Ultrafast Transient Absorption Spectroscopy of Polymer-Based Organophotoredox Catalysts Mimicking Transition Metal Complexes

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Outline

- Motivation
  - Transition-metals based photocatalysts
  - Organophotoredox catalysts
  - Novel polymer-based organophotoredox catalysts
- Experimental
  - Femtosecond transient absorption (TA) spectroscopy
- Results and Discussion
  - Steady-state absorption (Abs)
  - Steady-state Photoluminescence spectroscopy (PL)
  - Time-resolved photoluminescence (TRPL)
  - Femtosecond transient absorption (TA) spectroscopy
  - Simulation and fitting of the TA spectra
  - Rate constants of photoinduced processes
- Summary and Future Work

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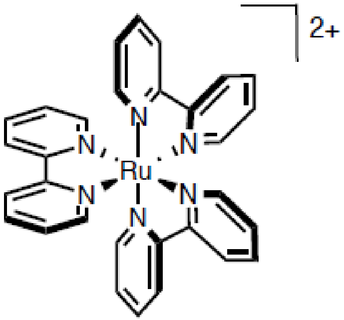
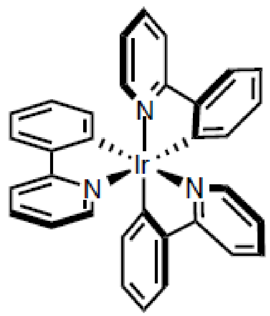
Motivation

Transition Metal Complexes

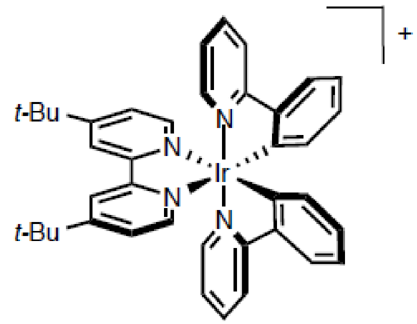
The “Big Four”



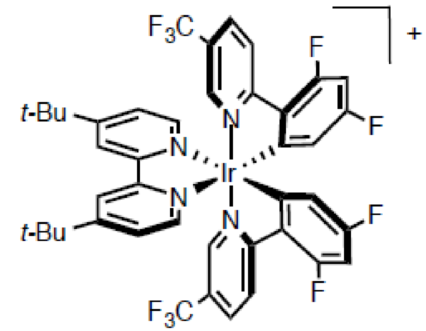
$Ru(bpy)_3^{2+}$



$Ir(ppy)_3$



$Ir(ppy)_2(dtbbpy)^+$



$Ir[di-F(CF3)(ppy)_2(dtbbpy)^+$

- Applications in:
  - Solar energy conversion
  - Organic light-emitting diodes (OLEDs)
  - Molecular electronics
  - Biology
  - Photochemistry

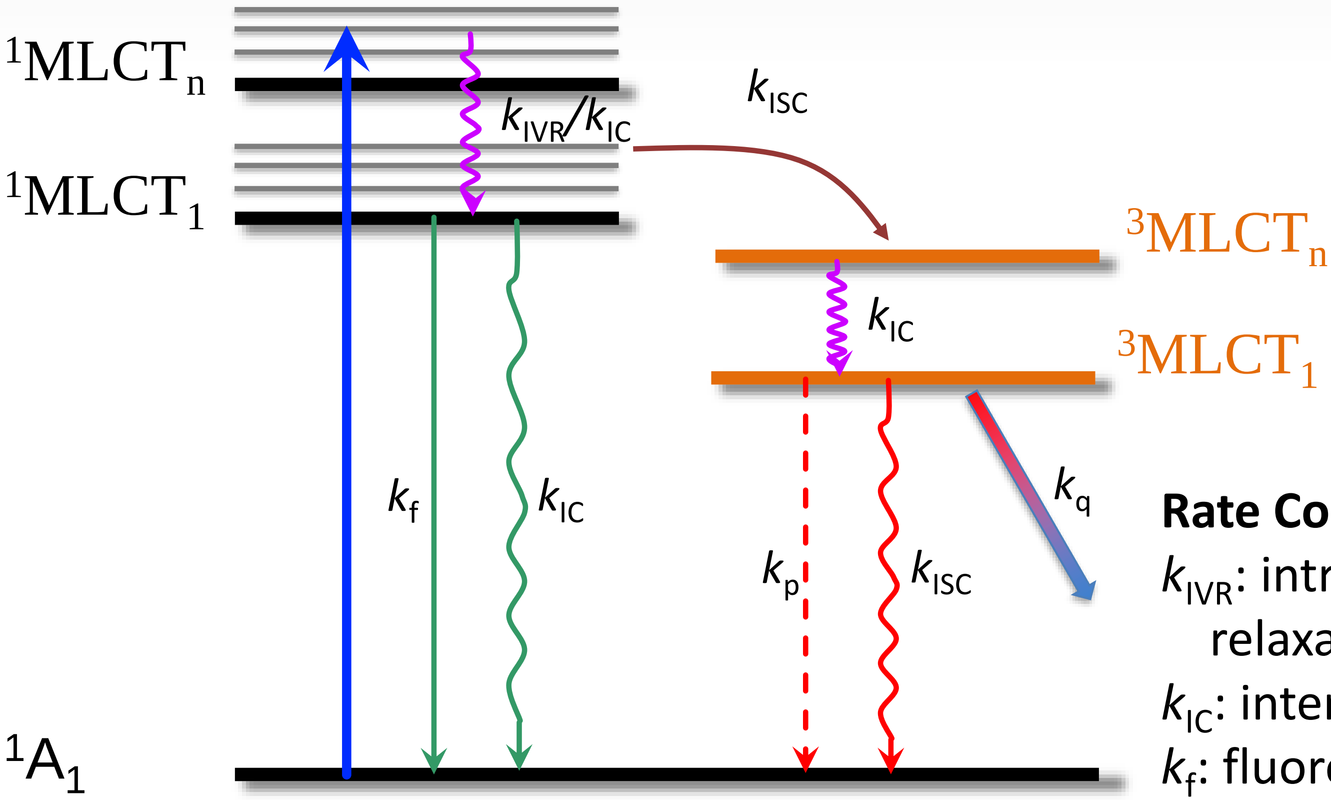
- Disadvantages

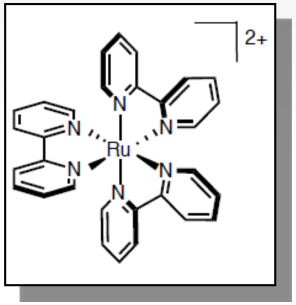
Ruthenium and Iridium
  - High cost
  - Potential toxicity
  - Limited availability in the future
  - Carrying over traces of metal

- Tucker, J. W.; Stephenson, C. R. J. J. Org. Chem. 2012, 77, 1617
- Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Chem. Rev. 2013, 113 , 5322

Photophysics of Transition Metal Complexes

Jablonski Diagram





$Ru(bpy)_3^{2+}$

Rate Constants:

k_{IVR}: intramolecular vibrational relaxation

k_{IC}: internal conversion

k_f: fluorescence

k_{ISC}: intersystem crossing

k_p : phosphorescence

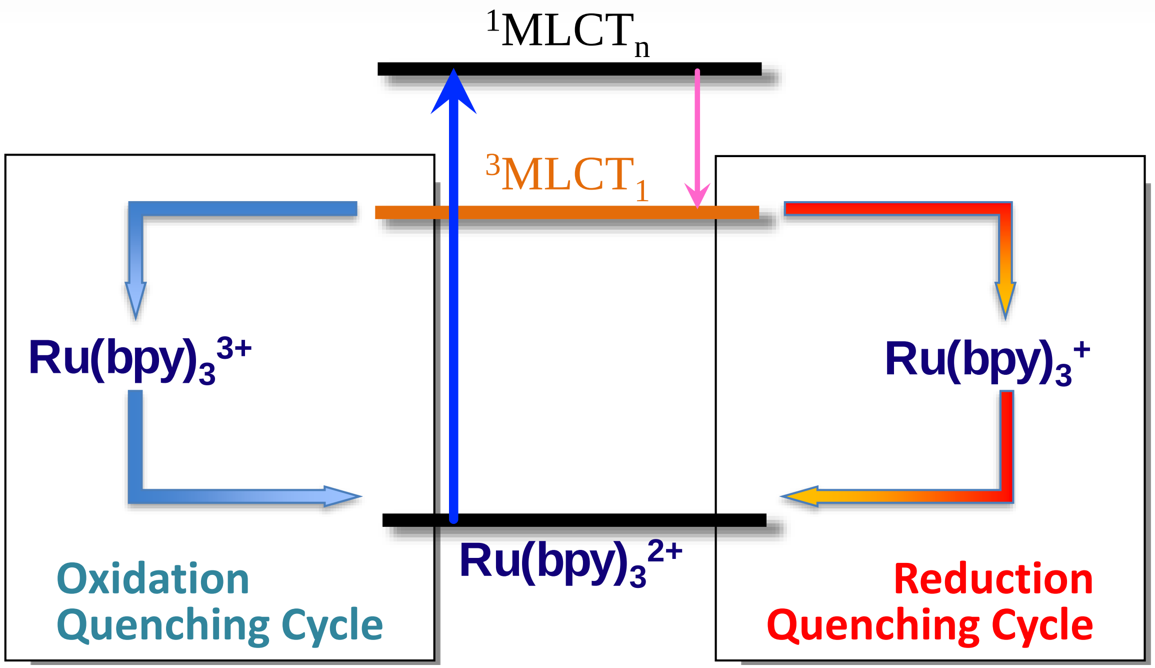
k_q : intermolecular quenching

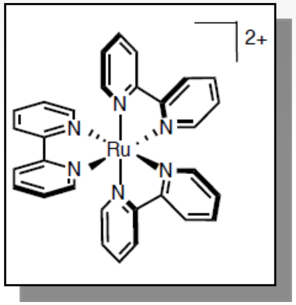
Lifetimes (τ):

S_1: 100-300 fs T_1: ~1.1 μs!

Photochemistry of Transition Metal Complexes

Photoredox Catalysis





$Ru(bpy)_3^{2+}$

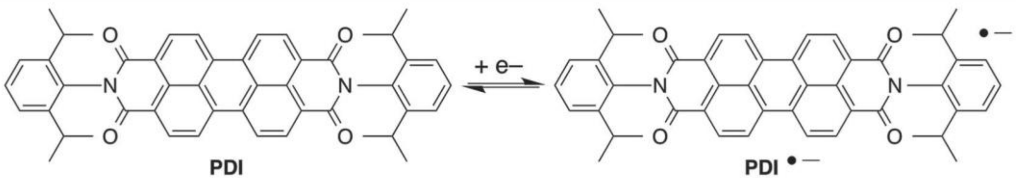
Triplet-state transition metal complexes are both potent reducing agents and potent oxidizing agents.

