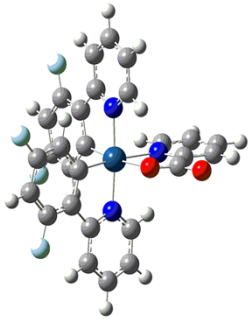
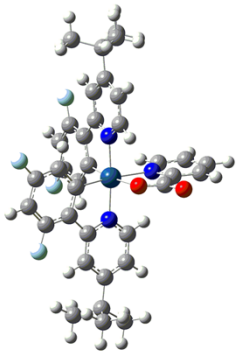
Electronic Supplementary Material (ESI) for Dalton Transactions.

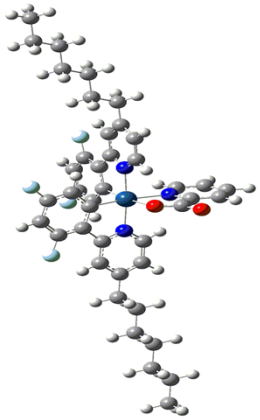
Supporting Information



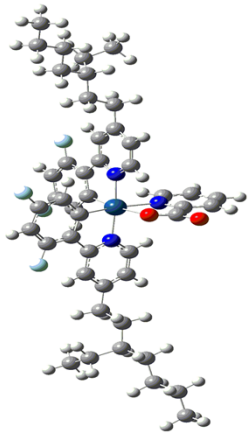
FIrpic



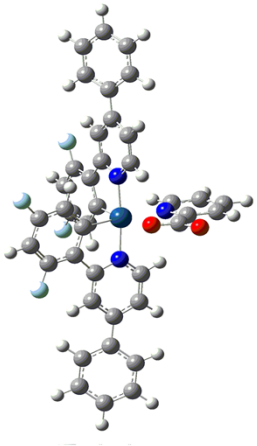
1a



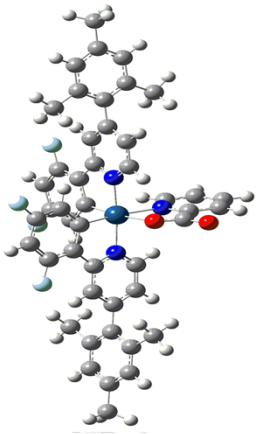
2a



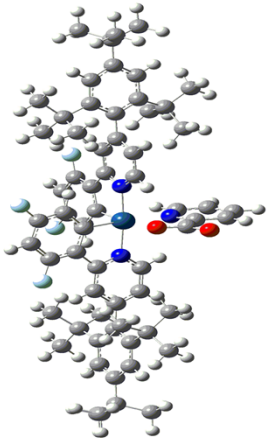
3a



4a



5a



