Effects of extending the π-conjugation of the acetylide ligand on the photophysics and reverse saturable absorption of Pt(II) bipyridine bis(acetylide) complexes

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Table S1. Optimized ground state geometries and torsion angles between aromatic building blocks for **Pt-1** – **Pt-4** in toluene.

	Torsion Angles	Geometry
Pt-1	A = -0.9º B = -8.4º C = -8.5º D = -1.7º	
Pt-2	A = -0.2º B = -9.7º C = -9.0º D = -7.2º E = -2.7º F = -1.2º	
Pt-3	A = -9.2º B = -7.7º C = 10.2º D = -6.2º	
Pt-4	A = -0.1º B = -4.1º C = 7.9º D = -6.3º E = -2.6º F = -1.2º	

Table S2. Optimized triplet excited state geometries and torsion angles between aromatic building blocks for **Pt-1** – **Pt-4** in toluene.

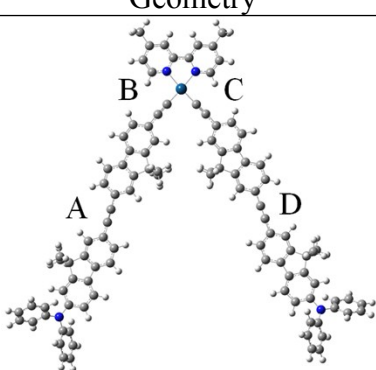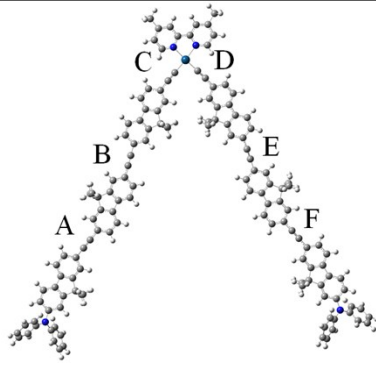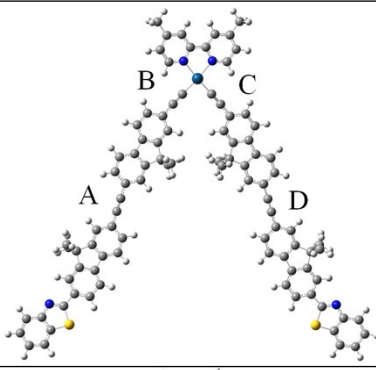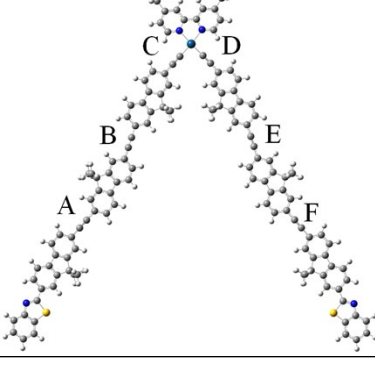|	Torsion Angles	Geometry
Pt-1	A = 0.6º B = 5.6º C = 9.1º D = 3.9º	
Pt-2	A = -0.1º B = -4.7º C = 7.7º D = -4.0º E = -1.3º F = -0.2º	
Pt-3	A = 9.5º B = 8.7º C = 5.2º D = 5.0º	
Pt-4	A = -1.4º B = -2.9º C = -1.8º D = -0.5º E = 0.2º F = 0.2º	

Table S3. Comparison of the energy difference between the DFT optimized geometry and the symmetric geometries of **Pt-3** in toluene. The total energy of **Pt-3-L** is calculated by preserving the overall geometry and torsion angles A and B of the left ligand as they are in the optimized structure (see Table S1), while torsion angles of the right ligand are fixed to C = B and D = A. In **Pt-3-R**, the geometry and torsion angles C and D of the right ligand are preserved as they are in the optimized structure (see Table S1), while torsion angles of the left ligand are fixed to B = C and A = D.
