Electronic Supplementary Information for

Heteroleptic Cationic Iridium(III) Complexes Bearing Phenanthroline Derivatives with Extended π-Conjugation as Potential Broadband Reverse Saturable Absorbers

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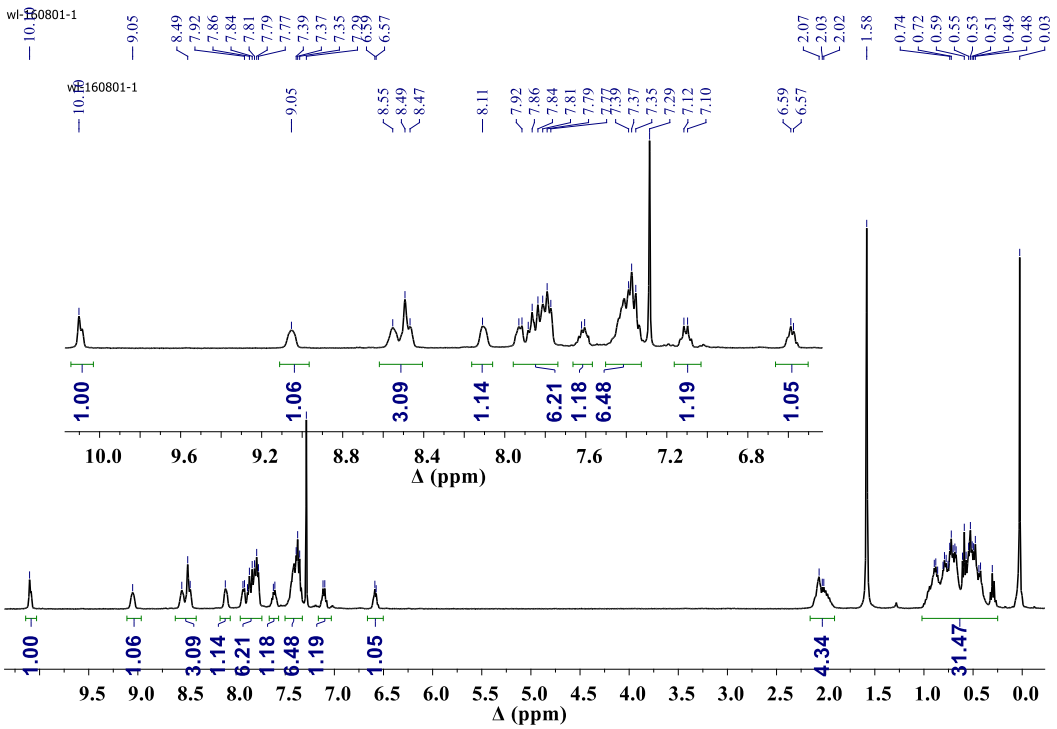

Fig. S1 ^{1}H NMR spectrum of complex **2** in $CDCl_3$.

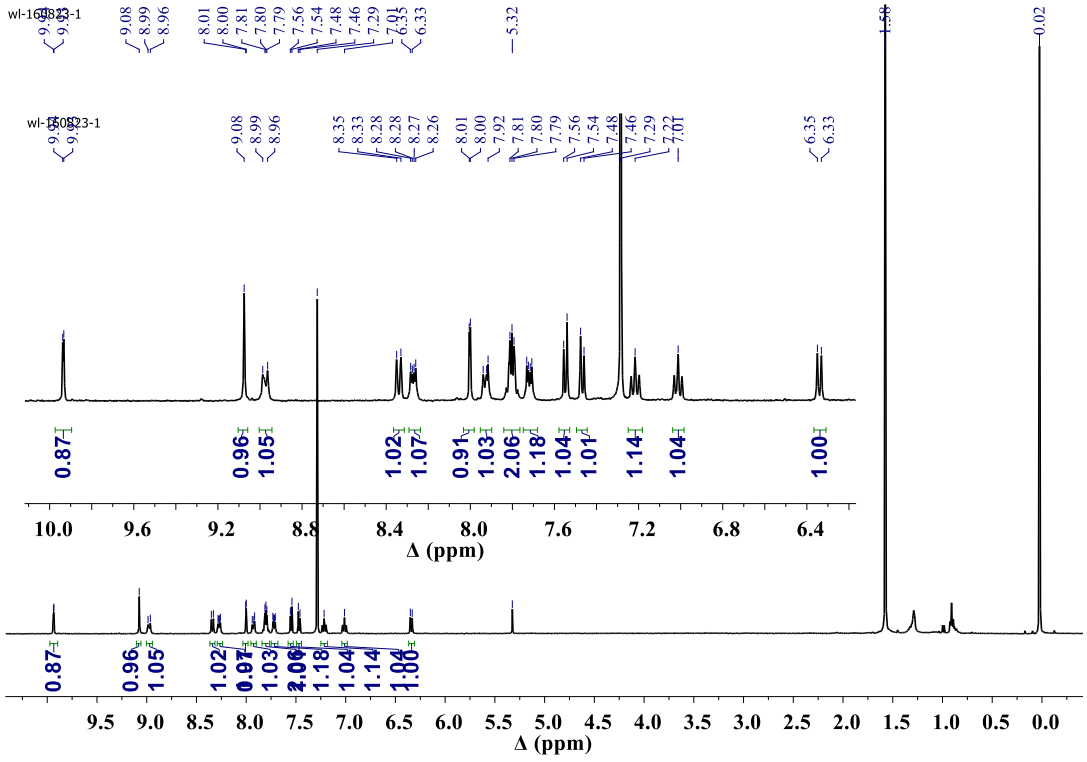

Fig. S2 ^{1}H NMR spectrum of complex $Ir(piq)_2$(dppn-2Br) in $CDCl_3$.

