Synthetic Control of Excited States in Cyclometalated Ir(III) Complexes using Ancillary Ligands

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Supporting information.

Figure Captions.

Figure S 1. Abbreviations of Iridium complexes used through out the paper.

Figure S 2. Absorption spectra of $(tpy)_2Ir(pz)_2Bpz_2$ in hexane, CH_2Cl_2, DMSO. ^{1}MLCT absorption spectra are demonstrated in the inset.

Figure S 3. Absorption, emission (77 K) and excitation (77 K) spectra of $[(tpy)_2Ir(CN\text{-}t\text{-}Bu)_2](CF_3SO_3)$.

Figure S 4 Rigidochromic shift vs emission energy of $(tpy)_2Ir(LX)$ complexes in 2-MeTHF. The ancillary ligands (LX) are numbered as in Figure 1.

Figure S 5. Absorption spectra of $(dfppy)_2Ir[(PPh_2CH_2)_2BPh_2]$, $(dfppy)_2Ir(pz_2Bpz_2)$, and $(dfppy)_2Ir(acac)$ complexes in CH_2Cl_2.

Figure S 6. RT emission spectra of $(dfppy)_2Ir(PPh_2CH_2)_2BPh_2$, $(dfppy)_2Ir(pz)_2Bpz_2$, $(dfppy)_2Ir(pz)_2H$, and $(dfppy)_2Ir(acac)$ complexes in 2-MeTHF.

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Figure S 8. ORTEP drawings of $(tpy)_2Ir(PPh_2CH_2)_2BPh_2\cdot H_2O$ The thermal ellipsoids for the image represent 25 % probability limit. The hydrogen atoms, counter anion and solvent are omitted for clarity.

Figure S 9. ORTEP drawings of $(tpy)_2Ir(CN\text{-}t\text{-}Bu)_2(CF_3SO_3)\cdot CHCl_3$. The thermal ellipsoids for the image represent 25 % probability limit. The hydrogen atoms, counter anion and solvent are omitted for clarity.

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Table S 1. Selected parameters for plot of k_r vs. $\frac{1}{\Delta E^2}\left(\frac{\upsilon_{T_1}}{\upsilon_{^1MLCT}}\right)^3$ and plot of ε vs. $\frac{1}{\Delta E^2}\frac{\upsilon_{T_1}}{\upsilon_{^1MLCT}}^3$ of $(tpy)_2Ir(LL')$ complexes.

Table S 2. Redox properties of $(dfppy)_2Ir(LL')$ complexes. Redox measurements were carried out in DMF solution unless noted: (a) in CH_2Cl_2; (b) in CH_3CN. The redox values are reported relative to Fc^+/Fc. The electrochemical process is reversible unless noted:(c) Quasi-reversible; (d) Irreversible.

Table S 3. Photophysical properties of $(dfppy)_2Ir(LX)$ complexes. Absorption measurements were carried out in CH_2Cl_2. Emission and lifetime measurements were carried out in 2-methyltetrahydrofuran (2-MeTHF).

Table S 4. Selected excited state properties and IR absorption of selected $(dfppy)_2Ir(LX)$ complexes.

Table S 5. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $(tpy)_2Ir(PPh_2CH_2)_2BPh_2\cdot H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S 6. Bond lengths [Å] for $(tpy)_2Ir(PPh_2CH_2)_2BPh_2\cdot H_2O$.

Table S 7. Bond angles [°] for $(tpy)_2Ir(PPh_2CH_2)_2BPh_2\cdot H_2O$.

Table S 8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(tpy)_2Ir(PPh_2CH_2)_2BPh_2\cdot H_2O$.. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+ ...+2hka^*b^*U^{12}]$

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Table S 10. Bond lengths [Å] and angles [°] for $[(tpy)_2Ir(CN\text{-}t\text{-}Bu)_2](CF_3SO_3)\cdot CHCl_3$.

Table S 11. Bond angles [°] for $[(tpy)_2Ir(CN\text{-}t\text{-}Bu)_2](CF_3SO_3)\cdot CHCl_3$.

Table S 12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[(tpy)_2Ir(CN\text{-}t\text{-}Bu)_2](CF_3SO_3)\cdot CHCl_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+ ...+2hka^*b^*U^{12}]$.

Table S 13. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for $[(tpy)_2Ir(CN\text{-}t\text{-}Bu)_2](CF_3SO_3)\cdot CHCl_3$.

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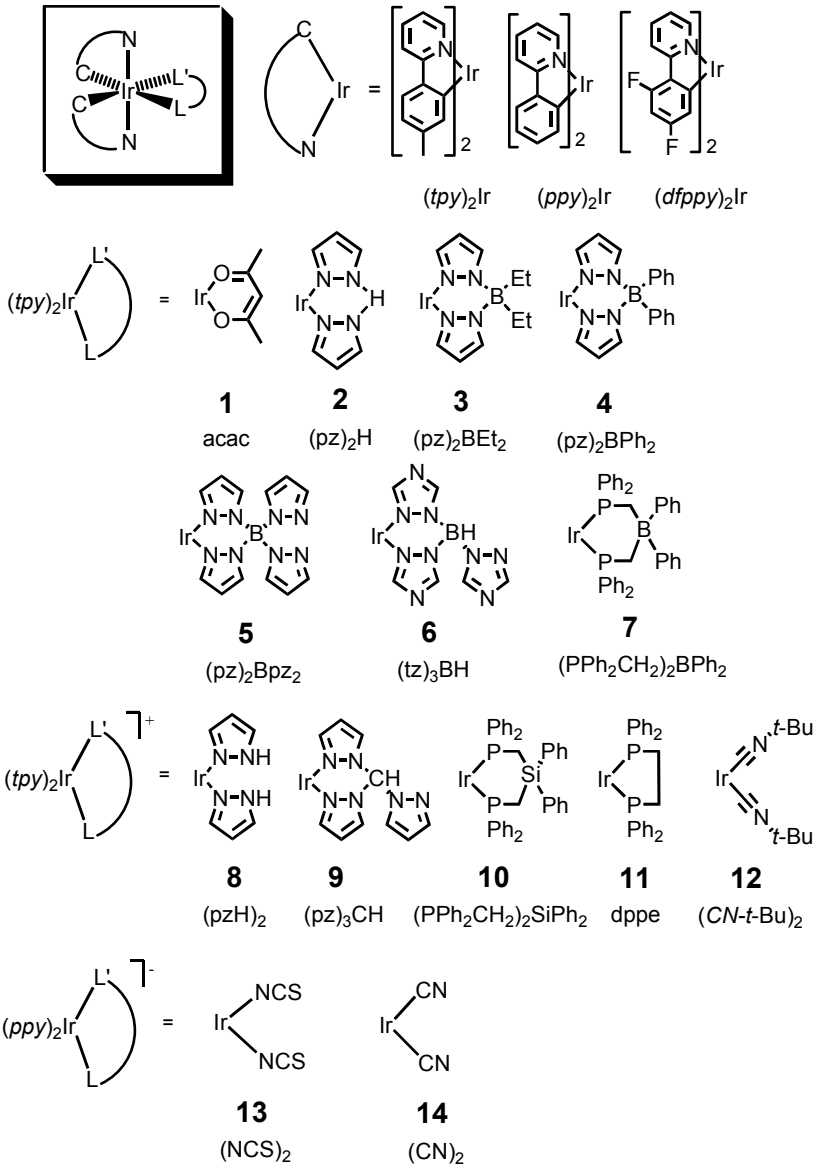