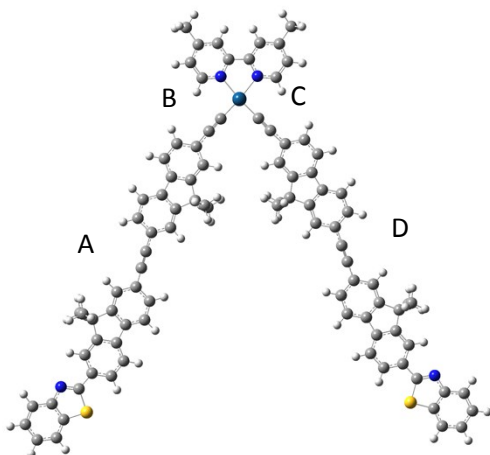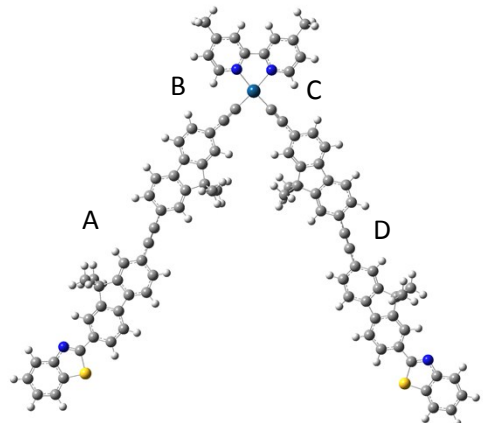
	Torsion Angles	**Geometry**	**E(Opt) – E(symmetric) / eV**
Pt-3-L	A = -6.2º B = 10.2º C = 10.2º D = -6.2º		-2.132
Pt-3-R	A = -9.2º B = -7.7º C = -7.7º D = -9.2º		-2.129

Table S4. Theoretical phosphorescence emission for ligands **L-1 - L-4** in toluene, calculated by TDDFT excited state optimization (ES-optimization) and by delta-SCF method, where the ground triplet state is optimized and TDDFT is calculated using this triplet optimized geometry. The phosphorescence energies and states are calculated with PBE with 35% HF for both methods.

	Triplet (delta-SCF)	Hole	Electron
L-1	938 nm		
L-2	954 nm		
L-3	907 nm		
L-4	946 nm		

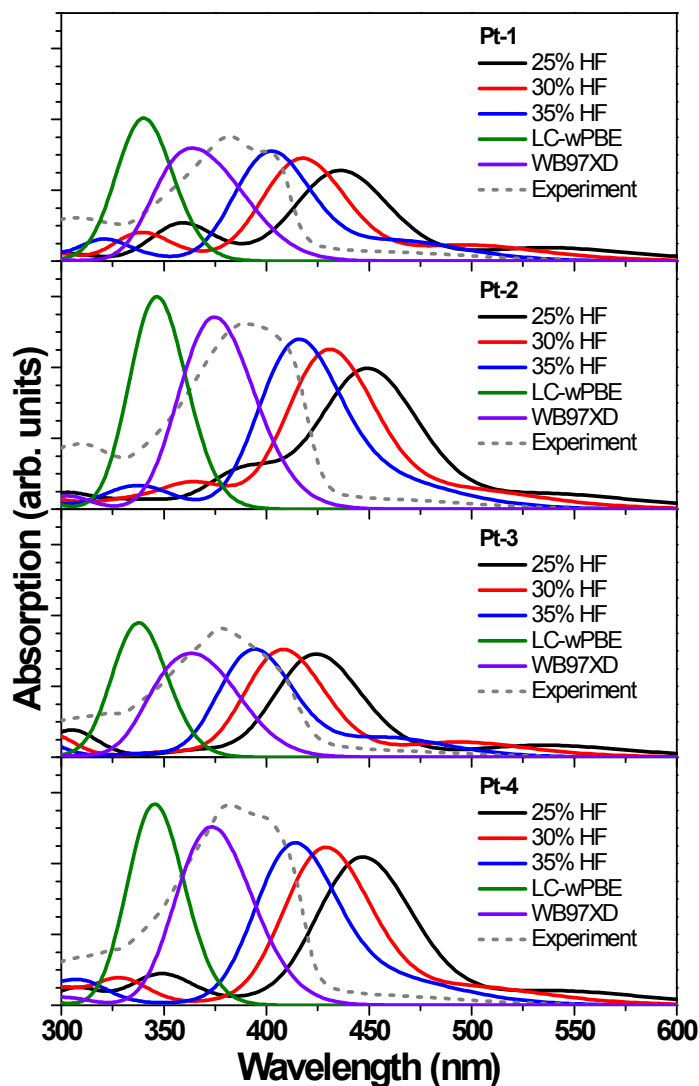|	Triplet (ES-optimization)	Hole	Electron
L-1	925 nm		
L-2	915 nm		
L-3	922 nm		
L-4	909 nm		

Figure S1. Absorption spectra of **Pt-1 – Pt-4** calculated by the PBE functional with different percentages of the Hartree-Fock (HF) exchange (*i.e.* 25%, 30% and 35%) and also by the long-range corrected functionals LcwPBE and WB97XD (with additional dispersion correction). The hybrid functional with 35% HF demonstrated the best qualitative and quantitative agreement with the experimental spectra. Changing the percentage of the HF exchange changed the energy of the peaks, while the character of the transitions remained the same: All spectra show the lowest-energy and low-intensity band originated from the charge transfer (^{1}CT) transitions well split from the high-intensity band originated from the $^1\pi,\pi^*$ transitions. Both bands are consistently blue-shifted with increased HF exchange portion in the functional, with the lowest-energy CT transitions being blue-shifted slightly more than the $^1\pi,\pi^*$ transitions. In contrast, long-range corrected functionals, LC-wPBE and WB97XD, result in the disappearance of the lowest-energy CT band in the spectra, while the $^1\pi,\pi^*$ band is over blue-shifted compared to the experimental spectra.
