Electronic Supplementary Information for Dalton Transactions

Syntheses, Crystal Structure, Electrochemical, Photophysical, Electroluminescence and Theoretical Calculations of a Set of *bis*-Cyclometalated Ir(III) Complexes with a Common Ancillary Ligand

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1. Syntheses

[Ir(F_2ppy)$_2$ZN] FZN: To a solution of the ligand 3,5-dimethyl-pyrazole *N*-carboxamide, **ZN** (1.25 mmol, 0.175 g) in 200 ml of tetrahydrofuran was added the dimer [Ir(F_2ppy)$_2$Cl]$_2$ (0.5 mmol, 0.61 g). The mixture was stirred at ambient temperature for 24 hrs under nitrogen environment. Evaporation of the solvent afforded a yellow solid. The crude product was chromatographed on silica with 5~10 % acetone in dichloromethane as eluent. The complex FZN was obtained as a yellow solid (0.59g, 80 %) after the evaporation of the solvents at low pressure and was further purified by its reprecipitation from a solution of chloroform and n-hexane. light yellow solid. The complex was crystalised by the slow evaporation of n-hexane into a methylene chloride solution. δ_H (300 MHz, CH_2Cl_2) 8.99 (d, 1H), 8.26 (d, 2H), 7.80 (t, 3H), 7.21(t,1H), 7.11 (t, 1H), 6.39 (t, 2H), 5.87-5.83 (d, 2H),

5.57 (d, 1H), 4.51 (s, 1H), 2.60 (s, 3H), 1.63 (s, 3H). T_d (dissociation temperature), 255 ^oC (methylene chloride, n-hexane). Elemental analysis, Found : C, 47.09; H, 2.91; N, 9.48. Calc. For C28 H20 F4 Ir N5 O: C, 47.32; H, 2.84; N, 9.85%.

[Ir(F_2CNppy)$_2$ZN] FCZN: The complex is synthesized as mentioned above and obtained as a light yellow solid. Single crystals are obtained from a solution of methylene chloride and diethyl ether. Elemental analysis is performed by reprecipitating the complex several times from its solution in chloroform and ether and evaporating at 80 ^oC in vacuum for 24h. δ_H (300 MHz, CH_2Cl_2) 9.00 (d, 1H), 8.34 (d, 2H), 7.80 (t, 2H), 7.77 (d, 1H), 7.38 (t, 1H), 7.28 (t, 1H), 6.10 (d, 1H), 5.91 (s, 1H), 5.75 (d, 1H), 4.80 (s, 1H), 2.61 (s, 3H), 1.86 (s, 3H). T_d (dissociation temperature), 270 ^oC (methylene chloride, diethylether). Elemental analysis, Found : C, 46.91; H, 2.04; N, 12.78. Calc. for C30H18F4IrN7O: C, 47.37; H, 2.38; N, 12.89

[Ir(DMAF_2ppy)$_2$ZN] FDZN: The complex is synthesized as mentioned above and obtained as a light yellow solid. δ_H (300 MHz, CH_2Cl_2) 8.38 (d, 1H), 7.52 (s, 2H), 7.30 (t, 1H), 6.45 (d, 1H), 6.29 (t, 3H), 5.98 (d, 1H), 5.78 (s, 1H), 5.73 (d, 1H), 4.44 (s, 1H), 3.16 (s, 12H), 2.59 (s, 3H), 1.50 (s, 3H). T_d (dissociation temperature), 265 ^oC (Methanol, n-hexane). Elemental analysis, Found : C, 47.78; H, 3.45; N, 11.92. Calc. For C32 H30 F4 Ir N7 O: C, 48.23; H, 3.79; N, 12.30.

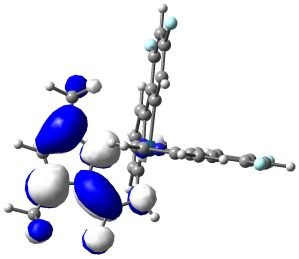
[Ir(MeOF_2ppy)$_2$ZN] MeOFZN: The complex is synthesized as mentioned above and obtained as a light yellow solid. Single crystals were obtained by the slow evaporation of n-hexane into a methylene chloride solution. δ_H (300 MHz, CH_2Cl_2) 8.73 (d, 1H), 7.75 (d, 2H), 7.48 (d, 1H), 6.73 (d, 1H), 6.71 (d, 1H), 6.36 (t, 2H), 5.88 (d, 1H), 5.84 (s, 1H), 5.78

(d, 1H), 4.60 (s, 1H), 3.99 (s, 6H), 2.64 (s, 3H), 1.63 (s, 3H). T_d (dissociation temperature), 258 ^oC (methylene chloride, n-hexane). Elemental analysis, Found : C, 46.58; H, 2.87; N, 8.82. Calc. For C30H24F4IrN5O3: C, 46.75; H, 3.14; N, 9.09%.