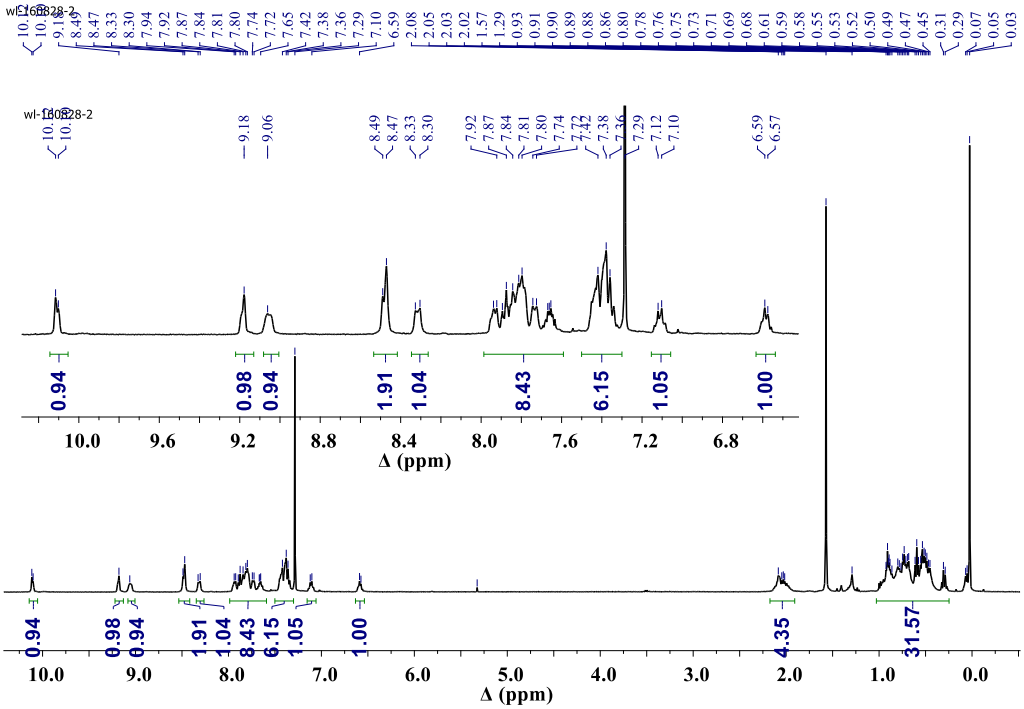

Fig. S3 ^{1}H NMR spectrum of complex **3** in $CDCl_3$.

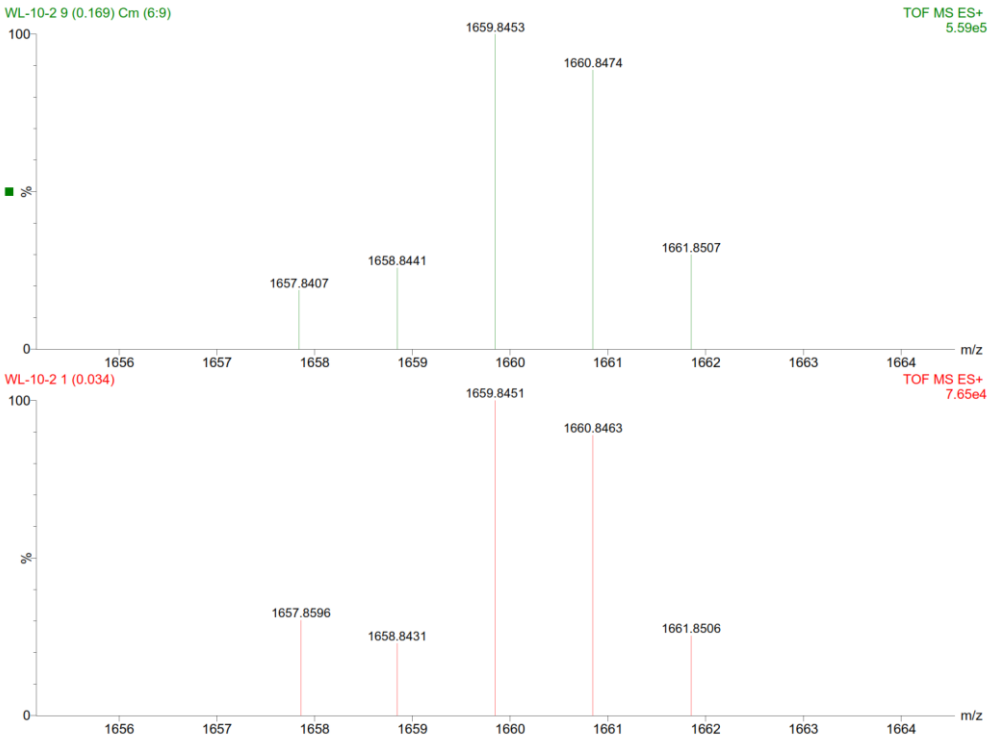

Fig. S4 HRMS spectra of complex **2**. Top: theoretical spectrum calculated for $C_{106}H_{110}IrN_6$ ($M\text{-}PF_6$); Bottom: experimental spectrum.

