Supplementary Information

DFT *vs.* TDDFT *vs.* TDA to simulate phosphorescence spectra of Pt- and Ir-based complexes

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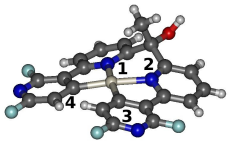
Contents

1 Complex 10



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Pt-N(1)	2.077	2.096	2.107	2.080	2.080
Pt-N(2)	2.065	2.083	2.046	2.069	2.069
Pt-C(3)	1.995	1.990	1.986	1.988	1.983
Pt-C(4)	1.996	1.990	1.982	1.988	1.983

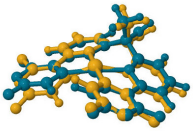


Fig-SI 1: Relaxed ground state structure (left) of **10**. Experimental[1] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

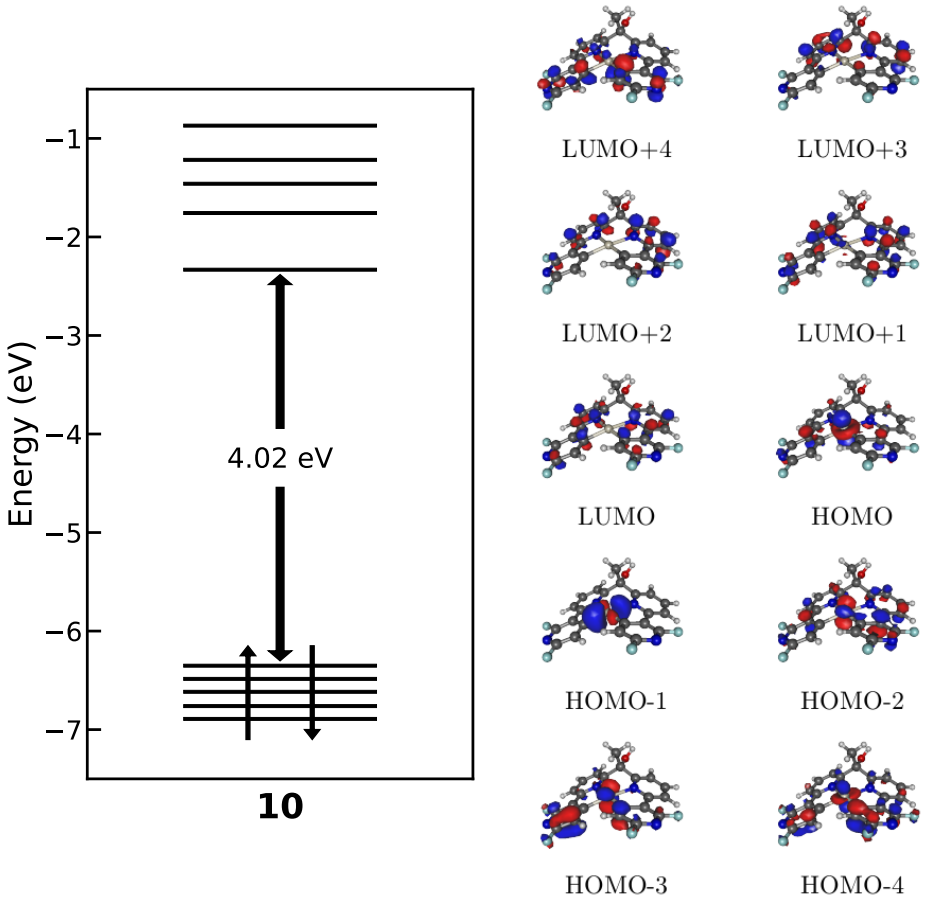


Fig-SI 2: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **10**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.29	3.54	HOMO-2 → LUMO HOMO-3 → LUMO
3.73	3.86	HOMO → LUMO+1 HOMO-3 → LUMO HOMO-1 → LUMO+1
4.05	3.93	HOMO-4 → LUMO HOMO → LUMO+2
4.54	4.47	HOMO-3 → LUMO+1 HOMO-2 → LUMO+1 HOMO-1 → LUMO+3

Table-SI 1: Experimental[1] and computed absorption energies and excitation assignments obtained on complex **10**.

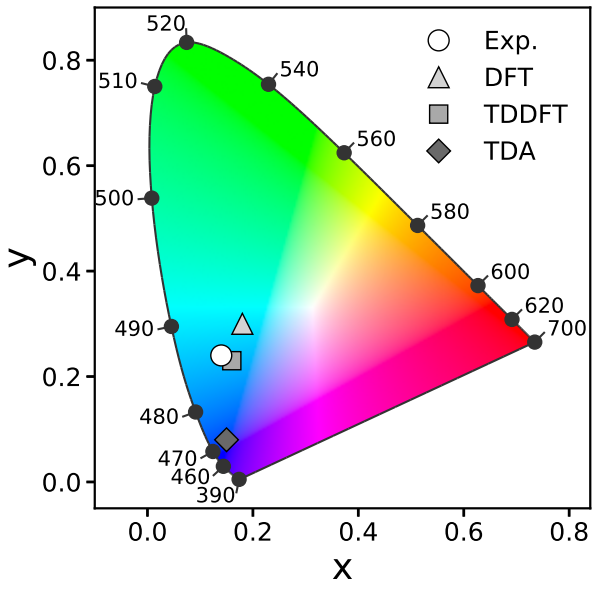
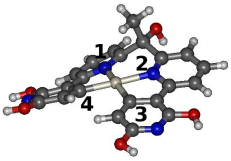


Fig-SI 3: Experimental[1] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **10** over a CIE 1931 chromaticity horseshoe diagram.

2 Complex 13



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Pt-N(1)	2.054	2.083	2.039	2.063	2.061
Pt-N(2)	2.057	2.093	2.052	2.070	2.068
Pt-C(3)	1.998	1.994	1.979	1.992	1.990
Pt-C(4)	1.980	1.995	1.985	1.992	1.990

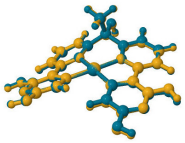


Fig-SI 4: Relaxed ground state structure (left) of **13**. Experimental[1] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

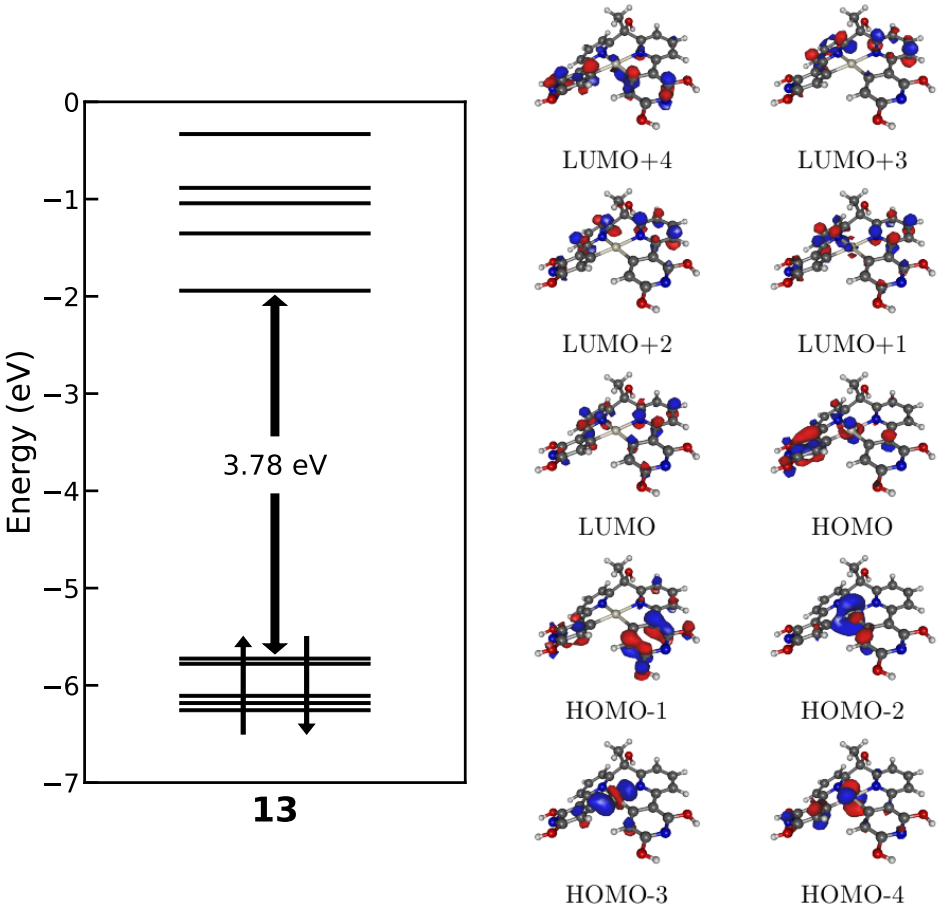


Fig-SI 5: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **13**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.93	3.07	HOMO → LUMO HOMO-2 → LUMO
3.49	3.56	HOMO-4 → LUMO HOMO-3 → LUMO HOMO-2 → LUMO HOMO → LUMO+1
4.23	4.42	HOMO-1 → LUMO+3 HOMO-2 → LUMO+3 HOMO-4 → LUMO+1 HOMO-3 → LUMO+2

Table-SI 2: Experimental[1] and computed absorption energies and excitation assignments obtained on complex **13**.

