Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supplementary Information

for

Highly Efficient Blue Phosphorescent and Electroluminescent Ir(III) Compounds

Youngjin Kang,[‡]* Yi-Lu Chang[+], Jia-Sheng, Lu, Soo-Byung Ko, Yingli, Rao, Maria Varlan, Zheng-Hong Lu[+], and Suning Wang*

[‡]*Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada*

[+]*Department of Materials Science and Engineering, University of Toronto, Ontario, M5S 3E4 Canada*

Division of Science education, Kangwon National University, Chuncheon 200-701, Republic of Korea

Corresponding Authors: Youngjin kang(kangy@kangwon.ac.kr)

and Suning Wang(suning.wang@chem.queensu.ca)

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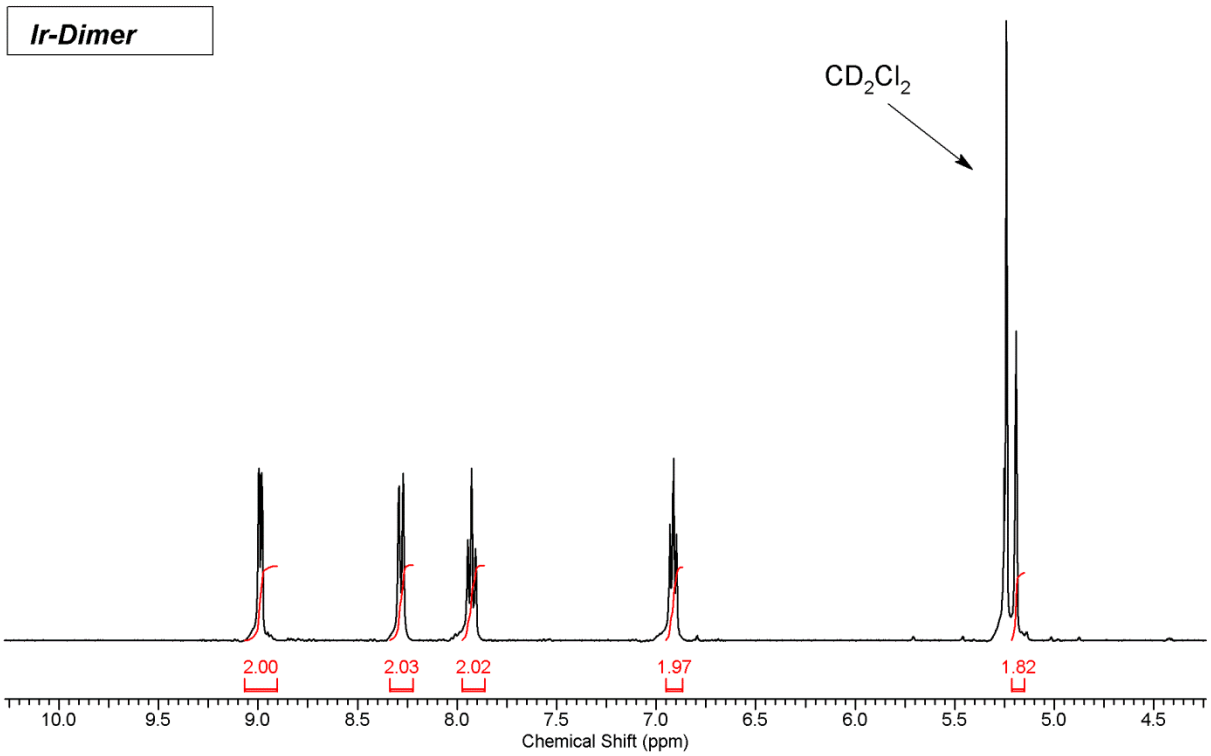


Figure S1. ^{1}H NMR of **[(dfpypy)$_2$Ir(μ-Cl)]$_2$** in CD_2Cl_2**.**

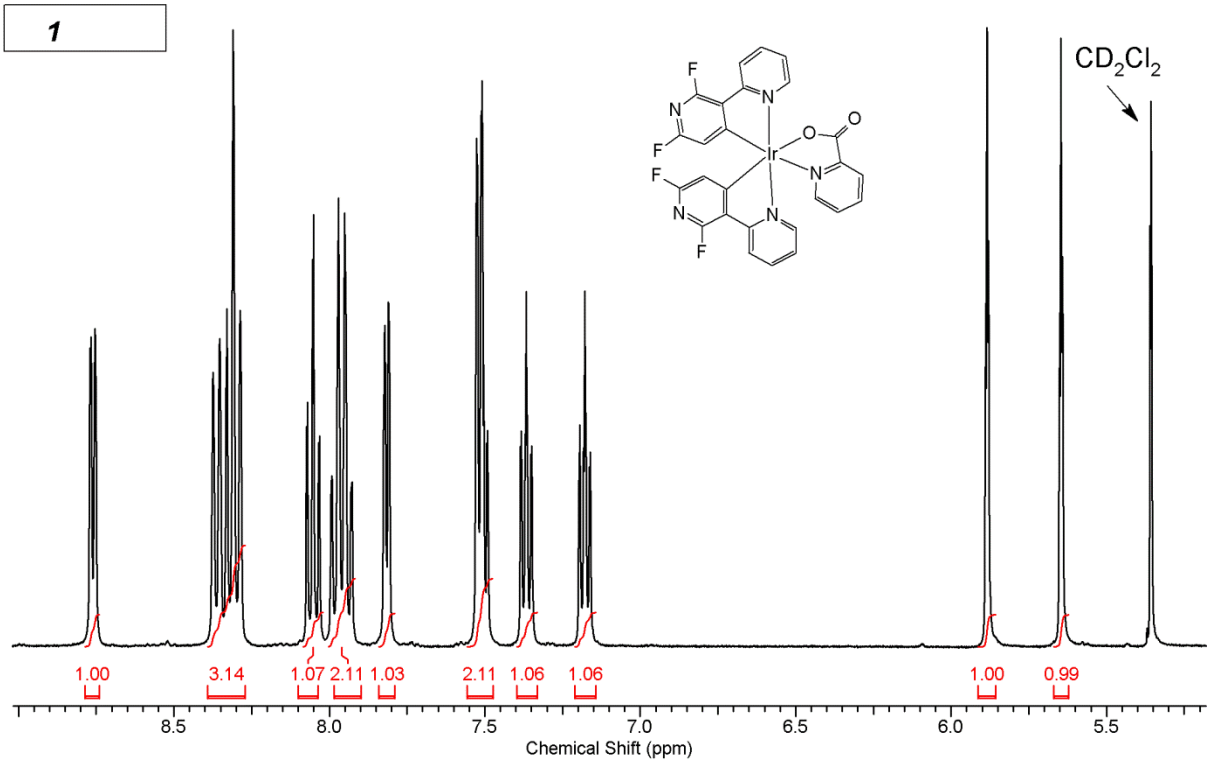


Figure S2. ^{1}H NMR of **1** in CD_2Cl_2**.**

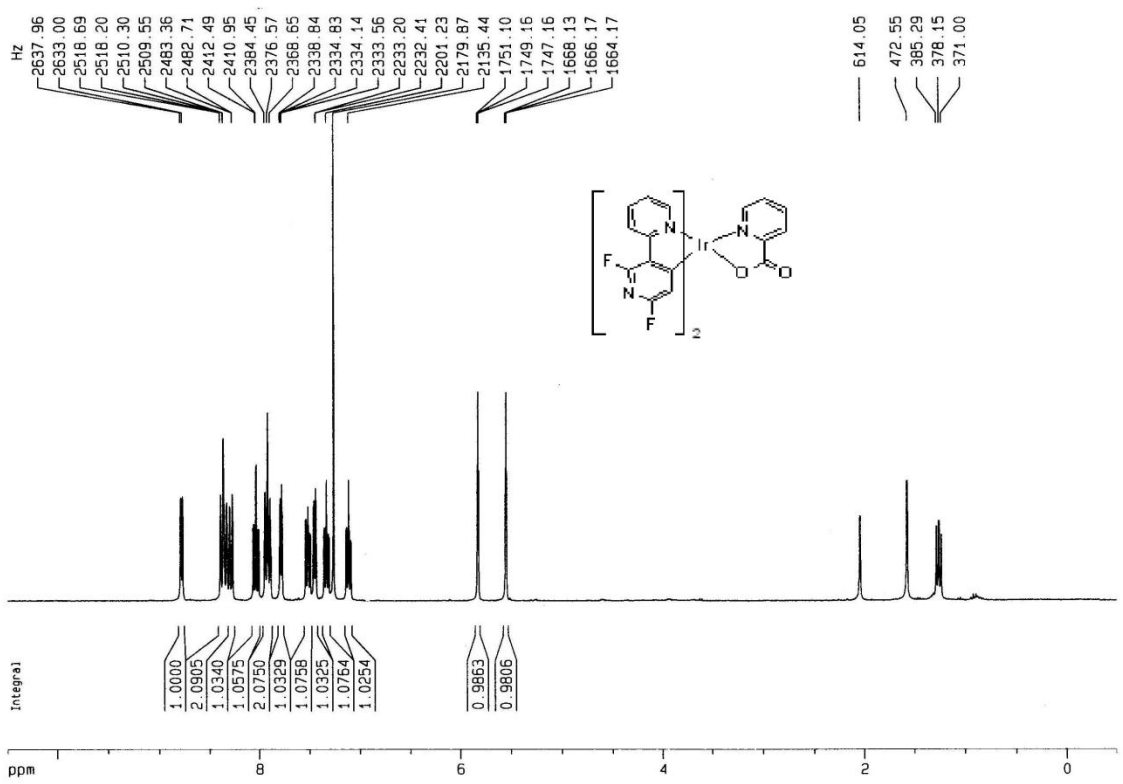


Figure S3. ^{1}H NMR of **1** in $CDCl_3$; compound **1** was obtained by using different reaction conditions (in the presence of NEt_3 at 120 ^{o}C ; refluxing toluene).

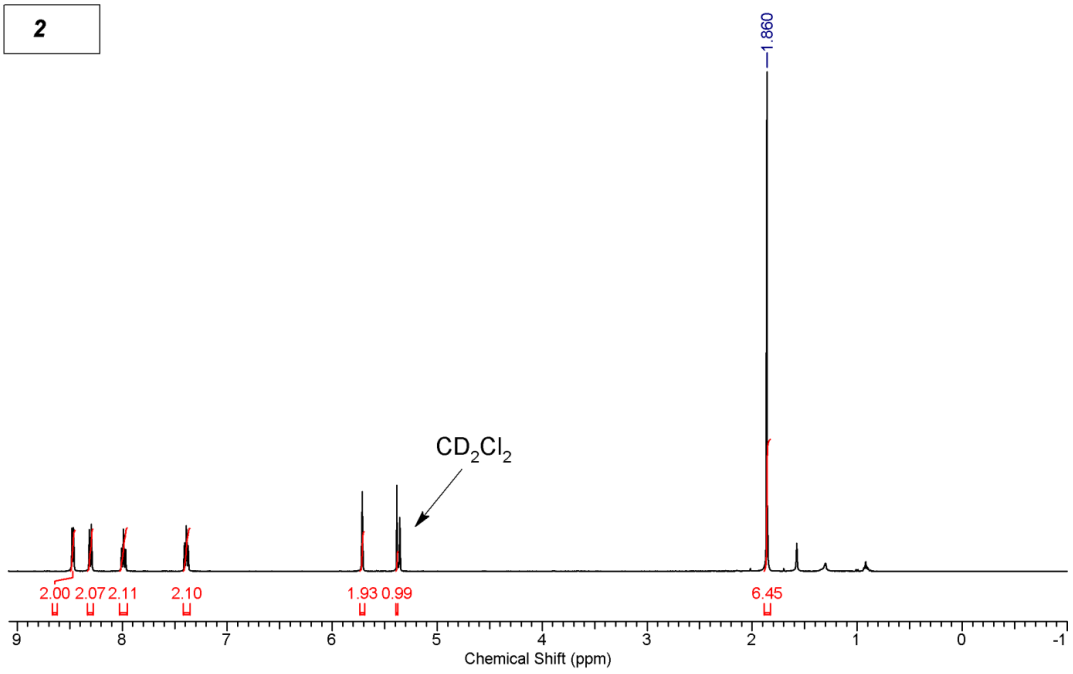


Figure S4. ^{1}H NMR of **2** in CD_2Cl_2.

