

## Supporting Information

# **Synthesis, Photophysics, and Reverse Saturable Absorption of Platinum Complexes Bearing Extended $\pi$ -Conjugated C<sup>N</sup>N Ligand**

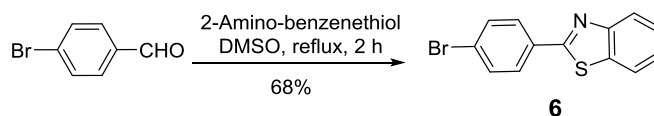
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*ND 58108-6050*

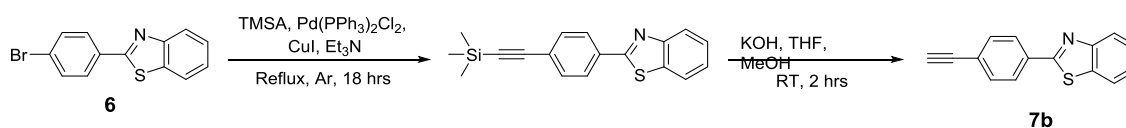
## Synthesis of intermediates 6, 7b and 9

### Synthesis of 6.



The mixture of 4-bromobenzaldehyde (3.7 g, 20 mmol), 2-amino-benzenethiol (2.5 g, 20 mmol), and DMSO (20 mL) was heated to reflux for 2 hrs. After the reaction, the off-white precipitate formed upon cooling was collected and dissolved into dichloromethane. The solution was discolored by stirring with activated carbon pellets under reflux. The carbon pellets were removed by filtration after the solution cooled down to room temperature. The solvent of the filtrate was then removed by distillation. 3.96 g white powder was collected as the product (yield: 68%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.03 – 8.06 (m, 1H), 7.92 – 7.96 (m, 2H), 7.87 – 7.90 (m, 1H), 7.59 – 7.62 (m, 2H), 7.46 – 7.50 (m, 1H), 7.36 – 7.40 (m, 1H).

### Synthesis of 7b.

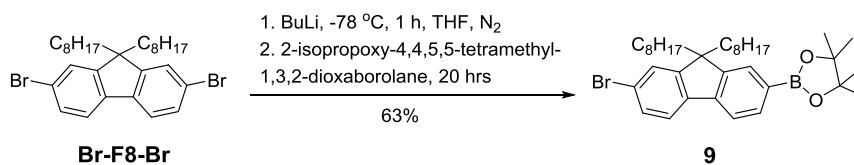


*Trimethyl-(4-BTZ-phenylethynyl)-silane.* Compound **6** (0.38 g, 1.3 mmol) was dissolved in 30 mL triethylamine and the solution was degassed.  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (58 mg),  $\text{PPh}_3$  (98 mg) and  $\text{CuI}$  (48 mg) was then added. The system was purged with argon again and TMSA (0.5 mL, 3.6 mmol) was injected. The mixture was then heated to reflux for 18 hrs. After reaction, the black precipitate was removed by

filtration. The solvent from the filtrate was removed by distillation. The residue was purified by running a silica gel column eluted with a mixed solvent of dichloromethane and hexane (v/v = 1/1). 0.35 g white powder was collected as the product (yield: 88%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.04 – 8.06 (m, 1H), 8.00 – 8.02 (m, 2H), 7.88 – 7.90 (m, 1H), 7.54 – 7.56 (m, 2H), 7.46 – 7.50 (m, 1H), 7.35 – 7.39 (m, 1H), 0.25 (s, 9H).

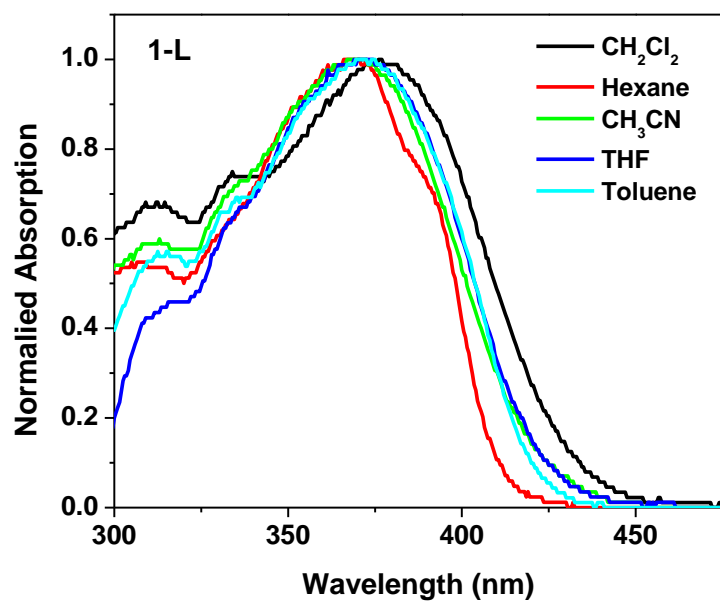
**7b.** The mixture of trimethyl-(4-BTZ-phenylethynyl)-silane (0.35 g, 1.1 mmol), KOH (0.56 g, 10 mmol), THF (6 mL),  $\text{CH}_3\text{OH}$  (6 mL), and water (1 mL) was stirred at room temperature for 2 hours. After reaction, the solvent was removed by distillation and the residue was dissolved in dichloromethane. The dichloromethane solution was washed with brine twice and dried over  $\text{MgSO}_4$ . After removal of the solvent, 0.26 g yellow powder was collected as the product (yield: 97%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.03 – 8.07 (m, 3H), 7.88 – 7.90 (m, 1H), 7.58 – 7.60 (m, 2H), 7.46 – 7.50 (m, 1H), 7.36 – 7.40 (m, 1H), 3.20 (s, 1H).

### Synthesis of 9.

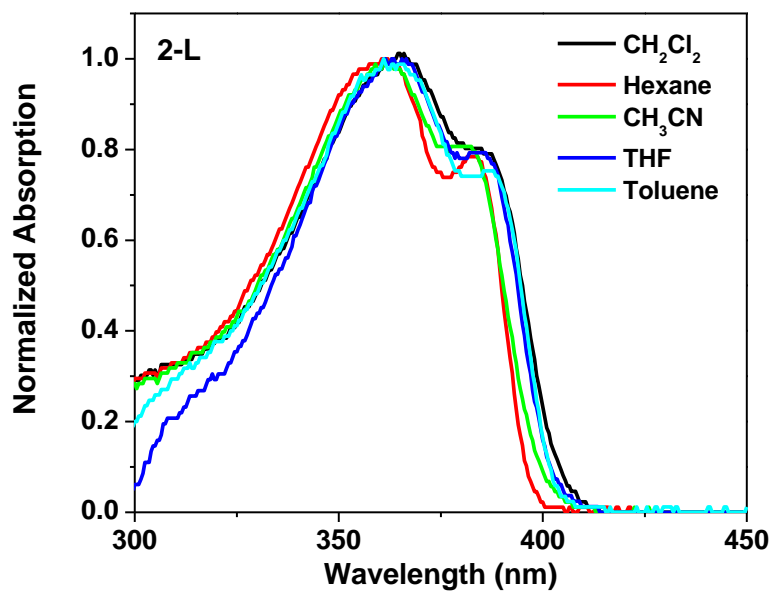


Compound Br-F8-Br (5.14 g, 9.4 mmol) was dissolved in 20 mL THF and the solution was degassed and cooled down to  $-78$  °C. BuLi (4.1 mL, 10.3 mmol) was then added dropwise. The solution was stirred under argon for 1 hour.

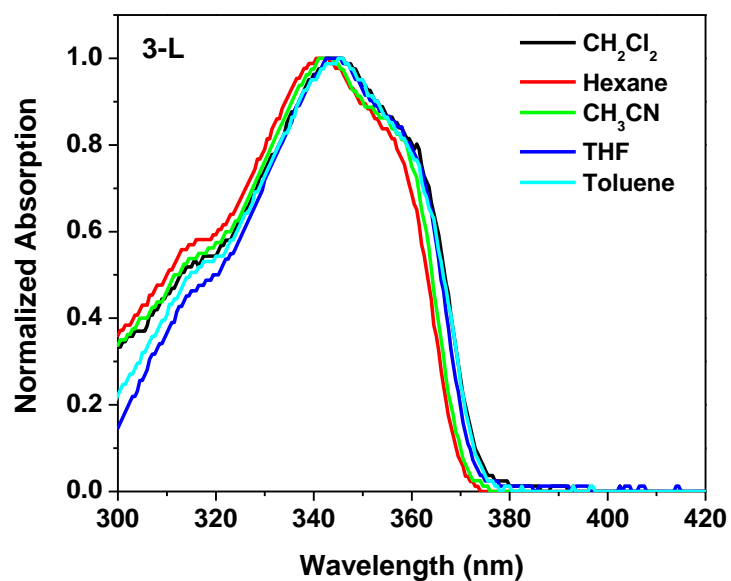
2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.92 mL, 0.912 g/mL, 9.4 mmol) was then added dropwise and the reaction mixture was allowed to warm up to room temperature for 20 hours. After the reaction, the organic layer was washed with saturated NH<sub>4</sub>Cl aqueous solution and dried over MgSO<sub>4</sub>. The solvent was removed and the residue was purified by running a silica gel column eluted with a mixed solvent of hexane/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 3/1). 3.55 g colorless oil was collected as the product (yield: 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 7.75 – 7.80 (m, 2H), 7.61 – 7.63 (m, 1H), 7.53 – 7.55 (m, 1H), 7.47 – 7.48 (m, 1H), 7.40 – 7.43 (m, 1H), 1.87 – 2.01 (m, 4H), 1.33 (s, 12H), 0.63 – 0.95 (m, 22H), 0.42 – 0.53 (m, 8H).



