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Upper limit to the ultimate achievable emission wavelength in Near-IR emitting cyclometalated Iridium complexes

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Supporting Informations

General section:

Reagents and solvents were purchased from Aldrich and TCI, and used without further purification. All solvents, unless otherwise stated are degassed under argon prior the use. $[(iqbt)_2IrCl]_2$ and **Ir2** were prepared according to the literature.[1]
Thin films 4% wt in PMMA were fabricated by spin-coating a toluene mixture of PMMA (100 mg/ml) and the organometallic complex (4 mg/ml) onto quartz plates.
NMR spectra were recorded at 300 K on Bruker AV400 and Bruker AC300 spectrometers. Chemical shifts are expressed in parts per million (ppm) and referred to the residual signal of the solvent (7.26 ppm for ^1H and 77.0 ppm for ^{13}C in $CDCl_3$); coupling constants are given in Hz. Mass analysis were recorded on BRUKER Esquire 3000 PLUS (Esi Ion Trap LC/MSn System). Reverse phase gradient HPLC analysis were performed on Agilent 1100 equipped with VWD UV-Vis detector (set 300 nm) and a Waters Atlantis column (4.6 mm x 10.0 cm, 3 μm particle size). Analysis runned in a 20 minutes gradient elution, flow 1.0 ml/min starting from 70-30 acetonitile – water mixture up to 100% acetonitrile.

Synthesis of the complex $Ir(iqbt)_3$ (Ir3)

Under Argon atmosphere, $[(iqbt)_2IrCl]_2$ (60 mg, 0.040 mmol, 1eq) and 1-(benzo[b]thiophen-2-yl) isoquinoline (*Hiqbt*) (62.86 mg, 0.240 mmol, 6 eq) in 8 ml of glycerol were heated at 250°C overnight. After cooling the reaction mixture at room temperature, water was added, the solid filtered and washed with water, diethyl ether and hexane. The solid was dried under high vacuum and further purified by flash column chromatography (CH_2Cl_2) and finally recristallized from CH_2Cl_2/Hexane obtaining Ir3 in 88 % yield.
^1H NMR (400 MHz, $CDCl_3$) δ 6.70 (t, *J* = 7.60 Hz, 3H), 6.79 (d, *J* = 8.17 Hz, 3H), 7.00 (d, *J* = 6.32 Hz, 3H), 7.10 (t, *J* = 7.49 Hz, 3H), 7.21 (d, *J* = 6.30 Hz, 3H), 7.65 (m, 9H), 7.79 (d, *J* = 7.96 Hz, 3H), 9.11 (d, *J* = 8.90 Hz, 3H).
HPLC: 99%.
ESI-MS: M_w 974.2 $[M+H]^+$.

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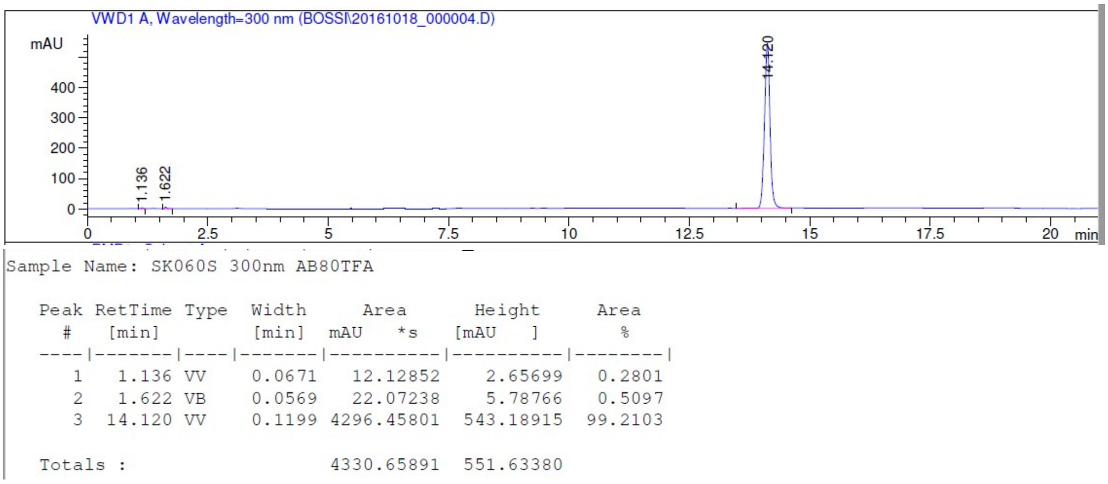
[1] S. Kesarkar, W. Mróz, M. Penconi, M. Pasini, S. Destri, M. Cazzaniga, D. Ceresoli, P. R. Mussini, C. Baldoli, U. Giovanella and A. Bossi, *Angew. Chem.*, 2016, **128**, 2764-2768.