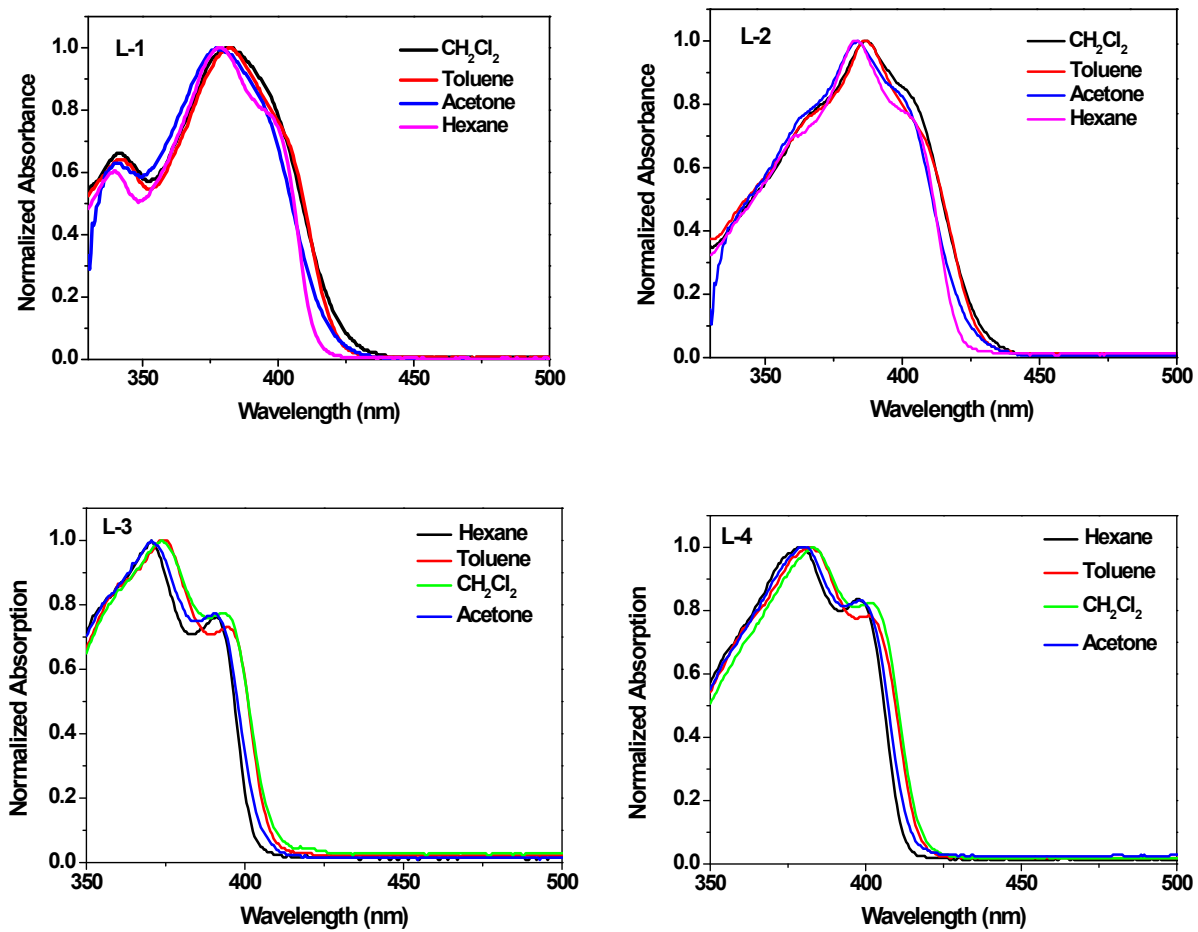
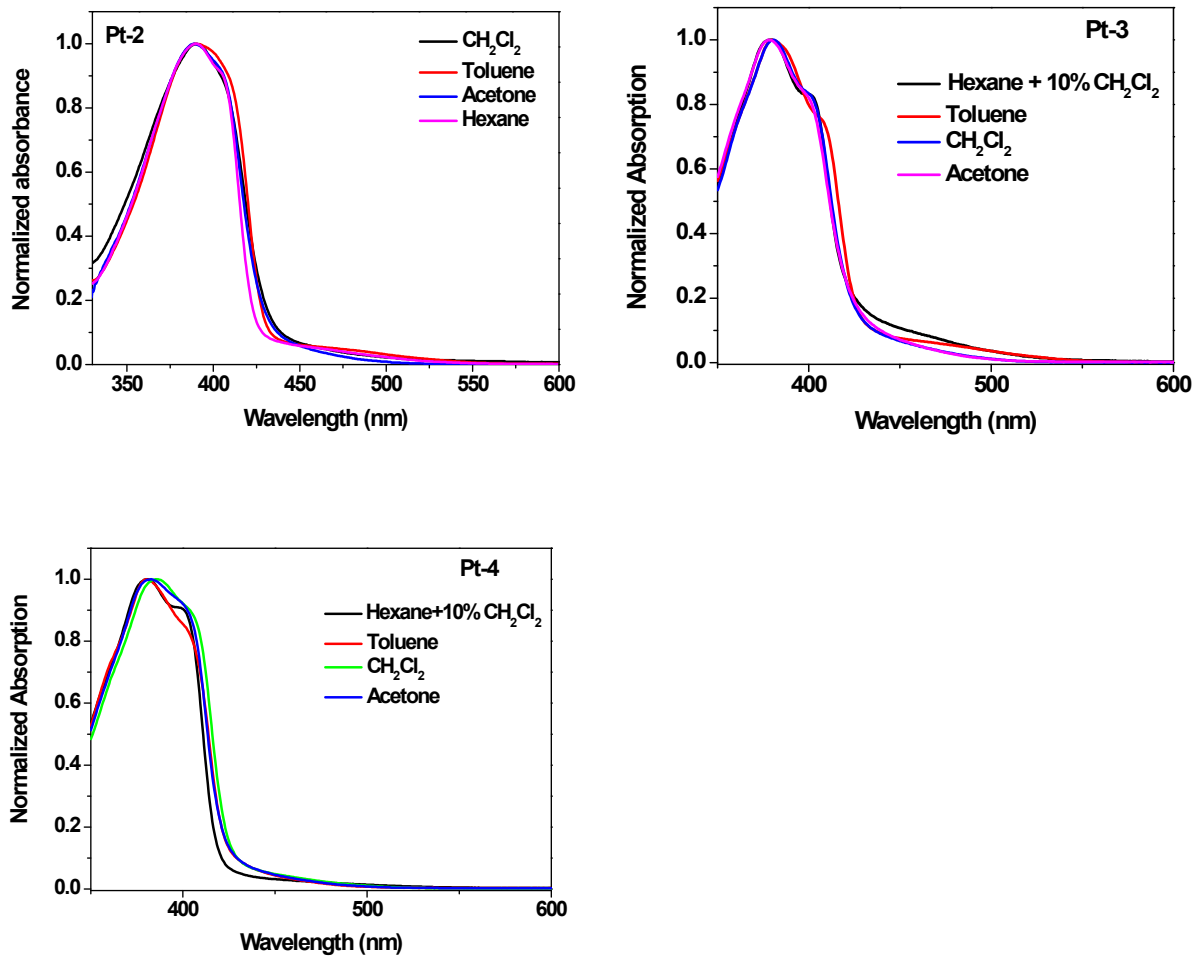**Figure S2**. Normalized UV-vis absorption spectra of ligands **L-1** − **L-4** in different solvents.

Figure S3. Normalized UV-vis absorption spectra of complexes **Pt-1** − **Pt-4** in different solvents.