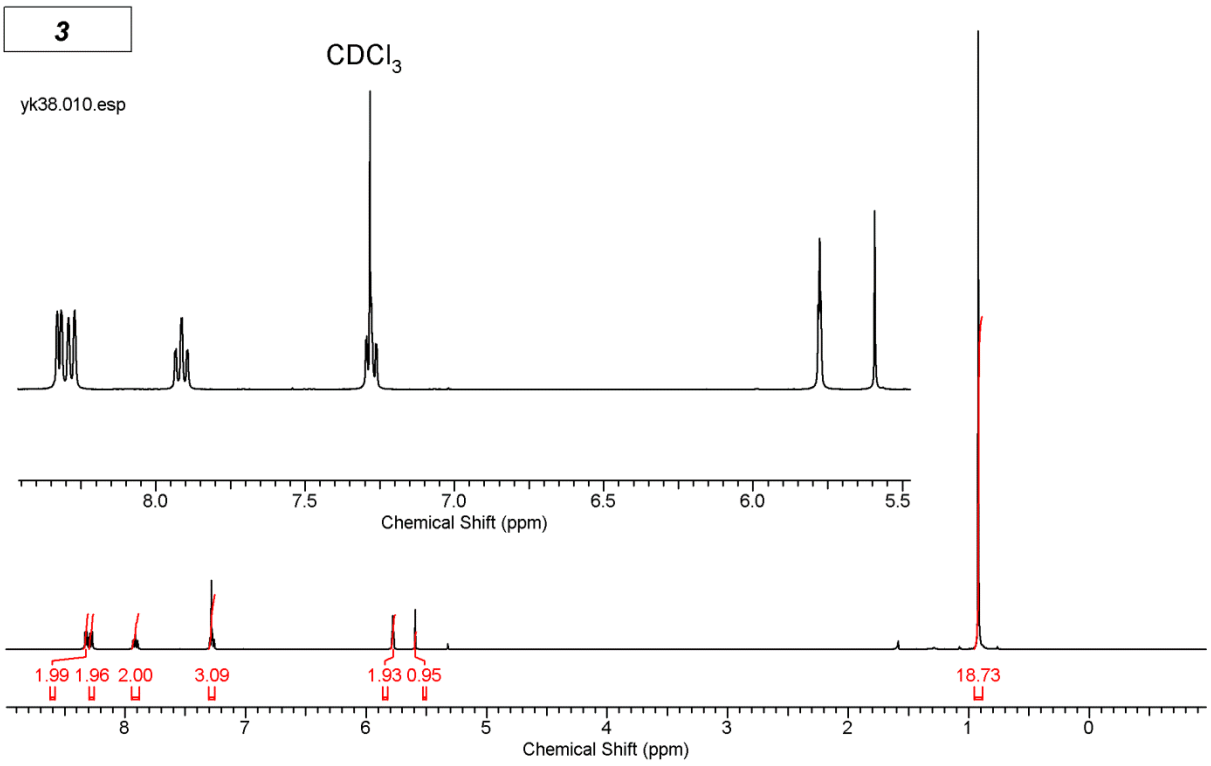


Figure S5. ^{1}H NMR of **3** in $CDCl_3$.

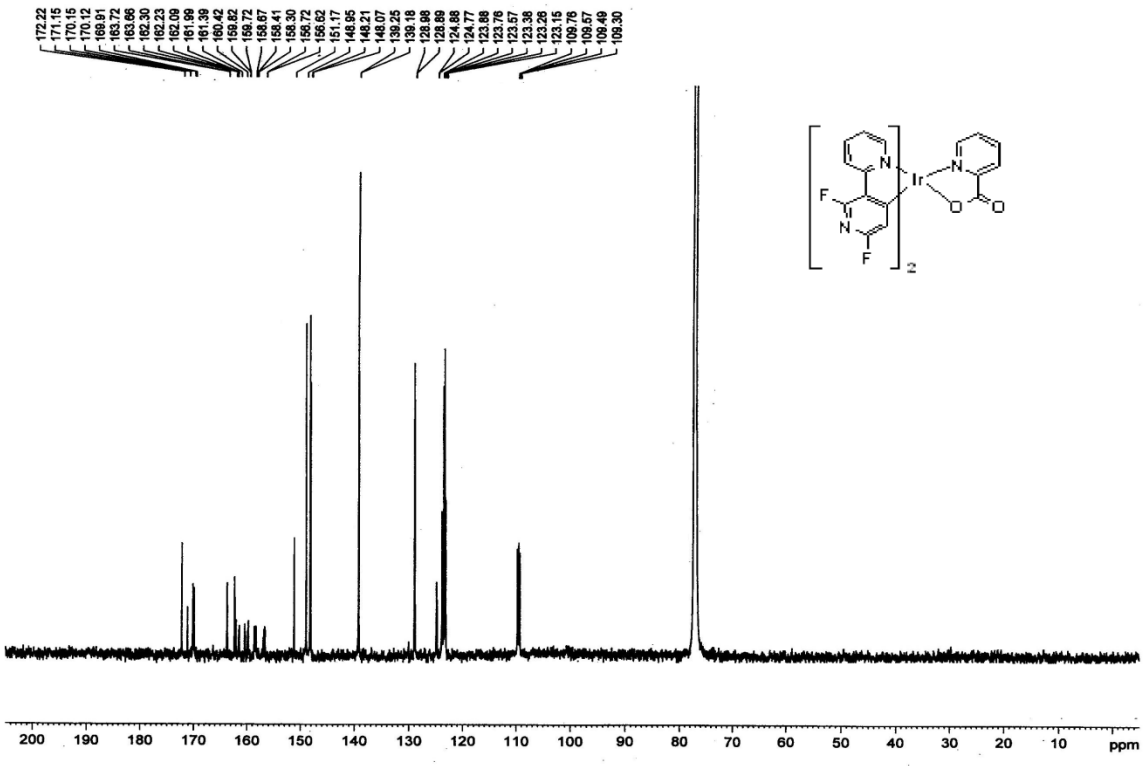


Figure S6. ^{13}C NMR of **1** in $CDCl_3$.

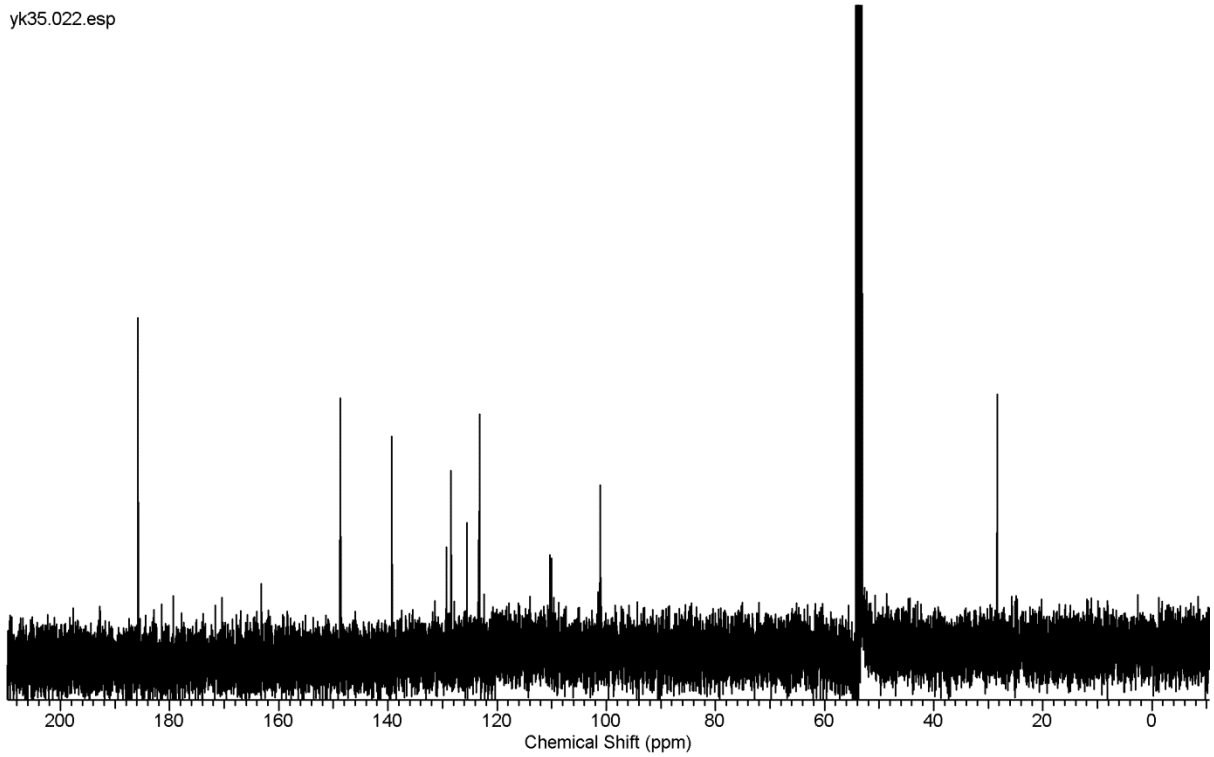


Figure S7. ^{13}C NMR of **2** in CD_2Cl_2.

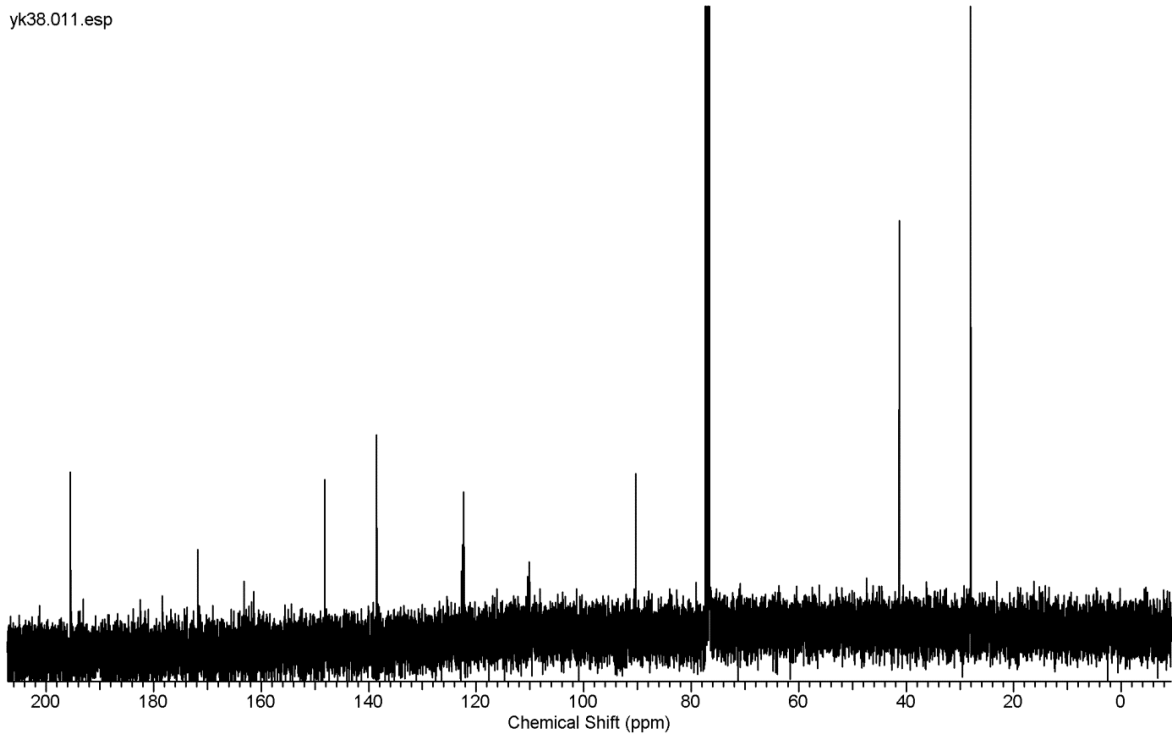


Figure S8. ^{13}C NMR of **3** in CD_2Cl_2.