- Oxidation of the metal center.
- Reduction of the ligands.

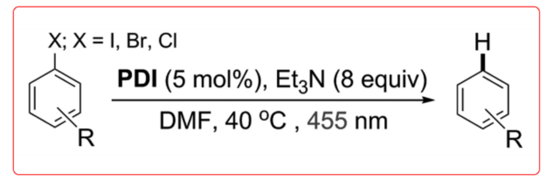
Photocatalysis:

1. Photoexcitation and ISC
2. Reduction or oxidation by an outer-sphere electron transfer
3. Catalyst regeneration by another outer-sphere electron transfer

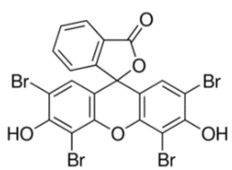
Organophotoredox catalysts



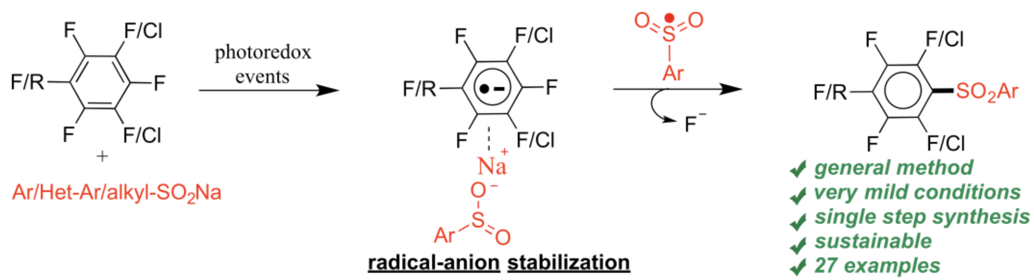
(catalyst)



Konig, et al., *Science*, **2014**, *346*, 725



eosin Y
(catalyst)

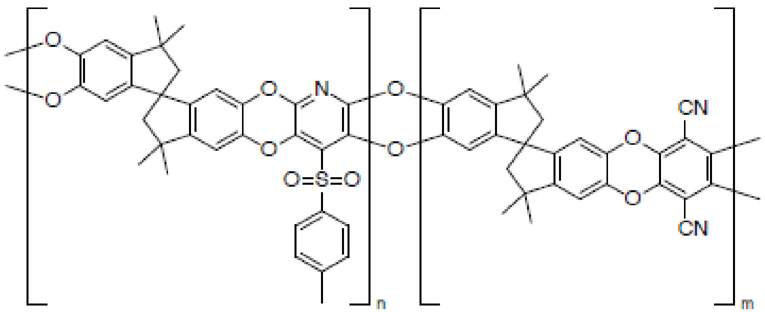


Handa, et al., **2017**, *submitted*

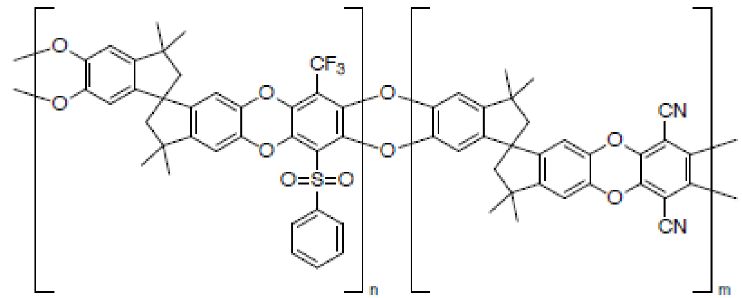
- **Non-recyclable**
- **Difficulty in isolation**
- **Not active for broad range of transformations**

Novel Polymer-Based Organophotoredox Catalysts

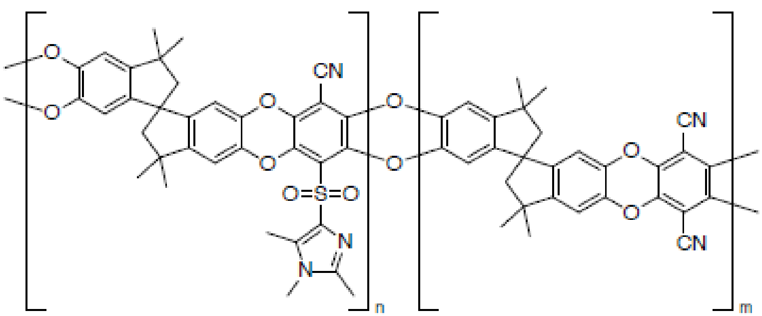
js-lnb1-095



yd-lnb1-151



yd-lnb1-153



- **Recyclable catalyst**
- **Ease in product isolation**
- **Active in broad range of transformations**
- **Ease of synthesis**
- **Non-toxicity of chemical process**
- **Catalytic activity in water at room temperature**

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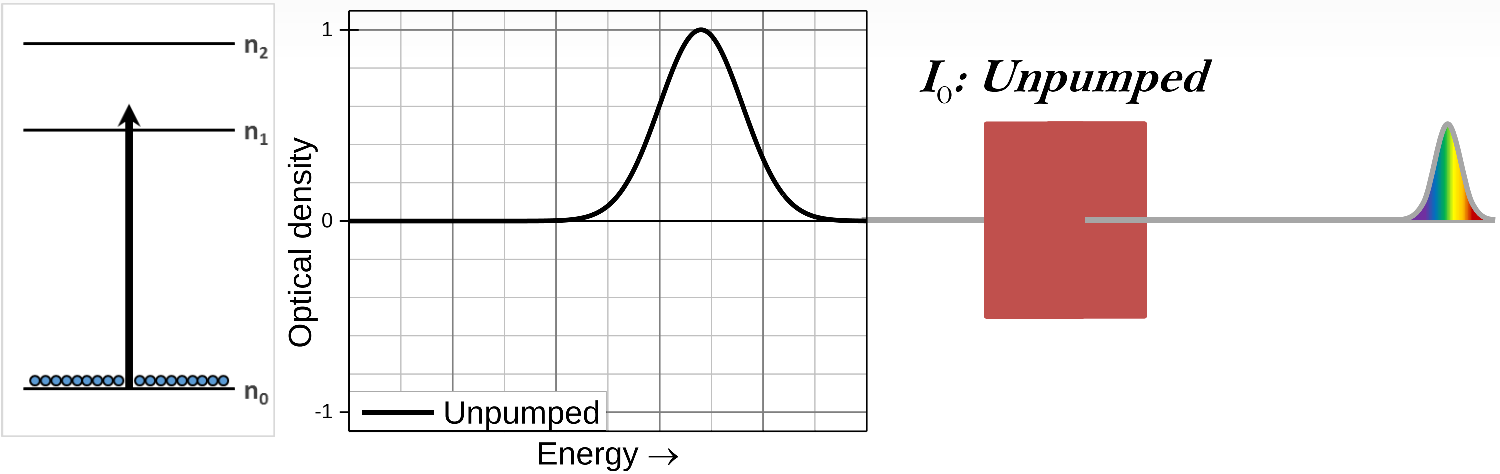
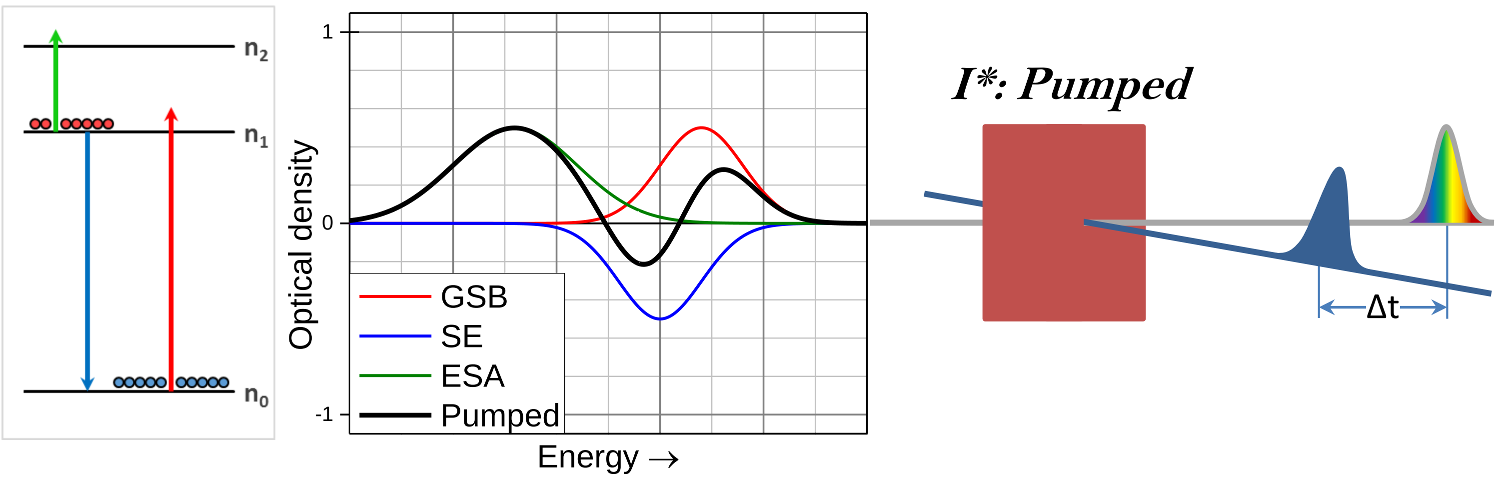
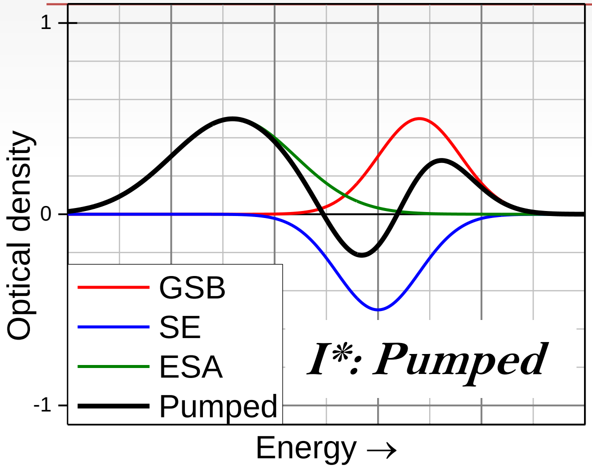
Pump-Probe TA Spectroscopy Experiment (Concept)