6a

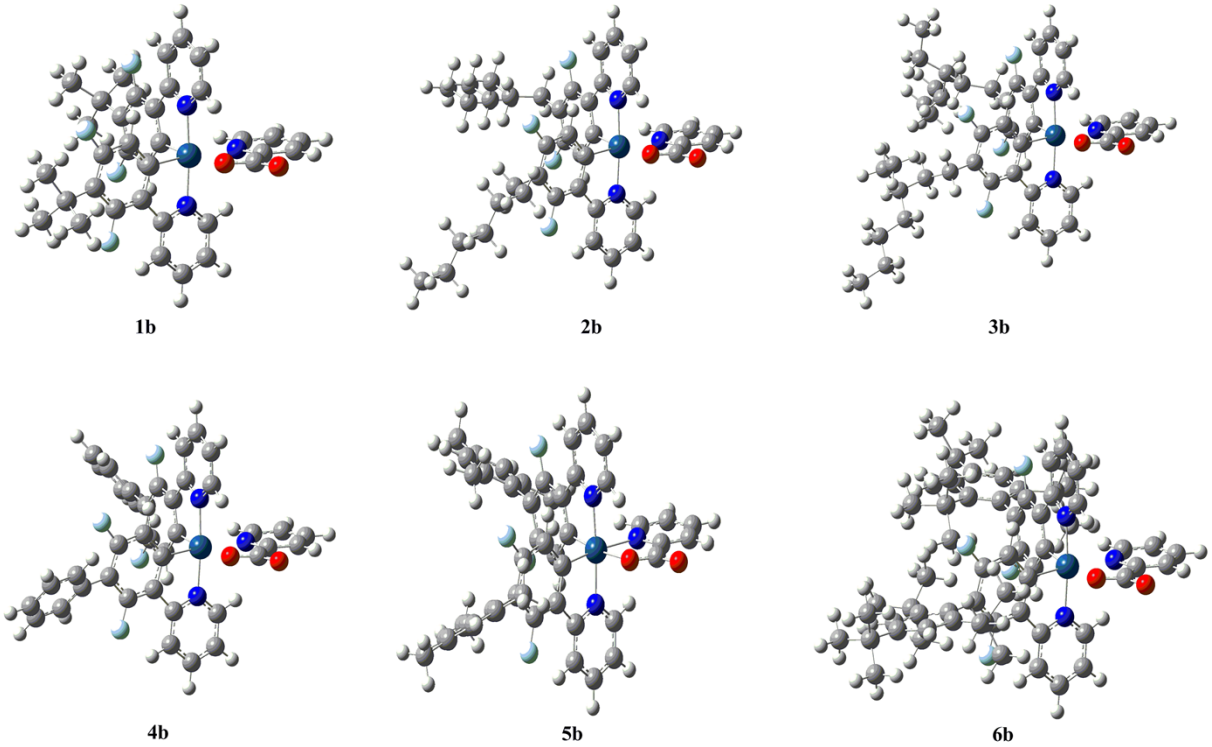
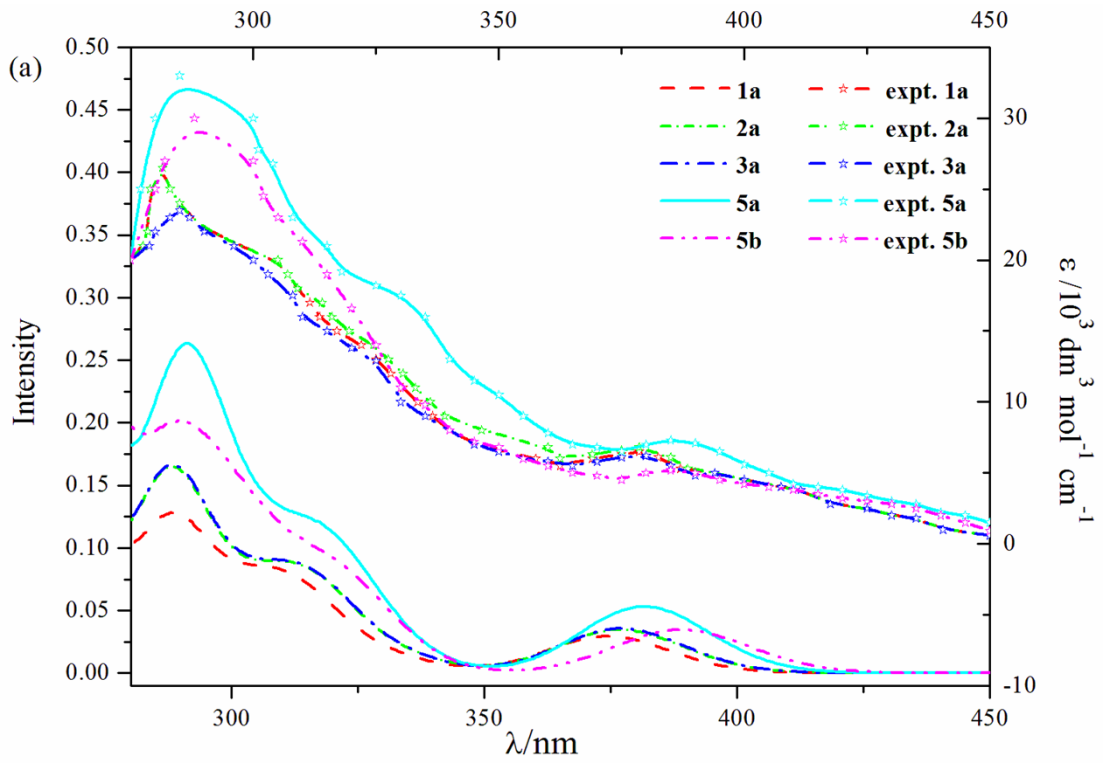
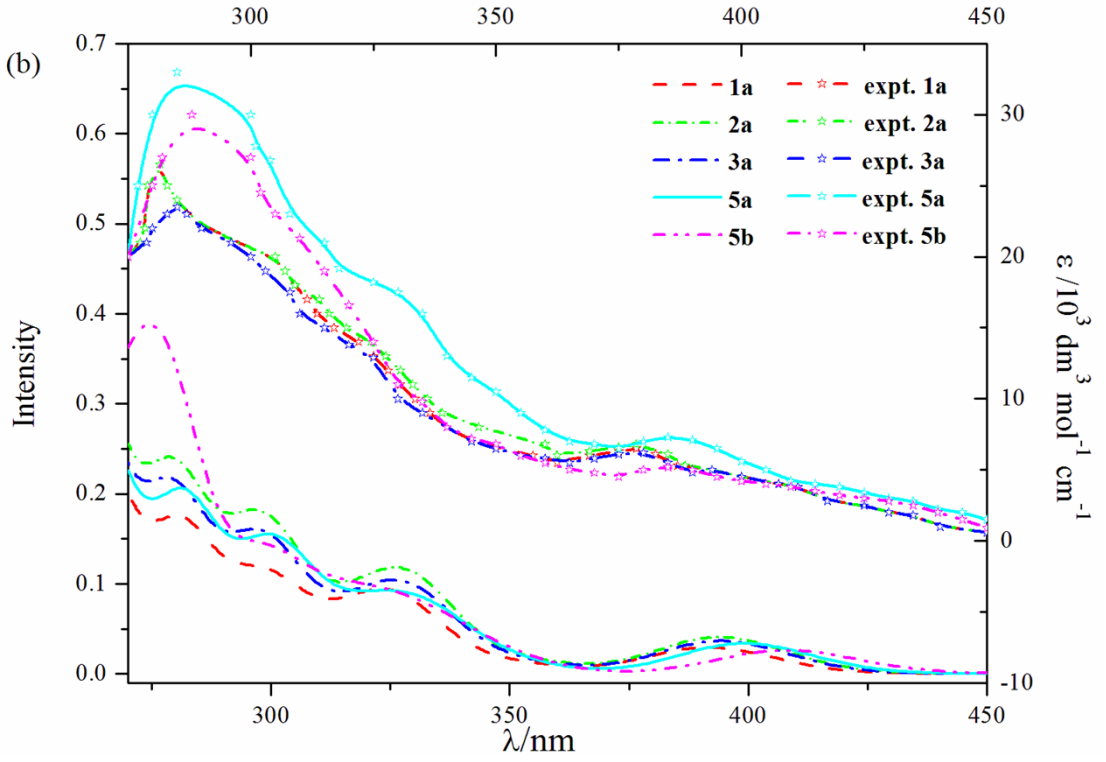
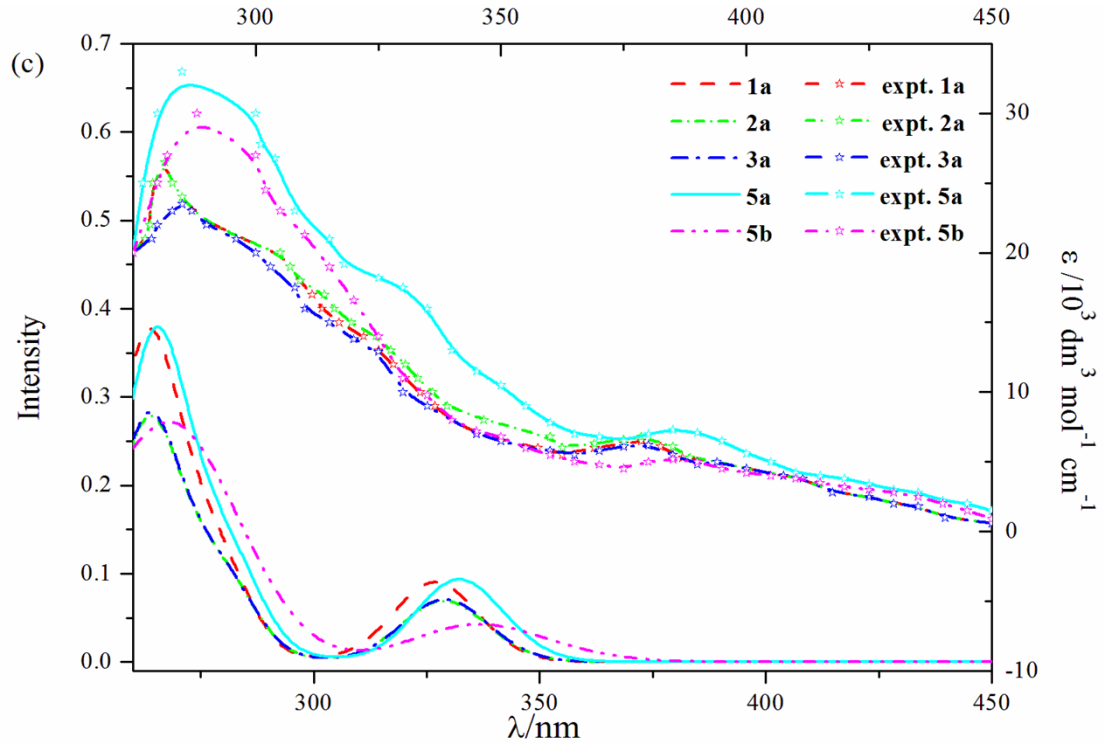
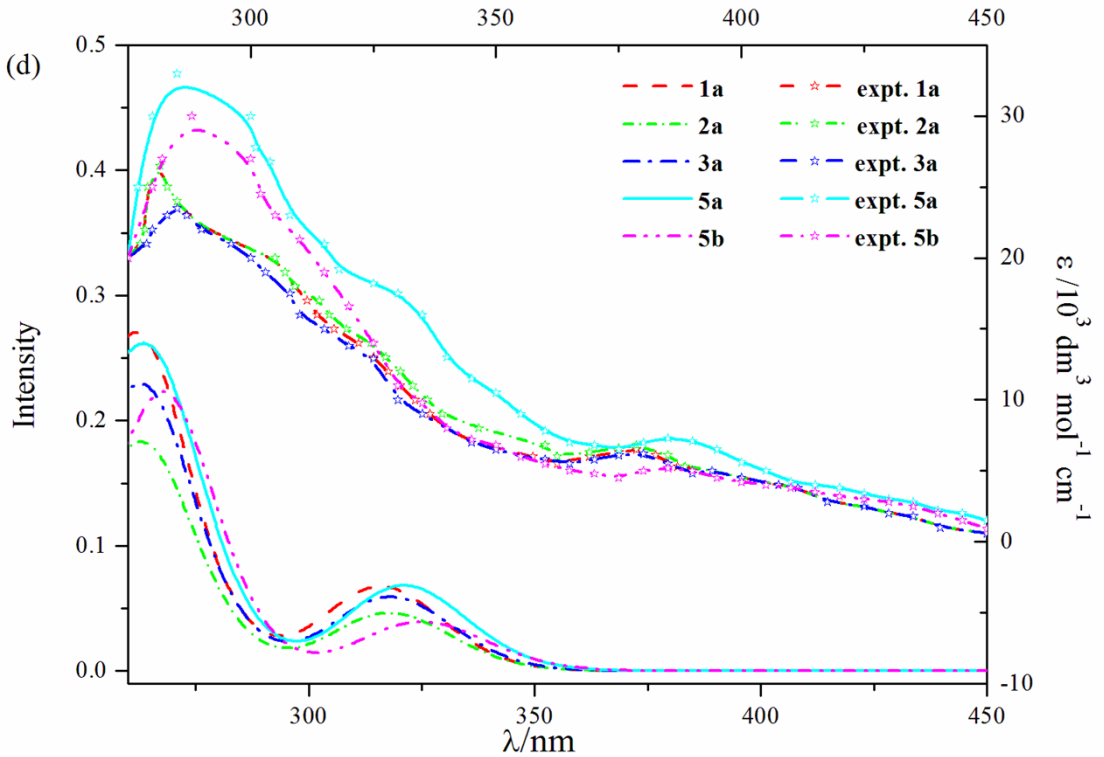