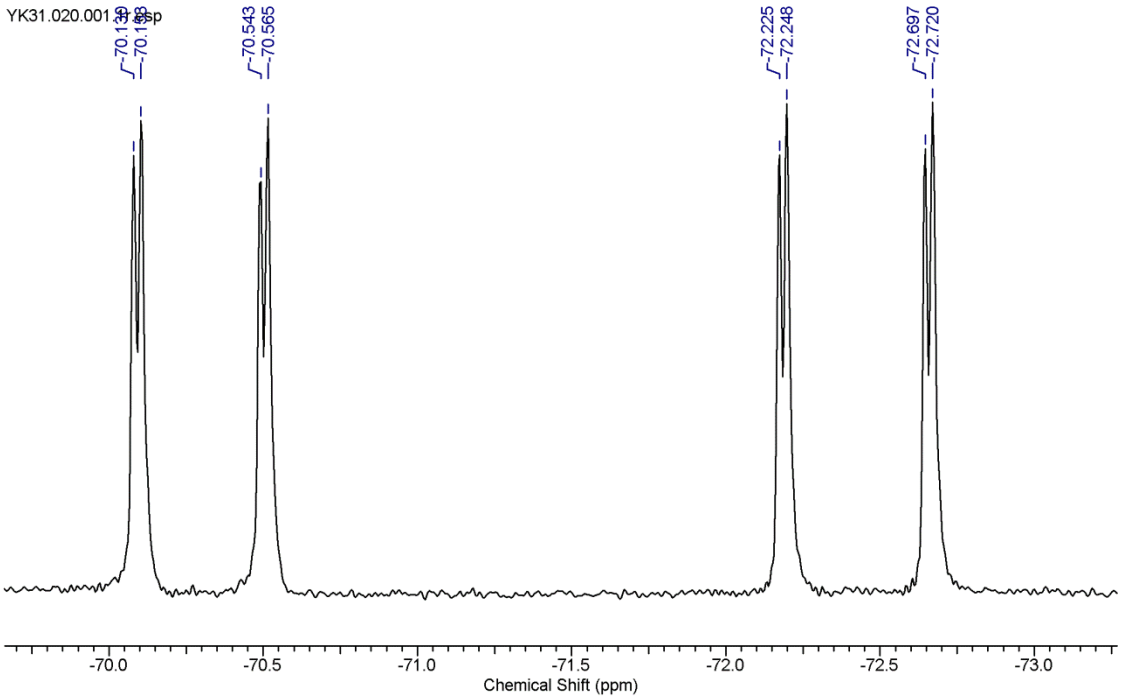


Figure S9. ^{19}F NMR of **1** in $CDCl_3$

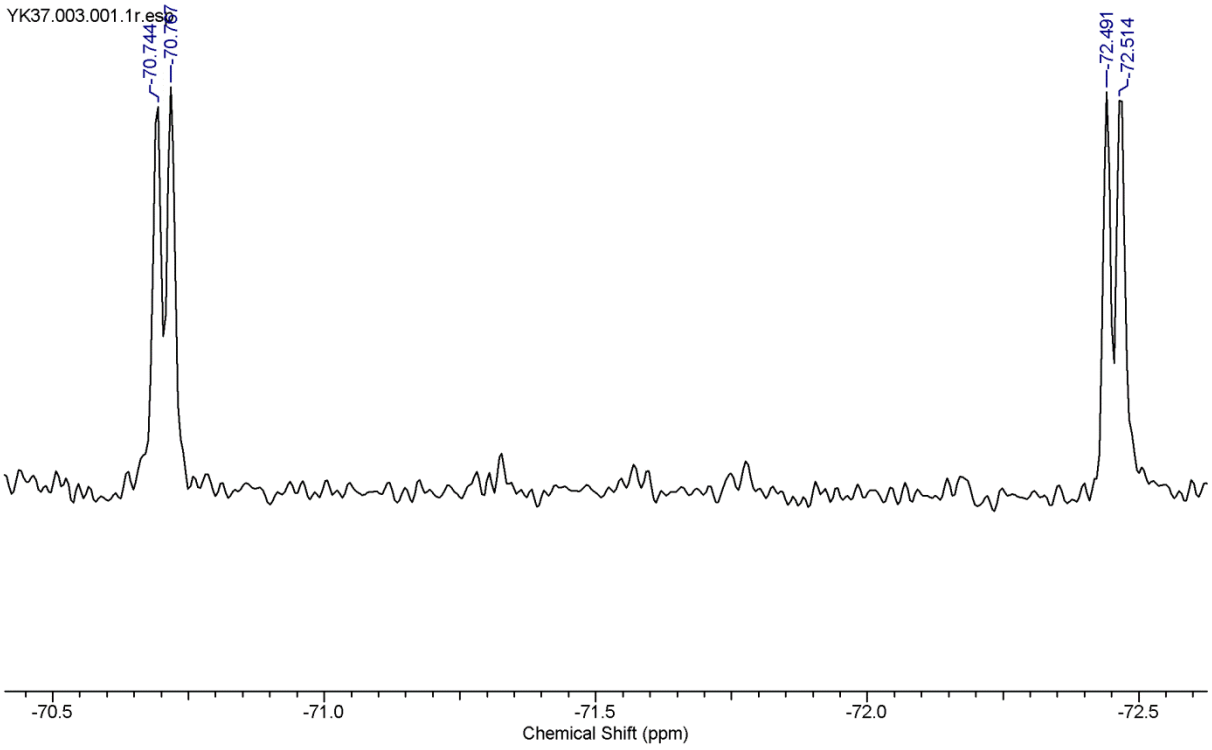


Figure S10. ^{19}F NMR of **2** in $CDCl_3$

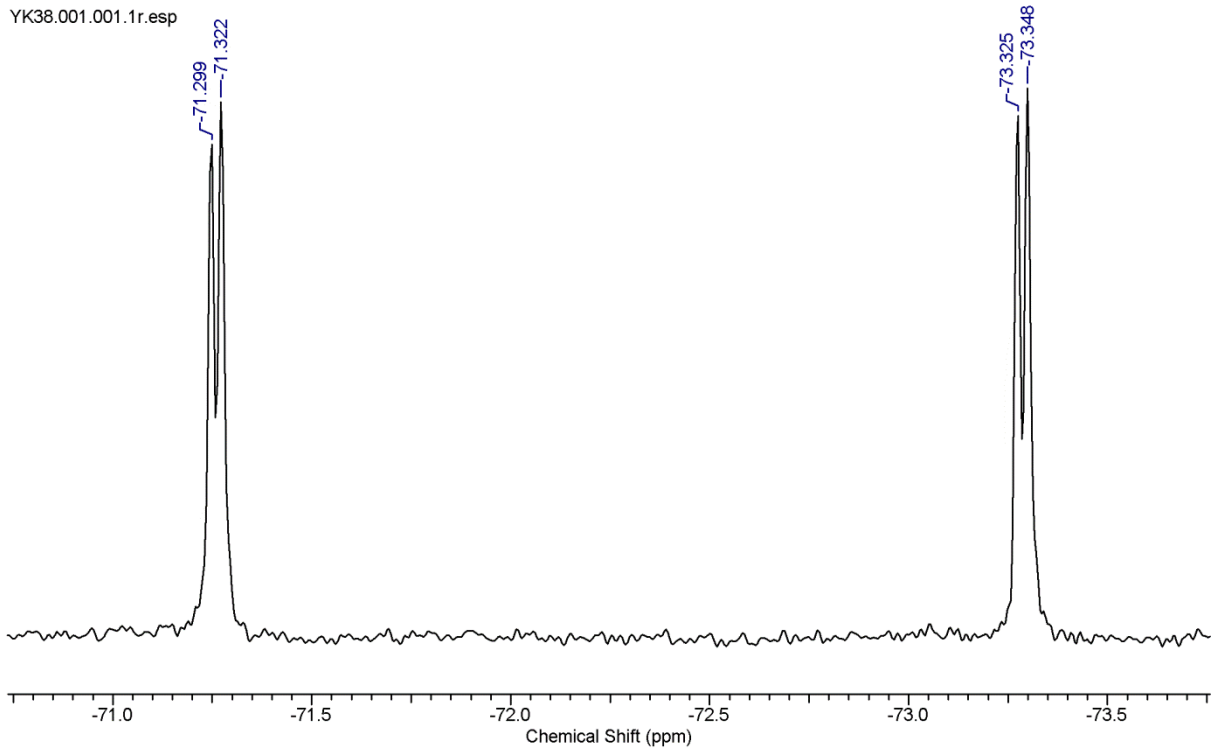


Figure S11. ^{19}F NMR of **3** in $CDCl_3$

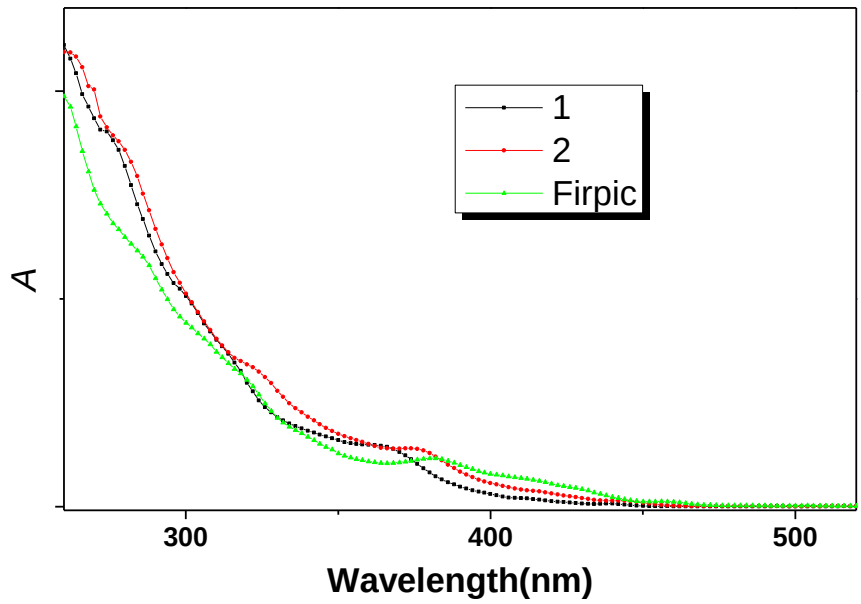


Figure S12. Absorption spectra of **1**, **2** and **Firpic**(reference).