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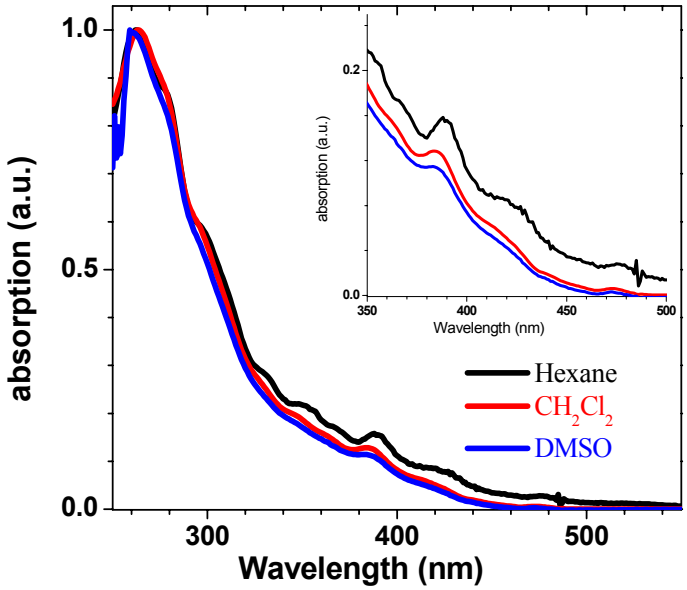
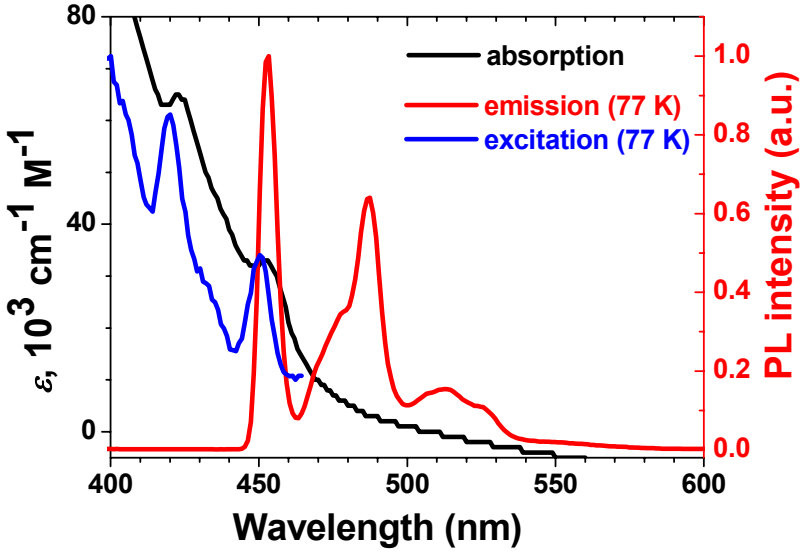


Figure S 3. Absorption, emission (77 K) and excitation (77 K) spectra of [(tpy)2Ir(CN-t-Bu)2](CF3SO3).



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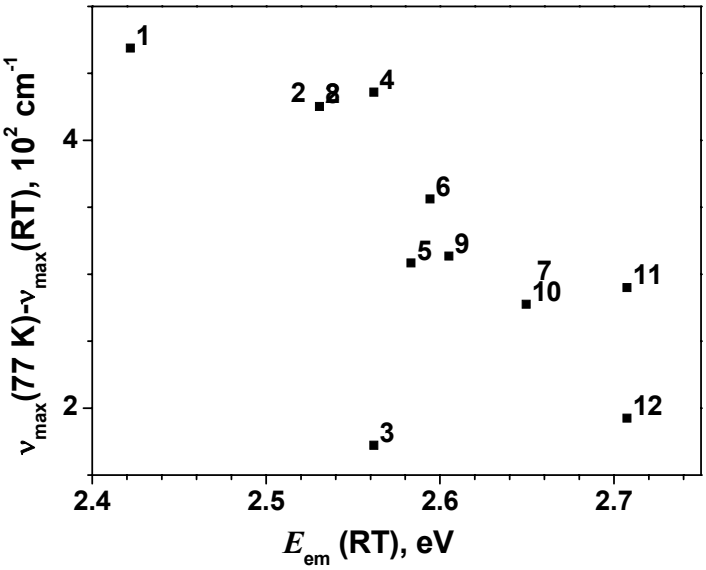

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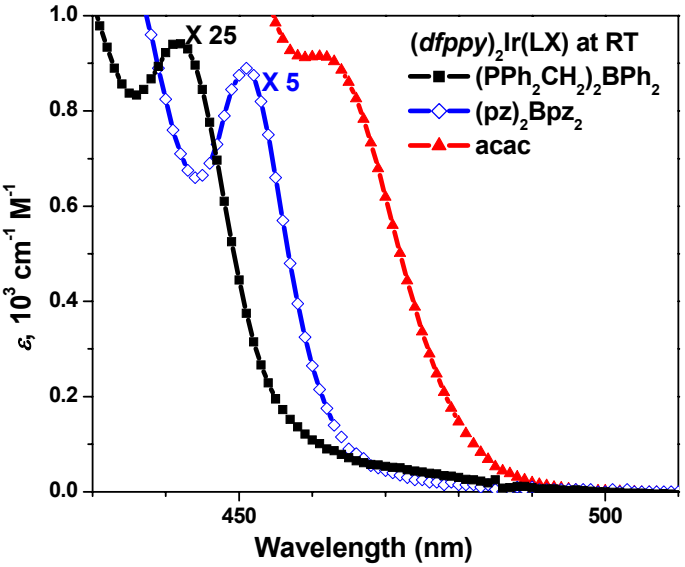

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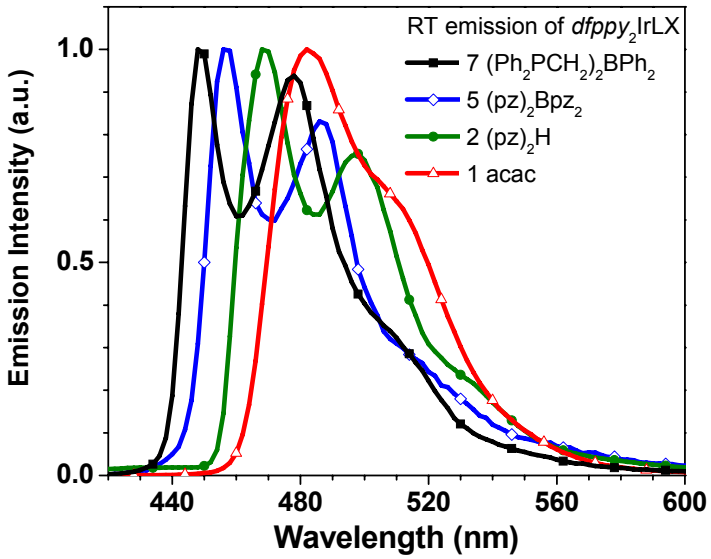

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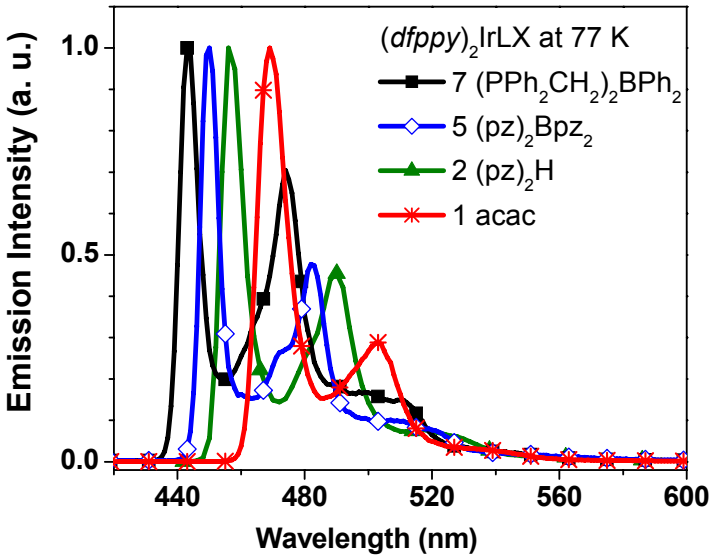

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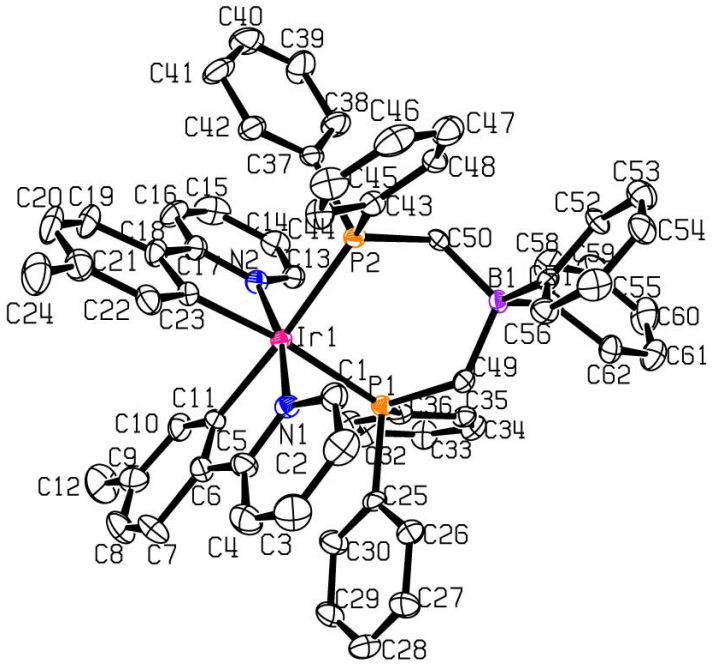

Figure S 9. ORTEP drawings of (tpy)2Ir(CN-t-Bu)2(CF3SO3)·CHCl3. The thermal ellipsoids for the image represent 25 % probability limit. The hydrogen atoms, counter anion and solvent are omitted for clarity.

