Supporting Information

High efficient deep blue phosphorescence from heptafluoropropyl-substituted iridium complexes

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Synthesis of Materials

2-(2,4-Difluorophenyl)-4-methylpyridine

2-Bromo-4-methylpyridine (10.00 g, 60.68 mmol), 2,4-difluorophenylboronic acid (11.50 g, 72.81 mmol) and tetrakis(triphenylphosphine)palladium(0) (2.10 g, 3 mol%) were dissolved in freshly distilled THF (150 mL). A solution of 4 M K_2CO_3 (30 mL) and ethanol (15 mL) were added and the mixture was refluxed with stirring for 24 h in the nitrogen atmosphere. After it was cooled, the mixture was poured into 2 N HCl and extracted with ether. The solution was dried over magnesium sulfate and removed solvent. The product was purified by chromate-graphy on silicagel using methylene chloride as the eluent. Yield: 11.10 g, 89%. ^{1}H-NMR (300MHz, $CDCl_3$, ppm): 8.55-8.57 (d, 1H), 7.99-8.07 (m, 1H), 7.61 (s, 1H), 7.12-7.14 (d, 1H), 6.93-7.08 (m, 2H), 2.44 (s, 3H).

2-(2,4-Difluoro-3-iodophenyl)-4-methylpyridine

2-(2,4-Difluorophenyl)-4-methylpyridine (11.02 g, 53.70 mmol) was dissolved in freshly distilled THF (160 mL) under a nitrogen atmosphere. Lithium diisopropylamide (30.9 mL, 2 M) in n-hexane/ THF was added to the solution at -78^{o}C and the mixture was stirred for 1 h. Then, iodine (16.35 g, 64.44 mmol) dissolved in THF (60 ml) was added to the solution, and the mixture was stirred for 3 h at -78^{o}C, and warmed to room temperature. After reaction, water (200 ml) was added and the solution was extracted with diethylether. The ether solution was washed with saturated sodium thiosulfate and brine. The product was purified by chromate-graphy on silicagel using hexane/ethyl acetate (5:1 v/v) as the eluent. Yield: 12.42 g, 70%. ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.56-8.58 (d, 1H), 7.97-8.05 (m, 1H), 7.61 (s, 1H), 7.15-7.17 (d, 1H), 7.04-7.10 (m, 1H), 2.44 (s, 3H). (EI^+) m/z calcd for $C_{12}H_8F_2NI$ 331 ($[M]^+$), found 331.

2-(2,4-Difluoro-3-(perfluoropropyl)phenyl)-4-methylpyridine

2-(2,4-Difluoro-3-iodophenyl)-4-methylpyridine (5.00 g, 15.10 mmol) and heptafluoropropyl iodide (4.50 g, 15.10 mmol) were dissolved into DMF (25 mL), and freshly precipitated copper powder (4.9 g, 75.5 mmol) was added and the resulting mixture stirred at 130°C for 20 h, cooled to room temperature, poured into water (30 mL), and extracted with methylene chloride. The product was purified by chromatography on silicagel using methylene chloride as the eluent. Yield: 2.82g, 50%. ^{1}H-NMR (300MHz, $CDCl_3$, ppm): 8.58-8.60 (d, 1H), 8.23-8.31 (m, 1H), 7.61 (s, 1H), 7.17-7.23 (m, 2H), 2.45 (s, 3H). ^{19}F-NMR (500 MHz, $CDCl_3$, ppm): -81.14 (3F), -108.13 (2F), -109.33 (1F), -113.89 (1F), -127.92 (2F). HRMS (EI^+) m/z calcd for $C_{15}H_8F_9N$ 373.0513 ($[M]^+$), found 373.0511.