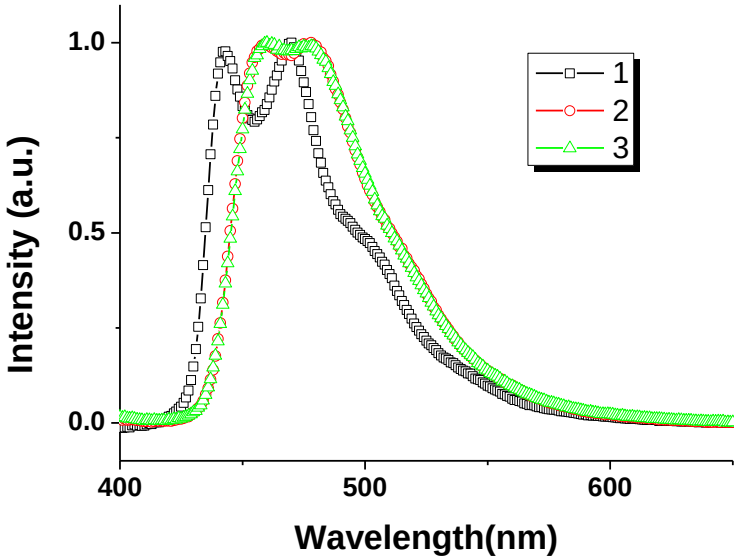


Figure S13. Emission spectra of **1**, **2** and **3** in the solid state at 298K (10 %wt- PMMA film).

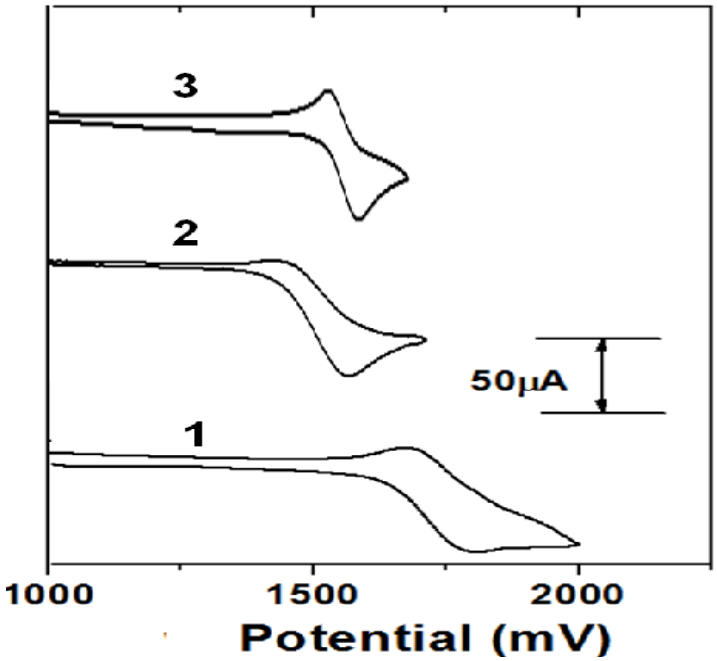


Figure S14. Comparison of oxidation potentials (*vs* Ag/AgCl in CH_3CN) of **1**, **2** and **3** (oxidation potential $FeCp_2/FeCp_2^+$ =0.45 V)

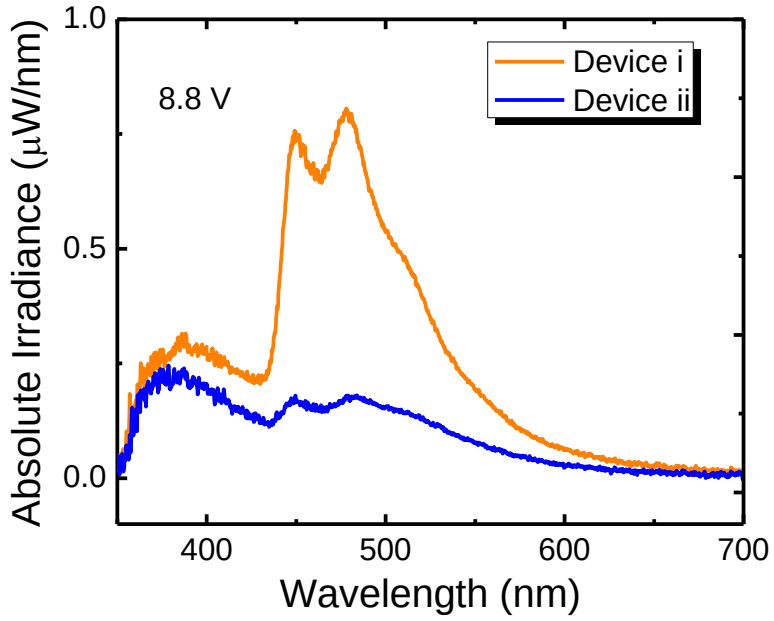


Figure S15. EL spectra of **1** using different hole-transporting and host materials. Device **i**: ITO(120 nm)/MoO_3(1 nm)/CBP(35 nm)/CDBP-doped with 20 wt% of **1**(15 nm)/TPBi(65 nm) /LiF (1 nm)/Al (100 nm); Device **ii**: ITO(120 nm)/MoO_3(1 nm)/CBP(35 nm)/CBP-doped with 20 wt% of **1**(15 nm)/TPBi(65 nm) /LiF (1 nm)/Al (100 nm).

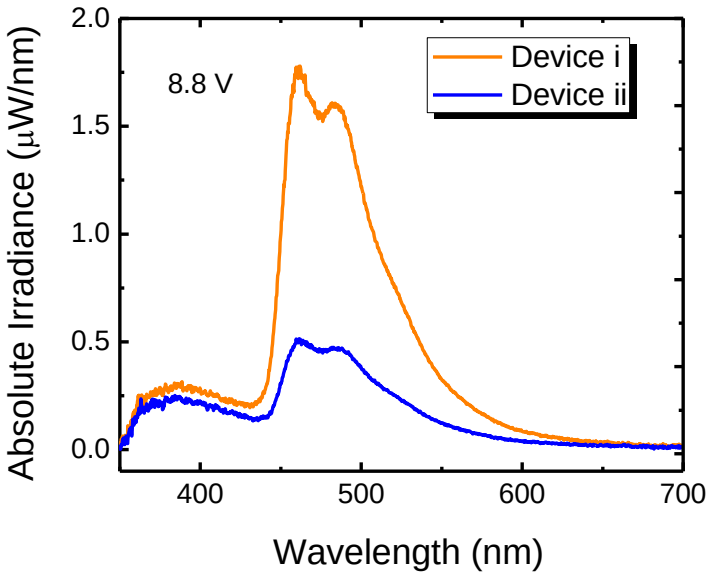


Figure S16. EL spectra of **2** using different hole-transporting and host materials. Device **i**: ITO(120 nm)/MoO_3(1 nm)/CBP(35 nm)/CDBP-doped with 20 wt% of **2**(15 nm)/TPBi(65 nm) /LiF (1 nm)/Al (100 nm); Device **ii**: ITO(120 nm)/MoO_3(1 nm)/CBP(35 nm)/CBP-doped with 20 wt% of **2**(15 nm)/TPBi(65 nm) /LiF (1 nm)/Al (100 nm).

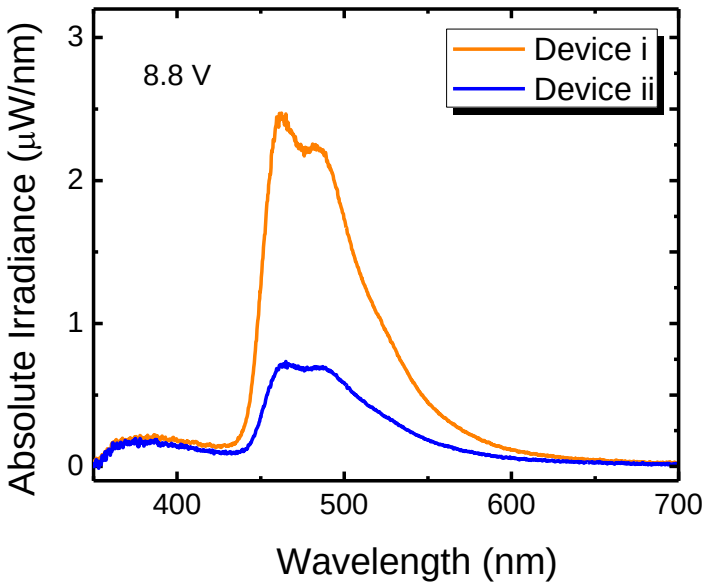


Figure S17. EL spectra of **3** using different hole-transporting and host materials. Device **i**: ITO(120 nm)/MoO_3(1 nm)/CBP(35 nm)/ CDBP-doped with 20 wt% of **3**(15 nm)/TPBi(65 nm) /LiF (1 nm)/Al (100 nm); Device **ii**: ITO(120 nm)/MoO_3(1 nm)/CBP(35 nm)/ CBP-doped with 20 wt% of **3**(15 nm)/TPBi(65 nm) /LiF (1 nm)/Al (100 nm).

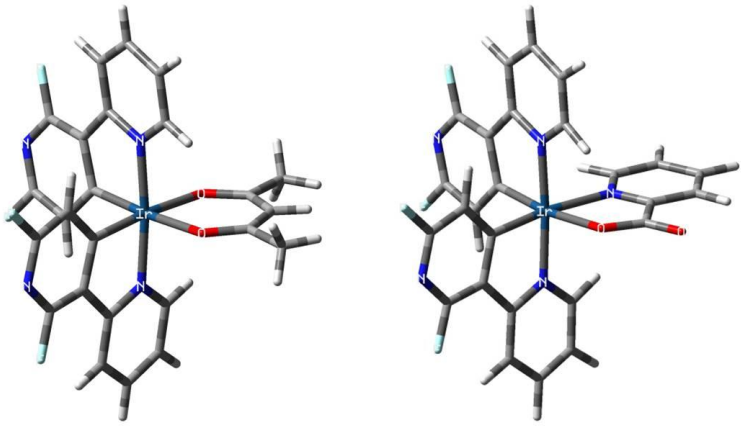
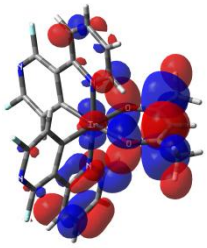
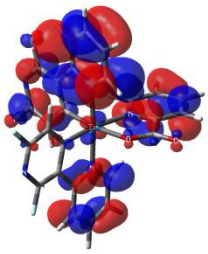
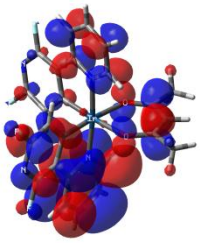
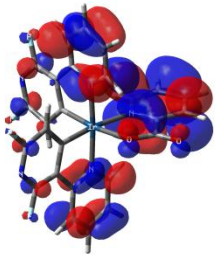
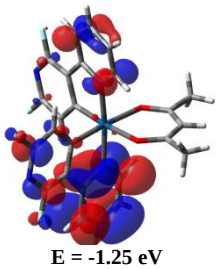
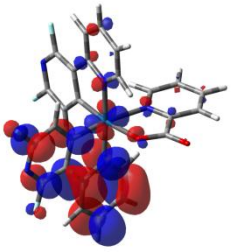
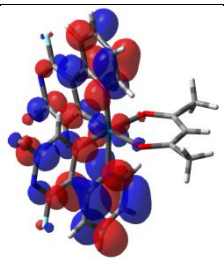
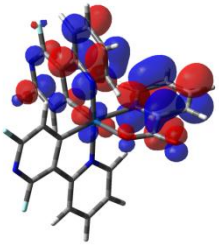
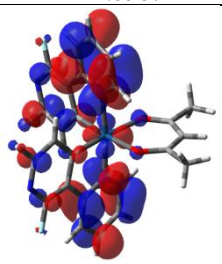
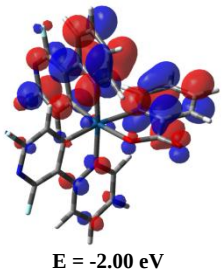


Figure S18. Optimized molecular structure of **1** and **2** at the B3LYP/6-31G(d) level.