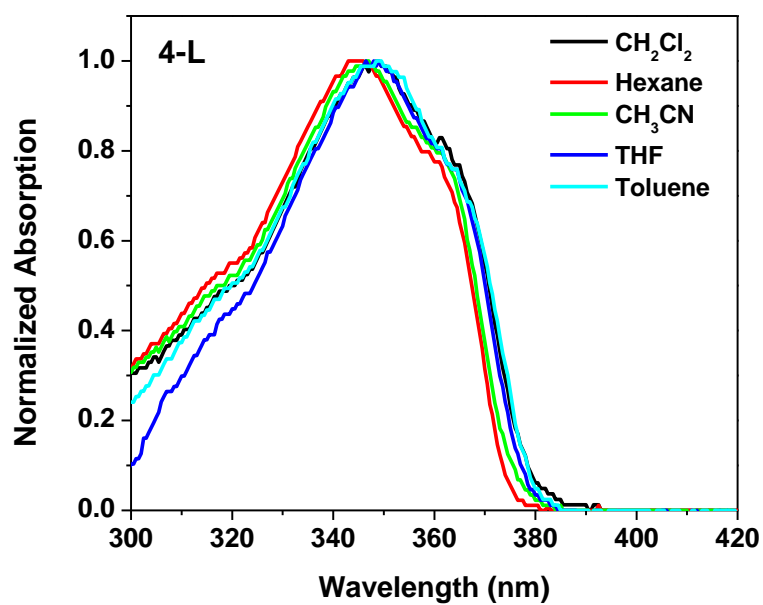
**Figure S1.** Normalized absorption spectra of **1-L** in different solvents.



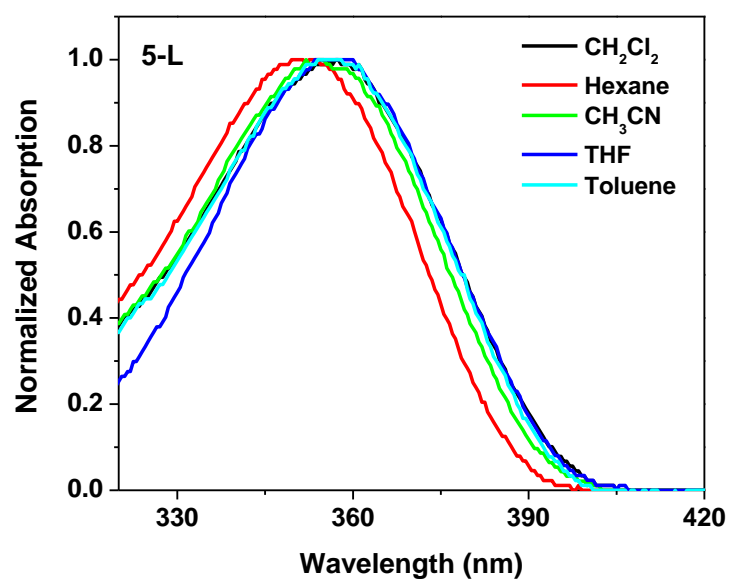
**Figure S2.** Normalized absorption spectra of **2-L** in different solvents.



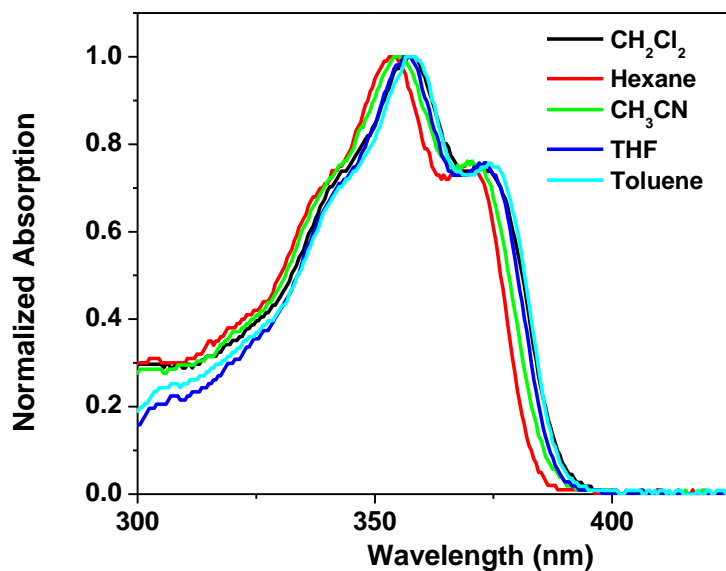
**Figure S3.** Normalized absorption spectra of **3-L** in different solvents.



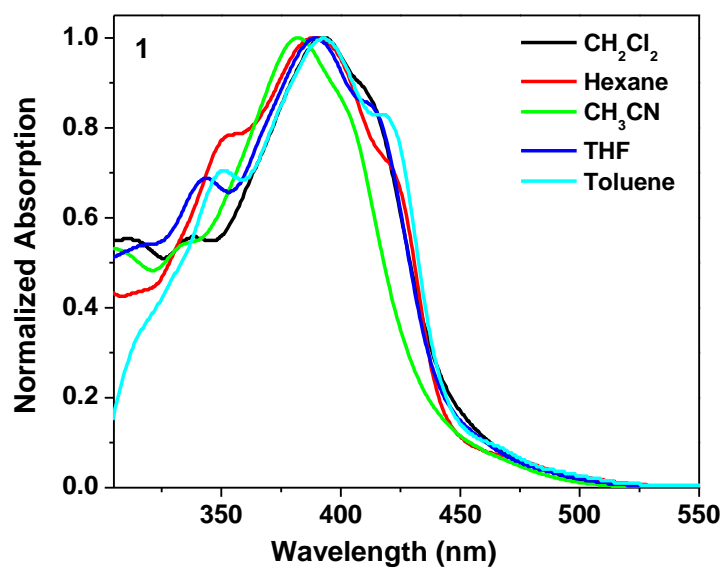
**Figure S4.** Normalized absorption spectra of **4-L** in different solvents.



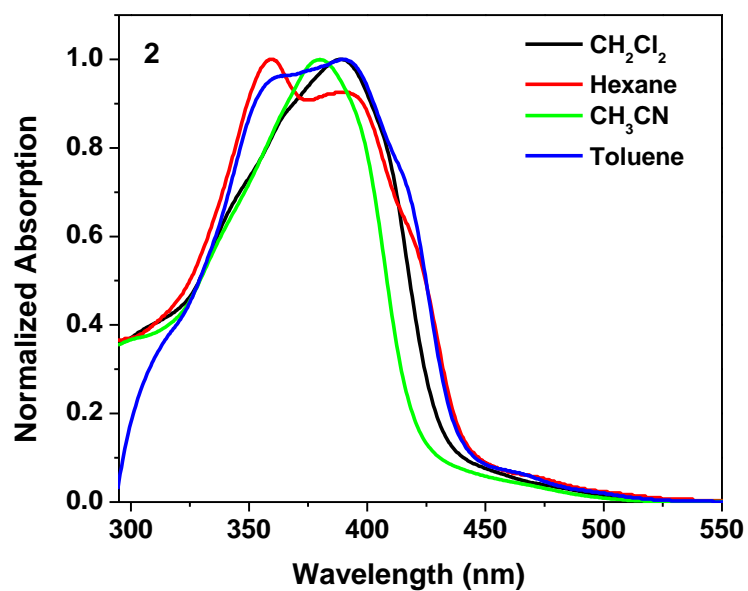
**Figure S5.** Normalized absorption spectra of **5-L** in different solvents.