Fig. S1 The optimized ground-state geometrical structures for all investigated Ir(III) complexes at the B3LYP/6-31G(d)(E)ULANL2DZ(Ir) level of theory.


(a)
Intensity
λ/nm
ε /10^3 dm^3 mol^-1 cm^-1
1a
2a
3a
5a
5b
expt. 1a
expt. 2a
expt. 3a
expt. 5a
expt. 5b


(b)
Intensity
λ/nm
ε /10^3 dm^3 mol^-1 cm^-1
1a
2a
3a
5a
5b
expt. 1a
expt. 2a
expt. 3a
expt. 5a
expt. 5b


(c)
1a
2a
3a
5a
5b
expt. 1a
expt. 2a
expt. 3a
expt. 5a
expt. 5b
Intensity
ε /10^3 dm^3 mol^-1 cm^-1
λ/nm


(d)
1a
2a
3a
5a
5b
expt. 1a
expt. 2a
expt. 3a
expt. 5a
expt. 5b
Intensity
ε /10^3 dm^3 mol^-1 cm^-1
λ/nm

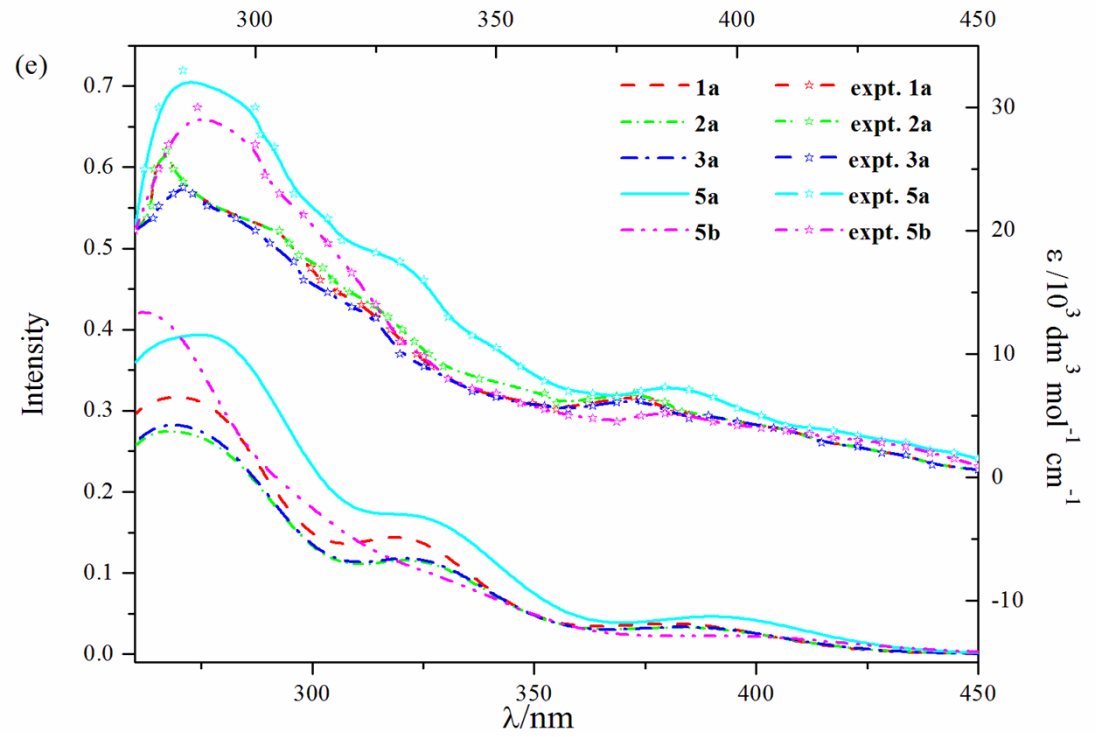
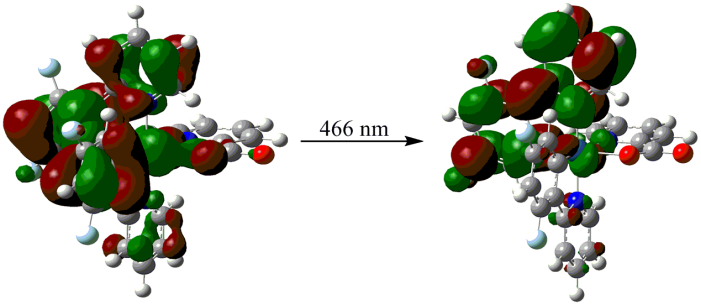