2. Figure S1. Calculated Molecular Orbitals of the complexes FZN FCZN, FDZN and MeOFZN

FZN

L+4



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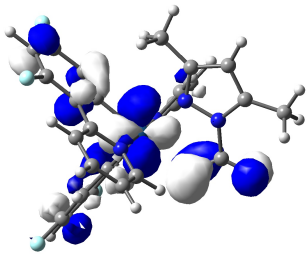

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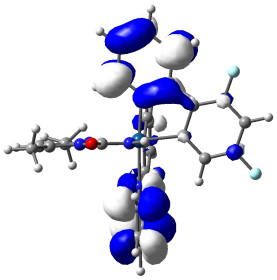

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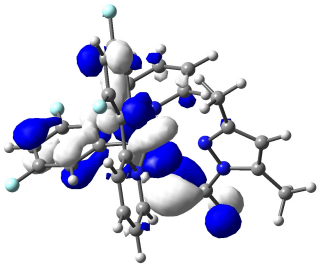

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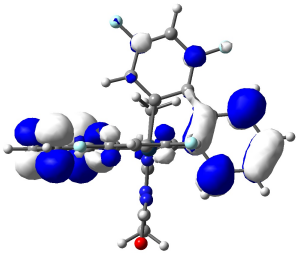

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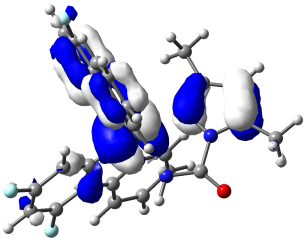

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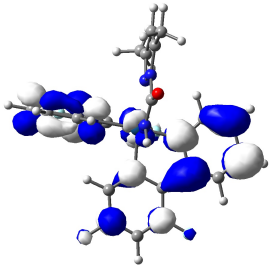

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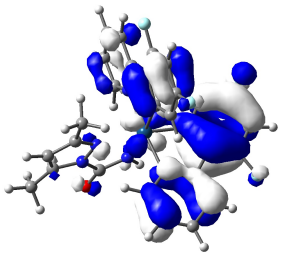
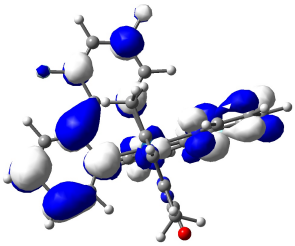
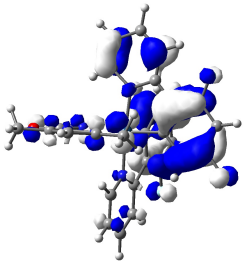
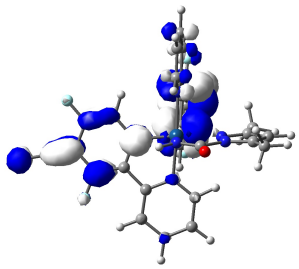
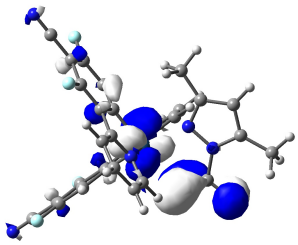
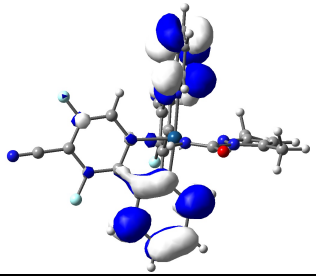
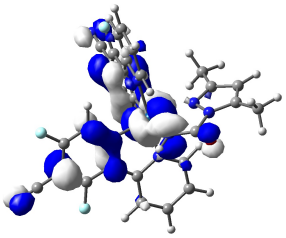
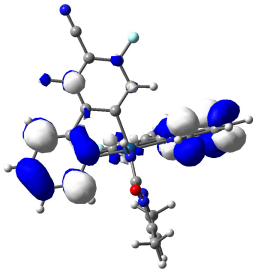
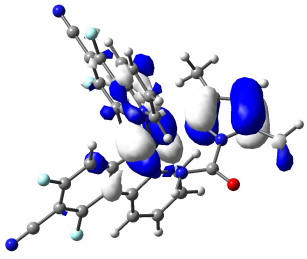
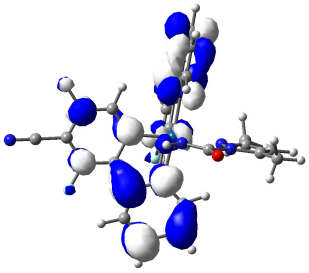
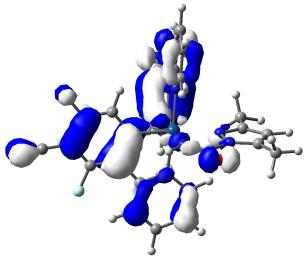
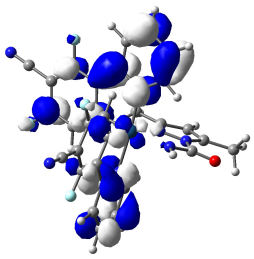
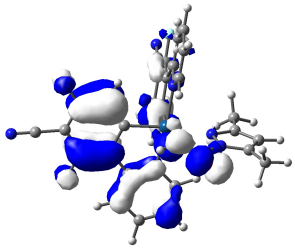


