Electronic Supplementary Material (ESI) for Materials Advances.

Tuning the optical bandgap and piezoresistance in iridium-based molecular semiconductors through ligand modification

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FTIR transmittance spectra

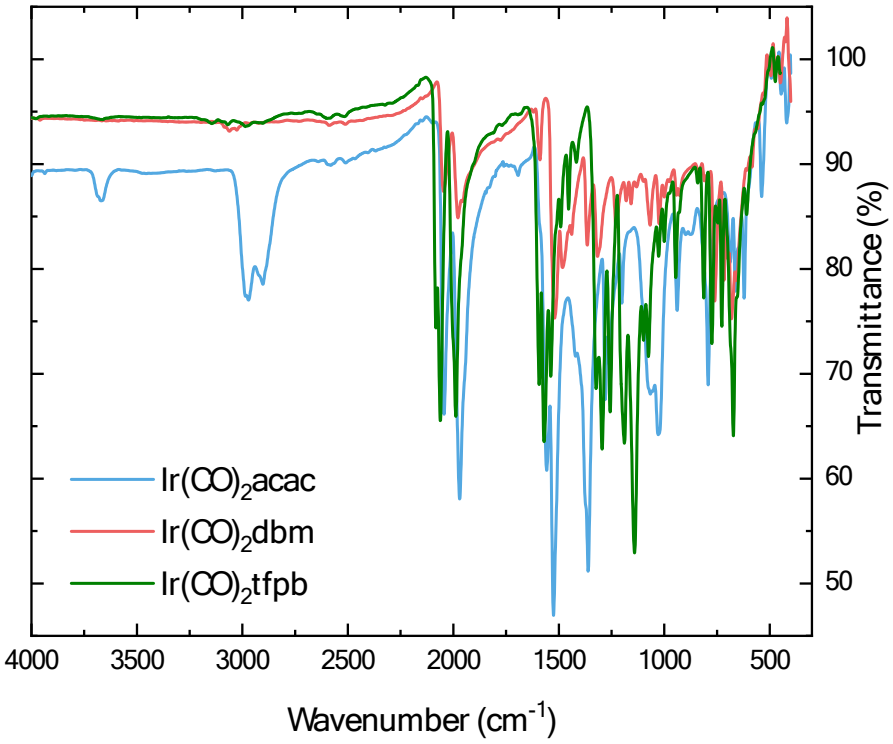

Figure S1: FTIR spectra of the complexes.

Tauc plots from solid-state absorption spectra

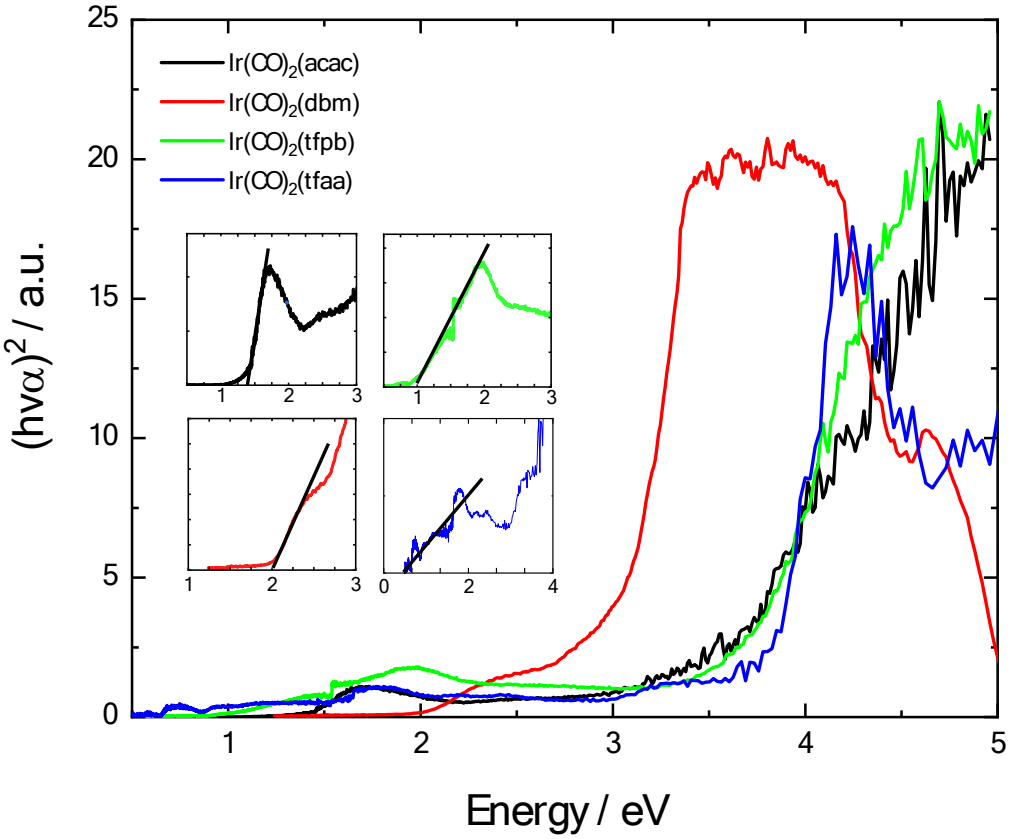

Figure S2: Estimating the optical bandgap. *Tauc plots of the four complexes. The product of the absorbance* α *and the incident photon energy squared* $(h\nu\alpha)^2$ *is plotted against the incident photon energy* $(h\nu)$*. Insets show a zoomed-in view of the plots at low energies. Extrapolation of the linear regime at low energies (solid black lines) gives the energy of the bandgap at the x-axis intercept. Note that for Ir(CO)$_2$tfpb, the discontinuity at 1.5 eV is an artefact from the spectrometer.*

Band-structure calculations

Table S1: Comparison of the optimised unit cell parameters under full geometry optimization.

		a	*b*	*c*	*α*	*β*	*γ*	*V*
$Ir(CO)_2acac$ [1]	*C* exp	6.533	7.787	9.277	105.970	90.475	100.663	445.054
	C cal	6.531	7.663	9.026	106.142	90.160	101.437	424.520
	V^{cal}/V^{exp}							-4.61%
$Ir(CO)_2dbm$	*C* exp	8.306	11.303	16.271	96.266	97.677	100.017	1477.080
	C cal	8.288	11.280	16.309	96.646	97.288	99.189	1478.427
	V^{cal}/V^{exp}							0.09%

[1] Crystal parameters taken from reference [4]

(TD-)DFT calculations

Predicted and measured absorption spectra in solution

The absorption spectra of the complexes in solution were modelled by TD-DFT calculations and are shown in Figure S3 below. There is good agreement between observed and predicted spectra, with similar ordering of transitions for all complexes.

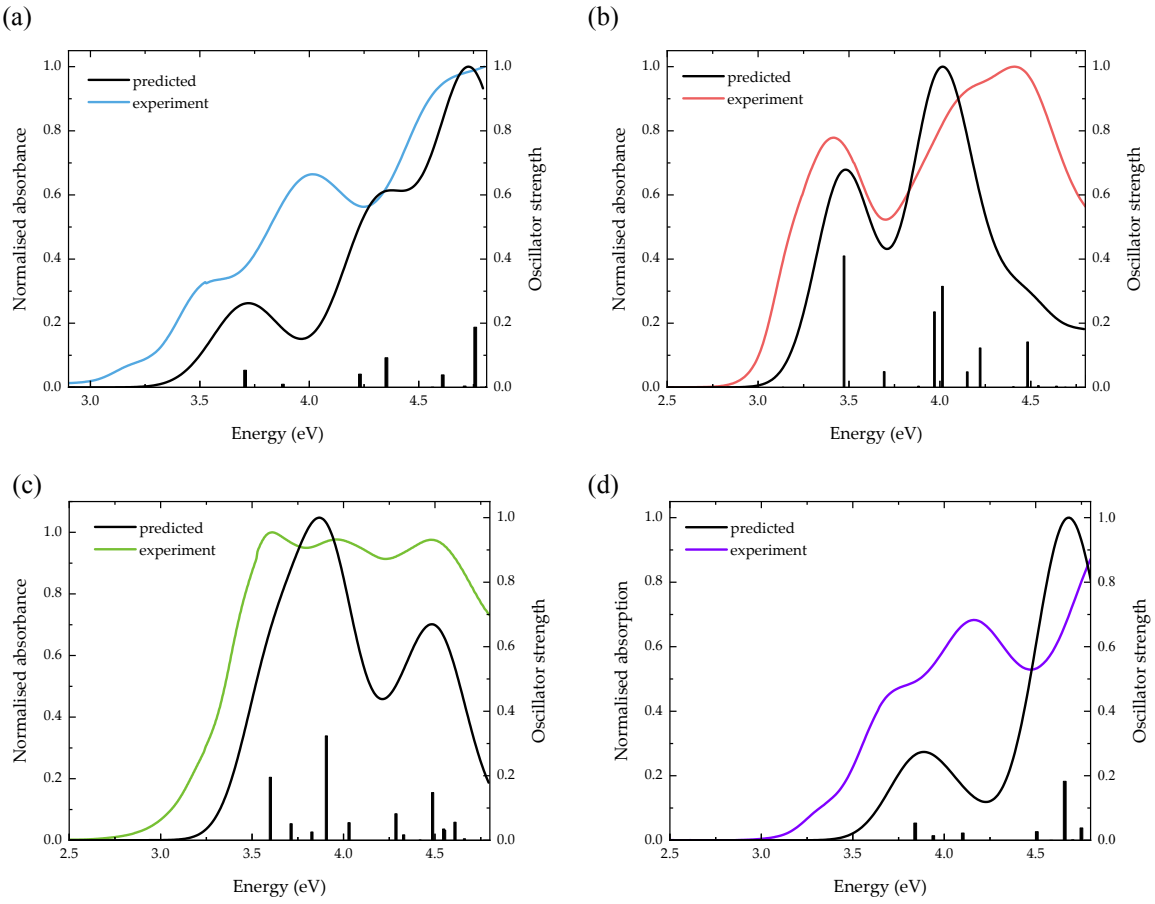

Figure S3: Optical transitions of the complexes in solution (a) $Ir(CO)_2acac$, b)$Ir(CO)_2dbm$, c) $Ir(CO)_2tfpb$, d) $Ir(CO)_2tfaa$): predicted spectra along with strength of the electronic transitions calculated with TD-DFT (black curve) and experimental absorbance in hexane solution (colour).