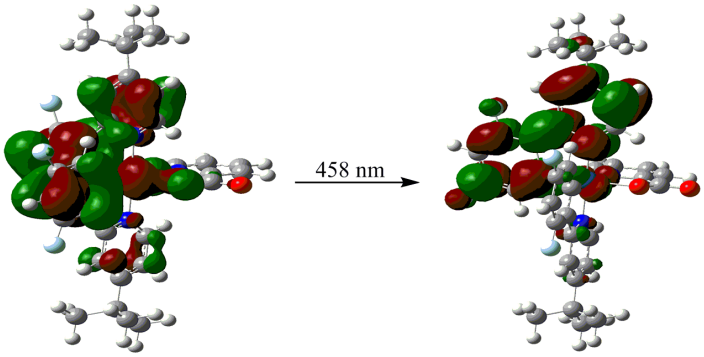
Fig. S2 Simulated (x- and y- axis: bottom-left) and experimental[14] (x- and y- axis: top-right) absorption spectra of complexes **1a-3a**, **5a**, and **5b**, respectively, in toluene solution determined at the TD-PBE0//B3LYP (a), TD-B3LYP//B3LYP (b), TD-CAM-B3LYP//B3LYP (c), TD-M06-2X//B3LYP (d) and TD-LC-BLYP//B3LYP (e) levels of theory with 6-31G(d)(E)ULANL2DZ(Ir) basis set.

