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Supporting Information

Reverse saturable absorbing cationic iridium(III) complexes bearing 2-(2-quinolinyl)quinoxaline ligand: Effects of different cyclometalating ligands on the linear and nonlinear absorption

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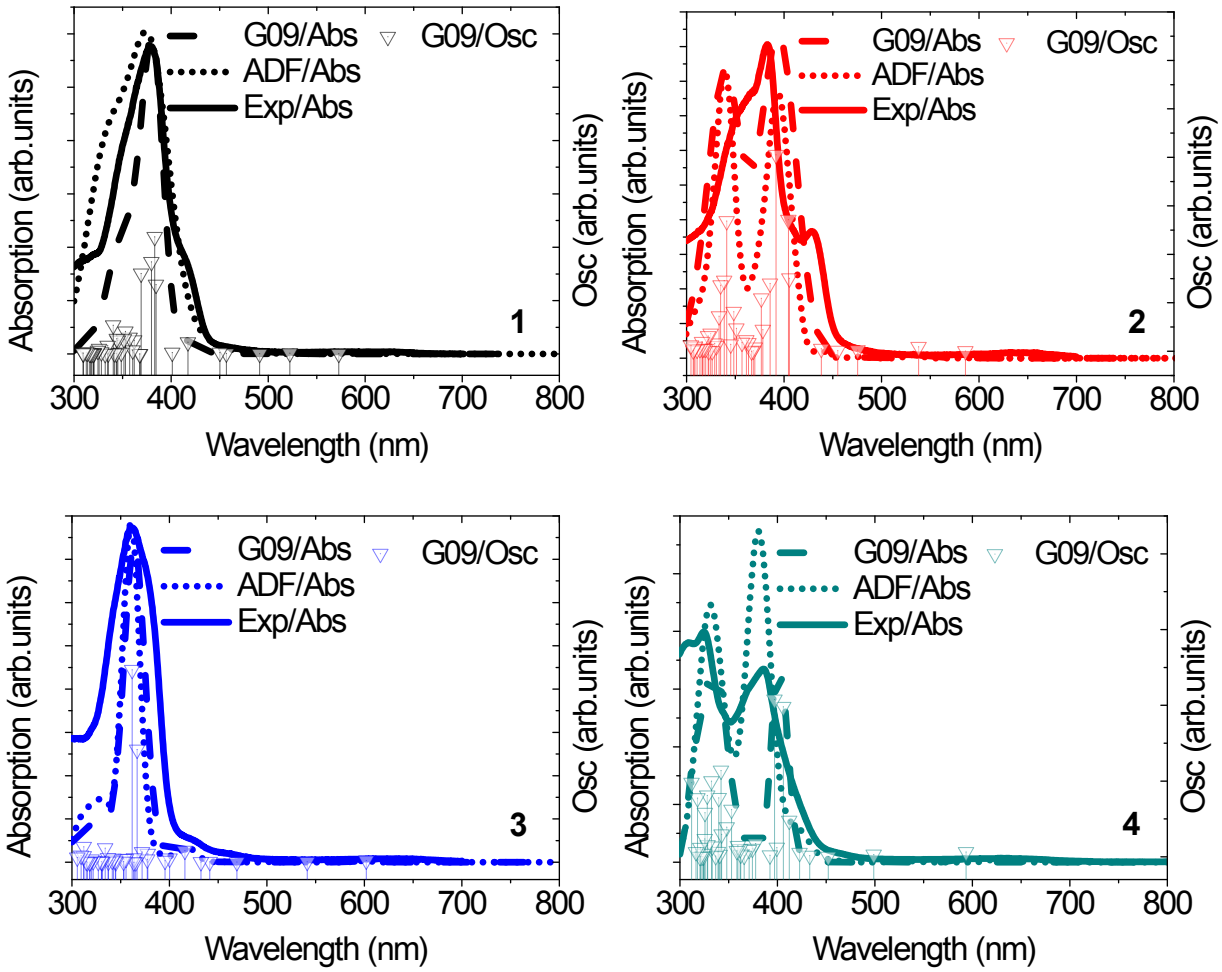


Figure S1. Comparison of UV-vis absorption spectra of **1** – **4** in CH_2Cl_2 calculated by Gaussian09 (dashed line) and ADF (dotted line) software packages, respectively. All calculations do not include spin-orbit coupling.