HPLC chromatogram of Ir3



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Sample Name: SK060S 300nm AB80TFA

  Peak RetTime Type  Width     Area      Height     Area
    #   [min]        [min]  mAU    *s   [mAU    ]     %
  ----|-------|----|-------|----------|----------|--------|
     1   1.136 VV    0.0671   12.12852    2.65699   0.2801
     2   1.622 VB    0.0569   22.07238    5.78766   0.5097
     3  14.120 VV    0.1199 4296.45801  543.18915  99.2103

  Totals :                  4330.65891  551.63380
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Synthesis of the intermediate (iqbt)PtCl(κ-Hiqbt):

Under argon atmosphere 1 eq. of K_2PtCl_4 (100 mg, 0.24 mmol) and 2.2 eq. of 1-(benzo[b]thiophen-2-yl) isoquinoline (*Hiqbt*) (138.51 mg, 0.53 mmol) were heated at 80°C in a deaerated 3:1 mixture of 2-ethoxyethanol (6 ml) and water (2 ml) overnight. After cooling to room temperature, water (20-25mL) was added to the reaction mixture; the precipitate was filtered and the solid washed thoroughly with water followed by isopropanol, diethyl ether and hexane, and dried under high vacuum to yield 180 mg of (iqdt)PtCl(κ-Hiqbt) used in the next steps without further purification.

Synthesis of the complex Pt(iqbt)dpm (Pt1)

Under argon atmosphere, 1 eq. of (iqdt)PtCl(κ-Hiqbt) (50 mg, 0.664 mmol), 2 eq. of ligand 2,2,6,6-Tetramethyl-3,5-heptanedione (Hdpm) (24.49 mg, 24.74 µl, 0.1329 mmol) and 9 eq. of K_2CO_3 (82.68 mg, 0.5982 mmol) in 5 ml of deareated 2-ethoxyethanol were heated overnight at 100°C. After cooling the reaction mixture at room temperature, water (20mL) was added to the reaction mixture; the precipitate was filtered and the solid washed thoroughly with water followed by ethyl ether and hexane. The crude product was purified by flash column chromatography using CH_2Cl_2 to yield 38 mg (89%) of Pt(iqdt)dpm.

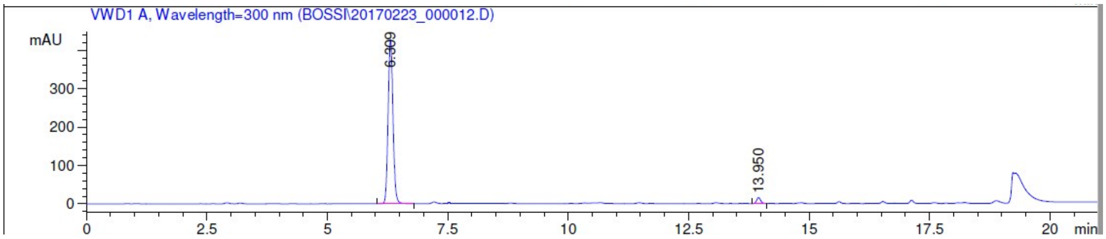
^{13}C-NMR (APT, $CDCl_3$, 75 MHz, δ ppm): 194.91, 193.60 (Cq, C=O), 145.07, 144.26, 143.14, 137.32, 124.50 (Cq arom), 41.76, 41.50 (Cq, t-Bu), 138.91, 131.75, 128.10, 127.77, 127.07, 126.90, 126.10, 123.79, 121.77, 117.11 (CH arom), 93.71 (CH dpm), 28.90, 28.36 (CH_3).

^{1}H NMR (300 MHz, CDCl3) δ 1.34 (s, 9H), 1.39 (s, 9H), 5.95 (s, 1H), 7.34 (d, *J* = 6.5 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.84 – 7.62 (m, 3H), 7.93 – 7.85 (m, 1H), 8.82 (d, *J* = 8.4 Hz,1H), 9.01 (d, *J* = 6.6 Hz, 1H) 9.17 (m, 1H).

HPLC: 97%.

ESI-MS: M_w 638.0 $[M+H]^+$.

HPLC chromatogram of Pt1



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Signal 2: VWD1 A, Wavelength=300 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.309 VB    0.1101 3017.74854  426.86362 96.9887
   2  13.950 VV    0.0934   93.69560   15.60329  3.0113