FIrpic



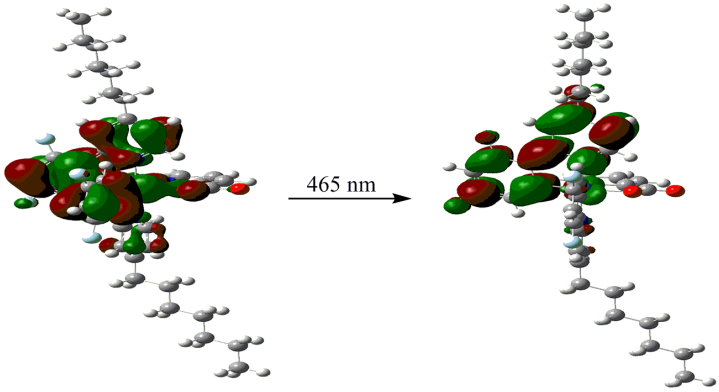
SOMO LUMO

1a



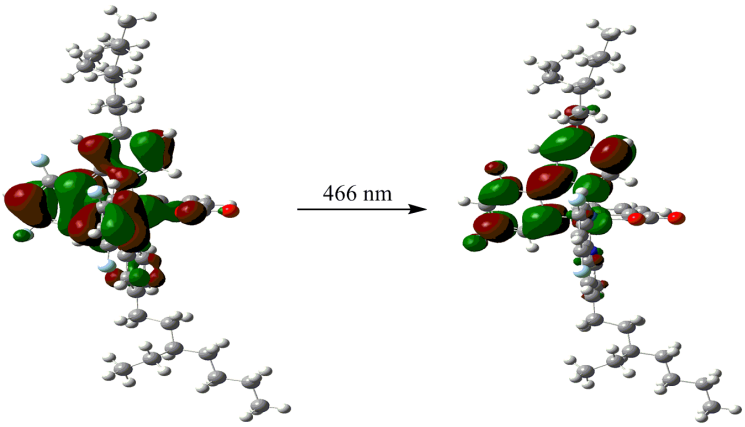
SOMO LUMO

2a



SOMO LUMO

3a



SOMO LUMO

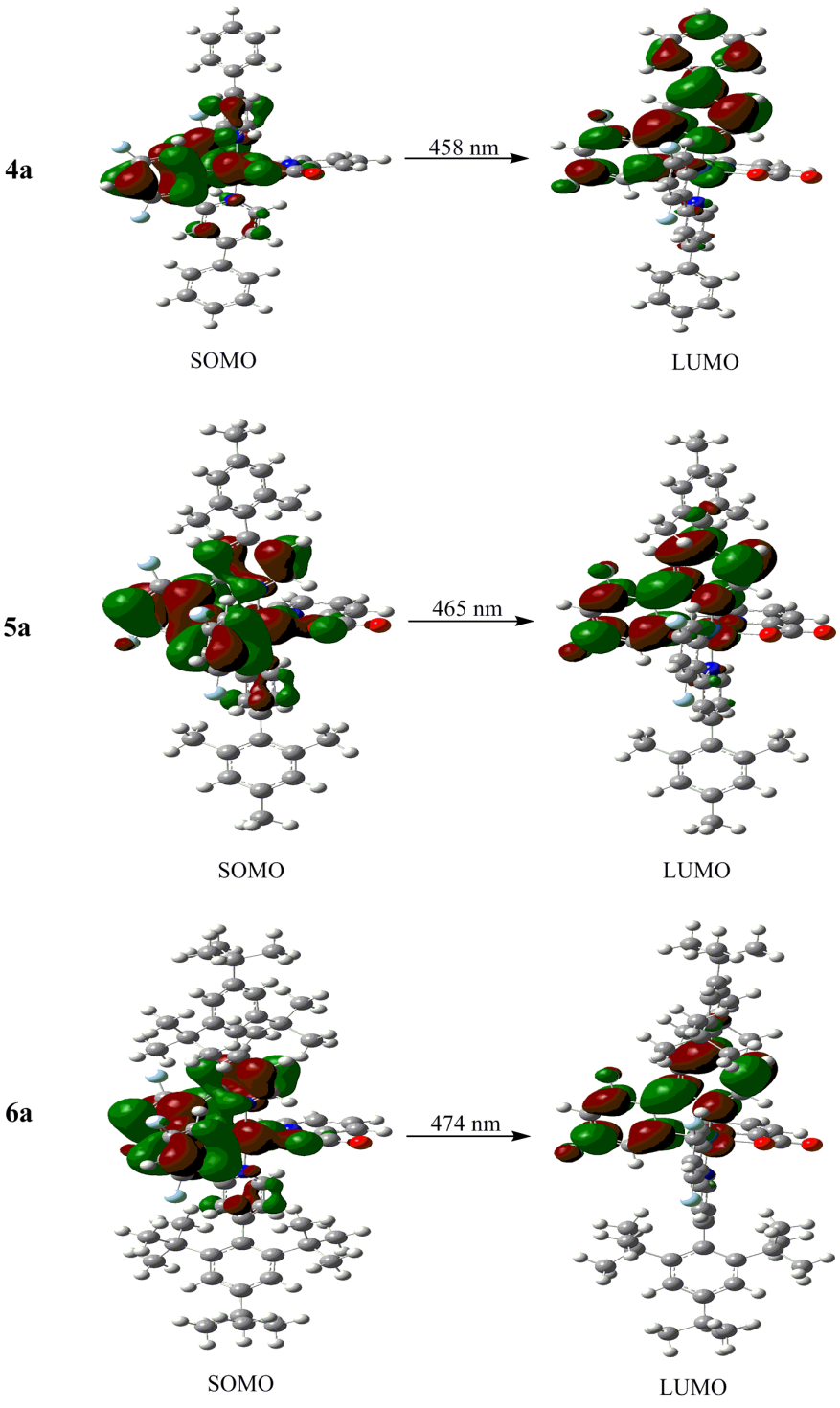
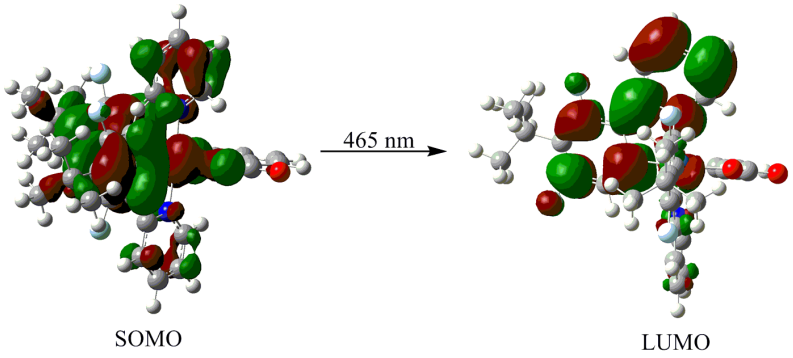