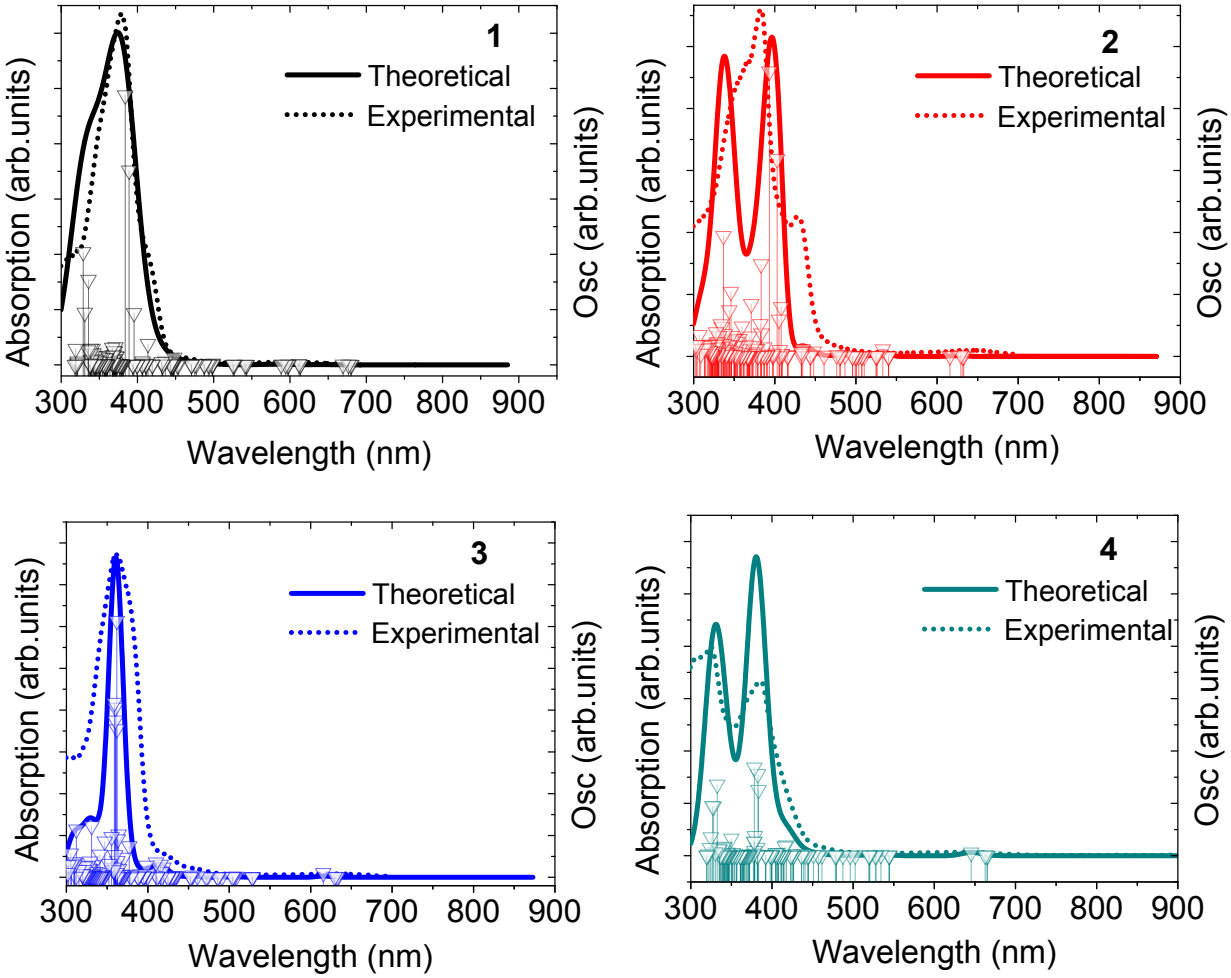


Figure S2. Comparison of the experimental and theoretical UV-vis absorption spectra of **1 – 4** in CH_2Cl_2 when spin-orbit coupling effect is taken into account.