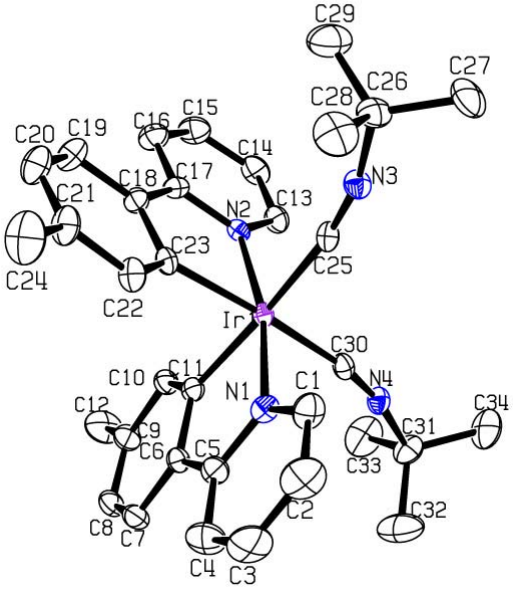

Table S 1. Selected parameters for plot of k_r vs. $\frac{1}{\Delta E^2}\left(\frac{\upsilon_{T_1}}{\upsilon_{^1MLCT}}\right)^3$ and plot of ε vs. $\frac{1}{\Delta E^2}\frac{\upsilon_{T_1}}{\upsilon_{^1MLCT}{}^3}$ of $(tpy)_2$Ir(LL') complexes.

$(C^N)_2$Ir(LL')	$\upsilon_{^1MLCT}$, 10^4 cm^{-1}	ΔE, 10^3cm^{-1}	υ_{T_1}, 10^4 cm^{-1}	$\left\|\frac{1}{\Delta E}\right\|^2\frac{\upsilon_{T_1}}{\upsilon_{^1MLCT}{}^3}$ 10^{-16}cm^{-4}	ε, 10^3cm^{-1}M^{-1}	$\left\|\frac{1}{\Delta E}\right\|^2\left(\frac{\upsilon_{T1}}{\upsilon_{^1MLCT}}\right)^3$ 10^{-7}cm^{-2}	k_r, 10^5s^{-1}
1 $(tpy)_2$Ir(acac)	2.46	2.1	2.05	3.09	1.0	1.30	2.7
2 $(tpy)_2$Ir(pz)$_2$H	2..55	2.99	2.09	1.41	0.42	0.618	2.0
3 $(tpy)_2$Ir(pz)$_2$BEt$_2$	2.56	3.12	2.10	1.28	0.35	0.562	2.0
4 $(tpy)_2$Ir(pz)$_2$BPh$_2$	2.56	3.05	2.11	1.35	0.31	0.599	1.4
5 $(tpy)_2$Ir(pz)$_2$Bpz$_2$	2.61	3.59	2.12	0.93	0.25	0.415	1.5
6 $(tpy)_2$Ir(tz)$_3$BH	2.62	3.66	2.12	0.89	0.16	0.399	1.3
7 $(tpy)_2$Ir(PPh$_2$CH$_2$)$_2$BPh$_2$	2.70	4.50	2.16	0.54	0.04	0.252	0.08
8 [$(tpy)_2$Ir(pzH)$_2$](CF$_3$SO$_3$)	2.62	3.65	2.12	0.88	0.17	0.397	1.1
9 [$(tpy)_2$Ir(pz)$_3$CH](CF$_3$SO$_3$)	2.65	4.00	2.13	0.71	0.16	0.324	1.1
10 [$(tpy)_2$Ir(PPh$_2$CH$_2$)$_2$SiPh$_2$](CF$_3$SO$_3$)	2.78	5.26	2.16	0.36	0.04	0.169	0.05
11 [$(tpy)_2$Ir(dppe)](CF$_3$SO$_3$)	2.79	5.41	2.19	0.34	0.03	0.165	0.03
12 [$(tpy)_2$Ir(CN-*t*-Bu)$_2$](CF$_3$SO$_3$)	2.87	6.21	2.21	0.24	0.03	0.118	0.08
13 (NBu$_4$)[$(ppy)_2$Ir(NCS)$_2$]	2.51	2.60	2.07	1.93	0.59	0.831	2.7
14 (NBu$_4$)[$(ppy)_2$Ir(CN)$_2$]	2.62	3.72	2.16	0.86	0.25	0.404	2.0

Table S 2. Redox properties of (dfppy)2Ir(LL') complexes. Redox measurements were carried out in DMF solution unless noted: (a) in CH2Cl2; (b) in CH3CN. The redox values are reported relative to Fc+/Fc. The electrochemical process is reversible unless noted:(c) Quasi-reversible; (d) Irreversible.

$(C^N)_2$Ir(LX)	$E_{½}^{Ox}$ (V)	$E_{½}^{Red}$ (V)	ΔE (V)
1 $(dfppy)_2$Ir(acac)	0.76	-2.48	3.24
2 $(dfppy)_2$Ir$(pz)_2$H	0.63[a,d], 0.93[a,d]	-2.44[c]	3.07, 3.37
5 $(dfppy)_2$Ir$(pz)_2$Bpz$_2$	1.08[a,c]	-2.39	3.47
7 $(dfppy)_2$Ir$(PPh_2CH_2)_2BPh_2$	0.95[a,d]	-2.38	3.33
12 [$(dfppy)_2$Ir(CN-*t*-Bu)$_2$](CF_3SO_3)	>1.40[b]	-2.19[d]	>3.59

Table S 3. Photophysical properties of (dfppy)2Ir(LX) complexes. Absorption measurements were carried out in CH2Cl2. Emission and lifetime measurements were carried out in 2-methyltetrahydrofuran (2-MeTHF).

$(C^N)_2$Ir(LX)	abs, λ_{max}[a]	Emission at RT		Φ_{PL}	k_r, 10^5 s^{-1}	k_{nr}, 10^5 s^{-1}	Emission at 77K		
	λ(nm) {ε, $10^3 cm^{-1}M^{-1}$}	λ_{max} (nm)	τ(μs)				λ_{max} (nm)	τ(μs)	$E_{m(0-0)}$ (eV)
$(dfppy)_2$Ir(acac)	254 (47.8), 387 (5.0), 461 (0.9)	482	1.2	0.62	5.2	3.2	469	2.8	2.64
$(dfppy)_2$Ir$(pz)_2$H	253 (42.3), 323 (11.8), 375 (5.3), 456 (0.4)	466	1.5	0.62	4.1	2.5	458	2.4	2.71
$(dfppy)_2$Ir$(pz)_2$Bpz$_2$	252 (39.8), 367 (4.9), 420 (0.52), 451(0.22)	456	3.7	0.73	2.0	0.73	450	4.0	2.76
$(dfppy)_2$Ir$(PPh_2CH_2)_2BPh_2$	251 (51.5), 312 (13.8), 413 (0.1), 442 (0.04)	448	8.4	0.19	0.22	1.0	443	19.7	2.79
[$(dfppy)_2$IrCN-*t*-Bu)$_2$](CF_3SO_3)	252 (44.9), 308 (20.1), 412 (0.1), 440 (0.06)	444(sh), 468	6.2	0.16	0.26	1.4	442	7.8,	2.79

Table S 4. Selected excited state properties and IR absorption of selected $(dfppy)_2$Ir(LX) complexes.