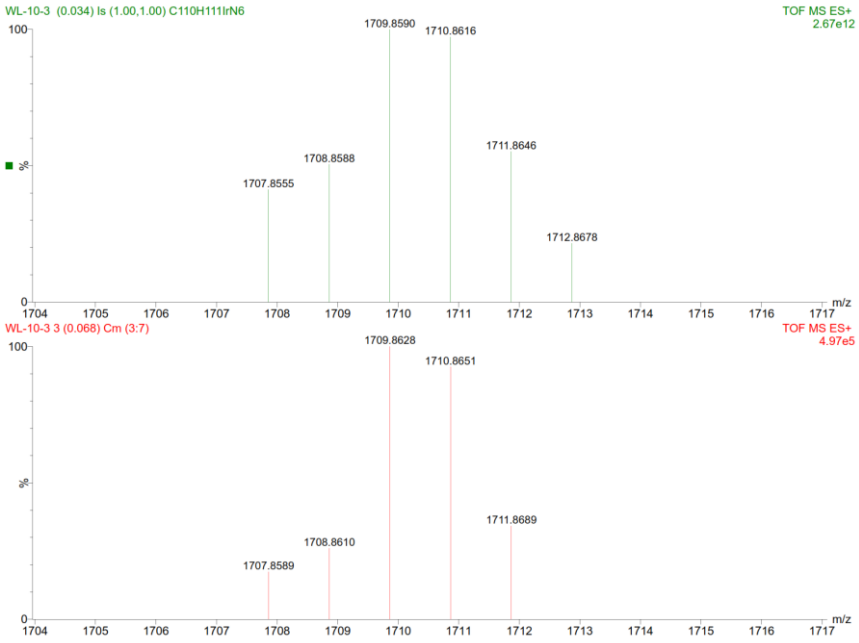

Fig. S5 HRMS spectra of complex **3**. Top: theoretical spectrum calculated for $C_{110}H_{112}IrN_6$ ($M\text{-}PF_6$); Bottom: experimental spectrum.

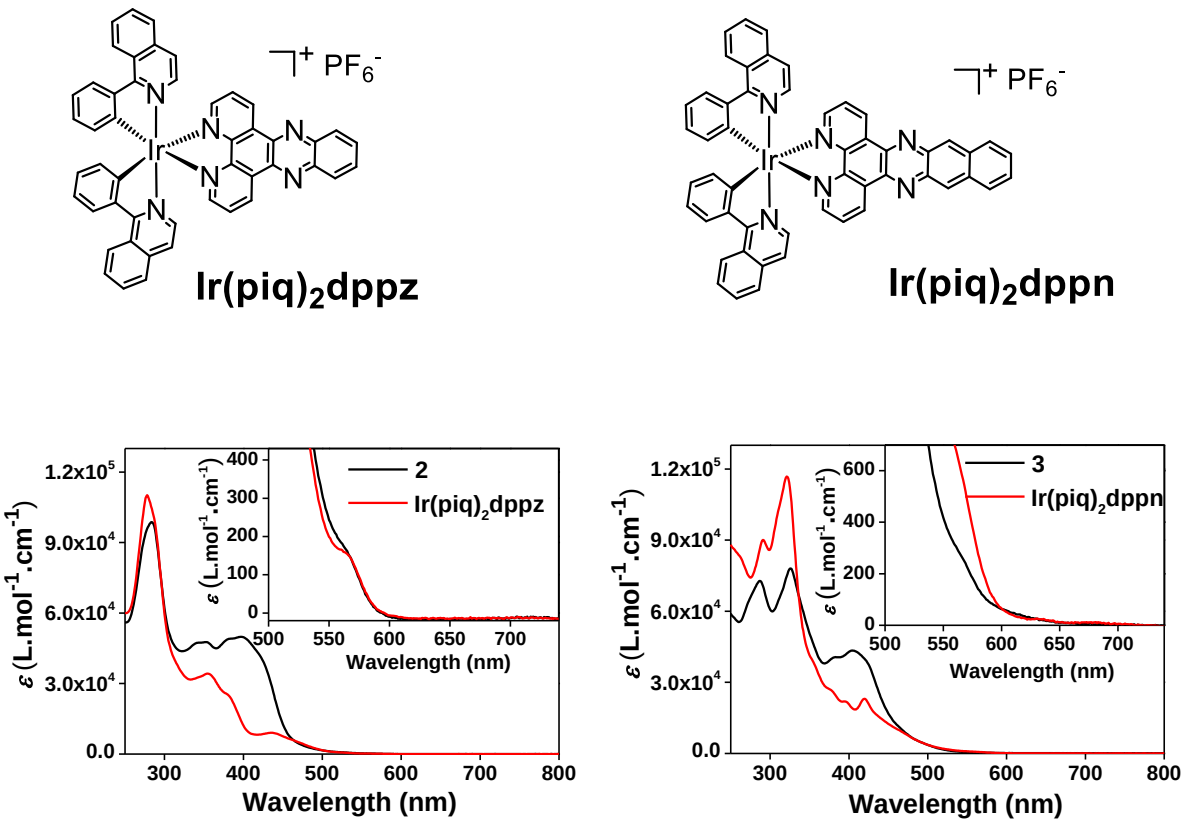

Fig. S6 Comparison of the UV-vis absorption spectra of complexes **2** and **3** to those of their corresponding complexes without the fluorenyl substituents **Ir(piq)$_2$dppz** and **Ir(piq)$_2$dppn** in acetonitrile solutions.