	2	1
LUMO+4	 **E = -1.06 eV**	 **E = -1.28 eV**
LUMO+3	 **E = -1.12 eV**	 **E = -1.52 eV**
LUMO+2	 **E = -1.25 eV**	 **E = -1.87 eV**
LUMO+1	 **E = -1.66 eV**	 **E = -1.95 eV**
LUMO	 **E = -1.67 eV**	 **E = -2.00 eV**

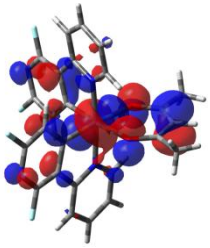
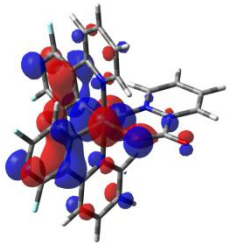
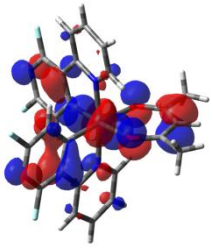
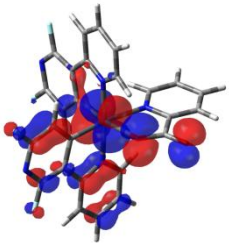
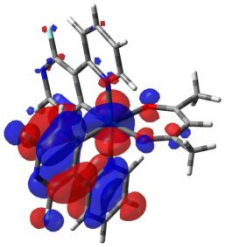
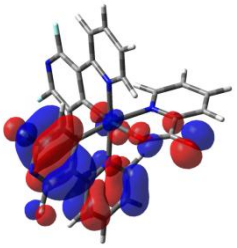
HOMO	 **E = -5.84 eV, Ir d orbital 38%**	 **E = -6.10 eV, Ir d orbital 44%**
HOMO-1	 **E = -5.87 eV, Ir d orbital 42%**	 **E = -6.27 eV, Ir d orbital 46%**
HOMO-2	 **E = -6.37 eV, Ir d orbital 27%**	 **E = -6.54 eV**

Figure S19. Isodensity surface plot of **1** and **2.**

Table S1. Calculated Energy Levels of the Low-Lying Singlet and Triplet States.

Complex	Spin state	Transition configurations	Excitation energy (nm, eV)	Oscillator strength
2	S_1	HOMO-1 → LUMO+1 (26%) HOMO→ LUMO (37%) HOMO→ LUMO+1 (35%)	370.9 (3.34)	0.0042
	S_2	HOMO-1 → LUMO (38%) HOMO-1 → LUMO+1 (32%) HOMO → LUMO (27%)	366.8 (3.38)	0.0030
	S_3	HOMO-1 → LUMO (45%) HOMO-1 → LUMO+1 (3%) HOMO → LUMO (31%) HOMO → LUMO+1 (16%)	361.1 (3.43)	0.0464
	T_1	HOMO-5 → LUMO+4 (5%) HOMO-1 → LUMO (4%) HOMO-1 → LUMO+1 (3%) HOMO-1 → LUMO+3 (5%) HOMO-1 → LUMO+4 (22%) HOMO → LUMO (8%) HOMO → LUMO+3 (7%) HOMO → LUMO+4 (35%)	412.9 (3.00)	
1	S_1	HOMO → LUMO (65%) HOMO → LUMO+1 (28%) HOMO → LUMO+2 (3%)	373.3 (3.32)	0.0227
	S_2	HOMO → LUMO (28%) HOMO → LUMO+1 (64%)	368.2 (3.37)	0.0008
	S_3	HOMO-1 → LUMO+2 (5%) HOMO → LUMO+2 (88%)	360.0 (3.44)	0.0016
	T_1	HOMO-4 → LUMO (6%) HOMO-4 → LUMO+1 (2%) HOMO-2 → LUMO+2 (15%) HOMO-2 → LUMO+4 (4%) HOMO-1 → LUMO+2 (21%) HOMO → LUMO (17%) HOMO → LUMO+1 (3%) HOMO → LUMO+2 (16%)	420.8 (2.95)	

Table S2. Crystal data and structure refinement for Compound **1**.

Identification code	Compound 1	
Empirical formula	C27 H16 Cl2 F4 Ir N5 O2	
Formula weight	781.55	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 34.9751(13) Å	α= 90°.
	b = 9.6151(3) Å	β= 109.068(2)°.
	c = 15.9638(6) Å	γ = 90°.
Volume	5073.9(3) $Å^3$	
Z	8	
Density (calculated)	2.046 Mg/m^3	
Absorption coefficient	5.541 mm^{-1}	
F(000)	3008	
Crystal size	0.05 x 0.02 x 0.02 mm^3	
Theta range for data collection	2.21 to 26.00°.	
Index ranges	-42<=h<=40, 0<=k<=11, 0<=l<=19	
Reflections collected	4972	
Independent reflections	4972 [R(int) = 0.0000]	
Completeness to theta = 26.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8972 and 0.7691	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4972 / 0 / 370	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0935	
R indices (all data)	R1 = 0.0575, wR2 = 0.0993	
Largest diff. peak and hole	2.752 and -1.737 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	1385(1)	8124(1)	2403(1)	18(1)
N(1)	2677(2)	6517(8)	4289(5)	32(2)
N(2)	1747(2)	9863(7)	2582(4)	21(1)
N(3)	1066(2)	6312(7)	2250(4)	22(1)
N(4)	1500(2)	6180(8)	-278(5)	36(2)
N(5)	1153(2)	8949(6)	3367(4)	20(1)
O(1)	852(2)	9174(5)	1619(3)	22(1)
O(2)	345(2)	10533(6)	1685(4)	30(1)
F(1)	1837(2)	8016(6)	-528(3)	47(1)
F(2)	1146(2)	4352(6)	-79(3)	49(1)
F(3)	2929(1)	8616(6)	4182(3)	39(1)
F(4)	2439(2)	4417(6)	4466(3)	44(1)
C(1)	1610(2)	11131(8)	2284(5)	25(2)
C(2)	1857(3)	12279(9)	2446(5)	29(2)
C(3)	2254(3)	12115(9)	2926(6)	34(2)
C(4)	2402(3)	10824(9)	3253(5)	31(2)
C(5)	2139(2)	9695(8)	3084(5)	24(2)
C(6)	2229(2)	8248(9)	3413(5)	24(2)
C(7)	2602(2)	7760(9)	3958(5)	30(2)
C(8)	2360(2)	5693(9)	4091(5)	29(2)
C(9)	1977(3)	5981(8)	3559(5)	28(2)
C(10)	1903(2)	7318(9)	3187(5)	23(2)
C(11)	870(3)	5864(9)	2803(6)	30(2)
C(12)	671(3)	4615(10)	2707(6)	41(2)
C(13)	670(3)	3757(9)	2005(6)	36(2)
C(14)	873(3)	4211(9)	1444(6)	32(2)
C(15)	1069(2)	5479(8)	1564(5)	26(2)
C(16)	1298(2)	6079(8)	1036(5)	27(2)
C(17)	1321(3)	5586(9)	230(6)	35(2)
C(18)	1671(2)	7384(10)	17(5)	31(2)
C(19)	1695(2)	7995(9)	810(5)	26(2)

C(20)	1493(2)	7373(8)	1328(5)	22(2)
C(21)	1314(3)	8809(9)	4249(5)	27(2)
C(22)	1132(3)	9378(9)	4818(5)	31(2)
C(23)	784(3)	10143(10)	4479(6)	36(2)
C(24)	618(3)	10310(9)	3580(6)	31(2)
C(25)	811(2)	9701(8)	3041(5)	23(2)
C(26)	647(2)	9826(8)	2038(5)	22(2)
C(100)	7(3)	2175(10)	-285(6)	44(2)
Cl(1)	-251(1)	3288(3)	229(2)	56(1)
Cl(2)	119(1)	3009(3)	-1152(2)	72(1)

Table S4. Bond lengths [Å] and angles [°] for Compound **1**.

Ir(1)-C(10)	1.992(7)	C(1)-C(2)	1.373(11)
Ir(1)-C(20)	2.010(7)	C(2)-C(3)	1.359(12)
Ir(1)-N(3)	2.040(6)	C(3)-C(4)	1.379(12)
Ir(1)-N(2)	2.058(6)	C(4)-C(5)	1.391(11)
Ir(1)-N(5)	2.115(6)	C(5)-C(6)	1.484(11)
Ir(1)-O(1)	2.130(5)	C(6)-C(7)	1.391(11)
N(1)-C(7)	1.298(11)	C(6)-C(10)	1.401(11)
N(1)-C(8)	1.316(11)	C(8)-C(9)	1.360(11)
N(2)-C(1)	1.339(10)	C(9)-C(10)	1.403(11)
N(2)-C(5)	1.354(10)	C(11)-C(12)	1.371(12)
N(3)-C(11)	1.354(10)	C(12)-C(13)	1.391(13)
N(3)-C(15)	1.360(10)	C(13)-C(14)	1.383(13)
N(4)-C(17)	1.305(12)	C(14)-C(15)	1.382(11)
N(4)-C(18)	1.318(12)	C(15)-C(16)	1.457(11)
N(5)-C(21)	1.342(9)	C(16)-C(17)	1.398(11)
N(5)-C(25)	1.347(10)	C(16)-C(20)	1.422(11)
O(1)-C(26)	1.291(9)	C(18)-C(19)	1.373(11)
O(2)-C(26)	1.228(9)	C(19)-C(20)	1.384(11)
F(1)-C(18)	1.339(9)	C(21)-C(22)	1.381(11)
F(2)-C(17)	1.352(10)	C(22)-C(23)	1.374(12)
F(3)-C(7)	1.359(10)	C(23)-C(24)	1.370(12)
F(4)-C(8)	1.354(10)	C(24)-C(25)	1.387(11)

C(25)-C(26)	1.518(10)	N(2)-C(5)-C(6)	112.2(7)
C(100)-Cl(2)	1.750(10)	C(4)-C(5)-C(6)	127.8(7)
C(100)-Cl(1)	1.766(11)	C(7)-C(6)-C(10)	117.6(8)
		C(7)-C(6)-C(5)	125.8(7)
C(10)-Ir(1)-C(20)	90.6(3)	C(10)-C(6)-C(5)	116.5(6)
C(10)-Ir(1)-N(3)	95.3(3)	N(1)-C(7)-F(3)	114.1(7)
C(20)-Ir(1)-N(3)	80.7(3)	N(1)-C(7)-C(6)	126.1(8)
C(10)-Ir(1)-N(2)	80.7(3)	F(3)-C(7)-C(6)	119.8(8)
C(20)-Ir(1)-N(2)	97.6(3)	N(1)-C(8)-F(4)	113.9(7)
N(3)-Ir(1)-N(2)	175.6(2)	N(1)-C(8)-C(9)	127.5(8)
C(10)-Ir(1)-N(5)	100.1(3)	F(4)-C(8)-C(9)	118.6(8)
C(20)-Ir(1)-N(5)	168.8(3)	C(8)-C(9)-C(10)	117.3(8)
N(3)-Ir(1)-N(5)	94.8(2)	C(6)-C(10)-C(9)	117.0(7)
N(2)-Ir(1)-N(5)	87.7(2)	C(6)-C(10)-Ir(1)	114.2(6)
C(10)-Ir(1)-O(1)	174.6(3)	C(9)-C(10)-Ir(1)	128.8(6)
C(20)-Ir(1)-O(1)	92.4(2)	N(3)-C(11)-C(12)	123.5(8)
N(3)-Ir(1)-O(1)	89.7(2)	C(11)-C(12)-C(13)	118.6(9)
N(2)-Ir(1)-O(1)	94.4(2)	C(14)-C(13)-C(12)	117.9(8)
N(5)-Ir(1)-O(1)	77.2(2)	C(15)-C(14)-C(13)	121.7(8)
C(7)-N(1)-C(8)	114.4(7)	N(3)-C(15)-C(14)	119.8(8)
C(1)-N(2)-C(5)	119.5(7)	N(3)-C(15)-C(16)	112.5(7)
C(1)-N(2)-Ir(1)	124.0(5)	C(14)-C(15)-C(16)	127.7(7)
C(5)-N(2)-Ir(1)	116.3(5)	C(17)-C(16)-C(20)	115.6(8)
C(11)-N(3)-C(15)	118.5(7)	C(17)-C(16)-C(15)	127.2(8)
C(11)-N(3)-Ir(1)	124.5(5)	C(20)-C(16)-C(15)	116.9(7)
C(15)-N(3)-Ir(1)	116.9(5)	N(4)-C(17)-F(2)	114.2(7)
C(17)-N(4)-C(18)	114.7(7)	N(4)-C(17)-C(16)	127.3(8)
C(21)-N(5)-C(25)	118.4(7)	F(2)-C(17)-C(16)	118.6(8)
C(21)-N(5)-Ir(1)	126.6(5)	N(4)-C(18)-F(1)	114.2(7)
C(25)-N(5)-Ir(1)	115.0(5)	N(4)-C(18)-C(19)	126.0(8)
C(26)-O(1)-Ir(1)	116.9(4)	F(1)-C(18)-C(19)	119.7(8)
N(2)-C(1)-C(2)	122.4(7)	C(18)-C(19)-C(20)	118.4(8)
C(3)-C(2)-C(1)	118.5(8)	C(19)-C(20)-C(16)	117.8(7)
C(2)-C(3)-C(4)	120.3(8)	C(19)-C(20)-Ir(1)	129.0(6)
C(3)-C(4)-C(5)	119.2(8)	C(16)-C(20)-Ir(1)	112.9(6)
N(2)-C(5)-C(4)	120.0(7)	N(5)-C(21)-C(22)	121.6(8)