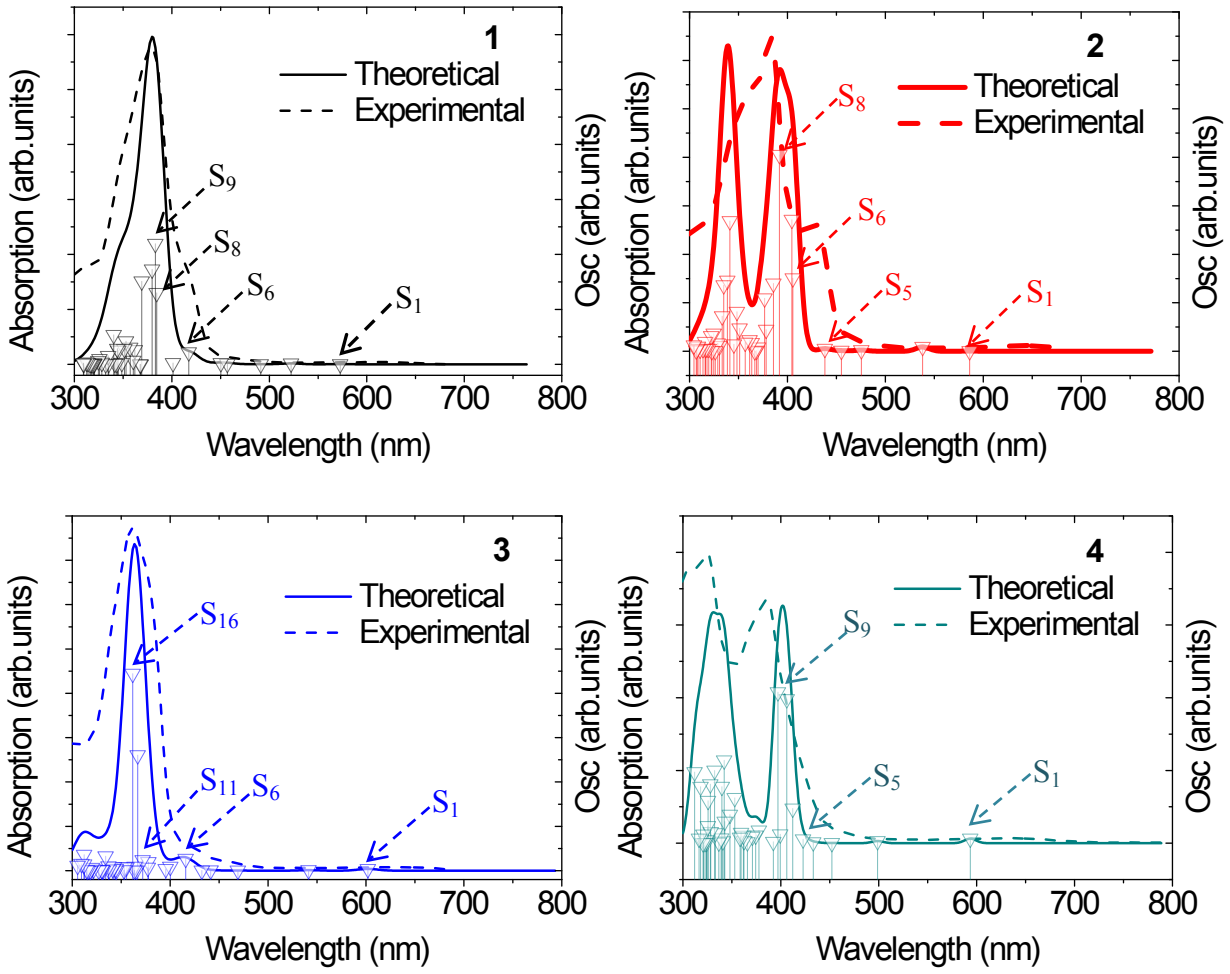
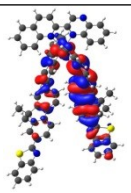
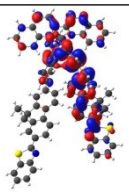
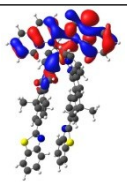
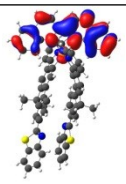
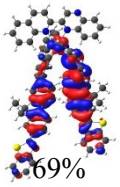
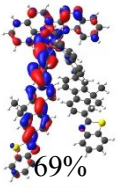
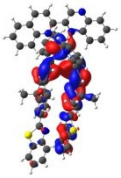
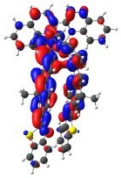
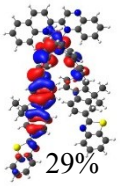
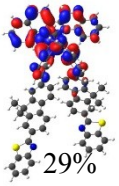
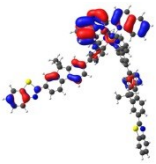
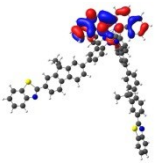
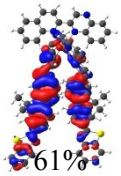
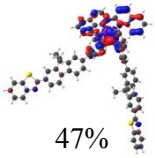
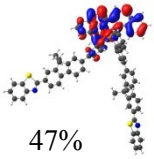
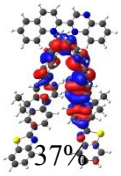
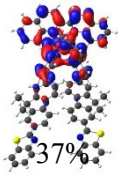
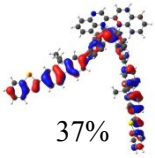
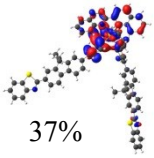
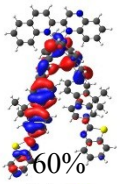
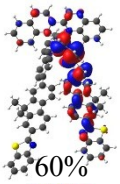
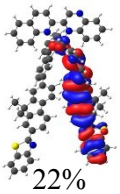
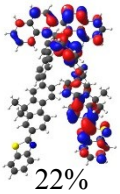
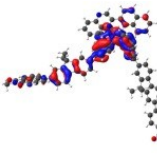
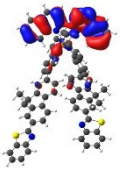
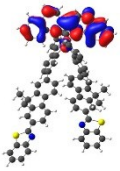


Figure S3. Comparison of the experimental and theoretical UV-vis absorption spectra of **1 – 4** in CH_2Cl_2 calculated by Gaussian09 software without spin-orbit coupling.

Table S1. Natural transition orbitals (NTOs) representing the high-energy major absorption bands.