Pump-Probe TA Spectroscopy Experiment (Concept)

$$\Delta OD(\Delta t, \lambda) = -\log\left(\frac{I^*(\Delta t, \lambda)}{I_0(\lambda)}\right)$$



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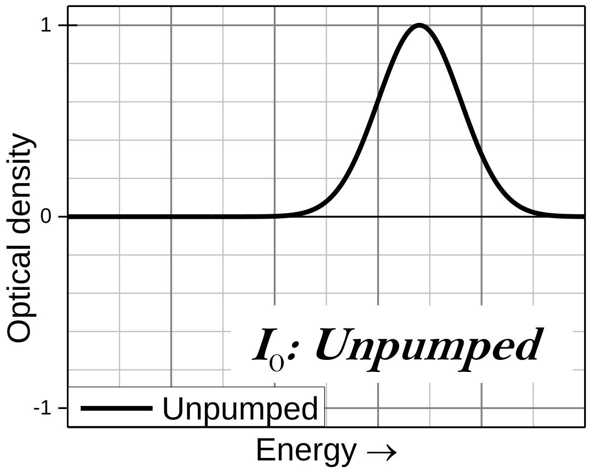

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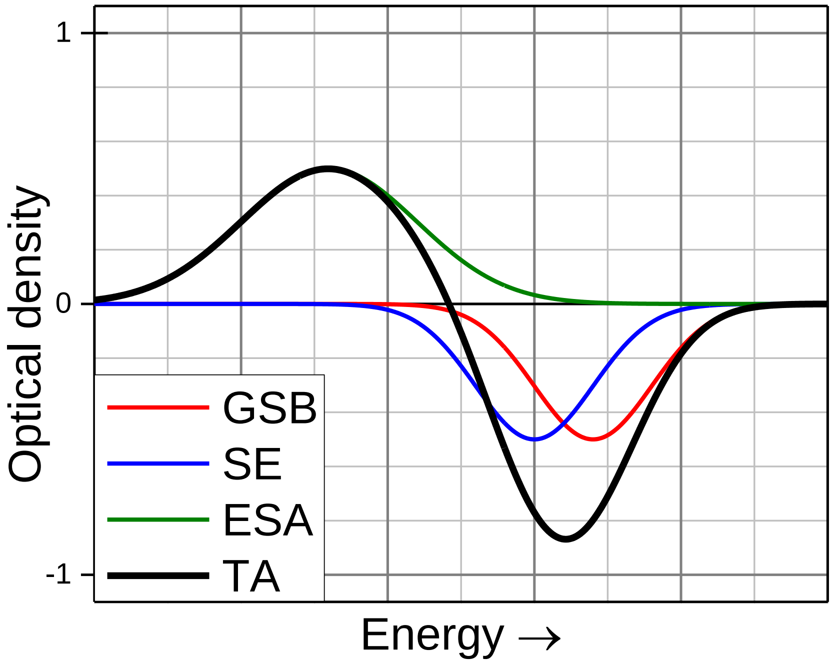
Ground-state bleach (GSB)

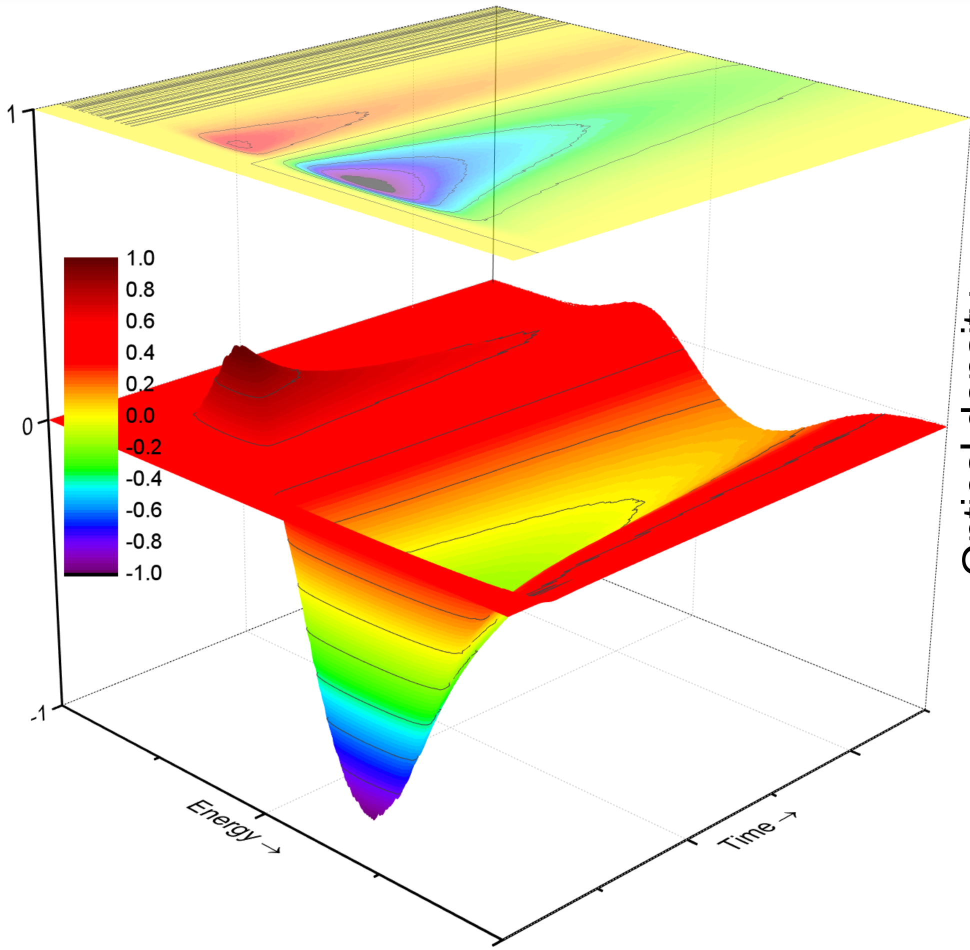
Stimulated Emission (SE)

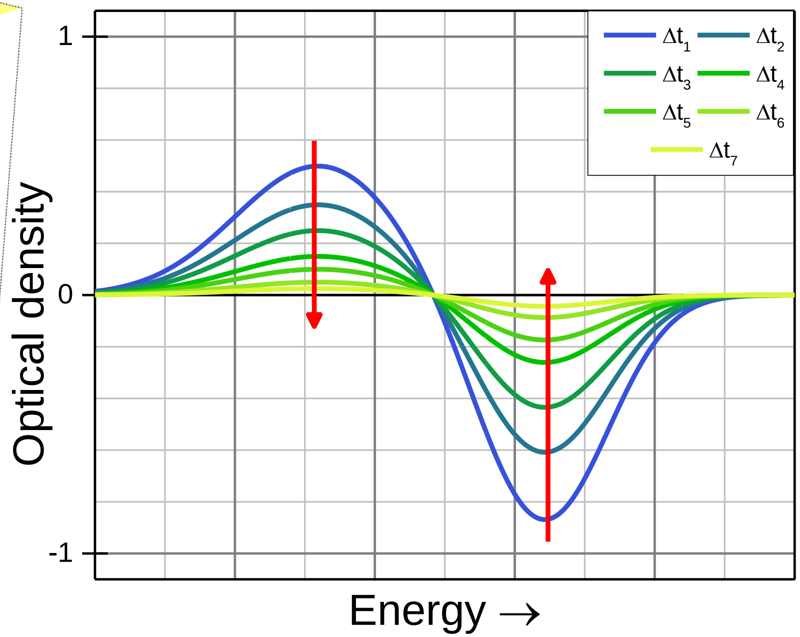
Excited-state absorption (ESA)



Berera R, van Grondelle R, Kennis JTM. Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems. Photosynth Res 2009, 101(2-3): 105-118.

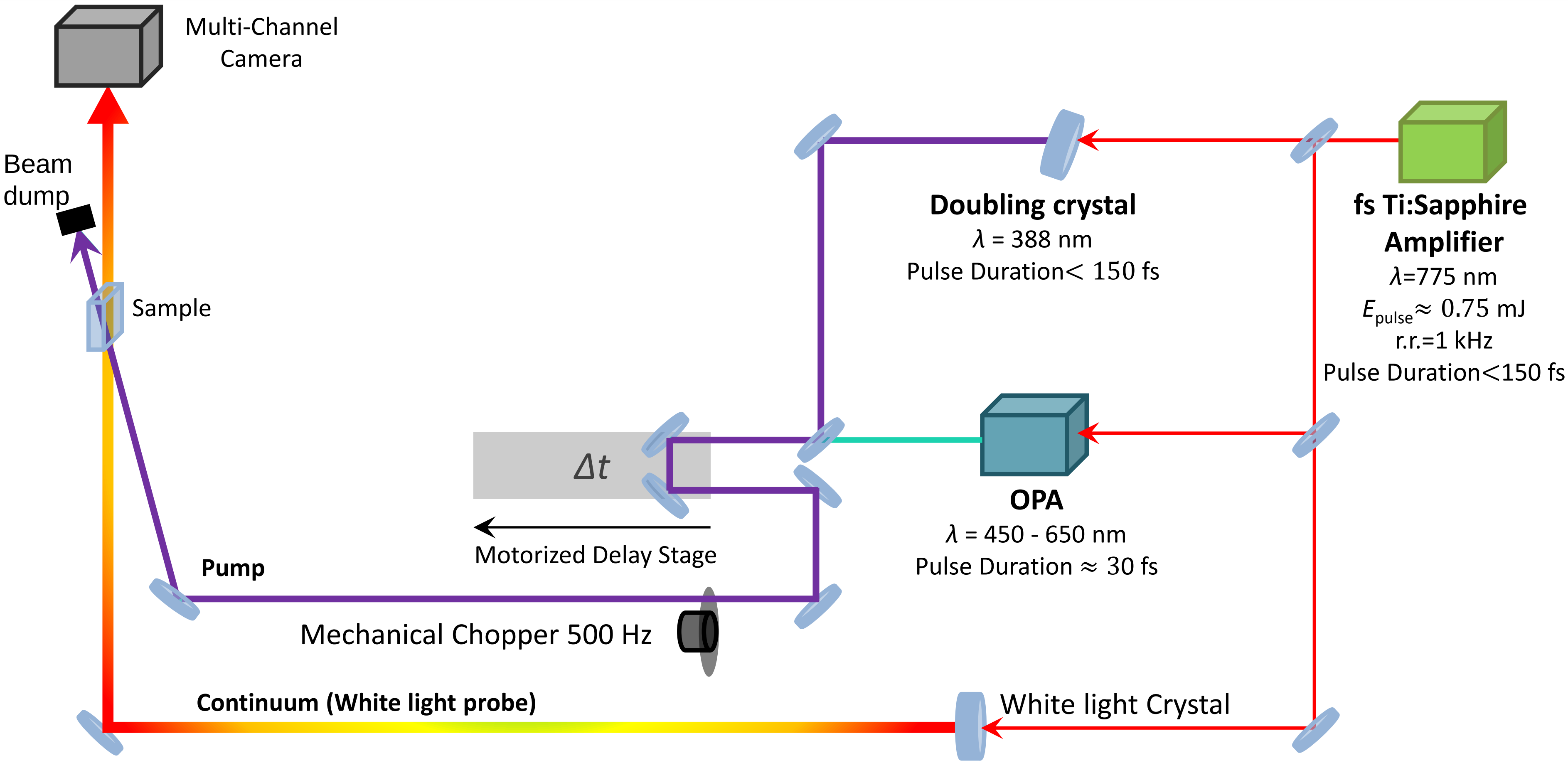
Pump-Probe TA Spectroscopy Experiment (Concept)





