic acid) (2). This compound was synthesized using a modified literature procedure.³ 2,2'-Bithiophene (330 mg, 2.00 mmol) and triisopropyl borate (1.1 mL, 4.8 mmol) were added to dry THF (20 mL). The mixture was cooled to $-78\text{ }^{\circ}\text{C}$, then *N*-butyllithium (4.0 mL, 4.8 mmol, 1.2 M in hexane) was added dropwise. After stirring for 4 h, the reaction was quenched with 1M HCl (20 mL) and extracted with dichloromethane (DCM, 3 x 15 mL). The combined organic layers were washed with water (3 x 10 mL) and brine (3 x 10 mL). DCM was removed under reduced pressure and the residue was recrystallized from hexanes. Yield: 430 mg (83%) – white solid.

¹H-NMR (DMSO-*d*₆, 400 MHz): 7.31 (*d*, *J* = 3.6 Hz, 1H), 7.55 (*d*, *J* = 3.6 Hz, 1H), 8.23 (*s*, 2H) ppm.

Synthesis of 4-(5-(2,2'-bithienyl))-N,N,N',N'-tetraethyl-2,6-pyridinedicarboxamide (2Tcbx). Compounds 1 (150 mg, 0.41 mmol), 2 (50 mg, 0.2 mmol), K₂CO₃ (280 mg, 2.0 mmol), and [Pd(PPh₃)₄] (50 mg, 0.04 mmol) were dissolved in DMF (10 mL) and heated at 80 °C for 24 h.

The reaction was allowed to cool to RT, then quenched with 1 M HCl (2 mL) and stirred for 30 minutes. The organic phases were extracted with chloroform (3 x 10 mL) and combined. The organic phase was washed with water (3 x 15 mL), brine (2 x 10 mL), dried over anhydrous MgSO₄, filtered, and the solvent removed under reduced pressure. The desired product was separated from the reaction mixture using a silica column and ethyl acetate ($R_f = 0.20$), as eluent. Yield: 28 mg (32%) – yellow solid.

¹H-NMR (CDCl₃, 400 MHz): 1.16 (t, $J = 7.0$ Hz, 6H), 1.27 (t, $J = 7.0$ Hz, 6H), 3.38 (q, $J = 7.0$ Hz, 4H), 3.58 (q, $J = 7.0$ Hz, 4H), 7.04 (m, 1H), 7.19 (d, $J = 3.9$ Hz, 1H), 7.23 (m, 1H), 7.27 (m, 1H), 7.49 (d, $J = 3.9$ Hz, 1H), 7.76 (s, 2H) ppm.

¹³C-NMR (CDCl₃, 100 MHz): 12.93, 14.42, 40.33, 43.43, 119.15, 124.60, 124.80, 125.00, 125.45, 126.99, 128.04, 136.48, 138.53, 140.04, 143.17, 154.31, 168.93 ppm.

ESI-MS: [M+H]⁺ 442 (exp.) 442 (calc.).

1.3 NMR spectroscopy of 2Tcbx

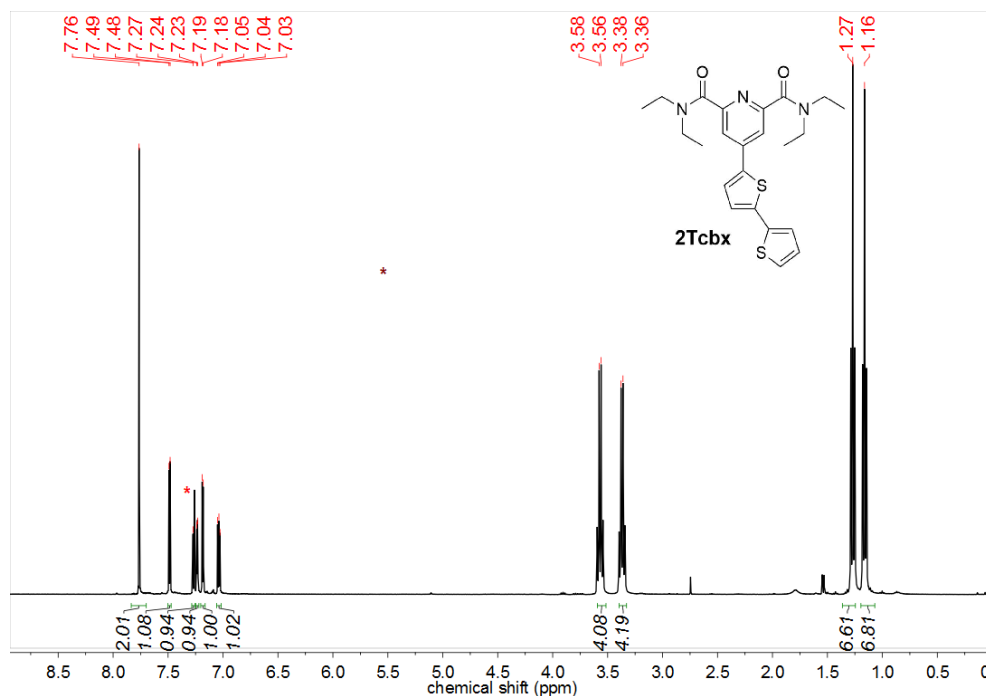


Figure S2. ¹H-NMR spectrum of 2Tcbx in CDCl₃. Asterisk indicates residual solvent peak.