$(dfppy)_2$Ir(LX)	E_{em} (0-0) (x 10^6 cm^{-1})	$\hbar\omega_M$ (cm^{-1})	S_M	IR absorption (1400-1550 cm^{-1})
$(dfppy)_2$Ir(acac)	2.13	1441	0.29	1515, 1478, 1428, 1403
$(dfppy)_2$Ir$(pz)_2$H	2.18	1426	0.46	1478, 1428, 1404
$(dfppy)_2$Ir$(pz)_2$Bpz$_2$	2.22	1475	0.48	1507, 1478, 1430, 1404
$(dfppy)_2$Ir$(PPh_2CH_2)_2BPh_2$	2.26	1475	0.70	1479, 1434, 1406
[$(dfppy)_2$Ir(CN-*t*-Bu)$_2$](CF_3SO_3)	2.26	1437	0.87	1480, 1431, 1408
free *dfppy* ligand	2.36	1468	2.22	1505, 1466, 1440, 1416

Table S 5. Atomic coordinates (x104) and equivalent isotropic displacement parameters (Å2x103) for (tpy)2Ir(PPh2CH2)2BPh2·H2O. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ir(1)	9848(1)	2704(1)	1783(1)	31(1)
N(1)	8858(4)	3499(5)	1828(3)	36(2)
N(2)	10800(4)	2011(6)	1581(3)	38(2)
B(1)	10164(6)	1691(7)	3483(4)	33(2)
P(1)	9243(1)	1434(2)	2232(1)	32(1)
P(2)	10785(1)	3052(2)	2693(1)	33(1)
C(1)	8755(6)	3944(8)	2305(5)	49(2)
C(2)	8077(7)	4429(9)	2329(6)	68(3)
C(3)	7468(8)	4449(11)	1821(6)	83(4)
C(4)	7572(7)	3997(10)	1346(6)	70(3)
C(5)	8279(6)	3500(8)	1349(5)	49(3)
C(6)	8441(6)	2955(8)	877(4)	50(3)
C(7)	7873(8)	2886(12)	319(6)	83(5)
C(8)	8075(10)	2321(11)	-94(6)	87(5)
C(9)	8749(8)	1779(11)	7(6)	70(3)
C(10)	9264(7)	1849(8)	538(4)	54(3)
C(11)	9118(6)	2433(7)	984(4)	41(2)
C(12)	8923(11)	1106(13)	-460(5)	108(6)
C(13)	11062(6)	1127(7)	1752(4)	43(2)
C(14)	11671(6)	672(9)	1595(5)	57(3)
C(15)	12057(7)	1230(10)	1224(6)	74(4)
C(16)	11793(7)	2110(9)	1059(5)	60(3)
C(17)	11177(6)	2536(7)	1245(4)	43(2)
C(18)	10879(6)	3508(8)	1096(4)	47(2)
C(19)	11171(8)	4182(9)	752(5)	63(3)
C(20)	10893(9)	5085(10)	648(5)	75(4)
C(21)	10263(8)	5397(9)	864(5)	65(3)
C(22)	9945(7)	4762(8)	1207(4)	53(3)
C(23)	10240(6)	3787(7)	1333(4)	38(2)

C(24)	9913(10)	6409(10)	748(6)	91(5)
C(25)	8167(5)	1394(7)	1926(4)	38(2)
C(26)	7663(6)	1798(8)	2214(4)	49(2)
C(27)	6875(7)	1761(11)	1984(5)	73(4)
C(28)	6562(7)	1281(10)	1477(6)	69(4)
C(29)	7045(7)	887(10)	1190(5)	64(3)
C(30)	7861(6)	925(9)	1404(5)	54(3)
C(31)	9537(6)	-226(8)	1612(5)	49(2)
C(32)	9644(7)	-1209(8)	1552(5)	60(3)
C(33)	9663(7)	-1840(8)	1985(5)	58(3)
C(34)	9565(6)	-1503(8)	2495(5)	53(3)
C(35)	9472(5)	-528(7)	2584(4)	40(2)
C(36)	9454(5)	125(6)	2148(4)	37(2)
C(37)	11774(5)	3226(8)	2573(4)	41(2)
C(38)	12350(7)	2536(9)	2736(6)	60(3)
C(39)	13088(8)	2658(12)	2612(7)	82(5)
C(40)	13216(8)	3521(14)	2360(6)	90(5)
C(41)	12649(7)	4189(10)	2186(5)	70(4)
C(42)	11926(6)	4087(8)	2301(4)	52(3)
C(43)	10743(6)	4191(7)	3095(4)	41(2)
C(44)	10448(6)	5032(8)	2804(5)	53(3)
C(45)	10462(7)	5907(8)	3082(6)	62(3)
C(46)	10763(8)	5966(9)	3668(6)	71(4)
C(47)	11056(8)	5152(10)	3970(5)	67(3)
C(48)	11068(6)	4258(8)	3684(4)	47(2)
C(49)	9315(5)	1666(6)	2991(3)	33(2)
C(50)	10902(5)	2040(6)	3204(3)	34(2)
C(51)	10094(5)	2430(6)	4016(4)	34(2)
C(52)	10679(6)	2366(7)	4542(4)	43(2)
C(53)	10694(8)	2961(8)	4997(5)	57(3)
C(54)	10102(7)	3656(8)	4976(4)	56(3)
C(55)	9557(7)	3743(8)	4490(5)	58(3)
C(56)	9540(6)	3137(8)	3997(4)	45(2)
C(57)	10340(6)	613(7)	3777(4)	39(2)
C(58)	10992(7)	32(8)	3780(5)	63(3)
C(59)	11074(9)	-882(11)	4038(6)	92(5)

C(60)	10540(10)	-1256(10)	4307(6)	82(4)
C(61)	9907(8)	-704(8)	4314(5)	62(3)
C(62)	9815(6)	193(8)	4069(4)	49(2)
O(1)	7390(4)	2999(10)	3581(3)	115(4)

Table S 6. Bond lengths [Å] for (tpy)2Ir(PPh2CH2)2BPh2·H2O.

Ir(1)-C(23)	2.047(9)
Ir(1)-C(11)	2.057(9)
Ir(1)-N(1)	2.082(7)
Ir(1)-N(2)	2.083(7)
Ir(1)-P(1)	2.420(2)
Ir(1)-P(2)	2.431(2)
N(1)-C(5)	1.334(12)
N(1)-C(1)	1.339(12)
N(2)-C(13)	1.324(12)
N(2)-C(17)	1.363(12)
B(1)-C(57)	1.631(14)
B(1)-C(49)	1.664(13)
B(1)-C(51)	1.651(13)
B(1)-C(50)	1.667(13)
P(1)-C(49)	1.809(8)
P(1)-C(36)	1.852(9)
P(1)-C(25)	1.860(9)
P(2)-C(50)	1.823(9)
P(2)-C(43)	1.841(9)
P(2)-C(37)	1.848(9)
C(1)-C(2)	1.380(15)
C(2)-C(3)	1.410(18)
C(3)-C(4)	1.341(17)
C(4)-C(5)	1.419(16)
C(5)-C(6)	1.435(15)
C(6)-C(11)	1.360(15)
C(6)-C(7)	1.460(15)

C(7)-C(8)	1.36(2)
C(8)-C(9)	1.37(2)
C(9)-C(10)	1.369(16)
C(9)-C(12)	1.532(18)
C(10)-C(11)	1.403(14)
C(13)-C(14)	1.369(14)
C(14)-C(15)	1.457(17)
C(15)-C(16)	1.317(17)
C(16)-C(17)	1.398(14)
C(17)-C(18)	1.444(14)
C(18)-C(19)	1.412(14)
C(18)-C(23)	1.429(13)
C(19)-C(20)	1.332(17)
C(20)-C(21)	1.399(18)
C(21)-C(22)	1.401(15)
C(21)-C(24)	1.516(18)
C(22)-C(23)	1.438(14)
C(25)-C(26)	1.363(13)
C(25)-C(30)	1.387(13)
C(26)-C(27)	1.365(14)
C(27)-C(28)	1.368(18)
C(28)-C(29)	1.330(17)
C(29)-C(30)	1.404(15)
C(31)-C(32)	1.371(14)
C(31)-C(36)	1.405(12)
C(32)-C(33)	1.340(16)
C(33)-C(34)	1.350(15)
C(34)-C(35)	1.368(14)
C(35)-C(36)	1.366(12)
C(37)-C(38)	1.373(15)
C(37)-C(42)	1.403(15)
C(38)-C(39)	1.410(16)
C(39)-C(40)	1.37(2)
C(40)-C(41)	1.34(2)
C(41)-C(42)	1.373(15)
C(43)-C(44)	1.378(14)