**Figure S6.** Normalized absorption spectra of **6-L** in different solvents.

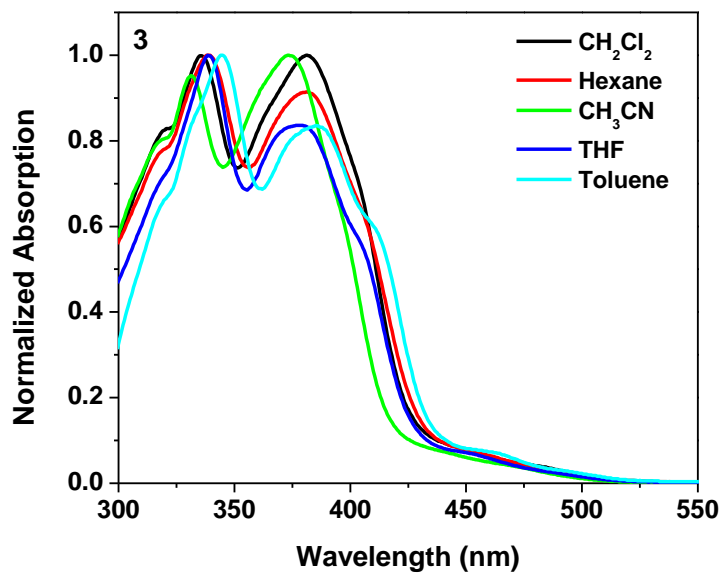


**Figure S7.** Normalized absorption spectra of **1** in different solvents.

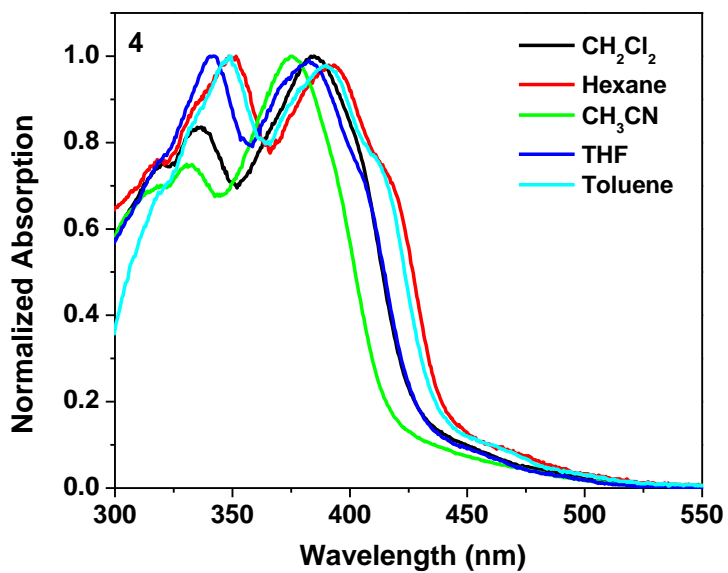


**Figure S8.** Normalized absorption spectra of **2** in different solvents.

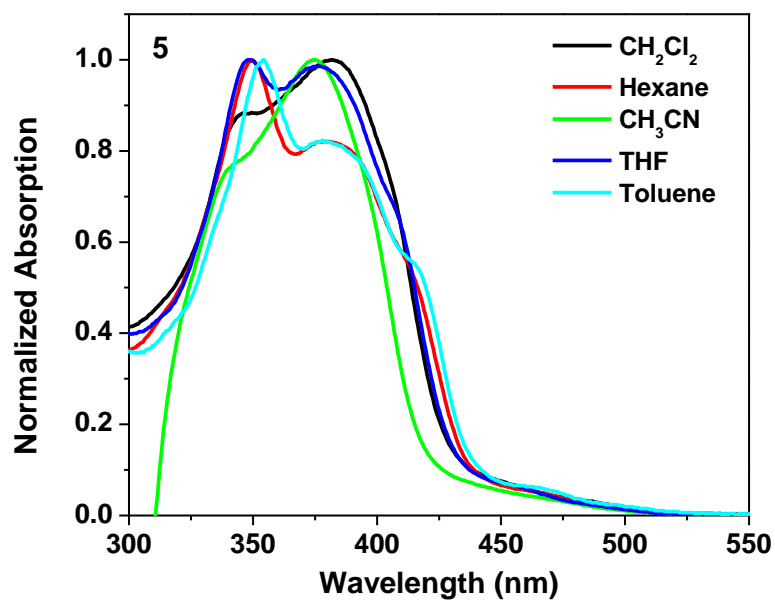




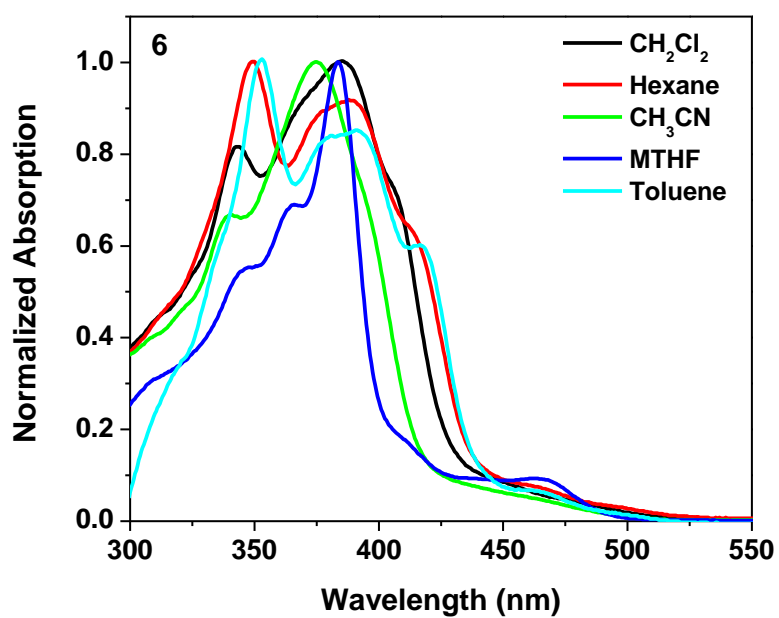
**Figure S9.** Normalized absorption spectra of **3** in different solvents.



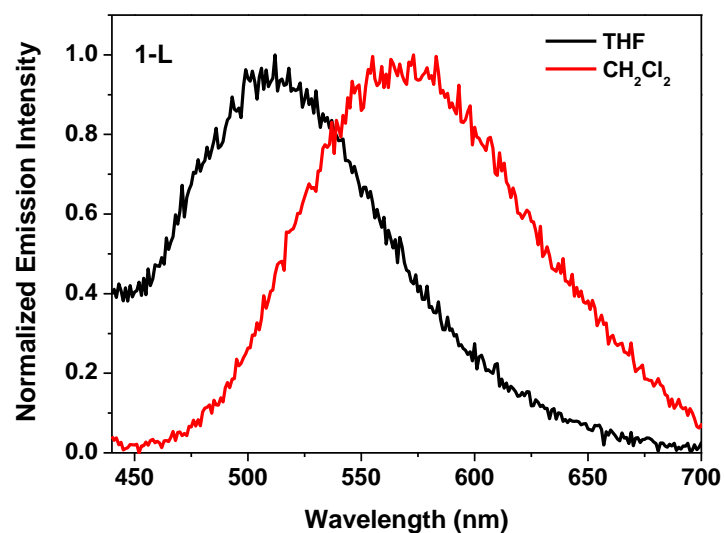
**Figure S10.** Normalized absorption spectra of **4** in different solvents.



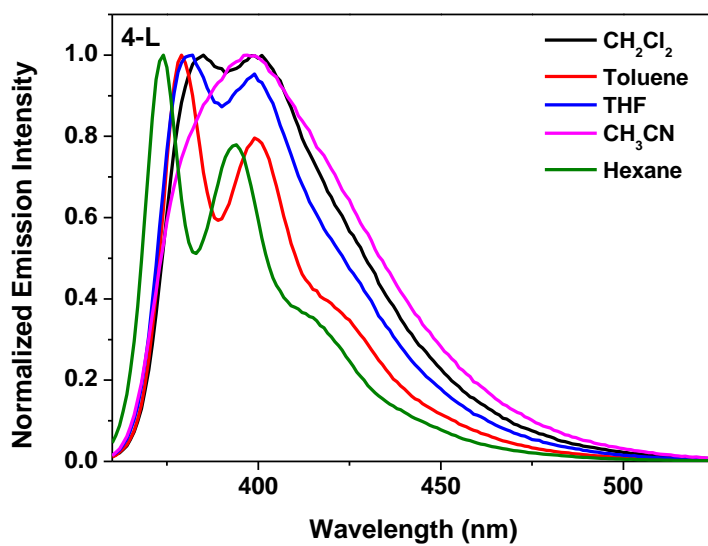
**Figure S11.** Normalized absorption spectra of **5** in different solvents.



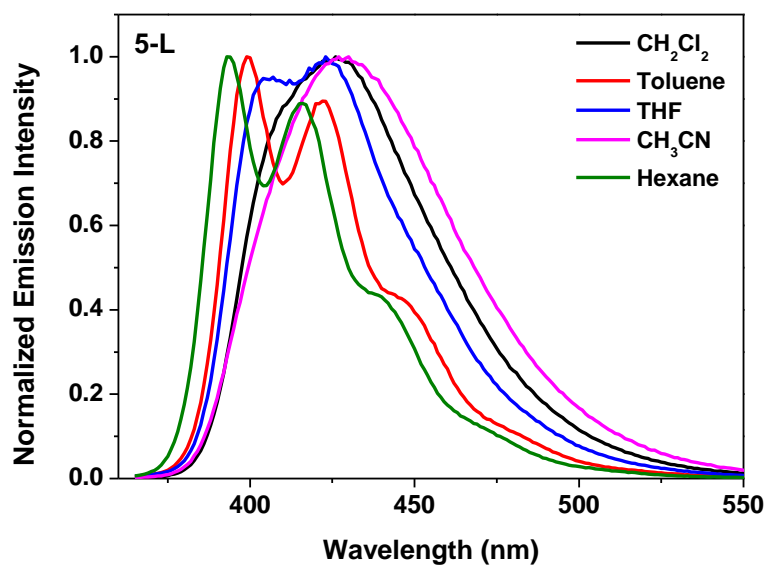
**Figure S12.** Normalized absorption spectra of **6** in different solvents.



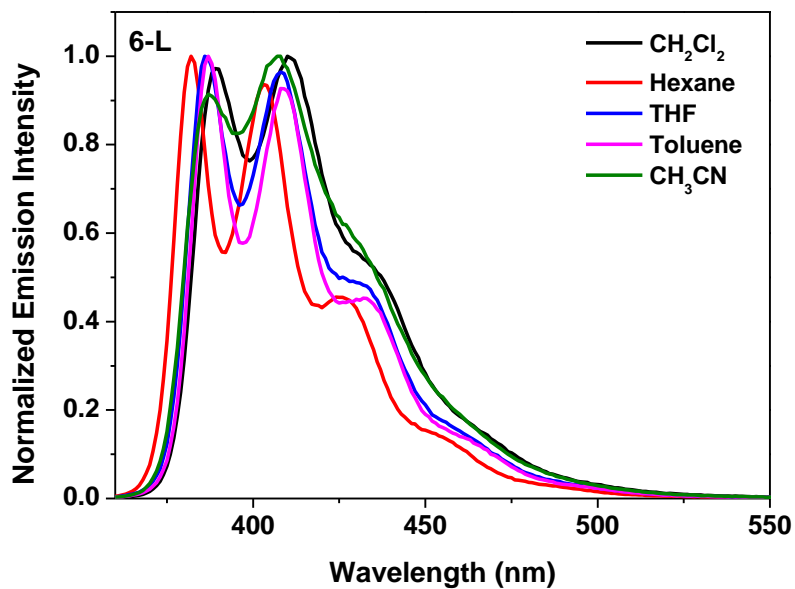
**Figure S13.** Normalized fluorescence spectra of **1-L** in different solvents.  $\lambda_{\text{ex}} = 347.5$  nm.