L 

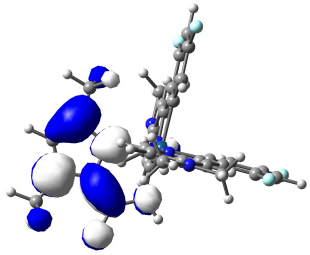
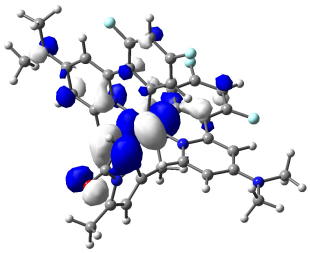
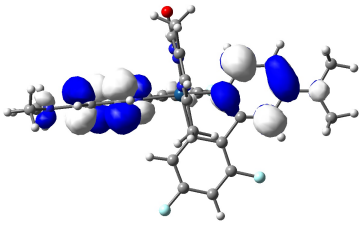
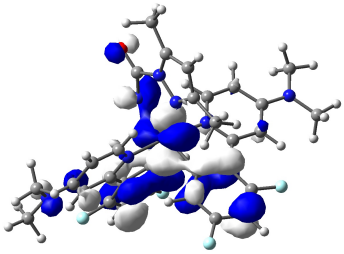
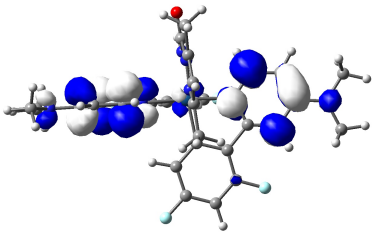
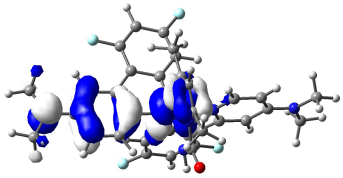
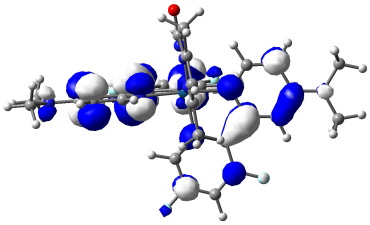
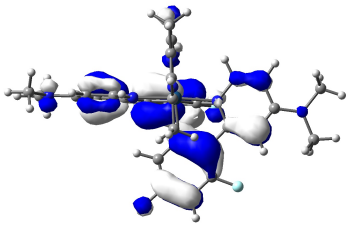
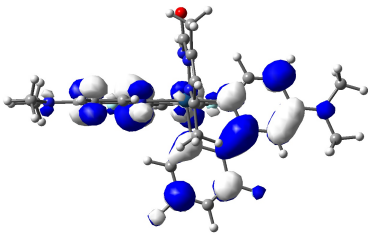
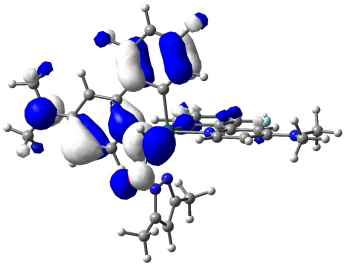
H-4 