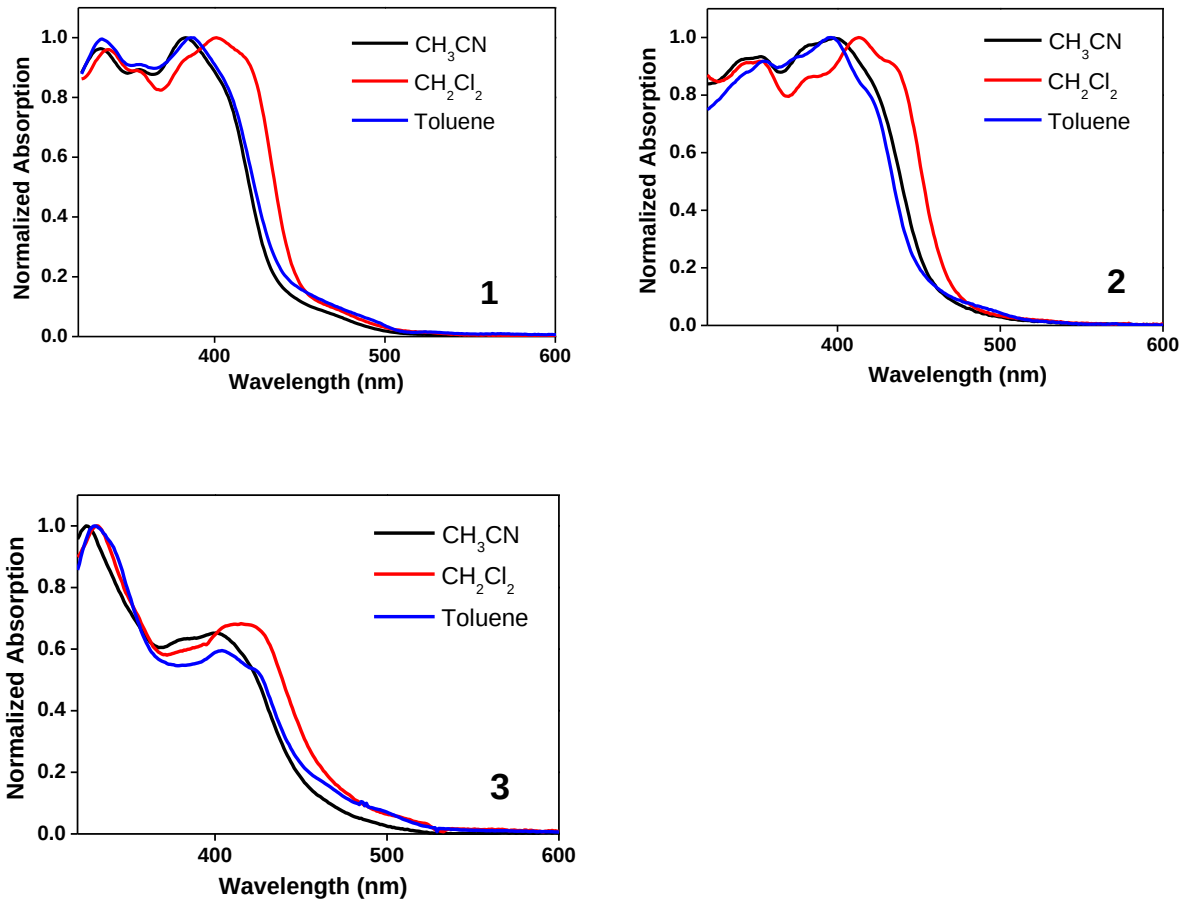

Fig. S7 Normalized UV-vis absorption spectra of complexes **1-3** in different solvents.

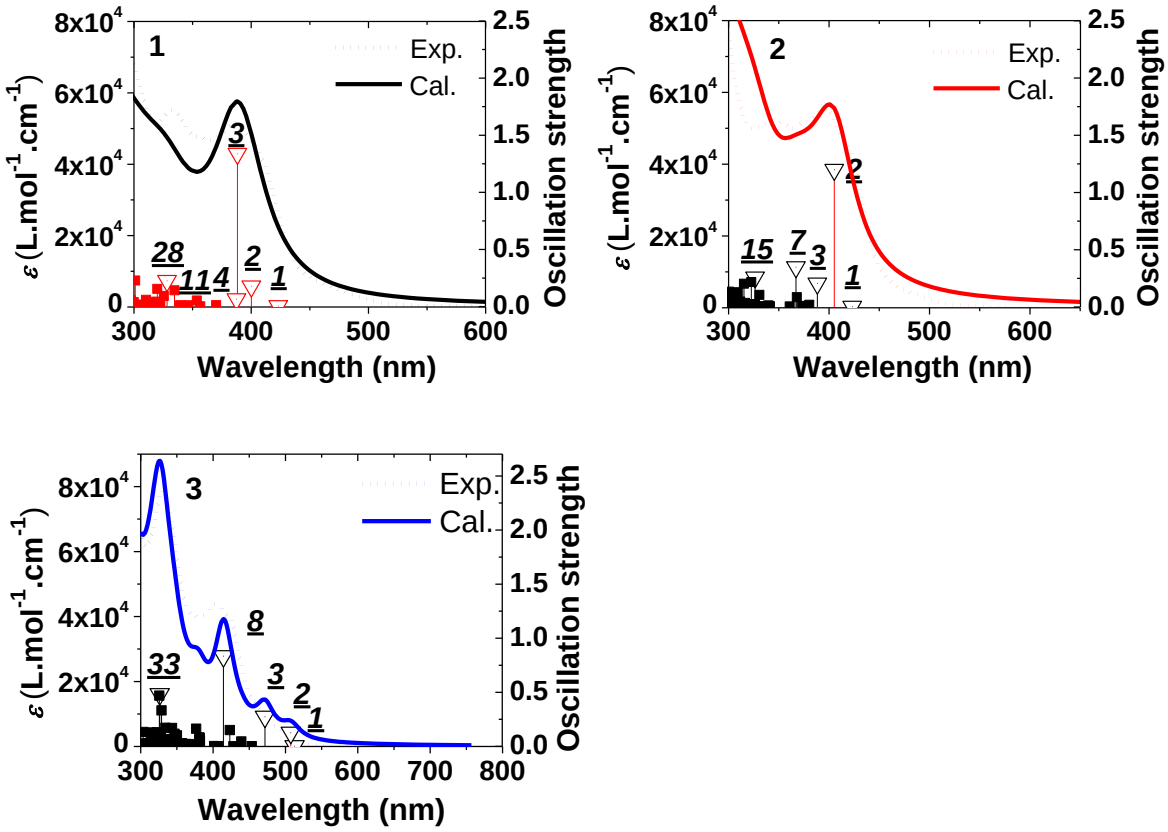

Fig. S8 Comparison of the experimental and calculated UV-vis absorption spectra of complexes **1-3** in toluene.