C(23)-C(22)-C(21)	119.5(7)	C(24)-C(25)-C(26)	121.9(7)
C(24)-C(23)-C(22)	119.5(8)	O(2)-C(26)-O(1)	124.8(7)
C(23)-C(24)-C(25)	118.4(8)	O(2)-C(26)-C(25)	120.0(7)
N(5)-C(25)-C(24)	122.5(7)	O(1)-C(26)-C(25)	115.1(6)
N(5)-C(25)-C(26)	115.6(6)	Cl(2)-C(100)-Cl(1)	111.7(5)

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Compound **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	20(1)	19(1)	15(1)	-1(1)	6(1)	1(1)
N(1)	28(4)	39(4)	27(4)	-3(3)	6(3)	11(3)
N(2)	22(3)	28(4)	15(3)	-5(3)	8(3)	-2(3)
N(3)	16(3)	25(3)	19(3)	1(3)	-1(2)	2(3)
N(4)	33(4)	47(5)	28(4)	-15(3)	10(3)	2(4)
N(5)	28(3)	19(3)	13(3)	-3(2)	8(3)	-5(3)
O(1)	23(3)	23(3)	19(2)	-1(2)	6(2)	0(2)
O(2)	23(3)	29(3)	34(3)	3(3)	6(2)	7(2)
F(1)	51(3)	70(4)	29(3)	-8(3)	25(2)	-10(3)
F(2)	63(4)	47(3)	40(3)	-29(3)	22(3)	-15(3)
F(3)	21(2)	55(3)	38(3)	-5(2)	4(2)	-5(2)
F(4)	51(3)	37(3)	38(3)	12(2)	6(2)	17(3)
C(1)	26(4)	26(4)	25(4)	-3(3)	12(3)	1(3)
C(2)	41(5)	24(4)	28(4)	-1(3)	17(4)	-5(4)
C(3)	45(5)	34(5)	27(4)	-6(4)	16(4)	-13(4)
C(4)	26(4)	38(5)	27(4)	-8(4)	5(3)	-9(4)
C(5)	22(4)	31(4)	22(4)	-1(3)	11(3)	-2(3)
C(6)	17(4)	34(4)	20(4)	-5(3)	7(3)	2(3)
C(7)	25(4)	45(5)	21(4)	-5(4)	7(3)	2(4)
C(8)	32(4)	33(5)	22(4)	0(4)	8(3)	9(4)
C(9)	32(4)	23(4)	28(4)	1(3)	10(4)	5(3)
C(10)	17(4)	37(5)	16(3)	0(3)	7(3)	9(3)
C(11)	33(4)	29(4)	31(4)	5(4)	12(4)	-4(4)
C(12)	44(5)	34(5)	44(5)	10(4)	13(4)	-6(4)

C(13)	34(5)	27(4)	38(5)	4(4)	-1(4)	-6(4)
C(14)	34(5)	26(4)	31(4)	-9(4)	5(4)	0(4)
C(15)	33(4)	18(4)	24(4)	0(3)	6(3)	9(3)
C(16)	22(4)	30(4)	25(4)	-7(3)	3(3)	5(3)
C(17)	39(5)	28(5)	34(5)	-14(4)	7(4)	2(4)
C(18)	27(4)	53(6)	19(4)	5(4)	14(3)	4(4)
C(19)	19(4)	32(4)	26(4)	0(4)	6(3)	5(3)
C(20)	26(4)	25(4)	13(3)	-3(3)	4(3)	8(3)
C(21)	33(4)	31(4)	15(4)	3(3)	5(3)	-3(4)
C(22)	42(5)	37(5)	15(4)	-3(4)	10(3)	-5(4)
C(23)	41(5)	41(5)	34(5)	-14(4)	22(4)	-5(4)
C(24)	33(5)	28(5)	35(5)	0(4)	16(4)	2(4)
C(25)	28(4)	20(4)	22(4)	-3(3)	9(3)	-3(3)
C(26)	22(4)	23(4)	21(4)	-1(3)	7(3)	-5(3)
C(100)	54(6)	39(6)	35(5)	1(4)	8(4)	-7(5)
Cl(1)	50(2)	55(2)	62(2)	5(1)	14(1)	6(1)
Cl(2)	84(2)	55(2)	90(2)	20(2)	48(2)	1(2)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Compound **1**.

	x	y	z	U(eq)
H(1B)	1333	11240	1947	30
H(2A)	1753	13169	2229	35
H(3A)	2432	12893	3036	41
H(4B)	2679	10708	3589	37
H(9A)	1768	5306	3443	33
H(11A)	870	6446	3284	36
H(12A)	537	4342	3111	49
H(13A)	534	2887	1913	43
H(14A)	878	3635	963	39
H(19A)	1846	8825	999	32
H(21A)	1560	8305	4488	32
H(22A)	1248	9242	5440	38

H(23A)	659	10554	4866	44
H(24A)	376	10829	3333	37
H(10A)	262	1856	161	53
H(10B)	-162	1346	-519	53

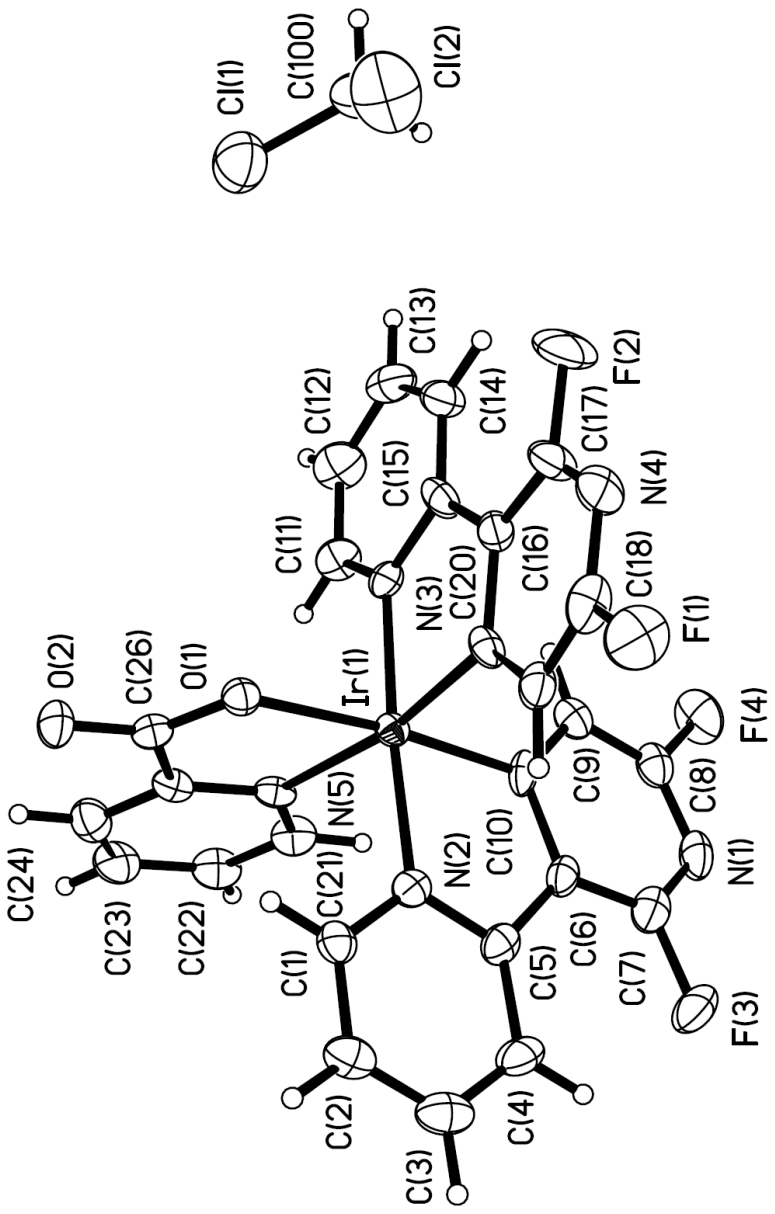


Figure S20. The structure of compound **1** with labeling scheme. Also shown is the solvent CH_2Cl_2 molecule, with 50% thermal ellipsoids.

Table S7. Crystal data and structure refinement for Compound **2**.

Identification code	Compound 2	
Empirical formula	C25 H17 F4 Ir N4 O2	
Formula weight	673.63	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.66610(10) Å	α= 90°.
	b = 18.1556(3) Å	β= 99.1990(10)°.
	c = 16.2735(3) Å	γ = 90°.
Volume	2235.86(6) $Å^3$	
Z	4	
Density (calculated)	2.001 Mg/m^3	
Absorption coefficient	6.038 mm^{-1}	
F(000)	1296	
Crystal size	0.10 x 0.10 x 0.02 mm^3	
Theta range for data collection	1.69 to 26.00°.	
Index ranges	-9<=h<=8, -20<=k<=22, -20<=l<=19	
Reflections collected	8837	
Independent reflections	4388 [R(int) = 0.0232]	
Completeness to theta = 26.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8888 and 0.5835	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4388 / 0 / 327	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0602	
R indices (all data)	R1 = 0.0296, wR2 = 0.0631	
Largest diff. peak and hole	1.755 and -0.896 $e.Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Compound **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	7784(1)	2317(1)	80(1)	20(1)
F(1)	12258(3)	312(2)	-841(2)	68(1)
F(2)	7268(4)	710(2)	-2611(2)	52(1)
F(3)	3494(3)	365(2)	1240(2)	60(1)
F(4)	8583(4)	865(2)	2882(2)	53(1)
N(1)	5673(4)	2212(2)	-852(2)	28(1)
N(2)	9756(5)	524(2)	-1717(2)	42(1)
N(3)	9910(4)	2305(2)	1009(2)	24(1)
N(4)	6051(5)	625(2)	2053(2)	41(1)
O(1)	8866(3)	3142(2)	-629(2)	30(1)
O(2)	6623(3)	3173(2)	718(2)	29(1)
C(1)	4137(6)	2572(2)	-860(3)	35(1)
C(2)	2713(6)	2450(3)	-1481(3)	45(1)
C(3)	2862(6)	1964(3)	-2100(3)	48(1)
C(4)	4441(6)	1589(3)	-2100(3)	42(1)
C(5)	5858(5)	1722(2)	-1462(2)	29(1)
C(6)	8705(5)	1542(2)	-576(2)	25(1)
C(7)	10297(5)	1151(2)	-394(3)	34(1)
C(8)	10709(5)	672(2)	-994(3)	40(1)
C(9)	8240(6)	867(2)	-1864(3)	36(1)
C(10)	8612(6)	3837(2)	-565(2)	33(1)
C(11)	9484(7)	4313(3)	-1135(3)	47(1)
C(12)	7628(5)	4184(3)	-24(2)	39(1)
C(13)	6731(5)	3858(2)	572(2)	32(1)
C(14)	5825(7)	4354(3)	1105(3)	53(1)
C(15)	9807(5)	1843(2)	1655(2)	26(1)

C(16)	6959(5)	1582(2)	819(2)	25(1)
C(17)	5357(5)	1183(2)	698(3)	32(1)
C(18)	5021(6)	741(2)	1330(3)	38(1)
C(19)	7551(6)	978(2)	2140(2)	35(1)
C(20)	11247(6)	1764(3)	2283(3)	40(1)
C(21)	12781(6)	2149(3)	2249(3)	43(1)
C(22)	12880(6)	2600(3)	1586(3)	41(1)
C(23)	11412(6)	2675(2)	980(3)	33(1)
C(25)	7591(5)	1363(2)	-1337(2)	28(1)
C(26)	8115(5)	1453(2)	1574(2)	27(1)

Table S9. Bond lengths [Å] and angles [°] for Compound **2**.