FCZN

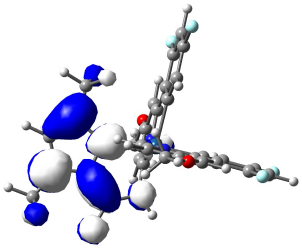
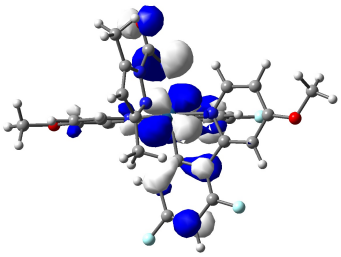
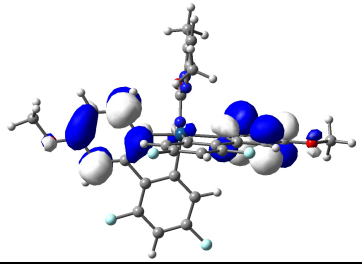
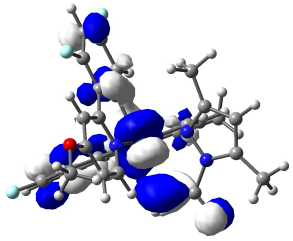
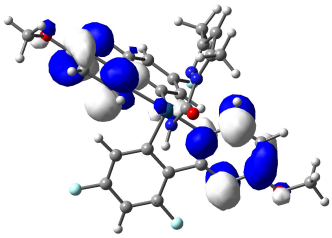
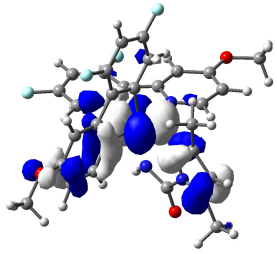
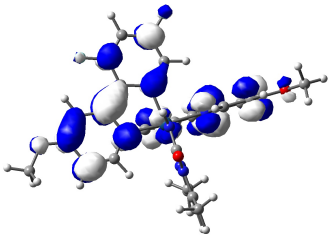
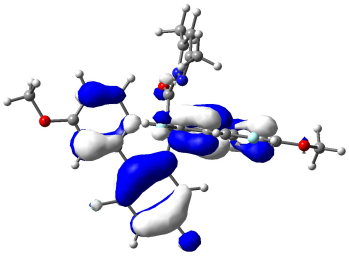
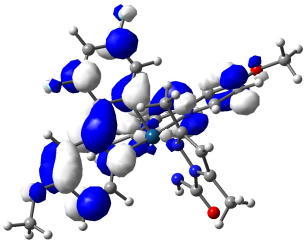
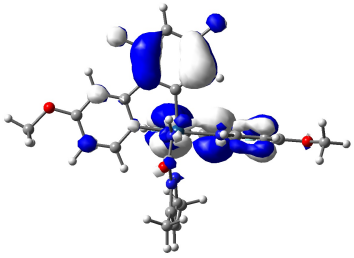
L+4		H	
L+3		H-1	
L+2		H-2	
L+1		H-3	

L		H-4	

FDZN

L+4		H	
L+3		H-1	
L+2		H-2	
L+1		H-3	
L		H-4	

MeOFZN

L+4		H	
L+3		H-1	
L+2		H-2	
L+1		H-3	
L		H-4	

3. Table S1. Calculated vertical transitions

Singlet transitions

FZN

#	(nm	1000 cm-1	eV)	(f)		(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	403.8	24.8	3.07	0.0090	S	H->L(+94%)
2	396.1	25.2	3.13	0.0038	S	H->L+1(+93%)
3	382.5	26.1	3.24	0.0190	S	H-1->L(+85%) H-1->L+1(+9%)
4	365.5	27.4	3.39	0.0373	S	H-1->L+1(+82%) H-1->L(9%)
5	336.3	29.7	3.69	0.0091	S	H-2->L(51%) H-2->L+1(+35%)
6	333.0	30.0	3.72	0.0259	S	H->L+2(+89%)
7	328.6	30.4	3.77	0.0337	S	H-2->L+1(+33%) H->L+3(+33%) H-2->L(+22%)
8	324.3	30.8	3.82	0.0048	S	H->L+3(+56%) H-2->L+1(13%) H-1->L+2(+10%) H-2->L(9%)