Table S1 Natural transition orbitals (NTOs) representing main absorption bands for complexes **1-3** in toluene.

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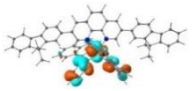
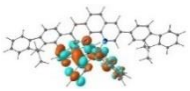
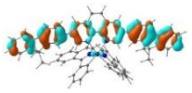
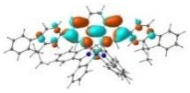
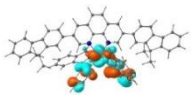
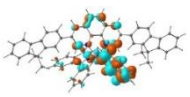
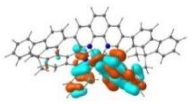
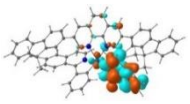
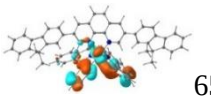
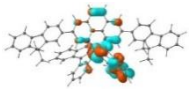
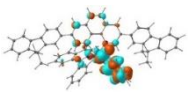
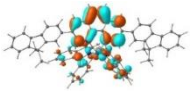
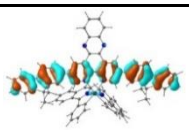
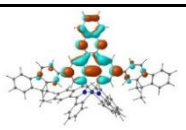
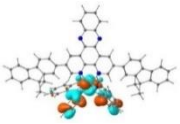
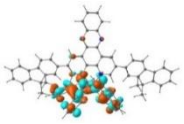
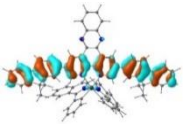
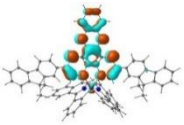
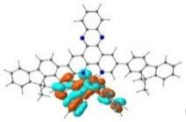
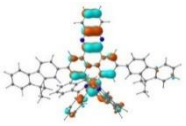
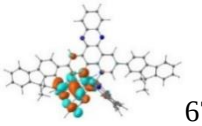
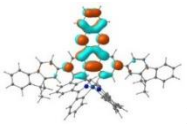
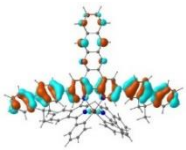
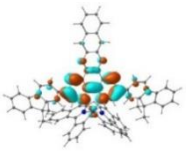
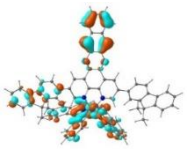
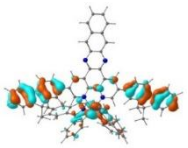
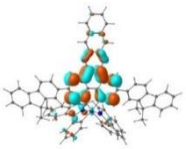
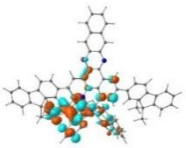
1	S_2 401 nm f = 0.18		
	S_3 389 nm f = 1.34		
	S_4 388 nm f = 0.07		
	S_{11} 329 nm f = 0.23		
	S_{28} 290 nm f = 0.06	 65%  19%	 65%  19%
2	S_2 406 nm f = 1.20		
	S_3 389 nm f = 0.21		
	S_7 368 nm f = 0.35		
	S_{15} 327 nm f = 0.26	 67%  17%	 67%  17%