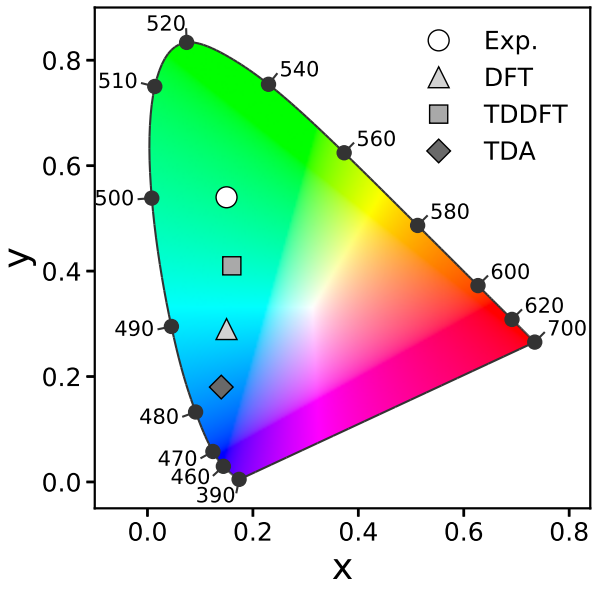
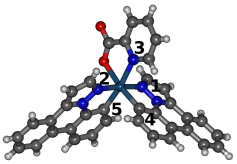


Fig-SI 6: Experimental[1] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **13** over a CIE 1931 chromaticity horseshoe diagram.

3 Complex I1



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-N(1)	2.028	2.036	2.040	2.037	2.040
Ir-N(2)	1.998	2.036	2.032	2.039	2.031
Ir-N(3)	2.106	2.152	2.147	2.168	2.150
Ir-C(4)	2.020	2.005	1.998	1.978	1.993
Ir-C(5)	2.009	2.018	2.004	2.015	2.002
Ir-O	2.142	2.172	2.074	2.174	2.081

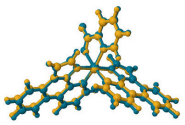


Fig-SI 7: Relaxed ground state structure (left) of **I1**. Experimental[2] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

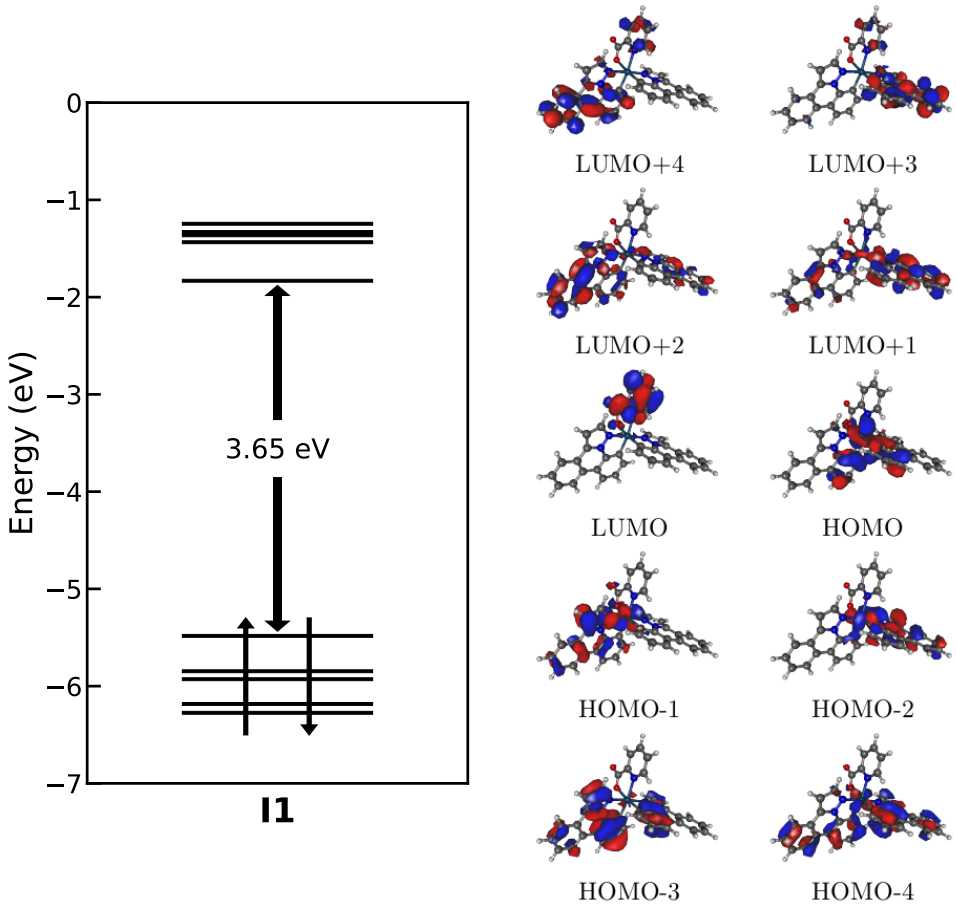


Fig-SI 8: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **I1**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.58	3.39	HOMO-1 → LUMO
4.47	4.29	HOMO-4→ LUMO+1 HOMO-3→ LUMO+4 HOMO-4 → LUMO+2

Table-SI 3: Experimental[2] and computed absorption energies and excitation assignments obtained on complex **I1**.

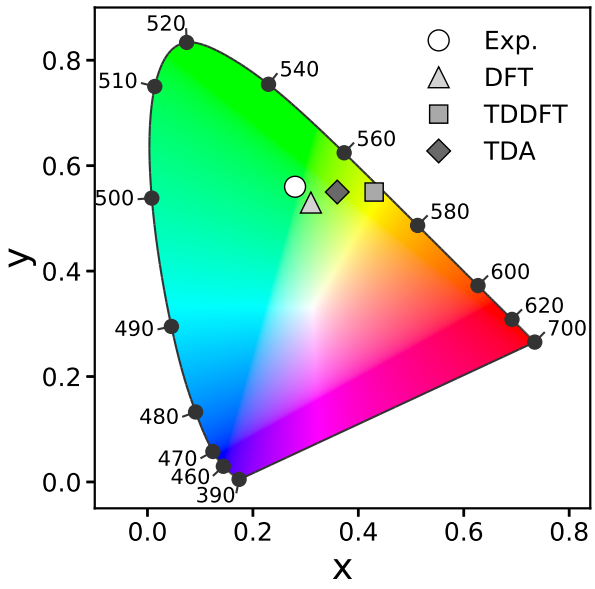
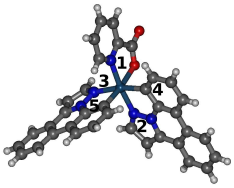


Fig-SI 9: Experimental[2] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **I1** over a CIE 1931 chromaticity horseshoe diagram.