$[(HFP)_2IrCl]_2$

Iridium trichloride hydrate (0.92 g, 3.08 mmol) and 2-(2,4-difluoro-3-(perfluoropropyl)phenyl)-4-methylpyridine (2.30 g, 6.16 mmol) were dissolved in a mixture of 2-ethoxyethanol (21 mL) and water (7 mL) and refluxed for 24 h. The solution was cooled to room temperature. Then, 100 mL of water was added to the cooled solution and the resulting yellow precipitate was collected on a glass filter. The precipitate was washed with water. Yield: 2.58 g, 85%

$(HFP)_2Ir(pic)$

$[(HFP)_2IrCl]_2$ complex (0.95 g, 0.49 mmol), picolinic acid (0.18 g, 1.46 mmol) and sodium carbonate (0.52 g, 4.88 mmol) were dissolved in 2-ethoxyethanol (8 mL) and the mixture was heated to 50°C under nitrogen for 10 h. The reaction mixture was then cooled to room temperature. The 20 mL of water was added to the mixture and the solution was extracted with methylene chloride. The organic layer was dried over and the solvent was removed under reduced pressure to give a yellow powder. The crude product was purified by chromatography on silica gel (ethyl acetate/hexane, 1/1, v/v) to obtain a light yellow powder. Yield: 0.62 g,

60%. ^{1}H-NMR (300MHz, $CDCl_3$, ppm): 8.58-8.60 (d, 1H), 8.35-8.37 (d, 1H), 8.19 (s, 1H), 8.13 (s, 1H), 7.98-8.04 (t, 1H), 7.73-7.75 (d, 1H), 7.49-7.53 (t, 1H), 7.27-7, 29 (d, 1H),12-7.14 (s, 1H), 6.89-6.91 (d, 1H), 6.00-6.04 (d, 1H), 5.72-5.76 (d, 1H), 2.60 (s, 6H) ^{19}F-NMR (500 MHz, $CDCl_3$, ppm): -81.06 (6F), -107.25 (4F), -109.75 (1F), -110.28 (1F), -112.36 (1F), -112.77 (1F), -127.80 (4F). HRMS (FAB^+) m/z calcd for $C_{36}H_{18}F_{18}N_3O_2Ir$ 1059.0741 ($[M+H]^+$), found 1060.0817. Elem. Anal. Cacld (%) for $C_{36}H_{18}F_{18}N_3O_2Ir$: C, 40.84; H,1.71; N, 3.97. Found: C, 41.02; H, 1.701; N, 3.87

$(HFP)_2Ir(mpic)$

The synthetic procedure was similarly proceeded with $(HFP)_2Ir(pic)$

Yield: 0.47 g, 53%. ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.54-8.56 (d, 1H), 8.23 (s, 1H), 8.16 (s, 1H), 8.11 (s, 1H), 7.57-7.59 (d, 1H) 7.35-7.37 (d, 1H), 7.27-7.30 (d, 1H), 7.15-7.17 (d, 1H), 6.97-6.99 (d, 1H), 6.06-6.09 (d, 1H), 5.83-5.87 (d, 1H), 2.59-2.60 (d, 6H), 2.50 (s, 3H). ^{19}F-NMR (500 MHz, $CDCl_3$, ppm): -81.08 (6F), -107.20 (4F), -109.8 (1F), -110.36 (1F), -112.48 (1F), -112.83 (1F), -127.79 (4F). HRMS (FAB^+) m/z calcd for $C_{37}H_{20}F_{18}N_3O_2Ir$ 1073.0897 ($[M+H]^+$), found 1074.1038. Elem. Anal. Cacld (%) for $C_{37}H_{20}F_{18}N_3O_2Ir$: C, 41.43; H,1.88; N, 3.92. Found: C, 41.75; H, 1.68; N, 3.93

$(HFP)_2Ir(fptz)$

The synthetic method was similar with that of $(HFP)_2Ir(pic)$

Yield: 1.40 g, 59%. ^{1}H-NMR (300MHz, CD_2Cl_2, ppm): 8.29-8.32 (d, 1H), 8.22 (s, 1H), 8.17 (s, 1H), 7.98-8.04 (t, 1H), 7.74-7.76 (d, 1H), 7.55-7.57 (d, 1H), 7.37-7.39 (d, 1H), 7.30-7.35 (t, 1H), 6.96-6.98 (d, 1H), 6.89-6.92 (d, 1H), 6.04-6.08 (d, 1H), 5.94-5.97 (d, 1H), 2.55-2.56 (d, 6H). ^{19}F-NMR (500 MHz, $CDCl_3$, ppm): -64.36 (3F), -81.06 (6F), -107.23 (4F), -108.79 (1F), -109.51 (1F), -111.82 (1F), -112.35 (1F), -127.65 (4F). HRMS (FAB^+) m/z calcd for