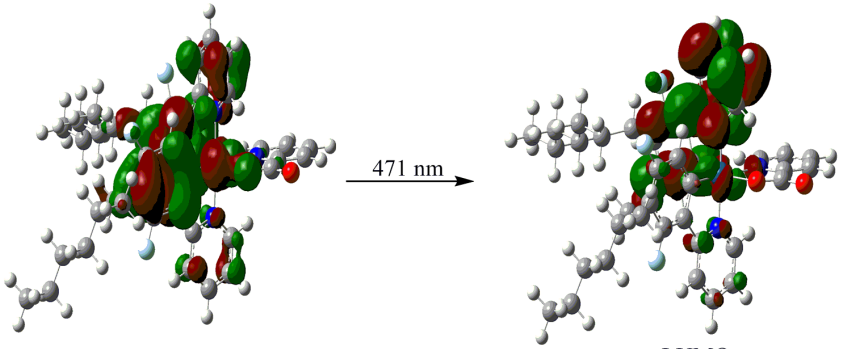
Fig. S3 Contributions of single orbital excitations to the $S_0 \rightarrow T_1$ excitation of complexes **FIrpic** and **1a-6a** determined at TD-M06-2X/6-31G(d)(E)ULANL2DZ(Ir)//B3LYP/6-31G(d)(E)ULANL2DZ(Ir) level of theory.