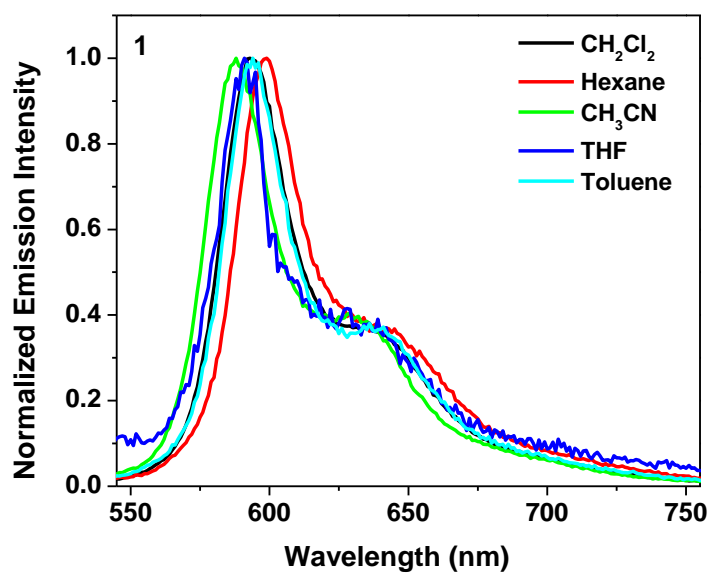
**Figure S14.** Normalized emission spectra of **4-L** in different solvents.  $\lambda_{\text{ex}} = 347.5$  nm.



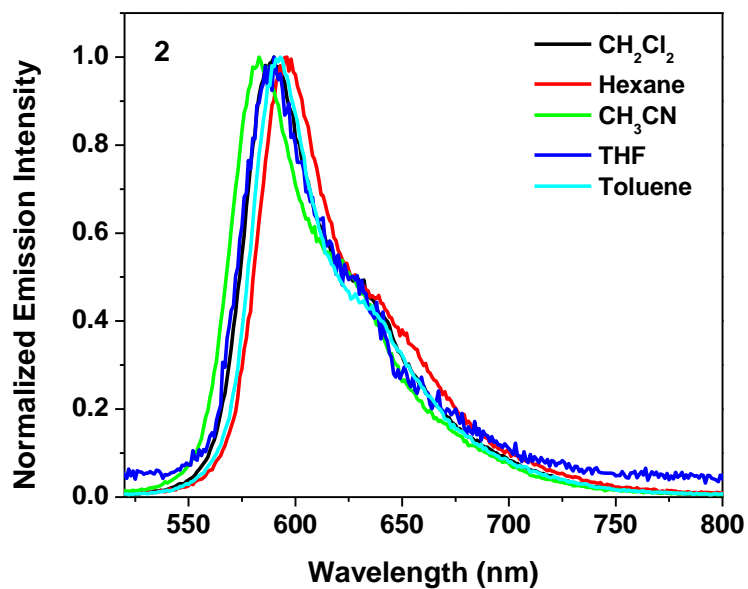
**Figure S15.** Normalized emission spectra of **5-L** in different solvents.  $\lambda_{\text{ex}} = 347.5$  nm.



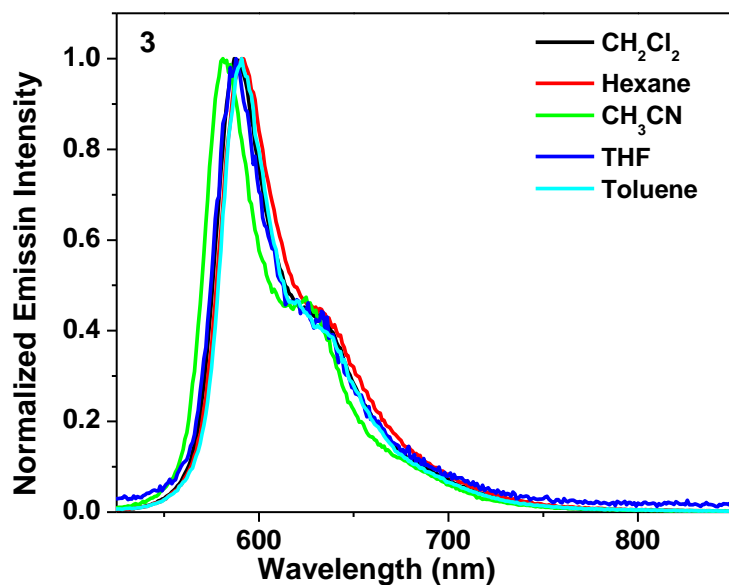
**Figure S16.** Normalized emission spectra of **6-L** in different solvents.  $\lambda_{\text{ex}} = 347.5$  nm.



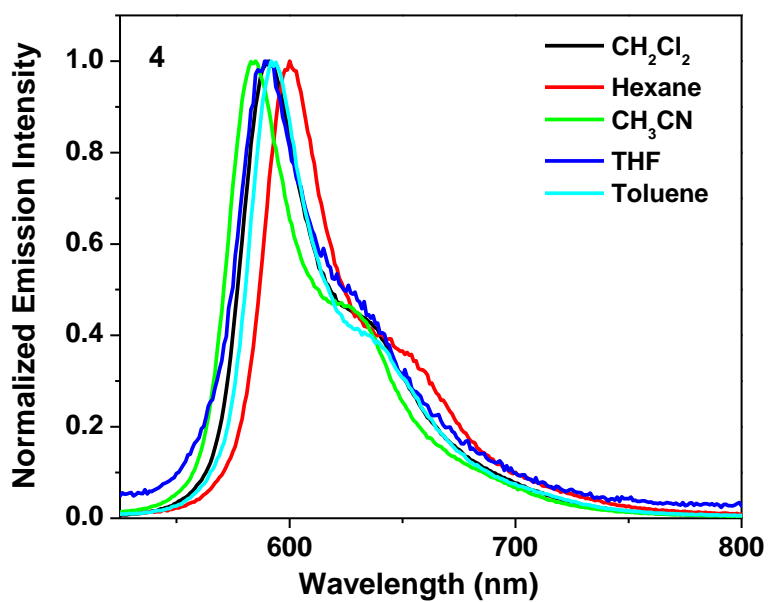
**Figure S17.** Normalized emission spectra of **1** in different solvents.  $\lambda_{\text{ex}} = 436$  nm.



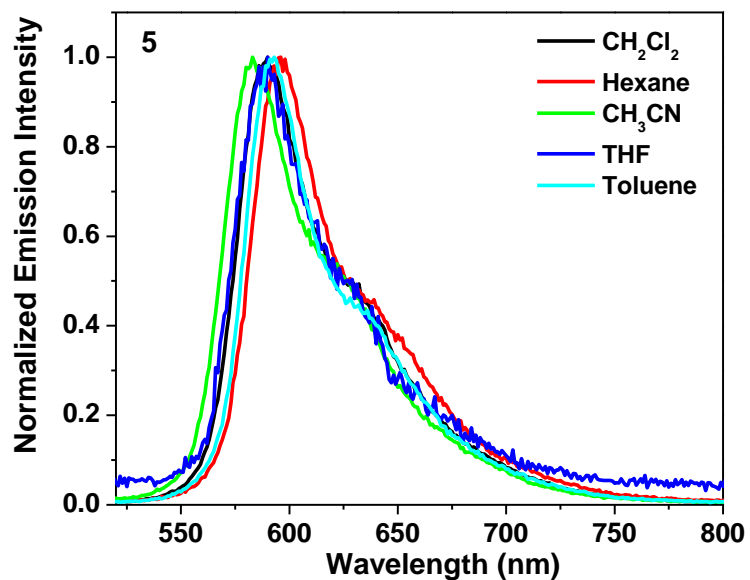
**Figure S18.** Normalized emission spectra of **2** in different solvents.  $\lambda_{\text{ex}} = 436$  nm.



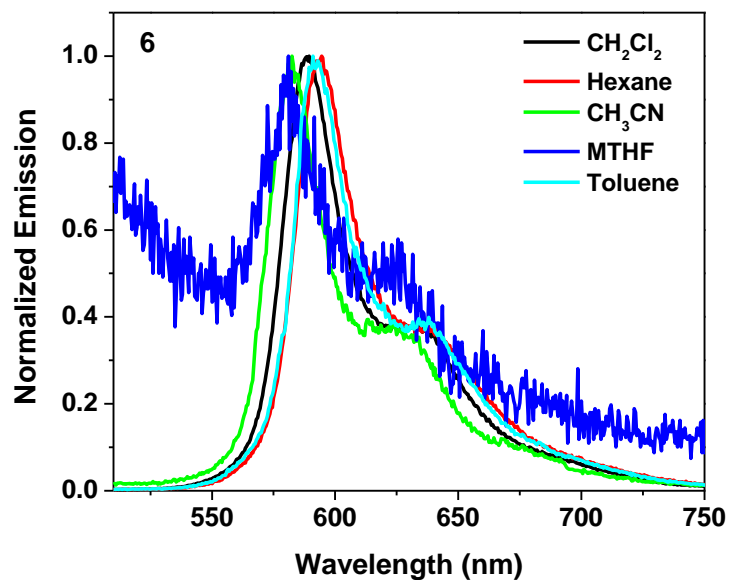
**Figure S19.** Normalized emission spectra of **3** in different solvents.  $\lambda_{\text{ex}} = 436$  nm.