FCZN

#	(nm	1000 cm-1	eV)	(f)		(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	400.9	24.9	3.09	0.0024	S	H->L(+96%)
2	392.7	25.5	3.16	0.0042	S	H->L+1(+95%)
3	375.8	26.6	3.30	0.0334	S	H-1->L(+87%) H-1->L+1(5%)
4	361.1	27.7	3.43	0.0252	S	H-1->L+1(+85%)
5	335.0	29.8	3.70	0.0175	S	H-2->L(+67%) H-2->L+1(+26%)
6	329.3	30.4	3.77	0.0192	S	H->L+2(+88%)
7	326.5	30.6	3.80	0.0198	S	H-2->L+1(+56%) H-2->L(20%) H->L+3(+8%) H->L+2(+5%)
8	320.9	31.2	3.86	0.0032	S	H->L+3(+85%)

FDZN

#	(nm	1000 cm-1	eV)	(f)		(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	378.2	26.4	3.28	0.0084	S	H->L(+95%)
2	368.2	27.2	3.37	0.0040	S	H->L+1(+93%)
3	361.3	27.7	3.43	0.0722	S	H-1->L(+87%)
4	347.7	28.8	3.57	0.0357	S	H-1->L+1(+86%)
5	333.3	30.0	3.72	0.0565	S	H-2->L(+88%) H-2->L+1(+5%)
6	325.1	30.8	3.81	0.0435	S	H-2->L+1(+83%)
7	320.3	31.2	3.87	0.0135	S	H->L+2(+86%) H->L+3(5%)

8 314.1 31.8 3.95 0.0227 S H->L+3(+80%) H-1->L+2(8%)

MeOFZN

(nm 1000 cm-1 eV) (f) (Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)

1 380.2 26.3 3.26 0.0161 S H ->L(+94%)
2 370.9 27.0 3.34 0.0031 S H->L+1(+93%)
3 362.9 27.6 3.42 0.0392 S H-1->L(+88%)
4 349.6 28.6 3.55 0.0260 S H-1->L+1(+83%)
5 332.0 30.1 3.73 0.0147 S H->L+2(+86%) H->L+3(+6%)
6 326.1 30.7 3.80 0.0068 S H->L+3(+69%) H-2->L(9%)
H-2->L+1(9%)
7 325.5 30.7 3.81 0.0484 S H-2->L(+72%) H->L+3(+14%)
H-2->L+1(+6%)
8 320.5 31.2 3.87 0.0113 S H-1->L+2(+60%) H-2->L+1(31%)

Triplet transitions

FZN

(nm 1000 cm-1 eV) (f) (Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)

1 445.5 22.4 2.78 0.0000 H->L(+47%) H->L+1(24%)
H-3->L+1(15%)
2 438.5 22.8 2.83 0.0000 H->L+1(+34%) H-1->L(16%)
H-2->L(+13%) H->L(+10%)
H-3->L(10%)
3 404.8 24.7 3.06 0.0000 H-1->L(+42%) H->L(+21%)
H-1->L+1(14%) H->L+1(+9%)
4 400.9 24.9 3.09 0.0000 H-1->L+1(+56%) H->L(+14%)
H->L+1(+10%) H-2->L(9%)
5 382.9 26.1 3.24 0.0000 H-1->L(+32%) H-2->L(+22%)
H-1->L+1(+21%) H-2->L+1(+8%)
6 377.8 26.5 3.28 0.0000 H-3->L+1(+21%) H->L+1(21%)
H-3->L(12%) H-4->L+1(+11%)
H-4->L(7%) H-3->L+3(+5%)
7 357.3 28.0 3.47 0.0000 H-4->L(+30%) H-2->L(16%)
H-3->L(15%) H-4->L+1(+8%)
H-3->L+1(6%)
8 351.9 28.4 3.52 0.0000 H->L+2(+48%) H-1->L+2(20%)
H-3->L+3(10%)