C(43)-C(48)	1.385(13)
C(44)-C(45)	1.367(15)
C(45)-C(46)	1.369(17)
C(46)-C(47)	1.360(18)
C(47)-C(48)	1.403(16)
C(51)-C(56)	1.368(13)
C(51)-C(52)	1.419(13)
C(52)-C(53)	1.351(14)
C(53)-C(54)	1.404(16)
C(54)-C(55)	1.317(16)
C(55)-C(56)	1.434(14)
C(57)-C(58)	1.397(14)
C(57)-C(62)	1.408(13)
C(58)-C(59)	1.386(18)
C(59)-C(60)	1.36(2)
C(60)-C(61)	1.352(19)
C(61)-C(62)	1.353(15)

Table S 7. Bond angles [°] for (tpy)2Ir(PPh2CH2)2BPh2·H2O.

C(23)-Ir(1)-C(11)	82.0(4)
C(23)-Ir(1)-N(1)	92.4(3)
C(11)-Ir(1)-N(1)	78.3(4)
C(23)-Ir(1)-N(2)	79.4(3)
C(11)-Ir(1)-N(2)	93.6(4)
N(1)-Ir(1)-N(2)	169.2(3)
C(23)-Ir(1)-P(1)	173.4(3)
C(11)-Ir(1)-P(1)	92.0(3)
N(1)-Ir(1)-P(1)	83.6(2)
N(2)-Ir(1)-P(1)	103.9(2)
C(23)-Ir(1)-P(2)	94.7(3)
C(11)-Ir(1)-P(2)	175.9(3)
N(1)-Ir(1)-P(2)	104.4(2)
N(2)-Ir(1)-P(2)	83.4(2)

P(1)-Ir(1)-P(2)	91.43(8)
C(5)-N(1)-C(1)	119.5(9)
C(5)-N(1)-Ir(1)	115.7(7)
C(1)-N(1)-Ir(1)	124.7(7)
C(13)-N(2)-C(17)	118.6(8)
C(13)-N(2)-Ir(1)	125.9(6)
C(17)-N(2)-Ir(1)	115.5(6)
C(57)-B(1)-C(49)	109.2(7)
C(57)-B(1)-C(51)	105.5(7)
C(49)-B(1)-C(51)	109.3(7)
C(57)-B(1)-C(50)	110.3(7)
C(49)-B(1)-C(50)	112.3(7)
C(51)-B(1)-C(50)	110.0(7)
C(49)-P(1)-C(36)	108.1(4)
C(49)-P(1)-C(25)	102.4(4)
C(36)-P(1)-C(25)	98.2(4)
C(49)-P(1)-Ir(1)	112.5(3)
C(36)-P(1)-Ir(1)	121.8(3)
C(25)-P(1)-Ir(1)	111.4(3)
C(50)-P(2)-C(43)	108.1(4)
C(50)-P(2)-C(37)	104.0(4)
C(43)-P(2)-C(37)	97.4(4)
C(50)-P(2)-Ir(1)	112.8(3)
C(43)-P(2)-Ir(1)	121.7(3)
C(37)-P(2)-Ir(1)	110.5(3)
N(1)-C(1)-C(2)	123.4(11)
C(1)-C(2)-C(3)	117.4(11)
C(4)-C(3)-C(2)	118.9(11)
C(3)-C(4)-C(5)	121.1(12)
N(1)-C(5)-C(6)	114.5(9)
N(1)-C(5)-C(4)	119.6(10)
C(6)-C(5)-C(4)	125.9(10)
C(11)-C(6)-C(5)	117.3(9)
C(11)-C(6)-C(7)	120.9(11)
C(5)-C(6)-C(7)	121.6(11)
C(8)-C(7)-C(6)	116.8(13)

C(9)-C(8)-C(7)	123.1(12)
C(8)-C(9)-C(10)	118.5(13)
C(8)-C(9)-C(12)	121.0(13)
C(10)-C(9)-C(12)	120.5(14)
C(9)-C(10)-C(11)	122.4(12)
C(6)-C(11)-C(10)	118.1(10)
C(6)-C(11)-Ir(1)	113.7(7)
C(10)-C(11)-Ir(1)	128.0(8)
N(2)-C(13)-C(14)	124.9(10)
C(13)-C(14)-C(15)	116.0(11)
C(16)-C(15)-C(14)	118.6(10)
C(15)-C(16)-C(17)	122.2(11)
N(2)-C(17)-C(16)	119.6(10)
N(2)-C(17)-C(18)	115.5(8)
C(16)-C(17)-C(18)	124.9(10)
C(19)-C(18)-C(23)	119.2(10)
C(19)-C(18)-C(17)	125.7(10)
C(23)-C(18)-C(17)	115.1(8)
C(20)-C(19)-C(18)	123.1(11)
C(19)-C(20)-C(21)	120.3(11)
C(20)-C(21)-C(22)	119.4(12)
C(20)-C(21)-C(24)	122.5(11)
C(22)-C(21)-C(24)	118.1(12)
C(21)-C(22)-C(23)	121.5(11)
C(18)-C(23)-C(22)	116.5(9)
C(18)-C(23)-Ir(1)	114.3(7)
C(22)-C(23)-Ir(1)	129.2(7)
C(26)-C(25)-C(30)	118.6(9)
C(26)-C(25)-P(1)	121.1(8)
C(30)-C(25)-P(1)	120.2(8)
C(25)-C(26)-C(27)	120.4(11)
C(26)-C(27)-C(28)	121.7(12)
C(29)-C(28)-C(27)	118.5(11)
C(28)-C(29)-C(30)	121.7(11)
C(25)-C(30)-C(29)	119.0(11)
C(32)-C(31)-C(36)	118.6(10)

C(33)-C(32)-C(31)	122.1(10)
C(32)-C(33)-C(34)	119.2(11)
C(33)-C(34)-C(35)	121.3(10)
C(36)-C(35)-C(34)	120.2(9)
C(35)-C(36)-C(31)	118.6(9)
C(35)-C(36)-P(1)	121.4(7)
C(31)-C(36)-P(1)	119.8(7)
C(38)-C(37)-C(42)	119.8(10)
C(38)-C(37)-P(2)	122.0(8)
C(42)-C(37)-P(2)	118.2(8)
C(37)-C(38)-C(39)	121.1(12)
C(40)-C(39)-C(38)	116.9(12)
C(39)-C(40)-C(41)	122.1(12)
C(40)-C(41)-C(42)	121.8(13)
C(41)-C(42)-C(37)	117.9(12)
C(44)-C(43)-C(48)	117.9(9)
C(44)-C(43)-P(2)	120.3(8)
C(48)-C(43)-P(2)	121.6(8)
C(45)-C(44)-C(43)	121.9(11)
C(44)-C(45)-C(46)	120.2(12)
C(47)-C(46)-C(45)	119.6(11)
C(46)-C(47)-C(48)	120.5(12)
C(43)-C(48)-C(47)	119.8(11)
B(1)-C(49)-P(1)	122.8(6)
B(1)-C(50)-P(2)	120.8(6)
C(56)-C(51)-C(52)	115.6(9)
C(56)-C(51)-B(1)	126.5(8)
C(52)-C(51)-B(1)	117.8(8)
C(53)-C(52)-C(51)	122.7(10)
C(52)-C(53)-C(54)	120.7(11)
C(55)-C(54)-C(53)	118.1(10)
C(54)-C(55)-C(56)	122.2(10)
C(51)-C(56)-C(55)	120.6(10)
C(58)-C(57)-C(62)	113.8(9)
C(58)-C(57)-B(1)	126.0(9)
C(62)-C(57)-B(1)	120.2(8)