4 Complex I3



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-N(1)	2.039	2.033	2.023	2.038	2.027
Ir-N(2)	2.040	2.043	2.072	2.042	2.066
Ir-N(3)	2.135	2.157	2.202	2.171	2.201
Ir-C(4)	2.013	2.014	1.971	1.990	1.967
Ir-C(5)	2.008	2.012	2.050	2.014	2.047
Ir-O	2.159	2.165	2.021	2.165	2.027

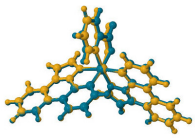


Fig-SI 10: Relaxed ground state structure (left) of **I3**. Experimental[2] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

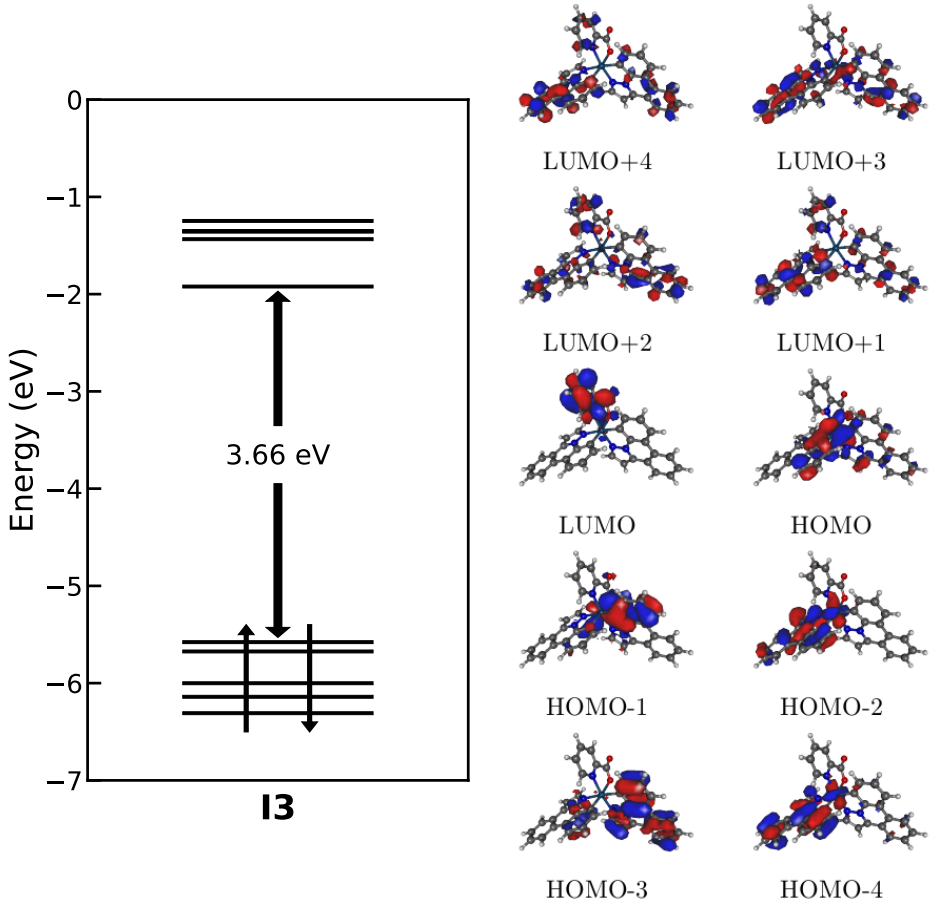


Fig-SI 11: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **I3**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.56	3.46	HOMO-2 → LUMO
4.58	4.58	HOMO-4→ LUMO+4 HOMO-3→ LUMO+7 HOMO-5 → LUMO+1

Table-SI 4: Experimental[2] and computed absorption energies and excitation assignments obtained on complex **I3**.

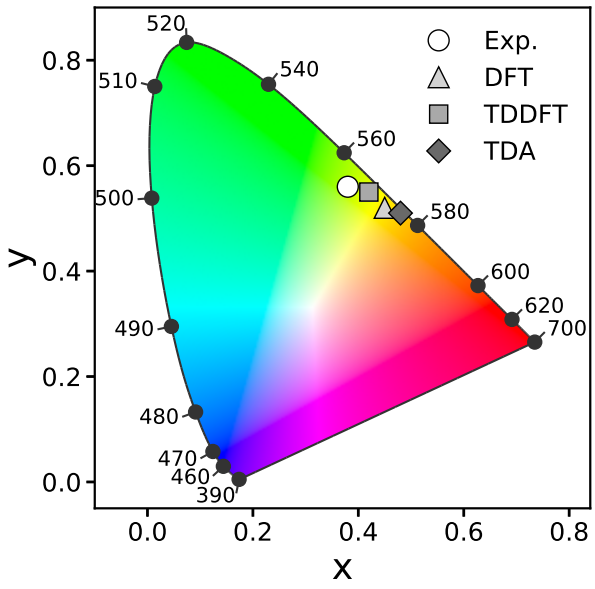
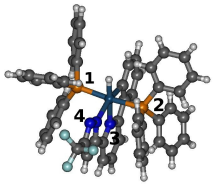


Fig-SI 12: Experimental[2] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **I3** over a CIE 1931 chromaticity horseshoe diagram.

5 Complex 1a



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.307	2.358	2.375	2.367	2.376
Ir-P(2)	2.316	2.356	2.368	2.362	2.366
Ir-N(3)	2.056	2.068	2.058	2.060	2.059
Ir-N(4)	2.090	2.178	2.176	2.182	2.177
Ir-C	2.055	2.039	2.011	2.028	2.014
Ir-H	1.512	1.619	1.622	1.622	1.622

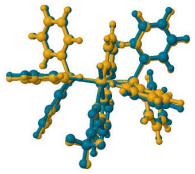


Fig-SI 13: Relaxed ground state structure (left) of **1a**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

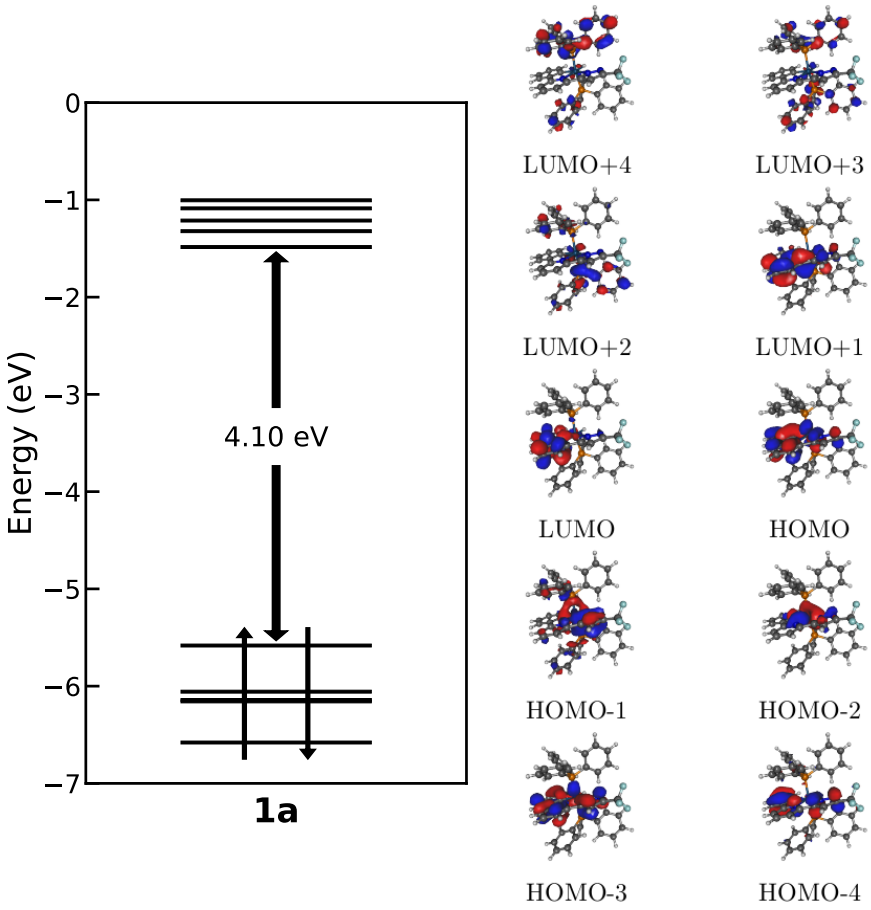


Fig-SI 14: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **1a**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.15	3.32	HOMO → LUMO HOMO → LUMO+1
3.63	3.67	HOMO → LUMO+1
4.46	4.20	HOMO-1 → LUMO+2 HOMO → LUMO+5 HOMO-2 → LUMO+2

Table-SI 5: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **1a**.

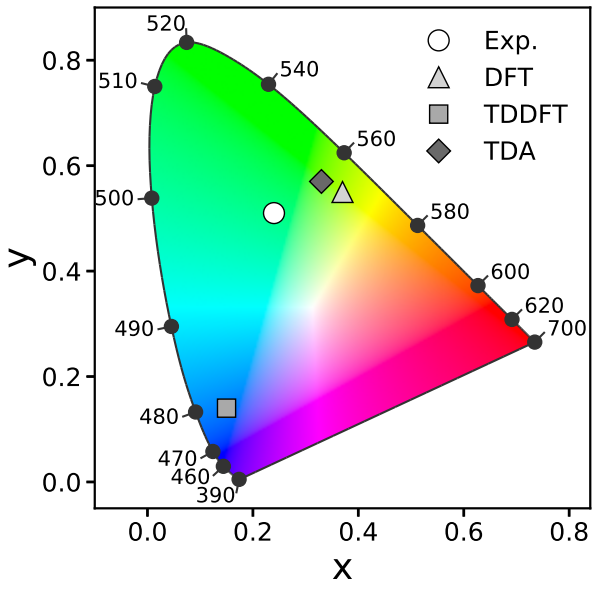
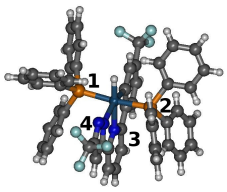


Fig-SI 15: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **1a** over a CIE 1931 chromaticity horseshoe diagram.