FCZN

#	(nm	1000 cm-1	eV)	(f)	(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	438.7	22.8	2.83	0.0000	H->L(+39%) H->L+1(+24%) H-3->L+1(+11%) H-1->L(7%) H-4->L+1(6%) H-4->L(6%)
2	430.3	23.2	2.88	0.0000	H-1->L(+21%) H->L+1(+20%) H-3->L(+14%) H-1->L+1(12%) H-2->L(+7%) H-5->L(+6%)
3	403.4	24.8	3.07	0.0000	H->L(+48%) H-1->L(+24%) H->L+1(9%)
4	397.8	25.1	3.12	0.0000	H-1->L+1(+42%) H->L+1(+31%) H-1->L(+9%)
5	375.4	26.6	3.30	0.0000	H-2->L(25%) H-1->L(+23%) H-1->L+1(18%) H-2->L+1(+11%)
6	371.2	26.9	3.34	0.0000	H-4->L+1(+18%) H-1->L+1(14%) H->L+1(+13%) H-4->L(+12%) H-1->L(7%) H-3->L+1(7%)
7	359.7	27.8	3.45	0.0000	H-1->L+4(14%) H-2->L(+12%) H-3->L(6%) H-1->L(+6%) H-5->L(6%) H-3->L+4(5%) H-6->L+4(5%) H->L+4(+5%)
8	349.4	28.6	3.55	0.0000	H-1->L+2(+18%) H-1->L+5(+13%) H-1->L+4(13%) H-3->L+5(8%) H->L+4(+6%) H->L+5(6%) H->L+2(5%) H-6->L+5(5%)

FDZN

#	(nm	1000 cm-1	eV)	(f)	(A ignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	419.2	23.9	2.96	0.0000	H->L(+39%) H->L+1(+16%) H-3->L+1(15%) H-1->L(10%) H-4->L(8%) H-4->L+1(7%)
2	413.0	24.2	3.00	0.0000	H->L+1(+21%) H-3->L(21%) H-1->L(+17%) H-1->L+1(13%) H-5->L(+6%) H-2->L(6%)
3	388.7	25.7	3.19	0.0000	H-1->L+1(+38%) H-1->L(+33%) H->L(+12%)
4	382.7	26.1	3.24	0.0000	H-2->L(+32%) H->L(21%) H->L+1(+20%) H-2->L+1(15%)
5	371.1	26.9	3.34	0.0000	H-1->L+1(19%) H->L(+19%) H-2->L(+16%) H->L+1(15%)

					H-1->L(+12%) H-2->L+1(9%)
6	359.2	27.8	3.45	0.0000	H->L+1(+17%) H-3->L+1(+14%)
					H-5->L(+13%) H-1->L(10%)
					H-4->L(+9%) H-4->L+1(+6%)
7	355.9	28.1	3.48	0.0000	H-1->L+1(18%) H-5->L(15%)
					H-3->L(+13%) H-1->L(+11%)
					H-5->L+1(+11%) H-6->L(+7%)
8	347.6	28.8	3.57	0.0000	H->L+2(+29%) H->L+3(+17%)
					H-1->L+2(+10%) H-1->L+3(+6%)
					H-1->L+1(5%) H-4->L+3(5%)

MeOFZN

#	(nm	1000 cm-1	eV)	(f)	(Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	421.7	23.7	2.94	0.0000	H->L(+47%) H-3->L+1(+20%)
					H->L+1(+11%) H-4->L(9%)
					H-1->L(+7%)
2	416.2	24.0	2.98	0.0000	H->L+1(+35%) H-3->L(+24%)
					H-4->L+1(10%) H-1->L(10%)
					H-1->L+1(+7%)
3	383.7	26.1	3.23	0.0000	H-1->L(+44%) H-1->L+1(+30%)
					H->L(11%)
4	379.2	26.4	3.27	0.0000	H->L(+25%) H->L+1(20%)
					H-1->L+1(+18%) H-2->L(+10%)
					H-4->L(+7%)
5	365.7	27.3	3.39	0.0000	H-1->L+1(33%) H-1->L(+28%)
					H-2->L(+12%) H-2->L+1(6%)
6	363.6	27.5	3.41	0.0000	H->L+1(+26%) H-3->L+1(14%)
					H-4->L(+13%) H-4->L+1(+11%)
					H-3->L(9%) H->L(+5%)
7	350.9	28.5	3.53	0.0000	H-2->L(+24%) H-4->L(16%)
					H-2->L+1(9%) H-3->L(9%)
					H-2->L+2(+7%) H-4->L+1(+7%)
8	346.0	28.9	3.58	0.0000	H->L+2(+61%) H-1->L+3(+9%)
					H-1->L+2(5%)