C(59)-C(58)-C(57)	120.9(12)
C(60)-C(59)-C(58)	122.6(13)
C(59)-C(60)-C(61)	117.5(12)
C(62)-C(61)-C(60)	121.1(11)
C(61)-C(62)-C(57)	124.0(11)

Symmetry transformations used to generate equivalent atoms:

Table S 8. Anisotropic displacement parameters (Å2x 103) for (tpy)2Ir(PPh2CH2)2BPh2·H2O.. The anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+ ...+2hka*b*U12]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	31(1)	33(1)	31(1)	-3(1)	9(1)	-1(1)
N(1)	29(4)	36(4)	42(4)	0(3)	10(3)	4(3)
N(2)	36(4)	44(5)	37(4)	-10(3)	15(3)	0(4)
B(1)	32(5)	37(6)	29(5)	2(4)	9(4)	5(4)
P(1)	30(1)	33(1)	32(1)	-4(1)	8(1)	-1(1)
P(2)	31(1)	36(1)	33(1)	-4(1)	10(1)	-2(1)
C(1)	50(6)	46(6)	50(6)	3(5)	13(5)	3(5)
C(2)	67(8)	59(7)	89(9)	-8(6)	40(7)	18(6)
C(3)	53(8)	105(11)	96(10)	11(9)	28(8)	38(8)
C(4)	55(7)	71(9)	76(8)	12(7)	1(6)	16(6)
C(5)	40(6)	49(6)	55(6)	13(5)	4(5)	1(5)
C(6)	49(6)	53(6)	42(5)	8(5)	2(5)	-7(5)
C(7)	61(8)	125(13)	47(7)	11(8)	-15(6)	-6(8)
C(8)	93(12)	119(12)	36(7)	-2(7)	-10(7)	-21(9)
C(9)	73(8)	87(9)	49(8)	-9(7)	12(7)	-26(7)
C(10)	66(7)	54(6)	43(5)	-7(5)	18(5)	-16(6)
C(11)	43(6)	49(6)	28(5)	-3(4)	4(4)	-12(4)
C(12)	137(16)	138(15)	50(7)	-44(8)	23(9)	-20(12)
C(13)	40(5)	47(6)	42(5)	-4(4)	14(4)	0(5)
C(14)	48(6)	61(7)	62(7)	-10(5)	15(5)	13(5)
C(15)	55(8)	89(10)	81(9)	-37(8)	26(7)	11(7)
C(16)	51(7)	70(9)	72(8)	-3(6)	36(6)	-4(6)

C(17)	43(6)	54(6)	36(5)	-7(4)	15(4)	-2(4)
C(18)	59(7)	51(6)	34(5)	-5(4)	19(5)	-10(5)
C(19)	77(8)	68(8)	58(7)	4(6)	41(6)	-10(7)
C(20)	109(12)	69(9)	59(8)	13(6)	42(8)	-22(8)
C(21)	87(9)	54(7)	51(7)	3(5)	7(6)	-15(6)
C(22)	64(8)	51(6)	40(5)	3(5)	5(5)	-5(6)
C(23)	39(5)	42(5)	33(5)	-1(4)	9(4)	0(4)
C(24)	137(14)	57(9)	78(9)	17(7)	22(9)	-15(9)
C(25)	32(5)	34(5)	45(5)	8(4)	6(4)	-7(4)
C(26)	38(5)	57(7)	54(6)	0(5)	14(5)	2(5)
C(27)	34(6)	120(11)	66(8)	19(7)	12(6)	12(7)
C(28)	37(6)	96(11)	70(9)	15(8)	9(6)	-6(6)
C(29)	58(8)	80(9)	44(6)	3(6)	-8(6)	-23(7)
C(30)	48(6)	62(7)	48(6)	-6(5)	3(5)	-5(5)
C(31)	53(6)	43(6)	54(6)	-10(5)	17(5)	-4(5)
C(32)	74(8)	51(7)	62(7)	-24(6)	27(6)	-2(6)
C(33)	76(8)	34(6)	68(7)	-6(5)	23(6)	2(6)
C(34)	53(6)	45(6)	62(7)	4(5)	18(5)	-4(5)
C(35)	36(5)	33(5)	49(6)	5(4)	6(4)	0(4)
C(36)	31(5)	35(5)	47(5)	-5(4)	13(4)	-4(4)
C(37)	30(5)	59(7)	34(5)	-12(4)	9(4)	-8(5)
C(38)	37(6)	70(8)	77(8)	5(6)	21(6)	2(5)
C(39)	39(7)	121(13)	96(11)	36(9)	33(7)	18(7)
C(40)	38(7)	160(16)	76(9)	-16(10)	21(7)	-18(9)
C(41)	54(7)	85(9)	79(8)	-8(7)	33(7)	-29(7)
C(42)	46(6)	59(7)	52(6)	-4(5)	15(5)	-15(5)
C(43)	42(5)	37(5)	46(5)	-9(4)	15(4)	-6(4)
C(44)	58(7)	49(6)	52(6)	0(5)	14(5)	3(5)
C(45)	62(8)	41(6)	86(9)	-14(6)	22(7)	4(5)
C(46)	67(8)	50(7)	105(11)	-30(7)	42(8)	-16(6)
C(47)	69(8)	79(9)	61(7)	-24(7)	28(6)	-28(7)
C(48)	48(6)	56(7)	38(5)	-9(4)	13(4)	-20(5)
C(49)	35(5)	35(5)	33(4)	-4(4)	14(4)	2(4)
C(50)	34(5)	38(5)	27(4)	-5(3)	3(4)	2(4)
C(51)	32(5)	36(5)	36(5)	2(4)	11(4)	-4(4)
C(52)	52(6)	45(5)	27(4)	-4(4)	-2(4)	-1(5)

C(53)	65(8)	52(7)	48(6)	-4(5)	3(6)	-6(6)
C(54)	71(8)	58(7)	38(5)	-16(5)	13(5)	-7(6)
C(55)	55(7)	52(7)	73(8)	-16(6)	23(6)	11(5)
C(56)	38(5)	49(6)	49(6)	-5(5)	10(4)	4(5)
C(57)	43(5)	43(6)	32(5)	-4(4)	9(4)	0(4)
C(58)	69(8)	47(7)	79(8)	8(6)	29(7)	14(6)
C(59)	99(11)	80(10)	91(10)	19(8)	10(9)	53(9)
C(60)	126(14)	48(8)	78(9)	18(7)	37(9)	0(8)
C(61)	79(9)	51(7)	64(7)	5(6)	31(6)	-10(6)
C(62)	58(6)	46(6)	46(6)	9(5)	16(5)	6(5)
O(1)	30(4)	287(12)	29(4)	-33(5)	10(3)	27(6)

Table S 9. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for [(tpy)2Ir(CN-t-Bu)2](CF3SO3)·CHCl3. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ir(1)	5231(1)	1788(1)	7549(1)	30(1)
Cl(1)	1204(4)	748(5)	8218(2)	251(3)
Cl(2)	393(4)	2633(4)	8336(3)	223(2)
Cl(3)	-872(3)	1016(4)	8041(2)	197(2)
S(1)	5915(1)	6118(1)	8711(1)	59(1)
F(1)	6422(4)	5901(5)	9835(2)	119(2)
F(2)	4895(4)	5879(4)	9560(2)	99(2)
F(3)	5686(5)	7280(4)	9594(2)	100(2)
O(1)	5925(4)	5051(3)	8658(2)	75(2)
O(2)	5047(5)	6609(4)	8378(3)	86(2)
O(3)	6794(4)	6643(4)	8652(3)	83(2)
N(1)	4142(3)	2856(3)	7574(2)	39(1)
N(2)	6087(3)	515(3)	7522(2)	31(1)
N(3)	6682(3)	2483(3)	8676(2)	41(1)
N(4)	5845(3)	2869(3)	6438(2)	41(1)
C(1)	4230(5)	3656(5)	7949(3)	57(2)
C(2)	3459(7)	4291(6)	7984(4)	83(3)