Table S2: *MO energies and % MO contributions from key groups for* ***Ir(CO)$_2$acac****. 'Chelate' refers to the C, O and H atoms included on the chelated ring.*

Orbital No.		Energy (eV)	Ir	CO	chelate	CH_3
54	L+4	0.23	14	84	2	0
53	L+3	-0.43	30	68	1	1
52	L+2	-1.07	30	64	5	1
51	L+1	-1.45	44	50	5	0
50	LUMO	-1.75	1	3	86	10
49	HOMO	-6.5	96	2	2	0
48	H-1	-6.71	19	9	70	1
47	H-2	-7.39	74	15	9	1
46	H-3	-7.8	57	12	28	3
45	H-4	-7.94	45	17	36	2

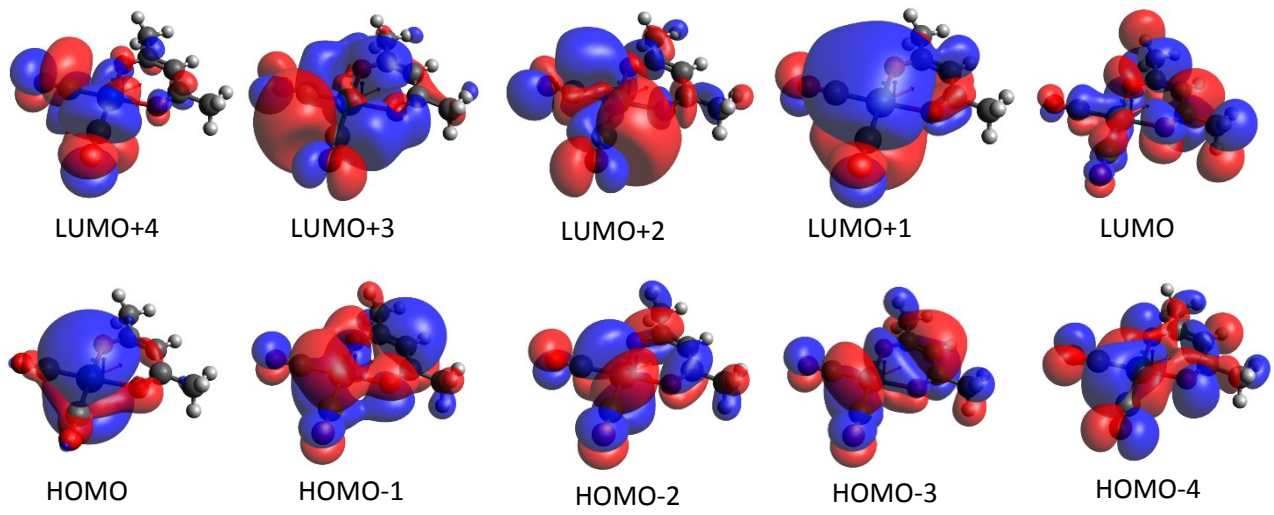

Figure S4: Frontier molecular orbitals for Ir(CO)$_2$acac (isocontour set at 0.01000)

Table S3: *MO energies and % MO contributions from key groups for* ***Ir(CO)$_2$dbm****. 'Chelate' refers to the C, O and H atoms included on the chelated ring.*

Orbital No.		Energy (eV)	Ir	CO	chelate	Ph
86	L+4	-0.59	0	0	1	99
85	L+3	-0.91	8	9	10	73
84	L+2	-1.08	30	64	5	1
83	L+1	-1.53	37	42	9	11
82	LUMO	-2.43	1	2	57	40
81	HOMO	-6.51	96	2	2	0
80	H-1	-6.54	9	5	62	25
79	H-2	-7.09	35	8	10	47
78	H-3	-7.2	29	9	8	54
77	H-4	-7.34	2	0	1	97

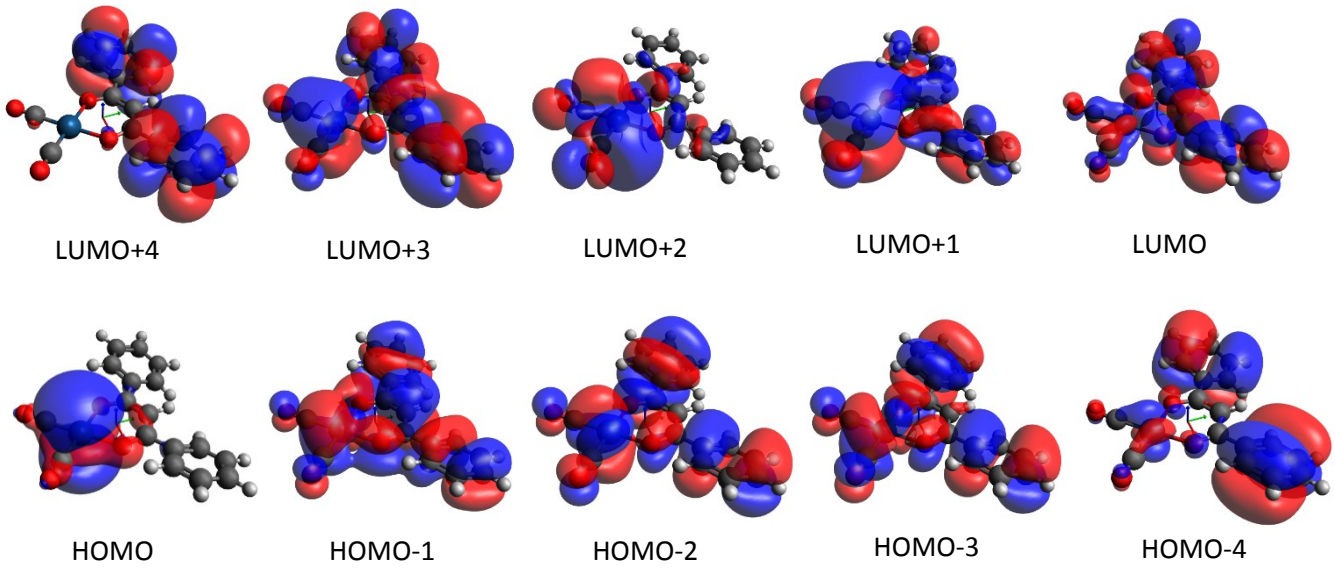

Figure S5: Frontier molecular orbitals for ***Ir(CO)$_2$dbm*** *(isocontour set at 0.01000)*

Table S4: *MO energies and % MO contributions from key groups for* ***Ir(CO)$_2$tfpb****. 'Chelate' refers to the C, O and H atoms included on the chelated ring.*

Orbital No.		Energy (eV)	Ir	CO	chelate	CF3	Ph
82	L+4	-0.66	27	67	1	0	4
81	L+3	-0.84	2	2	5	1	91
80	L+2	-1.35	31	62	5	1	1
79	L+1	-1.71	41	49	8	0	2
78	LUMO	-2.76	1	2	67	3	27
77	HOMO	-6.75	96	2	2	0	0
76	H-1	-7.02	18	7	57	0	18
75	H-2	-7.4	36	9	10	0	44
74	H-3	-7.58	5	1	1	0	92
73	H-4	-7.89	60	12	10	1	18

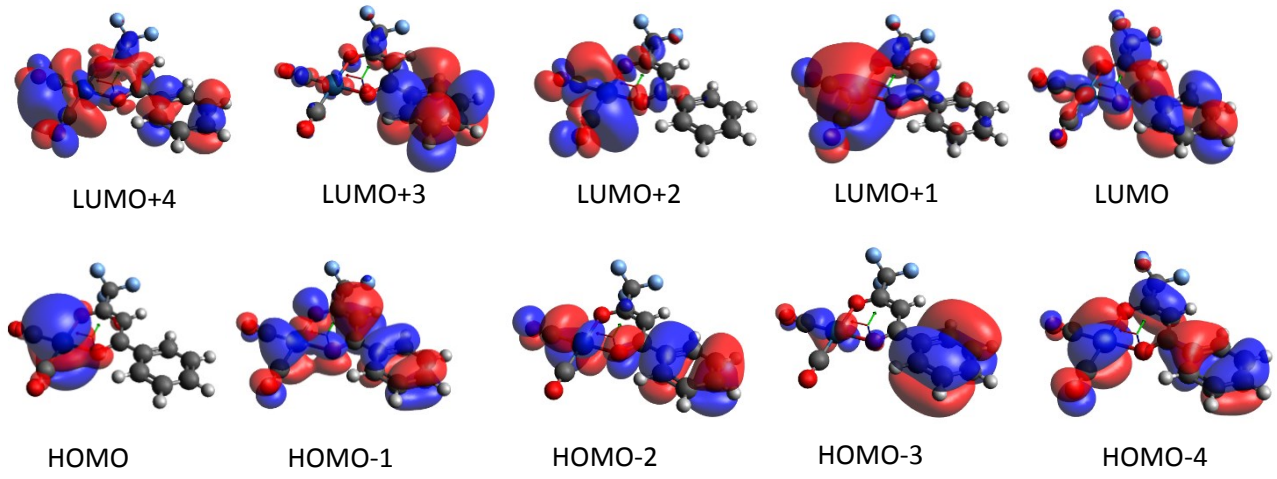

Figure S6: Frontier molecular orbitals for ***Ir(CO)$_2$tfpb*** *(isocontour set at 0.01500)*

Table S5: *MO energies and % MO contributions from key groups for* ***Ir(CO)$_2$tfaa****. 'Chelate' refers to the C, O and H atoms included on the chelated ring.*

Orbital No.		Energy (eV)	Ir	CO	chelate	CF_3	CH_3
66	L+4	-0.03	14	85	1	0	0
65	L+3	-0.7	29	70	1	0	1
64	L+2	-1.39	32	62	5	1	1
63	L+1	-1.72	43	51	6	0	0
62	LUMO	-2.46	1	3	86	6	5
61	HOMO	-6.79	96	3	2	0	0
60	H-1	-7.16	27	11	61	0	0
59	H-2	-7.73	76	15	8	0	1
58	H-3	-8.24	51	9	37	1	1
57	H-4	-8.32	46	17	35	0	2

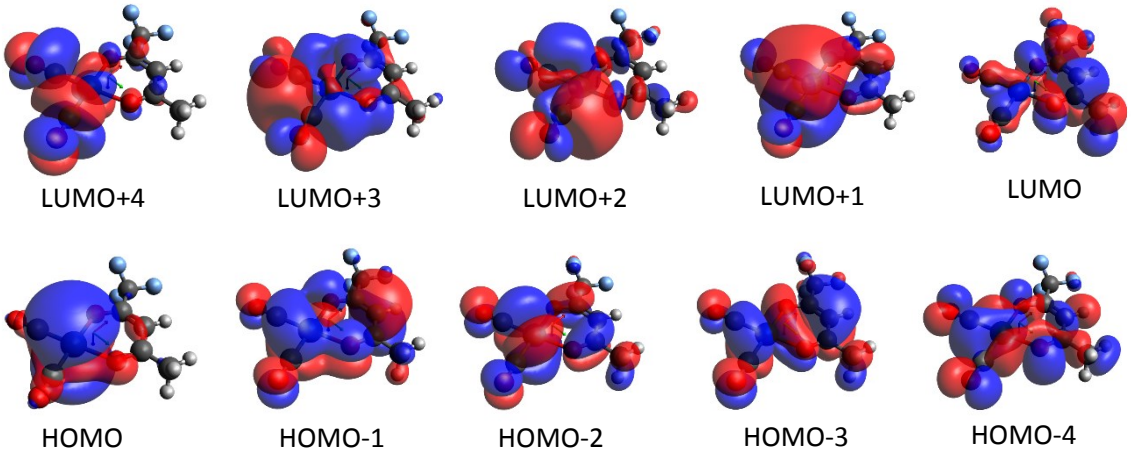

Figure S7: Frontier molecular orbitals for ***Ir(CO)$_2$tfaa*** *(isocontour set at 0.01000)*

Table S6: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***Ir(CO)$_2$acac:***