Totals :                  3111.44414  442.46690
```

Photophysical properties

Table S1 Photophysical parameter for the complexes Ir3, Ir2 and Pt1 as described in the main text and depicted in Figure 2.

	Rigidochromic effect /cm^{-1}	77 K						PMMA film	
		$\Delta E(S_1-T_1)$ /eV	$\Delta E(0-1)_{T1}$ /cm^{-1}	$\Delta E(0-1)_{S1}$ /cm^{-1}	$\Delta E(0-1)_{S0}$ /cm^{-1}	S_M	Stokes shift /cm^{-1}	$\Delta E(0-1)_{S0}$ /cm^{-1}	S_M
Ir3	298	0.50	1397	1150	1362	0.53	87	1188	0.67
Ir2	325	0.46	1426	1193	1384	0.38	63	1238	0.51
Pt1	223	0.64	1431	1274	1396	0.63	125	1331	0.81

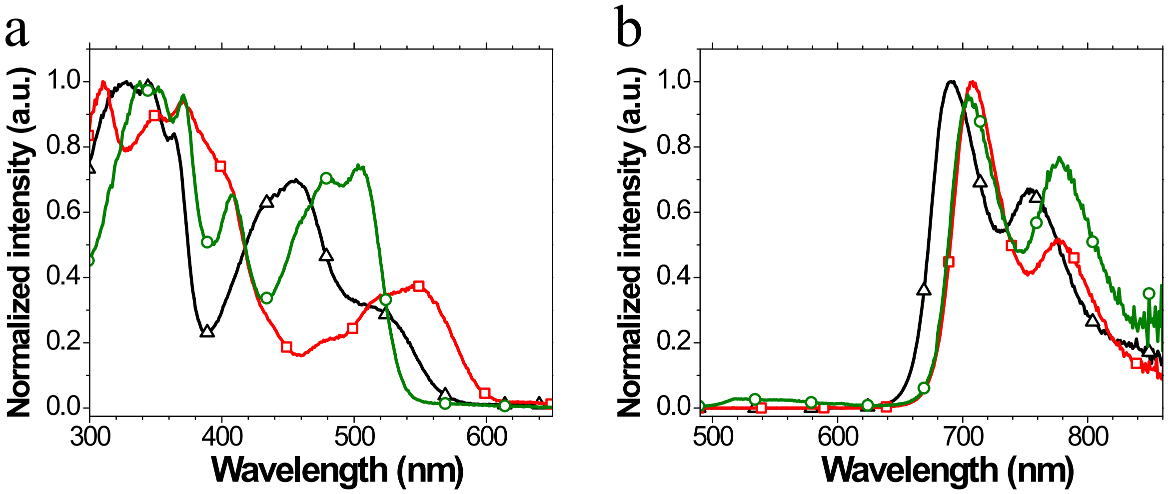


Figure S1. Excitation (a) and emission (b) spectra in PMMA films at room temperature of Ir3 (black triangles), Ir2 (red squares) and Pt1 (green circles).

Electrochemical properties

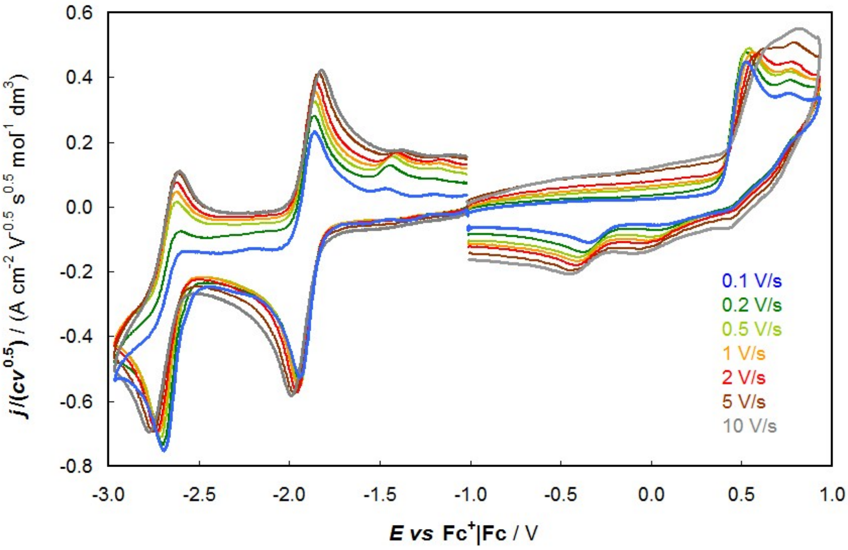


Figure S2. Scan rate effect on the first oxidation peak system and on the first two reduction peaks of complex Pt1.

DFT/TDDFT calculations

Calculated optical absorption energies, oscillator strength and dominant orbital transitions with coefficients from TDDFT (H = HOMO, L = LUMO)

Table S2a: Ir3 – Singlet states

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.31	537	0.0234	H→L (0.69)
S2	2.36	525	0.0088	H→L+1 (0.67)
S3	2.38	521	0.0035	H→L+2 (0.68)
S4	2.51	495	0.0302	H−2→L (0.47), H−1→L (0.45)
S5	2.52	492	0.0440	H−2→L (-0.44), H−1→L (0.45)
S6	2.55	485	0.0123	H−1→L+1 (0.50)
S7	2.62	473	0.0948	H−2→L+2 (0.40), H−1→L+2 (0.39)
S8	2.63	471	0.1271	H−2→L+1 (0.45)
S9	2.71	457	0.1450	H−2→L+1 (0.34), H−2→L+2 (0.39), H−1→L+2 (-0.39)
S10	3.34	371	0.0197	H−3→L (0.54)
S11	3.35	370	0.0163	H−4→L (0.53)
S12	3.37	368	0.0049	H→L+3 (0.60)
S13	3.40	364	0.0239	H−3→L+1 (0.48)
S14	3.43	362	0.0566	H−5→L (0.31), H−3→L+2 (0.35)
S15	3.44	361	0.0892	H−4→L+1 (0.37), H−3→L+1 (0.35)
S16	3.44	360	0.0476	H−4→L+2 (0.47)
S17	3.47	358	0.0637	H−1→L+3 (0.43)
S18	3.48	356	0.0690	H−2→L+3 (0.37), H→L+5 (-0.34)
S19	3.50	354	0.0371	H−3→L+2 (0.53)
S20	3.53	352	0.0074	H−5→L+1 (0.57)
S21	3.54	351	0.0019	H−5→L+2 (0.42)
S22	3.55	349	0.0328	H−5→L+2 (0.43), H→L+4 (-0.39)
S23	3.56	348	0.0180	H−2→L+3 (0.45), H→L+5 (0.44)
S24	3.63	342	0.0042	H−1→L+4 (0.39), H−1→L+5 (-0.36)
S25	3.67	338	0.0093	H−2→L+4 (0.45)
S26	3.68	337	0.0192	H−1→L+4 (0.41)
S27	3.68	337	0.0535	H−6→L (0.42), H−2→L+5 (-0.40)
S28	3.72	333	0.0163	H−7→L (0.39), H−6→L+1 (-0.38)
S29	3.73	332	0.1002	H−7→L (0.48)
S30	3.74	332	0.0067	H−8→L (0.45), H−6→L+2 (0.40)
S31	3.74	331	0.1157	H−6→L+1 (0.33), H−6→L+2 (-0.29), H−2→L+5 (0.30)