C(3)	2569(6)	4123(6)	7633(4)	84(3)
C(4)	2467(6)	3316(5)	7249(4)	70(2)
C(5)	3266(4)	2677(4)	7221(3)	44(1)
C(6)	3275(4)	1819(4)	6833(2)	38(1)
C(7)	2497(4)	1574(5)	6384(3)	49(2)
C(8)	2596(4)	787(5)	6004(3)	53(2)
C(9)	3472(5)	229(5)	6057(3)	50(2)
C(10)	4239(4)	465(4)	6516(2)	41(1)
C(11)	4164(4)	1246(4)	6904(2)	35(1)
C(12)	3587(6)	-614(6)	5632(3)	84(3)
C(13)	6801(4)	394(5)	7175(2)	44(1)
C(14)	7307(4)	-497(5)	7146(3)	53(2)
C(15)	7068(5)	-1302(5)	7478(3)	60(2)
C(16)	6361(5)	-1200(5)	7833(3)	54(2)
C(17)	5874(4)	-272(4)	7860(2)	38(1)
C(18)	5129(4)	-51(4)	8241(2)	39(1)
C(19)	4883(5)	-728(5)	8659(3)	56(2)
C(20)	4238(6)	-441(6)	9031(3)	65(2)
C(21)	3812(5)	512(5)	8994(3)	58(2)
C(22)	4036(4)	1170(5)	8557(2)	45(1)
C(23)	4697(4)	894(4)	8172(2)	35(1)
C(24)	3133(7)	839(7)	9425(4)	91(3)
C(25)	6178(4)	2295(4)	8238(2)	37(1)
C(26)	7128(5)	2554(5)	9296(3)	54(2)
C(27)	7917(6)	3361(6)	9364(3)	75(2)
C(28)	6295(7)	2815(7)	9633(3)	81(2)
C(29)	7546(7)	1518(6)	9463(4)	88(3)
C(30)	5697(4)	2519(4)	6871(2)	37(1)
C(31)	5864(6)	3203(5)	5834(3)	55(2)
C(32)	4937(7)	3824(8)	5656(4)	104(3)
C(33)	5875(8)	2258(6)	5465(3)	93(3)
C(34)	6800(6)	3813(6)	5826(3)	80(2)
C(35)	236(7)	1524(8)	7971(4)	96(3)
C(36)	5734(5)	6322(6)	9463(3)	61(2)

Table S 10. Bond lengths [Å] and angles [°] for [(tpy)2Ir(CN-t-Bu)2](CF3SO3)·CHCl3.

Ir(1)-C(25)	2.004(6)
Ir(1)-C(30)	2.018(6)
Ir(1)-C(11)	2.047(5)
Ir(1)-N(2)	2.059(4)
Ir(1)-N(1)	2.061(4)
Ir(1)-C(23)	2.072(5)
Cl(1)-C(35)	1.704(11)
Cl(2)-C(35)	1.691(11)
Cl(3)-C(35)	1.686(10)
S(1)-O(3)	1.412(6)
S(1)-O(1)	1.421(5)
S(1)-O(2)	1.463(6)
S(1)-C(36)	1.803(8)
F(1)-C(36)	1.299(8)
F(2)-C(36)	1.336(8)
F(3)-C(36)	1.310(8)
N(1)-C(1)	1.359(7)
N(1)-C(5)	1.362(7)
N(2)-C(13)	1.359(6)
N(2)-C(17)	1.359(6)
N(3)-C(25)	1.158(7)
N(3)-C(26)	1.464(7)
N(4)-C(30)	1.143(7)
N(4)-C(31)	1.461(7)
C(1)-C(2)	1.360(9)
C(2)-C(3)	1.372(12)
C(3)-C(4)	1.382(10)
C(4)-C(5)	1.392(8)
C(5)-C(6)	1.446(8)
C(6)-C(7)	1.405(8)
C(6)-C(11)	1.420(7)
C(7)-C(8)	1.380(9)
C(8)-C(9)	1.397(9)
C(9)-C(10)	1.405(7)

C(9)-C(12)	1.508(9)
C(10)-C(11)	1.382(7)
C(13)-C(14)	1.375(8)
C(14)-C(15)	1.380(9)
C(15)-C(16)	1.361(9)
C(16)-C(17)	1.405(8)
C(17)-C(18)	1.466(7)
C(18)-C(23)	1.385(7)
C(18)-C(19)	1.393(8)
C(19)-C(20)	1.370(9)
C(20)-C(21)	1.389(9)
C(21)-C(22)	1.397(8)
C(21)-C(24)	1.519(9)
C(22)-C(23)	1.404(7)
C(26)-C(27)	1.509(9)
C(26)-C(28)	1.510(10)
C(26)-C(29)	1.514(10)
C(31)-C(32)	1.514(11)
C(31)-C(34)	1.515(10)
C(31)-C(33)	1.516(9)

Table S 11. Bond angles [°] for [(tpy)2Ir(CN-t-Bu)2](CF3SO3)·CHCl3.

C(25)-Ir(1)-C(30)	102.0(2)
C(25)-Ir(1)-C(11)	174.1(2)
C(30)-Ir(1)-C(11)	83.2(2)
C(25)-Ir(1)-N(2)	89.84(19)
C(30)-Ir(1)-N(2)	97.11(18)
C(11)-Ir(1)-N(2)	92.07(18)
C(25)-Ir(1)-N(1)	97.5(2)
C(30)-Ir(1)-N(1)	90.22(19)
C(11)-Ir(1)-N(1)	79.82(19)
N(2)-Ir(1)-N(1)	168.38(17)

C(25)-Ir(1)-C(23)	84.2(2)
C(30)-Ir(1)-C(23)	172.8(2)
C(11)-Ir(1)-C(23)	90.7(2)
N(2)-Ir(1)-C(23)	79.20(18)
N(1)-Ir(1)-C(23)	92.51(19)
O(3)-S(1)-O(1)	117.7(3)
O(3)-S(1)-O(2)	111.4(4)
O(1)-S(1)-O(2)	114.6(4)
O(3)-S(1)-C(36)	105.0(4)
O(1)-S(1)-C(36)	103.6(3)
O(2)-S(1)-C(36)	102.5(3)
C(1)-N(1)-C(5)	120.0(5)
C(1)-N(1)-Ir(1)	124.0(4)
C(5)-N(1)-Ir(1)	115.8(4)
C(13)-N(2)-C(17)	118.6(5)
C(13)-N(2)-Ir(1)	125.1(4)
C(17)-N(2)-Ir(1)	116.2(3)
C(25)-N(3)-C(26)	164.8(6)
C(30)-N(4)-C(31)	168.8(6)
N(1)-C(1)-C(2)	121.7(7)
C(1)-C(2)-C(3)	119.3(7)
C(2)-C(3)-C(4)	119.8(7)
C(3)-C(4)-C(5)	119.8(7)
N(1)-C(5)-C(4)	119.4(6)
N(1)-C(5)-C(6)	114.7(5)
C(4)-C(5)-C(6)	125.9(6)
C(7)-C(6)-C(11)	119.9(5)
C(7)-C(6)-C(5)	124.1(5)
C(11)-C(6)-C(5)	115.9(5)
C(8)-C(7)-C(6)	120.4(6)
C(7)-C(8)-C(9)	120.6(5)
C(8)-C(9)-C(10)	118.7(6)
C(8)-C(9)-C(12)	120.5(6)
C(10)-C(9)-C(12)	120.8(6)
C(11)-C(10)-C(9)	122.2(5)
C(10)-C(11)-C(6)	118.2(5)