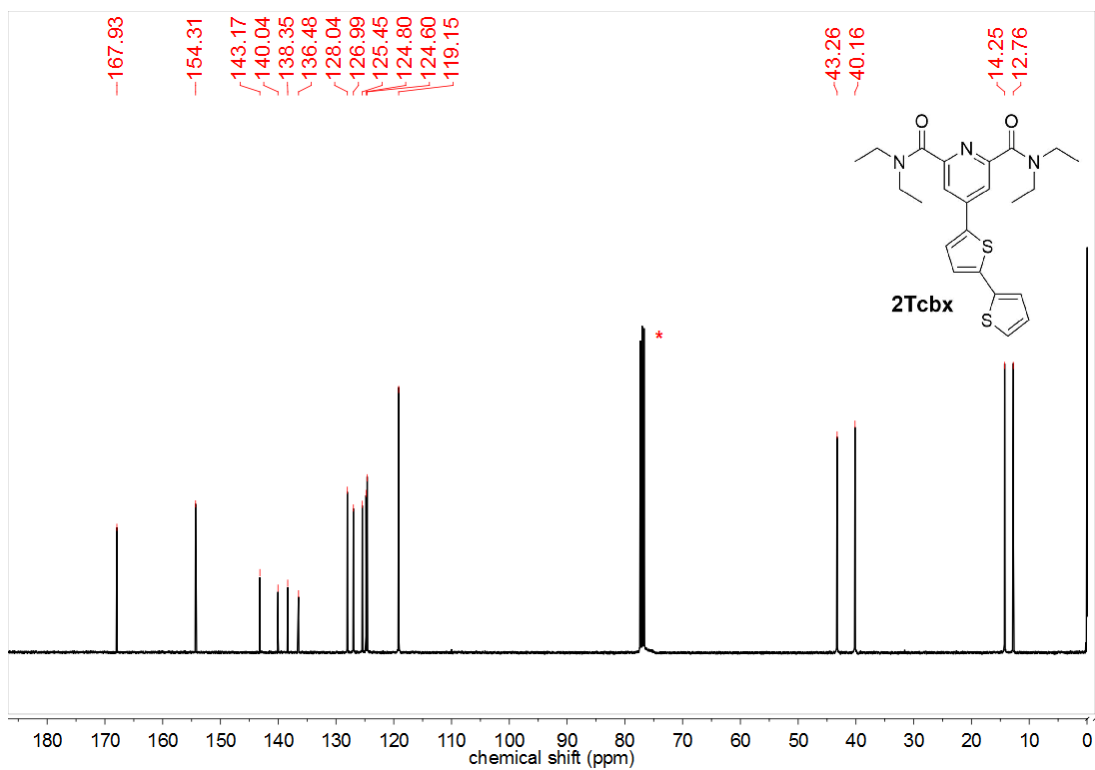


Figure S3. ^{13}C -NMR spectrum of **2Tcbx** in CDCl_3 . Asterisk indicates residual solvent peak.

1.4 Mass spectrometry of **2Tcbx**

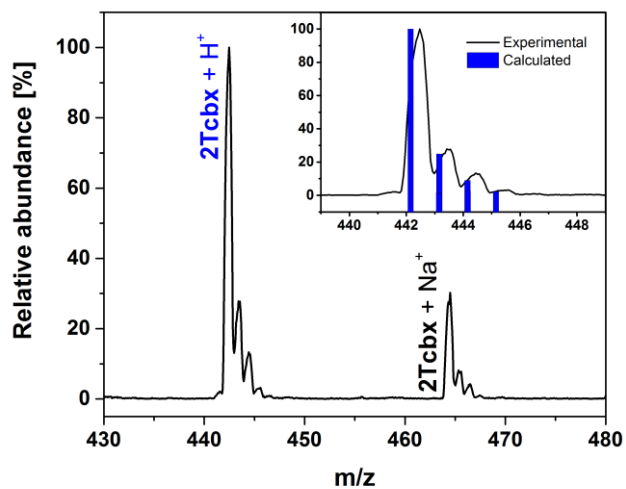


Figure S4. Mass spectrum of **2Tcbx**. Inset shows calculated and experimental isotope pattern.

1.5 Single crystal X-ray diffraction

Crystal data, data collection, and refinement details for 2Tcbx are given below. A suitable crystal was mounted on a glass fiber and placed in a low-temperature nitrogen stream of a Bruker SMART CCD area detector diffractometer. A full sphere of data was collected using a graphite-monochromated Mo-K α radiation source ($\lambda = 0.71073 \text{ \AA}$). Multi-scan absorption corrections were applied using SADABS.⁴ The structure was solved by direct methods and refined by least-square methods on F^2 using the SHELXTL⁵ programming package. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added geometrically, and their parameters constrained to the parent site. The disorder of the external thiophene ring was modeled in two positions rotated by 180° from each other along the C-C bond to the neighboring thiophene. The occupancy for the main component refined to 80%.

Table S1. Crystallographic information for **2Tcbx**.

Compound Name	2Tcbx
CCDC number	1990459
Empirical Formula	C ₂₃ H ₂₇ N ₃ O ₂ S ₂
M (g/mol)	441.59
Crystal system	orthorhombic
Space group	Pna2(1)
<i>a</i> (Å)	7.6657(2)
<i>b</i> (Å)	17.2857(5)
<i>c</i> (Å)	17.1528(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
<i>V</i> (Å ³)	2272.87(11)
<i>T</i> (K)	100(2)
<i>Z</i>	4
<i>D</i> _c (g/cm ³)	1.291
μ (Mo-K α) (1/mm)	0.259
Independent reflections, $R_{\text{int}} [F_o \geq 4\sigma(F_o)]$	4573, 0.0263
Reflections collected	19209
Data/restraints/parameters	4573/11/276
Goodness-of-fit on F^2	1.095
R_1, wR_2 (all data)	0.03102, 0.0900
Largest diff. peak and hole (e/Å ³)	0.281, -0.236