6 Complex 2a



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.307	2.307	2.386	2.381	2.383
Ir-P(2)	2.316	2.361	2.374	2.374	2.374
Ir-N(3)	2.056	2.066	2.058	2.048	2.058
Ir-N(4)	2.090	2.166	2.156	2.141	2.159
Ir-C	2.055	2.036	2.003	2.015	2.003
Ir-H	1.512	1.618	1.618	1.623	1.619

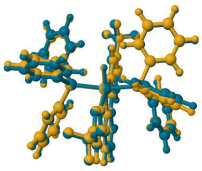


Fig-SI 16: Relaxed ground state structure (left) of **2a**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

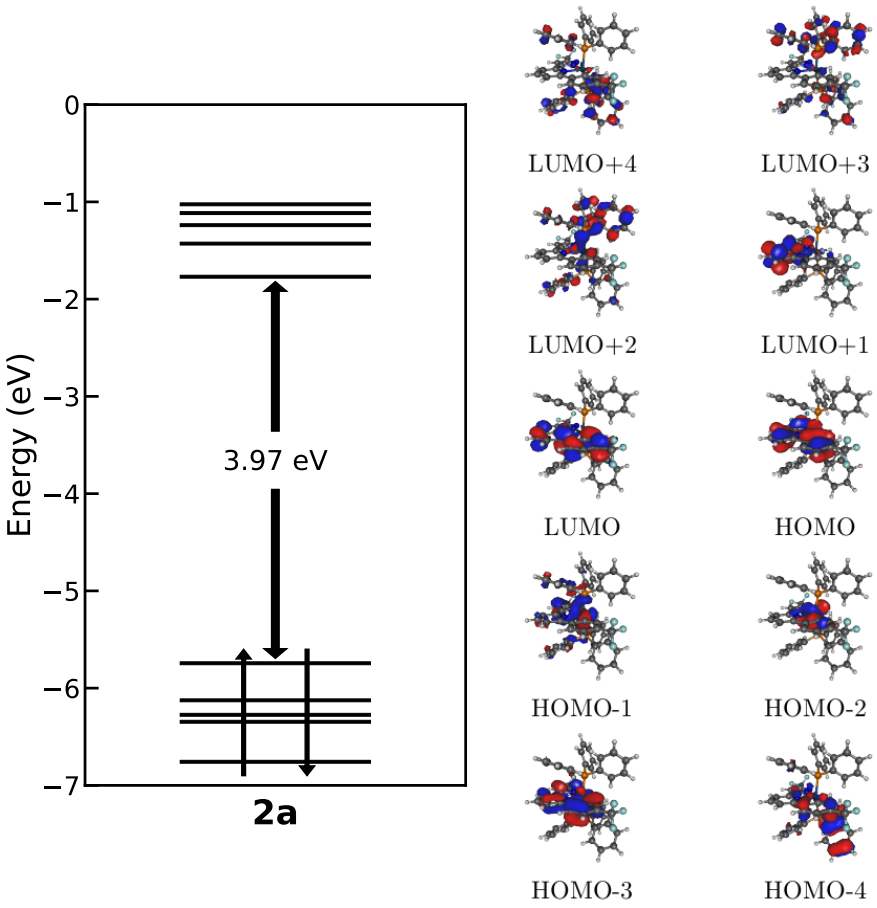


Fig-SI 17: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **2a**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.05	3.25	HOMO → LUMO HOMO → LUMO+1
3.66	3.76	HOMO → LUMO+1 HOMO-1 → LUMO
4.54	4.26	HOMO-2 → LUMO+2 HOMO-1 → LUMO+2

Table-SI 6: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **2a**.

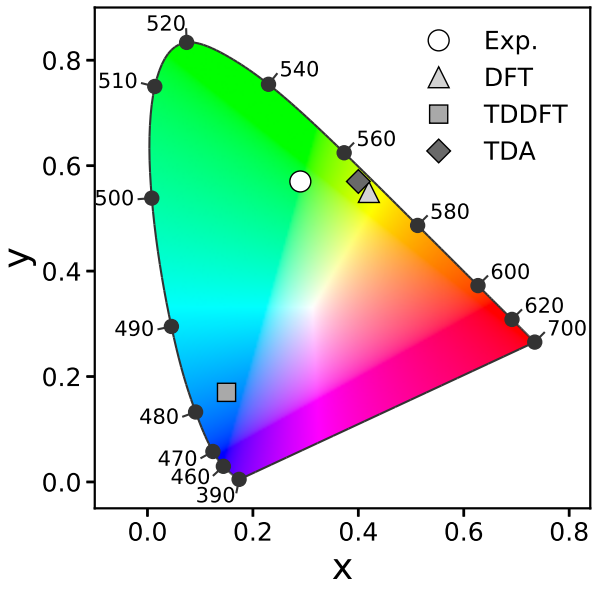
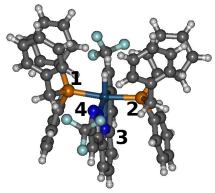


Fig-SI 18: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **2a** over a CIE 1931 chromaticity horseshoe diagram.

7 Complex 2c



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.309	2.361	2.384	2.374	2.382
Ir-P(2)	2.318	2.360	2.381	2.373	2.382
Ir-N(3)	2.066	2.063	2.058	2.058	2.058
Ir-N(4)	2.123	2.149	2.143	2.149	2.143
Ir-C	2.049	2.036	2.000	2.015	2.003
Ir-H	1.473	1.619	1.620	1.620	1.620

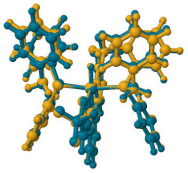


Fig-SI 19: Relaxed ground state structure (left) of **2c**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

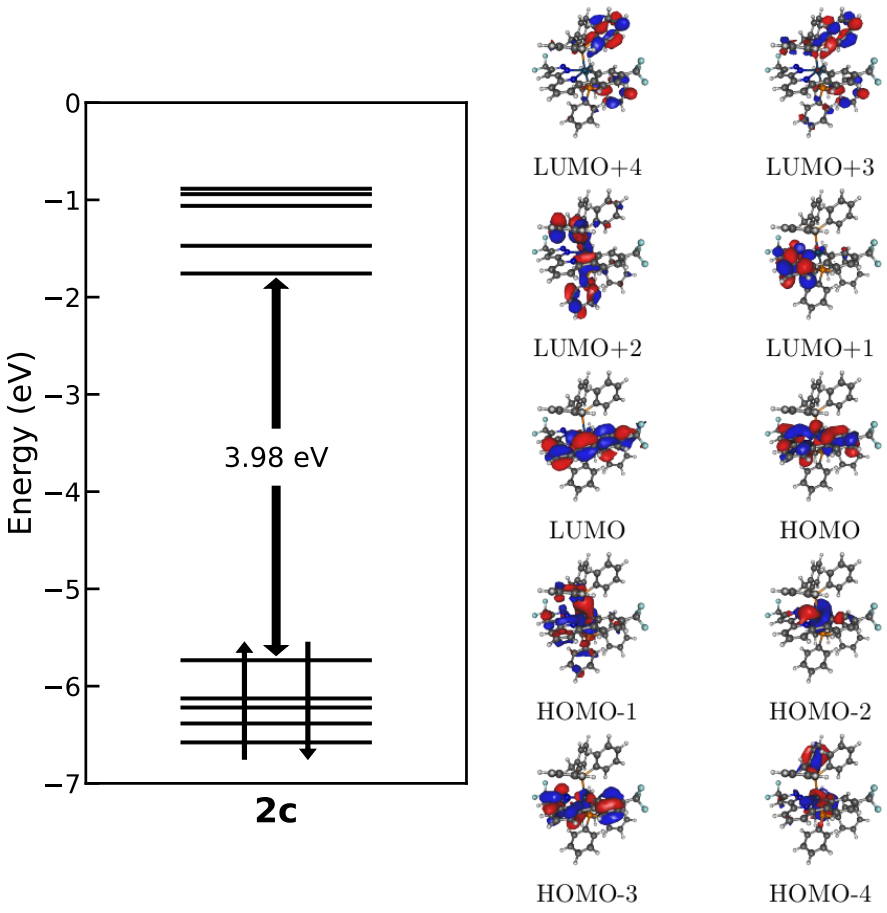


Fig-SI 20: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **2c**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.10†	3.24	HOMO → LUMO HOMO → LUMO+1
3.64	3.75	HOMO-1 → LUMO HOMO → LUMO+1
4.61	4.40	HOMO-1 → LUMO+2

Table-SI 7: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **2c**. † Approximately attributed from experimental spectra.