	Transition states	Hole	Electron			Hole	Electron
1	S_{10} 380 nm $f = 0.86$			**2**	S_{19} 348 nm $f = 0.17$		
	S_{14} 362 nm $f = 0.13$	 69%	 69%		S_{21} 341 nm $f = 0.54$		
		 29%	 29%	**3**	S_{26} 334 nm $f = 0.16$		
	S_{16} 357 nm $f = 0.15$	 61%	 61%		S_{37} 312 nm $f = 0.18$	 47%	 47%
		 37%	 37%			 37%	 37%
	S_{21} 344 nm $f = 0.14$	 60%	 60%	**4**	S_{28} 332 nm $f = 0.20$		
		 22%	 22%		S_{38} 318 nm $f = 0.16$		
	S_{24} 340 nm $f = 0.27$						

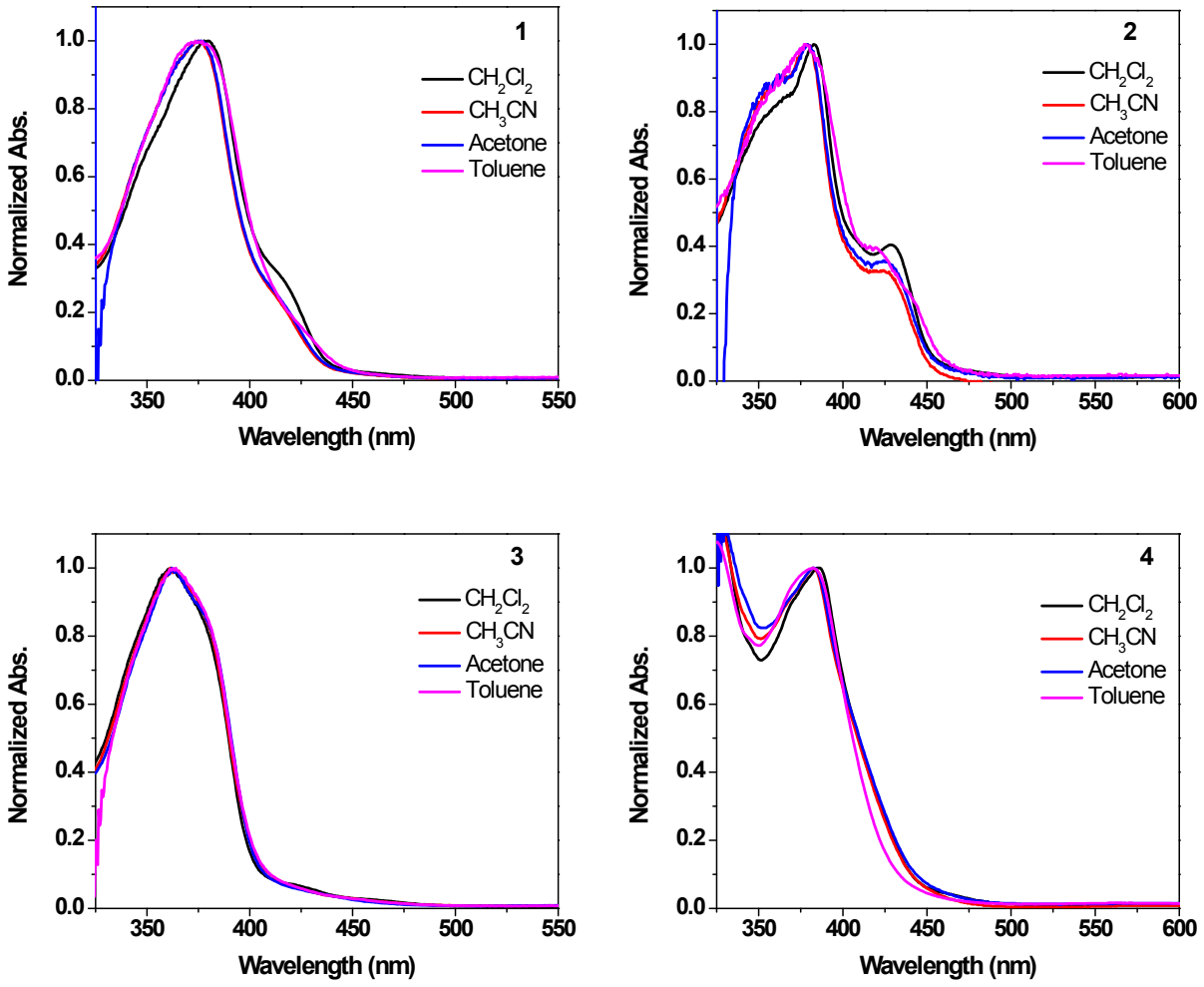


Figure S4. Normalized UV-vis absorption spectra of complexes **1** – **4** in different solvents at r.t.

Table S2. Emission energies, lifetimes and quantum yields of complexes **1** and **2** in different solvents at R.T.