1b



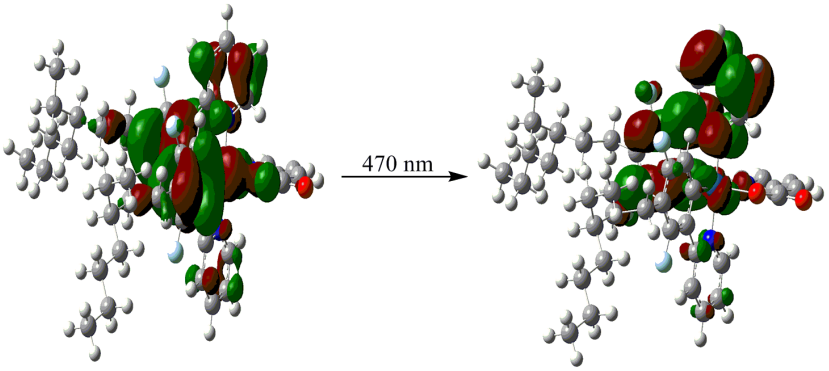
SOMO LUMO

2b



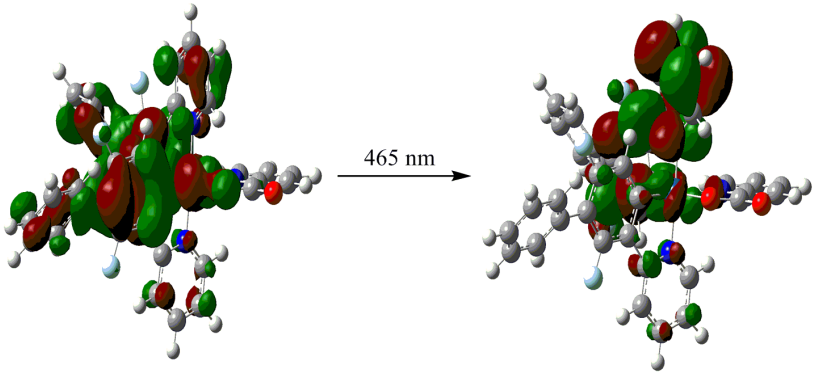
SOMO LUMO

3b



SOMO LUMO

4b



SOMO LUMO

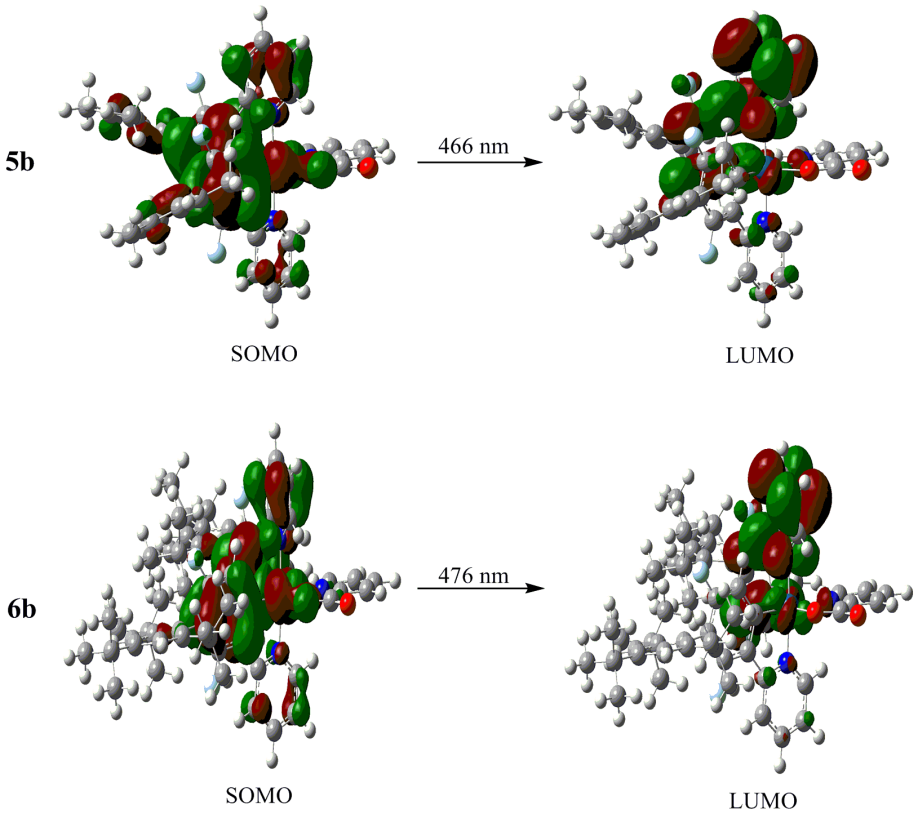


Fig. S4 Contributions of single orbital excitations to the $S_0 \rightarrow T_1$ excitation of complexes **1b-6b** determined at TD-M06-2X/6-31G(d)(E)ULANL2DZ(Ir)//B3LYP/6-31G(d)(E)ULANL2DZ(Ir) level of theory.

Table S1 Main optimized geometric parameters of complexes **1a** in the S_0 state determined at B3LYP/6-31G(d)(E)ULANL2DZ(Ir) and B3LYP/Def2-SVP levels of theory together with the available experimental values.[34]

	B3LYP/ 6-31G(d)(E) ULANL2DZ(Ir)	B3LYP/ Def2-SVP	Expt.
	Bond Length / Å		
Ir–C1	2.010	2.014	1.987
Ir–C2	2.013	2.019	2.003
Ir–N1	2.060	2.067	2.032
Ir–N2	2.072	2.079	2.036
Ir–N3	2.208	2.218	2.146
Ir–O1	2.182	2.172	2.148
	Bond Angle / deg		
C1–Ir–O1	171.55	171.73	173.54
C1–Ir–C2	90.89	90.77	89.94

Table S2 Lowest singlet-triplet (S_0-T_1) and singlet-singlet (S_0-S_1 and S_0-S_2) excitation energies (eV) for complexes **1a-6a** and **1b-6b** calculated in toluene solution at the S_0 and T_1 optimized geometries. For S-S excitations oscillator strengths are also reported in parenthesis.

	1a		**2a**		**3a**	
	S_0	T_1	S_0	T_1	S_0	T_1
S_0-T_1	2.85	2.34	2.83	2.31	2.83	2.31
S_0-S_1	3.08 (0.003)	2.77 (0.079)	3.09 (0.007)	2.76 (0.079)	3.09 (0.005)	2.75 (0.079)
S_0-S_2	3.16 (0.066)	3.00 (0.003)	3.14 (0.065)	3.01 (0.003)	3.14 (0.069)	3.01 (0.003)
	4a		**5a**		**6a**	
	S_0	T_1	S_0	T_1	S_0	T_1
S_0-T_1	2.72	2.28	2.80	2.31	2.78	2.27
S_0-S_1	2.96 (0.064)	2.59 (0.070)	3.10 (0.064)	2.72 (0.084)	3.07 (0.084)	2.71 (0.086)
S_0-S_2	3.05 (0.009)	2.92 (0.035)	3.11 (0.014)	3.02 (0.005)	3.11 (0.014)	3.04 (0.006)
	1b		**2b**		**3b**	
	S_0	T_1	S_0	T_1	S_0	T_1
S_0-T_1	2.76	2.28	2.72	2.25	2.72	2.25
S_0-S_1	3.03 (0.043)	2.65 (0.058)	3.00 (0.045)	2.64 (0.064)	3.00 (0.033)	2.64 (0.063)
S_0-S_2	3.04 (0.008)	2.95 (0.003)	3.01 (0.010)	2.91 (0.003)	3.01 (0.021)	2.91 (0.003)
	4b		**5b**		**6b**	
	S_0	T_1	S_0	T_1	S_0	T_1
S_0-T_1	2.72	2.26	2.75	2.27	2.74	2.26
S_0-S_1	3.00 (0.060)	2.64 (0.070)	3.03 (0.054)	2.66 (0.064)	3.05 (0.047)	2.71 (0.062)
S_0-S_2	3.04 (0.001)	2.94 (0.004)	3.06 (0.002)	2.96 (0.004)	3.08 (0.007)	3.00 (0.004)