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs	Ir	CO	chelate	Ch3
1	327.2819	0	HOMO->LUMO (100%)		96-->1 (-95)	2-->3 (1)	2-->86 (84)	0-->10 (10)
2	323.7354	0.0534	HOMO->L+1 (97%)		96-->44 (-52)	2-->50 (48)	2-->5 (3)	0-->0 (0)
3	309.3418	0.0099	HOMO->L+2 (96%)		96-->30 (-66)	2-->64 (62)	2-->5 (3)	0-->1 (1)
4	283.6128	0.0412	H-1->LUMO (88%)	H-3->LUMO (4%), H-2->L+1 (5%)	24-->3 (-21)	9-->6 (-3)	65-->82 (17)	2-->10 (8)
5	275.7288	0.0923	H-1->L+1 (86%)	H-2->LUMO (3%), HOMO->L+3 (6%)	26-->42 (16)	9-->50 (41)	64-->8 (-56)	1-->1 (0)
6	273.4966	0	H-1->L+2 (90%)	H-3->L+2 (8%)	23-->30 (7)	9-->64 (55)	67-->5 (-62)	2-->1 (-1)
7	262.996	0.0003	HOMO->L+3 (91%)	H-1->L+1 (6%)	91-->31 (-60)	3-->67 (64)	6-->1 (-5)	0-->1 (1)
8	260.3343	0.0388	H-2->L+1 (84%)	H-4->L+2 (3%), H-3->LUMO (5%), H-1->LUMO (3%)	70-->40 (-30)	15-->46 (31)	13-->13 (0)	2-->1 (-1)
9	254.8074	0.0043	H-2->L+2 (82%), H-1->L+3 (11%)	H-3->L+3 (4%)	67-->30 (-37)	14-->65 (51)	17-->4 (-13)	2-->1 (-1)
10	252.2106	0.1878	H-2->LUMO (95%)	H-1->L+1 (3%)	73-->2 (-71)	15-->5 (-10)	11-->84 (73)	1-->10 (9)
11	249.405	0.0026	H-5->LUMO (98%)		1-->1 (0)	7-->3 (-4)	77-->86 (9)	15-->10 (-5)
12	244.6799	0	H-4->LUMO (97%)		45-->1 (-44)	17-->3 (-14)	36-->86 (50)	2-->10 (8)
13	240.7694	0.0001	H-4->L+1 (64%), H-1->L+3 (27%)	H-3->L+3 (3%), H-2->L+2 (2%)	39-->39 (0)	15-->56 (41)	45-->4 (-41)	2-->1 (-1)
14	233.7208	0	HOMO->L+4 (94%)	H-2->L+3 (2%)	95-->15 (-80)	3-->83 (80)	2-->2 (0)	0-->0 (0)
15	232.7686	0.003	H-4->L+1 (32%), H-2->L+2 (12%), H-1->L+3 (53%)		34-->35 (1)	12-->62 (50)	52-->3 (-49)	2-->1 (-1)
16	232.607	0.0126	HOMO->L+5 (86%)	H-3->LUMO (7%), HOMO->L+8 (3%)	93-->35 (-58)	3-->52 (49)	4-->9 (5)	0-->5 (5)
17	228.977	0.1836	H-3->LUMO (80%)	H-4->L+2 (2%), H-2->L+1 (2%), H-1->LUMO (6%), HOMO->L+5 (6%)	58-->5 (-53)	11-->9 (-2)	29-->77 (48)	3-->9 (6)
18	227.4856	0.0005	H-3->L+1 (89%)	H-4->L+3 (4%), H-2->L+4 (3%)	57-->43 (-14)	12-->52 (40)	28-->5 (-23)	3-->0 (-3)
19	225.7008	0	H-2->L+3 (81%)	H-3->L+5 (4%), H-1->L+5 (9%)	68-->31 (-37)	14-->67 (53)	16-->1 (-15)	2-->1 (-1)
20	222.9972	0	H-3->L+2 (85%)	H-1->L+2 (7%), HOMO->L+4 (3%)	55-->29 (-26)	11-->64 (53)	31-->5 (-26)	3-->1 (-2)
21	221.349	0.0096	H-4->L+2 (70%), H-1->L+4 (15%)	H-4->L+5 (4%), H-3->L+4 (4%)	41-->27 (-14)	15-->68 (53)	41-->4 (-37)	2-->1 (-1)
22	216.6912	0	H-5->L+1 (98%)		1-->44 (43)	7-->50 (43)	77-->5 (-72)	15-->0 (-15)
23	209.0972	0	H-2->L+3 (13%), H-1->L+5 (75%)	H-3->L+5 (7%)	30-->36 (6)	10-->59 (49)	59-->3 (-56)	2-->2 (0)
24	200.9957	0.1368	H-5->L+2 (94%)		1-->30 (29)	7-->64 (57)	77-->5 (-72)	15-->1 (-14)

25	199.7039	0.0001	H-3->L+3 (41%), H-2->L+5 (49%)	H-1->L+3 (4%), H-1->L+6 (2%)	64-->34 (-30)	13-->61 (48)	21-->2 (-19)	2-->3 (1)
26	199.3668	0.0877	H-4->L+5 (17%), H-1->L+4 (69%)	H-4->L+2 (7%), H-2->L+1 (2%)	27-->20 (-7)	11-->77 (66)	60-->2 (-58)	2-->1 (-1)
27	197.8808	0.0015	H-3->L+3 (43%), H-2->L+5 (45%)	H-1->L+3 (4%), H-1->L+6 (3%)	62-->34 (-28)	13-->61 (48)	22-->2 (-20)	2-->3 (1)
28	196.0379	0.0021	H-4->L+3 (44%), H-2->L+4 (44%)	H-5->L+2 (4%), HOMO->L+6 (5%)	59-->24 (-35)	15-->72 (57)	24-->2 (-22)	2-->2 (0)
29	190.6511	0.0578	HOMO->L+6 (90%)	H-4->L+3 (3%), H-2->L+4 (2%), HOMO->L+9 (2%)	93-->53 (-40)	3-->11 (8)	3-->11 (8)	0-->24 (24)
30	188.1399	0	H-6->LUMO (91%)	H-4->L+4 (5%)	32-->1 (-31)	10-->8 (-2)	45-->81 (36)	12-->10 (-2)
31	186.7091	0.0001	H-1->L+6 (88%)	H-3->L+3 (5%), HOMO->L+7 (4%)	25-->55 (30)	9-->11 (2)	65-->10 (-55)	1-->23 (22)
32	185.0731	0.1063	HOMO->L+7 (94%)	H-1->L+6 (4%)	92-->77 (-15)	2-->16 (14)	5-->1 (-4)	0-->6 (6)
33	182.3082	0.0148	H-5->L+3 (83%)	H-4->L+5 (6%), H-3->L+4 (4%), HOMO->L+8 (2%)	8-->30 (22)	8-->67 (59)	71-->1 (-70)	13-->2 (-11)
34	181.5926	0	H-4->L+4 (54%), H-3->L+5 (29%)	H-6->LUMO (3%), H-1->L+5 (7%)	46-->23 (-23)	14-->71 (57)	37-->5 (-32)	2-->2 (0)
35	179.0127	0.0423	H-5->L+3 (13%), H-4->L+5 (21%), H-3->L+4 (47%)	H-1->L+4 (9%), HOMO->L+8 (4%)	45-->23 (-22)	12-->72 (60)	40-->2 (-38)	4-->3 (-1)
36	178.2355	0	H-4->L+4 (35%), H-3->L+5 (50%)	H-1->L+5 (5%), H-1->L+8 (3%)	49-->29 (-20)	13-->66 (53)	35-->2 (-33)	2-->3 (1)
37	177.8061	0.0078	HOMO->L+8 (87%)	H-4->L+5 (3%), H-3->L+4 (3%), HOMO->L+5 (3%)	93-->49 (-44)	3-->11 (8)	4-->-1 (-5)	0-->41 (41)
38	176.5729	0.0473	H-2->L+4 (11%), H-1->L+7 (75%)	H-4->L+3 (8%)	28-->66 (38)	10-->28 (18)	60-->1 (-59)	1-->5 (4)
39	175.8591	0.0015	H-6->L+1 (94%)		31-->44 (13)	10-->50 (40)	46-->5 (-41)	12-->0 (-12)
40	172.5238	0.0195	H-6->L+2 (38%), H-4->L+5 (17%), H-3->L+4 (26%)	H-4->L+2 (8%), H-2->L+7 (4%)	44-->29 (-15)	13-->66 (53)	37-->4 (-33)	6-->1 (-5)

Table S7: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***Ir(CO)$_2$dbm***

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs	Ir	CO	chelate	Ph
1	382.5728	0.0002	HOMO->LUMO (99%)		96-->1 (-95)	2-->2 (0)	2-->57 (55)	0-->40 (40)
2	345.562	0.4098	H-1->LUMO (97%)		9-->1 (-8)	5-->2 (-3)	62-->57 (-5)	25-->40 (15)
3	324.8806	0.0489	HOMO->L+1 (92%)	HOMO->L+3 (5%)	96-->35 (-61)	2-->41 (39)	2-->9 (7)	0-->15 (15)
4	309.1027	0.004	HOMO->L+2 (92%)	H-3->LUMO (4%)	93-->28 (-65)	2-->61 (59)	2-->7 (5)	3-->3 (0)
5	302.2457	0.2356	H-2->LUMO (96%)		35-->1 (-34)	8-->2 (-6)	10-->57 (47)	47-->40 (-7)
6	298.9444	0.3152	H-3->LUMO (92%)	HOMO->L+2 (4%)	32-->2 (-30)	9-->5 (-4)	8-->55 (47)	52-->38 (-14)
7	289.1153	0.0484	H-4->LUMO (92%)		2-->1 (-1)	0-->2 (2)	1-->57 (56)	97-->40 (-57)
8	288.5366	0.0001	H-5->LUMO (94%)		4-->1 (-3)	1-->2 (1)	1-->57 (56)	93-->40 (-53)
9	284.2761	0.1228	H-1->L+1 (87%)	H-6->LUMO (5%), H-3->L+1 (3%)	11-->35 (24)	5-->40 (35)	58-->12 (-46)	27-->13 (-14)
10	275.7594	0	H-3->L+2 (16%), H-1->L+2 (75%)	H-7->LUMO (3%), H-5->L+2 (2%)	13-->29 (16)	6-->62 (56)	51-->7 (-44)	31-->3 (-28)
11	272.4568	0.0017	H-7->LUMO (90%)	H-2->L+1 (3%), H-1->L+2 (3%)	44-->3 (-41)	16-->5 (-11)	36-->55 (19)	4-->38 (34)
12	268.1551	0.0003	H-9->LUMO (93%)		0-->1 (1)	7-->2 (-5)	75-->57 (-18)	17-->40 (23)
13	267.6919	0.1416	H-6->L+1 (10%), H-2->L+1 (74%)	H-8->LUMO (3%), H-7->LUMO (3%), H-7->L+2 (2%), H-2->L+3 (2%)	36-->34 (-2)	8-->40 (32)	12-->12 (0)	44-->14 (-30)
14	264.2121	0.0053	HOMO->L+6 (85%)	H-3->L+1 (3%), HOMO->L+3 (6%)	94-->27 (-67)	2-->65 (63)	2-->1 (-1)	2-->7 (5)
15	258.5482	0.0039	H-6->L+2 (16%), H-2->L+2 (65%)	H-6->LUMO (3%), H-3->L+6 (3%), H-1->L+6 (5%)	34-->29 (-5)	8-->63 (55)	12-->6 (-6)	46-->3 (-43)
16	255.838	0.0002	H-6->LUMO (77%)	H-2->L+2 (3%), H-1->L+1 (3%), H-1->L+3 (9%)	35-->4 (-31)	7-->6 (-1)	14-->50 (36)	44-->41 (-3)
17	249.646	0.038	H-3->L+1 (35%), HOMO->L+3 (51%)	HOMO->L+1 (4%)	70-->20 (-50)	5-->24 (19)	4-->10 (6)	21-->46 (25)
18	248.2365	0.0391	H-3->L+1 (42%), HOMO->L+3 (35%), HOMO->L+6 (10%)		63-->24 (-39)	5-->32 (27)	5-->9 (4)	26-->35 (9)
19	245.1783	0.0115	H-1->L+3 (76%)	H-6->LUMO (7%), H-3->L+1 (5%), H-1->L+5 (2%), H-1->L+6 (3%)	12-->9 (-3)	5-->13 (8)	55-->13 (-42)	28-->65 (37)
20	241.4775	0.0067	H-7->L+1 (55%), H-1->L+6 (21%)	H-7->L+3 (3%), H-3->L+6 (6%), H-1->L+3 (5%)	33-->32 (-1)	13-->48 (35)	41-->7 (-34)	12-->14 (2)
21	240.7928	0.0045	H-8->LUMO (65%), H-3->L+2 (11%)	H-8->L+2 (2%), H-4->L+1 (3%), H-2->L+1 (2%), H-1->L+2 (3%), H-1->L+4 (3%)	33-->8 (-25)	7-->16 (9)	28-->43 (15)	32-->33 (1)
22	239.1071	0.002	H-8->LUMO (14%), H-3->L+2	H-8->L+2 (7%), H-5->L+2 (3%),	31-->24 (-7)	7-->55 (48)	22-->13 (-9)	40-->8 (-32)