S32	3.75	330	0.0960	H−8→L (0.45), H−6→L+2 (-0.39)
S33	3.81	325	0.0404	H−8→L+1 (-0.37), H−7→L+1 (0.38), H−7→L+2 (-0.37)
S34	3.83	324	0.0685	H−8→L+1 (0.48)

S35	3.83	324	0.0522	H−8→L+2 (0.36), H−7→L+1 (0.36), H−7→L+2 (0.39)
S36	3.92	316	0.0032	H−8→L+2 (0.49)
S37	3.98	312	0.0263	H→L+6 (0.66)
S38	4.00	310	0.0253	H→L+7 (0.66)
S39	4.04	307	0.0290	H→L+8 (0.64)
S40	4.10	303	0.0052	H−1→L+6 (0.60)
S41	4.12	301	0.0041	H−2→L+6 (0.43), H−1→L+7 (-0.38)
S42	4.13	300	0.0023	H−2→L+7 (0.50)
S43	4.15	299	0.0029	H−2→L+6 (0.42), H−1→L+7 (0.45)
S44	4.17	298	0.0040	H−10→L (0.31), H−2→L+7 (-0.32), H−1→L+8 (0.35)
S45	4.17	297	0.0066	H−9→L (0.36)
S46	4.18	296	0.0122	H−10→L (-0.41), H−1→L+8 (0.45)
S47	4.19	296	0.0123	H−2→L+8 (0.54)
S48	4.23	293	0.0159	H−9→L+1 (0.49)
S49	4.27	290	0.0088	H−10→L+2 (0.42), H−9→L+1 (0.36)
S50	4.28	290	0.0032	H−10→L+1 (0.61)

Table S2b: Ir3 – Triplet states

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	1.81	686	- -	H→L (0.44)
T2	1.82	682	- -	H−1→L (0.43), H→L+2 (-0.40)
T3	1.82	680	- -	H−2→L+1 (0.39), H→L+1 (0.44)
T4	2.34	529	- -	H−1→L+2 (0.31), H→L (0.36)
T5	2.35	527	- -	H→L+2 (0.44)
T6	2.37	523	- -	H−2→L+1 (-0.35), H→L+1 (0.39)
T7	2.47	502	- -	H−2→L (0.40), H−1→L+2 (-0.38)
T8	2.48	501	- -	H−1→L+1 (0.48)
T9	2.50	495	- -	H−2→L+2 (0.51)
T10	2.81	440	- -	H−3→L (0.39)
T11	2.82	440	- -	H−4→L+1 (0.32), H−3→L+2 (0.31)
T12	2.82	439	- -	H−4→L (0.31), H−4→L+1 (0.32)
T13	3.09	401	- -	H→L+3 (0.48)
T14	3.11	399	- -	H−1→L+3 (0.36), H→L+4 (0.32)
T15	3.11	398	- -	H−2→L+3 (-0.34), H→L+5 (0.34)
T16	3.19	389	- -	H−11→L (-0.21), H−10→L+2 (0.22), H−1→L+6 (-0.22), H→L+8 (0.21)
T17	3.19	388	- -	H−10→L (0.25)
T18	3.20	388	- -	H−9→L (0.19), H−9→L+1 (0.21)
T19	3.30	376	- -	H−5→L (0.43)
T20	3.32	373	- -	H−4→L (0.39)
T21	3.33	372	- -	H−3→L+1 (0.33)
T22	3.37	368	- -	H−7→L (0.31), H−5→L+2 (-0.27), H−4→L (0.30)
T23	3.38	366	- -	H−8→L (-0.26), H−5→L+1 (0.26), H−4→L+2 (0.30), H−3→L (0.29)
T24	3.39	365	- -	H−3→L+1 (0.44)
T25	3.48	356	- -	H→L+3 (0.36)
T26	3.50	355	- -	H→L+4 (0.40)
T27	3.51	354	- -	H−2→L+3 (0.34), H→L+5 (0.36)
T28	3.53	351	- -	H−6→L (0.43)
T29	3.55	350	- -	H−6→L+2 (-0.30), H−5→L+2 (0.35)
T30	3.55	349	- -	H−5→L+1 (0.36)
T31	3.58	346	- -	H−6→L (0.35)
T32	3.60	345	- -	H−6→L+1 (0.42)
T33	3.61	344	- -	H−6→L+2 (0.40)
T34	3.65	340	- -	H−2→L+4 (-0.35), H−1→L+5 (0.36)
T35	3.66	339	- -	H−2→L+5 (0.36), H−1→L+4 (0.39)
T36	3.68	337	- -	H−2→L+4 (0.36), H−1→L+5 (0.35)
T37	3.73	333	- -	H−9→L+1 (-0.20), H−1→L+6 (0.23), H→L+7 (-0.20)

T38	3.73	333	- -	H→L+6 (0.28)