3	S_8 415 nm f = 0.83		
	S_{33} 327 nm f = 0.48	 53%  27%	 53%  27%

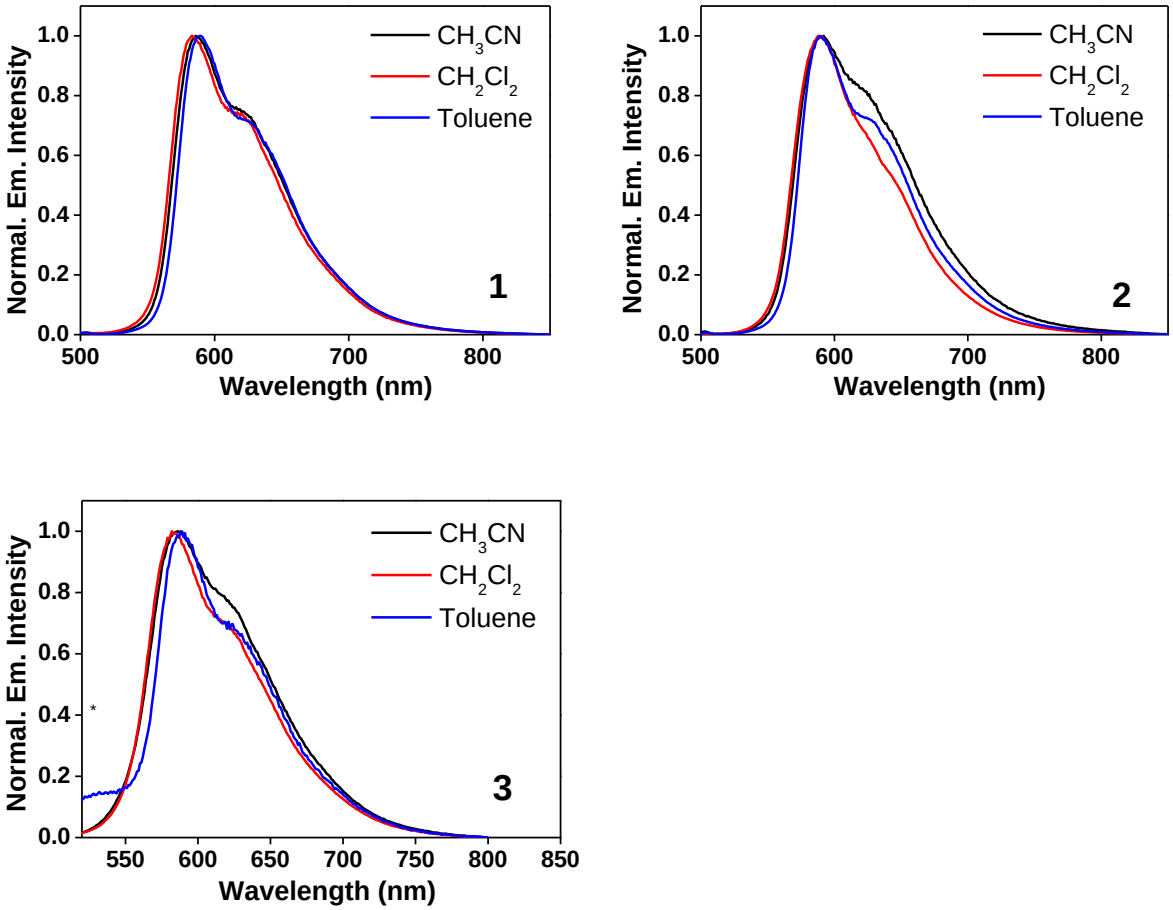
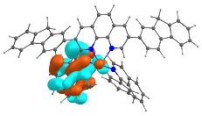
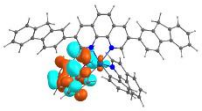
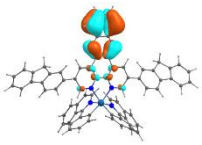
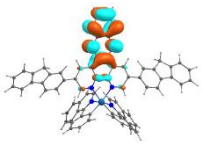
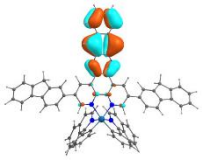
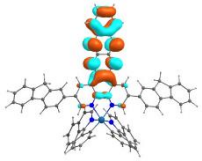
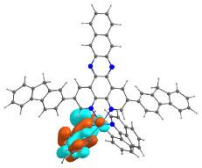
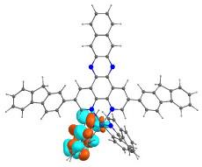


Fig. S9 Normalized emission spectra of complexes **1-3** in different solvents at room temperature. λ_{ex} = 436 nm.

Table S2 Emission band maxima (λ_{em}), lifetimes (τ_{em}) and quantum yields (Φ_{em}) for complexes **1-3** in different solvents at room temperature.

	λ_{em}/nm (τ_{em}/μs); Φ_{em}		
	CH_3CN	CH_2Cl_2	Toluene
1	586 (3.30); 0.35	583 (3.80); 0.40	590 (3.10); 0.46
2	590 (1.05); 0.13	590 (4.42); 0.57	590 (2.93); 0.40
3	587 (2.37); 0.035	588 (2.84); 0.077	590 (2.00); 0.003

Table S3 Natural transition orbitals (NTOs) of the low(est)-energy triplet transitions of **1-3** in acetonitrile.