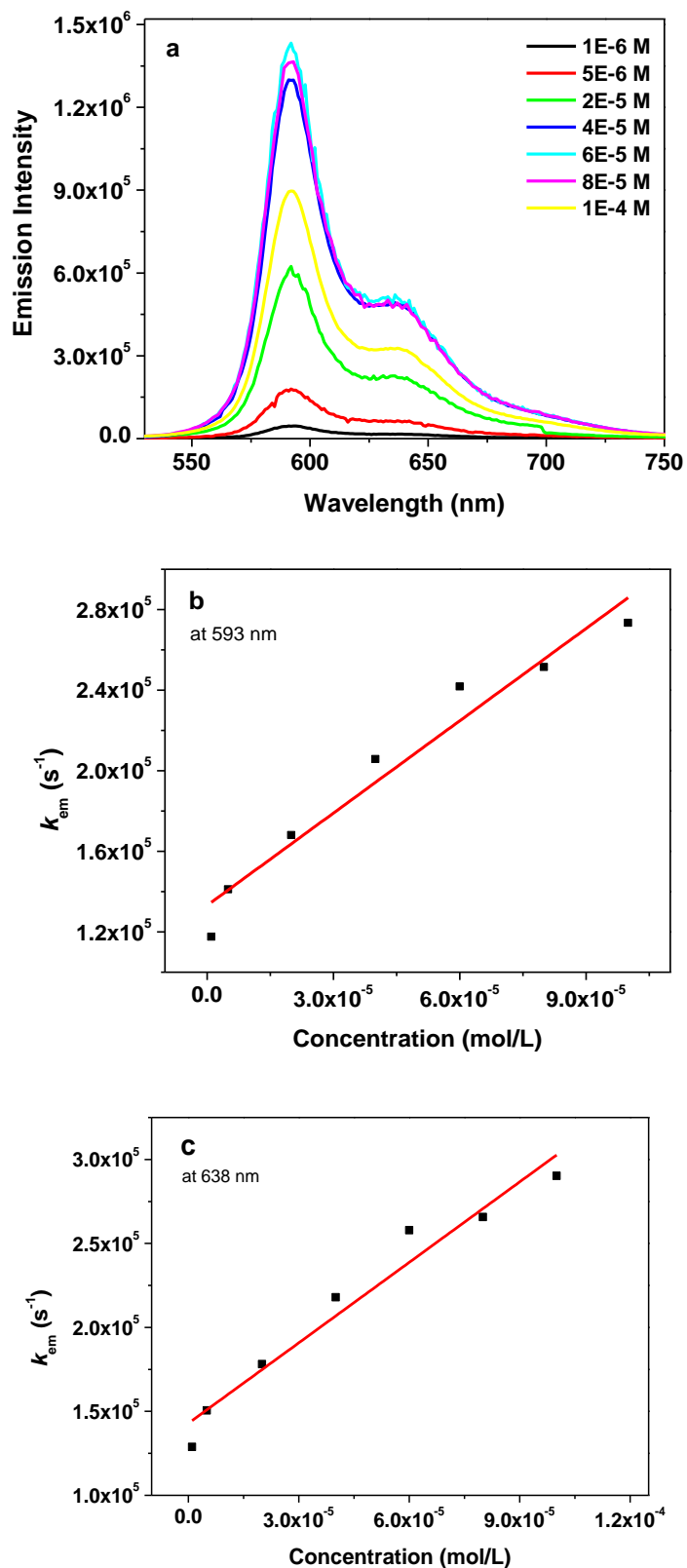
**Figure S20.** Normalized emission spectra of **4** in different solvents.  $\lambda_{\text{ex}} = 436$  nm.



**Figure S21.** Normalized emission spectra of **5** in different solvents.  $\lambda_{\text{ex}} = 436$  nm.

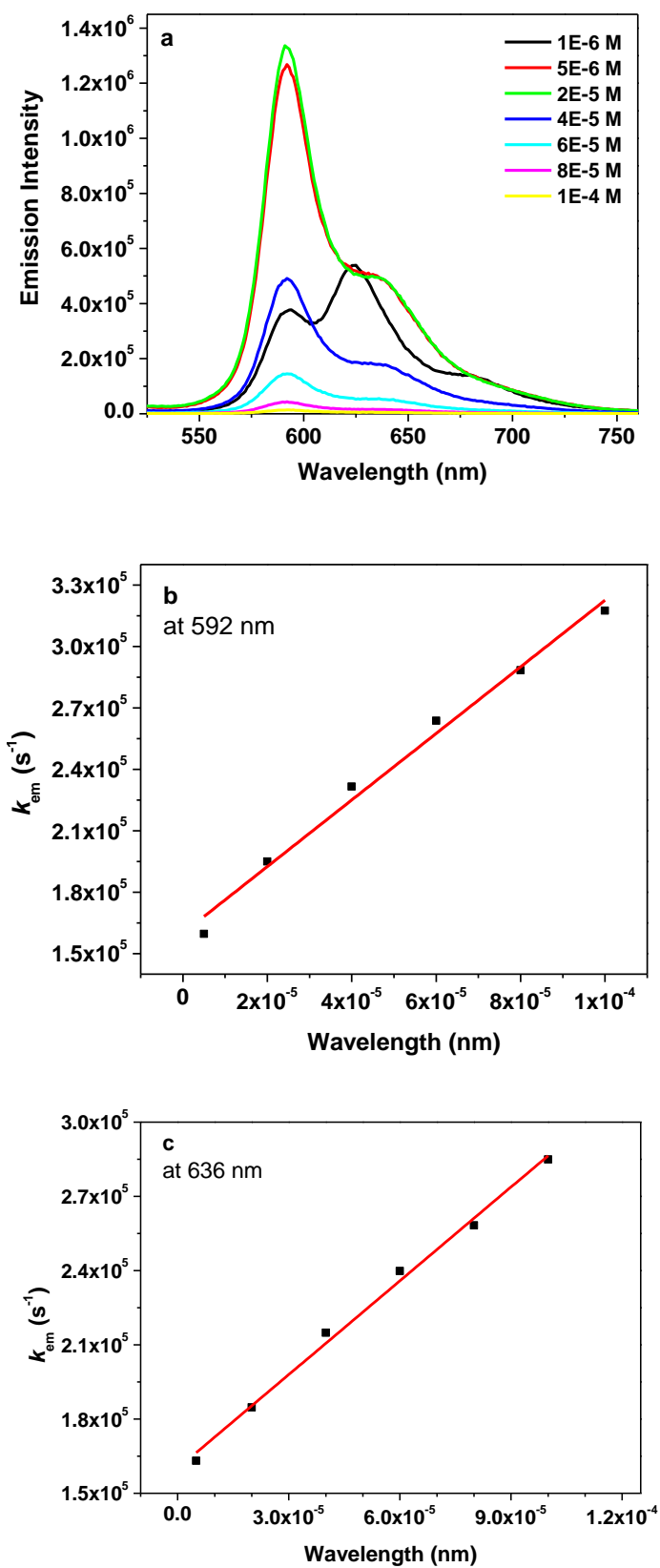


**Figure S22.** Normalized emission spectra of **6** in different solvents.  $\lambda_{\text{ex}} = 436$  nm.

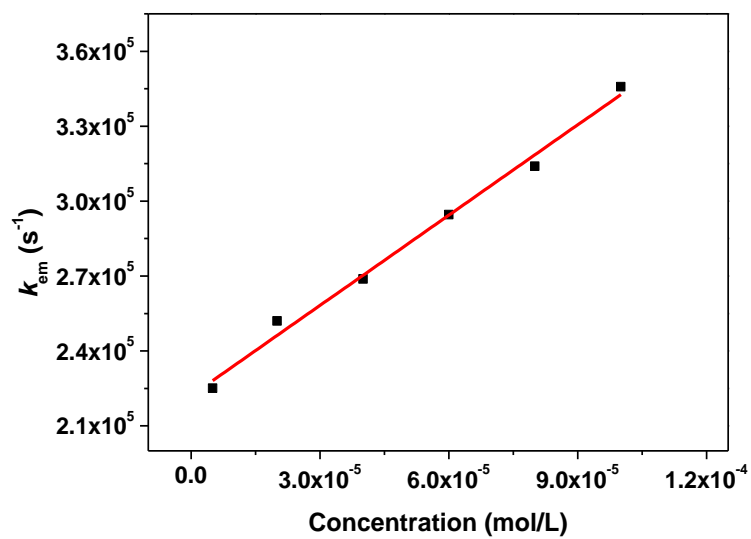


**Figure S23.** (a) Emission spectra of **1** at different concentrations in CH<sub>2</sub>Cl<sub>2</sub>. (b) & (c) Stern-Volmer plots for the emission of **1** at 593 nm and 638 nm in CH<sub>2</sub>Cl<sub>2</sub>