	λ_{em} / nm (τ_{em} / ns; Φ_{em})			
	CH_3CN	CH_2Cl_2	Toluene	Acetone
1	701 (102; 0.041)	704 (192; 0.066)	688 (64; 0.028)	702 (112; 0.048)
2	753 (29; 0.008)	742 (61; 0.024)	- (-; -)	752 (26; 0.010)

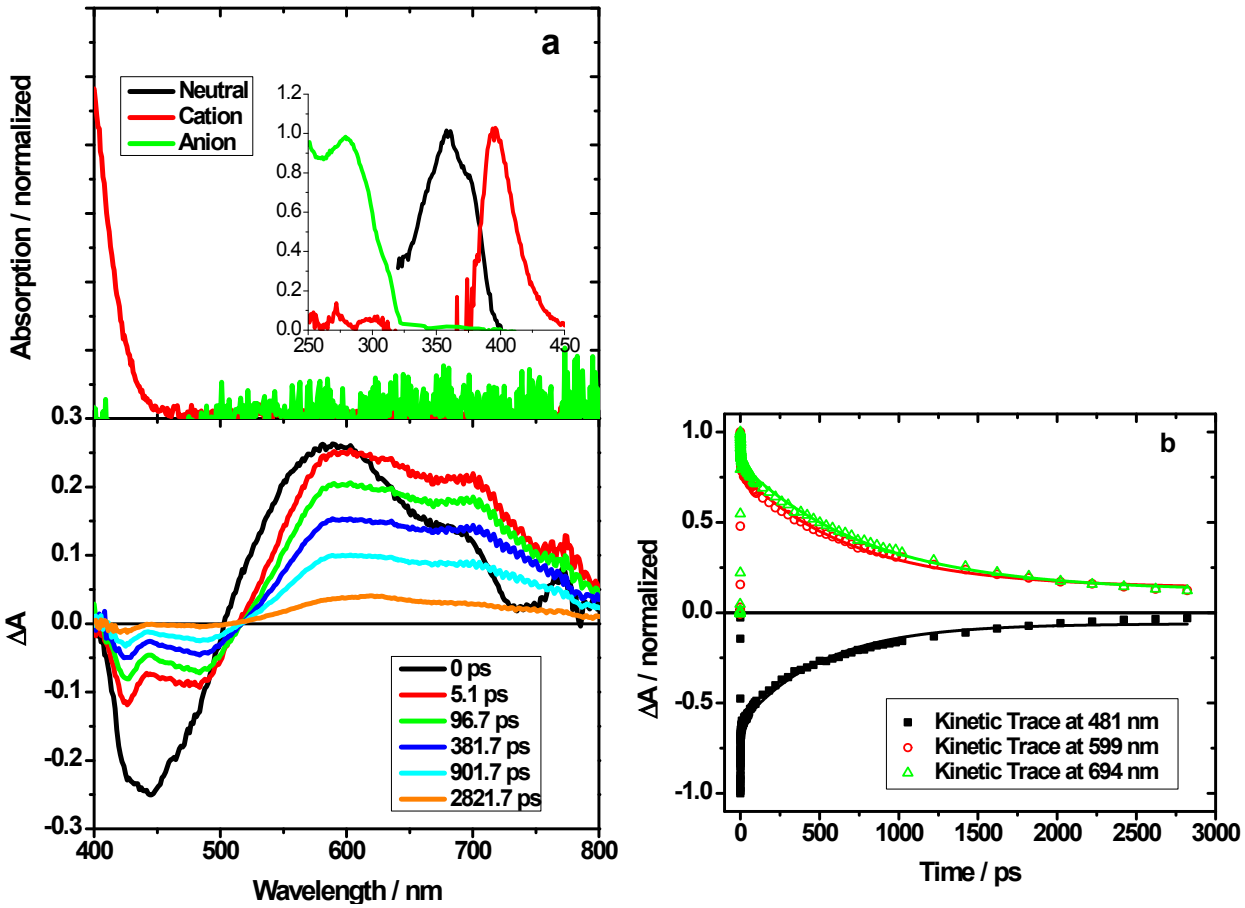


Figure S5. (a) Top Panel: Absorption spectra of the neutral (black), cation (red), and anion (green) of ligand **6**. Bottom Panel: Time-resolved fs TA spectra of **6** at various time delays after 390 nm excitation (noted in legend). The inset shows the steady state absorption from 250 to 450 nm. (b) Kinetic traces and their fits for **6**. The parameters of these fits are summarized in Table S3 below.

Table S3. Kinetic fit of ligand **6**.

λ / nm	τ_1 / ps	τ_2 / ps
481	2.03 ± 0.06	510.8 ± 14.4
599	5.5 ± 0.3	706.4 ± 16.5
694	4.0 ± 0.2	812.5 ± 20.1