Berera R, van Grondelle R, Kennis JTM. Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems. Photosynth Res 2009, 101(2-3): 105-118.

Pump-Probe TA Spectroscopy Experiment (Setup)



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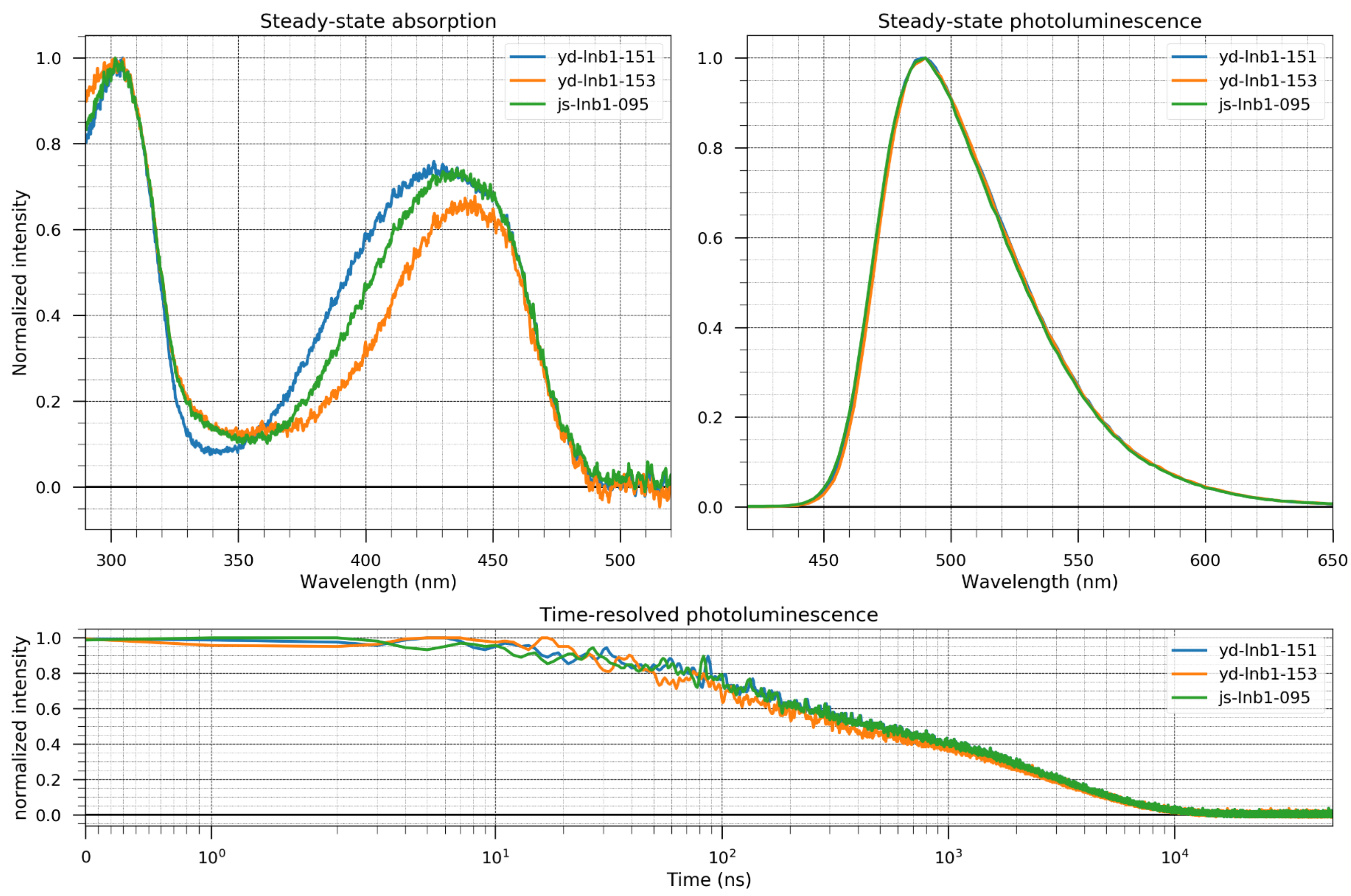
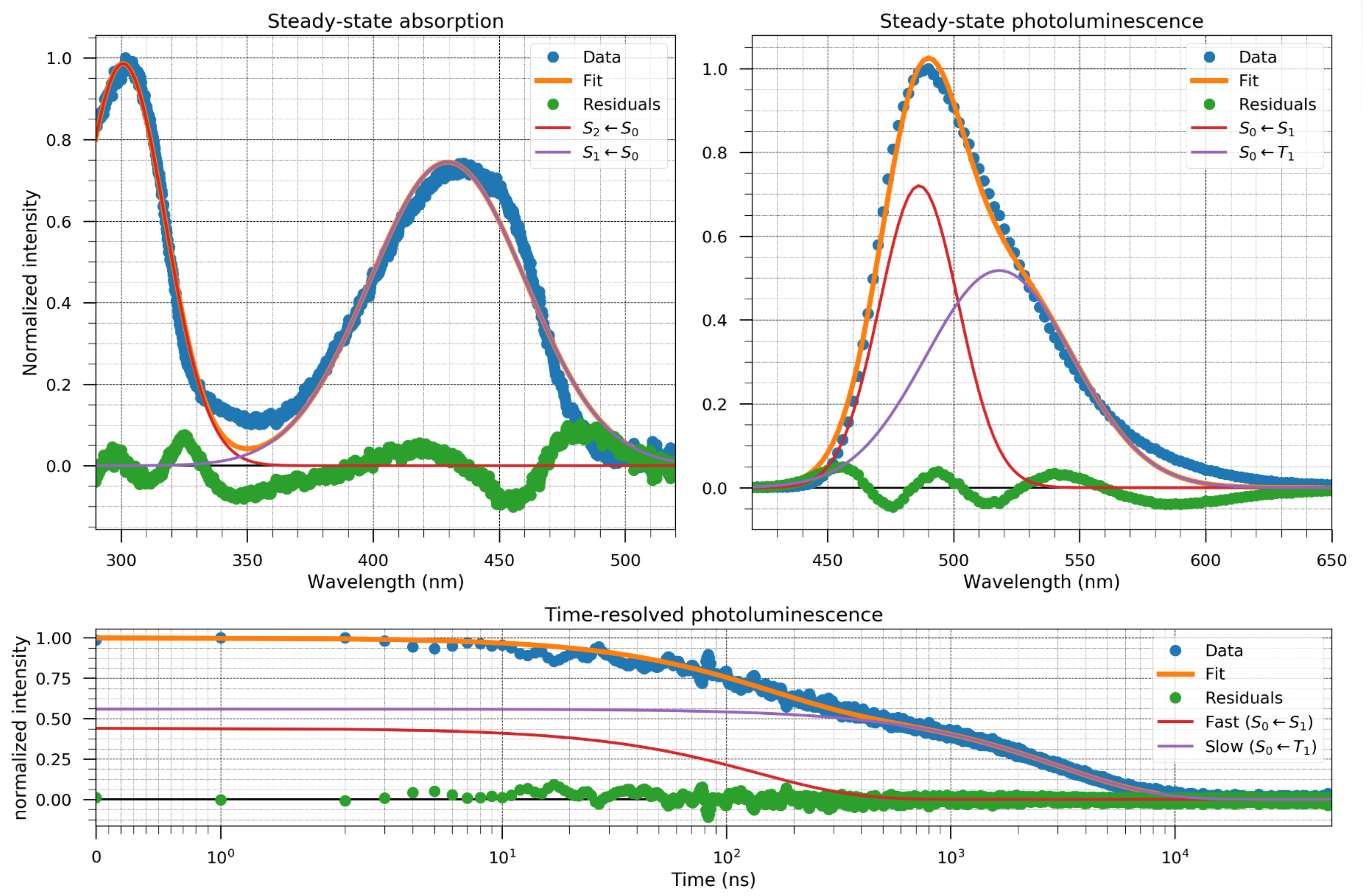
Steady-state Abs, PL, and TRPL spectra