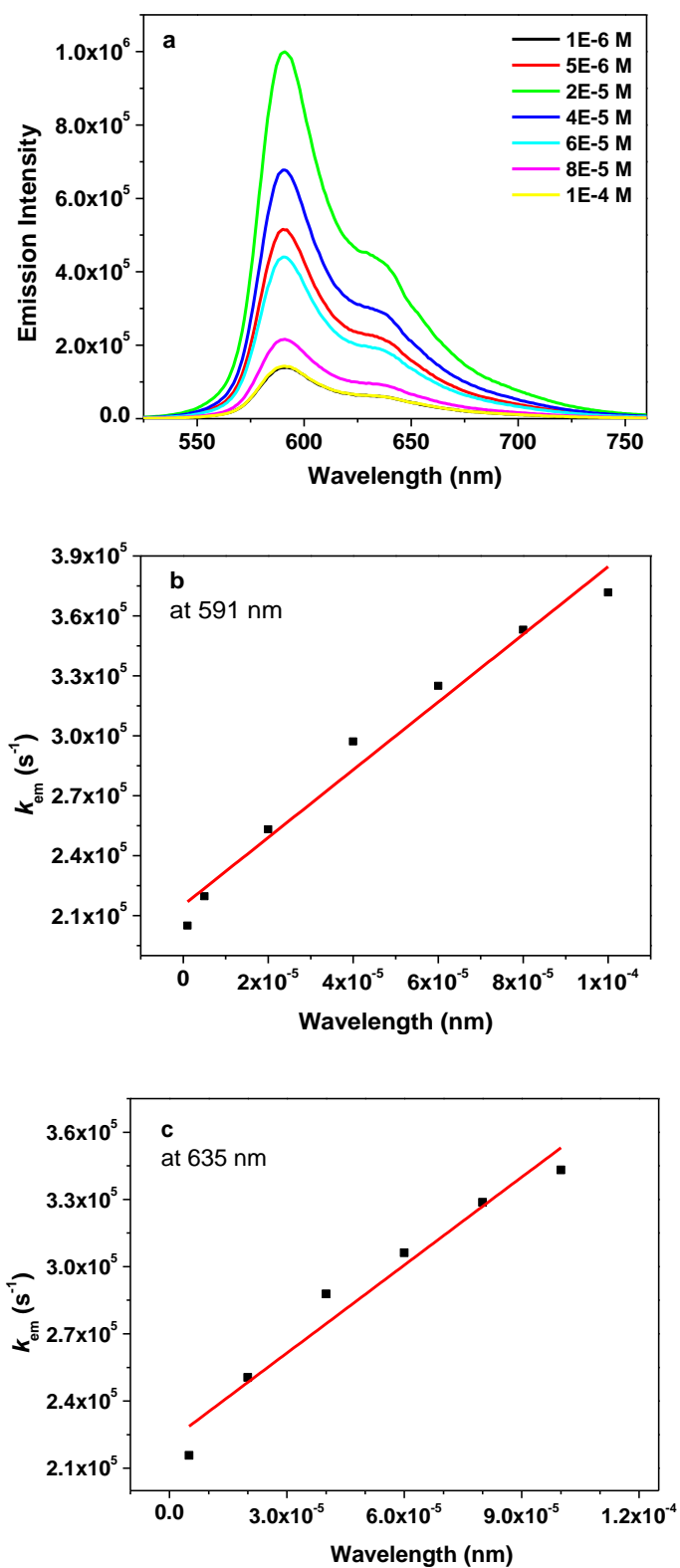




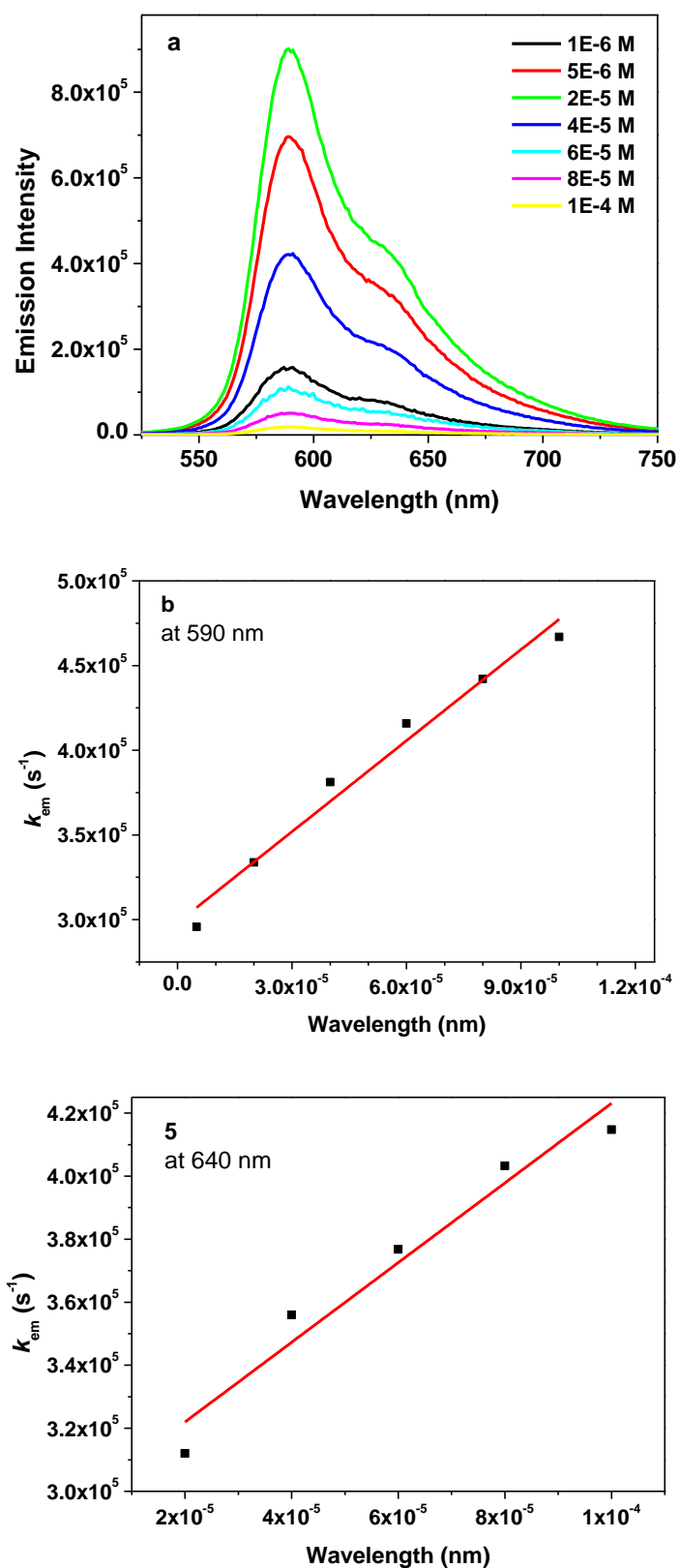
**Figure S24.** (a) Emission spectra of **2** at different concentrations in CH<sub>2</sub>Cl<sub>2</sub>. (b) & (c) Stern-Volmer plots for the emission of **2** at 592 nm and 636 nm in CH<sub>2</sub>Cl<sub>2</sub>.



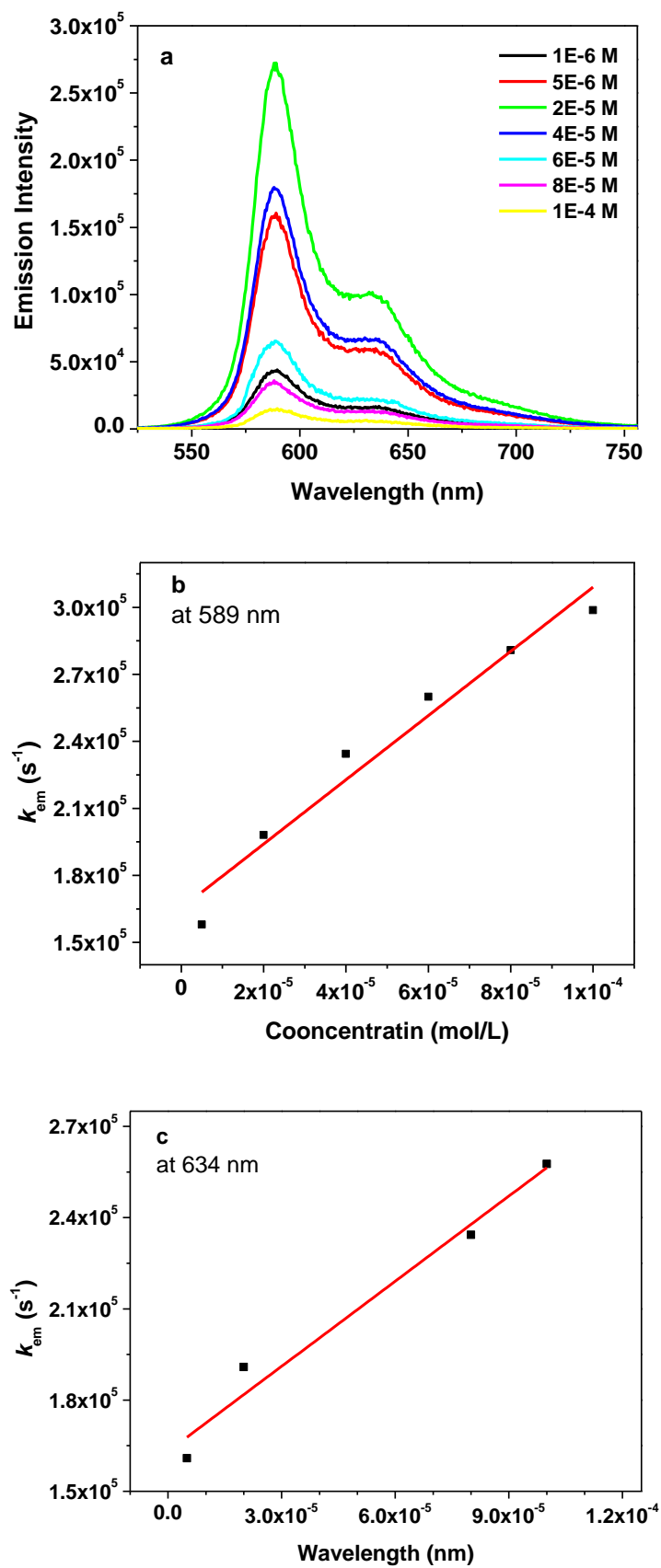
**Figure S25.** Stern-Volmer plot for the emission of **3** at 630 nm in  $CH_2Cl_2$ .