Table S2. Selected bond distances and angles for **2Tcbx**.

	bond distance (Å)	bond angle (°)
C _{py} –C _{py} (<i>ar.</i>)	1.396(3)	
C _{Th} –C _{Th} (<i>ar.</i>)	1.38(3)	
C=O (carbonyl)	1.23(1)	
C(O)–N		123.5(2)
		121.6(3)
C _{py} –C(O)		117.4
N _{py} –C–C–O		112.9(2)
		145.2(2)

1.6 Synthesis of lanthanide complexes

All metal complexes were prepared by mixing one equivalent of Ln(NO₃)₃ (Ln = Eu^{III}, Gd^{III}, Yb^{III}, Nd^{III}, or Er^{III}) with 2 equivalents of **2Tcbx**. Once combined, the mixtures were refluxed for 16 h in MeCN. After complexation, acetonitrile was removed under reduced pressure with no further work up. The resulting solids were dried in a vacuum oven overnight.



Yield: 90%

ESI-MS: [Yb(C₂₃H₂₇N₃O₂S₂)₂(NO₃)⁺, m/z: 1180.2220 (exp), 1180.2229 (calc)



Yield: 93%

ESI-MS: [Nd(C₂₃H₂₇N₃O₂S₂)₂(NO₃)⁺, m/z: 1148.1924 (exp), 1148.1917 (calc)



Yield: 97%

ESI-MS: [Er(C₂₃H₂₇N₃O₂S₂)₂(NO₃)⁺, m/z: 1172.2129 (exp), 1172.2143 (calc)



Yield: 95%

ESI-MS: [Gd(C₂₃H₂₇N₃O₂S₂)₂(NO₃)⁺, m/z: 1164.2104 (exp), 1164.2081 (calc)

1.7 Mass spectrometry of the Ln^{III} complexes

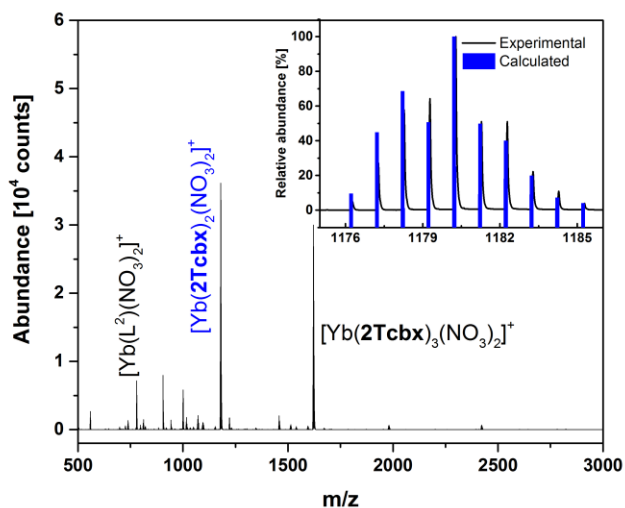


Figure S5. Mass spectrum of $[\text{Yb}(\text{2Tcbx})_2]^{3+}$. Inset shows calculated and experimental isotope pattern.

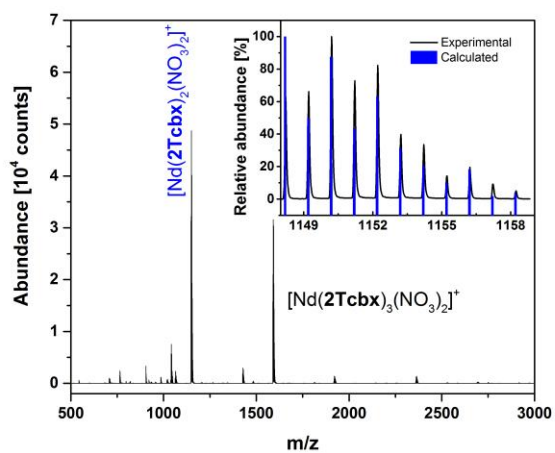


Figure S6. Mass spectrum of $[\text{Nd}(\text{2Tcbx})_2]^{3+}$. Inset shows calculated and experimental isotope pattern.

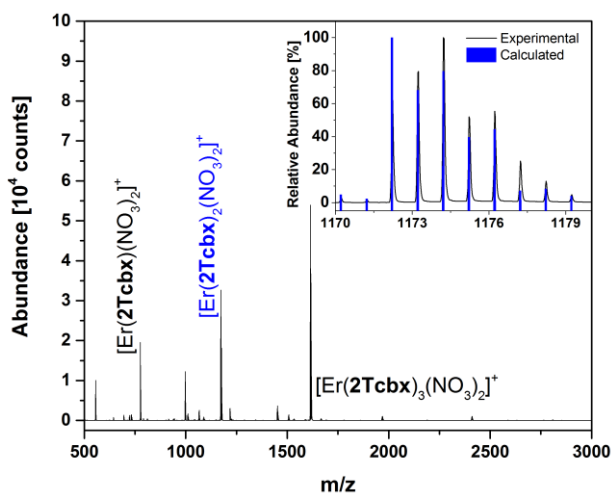


Figure S7. Mass spectrum of $[\text{Er}(2\text{Tcbx})_2]^{3+}$. Inset shows calculated and experimental isotope pattern.