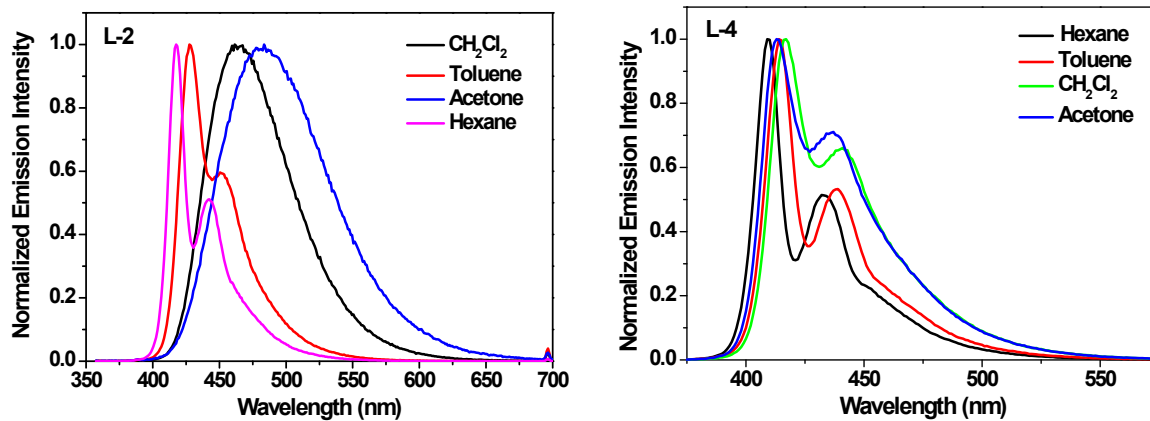
Figure S4. Normalized fluorescence spectra of **L-2** and **L-4** in different solvents at room temperature.
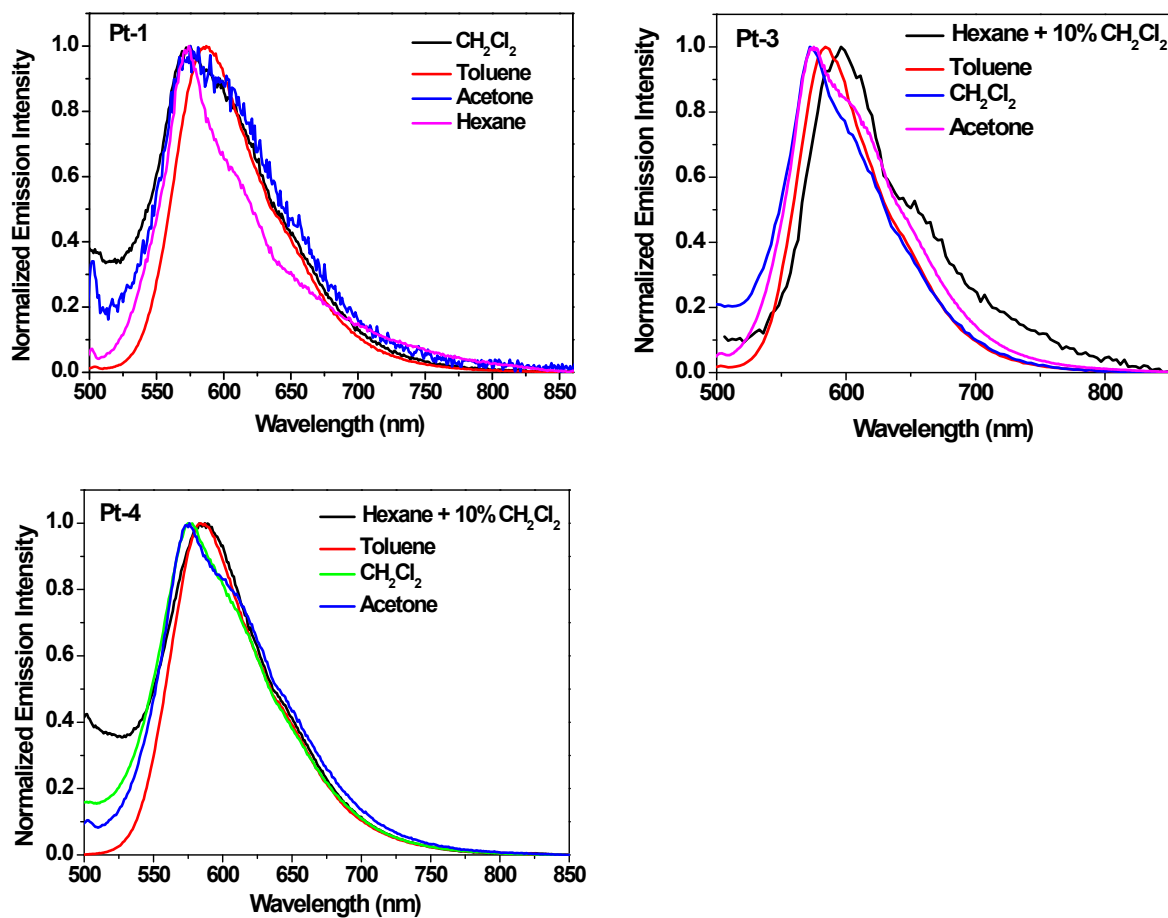