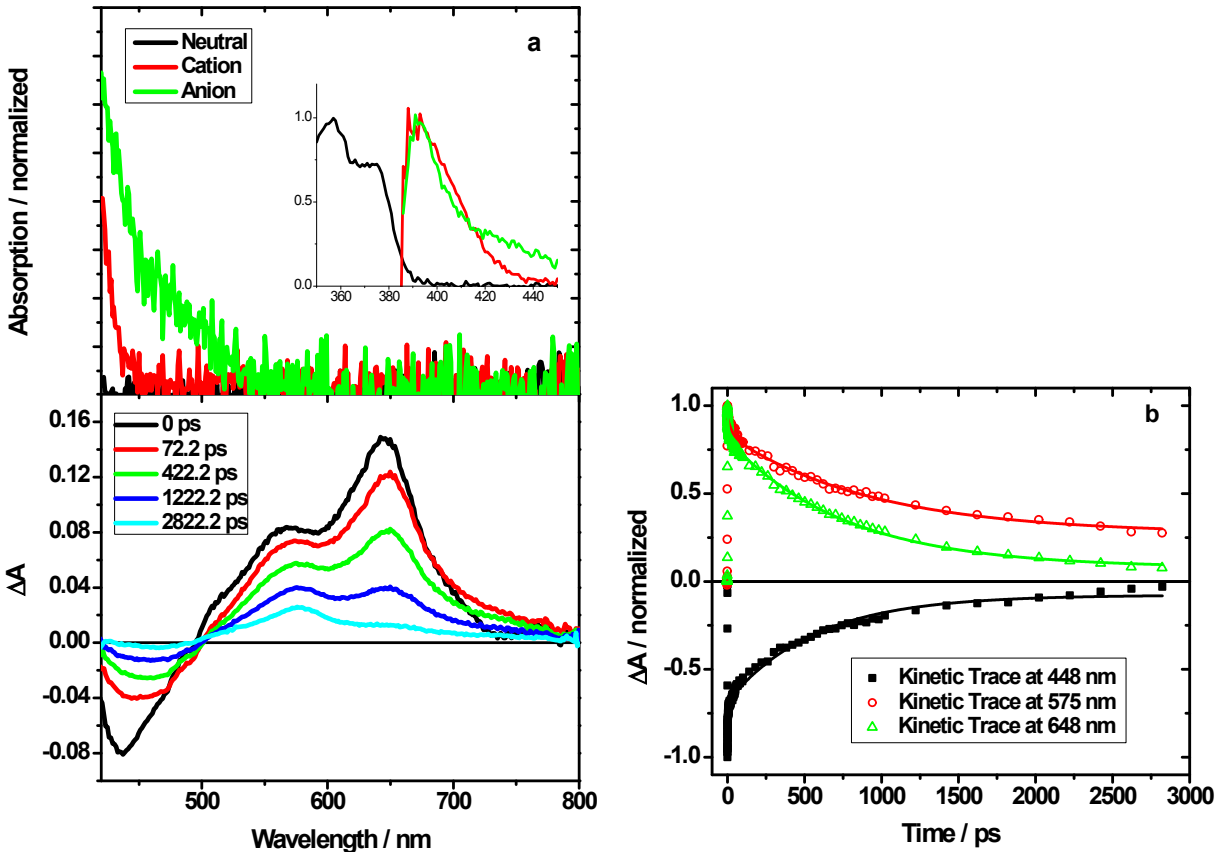


Figure S6. (a) Top Panel: Absorption spectra of the neutral (black), cation (red), and anion (green) of ligand **7** in CH_2Cl_2. Bottom Panel: Time-resolved fs TA spectra of **7** at various time delays after 390 nm excitation (noted in legend). The inset shows the steady state absorption from 350 to 450 nm. (b) Kinetic traces and their fits for **7**. The parameters of these fits are summarized in Table S4 below.

Table S4. Kinetic fit of ligand **7**.

λ / nm	τ_1 / ps	τ_2 / ps
448	4.2 ± 0.3	562.0 ± 20.6
575	31.8 ± 6.8	942.9 ± 63.7
648	7.4 ± 0.4	762.0 ± 17.0