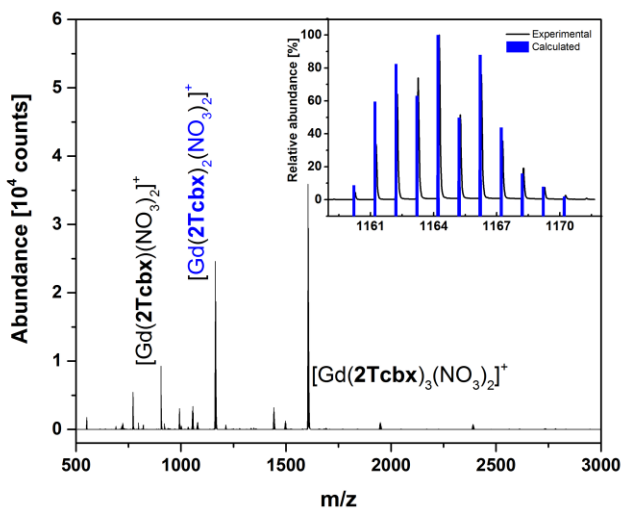


Figure S8. Mass spectrum of $[\text{Gd}(2\text{Tcbx})_2]^{3+}$. Inset shows calculated and experimental isotope pattern.

2 Photophysical characterization

1×10^{-4} M solutions of the complexes were prepared in acetonitrile and their purity assessed by high resolution mass spectrometry. The absorption spectra were measured on a Perkin Elmer Lambda 35 spectrometer. The speciation of the Nd^{III} and Yb^{III} complexes was determined through absorption titrations in acetonitrile. To determine the stability constants, solutions of the ligand

and Ln(NO₃)₃ (Ln = Nd^{III} or Yb^{III}) with a wide range of stoichiometric ratios were prepared and the absorption spectra obtained. Refinement of the stability constants was performed using the HypSpec2014 software.⁶ The speciation graphs were generated using the HySS software.⁷

Emission and excitation spectra of the complexes were obtained at 25.0 ± 0.1 °C in a Fluorolog-3 fluorimeter (Horiba FL3-22-iHR550), with a 1200 grooves/mm excitation monochromator with gratings blazed at 330 nm and a 1200 grooves/mm or 600 grooves/mm emission monochromator with gratings blazed at 500 nm or 1000 nm for UV-Vis or NIR range, respectively. An ozone-free xenon lamp of 450 W (Ushio) was used as the radiation source. The excitation spectra corrected for instrumental function were measured between 250 and 600 nm. The emission spectra were measured in the range 350-800 nm using a Hamamatsu 928P and in the range 800-1600 nm using a Hamamatsu 5509-73 cooled with liquid N₂. All emission spectra were corrected for instrumental functional. The ligand's singlet and triplet energy levels values were obtained at ~77 K by deconvolution of the fluorescence and phosphorescence spectra, respectively, into their Franck-Condon progression and are reported as the 0-0 transition.⁸

Standards for emission quantum yield measurements were quinine sulfate ($\phi = 55\%$, 5×10^{-6} M in aqueous 0.5 M H₂SO₄),⁹ Cs₃[Eu(dpa)₃] ($\phi = 24\%$, 7.5×10^{-5} M in aqueous TRIS/HCl buffer (0.1 M, pH ~7.4))¹⁰⁻¹¹, [Yb(tta)₃(H₂O)₂] ($\phi = 0.12\%$, 1×10^{-4} M in air-saturated toluene)¹² and 2,2':5',2''-terthiophene ($\phi = 0.74$, 1×10^{-4} M in air-saturated acetonitrile) for ligands, Eu^{III}, NIR emitting complexes (Nd^{III} and Yb^{III}) and ¹O₂ emission, respectively. The excitation wavelength for both samples and quantum yield standard were chosen to ensure a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species ($A \leq 0.05$). The quantum yield of the samples was determined by the dilution method using Equation 1.

$$\phi_x = \frac{Grad_x}{Grad_{std}} \times \frac{n_x^2}{n_{std}^2} \times \frac{I_{std}}{I_x} \phi_{std} \quad (1)$$

Grad is the slope of the plot of the integrated emission as a function of absorbance, *n* is the refractive index of the solvent, *I* is the intensity of the excitation source at the excitation wavelength and ϕ is the quantum yield for sample, *x*, and standard, *std*. All data are the average of at least three independent measurements.

2.1 Absorption, excitation, and emission of 2Tcbx

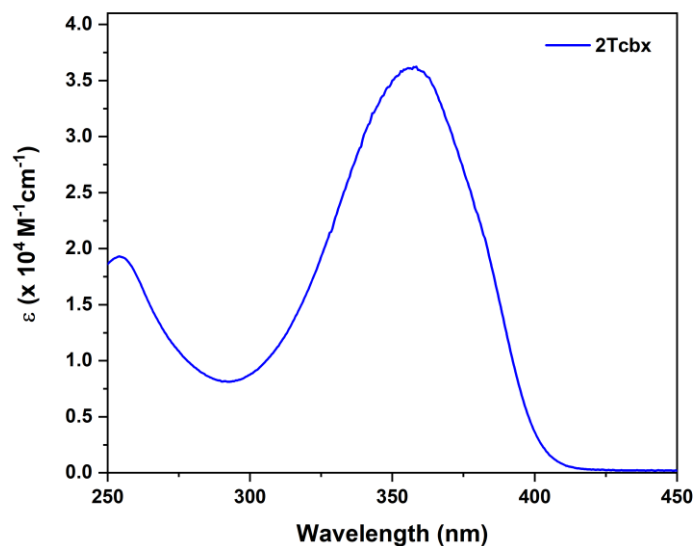


Figure S9. Molar absorptivity (ϵ) of **2Tcbx** plotted as a function of wavelength in acetonitrile at 25.0 ± 0.1 °C.