4. Table S2. Calculated Atomic Charges from Mulliken Population Analysis for Ir Complexes

FZN		FCZN		MeOFZN	
Ir	0.859	Ir	0.886	Ir	-0.854
C13	-0.201	C17	-0.206	C17	-0.199
C24	-0.195	C29	-0.201	C29	-0.196
N1	-0.303	N1	-0.307	N1	-0.299
N3	-0.376	N3	-0.300	N3	-0.375
N4	-0.554	N4	-0.554	N4	-0.564
N5	-0.551	N6	-0.551	N5	-0.560

5. Table S3. Calculated molecular orbital energies of Ir complexes at the DFT-B3LYP level

Orbitals	FZN	FCZN	MeOFZN	FDZN
L+4	-0.377	-1.282	-0.279	-0.060
L+3	-0.937	-1.475	-0.751	-0.324
L+2	-1.025	-1.579	-0.817	-0.395
L+1	-1.523	-2.098	-1.163	-0.864
L	-1.595	-2.181	-1.260	-0.973
H	-5.441	-6.032	-5.273	-4.985
H-1	-5.586	-6.209	-5.399	-5.112
H-2	-6.047	-6.640	-5.817	-5.381
H-3	-6.168	-6.785	-6.019	-5.778
H-4	-6.254	-6.935	-6.103	-5.871

6. Measurements

Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) measurements were carried out using an EG&G potentiostat/galvanostat model 283. The reduction and oxidation potential measurements were carried out in anhydrous CH_2Cl_2 (for

oxidation) or THF (for reduction) solution containing 1 mM electroactive compound and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the electrolyte at room temperature in an argon environment. A platinum disc (diameter: 1.6 mm) and a platinum wire were used as working and counter electrodes, respectively. A silver wire was used as the pseudo-reference electrode, and all the potential values were calibrated based on the ferrocene/ferrocenium (Fc/Fc^+) redox couple as a internal standard. The parameters of SWV were as follows: step pulse height = 75 mV, step increment = 4mV, scan rate = 20 mV/s.

^1H NMR spectra were recorded at 300 MHz with a Bruker FT-NMR spectrometer; chemical shifts were referenced to internal $SiMe_4$. Elemental analyses were performed by EA1110, CE Instrument, Italy. Absorption spectra were monitored with a Shimadzu UV-3150 spectrophotometer and corrected for background absorption. Photoluminescence spectra were obtained by an ISS PC1 spectrofluorometer with Xenon lamp as excitation source. Absolute PL quantum efficiencies of the PMMA films doped with 6% of the complexes were measured by the integration sphere method using 325 nm from He-Cd lasing source. Transient PL measurements were recorded from the PMMA films doped with 6% of the complexes using 325 nm excitation wavelength from He-Cd laser. The current-voltage characteristics of the EL devices were measured with a PR650 (Spectra Scan) Source Measurement Unit.

7. OLED Fabrication

For the electroluminescence studies, the EL devices were fabricated as described below. A precleaned indium tin oxide (ITO) from Samsung Corning with a sheet resistance of 10

Ω/cm^2 was treated with UV-ozone plasma. A 50 nm thick hole injecting PEDOT-PSS (AI4083) from Bayer was spin coated on the ITO surface and dried at 120 ^oC for 5 minutes in a glove box. The emissive layers were prepared from the solution of polystyrene (PS, typical Mw: 240K, Mn: 120K), mCP and the phosphor dopant with in a weight percent ratio of PS-mCP-dopant (20:74:6) in toluene and spun cast on top of the PEDOT-PSS layer to yield a 40 nm thick film. A 40 nm thick BAlq layer was then deposited as a hole blocking as well as electron transporting layer followed by the thermal evaporation at 10^{-6} torr. Finally, LiF (0.9 nm) and Al (200 nm) were deposited as the cathode through a shadow mask by thermal evaporation. The multilayer light emitting devices have the configuration of ITO/PEDOT-PSS (50 nm)/PS-mCP-dopant (20:74:6)/BAlq (40 nm)/LiF (0.9nm)/ Al (200 nm). Three different EL devices were fabricated using **FZN**, **FCZN** and **FDZN** phosphorescent dopants, and the device performances were investigated. All the measurements were made under ambient conditions.

8. Figure S2. Oxidative cyclicvoltammograms of FZN, FCZN, FDZN and MeOFZN