			(45%), H-1->L+2 (16%)	HOMO->L+7 (6%)				
23	237.0091	0.0008	H-8->LUMO (10%), H-4->L+1 (41%), H-1->L+4 (32%)	H-5->LUMO (2%), H-4->L+3 (4%)	8-->18 (10)	3-->20 (17)	26-->13 (-13)	63-->49 (-14)
24	236.7602	0.0001	H-5->L+1 (46%), H-1->L+5 (36%)	H-5->L+3 (4%), H-4->LUMO (2%), H-3->L+3 (2%), H-1->L+6 (3%)	7-->20 (13)	3-->24 (21)	26-->7 (-19)	64-->49 (-15)
25	234.7341	0.0019	H-7->L+1 (31%), H-1->L+6 (45%)	H-3->L+6 (6%), H-2->L+2 (8%), H-1->L+5 (3%)	24-->30 (6)	9-->58 (49)	45-->4 (-41)	21-->8 (-13)
26	234.1843	0	HOMO->L+7 (58%), HOMO->L+8 (18%)	H-3->L+2 (7%), H-2->L+6 (4%), HOMO->L+4 (3%), HOMO->L+9 (7%)	89-->16 (-73)	3-->60 (57)	3-->5 (2)	6-->19 (13)
27	233.2898	0.0052	HOMO->L+7 (15%), HOMO->L+8 (61%)	H-1->L+4 (3%), HOMO->L+4 (5%), HOMO->L+9 (4%)	92-->27 (-65)	2-->53 (51)	4-->4 (0)	1-->16 (15)
28	230.9346	0.0462	H-4->L+1 (40%), H-1->L+4 (50%)	H-2->L+1 (2%)	6-->17 (11)	3-->20 (17)	34-->5 (-29)	57-->59 (2)
29	229.4729	0.0019	H-5->L+1 (43%), H-1->L+5 (46%)	H-3->L+1 (2%)	7-->19 (12)	3-->21 (18)	32-->5 (-27)	58-->55 (-3)
30	228.7827	0.0009	HOMO->L+5 (98%)		96-->1 (-95)	2-->0 (-2)	2-->2 (0)	0-->97 (97)
31	228.7109	0.0037	H-6->L+6 (14%), H-2->L+6 (56%)	H-3->L+8 (3%), H-2->L+3 (8%), H-1->L+8 (5%), HOMO->L+7 (4%)	37-->26 (-11)	7-->63 (56)	12-->2 (-10)	44-->9 (-35)
32	228.3865	0.0006	HOMO->L+4 (88%)	HOMO->L+8 (6%)	96-->2 (-94)	2-->4 (2)	2-->1 (-1)	0-->93 (93)
33	225.348	0.0247	H-7->L+2 (19%), H-6->L+1 (40%), H-2->L+1 (10%)	H-4->L+1 (5%), H-2->L+3 (9%), H-2->L+6 (4%), HOMO->L+8 (5%)	40-->32 (-8)	9-->45 (36)	13-->8 (-5)	38-->15 (-23)
34	221.5151	0.0119	H-7->L+2 (45%), H-2->L+3 (15%)	H-7->L+8 (2%), H-6->L+1 (7%), H-3->L+7 (5%), H-1->L+7 (9%), H-1->L+9 (2%)	37-->23 (-14)	12-->52 (40)	31-->7 (-24)	20-->19 (-1)
35	219.1463	0.0379	H-6->L+1 (20%), H-4->L+3 (14%), H-2->L+3 (30%)	H-7->L+2 (3%), H-3->L+4 (6%), H-2->L+5 (6%), H-2->L+6 (3%), H-1->L+4 (4%), H-1->L+7 (2%)	29-->14 (-15)	7-->20 (13)	13-->8 (-5)	52-->58 (6)
36	217.7071	0.0348	H-5->L+3 (28%), H-3->L+3 (18%), H-2->L+4 (17%)	H-5->L+1 (4%), H-5->L+5 (5%), H-3->L+5 (9%), H-1->L+5 (8%)	18-->6 (-12)	5-->7 (2)	10-->6 (-4)	66-->81 (15)
37	216.5701	0.0102	H-6->L+1 (12%), H-4->L+3 (30%), H-2->L+3 (26%), H-2->L+5 (13%)	H-4->L+1 (2%), H-3->L+4 (8%)	23-->11 (-12)	5-->12 (7)	6-->8 (2)	65-->69 (4)
38	215.2578	0.0081	H-4->L+2 (78%)	H-6->L+2 (4%), H-5->L+3 (3%), H-3->L+6 (3%), H-2->L+2 (6%)	6-->29 (23)	1-->62 (61)	2-->5 (3)	90-->4 (-86)
39	214.7805	0.049	H-8->L+1 (12%), H-5->L+3 (13%), H-3->L+3 (46%)	H-4->L+2 (4%), H-3->L+1 (3%), H-3->L+5 (2%), H-3->L+6 (3%), H-2->L+4 (4%), H-1->L+6 (2%)	25-->14 (-11)	7-->21 (14)	11-->9 (-2)	57-->56 (-1)
40	214.5129	0.0009	H-5->L+2 (85%)	H-3->L+2 (8%)	7-->30 (23)	2-->64 (62)	2-->5 (3)	90-->1 (-89)

Table S8: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***Ir(CO)$_2$tfpb***

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs	Ir	CO	chelate	CF3	Ph
1	399.6525	0.0002	HOMO->LUMO (99%)		96-->1 (-95)	2-->2 (0)	2-->67 (65)	0-->3 (3)	0-->27 (27)
2	333.3356	0.1955	H-1->LUMO (91%)	H-2->LUMO (2%)	18-->1 (-17)	7-->2 (-5)	56-->67 (11)	0-->3 (3)	19-->27 (8)
3	323.1701	0.0513	HOMO->L+1 (96%)		96-->41 (-55)	2-->49 (47)	2-->8 (6)	0-->0 (0)	0-->2 (2)
4	313.5427	0.0259	HOMO->L+2 (89%)	H-2->LUMO (5%), H-1->LUMO (3%)	90-->29 (-61)	3-->57 (54)	4-->10 (6)	0-->1 (1)	3-->3 (0)
5	307.2109	0.3237	H-2->LUMO (89%)	HOMO->L+2 (6%)	40-->3 (-37)	9-->6 (-3)	10-->63 (53)	0-->3 (3)	42-->25 (-17)
6	297.7598	0.0547	H-3->LUMO (95%)		5-->1 (-4)	1-->2 (1)	1-->67 (66)	0-->3 (3)	92-->27 (-65)
7	279.9309	0.0822	H-4->LUMO (62%), H-1->L+1 (26%)	H-5->LUMO (6%)	47-->12 (-35)	11-->15 (4)	24-->50 (26)	1-->3 (2)	17-->20 (3)
8	277.2207	0.0168	H-7->LUMO (12%), H-5->LUMO (77%)	H-4->LUMO (3%), H-1->L+1 (4%)	40-->3 (-37)	16-->4 (-12)	38-->64 (26)	1-->3 (2)	4-->26 (22)
9	271.5557	0.0005	H-2->L+2 (10%), H-1->L+2 (76%)	H-6->L+2 (3%), H-4->L+2 (5%), H-3->L+2 (2%)	22-->31 (9)	7-->62 (55)	47-->5 (-42)	0-->1 (1)	23-->1 (-22)
10	267.4436	0.1478	H-4->LUMO (26%), H-1->L+1 (45%), HOMO->L+4 (18%)	H-2->L+1 (2%)	45-->27 (-18)	8-->39 (31)	31-->23 (-8)	0-->1 (1)	15-->9 (-6)
11	263.8972	0.0349	H-7->LUMO (41%), H-2->L+1 (17%), HOMO->L+4 (18%)	H-5->LUMO (6%), H-4->LUMO (3%), H-4->L+1 (5%), H-1->L+1 (6%)	34-->18 (-16)	8-->28 (20)	40-->37 (-3)	4-->2 (-2)	14-->15 (1)
12	263.5886	0.0311	H-7->LUMO (43%), H-2->L+1 (13%), HOMO->L+4 (19%)	H-5->LUMO (8%), H-4->L+1 (4%), H-1->L+1 (5%)	33-->16 (-17)	8-->27 (19)	42-->39 (-3)	5-->2 (-3)	12-->16 (4)
13	260.3452	0.0561	H-2->L+1 (34%), HOMO->L+4 (38%)	H-6->LUMO (5%), H-4->L+1 (9%), H-1->L+1 (7%)	62-->33 (-29)	6-->54 (48)	11-->8 (-3)	0-->1 (1)	20-->4 (-16)
14	257.4583	0.0048	H-4->L+2 (24%), H-2->L+2 (56%)	H-6->L+2 (2%), H-3->L+2 (3%), H-1->L+2 (4%), H-1->L+4 (4%)	39-->31 (-8)	9-->62 (53)	14-->5 (-9)	0-->1 (1)	37-->1 (-36)
15	242.8111	0.0201	H-6->LUMO (79%)	H-2->L+1 (8%), H-1->L+5 (2%)	37-->5 (-32)	7-->6 (-1)	34-->60 (26)	0-->3 (3)	22-->25 (3)
16	237.463	0.0011	H-5->L+1 (51%), H-1->L+4 (25%)	H-4->L+1 (3%), H-4->L+4 (2%), H-2->L+4 (4%)	39-->36 (-3)	14-->56 (42)	37-->5 (-32)	0-->0 (0)	10-->3 (-7)
17	234.7163	0.0089	H-4->L+1 (47%), H-2->L+1 (14%), HOMO->L+7 (16%)	H-5->L+2 (4%), H-1->L+1 (4%), H-1->L+4 (3%)	58-->39 (-19)	10-->53 (43)	13-->7 (-6)	0-->0 (0)	18-->2 (-16)
18	234.1135	0.0002	HOMO->L+3 (11%), HOMO->L+5 (19%), HOMO->L+6 (53%)	H-5->L+1 (4%), HOMO->L+7 (6%)	94-->13 (-81)	3-->55 (52)	3-->7 (4)	0-->1 (1)	0-->24 (24)
19	232.0845	0.002	H-4->L+1 (14%), HOMO->L+6 (18%), HOMO->L+7 (51%)	HOMO->L+3 (8%)	90-->27 (-63)	4-->59 (55)	3-->4 (1)	0-->0 (0)	3-->9 (6)
20	231.3052	0.0035	H-3->L+1 (69%), H-1->L+4	H-5->L+1 (5%), H-2->L+1 (2%), H-2-	11-->39 (28)	3-->51 (48)	10-->7 (-3)	0-->0 (0)	76-->2 (-74)