C(10)-C(11)-Ir(1)	128.1(4)
C(6)-C(11)-Ir(1)	113.5(4)
N(2)-C(13)-C(14)	122.7(5)
C(13)-C(14)-C(15)	118.4(6)
C(16)-C(15)-C(14)	120.2(6)
C(15)-C(16)-C(17)	119.8(6)
N(2)-C(17)-C(16)	120.3(5)
N(2)-C(17)-C(18)	114.5(5)
C(16)-C(17)-C(18)	125.2(5)
C(23)-C(18)-C(19)	121.3(5)
C(23)-C(18)-C(17)	115.7(5)
C(19)-C(18)-C(17)	122.9(5)
C(20)-C(19)-C(18)	119.7(6)
C(19)-C(20)-C(21)	121.1(6)
C(20)-C(21)-C(22)	118.6(6)
C(20)-C(21)-C(24)	120.7(6)
C(22)-C(21)-C(24)	120.7(7)
C(21)-C(22)-C(23)	121.4(6)
C(18)-C(23)-C(22)	117.8(5)
C(18)-C(23)-Ir(1)	114.1(4)
C(22)-C(23)-Ir(1)	127.8(4)
N(3)-C(25)-Ir(1)	171.0(5)
N(3)-C(26)-C(27)	109.5(5)
N(3)-C(26)-C(28)	106.1(5)
C(27)-C(26)-C(28)	111.4(6)
N(3)-C(26)-C(29)	106.0(5)
C(27)-C(26)-C(29)	112.4(7)
C(28)-C(26)-C(29)	111.2(7)
N(4)-C(30)-Ir(1)	170.0(5)
N(4)-C(31)-C(32)	106.8(6)
N(4)-C(31)-C(34)	108.0(6)
C(32)-C(31)-C(34)	112.3(7)
N(4)-C(31)-C(33)	106.5(5)
C(32)-C(31)-C(33)	112.1(7)
C(34)-C(31)-C(33)	110.9(7)
Cl(3)-C(35)-Cl(2)	110.5(6)

Cl(3)-C(35)-Cl(1)	112.9(7)
Cl(2)-C(35)-Cl(1)	109.0(6)
F(1)-C(36)-F(3)	108.7(6)
F(1)-C(36)-F(2)	104.7(6)
F(3)-C(36)-F(2)	108.3(6)
F(1)-C(36)-S(1)	112.2(6)
F(3)-C(36)-S(1)	112.7(5)
F(2)-C(36)-S(1)	109.8(5)

Symmetry transformations used to generate equivalent atoms:

Table S 12. Anisotropic displacement parameters (Å2x 103) for [(tpy)2Ir(CN-t-Bu)2](CF3SO3)·CHCl3. The anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+ ...+2hka*b*U12].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	28(1)	32(1)	32(1)	-4(1)	9(1)	-3(1)
Cl(1)	197(5)	327(7)	216(5)	-63(5)	-9(4)	147(5)
Cl(2)	199(5)	165(4)	274(6)	-73(4)	-60(4)	5(4)
Cl(3)	147(3)	301(5)	128(3)	75(3)	-26(2)	-123(4)
S(1)	66(1)	51(1)	67(1)	-5(1)	27(1)	-5(1)
F(1)	129(5)	140(5)	76(4)	22(3)	-27(3)	27(4)
F(2)	96(4)	116(4)	96(4)	8(3)	53(3)	-8(3)
F(3)	168(5)	73(3)	70(3)	-15(2)	47(3)	4(3)
O(1)	90(4)	49(3)	92(4)	-10(3)	31(3)	-3(3)
O(2)	94(4)	96(4)	68(4)	8(3)	9(3)	32(3)
O(3)	82(4)	77(4)	99(5)	-10(3)	46(3)	-15(3)
N(1)	45(3)	35(2)	39(3)	-2(2)	14(2)	6(2)
N(2)	26(2)	38(2)	28(2)	-3(2)	3(2)	0(2)
N(3)	45(3)	44(3)	35(3)	-7(2)	5(2)	-5(2)
N(4)	42(3)	42(2)	39(3)	1(2)	11(2)	-8(2)
C(1)	67(4)	40(3)	66(4)	-12(3)	19(3)	3(3)
C(2)	95(7)	64(5)	95(6)	-16(4)	33(5)	29(5)
C(3)	78(6)	65(5)	115(7)	-4(5)	34(5)	40(5)
C(4)	53(4)	77(5)	83(6)	-2(4)	17(4)	25(4)

C(5)	36(3)	47(3)	51(4)	3(3)	16(2)	6(3)
C(6)	29(2)	44(3)	43(3)	6(2)	11(2)	-1(2)
C(7)	31(3)	65(4)	51(4)	13(3)	2(2)	0(3)
C(8)	40(3)	66(4)	48(4)	8(3)	-9(3)	-14(3)
C(9)	51(3)	56(4)	39(3)	-4(3)	-7(3)	-8(3)
C(10)	40(3)	41(3)	41(3)	-4(2)	2(2)	-3(2)
C(11)	33(3)	38(3)	36(3)	3(2)	11(2)	0(2)
C(12)	93(6)	82(5)	65(5)	-34(4)	-25(4)	-3(5)
C(13)	37(3)	51(3)	45(3)	-2(3)	13(2)	-3(3)
C(14)	35(3)	63(4)	64(4)	-12(3)	18(3)	8(3)
C(15)	55(4)	60(4)	66(5)	2(4)	11(3)	19(3)
C(16)	56(4)	50(4)	57(4)	7(3)	11(3)	12(3)
C(17)	39(3)	39(3)	34(3)	3(2)	0(2)	5(2)
C(18)	41(3)	43(3)	33(3)	3(2)	6(2)	-3(2)
C(19)	79(5)	46(3)	46(4)	8(3)	19(3)	0(3)
C(20)	81(5)	67(4)	54(4)	11(3)	31(4)	-10(4)
C(21)	64(4)	66(4)	51(4)	0(3)	33(3)	-11(3)
C(22)	49(3)	48(3)	42(3)	-9(3)	19(3)	-7(3)
C(23)	30(2)	40(3)	35(3)	-4(2)	10(2)	-7(2)
C(24)	103(7)	111(7)	74(6)	-10(5)	63(5)	-10(5)
C(25)	42(3)	32(3)	39(3)	-6(2)	14(2)	-8(2)
C(26)	63(4)	58(4)	37(3)	-8(3)	-4(3)	2(3)
C(27)	68(5)	89(6)	61(5)	-18(4)	-9(4)	-25(4)
C(28)	99(6)	105(6)	42(4)	-20(4)	16(4)	-6(5)
C(29)	107(7)	77(5)	70(6)	-4(4)	-20(5)	14(5)
C(30)	29(3)	35(3)	47(3)	-7(2)	11(2)	-3(2)
C(31)	75(5)	58(4)	33(3)	9(3)	14(3)	0(3)
C(32)	105(7)	128(8)	77(6)	38(6)	5(5)	38(7)
C(33)	151(9)	86(6)	43(4)	-17(4)	18(5)	-12(6)
C(34)	100(6)	87(6)	63(5)	15(4)	41(4)	-22(5)
C(35)	91(7)	131(8)	67(6)	-7(5)	12(5)	-9(6)
C(36)	62(4)	63(4)	56(4)	8(3)	5(3)	0(4)

Table S 13. Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 103) for [(tpy)2Ir(CN-t-Bu)2](CF3SO3)·CHCl3.

	x	y	z	U(eq)
H(1)	4845	3774	8192	68
H(2)	3536	4846	8249	99
H(3)	2025	4561	7655	101
H(4)	1852	3198	7005	85
H(7)	1900	1952	6341	59
H(8)	2063	623	5704	64
H(10)	4829	74	6560	49
H(12A)	3216	-1206	5733	125
H(12B)	4290	-789	5657	125
H(12C)	3330	-397	5231	125
H(13)	6957	947	6943	53
H(14)	7809	-557	6903	63
H(15)	7397	-1930	7458	72
H(16)	6198	-1755	8062	65
H(19)	5161	-1386	8686	67
H(20)	4080	-902	9320	79
H(22)	3735	1817	8520	54
H(24A)	2690	282	9489	136
H(24B)	2739	1421	9264	136
H(24C)	3531	1026	9800	136
H(27A)	8443	3174	9137	112
H(27B)	8196	3429	9780	112
H(27C)	7624	4004	9218	112
H(28A)	6024	3477	9507	122
H(28B)	6548	2833	10055	122
H(28C)	5773	2305	9556	122
H(29A)	7005	1026	9430	132
H(29B)	7889	1532	9869	132
H(29C)	8015	1327	9198	132
H(32A)	4354	3424	5712	156

H(32B)	4891	4017	5241	156
H(32C)	4965	4432	5900	156
H(33A)	6425	1824	5635	139
H(33B)	5958	2443	5062	139
H(33C)	5248	1895	5458	139
H(34A)	6834	4352	6121	120
H(34B)	6793	4111	5435	120
H(34C)	7379	3373	5918	120
H(35)	247	1660	7544	116