T39	3.73	333	- -	H−7→L (0.28)
T40	3.76	330	- -	H−7→L+2 (0.37)
T41	3.77	329	- -	H−8→L (-0.26), H−8→L+2 (0.29)
T42	3.79	327	- -	H−8→L+1 (0.35)
T43	3.83	323	- -	H−1→L+11 (0.19)
T44	3.84	323	- -	H−2→L+11 (0.16), H−1→L+10 (0.17), H→L+11 (0.17)
T45	3.85	322	- -	H−8→L+2 (-0.18), H−2→L+10 (0.19), H→L+12 (0.16)
T46	4.02	309	- -	H→L+6 (0.49)
T47	4.04	307	- -	H→L+7 (0.45)
T48	4.05	306	- -	H→L+8 (0.48)
T49	4.08	304	- -	H−3→L+3 (0.25)
T50	4.08	304	- -	H−4→L+3 (0.28), H−4→L+5 (-0.25)

Table S3a: Ir2 – Singlet states

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.23	557	0.0093	H→L (0.70)
S2	2.27	545	0.1292	H→L+1 (0.70)
S3	2.89	428	0.0665	H−1→L (0.55)
S4	2.93	424	0.1606	H−2→L (0.55)
S5	2.97	417	0.0409	H−1→L+1 (0.68)
S6	3.03	409	0.0035	H→L+2 (0.60)
S7	3.06	406	0.0010	H−2→L+1 (0.55)
S8	3.23	384	0.0181	H−3→L (0.46)
S9	3.28	378	0.0194	H→L+4 (0.57)
S10	3.31	375	0.0097	H→L+3 (0.56)
S11	3.31	374	0.0781	H−3→L+1 (0.50)
S12	3.45	360	0.0717	H−4→L (0.68)
S13	3.48	356	0.0662	H−5→L (0.53)
S14	3.55	349	0.0000	H−4→L+1 (0.62)
S15	3.59	345	0.1173	H−5→L+1 (0.56)
S16	3.75	330	0.0007	H−1→L+2 (0.68)
S17	3.81	325	0.0052	H−7→L (0.41), H→L+6 (0.45)
S18	3.82	325	0.0243	H→L+5 (0.53)
S19	3.83	324	0.0304	H−2→L+2 (0.49)
S20	3.86	321	0.0296	H−6→L (0.55)
S21	3.86	321	0.0057	H−7→L (0.39), H−2→L+2 (0.39)
S22	3.90	318	0.0203	H−6→L+1 (0.55)
S23	3.91	317	0.0065	H−7→L+1 (-0.43), H−1→L+4 (0.49)
S24	3.97	312	0.2379	H−1→L+3 (0.60)
S25	4.03	308	0.0004	H−7→L+1 (0.42), H−1→L+4 (0.47)
S26	4.07	304	0.1158	H−2→L+3 (0.67)
S27	4.08	304	0.0000	H−2→L+4 (0.56)
S28	4.16	298	0.0119	H−3→L+2 (0.43)
S29	4.17	297	0.0019	H→L+7 (0.62)
S30	4.19	296	0.0015	H−9→L (0.52)
S31	4.20	295	0.0048	H−8→L (0.44)
S32	4.24	293	0.0051	H−10→L (0.56)
S33	4.28	290	0.0083	H→L+9 (0.52)
S34	4.29	289	0.0042	H−10→L+1 (0.48), H−9→L+1 (-0.44)
S35	4.31	288	0.0050	H→L+8 (0.62)
S36	4.33	286	0.0032	H−8→L+1 (0.50)
S37	4.36	285	0.0003	H−10→L+1 (0.35), H−9→L+1 (0.36), H−3→L+3 (0.31)
S38	4.39	282	0.0235	H→L+9 (-0.35), H→L+13 (0.37)
S39	4.42	281	0.0048	H→L+14 (0.45)

S40	4.42	281	0.1374	H−3→L+4 (0.55)
S41	4.44	279	0.0004	H→L+14 (0.38)
S42	4.46	278	0.0417	H−1→L+5 (0.63)
S43	4.46	278	0.0056	H−1→L+6 (0.59)
S44	4.49	276	0.0074	H−4→L+2 (0.62)
S45	4.51	275	0.0284	H−5→L+2 (0.54)
S46	4.53	274	0.0136	H→L+10 (0.62)
S47	4.55	272	0.0006	H−10→L+2 (0.52)
S48	4.58	271	0.0047	H−4→L+3 (0.65)
S49	4.60	270	0.0089	H−4→L+4 (0.65)
S50	4.61	269	0.0521	H−2→L+5 (0.61)

Table S3b: Ir2 – Triplet states

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	1.71	724	- -	H→L (0.64)