			(10%)	>L+2 (3%)					
21	230.6897	0.0011	H-5->L+1 (17%), H-3->L+1 (16%), H-1->L+4 (13%), HOMO->L+3 (26%)	H-4->L+2 (4%), H-2->L+2 (6%), H-1->L+2 (3%), H-1->L+3 (2%), HOMO->L+5 (3%), HOMO->L+7 (3%)	50-->24 (-26)	7-->38 (31)	19-->6 (-13)	0-->1 (1)	24-->31 (7)
22	230.2485	0.0003	H-5->L+1 (10%), HOMO->L+3 (42%), HOMO->L+6 (10%), HOMO->L+7 (16%)	H-3->L+1 (3%), H-2->L+2 (2%), H-1->L+4 (7%)	80-->17 (-63)	5-->35 (30)	9-->5 (-4)	0-->1 (1)	6-->43 (37)
23	226.9277	0.0015	H-4->L+2 (22%), H-4->L+4 (17%), H-2->L+4 (24%), H-1->L+4 (11%)	H-6->L+2 (3%), H-2->L+2 (3%), H-1->L+2 (6%), H-1->L+7 (2%)	42-->29 (-13)	10-->65 (55)	21-->3 (-18)	0-->0 (0)	26-->3 (-23)
24	223.8426	0.0027	H-4->L+2 (28%), H-2->L+4 (25%)	H-6->L+2 (4%), H-5->L+1 (4%), H-4->L+4 (7%), H-1->L+2 (4%), H-1->L+7 (3%), HOMO->L+3 (3%), HOMO->L+5 (9%)	53-->26 (-27)	9-->56 (47)	15-->6 (-9)	0-->1 (1)	23-->12 (-11)
25	222.6848	0.0222	H-1->L+3 (71%)	H-3->L+1 (4%), H-3->L+5 (7%), H-2->L+3 (2%), H-1->L+4 (3%), H-1->L+5 (2%)	16-->4 (-12)	6-->7 (1)	48-->7 (-41)	0-->1 (1)	28-->81 (53)
26	221.8837	0.0002	HOMO->L+5 (63%), HOMO->L+6 (14%)	H-4->L+2 (4%), H-2->L+4 (3%), HOMO->L+3 (6%), HOMO->L+4 (3%)	93-->7 (-86)	3-->24 (21)	2-->16 (14)	0-->3 (3)	2-->51 (49)
27	220.2128	0.008	H-5->L+2 (67%)	H-5->L+7 (4%), H-4->L+1 (3%), H-3->L+2 (3%), H-2->L+6 (3%), H-1->L+6 (9%)	43-->29 (-14)	16-->64 (48)	33-->5 (-28)	0-->1 (1)	9-->1 (-8)
28	216.6268	0.0046	H-3->L+2 (82%)	H-2->L+2 (9%)	8-->31 (23)	2-->62 (60)	2-->5 (3)	0-->1 (1)	88-->1 (-87)
29	214.3127	0.0261	H-2->L+3 (37%), H-1->L+3 (12%), H-1->L+5 (27%)	H-3->L+2 (2%), H-3->L+5 (9%)	24-->2 (-22)	7-->6 (-1)	30-->12 (-18)	0-->2 (2)	38-->78 (40)
30	210.3745	0.0394	H-6->L+1 (67%), H-1->L+5 (10%)	H-3->L+5 (3%), H-2->L+1 (2%), H-2->L+3 (7%)	34-->33 (-1)	7-->39 (32)	34-->10 (-24)	0-->1 (1)	25-->18 (-7)
31	207.6335	0.0012	H-1->L+7 (44%)	H-7->L+1 (4%), H-6->L+1 (5%), H-6->L+7 (2%), H-4->L+7 (3%), H-3->L+5 (2%), H-2->L+3 (5%), H-2->L+4 (5%), H-2->L+7 (8%), H-1->L+4 (3%), H-1->L+5 (6%)	23-->28 (5)	8-->54 (46)	43-->5 (-38)	1-->1 (0)	25-->12 (-13)
32	206.9611	0.0026	H-6->L+1 (13%), H-2->L+3 (11%), H-1->L+5 (36%), H-1->L+7 (10%)	H-3->L+5 (6%), H-2->L+4 (3%), H-2->L+7 (2%), H-1->L+6 (2%)	23-->14 (-9)	7-->25 (18)	40-->14 (-26)	0-->2 (2)	29-->46 (17)
33	206.1045	0	H-7->L+1 (91%)	H-1->L+7 (3%)	3-->41 (38)	7-->49 (42)	73-->8 (-65)	9-->0 (-9)	8-->2 (-6)
34	203.503	0.0003	H-9->LUMO (16%), H-8->LUMO (72%)		14-->1 (-13)	5-->2 (-3)	25-->67 (42)	5-->3 (-2)	51-->27 (-24)
35	202.8604	0.0014	H-6->L+2 (60%), H-4->L+4 (10%)	H-4->L+2 (3%), H-3->L+2 (3%), H-2->L+2 (6%), H-1->L+4 (3%), H-1->L+7	38-->31 (-7)	7-->63 (56)	30-->5 (-25)	0-->1 (1)	24-->1 (-23)

				(3%)					
36	201.0935	0.0008	H-3->L+3 (20%), H-2->L+5 (55%)	H-5->L+4 (2%), H-4->L+7 (2%), H-3->L+5 (5%), H-2->L+3 (3%), H-2->L+7 (3%)	28-->4 (-24)	7-->11 (4)	8-->16 (8)	0-->2 (2)	56-->66 (10)
37	199.8037	0.0002	H-6->L+2 (15%), H-4->L+7 (15%), H-2->L+7 (30%)	H-6->L+4 (2%), H-4->L+2 (3%), H-4->L+4 (8%), H-2->L+4 (3%), H-1->L+4 (2%), H-1->L+6 (3%), H-1->L+7 (5%)	42-->31 (-11)	9-->64 (55)	20-->3 (-17)	0-->0 (0)	29-->1 (-28)
38	198.1845	0.0014	H-9->LUMO (14%), H-4->L+4 (32%), H-2->L+7 (14%)	H-8->LUMO (5%), H-6->L+2 (4%), H-6->L+4 (4%), H-4->L+7 (5%), H-2->L+4 (4%), H-1->L+4 (7%)	39-->23 (-16)	9-->52 (43)	18-->16 (-2)	1-->1 (0)	34-->8 (-26)
39	197.9882	0.0029	H-9->LUMO (64%), H-8->LUMO (13%)	H-4->L+4 (7%), H-2->L+7 (5%)	13-->5 (-8)	4-->10 (6)	18-->59 (41)	3-->3 (0)	62-->24 (-38)
40	197.0067	0.1002	H-5->L+4 (13%), H-1->L+6 (49%)	H-5->L+2 (2%), H-5->L+7 (8%), H-4->L+6 (5%), H-3->L+3 (6%), H-1->L+7 (3%)	27-->19 (-8)	10-->71 (61)	44-->3 (-41)	0-->0 (0)	19-->8 (-11)

Table S9: *Energy and composition of TD-DFT calculated singlet-singlet transitions of* ***Ir(CO)$_2$tfaa***