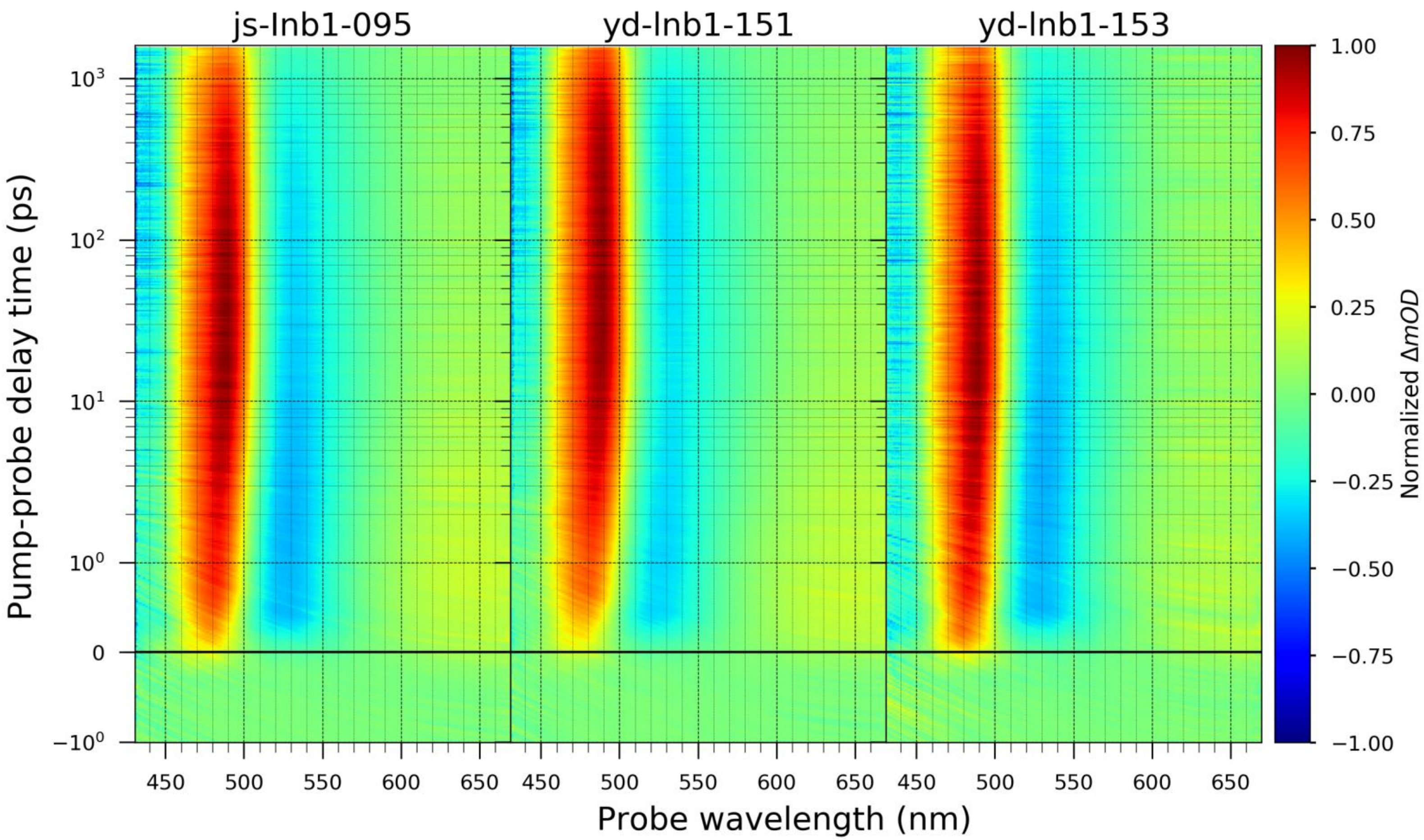
Steady-state Abs, PL, and TRPL fitting



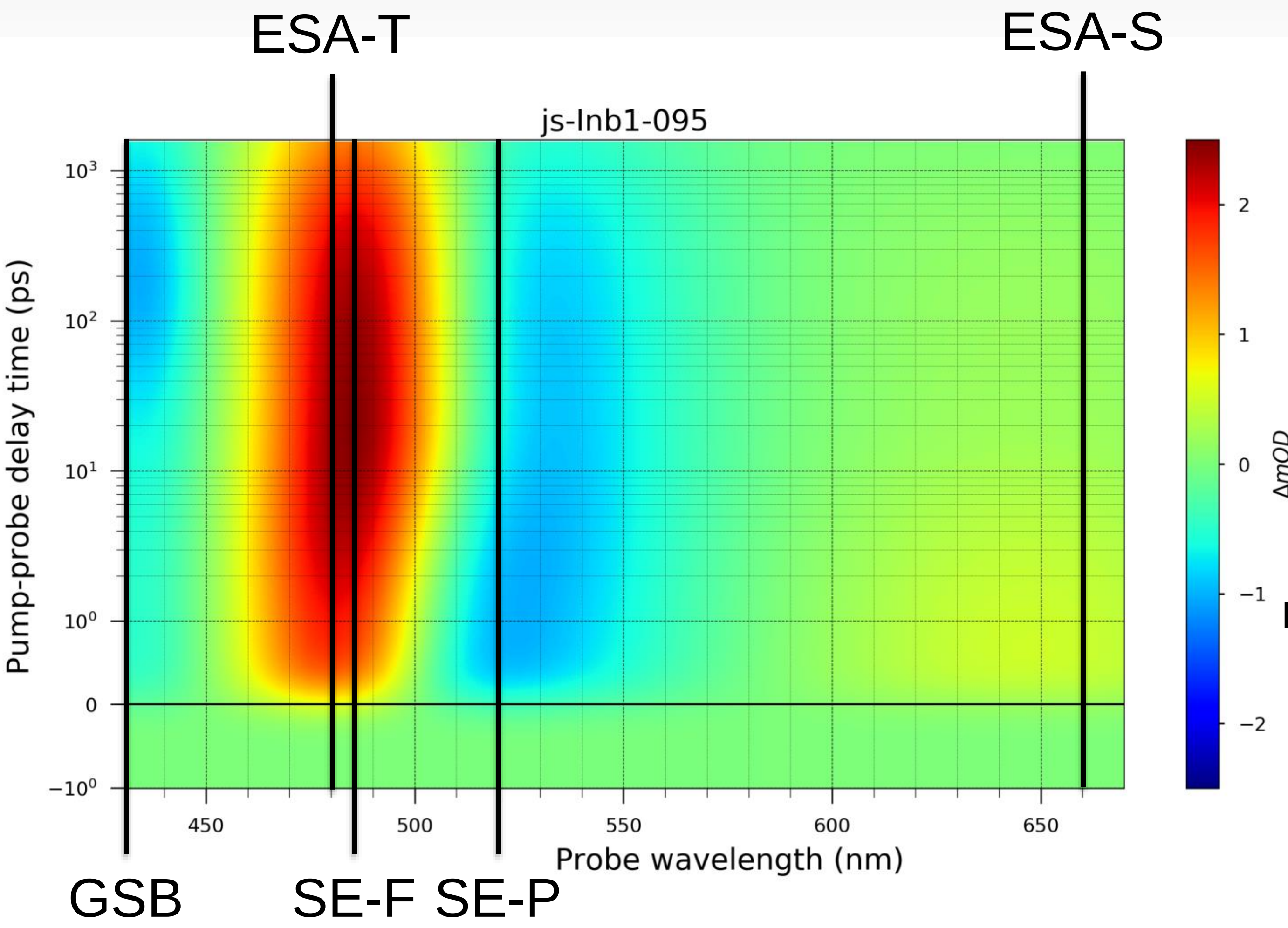
Steady-state and TRPL fitting results

Source	Component	Parameter	yd-lnb1-151 value	yd-lnb1-151 95% CI	yd-lnb1-153 value	yd-lnb1-153 95% CI	js-lnb1-095 value	js-lnb1-095 95% CI
Abs	$S_2 \leftarrow S_0$	μ (nm)	301.72652	-0.2995 +0.28869	298.997	-0.74365 +0.66057	300.7289	-0.42539 +0.40087
		σ (nm)	14.32834	-0.29325 +0.30596	18.49524	-0.64545 +0.70082	16.85601	-0.41082 +0.43227
	$S_1 \leftarrow S_0$	μ (nm)	424.86446	-0.33656 +0.33577	433.4939	-0.45492 +0.45155	429.556	-0.33081 +0.32972
		σ (nm)	33.20155	-0.32043 +0.32403	28.47144	-0.46996 +0.47917	31.01708	-0.33255 +0.33662
PL	$S_0 \leftarrow S_1$	μ (nm)	486.53389	-0.84603 0.87651	487.0351	-0.84000 +0.87001	486.3069	-0.80382 +0.81957
		σ (nm)	15.45525	-0.90044 +0.88358	15.38288	-0.89224 +0.87545	15.68872	-0.85016 +0.83415
	$S_0 \leftarrow T_1$	μ (nm)	518.21316	-2.78542 +3.17515	518.6962	-2.80942 +3.19602	518.1341	-2.76018 +3.14496
		σ (nm)	28.81613	-1.39943 +1.31578	28.74906	-1.41757 +1.33687	29.07063	-1.38992 +1.29600
TRPL	$S_0 \leftarrow S_1$	τ_{d1} (ns)	147.41689	-0.85127 0.85466	107.1091	-0.68647 +0.69667	138.85	-0.83685 +0.84175
	$S_0 \leftarrow T_1$	τ_{d2} (ns)	3052.30329	-4.08717 +4.09761	3011.612	-4.35685 +4.38888	3044.968	-4.09353 +4.10809