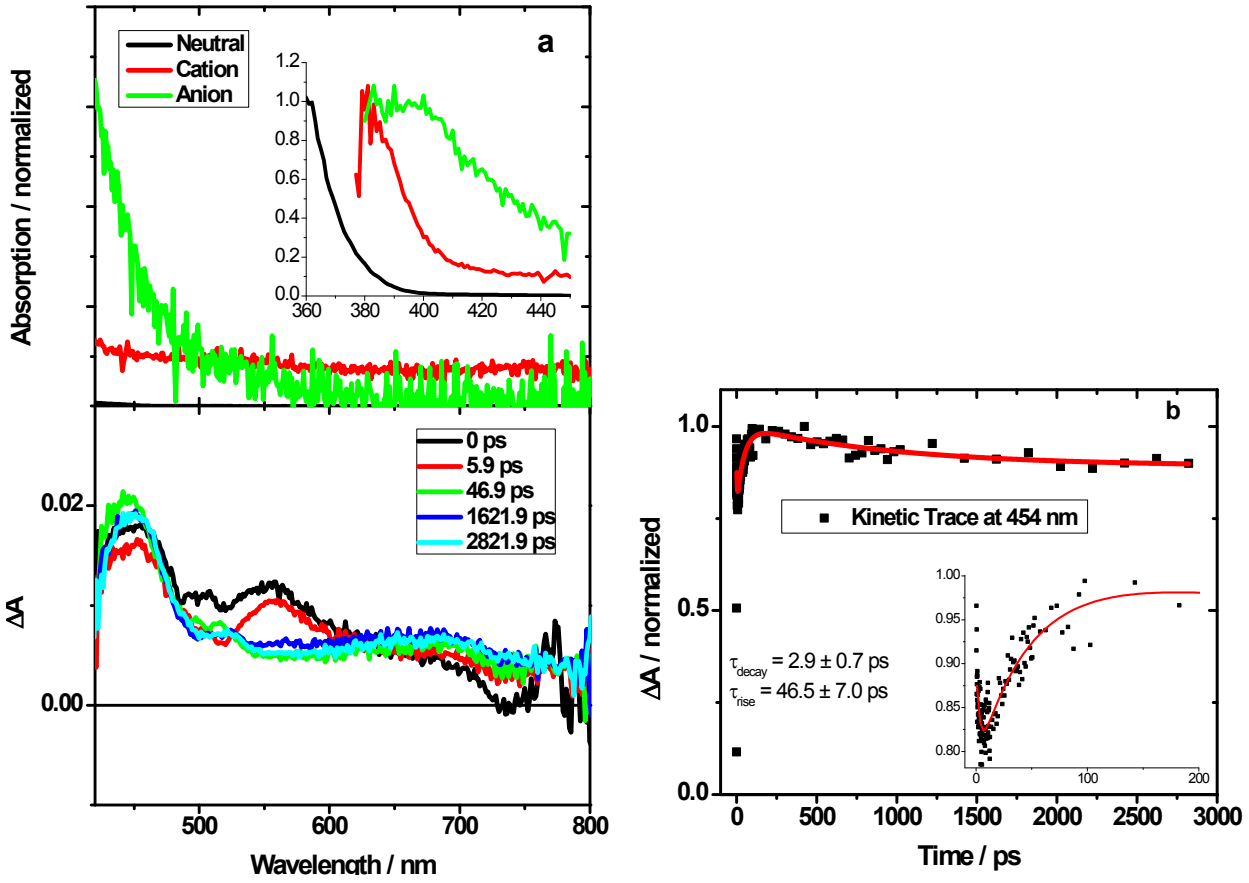


Figure S7. (a) Top Panel: Absorption spectra of the neutral **quqo** (black), cation (red), and anion (green). Bottom Panel: Time-resolved fs TA spectra of **quqo** at various time delays after 390 nm excitation (noted in legend). The inset shows the steady state absorption from 300 to 450 nm. (b) Kinetic traces and their fits for **quqo**. Kinetics was measured at 454 nm (black squares). The inset shows an enhanced view of the first 200 ps. In addition to the fast decay with a lifetime of ~3 ps followed by a rise with a lifetime of ~46 ps, there was a final decay that could not be measured within our time window.