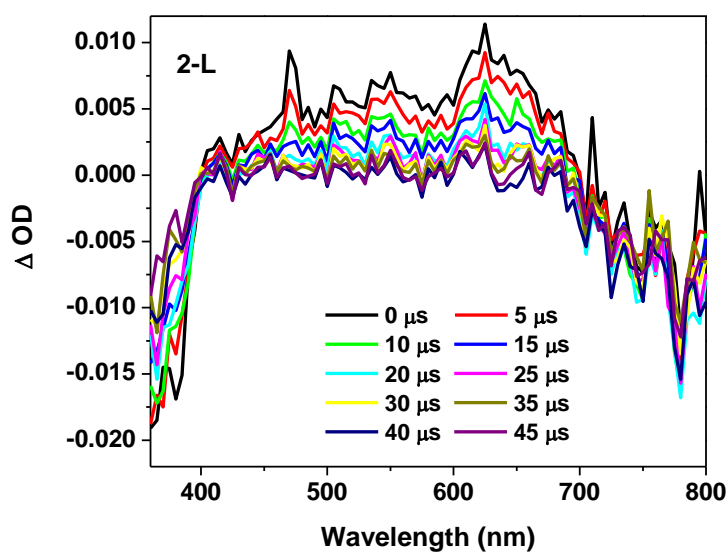
**Figure S26.** (a) Emission spectra of **4** at different concentrations in CH<sub>2</sub>Cl<sub>2</sub>. (b) & (c) Stern-Volmer plots for the emission of **4** at 591 nm and 635 nm in CH<sub>2</sub>Cl<sub>2</sub>.



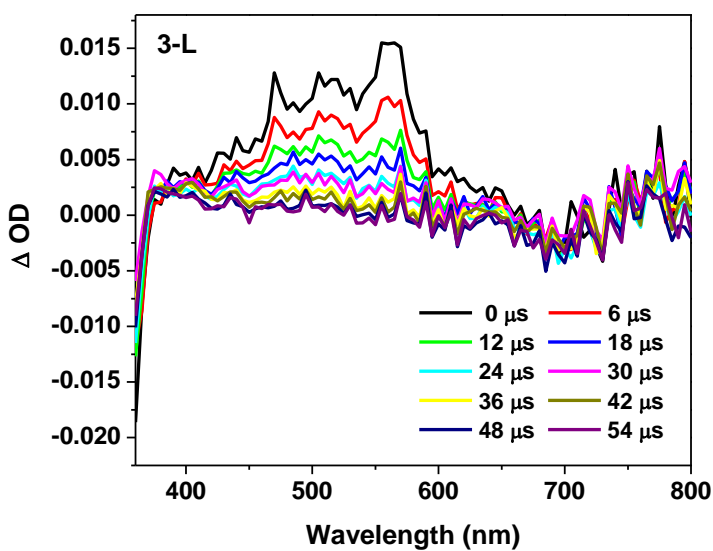
**Figure S27.** (a) Emission spectra of **5** at different concentrations in CH<sub>2</sub>Cl<sub>2</sub>. (b) & (c) Stern-Volmer plots for the emission of **5** at 590 nm and 640 nm in CH<sub>2</sub>Cl<sub>2</sub>.



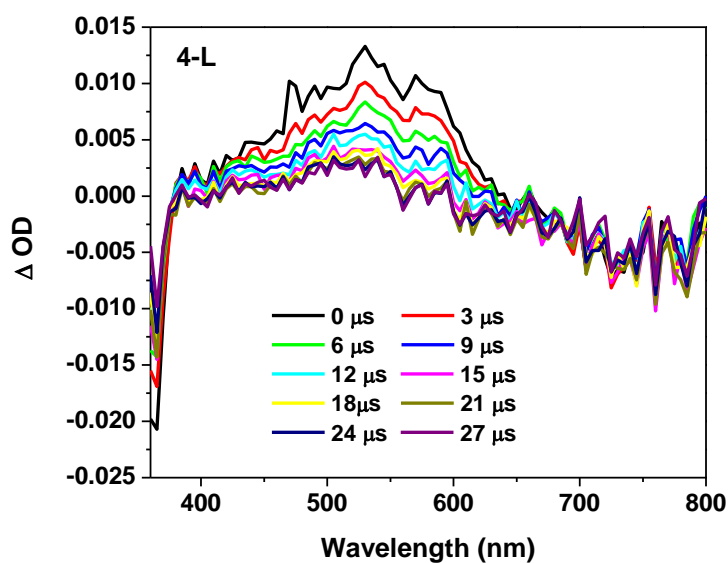
**Figure S28.** (a) Emission spectra of **6** at different concentrations in CH<sub>2</sub>Cl<sub>2</sub>. (b) & (c) Stern-Volmer plots for the emission of **6** at 589 nm and 634 nm in CH<sub>2</sub>Cl<sub>2</sub>.



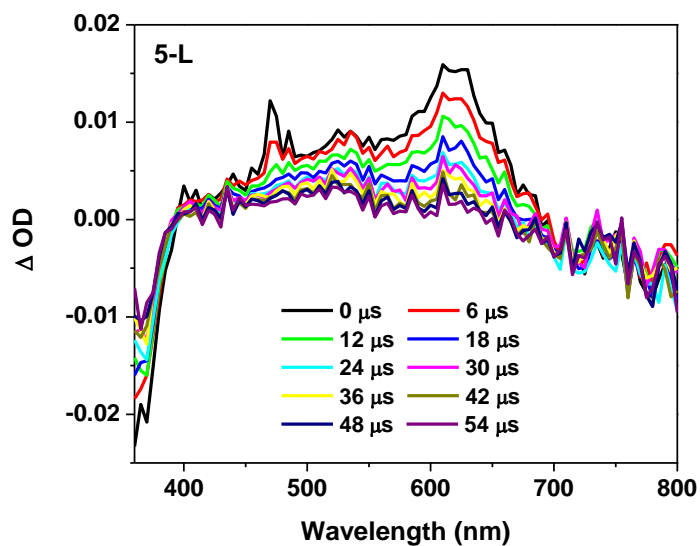
**Figure S29.** Nanosecond time-resolved transient absorption spectra of **2-L** in CH<sub>3</sub>CN.  $\lambda_{\text{ex}} = 355$  nm.  $A_{355} = 0.4$  in a 1-cm cuvette.



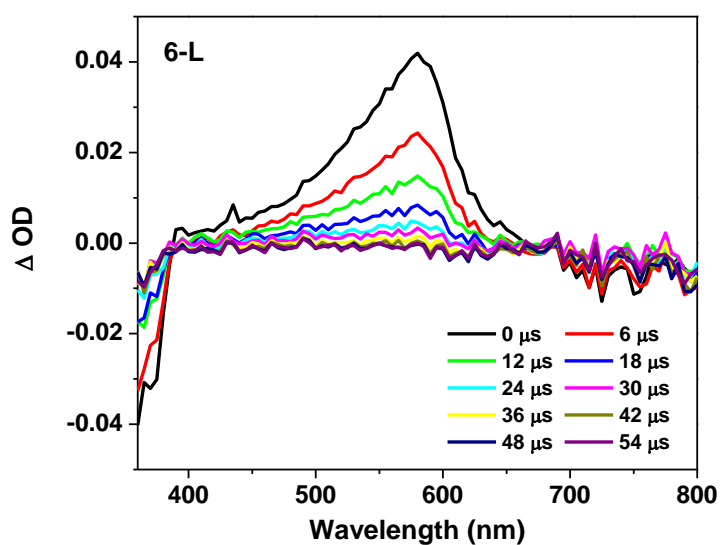
**Figure S30.** Nanosecond time-resolved transient absorption spectra of **3-L** in CH<sub>3</sub>CN.  $\lambda_{\text{ex}} = 355$  nm.  $A_{355} = 0.4$  in a 1-cm cuvette.



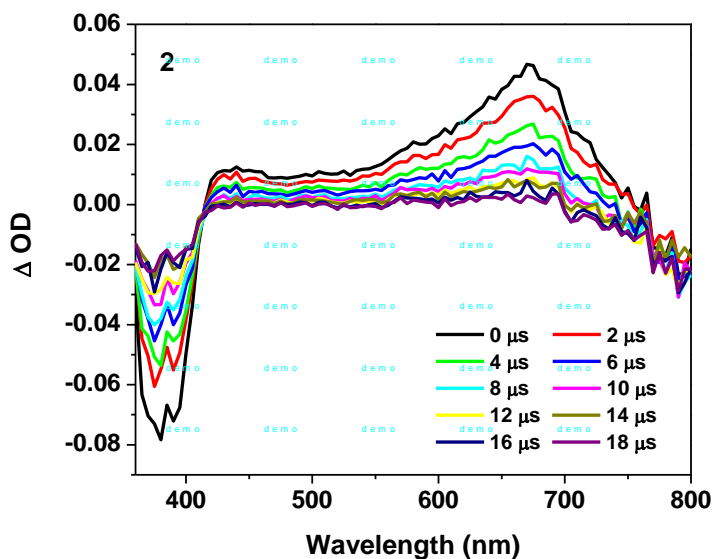
**Figure S31.** Nanosecond time-resolved transient absorption spectra of **4-L** in CH<sub>3</sub>CN.  $\lambda_{ex} = 355$  nm.  $A_{355} = 0.4$  in a 1-cm cuvette.