$C_{38}H_{18}F_{21}N_6Ir$ 1150.0887 ($[M+H]^+$), found 1151.1007. Elem. Anal. Cacld (%) for $C_{38}H_{18}F_{21}N_6Ir$: C, 39.70; H,1.58; N, 7.31. Found: C, 40.23; H, 1.49; N, 7.23

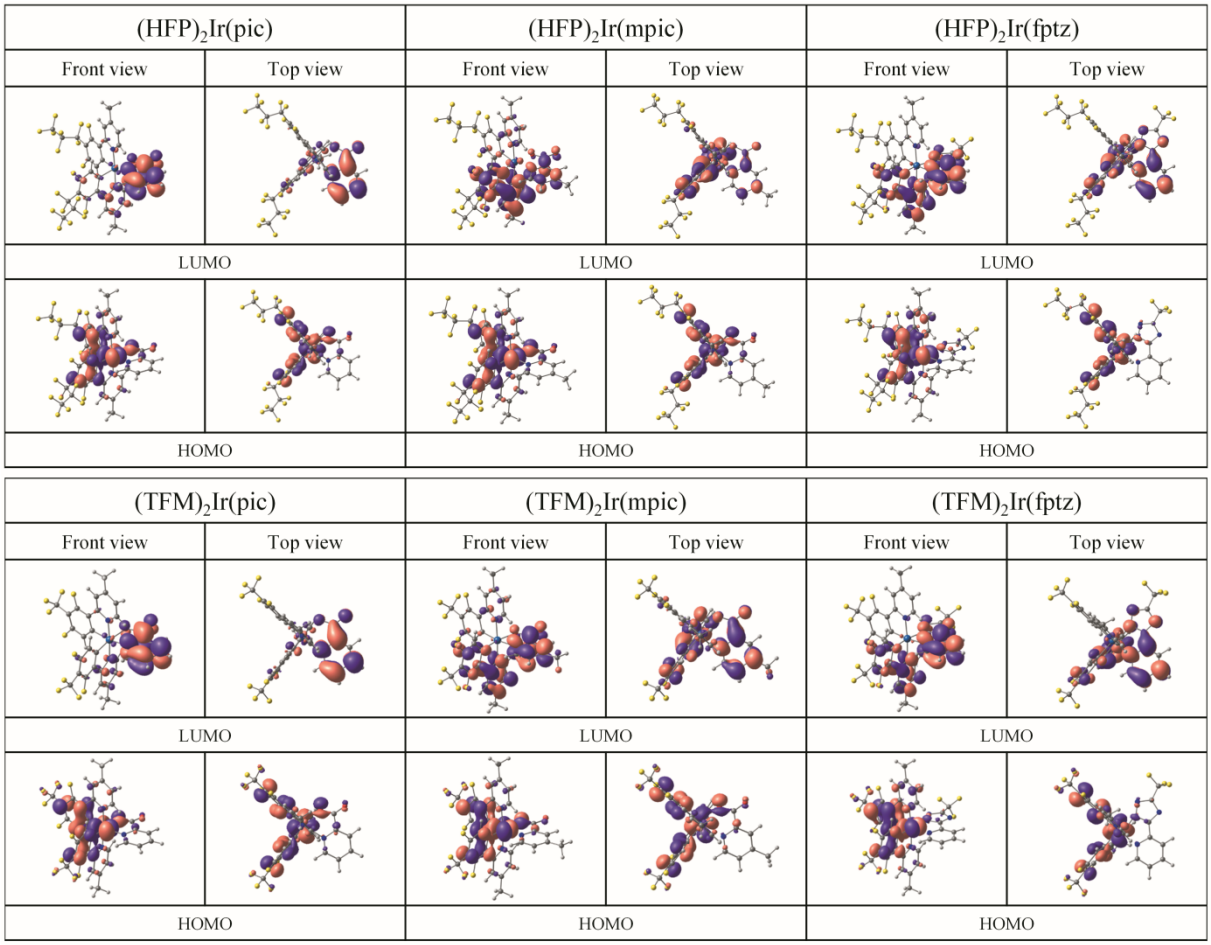

Figure S1. Contributions of the frontier molecular orbitals of the iridium complexes to the lowest triplet state, calculated using the density functional theory with B3LYP/ 6-31G as the base set.