No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs	Ir	CO	chelate	CF_3	CH_3
1	369.815	0	HOMO->LUMO (100%)		96-->1 (-95)	3-->3 (0)	2-->86 (84)	0-->6 (6)	0-->5 (5)
2	322.7746	0.0535	HOMO->L+1 (97%)		96-->43 (-53)	3-->51 (48)	2-->6 (4)	0-->0 (0)	0-->0 (0)
3	314.6727	0.0144	HOMO->L+2 (91%)	H-1->LUMO (5%)	92-->30 (-62)	3-->59 (56)	5-->10 (5)	0-->1 (1)	0-->1 (1)
4	302.312	0.0225	H-1->LUMO (86%)	H-3->LUMO (6%), HOMO->L+2 (6%)	33-->3 (-30)	10-->6 (-4)	56-->81 (25)	0-->5 (5)	1-->4 (3)
5	275.1475	0.0267	H-2->LUMO (78%), H-1->L+1 (18%)	HOMO->L+3 (2%)	67-->10 (-57)	14-->13 (-1)	17-->69 (52)	0-->5 (5)	1-->4 (3)
6	270.4008	0.0001	H-1->L+2 (90%)	H-3->L+2 (8%)	29-->32 (3)	11-->62 (51)	59-->5 (-54)	0-->1 (1)	1-->1 (0)
7	266.1405	0.183	H-2->LUMO (17%), H-1->L+1 (38%), HOMO->L+3 (38%)		64-->30 (-34)	8-->50 (42)	27-->18 (-9)	0-->1 (1)	0-->1 (1)
8	263.6615	0.0008	H-5->LUMO (24%), H-4->LUMO (74%)		36-->1 (-35)	15-->3 (-12)	44-->86 (42)	2-->6 (4)	3-->5 (2)
9	261.0194	0.0383	H-2->L+1 (13%), H-1->L+1 (28%), HOMO->L+3 (52%)	H-3->LUMO (2%)	72-->35 (-37)	7-->60 (53)	21-->5 (-16)	0-->0 (0)	0-->0 (0)
10	257.7741	0.0488	H-2->L+1 (70%)	H-4->L+2 (3%), H-3->LUMO (7%), H-1->L+1 (9%), HOMO->L+3 (6%)	70-->39 (-31)	14-->49 (35)	16-->11 (-5)	0-->1 (1)	1-->1 (0)
11	254.4153	0.0018	H-5->LUMO (21%), H-2->L+2 (61%)	H-4->LUMO (7%), H-1->L+3 (7%)	55-->23 (-32)	13-->45 (32)	28-->28 (0)	2-->2 (0)	2-->2 (0)
12	254.2223	0.005	H-5->LUMO (55%), H-4->LUMO (16%), H-2->L+2 (25%)		30-->9 (-21)	11-->18 (7)	49-->65 (16)	5-->4 (-1)	4-->4 (0)
13	236.5298	0.2036	H-3->LUMO (76%)	H-4->L+2 (2%), H-2->L+1 (4%), H-1->LUMO (6%), HOMO->L+5 (7%)	54-->6 (-48)	9-->11 (2)	35-->75 (40)	1-->5 (4)	1-->4 (3)
14	236.354	0.0003	H-4->L+1 (63%), H-1->L+3 (28%)	H-3->L+3 (3%)	40-->39 (-1)	15-->57 (42)	43-->4 (-39)	0-->0 (0)	2-->0 (-2)
15	232.3324	0	HOMO->L+4 (96%)		96-->14 (-82)	3-->85 (82)	2-->1 (-1)	0-->0 (0)	0-->0 (0)
16	231.7202	0.0147	HOMO->L+5 (87%)	H-3->LUMO (5%), H-2->L+1 (2%)	93-->31 (-62)	3-->59 (56)	4-->8 (4)	0-->1 (1)	0-->1 (1)
17	228.0043	0.0029	H-4->L+1 (31%), H-1->L+3 (54%)	H-3->L+3 (2%), H-2->L+2 (9%)	39-->34 (-5)	13-->63 (50)	47-->3 (-44)	0-->0 (0)	1-->0 (-1)
18	223.3225	0.0001	H-2->L+3 (82%), H-1->L+5 (10%)	H-3->L+5 (3%)	70-->29 (-41)	14-->69 (55)	14-->1 (-13)	0-->0 (0)	1-->1 (0)
19	220.5418	0.0076	H-3->L+1 (81%)	H-4->L+2 (6%), H-4->L+3 (3%), H-2->L+4 (2%), H-1->L+1 (2%)	51-->41 (-10)	10-->53 (43)	37-->5 (-32)	1-->0 (-1)	1-->0 (-1)
20	219.8301	0.0093	H-4->L+2 (66%), H-1->L+4 (12%)	H-4->L+5 (4%), H-3->L+1 (8%), H-3->L+4 (3%)	44-->30 (-14)	16-->65 (49)	38-->5 (-33)	0-->0 (0)	2-->0 (-2)
21	216.7745	0.0001	H-3->L+2 (88%)	H-1->L+2 (7%)	49-->32 (-17)	10-->62 (52)	39-->5 (-34)	1-->1 (0)	1-->1 (0)
22	206.9888	0	H-5->L+1 (91%)	H-1->L+5 (5%)	5-->43 (38)	8-->52 (44)	72-->5 (-67)	9-->0 (-9)	6-->0 (-6)

23	205.6873	0	H-2->L+3 (12%), H-1->L+5 (71%)	H-5->L+1 (6%), H-3->L+5 (7%)	34-->33 (-1)	11-->63 (52)	53-->3 (-50)	1-->0 (-1)	1-->1 (0)
24	197.2135	0.0007	H-2->L+5 (92%)	H-3->L+3 (2%)	75-->33 (-42)	15-->63 (48)	8-->3 (-5)	0-->0 (0)	1-->1 (0)
25	196.585	0.0002	H-6->LUMO (95%)		26-->1 (-25)	9-->3 (-6)	49-->86 (37)	10-->6 (-4)	6-->5 (-1)
26	195.7099	0.0783	H-4->L+5 (17%), H-1->L+4 (63%)	H-5->L+2 (6%), H-4->L+2 (6%)	31-->20 (-11)	12-->78 (66)	55-->2 (-53)	1-->0 (-1)	1-->0 (-1)
27	194.3113	0.1213	H-5->L+2 (53%), H-4->L+3 (19%), H-2->L+4 (17%)	HOMO->L+6 (3%)	29-->29 (0)	11-->66 (55)	50-->4 (-46)	5-->0 (-5)	4-->1 (-3)
28	192.543	0.0229	H-5->L+2 (34%), H-4->L+3 (25%), H-2->L+4 (31%)	H-4->L+5 (3%), H-1->L+4 (3%)	40-->25 (-15)	13-->72 (59)	40-->3 (-37)	3-->0 (-3)	3-->0 (-3)
29	191.6649	0.0006	H-3->L+3 (86%)	H-2->L+5 (2%), H-1->L+3 (7%), H-1->L+6 (2%)	49-->30 (-19)	10-->68 (58)	39-->1 (-38)	1-->0 (-1)	1-->1 (0)
30	185.6329	0.0676	HOMO->L+6 (92%)		96-->65 (-31)	3-->7 (4)	2-->7 (5)	0-->-1 (-1)	0-->23 (23)
31	181.3642	0.0991	HOMO->L+7 (98%)		96-->73 (-23)	3-->17 (14)	2-->6 (4)	0-->1 (1)	0-->4 (4)
32	178.0154	0.0001	H-4->L+4 (81%)	H-5->L+4 (2%), H-3->L+5 (6%), H-1->L+5 (3%), H-1->L+6 (3%)	44-->17 (-27)	16-->80 (64)	37-->2 (-35)	0-->0 (0)	2-->1 (-1)
33	176.2842	0.0066	H-1->L+6 (90%)	H-4->L+4 (4%), H-3->L+3 (2%)	29-->62 (33)	11-->12 (1)	59-->7 (-52)	0-->-1 (-1)	1-->21 (20)
34	176.2266	0.013	H-5->L+3 (53%), H-4->L+5 (11%), H-3->L+4 (10%)	H-6->L+2 (3%), H-4->L+3 (9%), H-2->L+4 (3%), H-1->L+4 (4%)	22-->27 (5)	10-->71 (61)	57-->1 (-56)	6-->0 (-6)	5-->1 (-4)
35	173.4409	0.0643	H-5->L+3 (28%), H-4->L+5 (17%), H-3->L+4 (34%)	H-6->L+2 (3%), H-1->L+4 (9%)	33-->23 (-10)	11-->75 (64)	50-->2 (-48)	3-->0 (-3)	3-->0 (-3)
36	173.2736	0.0152	HOMO->L+8 (93%)	H-6->L+1 (3%), H-3->L+5 (2%)	92-->15 (-77)	3-->3 (0)	4-->68 (64)	0-->8 (8)	0-->6 (6)
37	172.998	0.0015	H-3->L+5 (75%)	H-4->L+4 (7%), H-1->L+5 (8%), H-1->L+6 (2%), HOMO->L+8 (3%)	50-->31 (-19)	10-->61 (51)	39-->6 (-33)	1-->1 (0)	1-->2 (1)
38	171.7923	0.034	HOMO->L+9 (70%)	H-5->L+3 (3%), H-4->L+3 (6%), H-2->L+4 (6%), H-1->L+7 (8%)	83-->67 (-16)	5-->15 (10)	11-->0 (-11)	0-->0 (0)	0-->19 (19)
39	170.9207	0.0005	H-6->L+1 (92%)	HOMO->L+8 (3%)	29-->42 (13)	8-->49 (41)	47-->8 (-39)	10-->0 (-10)	6-->0 (-6)
40	170.8571	0.103	H-1->L+7 (42%), HOMO->L+9 (22%)	H-5->L+3 (6%), H-4->L+3 (6%), H-2->L+4 (9%), HOMO->L+10 (3%)	51-->60 (9)	9-->27 (18)	38-->4 (-34)	1-->0 (-1)	1-->9 (8)