Femtosecond transient absorption spectroscopy



Femtosecond transient absorption spectroscopy



GSB
Ground state bleach

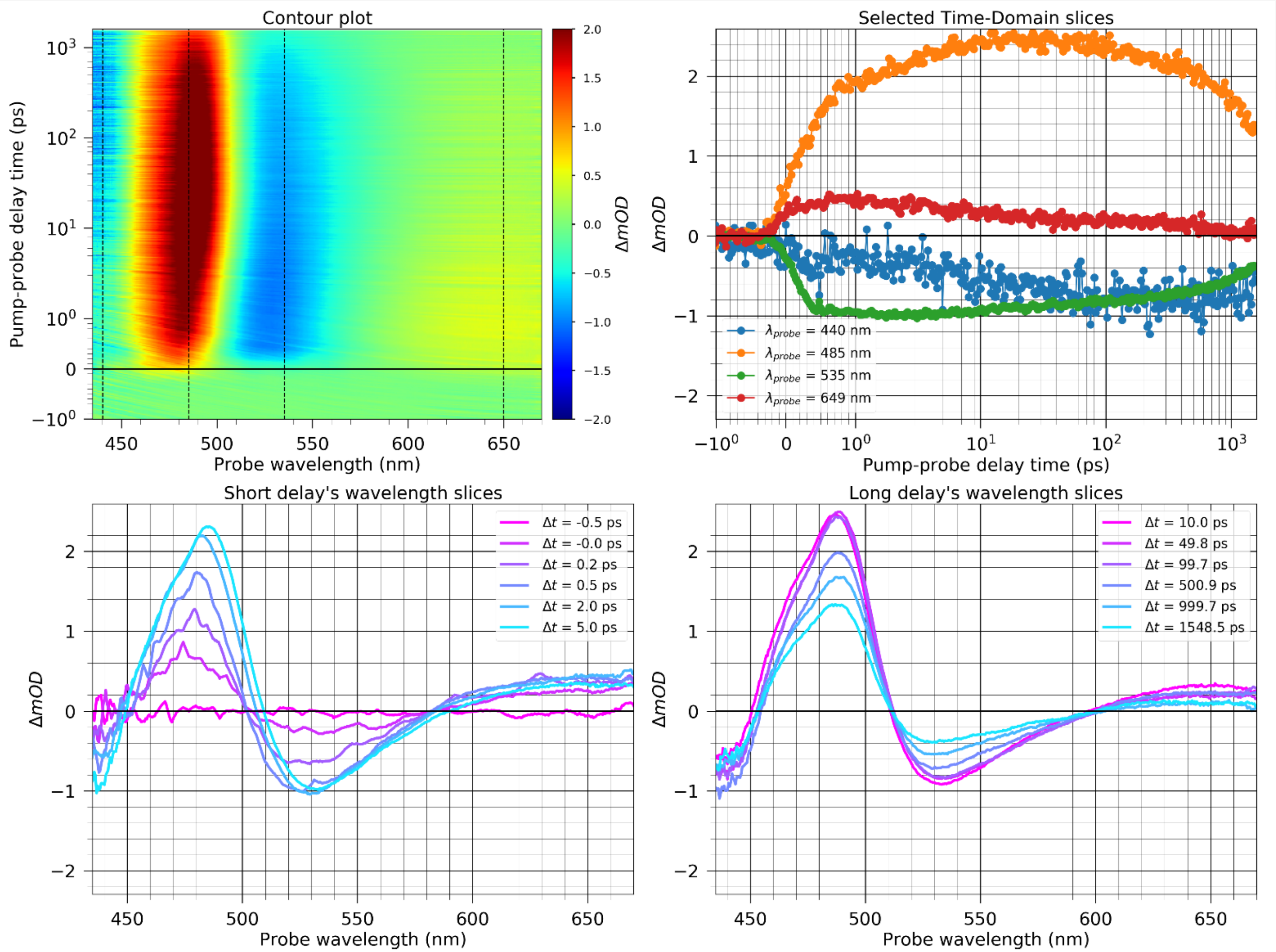
SE-F
Stimulated emission
($S_0 \leftarrow S_1$)

SE-P
Stimulated emission
($S_0 \leftarrow T_1$)

ESA-S
Excited state absorption
($S_n \leftarrow S_1$)

ESA-P
Excited state absorption
($T_n \leftarrow T_1$)

Femtosecond transient absorption spectroscopy



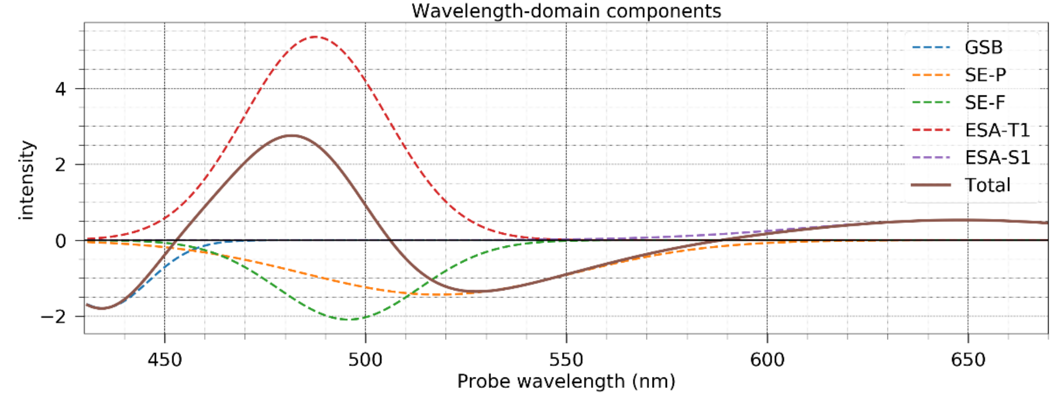
Global Model

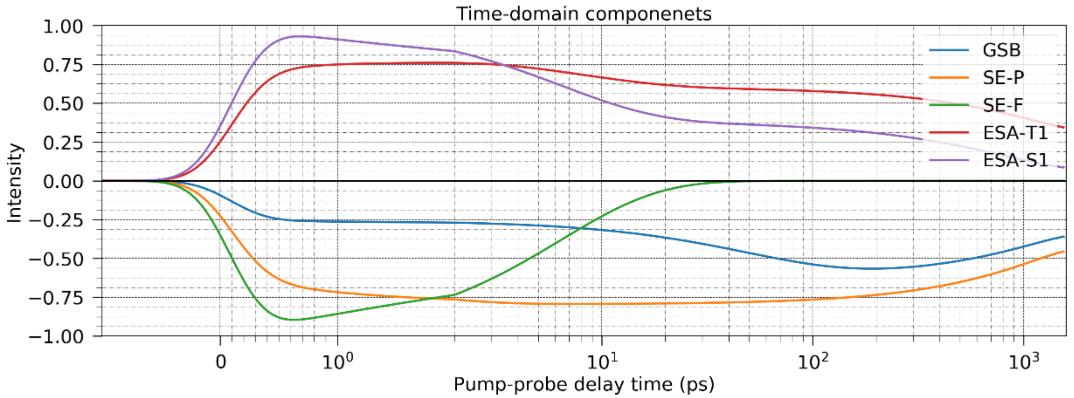
$$\Delta OD(\Delta t,\lambda) = \sum_{j=1}^{5}\left(\overbrace{\left[\left(\sum_{i=1}^{2\ or\ 3} A_{i_j} e^{-\frac{\Delta t}{\tau_{i_j}}}\right) * IRF(\Delta t)\right]}^{time-domain\ componenets} \otimes \overbrace{\left[\frac{A_j}{\sigma_j\sqrt{2\pi}} e^{-\frac{(\lambda-\mu_j)^2}{2\sigma_j^2}}\right]}^{wavelength-domain\ componenets}\right)$$

$$IRF(\Delta t) = \left(\frac{A_{IRF}}{\sigma_{IRF}\sqrt{2\pi}} e^{-\frac{(\Delta t-\mu_{IRF})^2}{2\sigma_{IRF}^2}}\right)$$

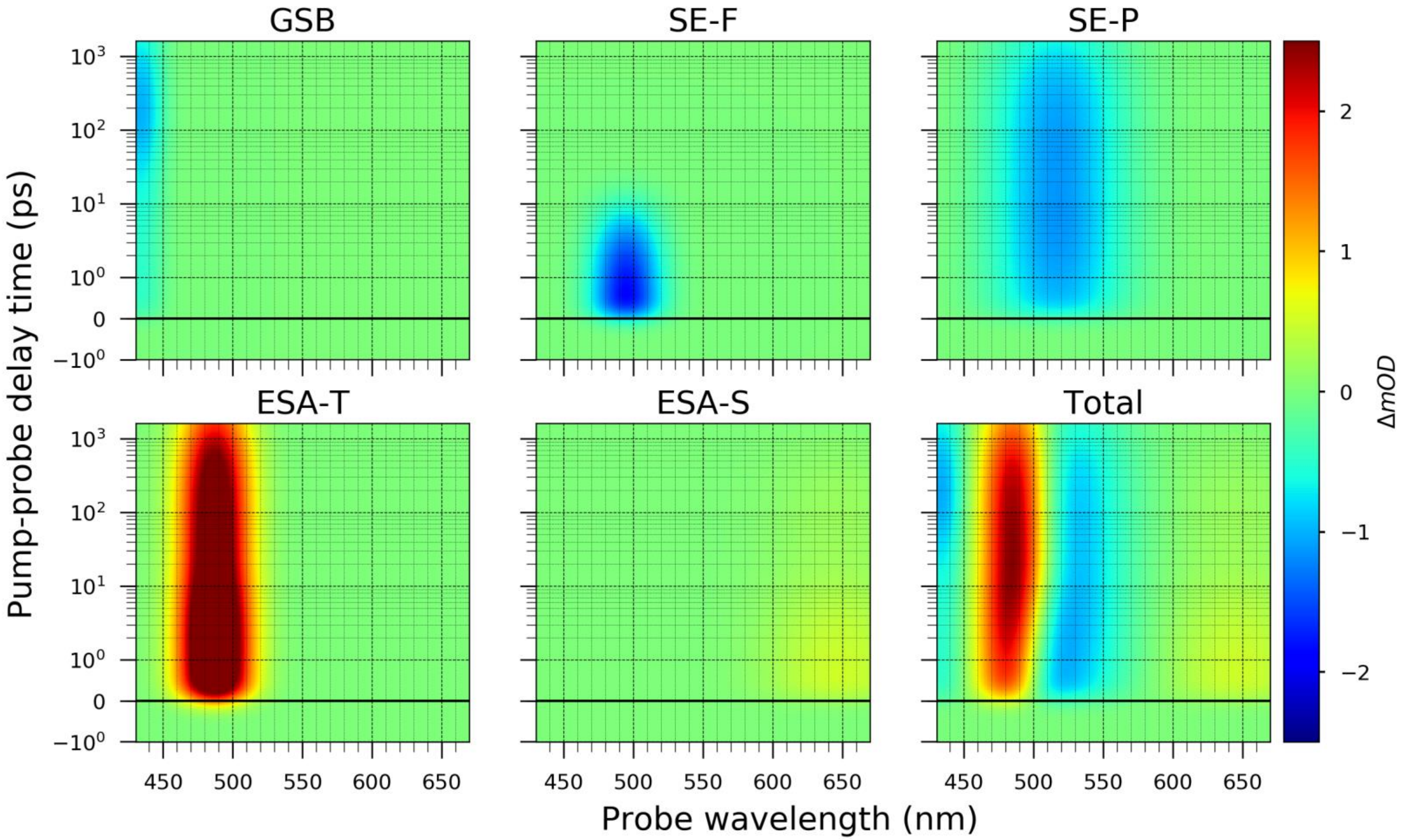
$$f * IRF = \mathcal{F}^{-1}\{\mathcal{F}\{f\}.\mathcal{F}\{IRF\}\}$$

$$and\ \boldsymbol{u} \otimes \boldsymbol{v} = \boldsymbol{u}\boldsymbol{v}^T = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} [v_1 \quad v_2 \quad v_3] = \begin{bmatrix} u_1v_1 & u_1v_2 & u_1v_3 \\ u_2v_1 & u_2v_2 & u_2v_3 \\ u_3v_1 & u_3v_2 & u_3v_3 \\ u_4v_1 & u_4v_2 & u_4v_3 \end{bmatrix}$$