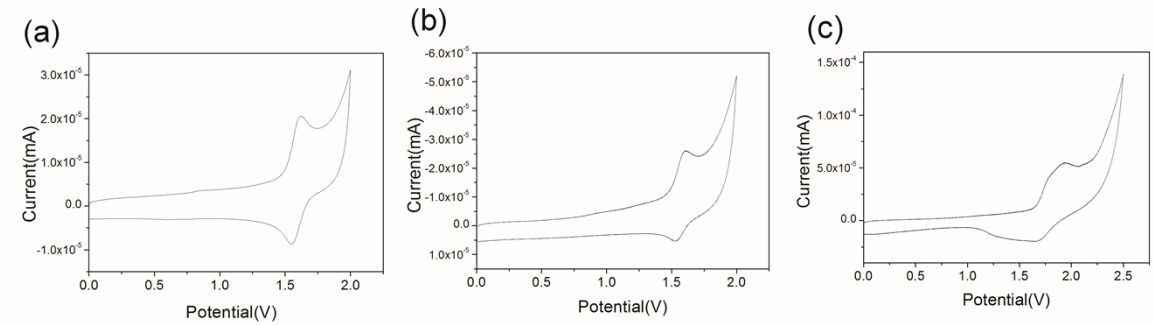

Figure S2 Cyclic voltammetry UV-vis spectra of (a) $(HFP)_2Ir(pic)$, (b) $(HFP)_2Ir(mpic)$, and $(HFP)_2Ir(fptz)$

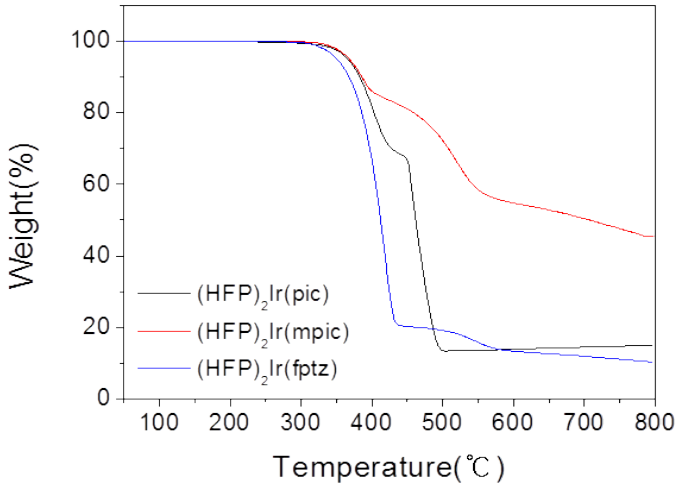

Figure S3 TGA thermograms of the iridium complexes.

Table S1. Photophysical and Electronic Properties of the Iridium Complexes

Ir complex	absorption[a] [nm]	PL[a] [nm]	fwhm[a] [nm]	HOMO [eV]	E_g[b] [eV]	LUMO [eV]	PL[c] [nm]	Qy[c] (%)	Life time[c] [μs]	τ_r[c] [μs]	τ_{nr}[c] [μs]	k_r[c] [$10^5 s^{-1}$]	k_{nr}[c] [$10^5 s^{-1}$]
$(HFP)_2Ir(pic)$	255,277, 370	451, 479	47.8	5.94	2.98	2.96	458, 486	81 ±3	1.46	1.8	7.68	0.55	0.13
$(HFP)_2Ir(mpic)$	255,278, 372	452, 480	47.8	5.92	2.99	2.93	458, 486	90 ±3	1.47	1.63	14.7	0.61	0.07
$(HFP)_2Ir(fptz)$	255,272, 356	446, 475	48.6	6.13	3.00	3.13	452, 481	53 ±3	1.99	3.75	4.23	0.27	0.24

[a]Measured in a $CHCl_3$ solution at room temperature; [b]Optical band gap; [c]Measured using 50-nm-thick mCPPO1films doped with the iridium complexes in the amount of 10 wt %.