T2	1.76	706	- -	H→L+1 (0.61)
T3	2.45	507	- -	H−1→L+1 (0.48)
T4	2.45	506	- -	H−1→L (0.48)
T5	2.73	455	- -	H−2→L (0.54)
T6	2.77	448	- -	H−2→L+1 (0.51)
T7	2.94	422	- -	H−3→L+1 (0.30), H−2→L (-0.27), H−2→L+2 (0.28)
T8	2.94	421	- -	H−3→L (0.36), H−2→L+1 (-0.35)
T9	2.96	419	- -	H−2→L+2 (0.51)
T10	3.00	414	- -	H→L+2 (0.68)
T11	3.02	411	- -	H→L+3 (0.55)
T12	3.04	408	- -	H→L+4 (0.52)
T13	3.19	389	- -	H−5→L (0.37)
T14	3.20	387	- -	H−5→L (0.44)
T15	3.21	386	- -	H−5→L+1 (0.38), H−4→L (0.36)
T16	3.22	385	- -	H−5→L+1 (0.36)
T17	3.48	356	- -	H−8→L+1 (-0.23), H−6→L+1 (0.26), H−5→L+1 (0.26)
T18	3.48	356	- -	H−6→L (0.42)
T19	3.52	352	- -	H−4→L (0.40)
T20	3.53	351	- -	H−4→L+1 (0.39), H→L+5 (-0.36)
T21	3.61	344	- -	H−6→L (0.37), H→L+5 (0.38)
T22	3.66	338	- -	H−6→L+1 (0.44)
T23	3.68	337	- -	H−1→L+3 (0.47)
T24	3.70	335	- -	H−1→L+4 (0.53)
T25	3.75	330	- -	H−1→L+2 (0.69)
T26	3.80	326	- -	H−7→L (0.51)
T27	3.83	324	- -	H−7→L+1 (0.37)
T28	3.86	321	- -	H−7→L+1 (0.40)
T29	3.88	320	- -	H−6→L+1 (0.38)
T30	3.94	315	- -	H−5→L+2 (0.46), H−3→L+2 (0.49)
T31	3.96	313	- -	H−2→L+3 (0.62)
T32	3.97	312	- -	H→L+14 (0.55)
T33	3.98	311	- -	H−2→L+4 (0.57)
T34	4.05	306	- -	H−7→L+2 (0.43)
T35	4.09	303	- -	H→L+13 (0.41)
T36	4.11	301	- -	H−14→L+1 (-0.24), H→L+8 (0.28)
T37	4.13	300	- -	H−10→L (0.39)
T38	4.15	299	- -	H−10→L (0.48)
T39	4.18	297	- -	H→L+7 (0.58)

T40	4.21	295	- -	H−1→L+5 (0.36)
T41	4.21	294	- -	H−10→L+1 (0.41)
T42	4.23	293	- -	H−10→L+1 (0.35), H−1→L+6 (0.39)
T43	4.24	292	- -	H−3→L+3 (0.42)
T44	4.26	291	- -	H−3→L+4 (0.37), H−1→L+5 (-0.36)
T45	4.30	288	- -	H−11→L+1 (-0.23), H−5→L+3 (0.25)
T46	4.30	288	- -	H−11→L (0.29)
T47	4.32	287	- -	H−9→L (0.41), H−8→L+1 (0.45)
T48	4.33	286	- -	H−10→L+2 (0.58)
T49	4.34	286	- -	H−9→L+1 (0.42), H−8→L (0.37)
T50	4.36	284	- -	H−5→L+2 (-0.27), H−3→L+2 (0.29)

Table S4a: Pt1 – Singlet states

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
S1	2.50	495	0.1336	H→L (0.69)
S2	3.16	393	0.0031	H−3→L (0.70)
S3	3.18	390	0.0625	H−1→L (0.65)
S4	3.29	377	0.0923	H→L+1 (0.65)
S5	3.43	361	0.0959	H−2→L (0.64)
S6	3.63	341	0.0702	H→L+2 (0.63)
S7	3.76	330	0.1405	H−4→L (0.63)
S8	3.81	325	0.0000	H−6→L (0.69)
S9	3.88	320	0.0000	H−3→L+1 (0.70)
S10	3.89	318	0.0482	H−1→L+1 (0.66)
S11	4.05	306	0.0002	H−5→L (0.60)
S12	4.16	298	0.0000	H→L+6 (0.48)
S13	4.20	295	0.0640	H→L+3 (0.59)
S14	4.27	290	0.0420	H−7→L (0.46), H−1→L+2 (-0.43)
S15	4.34	286	0.0047	H−2→L+1 (0.62)
S16	4.43	280	0.1288	H−7→L (0.46), H−1→L+2 (0.42)
S17	4.47	278	0.0000	H−6→L+1 (0.68)