Ir(1)-C(6)	1.965(4)	N(4)-C(18)	1.324(6)
Ir(1)-C(16)	1.967(4)	O(1)-C(10)	1.283(5)
Ir(1)-N(3)	2.038(3)	O(2)-C(13)	1.271(5)
Ir(1)-N(1)	2.042(3)	C(1)-C(2)	1.382(7)
Ir(1)-O(1)	2.138(3)	C(1)-H(1)	0.9500
Ir(1)-O(2)	2.139(3)	C(2)-C(3)	1.358(7)
F(1)-C(8)	1.343(5)	C(2)-H(2)	0.9500
F(2)-C(9)	1.350(5)	C(3)-C(4)	1.388(7)
F(3)-C(18)	1.342(5)	C(3)-H(3)	0.9500
F(4)-C(19)	1.349(5)	C(4)-C(5)	1.397(5)
N(1)-C(1)	1.345(5)	C(4)-H(4)	0.9500
N(1)-C(5)	1.358(5)	C(5)-C(25)	1.464(5)
N(2)-C(9)	1.307(6)	C(6)-C(7)	1.402(5)
N(2)-C(8)	1.311(6)	C(6)-C(25)	1.425(5)
N(3)-C(23)	1.340(5)	C(7)-C(8)	1.382(6)
N(3)-C(15)	1.357(5)	C(7)-H(7)	0.9500
N(4)-C(19)	1.304(6)	C(9)-C(25)	1.389(5)

C(10)-C(12)	1.397(6)	C(16)-Ir(1)-N(1)	95.49(14)
C(10)-C(11)	1.499(6)	N(3)-Ir(1)-N(1)	173.94(13)
C(11)-H(11A)	0.9800	C(6)-Ir(1)-O(1)	90.27(14)
C(11)-H(11B)	0.9800	C(16)-Ir(1)-O(1)	174.72(13)
C(11)-H(11C)	0.9800	N(3)-Ir(1)-O(1)	94.27(11)
C(12)-C(13)	1.407(5)	N(1)-Ir(1)-O(1)	89.73(11)
C(12)-H(12)	0.9500	C(6)-Ir(1)-O(2)	175.69(13)
C(13)-C(14)	1.497(6)	C(16)-Ir(1)-O(2)	89.85(13)
C(14)-H(14A)	0.9800	N(3)-Ir(1)-O(2)	89.66(11)
C(14)-H(14B)	0.9800	N(1)-Ir(1)-O(2)	94.98(12)
C(14)-H(14C)	0.9800	O(1)-Ir(1)-O(2)	88.87(11)
C(15)-C(20)	1.387(5)	C(1)-N(1)-C(5)	120.3(4)
C(15)-C(26)	1.464(5)	C(1)-N(1)-Ir(1)	123.4(3)
C(16)-C(17)	1.412(5)	C(5)-N(1)-Ir(1)	116.2(3)
C(16)-C(26)	1.415(5)	C(9)-N(2)-C(8)	114.7(4)
C(17)-C(18)	1.362(6)	C(23)-N(3)-C(15)	119.6(4)
C(17)-H(17)	0.9500	C(23)-N(3)-Ir(1)	123.9(3)
C(19)-C(26)	1.382(5)	C(15)-N(3)-Ir(1)	116.3(3)
C(20)-C(21)	1.377(6)	C(19)-N(4)-C(18)	114.2(4)
C(20)-H(20)	0.9500	C(10)-O(1)-Ir(1)	124.7(2)
C(21)-C(22)	1.366(7)	C(13)-O(2)-Ir(1)	125.1(2)
C(21)-H(21)	0.9500	N(1)-C(1)-C(2)	121.2(5)
C(22)-C(23)	1.380(7)	N(1)-C(1)-H(1)	119.4
C(22)-H(22)	0.9500	C(2)-C(1)-H(1)	119.4
C(23)-H(23)	0.9500	C(3)-C(2)-C(1)	119.8(5)
		C(3)-C(2)-H(2)	120.1
C(6)-Ir(1)-C(16)	91.38(16)	C(1)-C(2)-H(2)	120.1
C(6)-Ir(1)-N(3)	94.61(14)	C(2)-C(3)-C(4)	119.6(4)
C(16)-Ir(1)-N(3)	80.59(14)	C(2)-C(3)-H(3)	120.2
C(6)-Ir(1)-N(1)	80.80(15)	C(4)-C(3)-H(3)	120.2

C(3)-C(4)-C(5)	119.4(4)	O(2)-C(13)-C(12)	126.5(4)
C(3)-C(4)-H(4)	120.3	O(2)-C(13)-C(14)	115.5(4)
C(5)-C(4)-H(4)	120.3	C(12)-C(13)-C(14)	118.0(4)
N(1)-C(5)-C(4)	119.7(4)	C(13)-C(14)-H(14A)	109.5
N(1)-C(5)-C(25)	112.8(3)	C(13)-C(14)-H(14B)	109.5
C(4)-C(5)-C(25)	127.4(4)	H(14A)-C(14)-H(14B)	109.5
C(7)-C(6)-C(25)	116.7(4)	C(13)-C(14)-H(14C)	109.5
C(7)-C(6)-Ir(1)	128.6(3)	H(14A)-C(14)-H(14C)	109.5
C(25)-C(6)-Ir(1)	114.7(3)	H(14B)-C(14)-H(14C)	109.5
C(8)-C(7)-C(6)	117.4(4)	N(3)-C(15)-C(20)	119.8(4)
C(8)-C(7)-H(7)	121.3	N(3)-C(15)-C(26)	112.9(3)
C(6)-C(7)-H(7)	121.3	C(20)-C(15)-C(26)	127.3(4)
N(2)-C(8)-F(1)	114.6(4)	C(17)-C(16)-C(26)	116.5(4)
N(2)-C(8)-C(7)	127.3(4)	C(17)-C(16)-Ir(1)	128.4(3)
F(1)-C(8)-C(7)	118.1(4)	C(26)-C(16)-Ir(1)	115.1(3)
N(2)-C(9)-F(2)	114.2(4)	C(18)-C(17)-C(16)	117.6(4)
N(2)-C(9)-C(25)	126.3(4)	C(18)-C(17)-H(17)	121.2
F(2)-C(9)-C(25)	119.5(4)	C(16)-C(17)-H(17)	121.2
O(1)-C(10)-C(12)	126.7(4)	N(4)-C(18)-F(3)	113.8(4)
O(1)-C(10)-C(11)	115.3(4)	N(4)-C(18)-C(17)	127.3(4)
C(12)-C(10)-C(11)	117.9(4)	F(3)-C(18)-C(17)	118.9(4)
C(10)-C(11)-H(11A)	109.5	N(4)-C(19)-F(4)	113.8(4)
C(10)-C(11)-H(11B)	109.5	N(4)-C(19)-C(26)	126.8(4)
H(11A)-C(11)-H(11B)	109.5	F(4)-C(19)-C(26)	119.4(4)
C(10)-C(11)-H(11C)	109.5	C(21)-C(20)-C(15)	120.2(4)
H(11A)-C(11)-H(11C)	109.5	C(21)-C(20)-H(20)	119.9
H(11B)-C(11)-H(11C)	109.5	C(15)-C(20)-H(20)	119.9
C(10)-C(12)-C(13)	128.1(4)	C(22)-C(21)-C(20)	119.4(4)
C(10)-C(12)-H(12)	116.0	C(22)-C(21)-H(21)	120.3
C(13)-C(12)-H(12)	116.0	C(20)-C(21)-H(21)	120.3

C(21)-C(22)-C(23)	118.8(4)	C(9)-C(25)-C(6)	117.4(4)
C(21)-C(22)-H(22)	120.6	C(9)-C(25)-C(5)	127.5(4)
C(23)-C(22)-H(22)	120.6	C(6)-C(25)-C(5)	115.1(3)
N(3)-C(23)-C(22)	122.1(4)	C(19)-C(26)-C(16)	117.6(4)
N(3)-C(23)-H(23)	118.9	C(19)-C(26)-C(15)	127.5(4)
C(22)-C(23)-H(23)	118.9	C(16)-C(26)-C(15)	114.9(3)

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Compound **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	19(1)	21(1)	20(1)	0(1)	2(1)	0(1)
F(1)	44(2)	65(2)	95(2)	-34(2)	15(2)	18(2)
F(2)	70(2)	53(2)	34(1)	-21(1)	10(1)	-13(1)
F(3)	48(2)	56(2)	80(2)	16(2)	22(1)	-19(1)
F(4)	76(2)	51(2)	32(1)	14(1)	8(1)	5(2)
N(1)	26(2)	30(2)	27(2)	3(1)	0(1)	-4(1)
N(2)	50(2)	33(2)	50(2)	-14(2)	25(2)	-8(2)
N(3)	22(2)	25(2)	24(2)	-4(1)	0(1)	2(1)
N(4)	56(2)	31(2)	41(2)	7(2)	24(2)	0(2)
O(1)	34(1)	30(2)	27(1)	-2(1)	8(1)	-5(1)
O(2)	29(1)	31(2)	28(1)	1(1)	8(1)	4(1)
C(1)	30(2)	34(2)	39(3)	5(2)	2(2)	4(2)
C(2)	29(2)	49(3)	52(3)	9(2)	-11(2)	-1(2)
C(3)	38(2)	57(3)	42(3)	2(2)	-14(2)	-11(2)
C(4)	42(2)	49(3)	32(2)	-4(2)	-4(2)	-8(2)
C(5)	34(2)	30(2)	22(2)	-1(2)	4(2)	-8(2)
C(6)	26(2)	23(2)	28(2)	-2(2)	12(2)	-1(2)
C(7)	31(2)	32(2)	40(2)	-9(2)	8(2)	0(2)