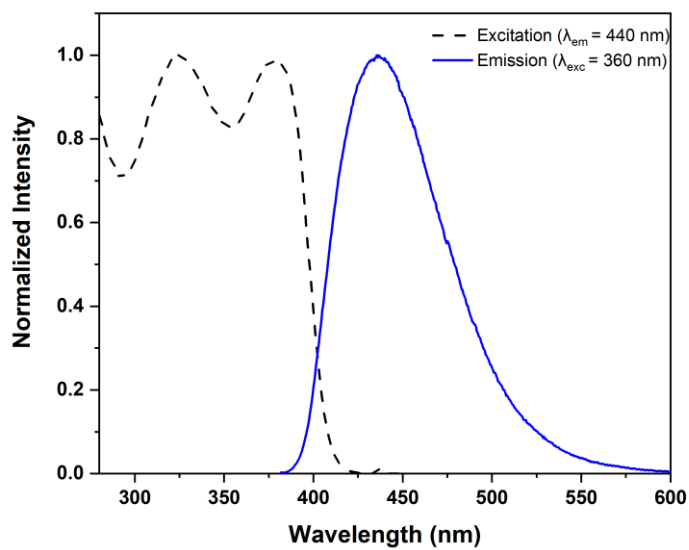


Figure S10. Excitation (black dashed) and emission (solid blue) spectra of **2Tcbx** in acetonitrile at 25.0 ± 0.1 °C.

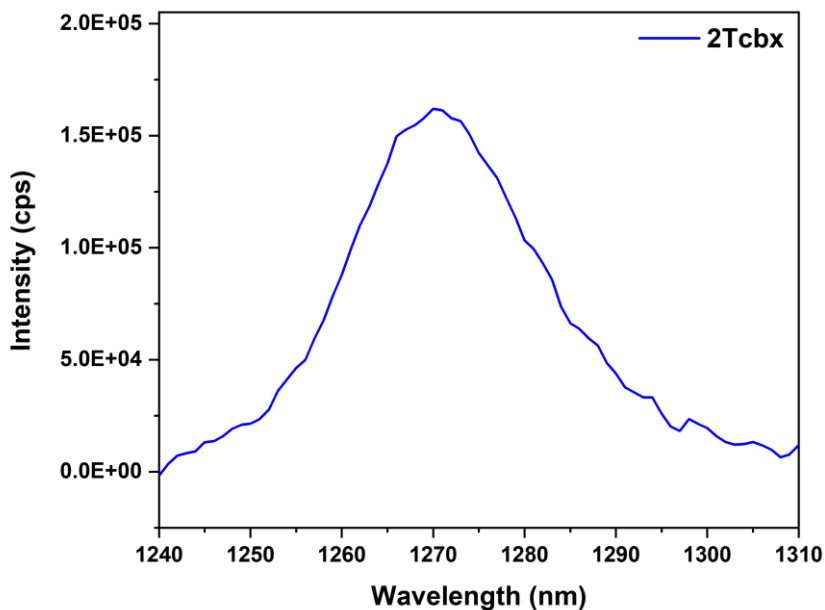


Figure S11. $^1\text{O}_2$ emission at 1270 nm for **2Tcbx** in acetonitrile at 25.0 ± 0.1 °C ($\lambda_{\text{exc}} = 360$ nm). $[\text{2Tcbx}] = 1 \times 10^{-4}$ M.

2.2 Absorption titrations of **2Tcbx** with Ln^{III} nitrates (speciation)

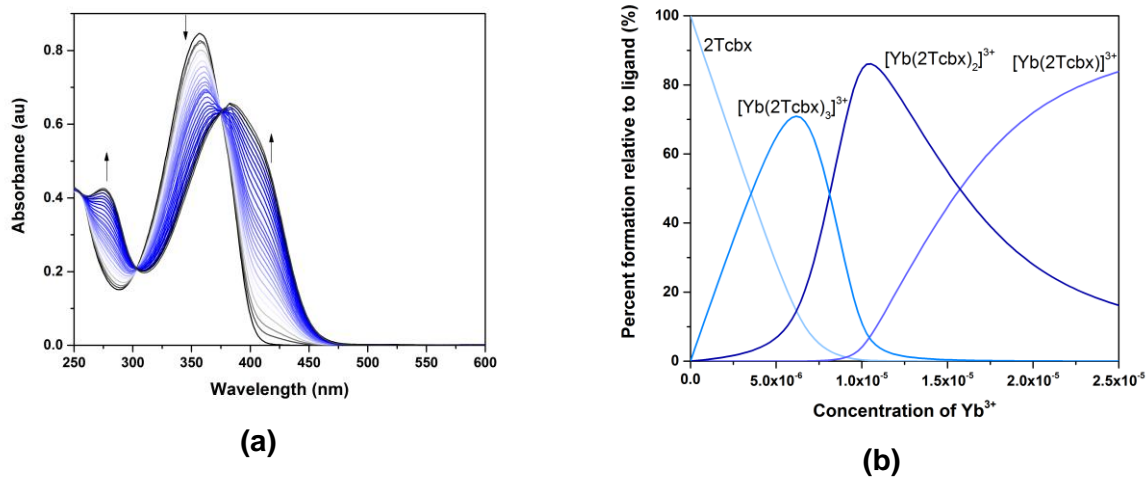


Figure S12. (a) Absorbance titration of **2Tcbx** ($[\text{2Tcbx}] = 2 \times 10^{-5}$ M) against $\text{Yb}(\text{NO}_3)_3$ in acetonitrile; (b) speciation diagram of percent complex formation as a function of concentration of added Yb^{III} .