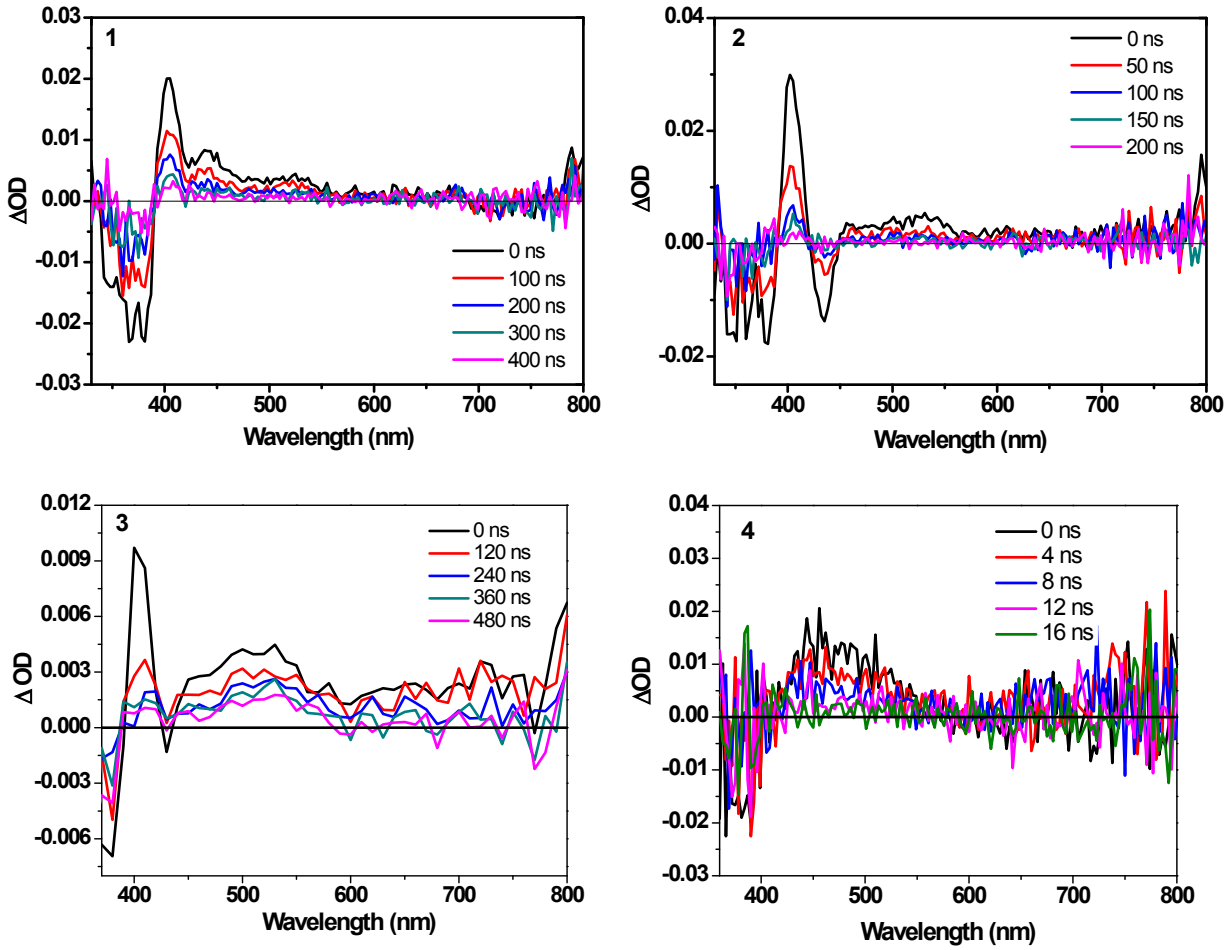


Figure S8. Time-resolved ns TA spectra of complexes **1** – **4** in CH_2Cl_2. The excitation wavelength was 355 nm, and the absorbance of the sample solutions was adjusted to 0.4 at 355 nm in a 1-cm cuvette.

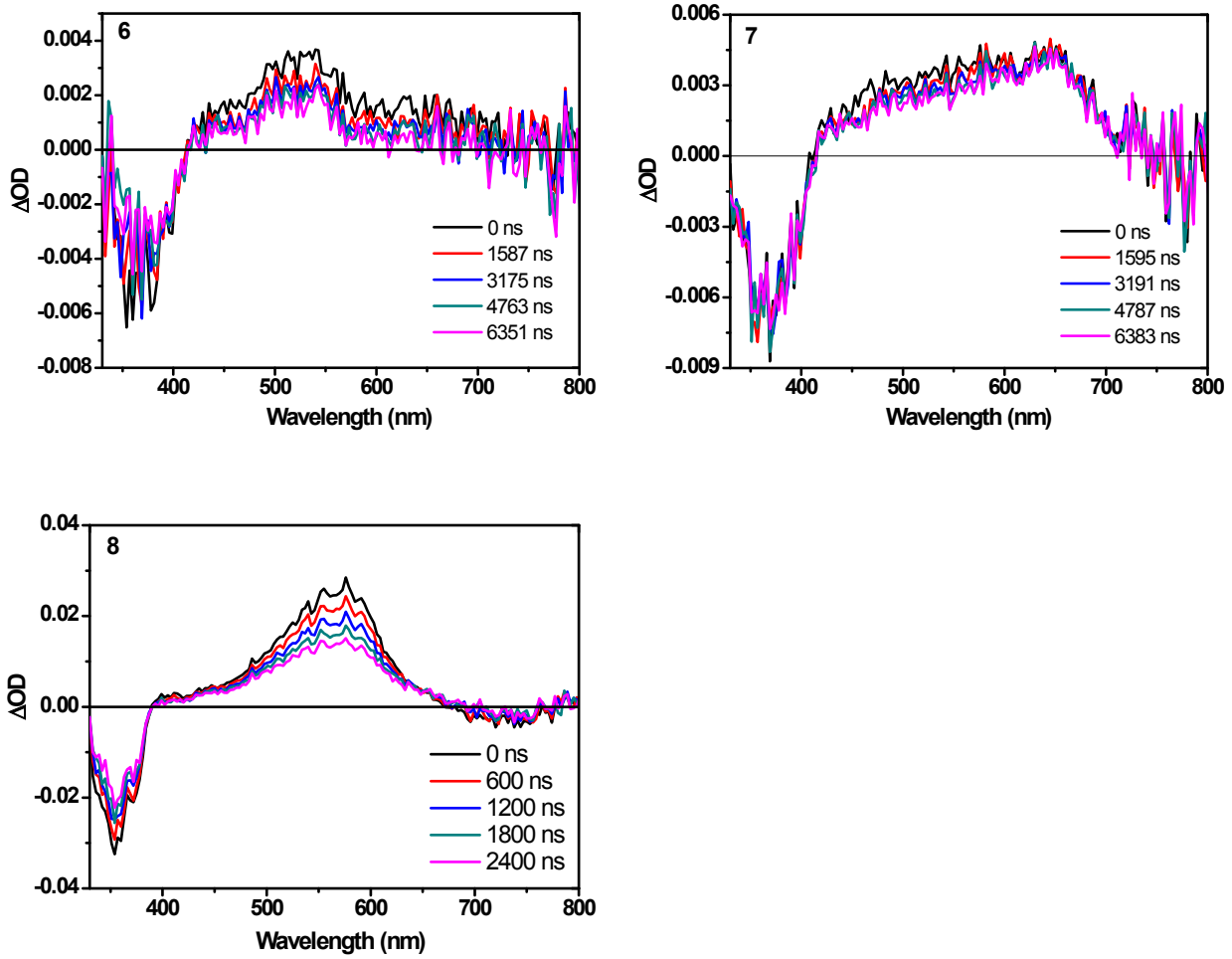


Figure S9. Time-resolved ns TA spectra of ligands **6** – **8** in CH_2Cl_2. The excitation wavelength was 355 nm, and the absorbance of the sample solutions was adjusted to 0.4 at 355 nm in a 1-cm cuvette.