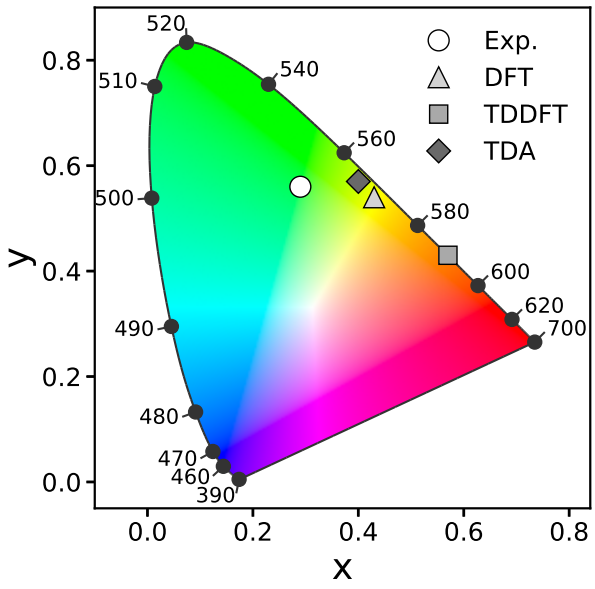
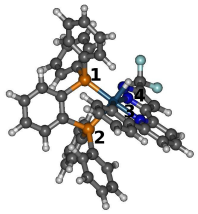


Fig-SI 21: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **2c** over a CIE 1931 chromaticity horseshoe diagram.

8 Complex 3a



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.240	2.296	2.309	2.305	2.309
Ir-P(2)	2.347	2.401	2.434	2.418	2.434
Ir-N(3)	2.048	2.043	2.028	2.030	2.028
Ir-N(4)	2.117	2.147	2.138	2.145	2.139
Ir-C	2.038	2.045	2.019	2.033	2.019
Ir-H	1.595	1.623	1.620	1.621	1.619

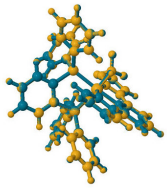


Fig-SI 22: Relaxed ground state structure (left) of **3a**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

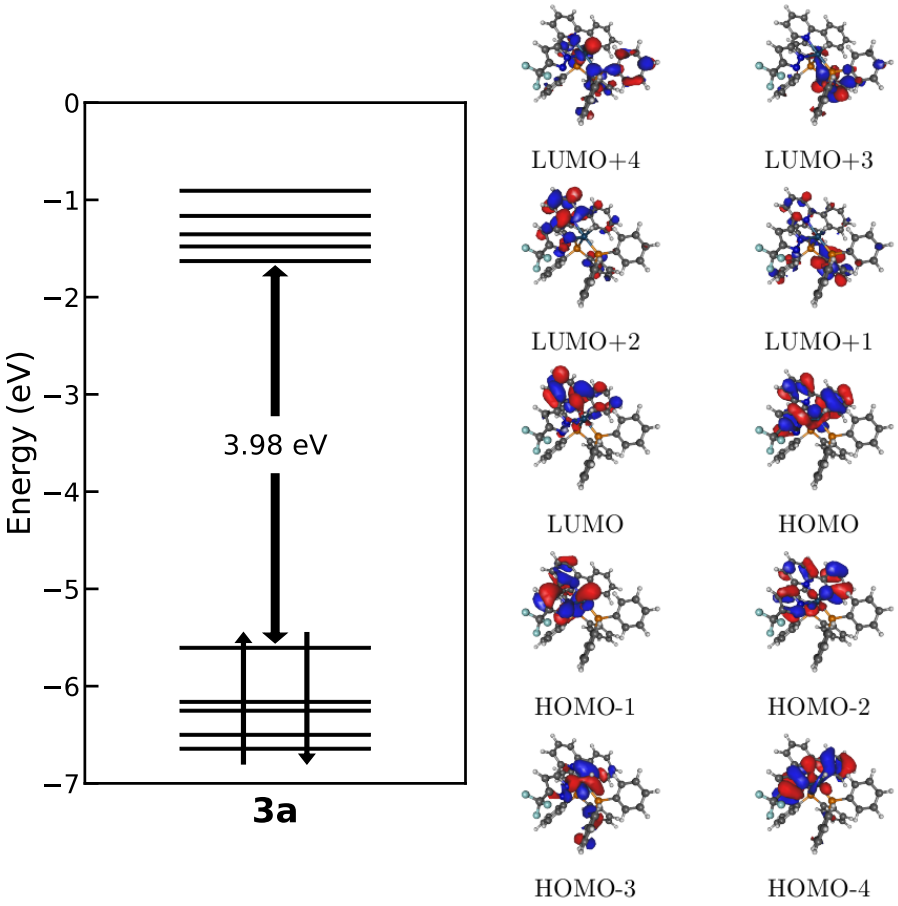


Fig-SI 23: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **3a**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.12	3.17	HOMO → LUMO
3.80	3.90	HOMO-1 → LUMO HOMO → LUMO+3
4.61	4.56	HOMO-4 → LUMO+1 HOMO-4 → LUMO+2

Table-SI 8: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **3a**.

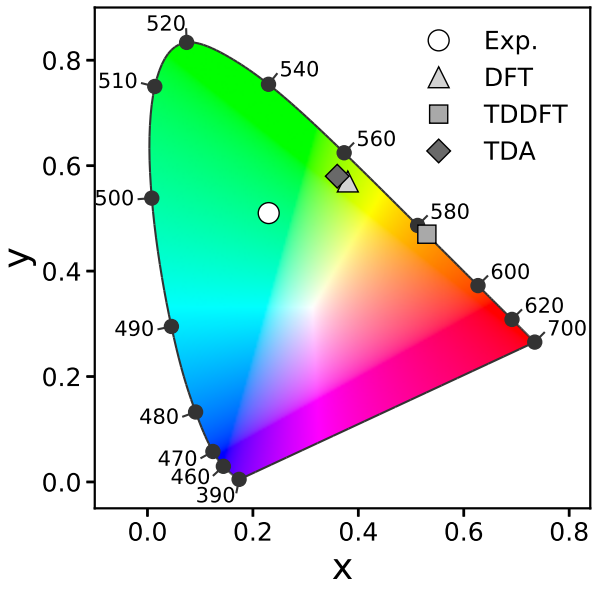
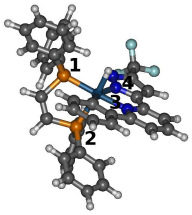


Fig-SI 24: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **3a** over a CIE 1931 chromaticity horseshoe diagram.

9 Complex 3b



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.240	2.295	2.308	2.304	2.309
Ir-P(2)	2.347	2.406	2.452	2.426	2.444
Ir-N(3)	2.048	2.040	2.023	2.027	2.025
Ir-N(4)	2.117	2.144	2.129	2.143	2.135
Ir-C	2.038	2.044	2.016	2.031	2.017
Ir-H	1.595	1.622	1.615	1.619	1.617

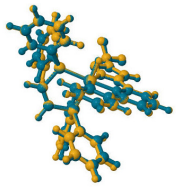


Fig-SI 25: Relaxed ground state structure (left) of **3b**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