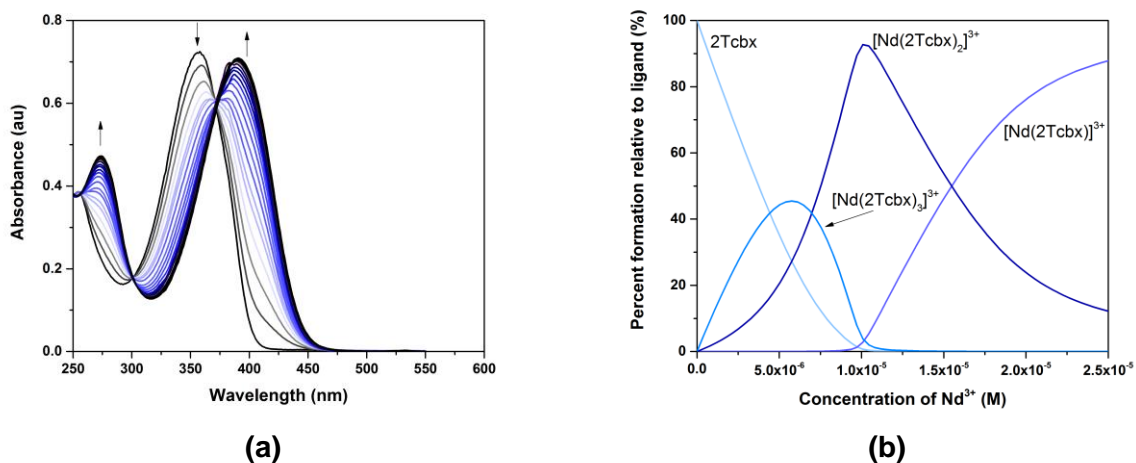


Figure S13. (a) Absorbance titration of **2Tcbx** ($[2Tcbx] = 2 \times 10^{-5} \text{ M}$) against $\text{Nd}(\text{NO}_3)_3$ in acetonitrile; (b) speciation diagram of percent complex formation as a function of concentration of added Nd^{III} .

Table S3. Stability constants for the formation of the 1:1, 2:1 and 3:1 complexes of **2Tcbx** with Nd^{III} or Yb^{III} .

Ln^{III}	2Tcbx	
Nd^{III}	β_1	9.70 ± 0.20
	β_2	17.79 ± 0.19
	β_3	23.10 ± 0.11
Yb^{III}	β_1	9.55 ± 0.01
	β_2	17.68 ± 0.01
	β_3	23.73 ± 0.41

2.3 Excited state energy measurements

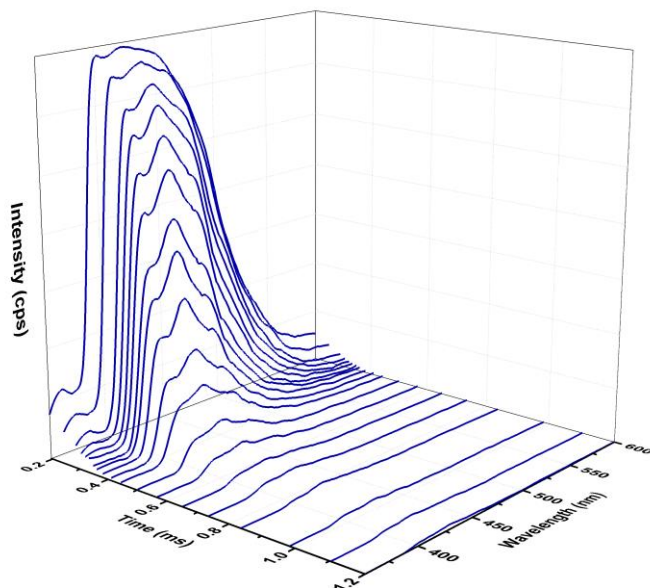


Figure S14. Time-resolved phosphorescence spectra of $[\text{Gd}(\text{2Tcbx})_2]^{3+}$ at ~ 77 K in degassed hexanes ($\lambda_{\text{exc}} = 330$ nm).

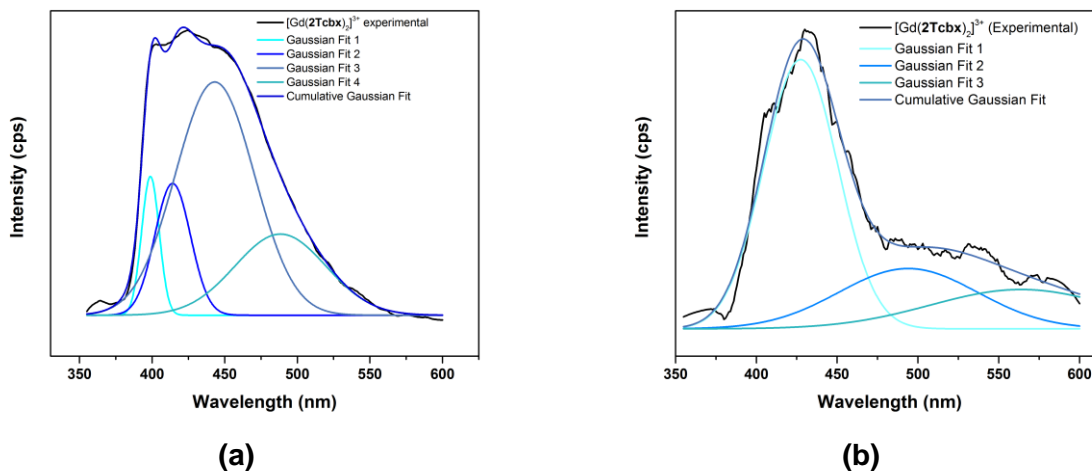


Figure S15. Deconvolution of $[\text{Gd}(\text{2Tcbx})_2]^{3+}$ singlet (a) and triplet (b) excited state emission into their vibrational components ($\lambda_{\text{exc}} = 330$ nm) obtained with delays of 0.0 ms and 0.75 ms, respectively.