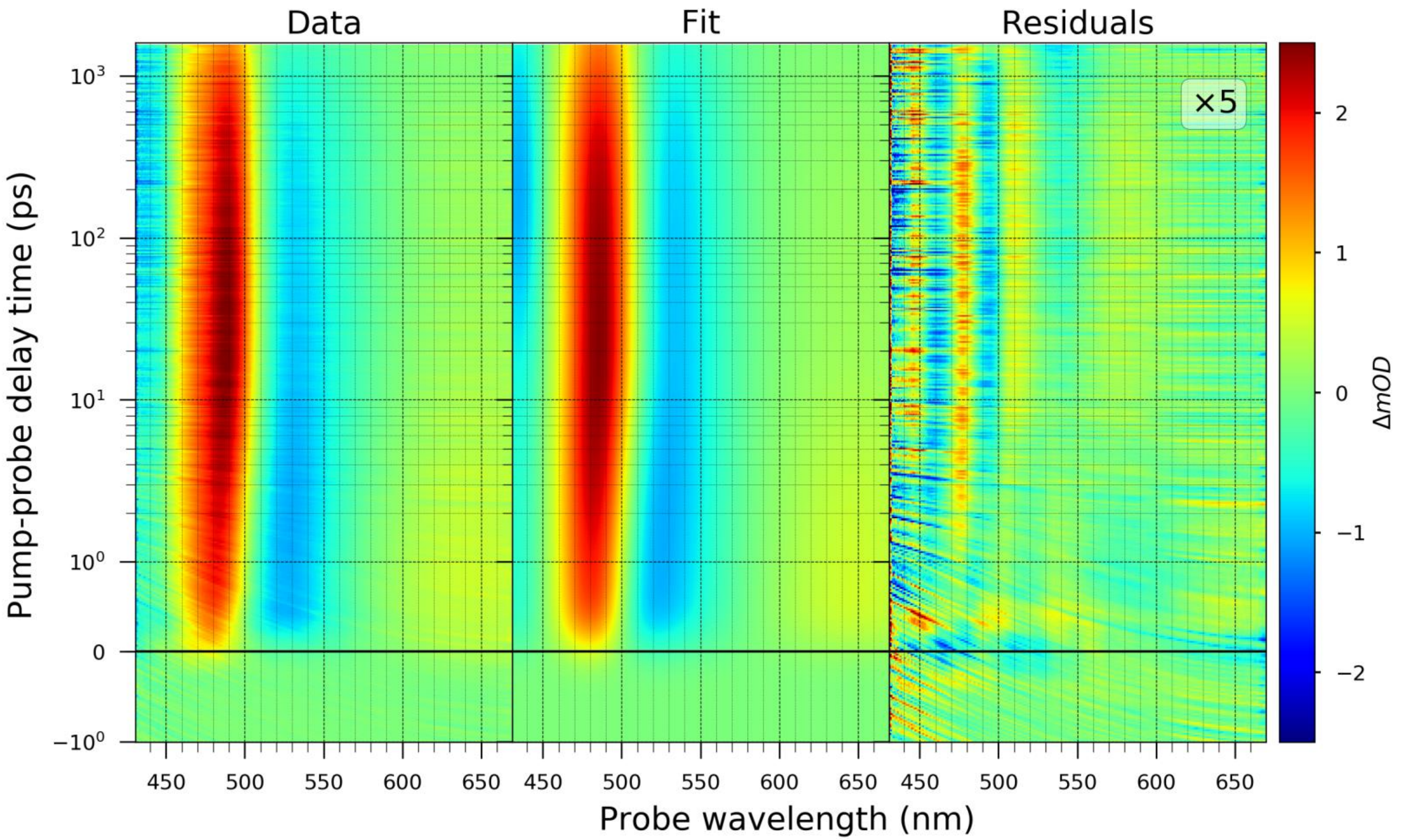




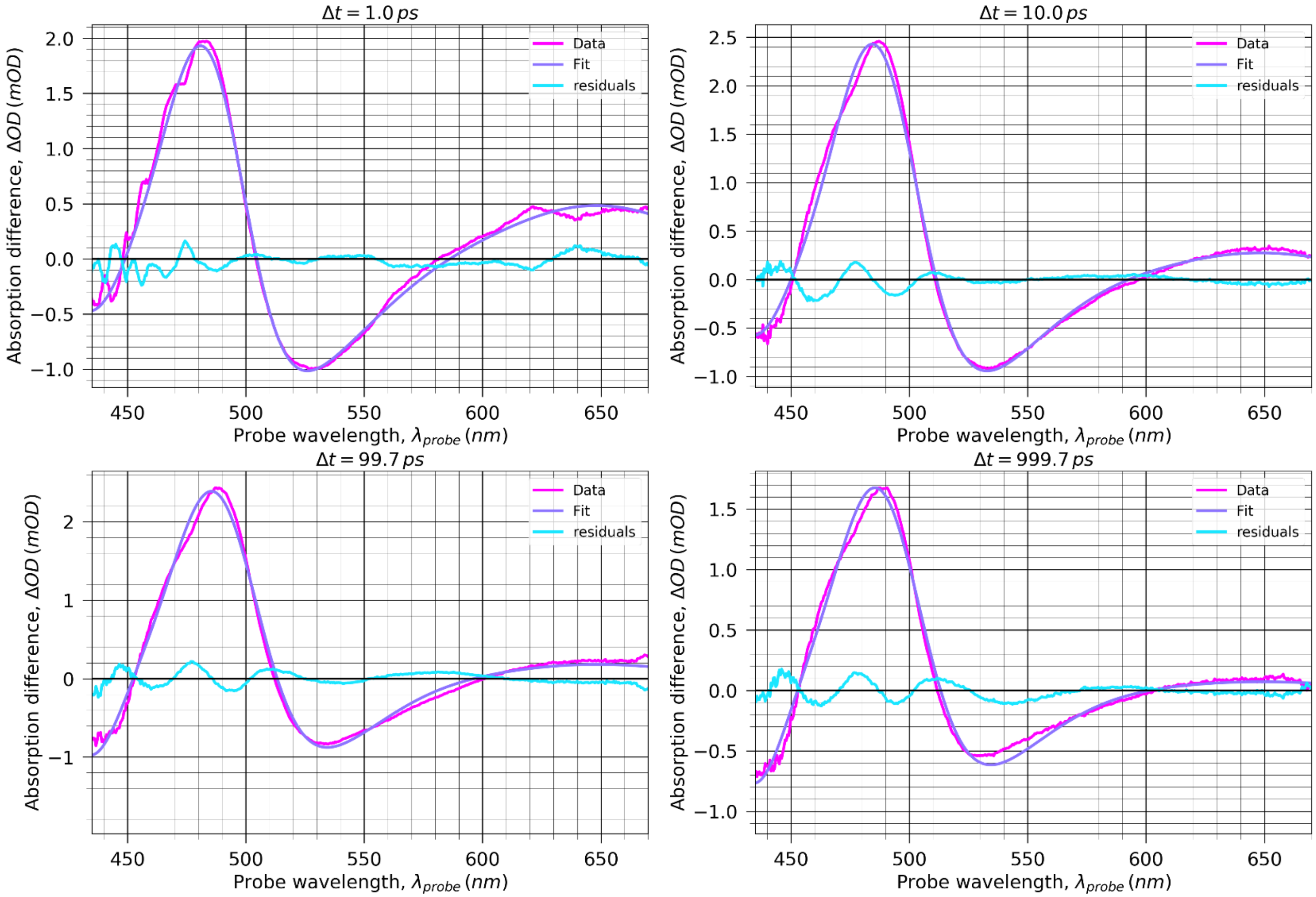
Global Model components



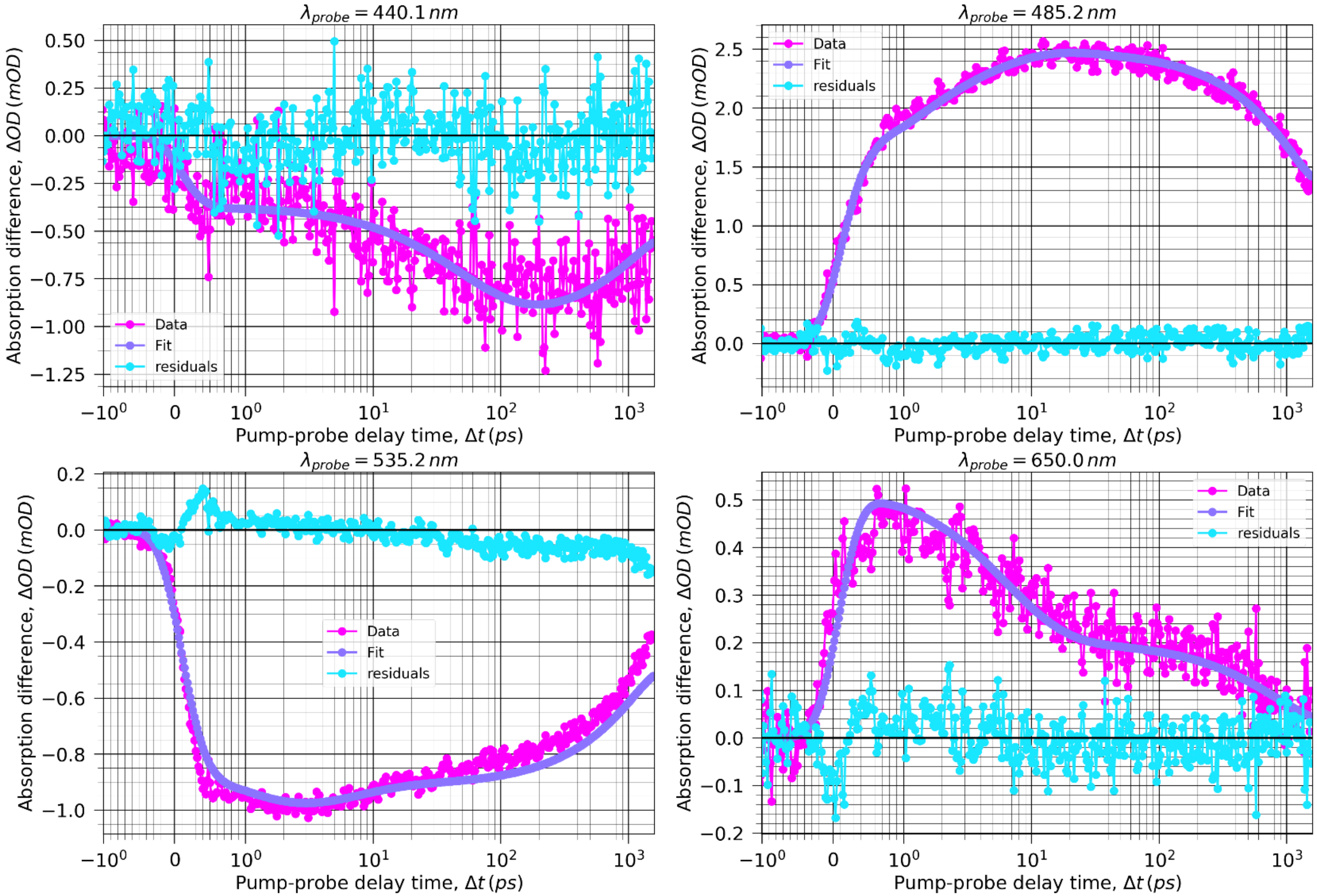
Transient Global Analysis



Global fitting (λ-domain)