	T_n	Hole	Electron
1	T_1 910 nm		
2	T_1 905 nm		
3	T_1 935 nm		
	T_2 909 nm		

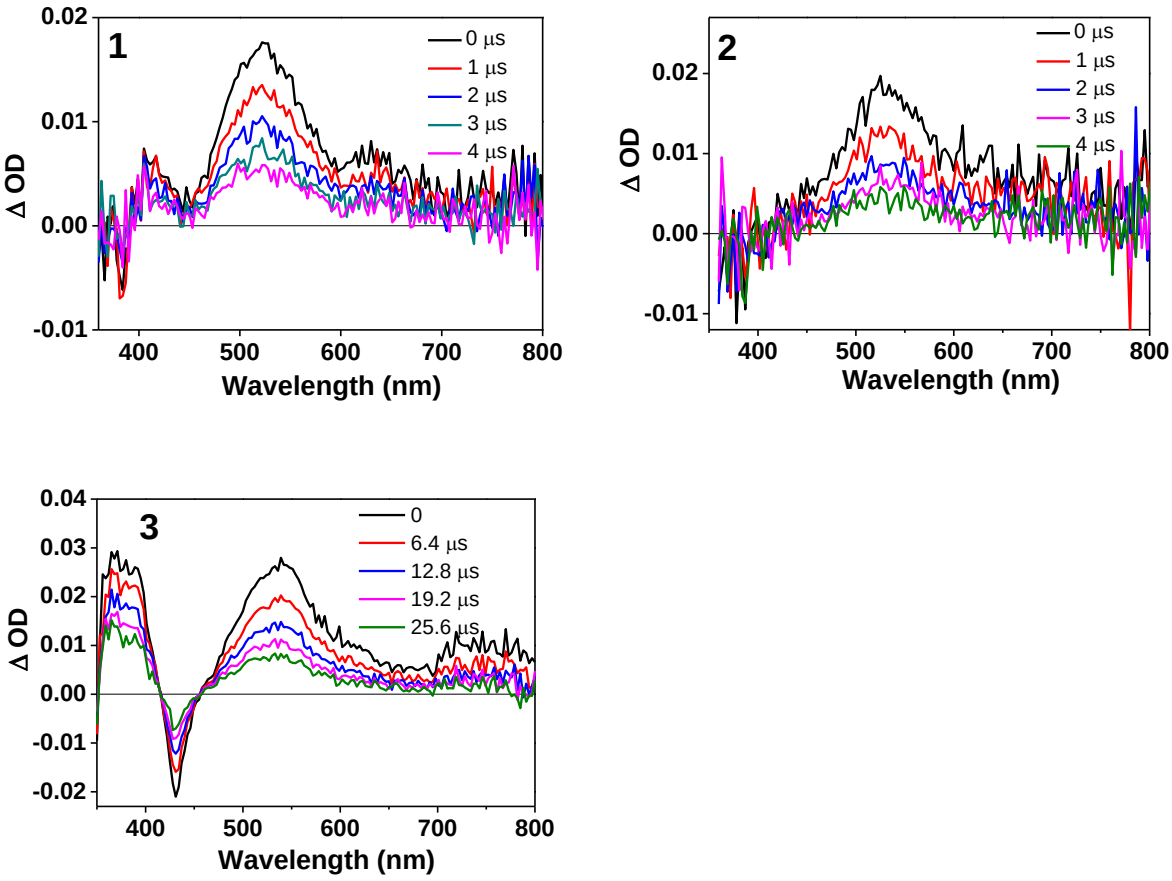


Fig. S10 Time-resolved ns transient absorption spectra of complexes **1-3** in deoxygenated toluene. λ_{ex} = 355 nm, $A_{355\ nm}$ = 0.4 in a 1-cm cuvette.

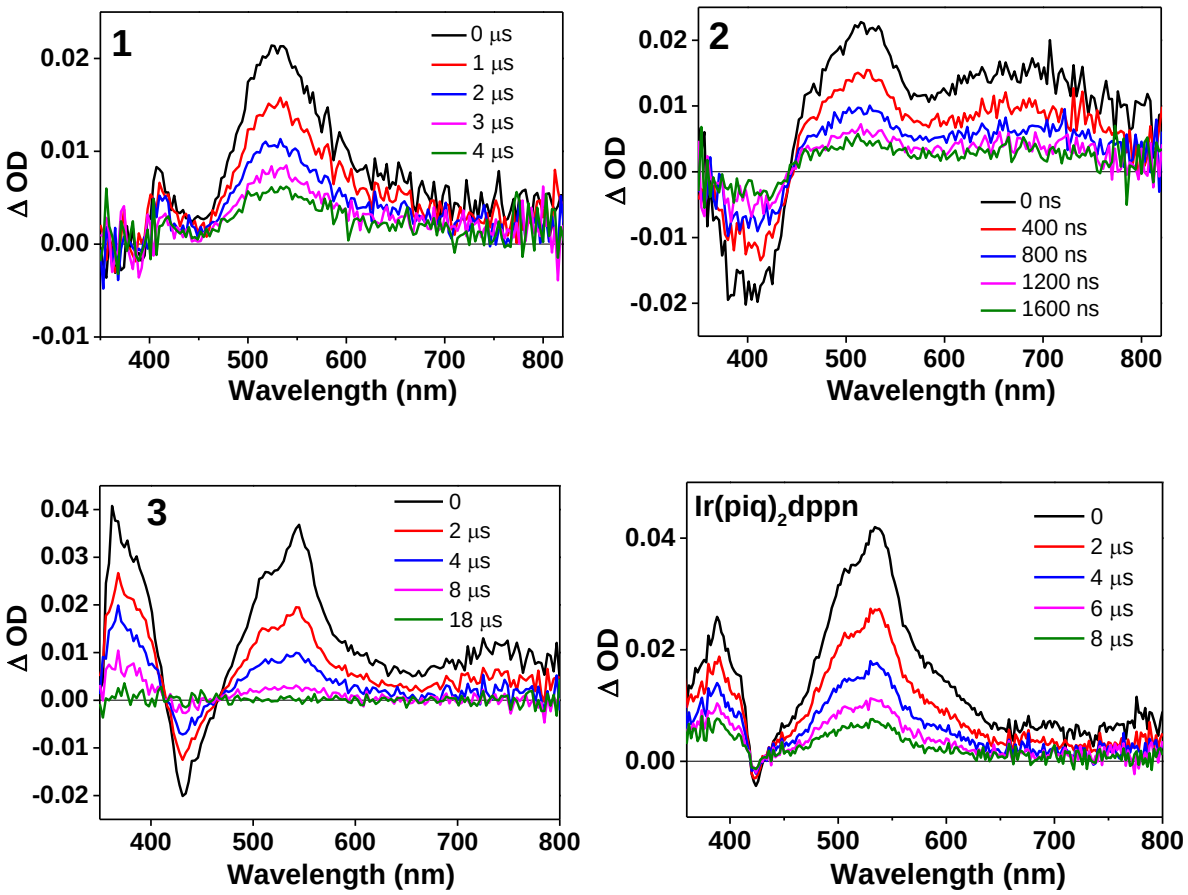


Fig. S11 Time-resolved ns transient absorption spectra of complexes **1-3** and complexes **Ir(piq)$_2$dppn** in deoxygenated acetonitrile. λ_{ex} = 355 nm, $A_{355\ nm}$ = 0.4 in a 1-cm cuvette.