S18	4.47	277	0.0000	H−8→L (0.67)
S19	4.52	275	0.0000	H−3→L+2 (0.66)
S20	4.55	272	0.0005	H→L+4 (0.63)
S21	4.58	271	0.0204	H→L+5 (0.63)
S22	4.65	267	0.0233	H−4→L+1 (0.56)
S23	4.66	266	0.0000	H−1→L+6 (0.43)
S24	4.66	266	0.0021	H−3→L+6 (0.41)
S25	4.71	263	0.0165	H−2→L+2 (0.65)
S26	4.76	260	0.0015	H→L+7 (0.52)
S27	4.77	260	0.0101	H−1→L+3 (0.52)
S28	4.79	259	0.0009	H−8→L+1 (0.68)
S29	4.85	256	0.0000	H→L+9 (0.63)
S30	4.86	255	0.0148	H−9→L (0.32), H−5→L+1 (-0.31), H−1→L+3 (-0.28)
S31	4.93	251	0.0923	H→L+8 (0.47)
S32	5.01	247	0.0091	H−10→L (0.31), H−6→L+6 (0.31), H−4→L+2 (0.29)
S33	5.04	246	0.0068	H−5→L+1 (0.45)
S34	5.06	245	0.0005	H−3→L+3 (0.70)
S35	5.07	245	0.0024	H−10→L (0.36)
S36	5.08	244	0.0200	H−4→L+2 (0.46)
S37	5.11	243	0.0001	H→L+11 (0.60)
S38	5.12	242	0.0393	H−10→L (-0.37), H−4→L+2 (0.36), H−2→L+3 (0.39)
S39	5.14	241	0.0001	H−1→L+4 (0.60)

S40	5.20	238	0.0000	H−6→L+2 (0.68)
S41	5.25	236	0.1428	H−7→L+1 (0.62)
S42	5.26	236	0.0014	H→L+10 (0.51)
S43	5.37	231	0.0001	H−2→L+6 (0.32)
S44	5.38	230	0.1283	H−1→L+5 (0.56)
S45	5.45	228	0.0465	H−4→L+3 (0.40)
S46	5.46	227	0.0000	H−1→L+7 (0.52)
S47	5.47	227	0.0114	H−3→L+4 (0.61)
S48	5.50	225	0.0042	H−2→L+4 (0.48)
S49	5.52	225	0.0003	H−12→L (0.58)
S50	5.53	224	0.0092	H−11→L (0.38)

Table S4b: Pt1 – Triplet states

Excited state	Transition (eV)	Transition λ (nm)	Oscillator strength	Dominant excitations (coefficient)
T1	1.74	711	- -	H→L (0.68)
T2	2.60	477	- -	H−1→L (0.62)
T3	2.94	421	- -	H−1→L+1 (-0.39), H→L+1 (0.43)
T4	3.01	412	- -	H−3→L (0.70)
T5	3.08	403	- -	H−2→L (0.33), H→L+2 (0.36)
T6	3.10	400	- -	H−2→L (0.54)
T7	3.14	395	- -	H−5→L (0.33), H→L+1 (0.28)
T8	3.27	379	- -	H→L+2 (0.43)
T9	3.44	360	- -	H−4→L (0.46)
T10	3.68	337	- -	H→L+3 (0.50)
T11	3.72	333	- -	H−6→L (0.52)
T12	3.76	330	- -	H−6→L (0.47)
T13	3.83	324	- -	H−3→L+1 (0.69)
T14	3.87	320	- -	H→L+5 (0.34)
T15	4.03	308	- -	H−1→L+2 (0.37)
T16	4.05	306	- -	H−1→L+6 (0.41)
T17	4.06	305	- -	H−3→L+6 (0.25), H−2→L+1 (0.23), H−1→L+1 (-0.23)
T18	4.07	305	- -	H−3→L+6 (0.42)
T19	4.14	299	- -	H−4→L+1 (0.38)
T20	4.17	297	- -	H−7→L (0.44)
T21	4.18	296	- -	H−11→L (-0.21), H−10→L (0.24), H−5→L+3 (0.21), H−2→L+1 (0.24)
T22	4.31	288	- -	H−2→L+1 (0.37)
T23	4.34	286	- -	H−6→L+1 (0.64)
T24	4.39	283	- -	H−8→L (0.64)
T25	4.41	281	- -	H−9→L (0.42)
T26	4.43	280	- -	H→L+5 (0.32)
T27	4.50	276	- -	H−3→L+2 (0.67)
T28	4.51	275	- -	H−8→L+1 (0.65)
T29	4.51	275	- -	H→L+4 (0.57)
T30	4.51	275	- -	H−1→L+3 (0.37)
T31	4.52	274	- -	H−6→L+6 (0.45)
T32	4.62	269	- -	H−7→L+1 (0.43)
T33	4.66	266	- -	H→L+11 (0.37)