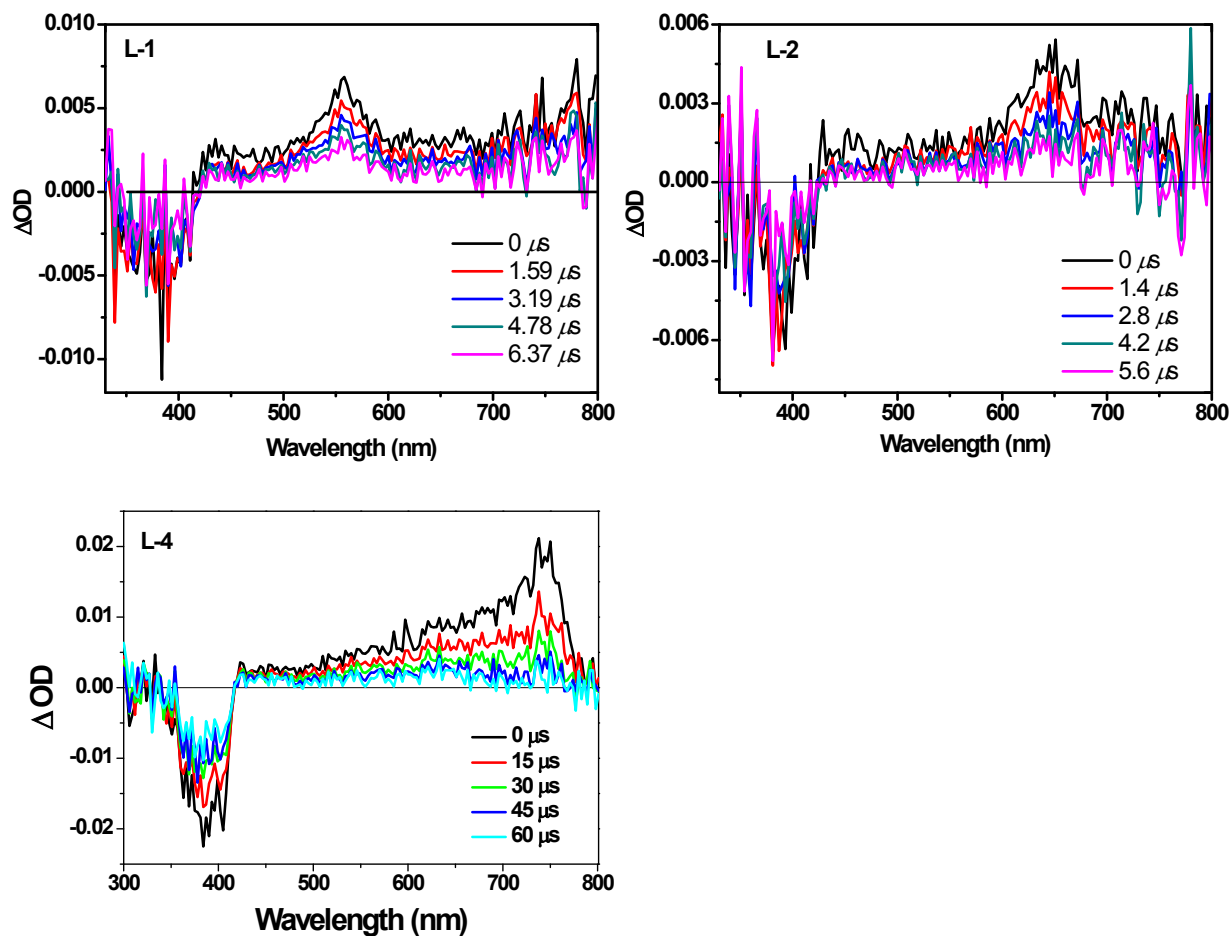**Figure S5**. Normalized emission spectra of **Pt-1**, **Pt-3** and **Pt-4** in different solvents at room temperature.