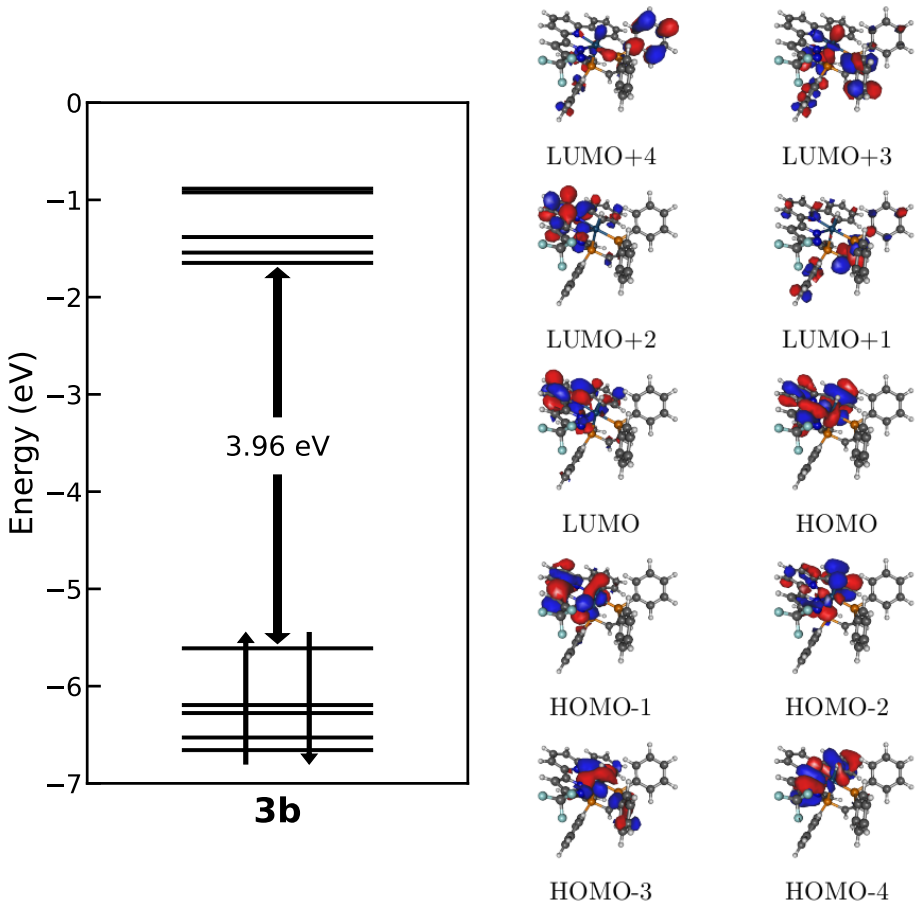


Fig-SI 26: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **3b**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.09	3.17	HOMO → LUMO
3.81	3.91	HOMO-1 → LUMO

Table-SI 9: CExperimental[3] and computed absorption energies and excitation assignments obtained on complex **3b**.

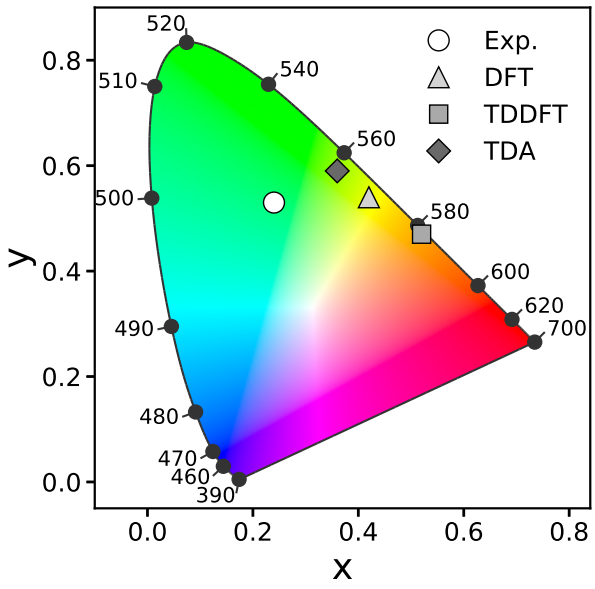
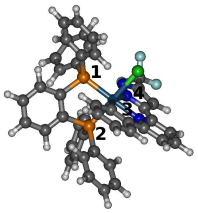


Fig-SI 27: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **3b** over a CIE 1931 chromaticity horseshoe diagram.

10 Complex 4a



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.240	2.328	2.338	2.334	2.338
Ir-P(2)	2.347	2.293	2.296	2.293	2.296
Ir-N(3)	2.048	2.044	2.026	2.030	2.025
Ir-N(4)	2.117	2.156	2.150	2.158	2.148
Ir-C	2.038	2.048	2.023	2.033	2.021
Ir-Cl	2.250	2.467	2.489	2.484	2.497

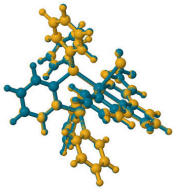


Fig-SI 28: Relaxed ground state structure (left) of **4a**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

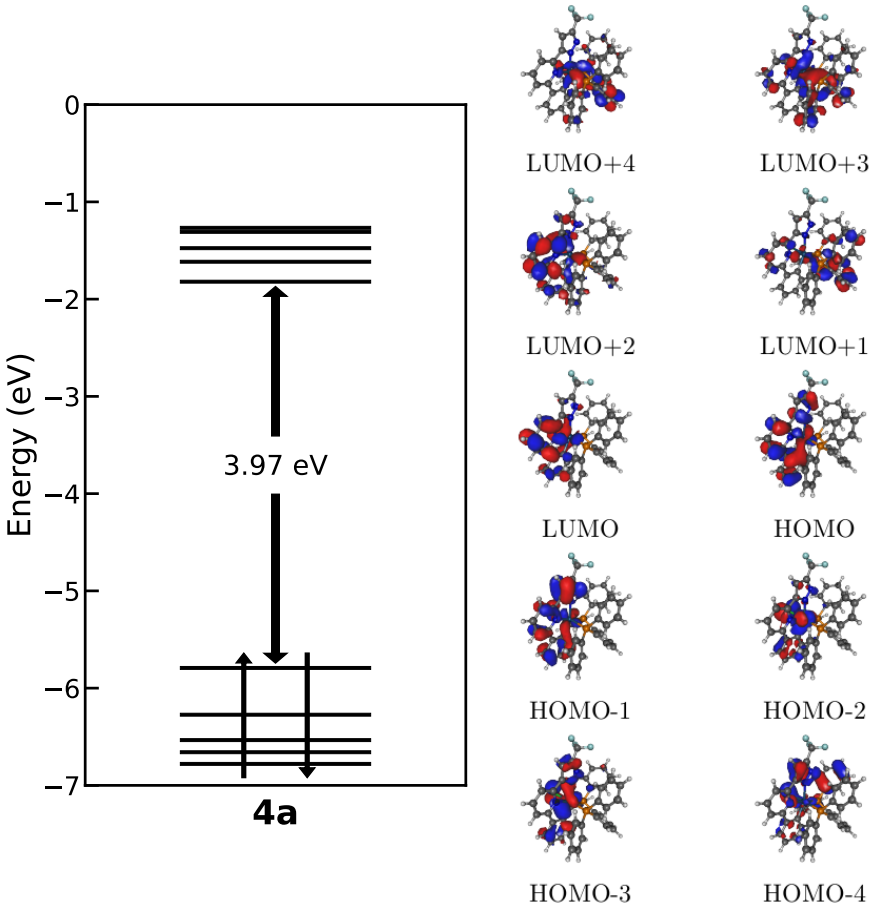


Fig-SI 29: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **4a**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.06	3.15	HOMO → LUMO
3.80	3.75	HOMO-1 → LUMO HOMO → LUMO+3

Table-SI 10: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **4a**.

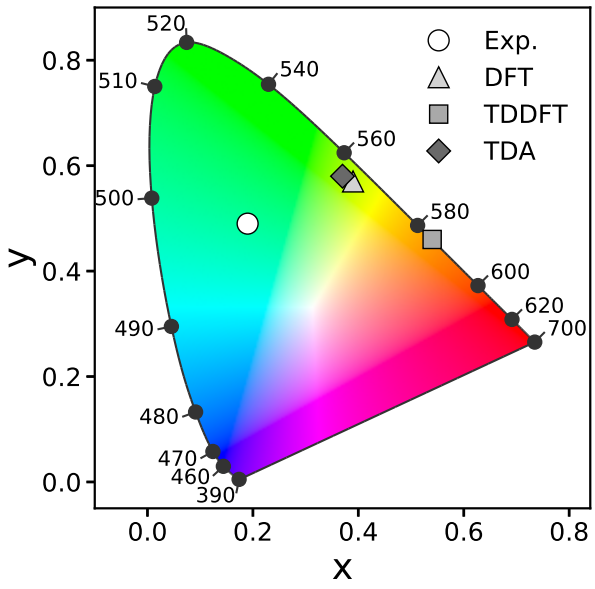
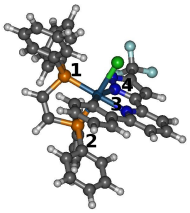


Fig-SI 30: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **4a** over a CIE 1931 chromaticity horseshoe diagram.