C(8)	30(2)	36(3)	58(3)	-15(2)	15(2)	-1(2)
C(9)	44(2)	31(2)	34(2)	-8(2)	11(2)	-12(2)
C(10)	42(2)	29(2)	24(2)	2(2)	-3(2)	-10(2)
C(11)	66(3)	40(3)	38(3)	0(2)	16(2)	-10(2)
C(12)	56(3)	17(2)	43(3)	0(2)	5(2)	0(2)
C(13)	37(2)	30(2)	28(2)	-2(2)	2(2)	5(2)
C(14)	78(4)	32(3)	53(3)	-3(2)	24(3)	15(2)
C(15)	30(2)	25(2)	22(2)	-1(2)	1(2)	6(2)
C(16)	24(2)	21(2)	32(2)	-2(2)	12(2)	0(2)
C(17)	22(2)	30(2)	46(2)	3(2)	8(2)	-2(2)
C(18)	40(2)	27(2)	52(3)	0(2)	23(2)	-2(2)
C(19)	50(3)	31(2)	26(2)	1(2)	11(2)	8(2)
C(20)	43(2)	45(3)	31(2)	2(2)	-4(2)	9(2)
C(21)	32(2)	49(3)	42(3)	-8(2)	-13(2)	7(2)
C(22)	29(2)	43(3)	48(3)	-8(2)	-2(2)	-3(2)
C(23)	26(2)	34(3)	37(2)	-4(2)	3(2)	-4(2)
C(25)	33(2)	26(2)	26(2)	-4(2)	6(2)	-8(2)
C(26)	35(2)	22(2)	26(2)	-1(2)	9(2)	5(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Compound **2**.

	x	y	z	U(eq)
H(1)	4030	2917	-432	42
H(2)	1633	2704	-1475	55
H(3)	1892	1881	-2532	58
H(4)	4558	1246	-2528	50
H(7)	11062	1214	121	41

H(11A)	10747	4197	-1064	71
H(11B)	9330	4832	-999	71
H(11C)	8944	4221	-1713	71
H(12)	7556	4706	-64	47
H(14A)	4578	4214	1056	79
H(14B)	5912	4865	923	79
H(14C)	6392	4307	1687	79
H(17)	4544	1221	194	39
H(20)	11175	1443	2737	48
H(21)	13762	2102	2684	52
H(22)	13941	2857	1544	49
H(23)	11467	2999	527	39

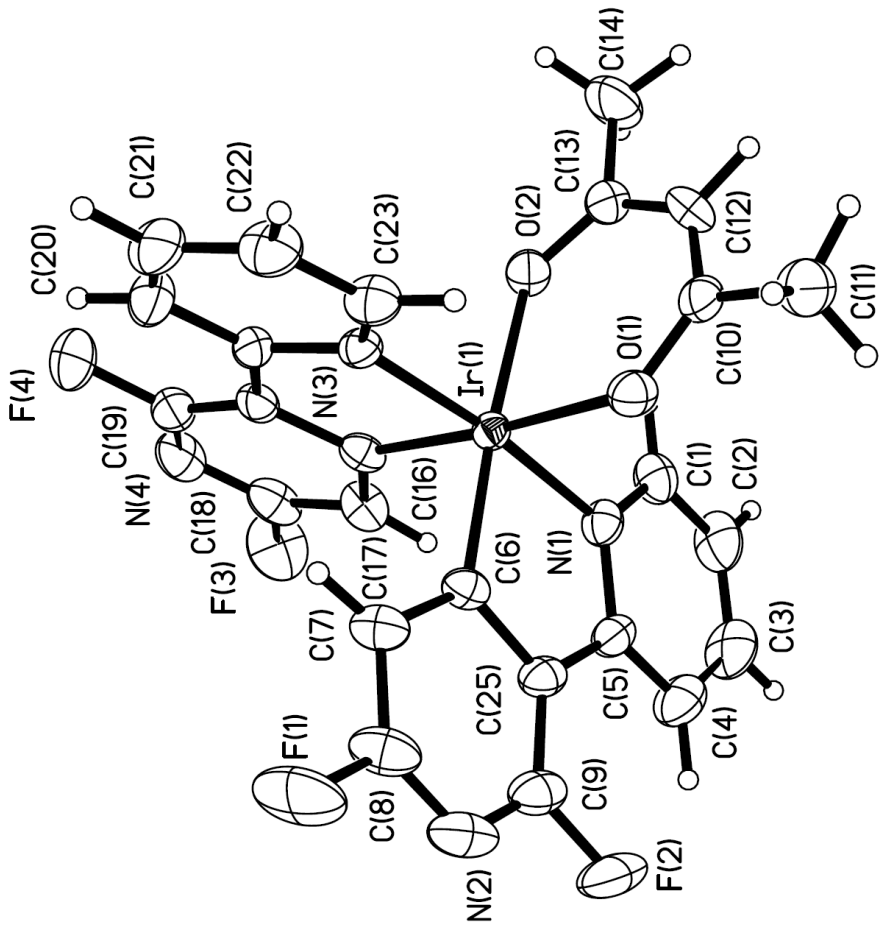


Figure S21. The structure of compound **2** with labeling scheme and 50% thermal ellipsoids.

Table S12. Intermolecular Hydrogen bonds and halogen…halogen interactions for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C3-H3A...F4i	0.95	2.66	3.18(2)	115.6
C11-H11A...F2ii	0.95	2.61	3.21(2)	121.4
C13-H13A...O2iii	0.95	2.37	3.30(2)	166.9
C23-H23A...O1iv	0.95	2.63	3.37(2)	134.9
C24-H24A...O2v	0.95	2.52	3.26(2)	135.0
C100-H10A...O2iii	0.99	2.70	3.39(3)	126.5
C100-H10B...O1vi	0.99	2.53	3.32(3)	136.6
C100-H10B...O2vi	0.99	2.52	3.39(3)	146.1
F1...F4vii			2.86(2)	

Symmetry transformations used to generate equivalent atoms: i) *x*, *y*+1, *z*; ii) *x*, -*y*+1, *z*+1/2; iii) *x*, *y*-1, *z*; iv) *x*, -*y*+2, *z*+1/2; v) -*x*, *y*, -*z*+1/2; vi) -*x*, -*y*+1, -*z*; vii) -*x*+1/2, *y*+1/2, -*z*+1/2.

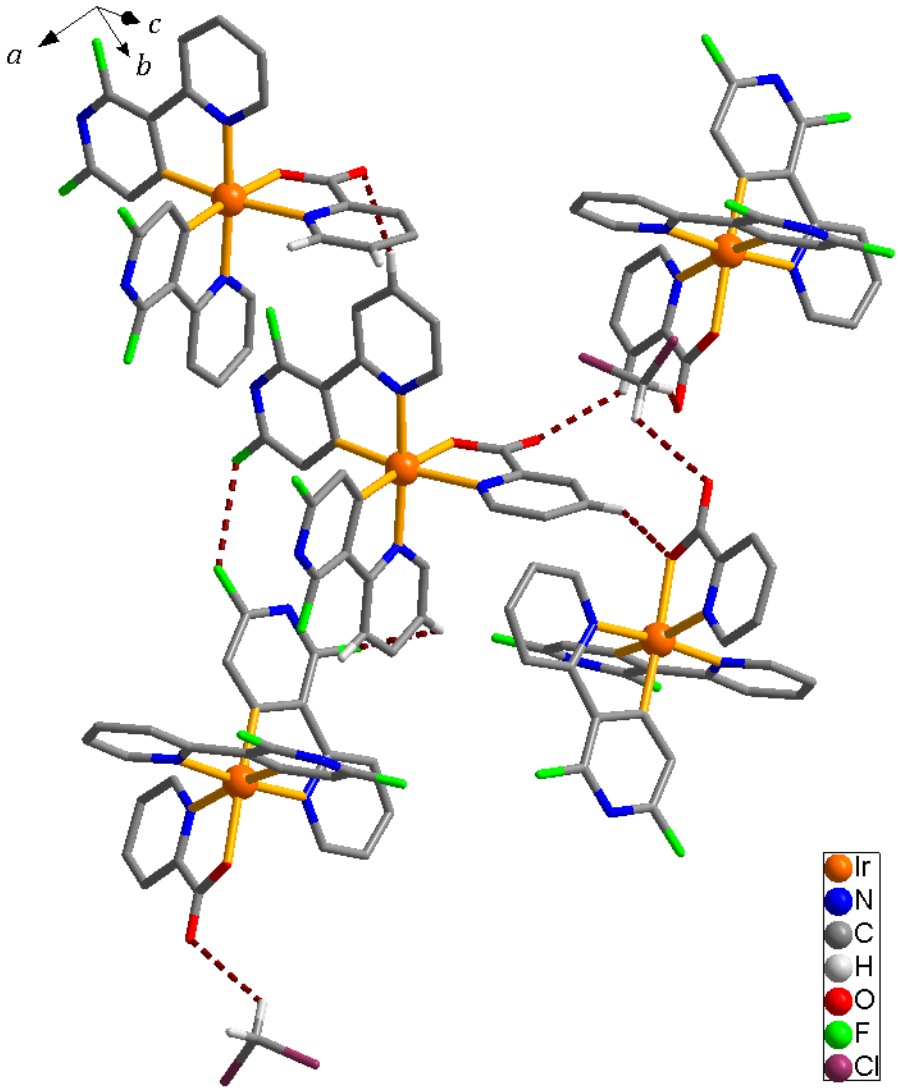


Figure S22. Packing diagram of complex **2** with intermolecular C-H…O and C-H…F hydrogen bonds shown as dashed lines.

Table S13. Intermolecular interactions of complex **2** (Å and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14B)...F(4)#1	0.98	2.64	3.195(5)	115.9
C(22)-H(22)...O(2)#2	0.95	2.69	3.551(5)	150.7

Symmetry transformations used to generate equivalent atoms: #1) -*x*+3/2, *y*+1/2, -*z*+1/2; #2) *x*+1, *y*, *z*.

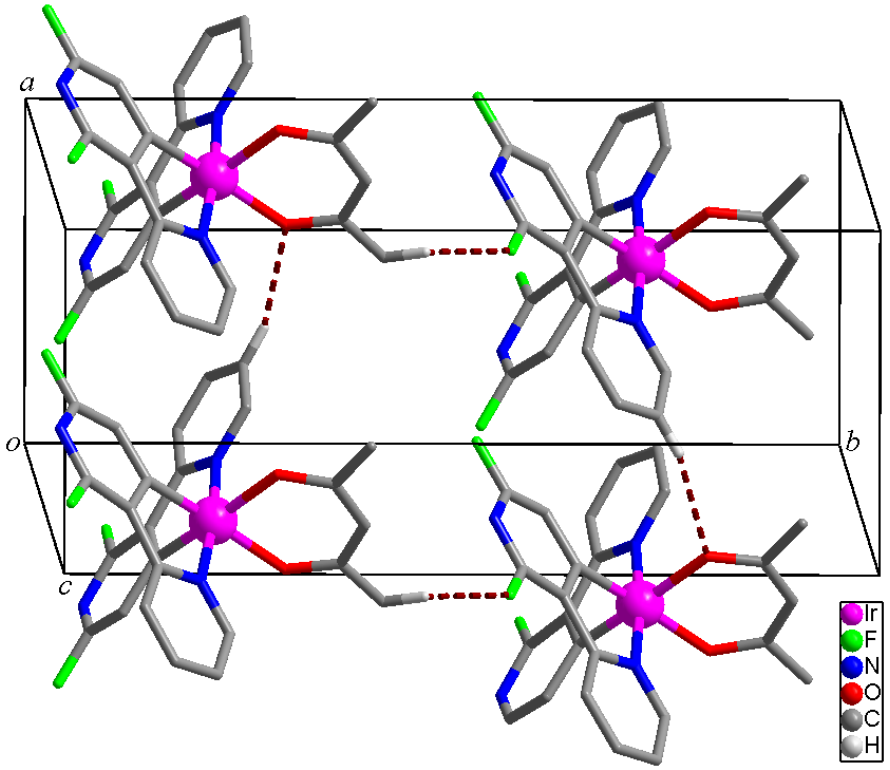


Figure S23. Packing diagram of complex **2** with intermolecular C-H…O and C-H…F hydrogen bonds shown as dashed lines.