Figure S6. Time-resolved ns transient absorption spectra of **L-1**, **L-2** and **L-4** in toluene at room temperature. λ_{ex} = 355 nm, $A_{355\ nm}$ = 0.4 in a 1-cm cuvette.
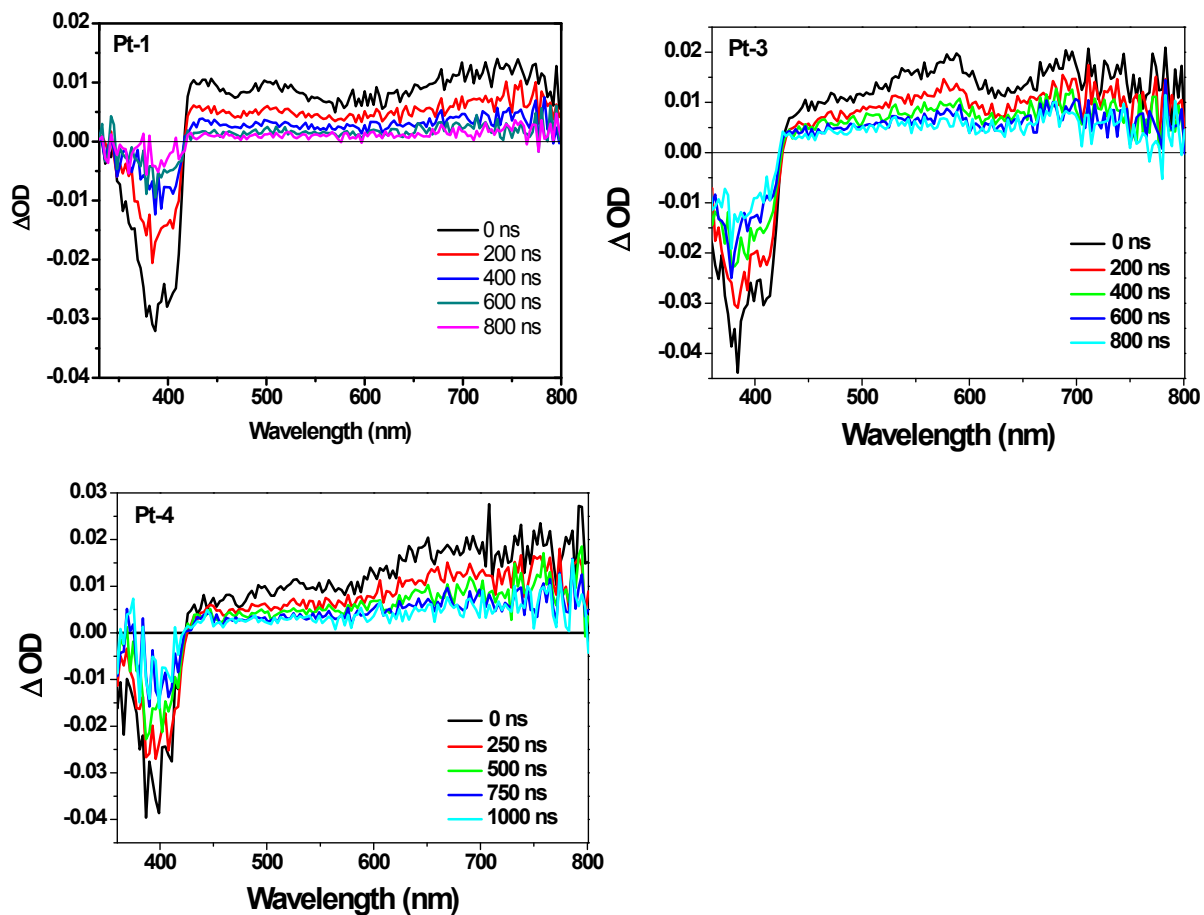
Figure S7. Time-resolved ns transient absorption spectra of **Pt-1**, **Pt-3** and **Pt-4** in toluene at room temperature. λ_{ex} = 355 nm, $A_{355\ nm}$ = 0.4 in a 1-cm cuvette.