11 Complex 4b



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.240	2.326	2.337	2.332	2.338
Ir-P(2)	2.347	2.295	2.299	2.296	2.300
Ir-N(3)	2.048	2.042	2.024	2.028	2.023
Ir-N(4)	2.117	2.152	2.146	2.155	2.144
Ir-C	2.038	2.046	2.018	2.029	2.016
Ir-Cl	2.250	2.467	2.493	2.486	2.506

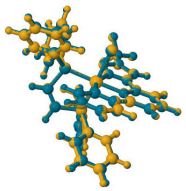


Fig-SI 31: Relaxed ground state structure (left) of **4b**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

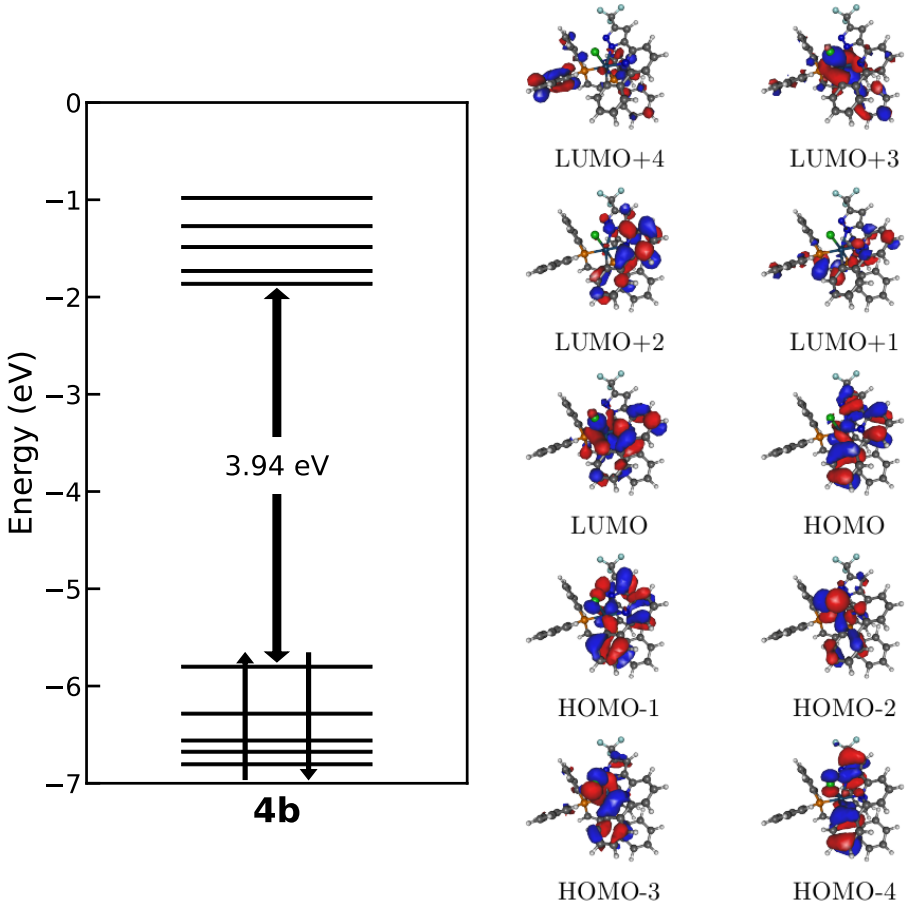


Fig-SI 32: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **4b**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
3.07	3.12	HOMO → LUMO
4.16	3.72	HOMO-1 → LUMO+3 HOMO → LUMO+2

Table-SI 11: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **4b**.

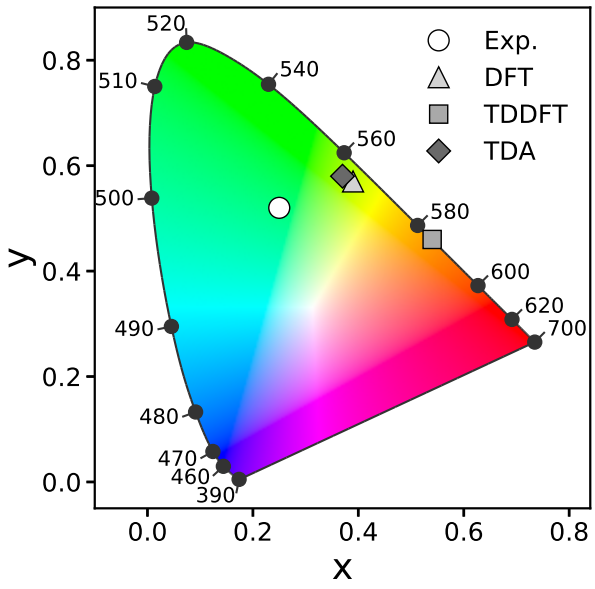
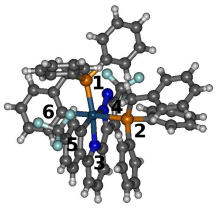


Fig-SI 33: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **4b** over a CIE 1931 chromaticity horseshoe diagram.

12 Complex 5c



Bond	Exp.	GS	Unr. DFT	TDDFT	TDA
Ir-P(1)	2.283	2.345	2.365	2.356	2.364
Ir-P(2)	2.416	2.494	2.570	2.533	2.565
Ir-N(3)	2.041	2.030	2.016	2.018	2.016
Ir-N(4)	2.125	2.137	2.123	2.131	2.126
Ir-C(5)	2.063	2.043	2.008	2.019	2.007
Ir-C(6)	2.102	2.093	2.080	2.088	2.078

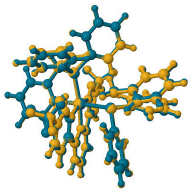


Fig-SI 34: Relaxed ground state structure (left) of **5c**. Experimental[3] and computed relevant geometrical parameters (middle) around the metal centre in Å. Ground and excited (Unr. DFT) states superimposed geometries (right).

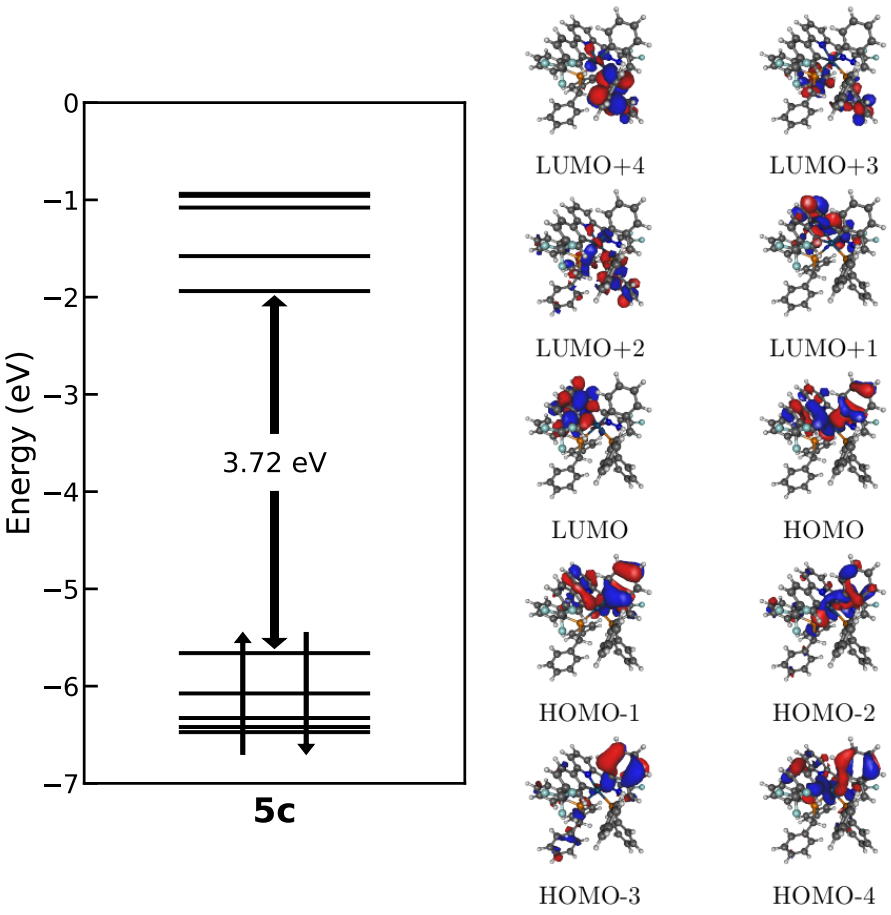


Fig-SI 35: Energetic diagram (left) and graphical representation of the frontier orbitals (right) of complex **5c**.

Exp. (eV)	TDDFT (eV)	Excitation assignments
2.95	2.96	HOMO → LUMO
3.67	3.73	HOMO-2 → LUMO

Table-SI 12: Experimental[3] and computed absorption energies and excitation assignments obtained on complex **5c**.