Global fitting (Δt-domain)



Transient absorption λ-domain fitting results

Process	Parameter	yd-lnb1-151		yd-lnb1-153		js-lnb1-095	
		value	95% CI	value	95% CI	value	95% CI
GSB	μ (nm)	437.66228	-0.04502 +0.04519	439.36414	-0.04189 +0.04182	434.6977	-0.06948 +0.08272
	σ (nm)	9.14088	-0.03291 +0.03333	8.88179	-0.04107 +0.04040	11.27772	-0.04666 +0.04827
SE-F	μ (nm)	493.18766	-0.03948 +0.03948	498.56881	-0.12228 +0.12247	495.2278	-0.05615 +0.05615
	σ (nm)	16.69671	-0.03273 +0.03306	18.21548	-0.07958 +0.08050	17.43199	-0.04541 +0.04603
SE-P	μ (nm)	521.46718	-0.15032 +0.15449	523.46982	-0.19862 +0.19916	519.9975	-0.16748 +0.17242
	σ (nm)	35.41022	-0.10723 +0.10223	32.30041	-0.11623 +0.11688	32.90997	-0.10229 +0.09734
ESA-S	μ (nm)	669.0364	-0.53963 +0.54042	646.26843	-0.37506 +0.37125	648.7864	-0.25646 +0.25932
	σ (nm)	68.53057	-0.38822 +0.38832	37.01925	-0.27999 +0.28587	39.22776	-0.19212 +0.19183
ESA-T	μ (nm)	486.96031	-0.01444 +0.02661	488.10308	-0.01864 +0.01864	487.5251	-0.01892 +0.01892
	σ (nm)	17.53088	-0.01641 +0.01618	16.84961	-0.02193 +0.02156	17.59995	-0.01884 +0.01865

Transient absorption Δt-domain fitting results

process	parameter	yd-lnb1-151		yd-lnb1-153		js-lnb1-095	
		value	95% CI	value	95% CI	value	95% CI
GSB	τ_g (ps)	19.36173	-0.49867 +0.51345	43.99549	-3.49678 +3.93088	50.14525	-1.50608 +1.54544
	τ_d (ps)	5108.32365	-44.79718 +45.57681	3220.57974	-24.90109 +25.27116	2486.243	-14.90020 +15.13987
SE-F	τ_d (ps)	4.568	-0.06072 +0.06124	6.59482	-0.12629 +0.12901	6.74512	-0.09560 +0.09592
SE-P	τ_g (ps)	0.74075	-0.01392 +0.01411	0.94857	-0.03556 +0.03669	0.66646	-0.02205 +0.02244
	τ_d (ps)	5108.32365	-44.79718 +45.57681	3220.57974	-24.90109 +25.27116	2486.243	-14.90020 +15.13987
ESA-S	τ_{d1} (ps)	4.568	-0.06072 +0.06124	6.59482	-0.12629 +0.12901	6.74512	-0.09560 +0.09592
	τ_{d2} (ps)	622.49904	-20.68767 +21.41418	1230.82751	-61.83303 +66.87382	929.1458	-32.26215 +33.86401
ESA-T	τ_g (ps)	0.74075	-0.01392 +0.01411	0.94857	-0.03556 +0.03669	0.66646	-0.02205 +0.02244
	τ_{d1} (ps)	4.366	-0.08966 +0.09062	8.94984	-0.31261 +0.31999	8.43351	-0.20654 +0.20825
	τ_{d2} (ps)	5108.32365	-44.79718 +45.57681	3220.57974	-24.90109 +25.27116	2486.243	-14.90020 +15.13987

Transient absorption Δt-domain fitting results

process	parameter	yd-lnb1-151 value	yd-lnb1-151 95% CI	yd-lnb1-153 value	yd-lnb1-153 95% CI	js-lnb1-095 value	js-lnb1-095 95% CI
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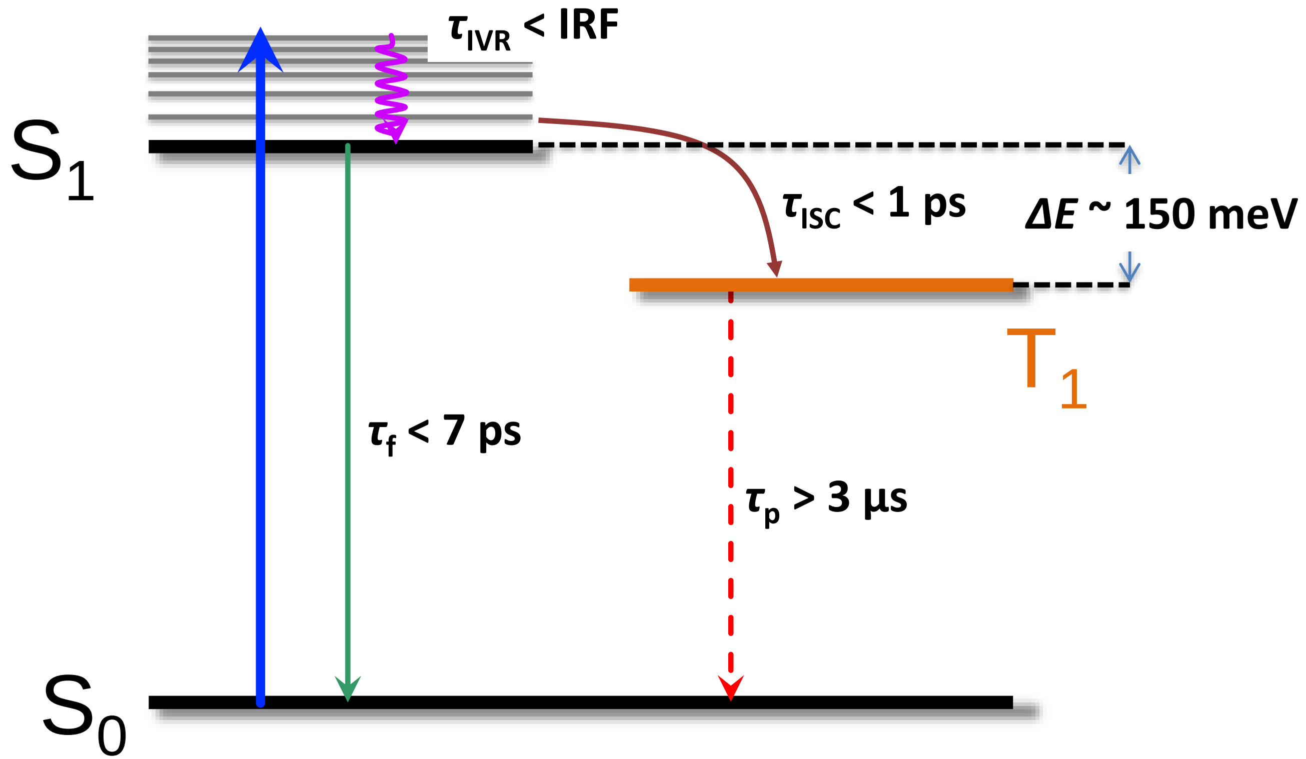
	τ_d (ps)	5108.32365	-44.79718 +45.57681	3220.57974	-24.90109 +25.27116	2486.243	-14.90020 +15.13987
ESA-S	τ_{d1} (ps)	4.568	-0.06072 +0.06124	6.59482	-0.12629 +0.12901	6.74512	-0.09560 +0.09592
	τ_{d2} (ps)	622.49904	-20.68767 +21.41418	1230.82751	-61.83303 +66.87382	929.1458	-32.26215 +33.86401
ESA-T	τ_g (ps)	0.74075	-0.01392 +0.01411	0.94857	-0.03556 +0.03669	0.66646	-0.02205 +0.02244
	τ_{d1} (ps)	4.366	-0.08966 +0.09062	8.94984	-0.31261 +0.31999	8.43351	-0.20654 +0.20825
	τ_{d2} (ps)	5108.32365	-44.79718 +45.57681	3220.57974	-24.90109 +25.27116	2486.243	-14.90020 +15.13987

?

Intermolecular quenching?

Kinetic model



Outline

- Motivation
  - Transition-metals based photocatalysts
  - Organophotoredox catalysts
  - Novel polymer-based organophotoredox catalysts
- Experimental
  - Femtosecond transient absorption (TA) spectroscopy
- Results and Discussion
  - Steady-state absorption (Abs)
  - Steady-state Photoluminescence spectroscopy (PL)
  - Time-resolved photoluminescence (TRPL)
  - Femtosecond transient absorption (TA) spectroscopy
  - Simulation and fitting of the TA spectra
  - Rate constants of photoinduced processes
- Summary and Future Work

Conclusions and Future Works

- Steady state absorption, emission, photoluminescence lifetimes, and transient absorption spectra were collected for three novel polymer-based organophotoredox catalysts.
- A preliminary TA global model was devised based on steady-state spectra, and general observations of the TA spectra. The model was used to fit the data, decently. Yet, some fitting parameters have yet to be correlated to a physical process.
- Long-lived triplet state through photoluminescence lifetimes measurements, and short-lived singlet states through femtosecond TA measurements, suggests a high photoredox catalytic capabilities for these class of polymers.

- Further investigation of these polymers catalytic activity.
- Refine the global model to better understand the photophysics of these polymers..
- Explore the uncovered portions of the spectrum in the UV region (<400 nm).
- Solvent-dependent dynamics.
- Uncover any electron transfer processes between the photoredox catalysts and the excited-state quenchers.

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