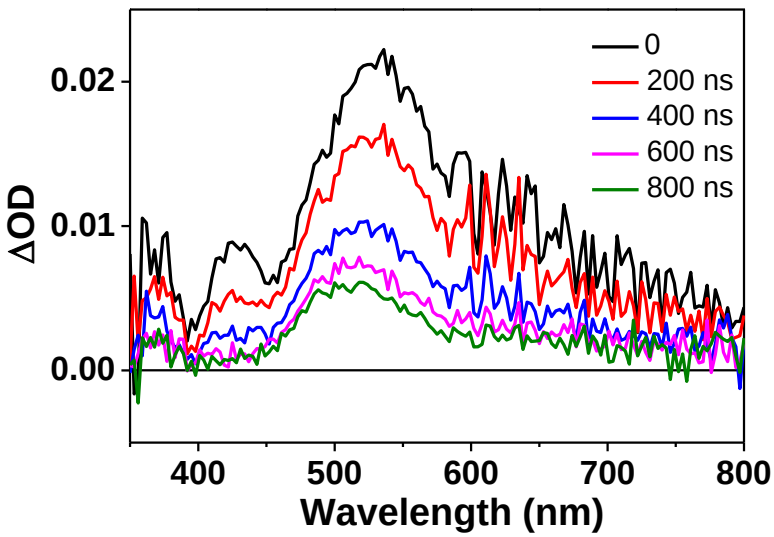


Fig. S12 Time-resolved ns transient absorption spectra of **[Ir(piq)$_2$Cl]$_2$** in deoxygenated acetonitrile. λ_{ex} = 355 nm, $A_{355\ nm}$ = 0.4 in a 1-cm cuvette.

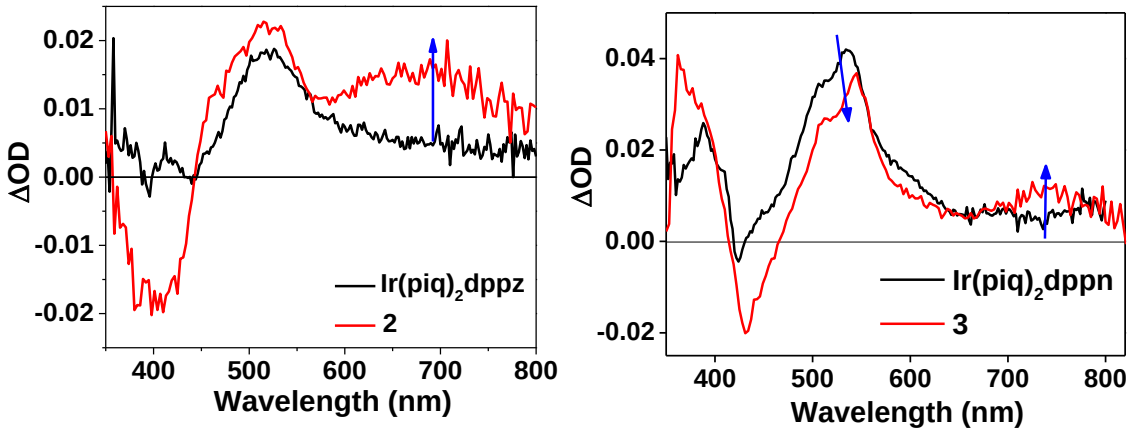


Fig. S13 Comparison of ns transient absorption spectra at zero-time delay for complexes **2** and **3** with **Ir(piq)$_2$dppz** and **Ir(piq)$_2$dppn**, respectively, in deoxygenated acetonitrile. λ_{ex} = 355 nm, $A_{355\ nm}$ = 0.4 in a 1-cm cuvette.

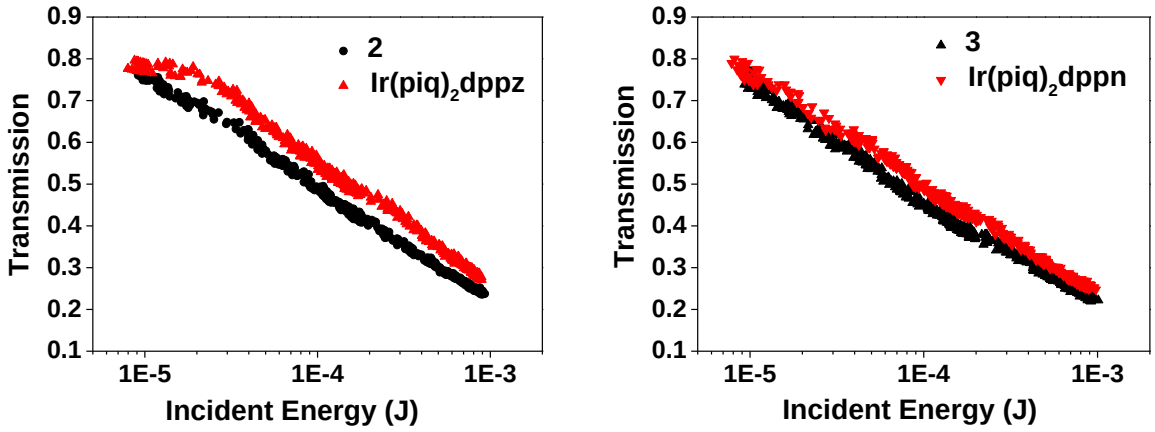


Fig. S14 Comparison of RSA performance of complex **2** with **Ir(piq)$_2$dppz** and complex **3** with **Ir(piq)$_2$dppn** in acetonitrile for 4.1-ns laser pulses at 532 nm in a 2-mm cuvette. The linear transmission was adjusted to 80% at 532 nm for each sample in a 2-mm cuvette.