2.4 Excitation, and emission of Ln^{III} complexes in acetonitrile

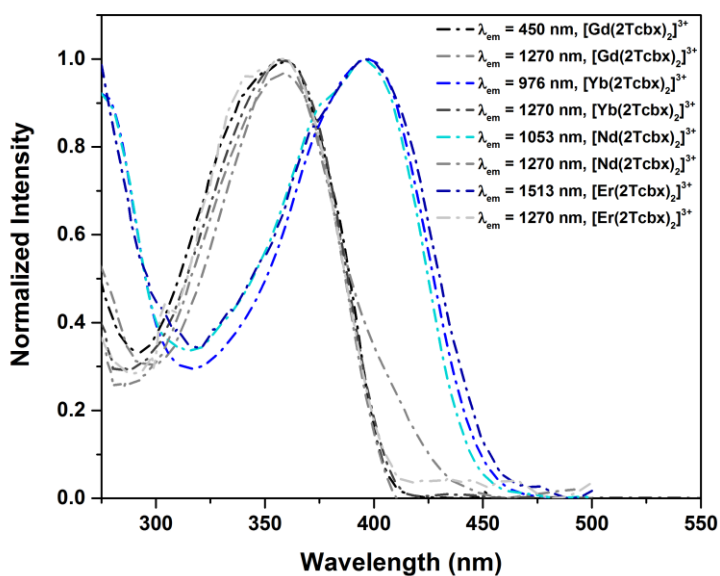


Figure S16. Excitation spectra of [Ln(2Tcbx)₂]³⁺ while monitoring at either ¹O₂ emission or Ln^{III} emission.

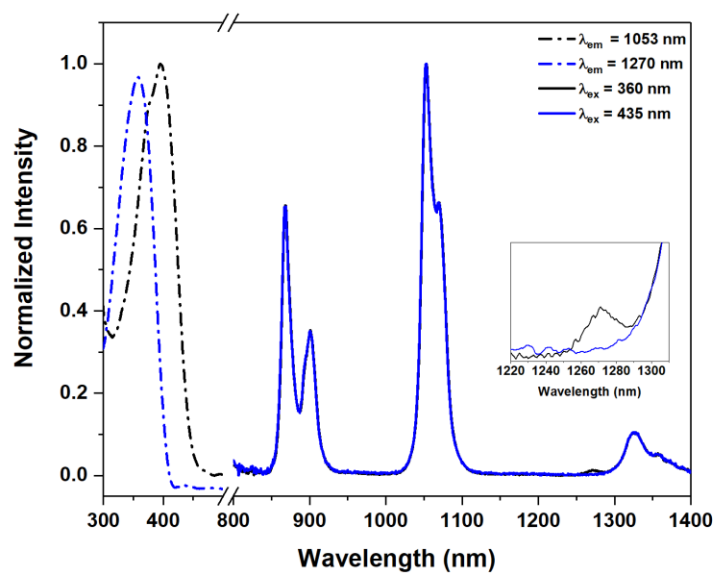


Figure S17. Excitation and emission spectra of [Nd(2Tcbx)₂]³⁺ at 25 ± 0.1 °C. Inset shows in detail the region of ¹O₂ phosphorescence.

2.5 Femtosecond pump-probe spectroscopy

A Ti:Sapphire one box regenerative amplifier (Spectra Physics Solstice, 7 mJ, 798 nm, 1 kHz, ~ 60 fs) light source is used to drive an Optical Parametric Amplifier (Light Conversion TOPAS Prime) and to generate a light continuum (CaF₂ 2 mm thick, 350 nm to 750 nm) inside the TAS. The TAS is a custom-built transient absorption detection system from Newport. Inside the TAS, the 798 nm light utilized for white light generation is directed through an eight-pass retroreflector to yield a maximum delay of 7.5 ns timed to the pump beam. The CaF₂ crystal is translated vertically to avoid burning. The pump and probe are overlapped in a pseudo collinear geometry. Post sample is a fiber coupled Oriel spectrograph.