**Figure S32.** Nanosecond time-resolved transient absorption spectra of **5-L** in CH<sub>3</sub>CN.  $\lambda_{ex} = 355$  nm.  $A_{355} = 0.4$  in a 1-cm cuvette.

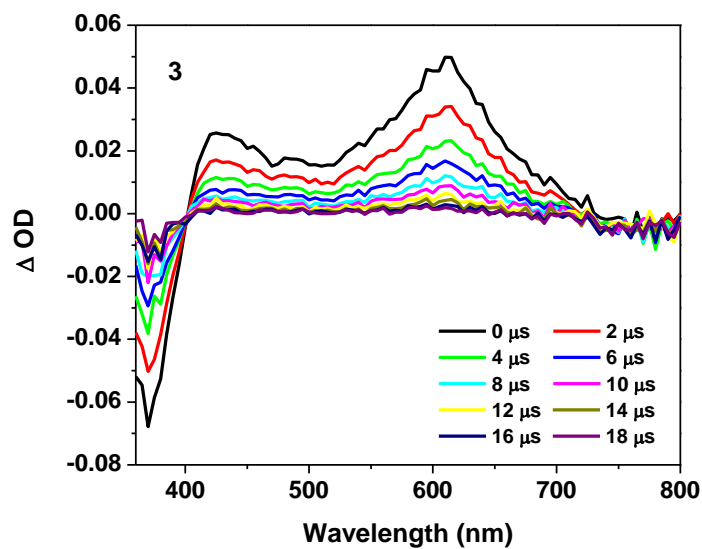


**Figure S33.** Nanosecond time-resolved transient absorption spectra of **6-L** in CH<sub>3</sub>CN.  $\lambda_{\text{ex}} = 355 \text{ nm}$ .  $A_{355} = 0.4$  in a 1-cm cuvette.

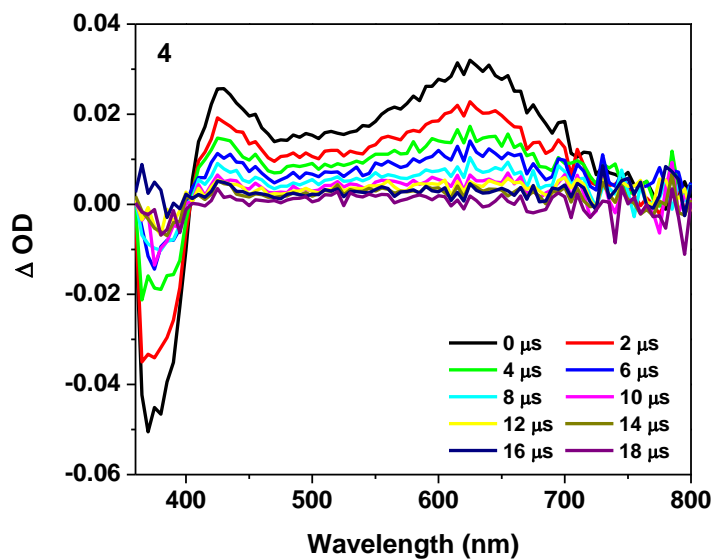


**Figure S34.** Nanosecond time-resolved transient absorption spectra of **2** in CH<sub>3</sub>CN.  $\lambda_{\text{ex}} = 355 \text{ nm}$ .  $A_{355} = 0.4$  in a 1-cm cuvette.

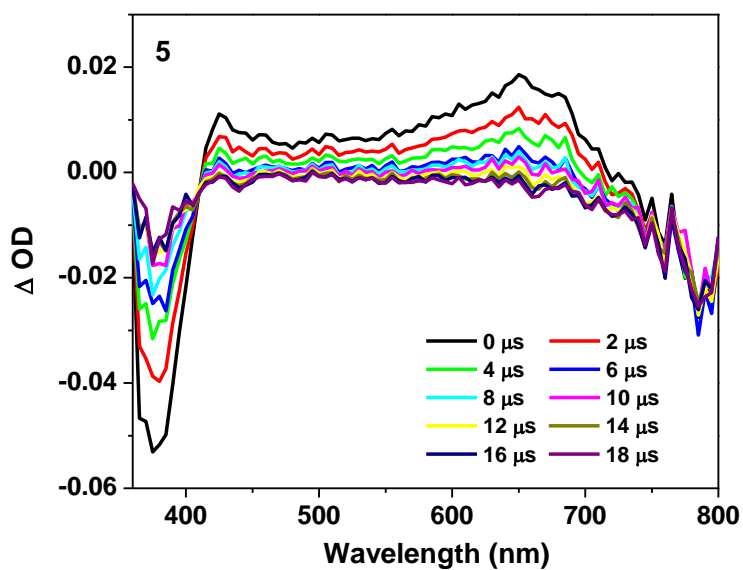




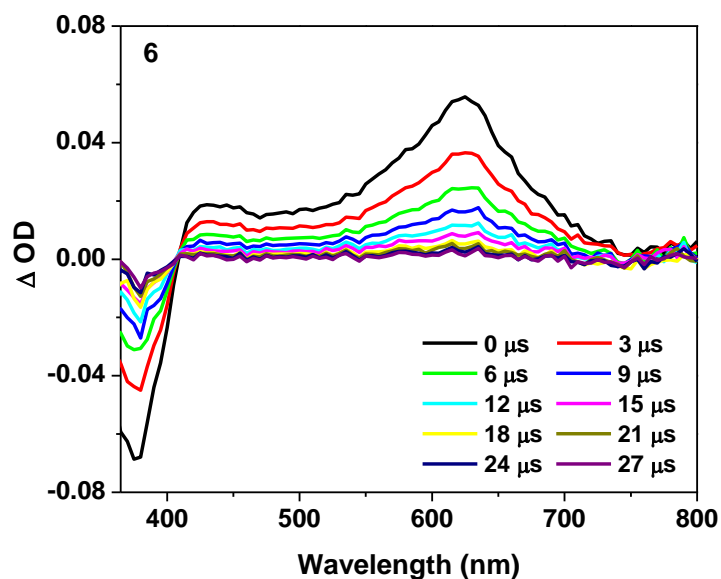
**Figure S35.** Nanosecond time-resolved transient absorption spectra of **3** in  $\text{CH}_3\text{CN}$ .  
 $\lambda_{\text{ex}} = 355 \text{ nm}$ .  $A_{355} = 0.4$  in a 1-cm cuvette.



**Figure S36.** Nanosecond time-resolved transient absorption spectra of **4** in  $\text{CH}_3\text{CN}$ .  
 $\lambda_{\text{ex}} = 355 \text{ nm}$ .  $A_{355} = 0.4$  in a 1-cm cuvette.



**Figure S37.** Nanosecond time-resolved transient absorption spectra of **5** in  $\text{CH}_3\text{CN}$ .  
 $\lambda_{\text{ex}} = 355 \text{ nm}$ .  $A_{355} = 0.4$  in a 1-cm cuvette.



**Figure S38.** Nanosecond time-resolved transient absorption spectra of **6** in  $\text{CH}_3\text{CN}$ .  
 $\lambda_{\text{ex}} = 355 \text{ nm}$ .  $A_{355} = 0.4$  in a 1-cm cuvette.

**Table S1.** Emission characteristics of complexes **1** – **6** in different solvents at room temperature

	$\lambda_{em}/nm$ ( $\tau_{em}/ns$ ); $\Phi_{em}$				
	<b>CH<sub>2</sub>Cl<sub>2</sub></b>	<b>Hexane</b>	<b>CH<sub>3</sub>CN</b>	<b>THF</b>	<b>Toluene</b>
<b>1</b>	594 (5640), 640 (5490); 0.133	598 (1190), 640 (1160); 0.038	588 (3770), 630 (3470); 0.066	591 (295), 639 (280); 0.0060	594 (3240), 634 (3250); 0.052
<b>2</b>	593( 3620), 636 (3530); 0.053	599 (1250), 645 (1290); 0.029	586 (6020), 630 (6320); 0.048	-	594 (2230), 635 (1800); 0.067
<b>3</b>	588 (4020); 0.084	591 (905); 0.042	583 (3620), 624 (3790); 0.043	588 (290), 632 (290); 0.0063	591 (2040); 0.056
<b>4</b>	591 (4120), 635 (4160); 0.051	600 (1100), 650 (1130); 0.020	585 (5010), 625 (5060); 0.048	590 (280), 620 (280); 0.0057	593 (1870), 636 (1810); 0.040
<b>5</b>	590 (3120), 640 (3120); 0.069	596 (1180), 645 (1210); 0.032	583 (3640), 625 (3960); 0.059	591 (195), 638 (200); 0.0059	592 (1490), 632 (1160); 0.061
<b>6</b>	589 (5430), 632 ( 5760), 660 (5780); 0.092	594 (1810), 636 (1780), 680 (1950); 0.037*	583 (1790), 600 (1750), 630 (1710); 0.02	-	591 (2310), 638 (2530), 680 (2160); 0.064

\*with 5% CH<sub>2</sub>Cl<sub>2</sub>

**Table S2.** Fluorescence quantum yields of ligands **1-L** – **6-L** different solvents

	<b>CH<sub>2</sub>Cl<sub>2</sub></b>	<b>Hexane</b>	<b>CH<sub>3</sub>CN</b>	<b>THF</b>	<b>Toluene</b>
<b>1-L</b>	0.032	0.0077	0.008	0.032	0.017
<b>2-L</b>	0.924	0.945	0.848	0.968	0.992
<b>3-L</b>	0.957	0.879	0.916	0.920	0.945
<b>4-L</b>	0.991	0.912	0.922	0.919	0.978
<b>5-L</b>	0.921	0.907	0.857	0.921	0.946
<b>6-L</b>	0.795	0.727	0.783	0.785	0.800