NMR spectra

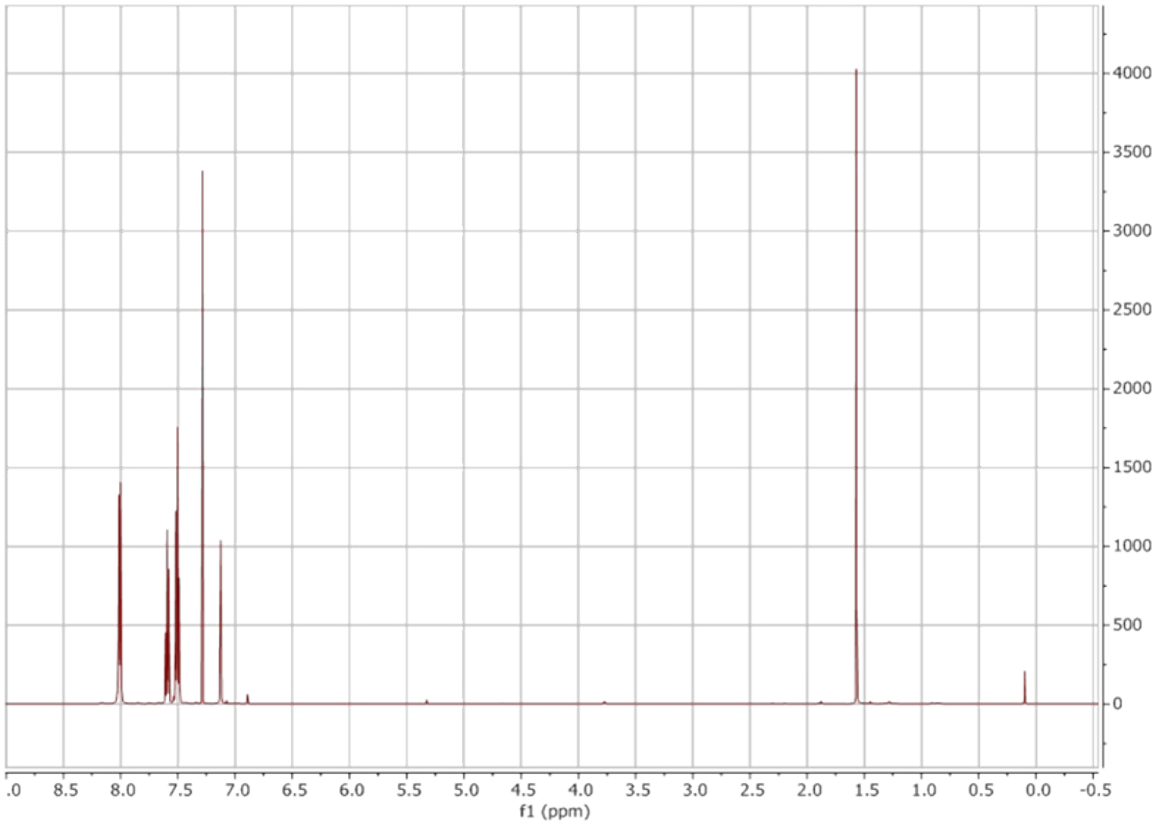

Figure S8: ^{1}H NMR spectrum for **Ir(CO)$_2$dbm**

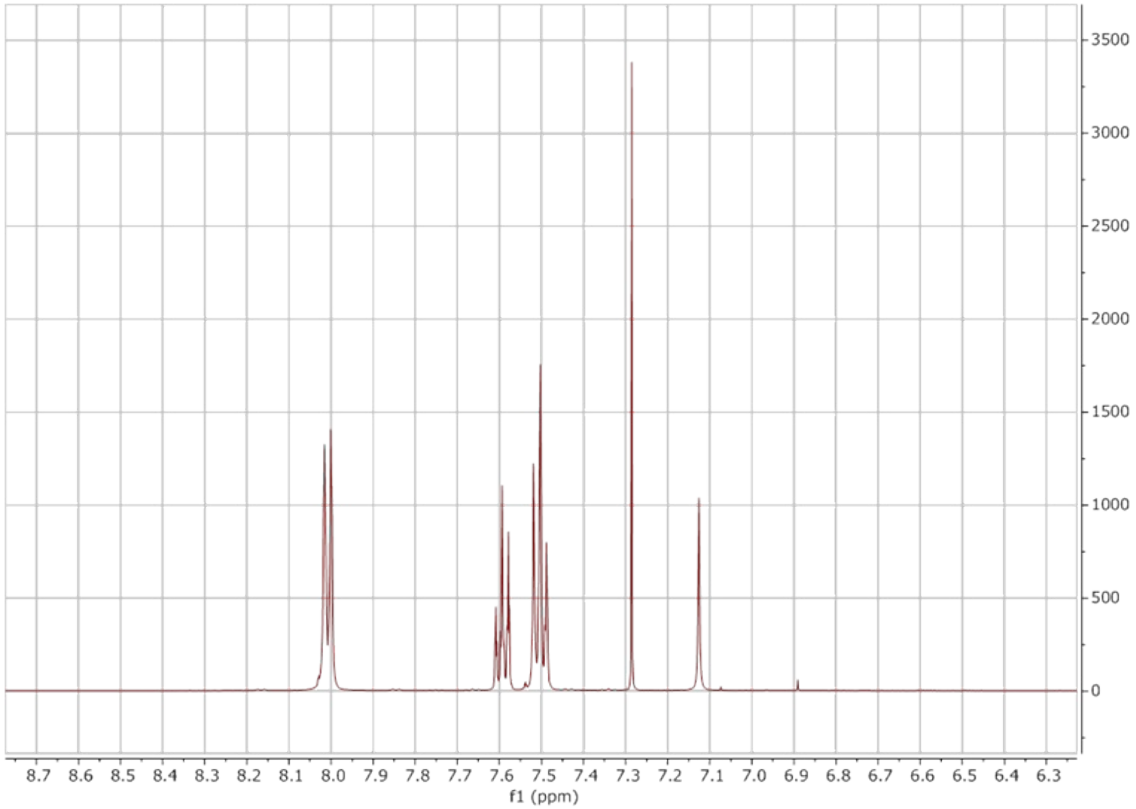

Figure S9: Aromatic region of the ^{1}H NMR spectrum for **Ir(CO)$_2$dbm**

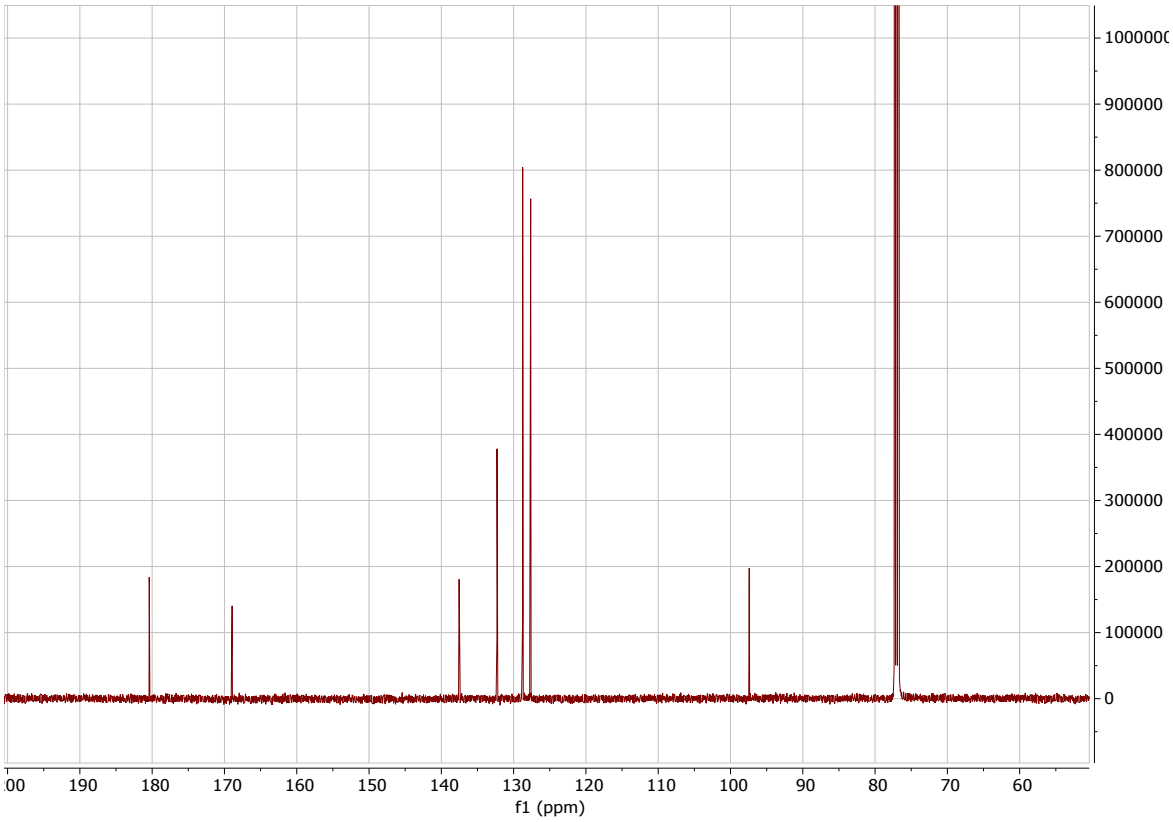

Figure S10: ^{13}C NMR spectrum for **Ir(CO)$_2$dbm**

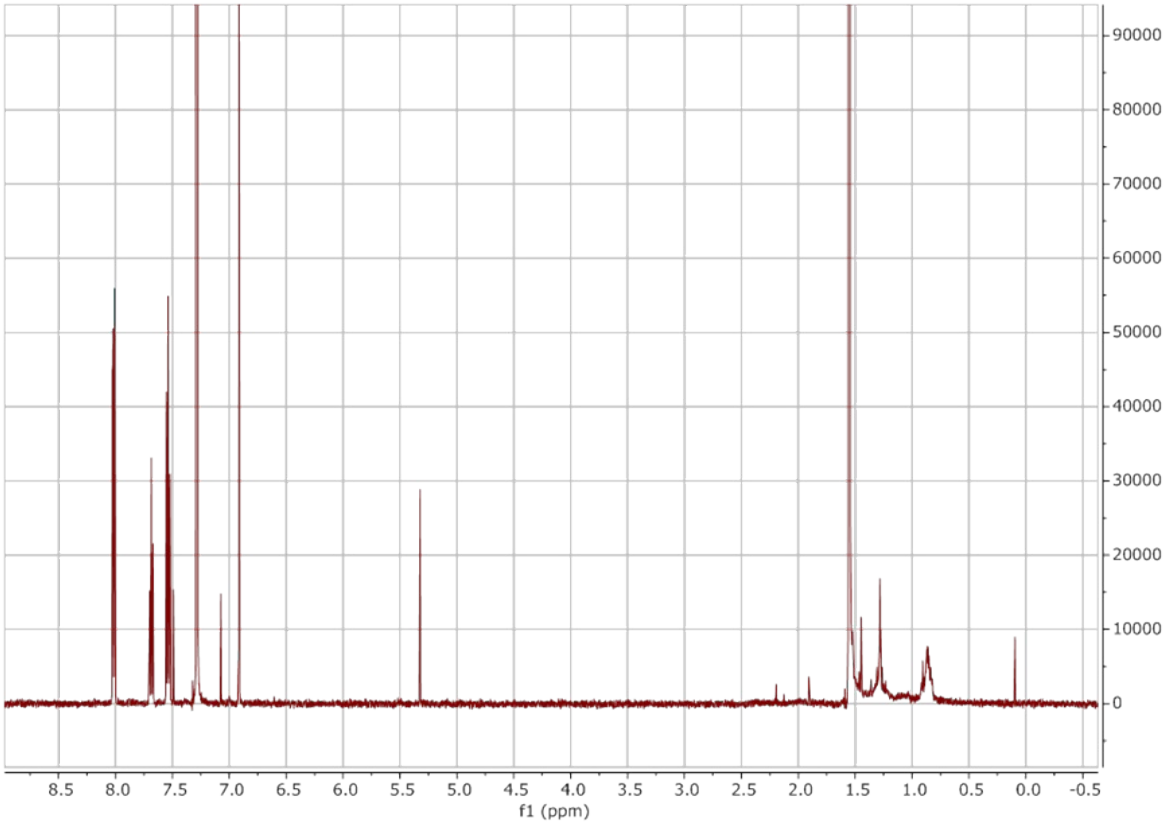

Figure S11: ^{1}H NMR spectrum for **Ir(CO)$_2$tfpb**