T34	4.68	265	- -	H−10→L (0.35)
T35	4.72	263	- -	H→L+8 (0.54)
T36	4.74	262	- -	H−10→L (0.33), H−5→L+2 (0.30)
T37	4.80	258	- -	H→L+7 (0.49)
T38	4.90	253	- -	H−4→L+2 (0.47)

T39	4.92	252	- -	H−2→L+3 (0.48)
T40	4.95	250	- -	H→L+9 (0.39), H→L+11 (0.35)
T41	5.01	248	- -	H→L+10 (0.39)
T42	5.03	246	- -	H−3→L+3 (0.68)
T43	5.05	245	- -	H−5→L+1 (0.54)
T44	5.10	243	- -	H−1→L+4 (0.62)
T45	5.14	241	- -	H→L+10 (0.34)
T46	5.14	241	- -	H−4→L+6 (0.27), H→L+11 (-0.24)
T47	5.18	239	- -	H−6→L+2 (0.68)
T48	5.19	239	- -	H−5→L+3 (-0.25), H−4→L+2 (0.29)
T49	5.28	235	- -	H−5→L+3 (0.39)
T50	5.34	232	- -	H−1→L+5 (0.42)

Fig. S3. Frontier molecular orbitals calculated at the B3LYP level. The value of the isosurface is ±0.03 bohr^{-3}. Blue and red denote positive and negative values, respectively.

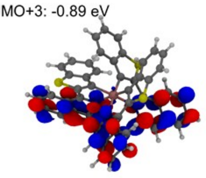
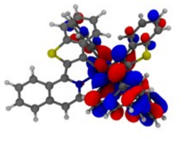
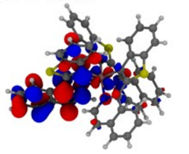
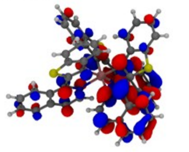
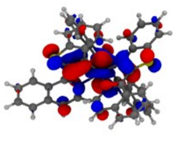
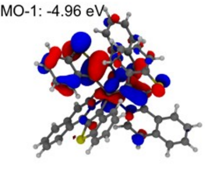
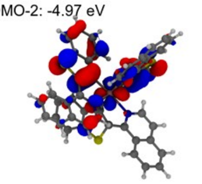
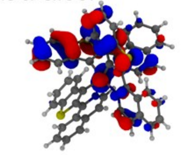
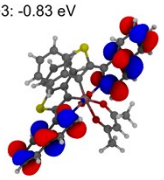
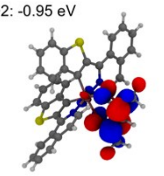
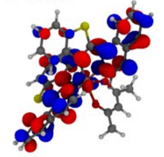
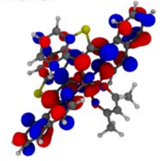
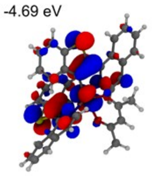
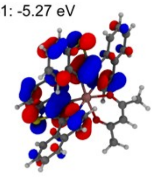
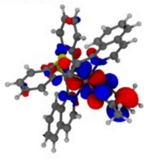
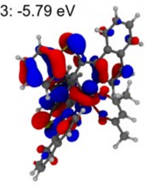
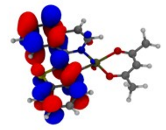
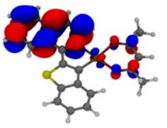
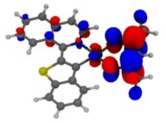
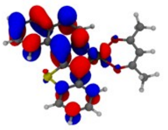
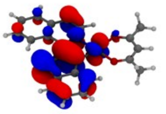
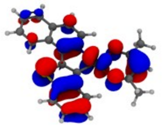
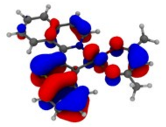
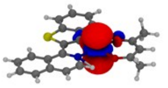
Ir3	Ir2	Pt1
LUMO+3: -0.89 eV  LUMO+2: -1.80 eV  LUMO+1: -1.82 eV  LUMO: -1.92 eV  HOMO: -4.85 eV  HOMO-1: -4.96 eV  HOMO-2: -4.97 eV  HOMO-3: -5.78 eV 	LUMO+3: -0.83 eV  LUMO+2: -0.95 eV  LUMO+1: -1.83 eV  LUMO: -1.91 eV  HOMO: -4.69 eV  HOMO-1: -5.27 eV  HOMO-2: -5.53 eV  HOMO-3: -5.79 eV 	LUMO+3: -0.41 eV  LUMO+2: -0.87 eV  LUMO+1: -1.25 eV  LUMO: -2.07 eV  HOMO: -5.09 eV  HOMO-1: -5.79 eV  HOMO-2: -6.08 eV  HOMO-3: -6.12 eV 

Fig S4. Spin density in the triplet geometry, from B3LYP calculations. The value of the isosurface is ±0.004 bohr^{-3}. Azure and green denote positive and negative values.

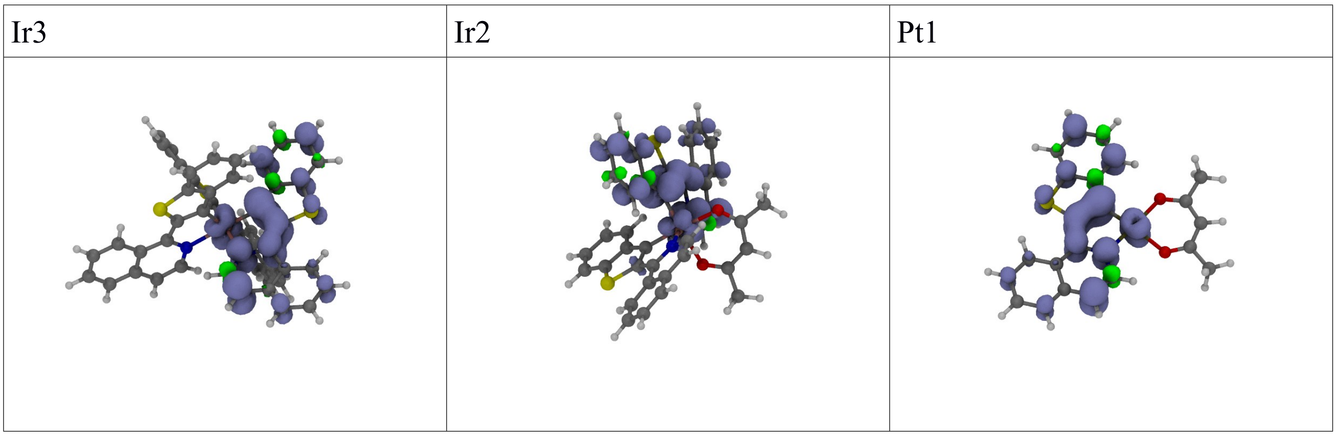


Fig S5. Calculated atom/ligand contribution (%) to frontier molecular orbitals.