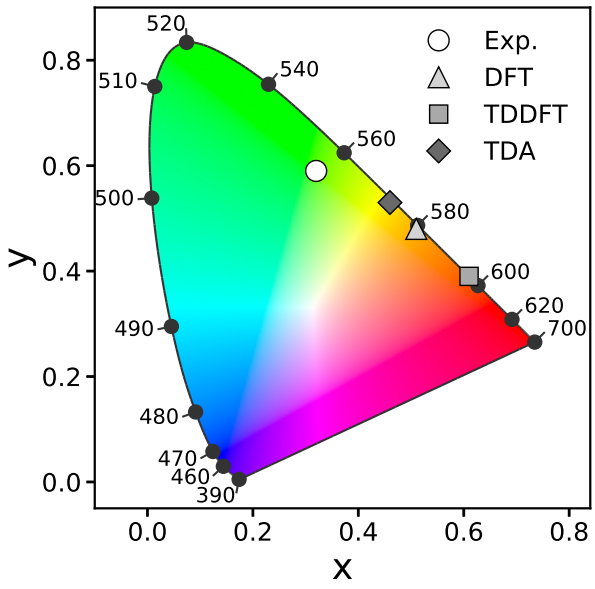
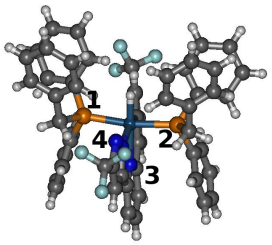


Fig-SI 36: Experimental[3] and computed (Unr. DFT, TDDFT and TDA) colour rendering of **5c** over a CIE 1931 chromaticity horseshoe diagram.

13 Basis set impact



		Ground State		
Bond	Exp.	**A**	**B**	**C**
Ir-P(1)	2.309	2.361	2.360	2.348
Ir-P(2)	2.318	2.360	2.359	2.348
Ir-N(3)	2.066	2.063	2.067	2.078
Ir-N(4)	2.123	2.149	2.149	2.161
Ir-C	2.049	2.036	2.037	2.051
Ir-H	1.473	1.619	1.605	1.610

	Unr. DFT		
Bond	**A**	**B**	**C**
Ir-P(1)	2.384	2.382	2.373
Ir-P(2)	2.381	2.382	2.368
Ir-N(3)	2.058	2.061	2.072
Ir-N(4)	2.143	2.141	2.161
Ir-C	2.000	2.002	2.011
Ir-H	1.620	1.606	1.611

Fig-SI 37: Relaxed ground and excited state structures of complex **2c** with respect to the basis set used together with relevant experimental data.[3] **A** refers to LANL2DZ+pol. (excepting H), **B** corresponds to LANL2DZ+pol. on all atoms and **C** is the Def2TZVP basis set.

14 Absorption spectra of complex 1a

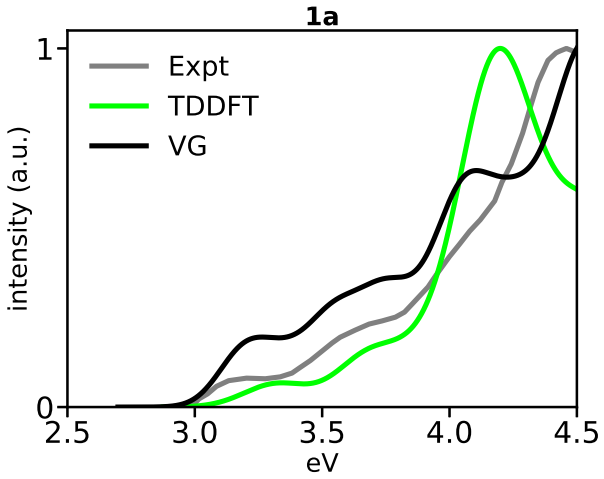


Fig-SI 38: Simulated and experimental absorption spectra of complex **1a** using TDDFT (green) and VG (black) model.[3]

15 Experimental and simulated phosphorescence

Table-SI 13: Experimental and simulated (electronic and vibronic) emission bands in eV together with the average and the mean absolute error (MAE) with respect to the highest energy band.[1, 2, 3], † Approximately attributed from experimental spectra.

	Exp.	Unr. DFT				TDDFT				TDA			
		Elec.	$\Delta_{\text{Elec.}}$	AH	Δ_{AH}	Elec.	$\Delta_{\text{Elec.}}$	AH	Δ_{AH}	Elec.	$\Delta_{\text{Elec.}}$	AH	Δ_{AH}
10	2.66, 2.51	2.71	0.05	2.66, 2.51	0.00, 0.00	2.58	-0.08	2.71, 2.55	0.05, 0.04	2.78	0.12	2.87, 2.72	0.21, 0.21
13	2.53, 2.41	2.76	0.23	2.66, 2.51	0.13, 0.10	2.48	-0.05	2.58, 2.41	0.05, 0.00	2.59	0.06	2.68, 2.52	0.15, 0.11
I1	2.37	2.64	0.27	2.39	0.02	2.31	-0.06	2.29	-0.08	2.17	-0.20	2.33	-0.04
I3	2.28	2.49	0.21	2.21	-0.07	2.33	0.05	2.31	0.03	1.86	-0.42	2.16	-0.12
1a	2.60, 2.42, 2.26	2.64	0.04	2.53, 2.35, 2.20	-0.07, -0.07, -0.06	2.65	0.05	2.80, 2.64, 2.47	0.20, 0.22, 0.21	2.36	-0.24	2.51, 2.33, 2.17	-0.09, -0.09, -0.09
2a	2.54, 2.37, 2.22	2.53	-0.01	2.41, 2.23, 2.08	-0.13, -0.14, -0.14	2.62	0.08	2.76, 2.59, 2.43	0.22, 0.22, 0.21	2.24	-0.30	2.41, 2.23, 2.07	-0.13, -0.14, -0.15
2c	2.55, 2.37, 2.21	2.53	-0.02	2.43, 2.25, 2.10	-0.12, -0.12, -0.11	2.01	-0.54	2.20, 2.02, 1.87	-0.35, -0.35, -0.34	2.25	-0.30	2.41, 2.23, 2.07	-0.14, -0.14, -0.14
3a	2.59, 2.41, 2.27	2.58	-0.01	2.45, 2.27, 2.11	-0.14, -0.14, -0.16	2.08	-0.51	2.24, 2.06, 1.90	-0.35, -0.35, -0.37	2.31	-0.28	2.45, 2.27, 2.11	-0.14, -0.14, -0.16
3b	2.58, 2.41, 2.25	2.58	0.00	2.47, 2.30, 2.16	-0.11, -0.11, -0.09	2.09	-0.49	2.24, 2.07, 1.91	-0.34, -0.34, -0.34	2.32	-0.26	2.45, 2.28, 2.12	-0.13, -0.13, -0.13
4a	2.59, 2.42, 2.27	2.58	-0.01	2.44, 2.27, 2.11	-0.15, -0.15, -0.16	2.05	-0.54	2.23, 2.05, 1.89	-0.36, -0.37, -0.38	2.30	-0.29	2.44, 2.26, 2.10	-0.15, -0.16, -0.17
4b	2.58, 2.41, 2.27 †	2.58	0.00	2.45, 2.27, 2.11	-0.13, -0.14, -0.16	2.06	-0.52	2.23, 2.05, 1.89	-0.35, -0.36, -0.38	2.30	-0.28	2.43, 2.26, 2.10	-0.15, -0.15, -0.17
5c	2.50, 2.33, 2.14	2.43	-0.07	2.32, 2.14, 2.04	-0.18, -0.19, -0.10	1.96	-0.54	2.13, 1.96, 1.77	-0.37, -0.37, -0.37	2.17	-0.33	2.31, 2.13, 1.97	-0.19, -0.20, -0.17
Avg.	-	-	0.06	-	-0.08	-	-0.18	-	-0.14	-	-0.23	-	-0.08
MAE	-	-	0.08	-	0.10	-	0.29	-	0.23	-	-0.26	-	0.14

References

[1] C. Lee, R. Zaen, K-M. Park, K H. Lee, J. Y. Lee, and Y. Kang. Blue phosphorescent platinum complexes based on tetradentate bipyridine ligands and their application to Organic Light-Emitting Diodes (OLEDs). *Organometallics*, 37(24):4639–4647, 2018.

[2] W. Wei, S. A. M. Lima, P. I. Djurovich, A. Bossi, M. T. Whited, and M. E. Thompson. Synthesis and characterization of phosphorescent isomeric iridium complexes with a rigid cyclometalating ligand. *Polyhedron*, 140:138–145, 2018.

[3] J-L. Liao, P. Rajakannu, S-H. Liu, G-H. Lee, P-T. Chou, A. K-Y. Jen, and Y. Chi. Iridium (III) complexes bearing tridentate chromophoric chelate: Phosphorescence fine-tuned by phosphine and hydride ancillary. *Inorganic chemistry*, 57(14):8287–8298, 2018.