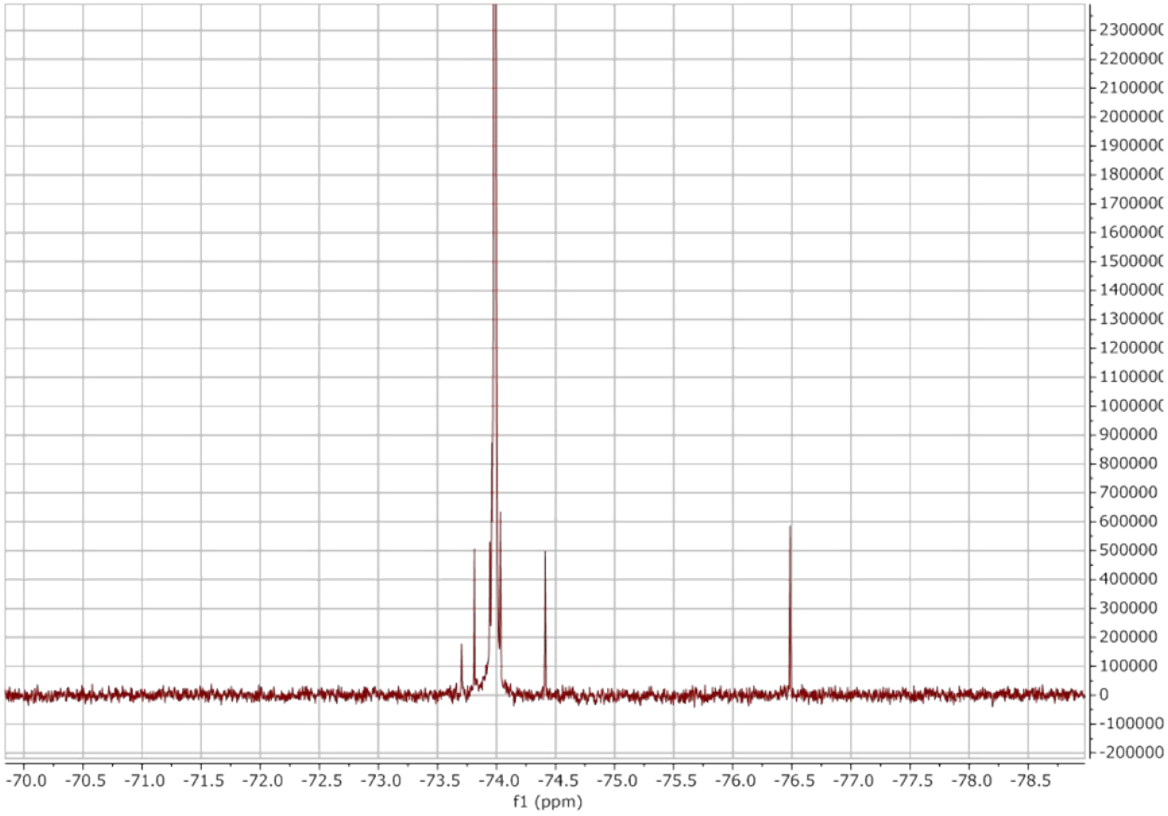

Figure S12: ^{19}F NMR spectrum for **Ir(CO)$_2$tfpb**

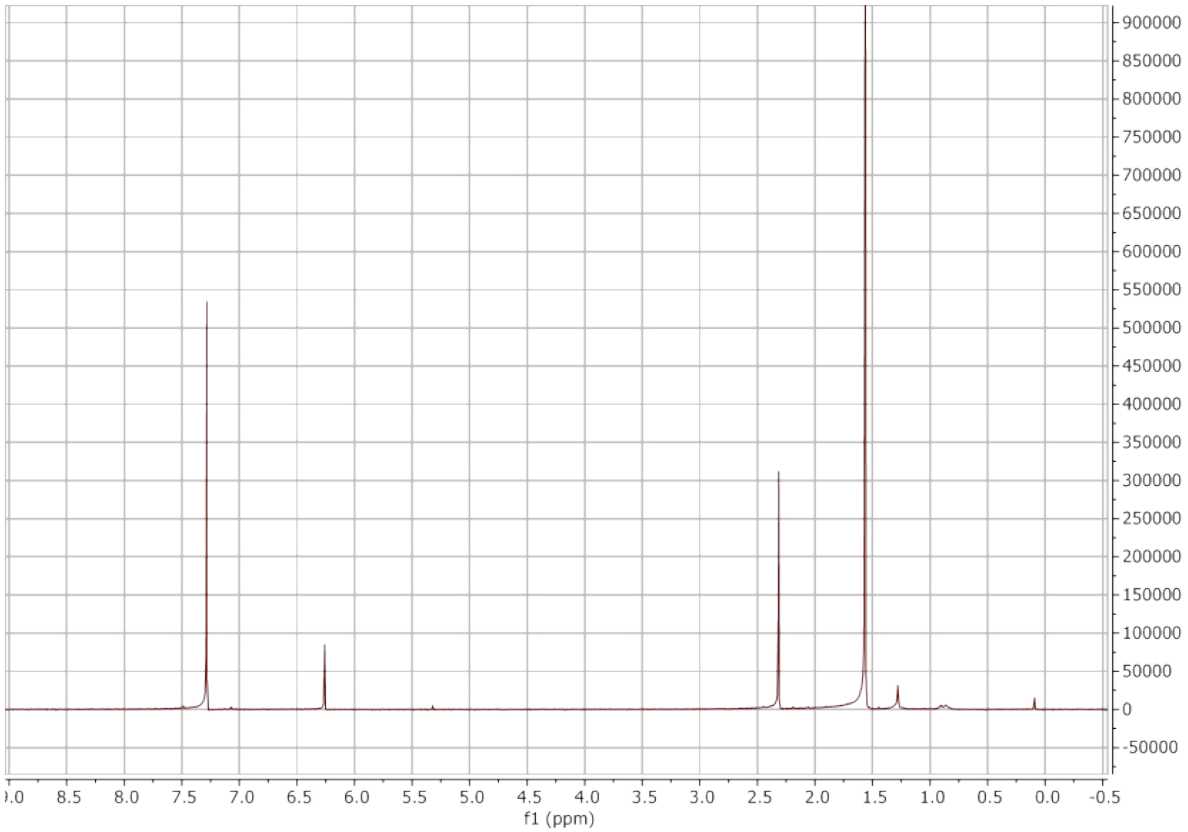

Figure S13: ^{1}H NMR spectrum for **Ir(CO)$_2$tfaa**

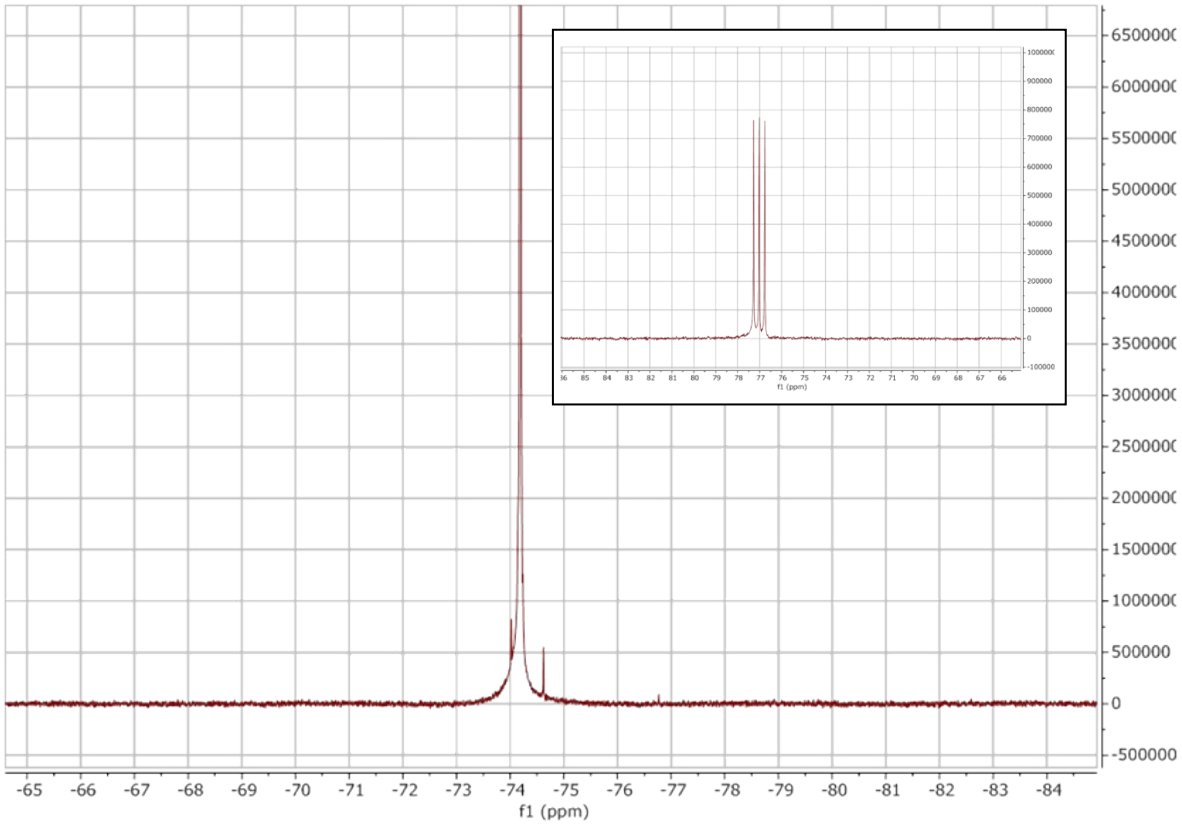

Figure S14: ^{19}F NMR spectrum for **Ir(CO)$_2$tfaa**

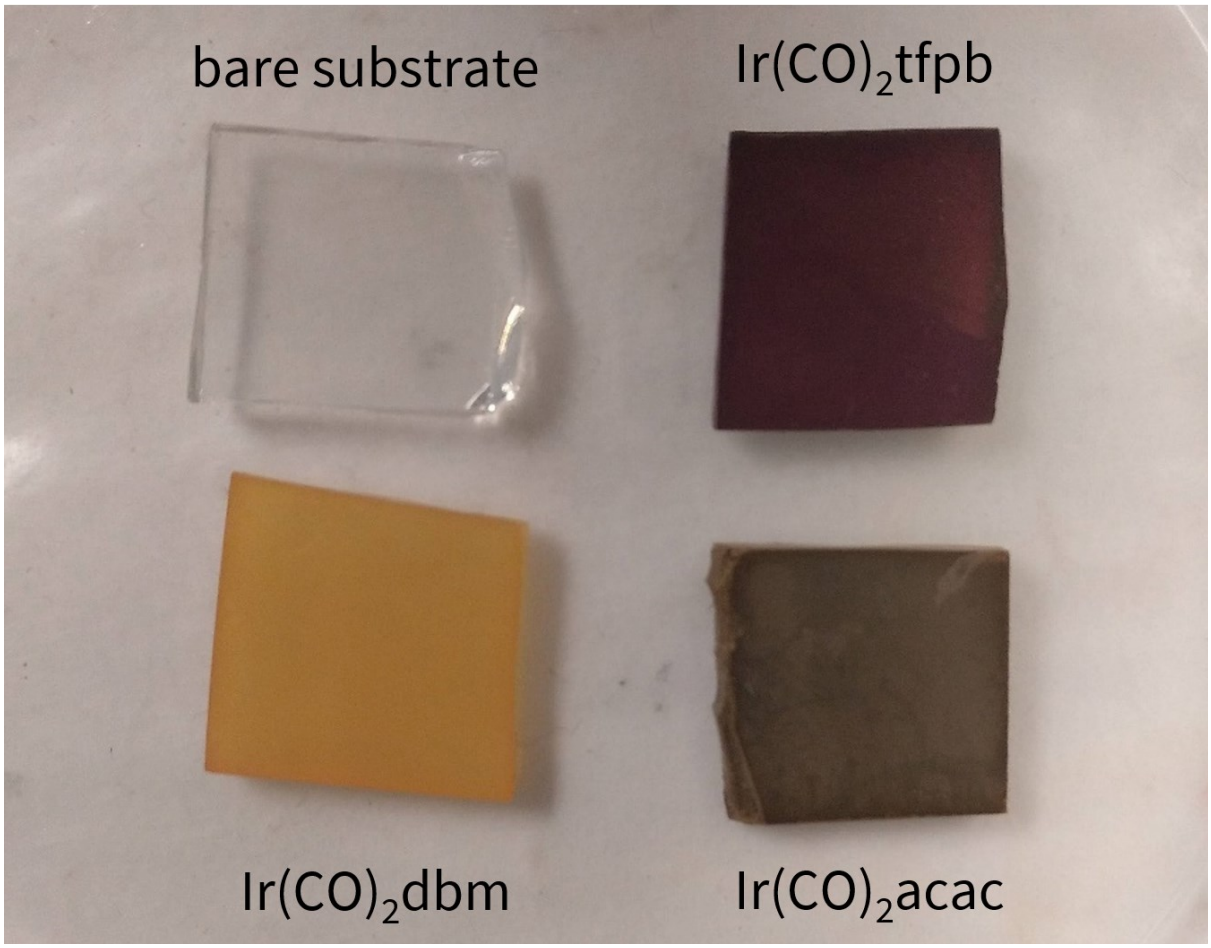

Figure S15: Photographs of vapour-deposited films