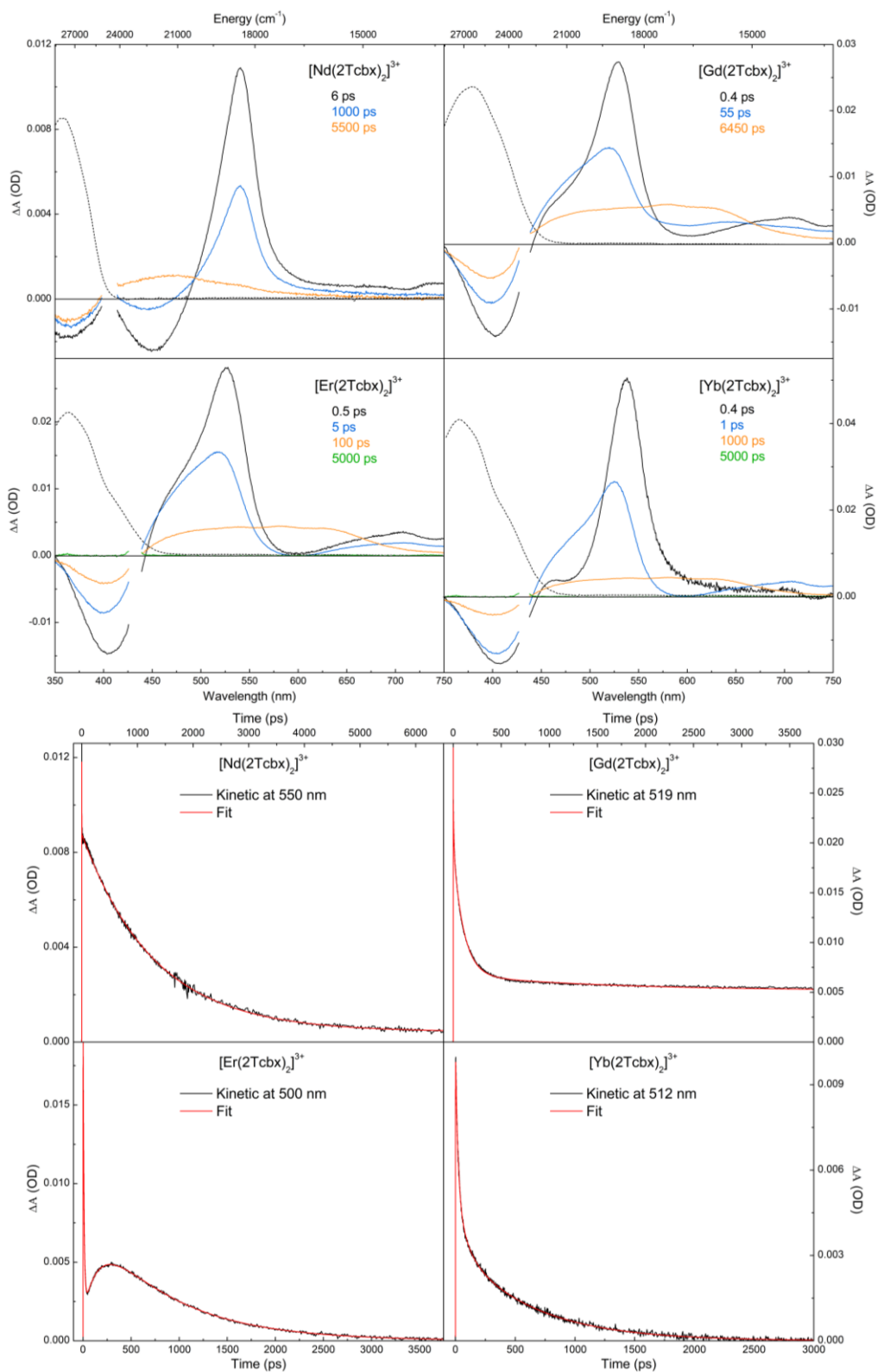


Figure S18. Femtosecond pump-probe spectroscopy of $[\text{Ln}(\text{2Tcbx})_2]^{3+}$ complexes in acetonitrile. (Top) selected transient spectra with ground state absorption spectrum (dashed trace); (bottom) single wavelength kinetic fits.

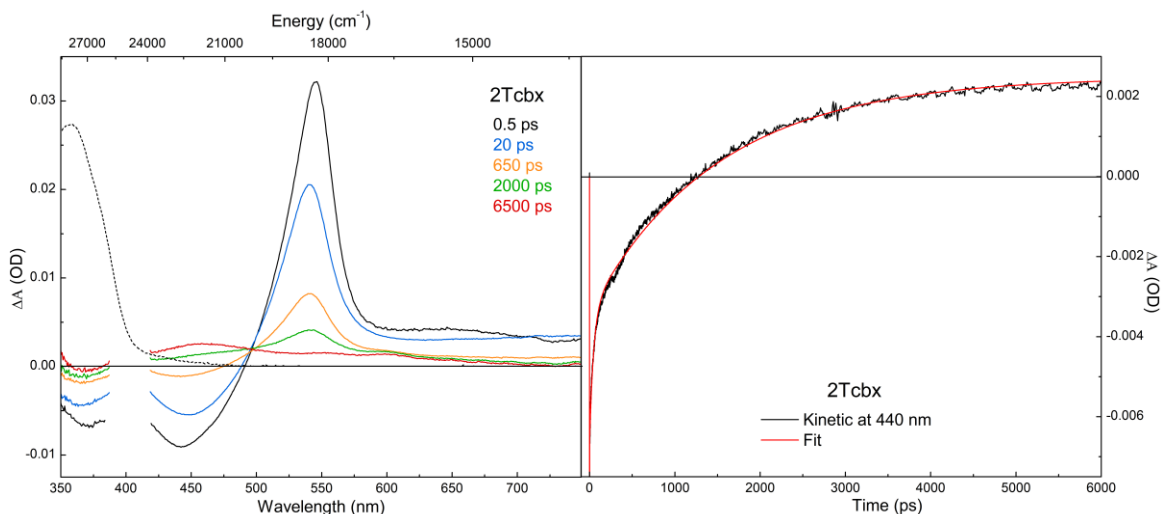


Figure S19. Femtosecond pump-probe spectroscopy of **2Tcbx** in acetonitrile. (left) Selected transient spectra with ground state absorption spectrum (dashed trace); (right) Single wavelength kinetic fitting analysis at 440 nm.

Table S4. Lifetimes obtained from single wavelength kinetic fittings for **2Tcbx** and corresponding Ln^{III} complexes.

	Selected Wavelength (nm)	τ_1 (ps)	\pm	τ_2 (ps)	\pm	τ_3 (ps)	\pm	τ_4 (ps)	\pm
2Tcbx	440	1496	21	48	1	0.39	0.03	-	-
Nd ^{III}	550	1286	25	288	63	0.95	0.07	-	-
Gd ^{III}	519	1594	120	106	2	7.0	0.3	0.60	0.02
Er ^{III}	500	822	45	161	13	9.3	0.1	0.37	0.02
Yb ^{III}	512	558	8	29.0	0.5	0.52	0.04	-	-

3 References

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