Table S2. Electroluminescence Characteristics of the Phosphorescent Blue OLEDs

Ir complex	Voltage (V)		EL_{max} (nm)	CIE (x,y)	EQE (%)			Current Efficiency (cd/A)		Power Efficiency (lm/W)	
	Turn on[a]	@100 cd/m²	@5 mA/cm²	@100 cd/m²	Max.	@100 cd/m²	@5 mA/cm²	Max.	@100 cd/m²	Max.	@100 cd/m²
$(HFP)_2Ir(pic)$	3.3	4.8	452	(0.147, 0.164)	19.7	13.2	7	23.4	15.7	22.3	10.4
$(HFP)_2Ir(mpic)$	3.3	4.6	452	(0.146, 0.165)	21.4	15.7	6.6	27.2	19.9	25.9	13.3
$(HFP)_2Ir(fptz)$	3.3	4.9	447	(0.152, 0.148)	14.2	8.5	4.7	15.3	9.1	14.5	5.9

[a] turn on voltage @ 1 cd/m²

Table S3. The DFT calculation results of irridium complexes with heptafluoropropyl group

Entry	isomer	Energy	del E [kcal/mol]	S1		T1		d(S1-T1)	MLCT(T1)	description
				[eV]	[nm]	[eV]	[nm]	[eV]	[%]	
$(HFP)_2Ir(pic)$	A	-3598.4906	0.00	3.121	397.28	2.896	428.12	0.22	41.00%	H-(L+1) 39%, H-L 15%
$(HFP)_2Ir(mpic)$	A	-3637.8017	0.00	3.173	390.73	2.893	428.51	0.28	40.60%	H-L 51%
$(HFP)_2Ir(fptz)$	A	-3987.9123	0.00	3.307	374.95	2.947	420.66	0.36	41.50%	H-L 21%, H-(L+1) 18%, H-(L+2) 12%

Table S4. Energy levels of frontier orbitals, calculated using the density functional theory with B3LYP/6-31G as the base set.

Entry	isomer	HOMO-1	HOMO	LUMO	LUMO+1	HOMO-1	HOMO	LUMO	LUMO+1	H-L(eV)
$(HFP)_2Ir(pic)$	A	-0.2362	-0.2286	-0.08636	-0.08321	-6.43	-6.22	-2.35	-2.26	3.87
$(HFP)_2Ir(mpic)$	A	-0.2342	-0.2267	-0.08266	-0.08007	-6.37	-6.17	-2.25	-2.18	3.92
$(HFP)_2Ir(fptz)$	A	-0.2476	-0.2386	-0.09022	-0.08823	-6.74	-6.49	-2.46	-2.40	4.04

Table S5 The DFT calculation results of irridium complexes with trifluoromethyl group using the density functional theory with B3LYP/6-31G as the base set.

Entry	isomer	Energy	S1		T1		d(S1-T1)	MLCT(T1)	description
			(eV)	(nm)	(eV)	(nm)	(eV)	(%)	
$(TFM)_2Ir(pic)$	A	-2647.5969	3.093	400.88	2.899	427.70	0.19	42.80%	H-(L+1) 33%, (H-1)-L 16%, H-L 13%
$(TFM)_2Ir(mpic)$	A	-3637.8017	3.152	393.31	2.892	428.78	0.26	41.10%	H-L 36%, H-(L+1) 23%
$(TFM)_2Ir(fptz)$	A	-3987.9123	3.290	376.84	2.946	420.84	0.34	42.00%	H-(L+1) 25%, H-L 19%, (H-2)-(L+1) 13%

Table S6 Energy levels of frontier orbitals, calculated using the density functional theory with B3LYP/6-31G as the base set.

Entry	isomer	HOMO-1	HOMO	LUMO	LUMO+1	HOMO-1	HOMO	LUMO	LUMO+1	H-L(eV)
$(TFM)_2Ir(pic)$	A	-0.2348	-0.2267	-0.08556	-0.08195	-6.39	-6.17	-2.33	-2.23	3.84
$(TFM)_2Ir(mpic)$	A	-0.2329	-0.2249	-0.08202	-0.07977	-6.34	-6.12	-2.23	-2.17	3.89
$(TFM)_2Ir(fptz)$	A	-0.2464	-0.2369	-0.08931	-0.08726	-6.70	-6.45	-2.43	-2.37	4.02

Table S7 Td(5% weight loss) of the iridium complexes.

Iridium complex	$(HFP)_2Ir(pic)$	$(HFP)_2Ir(mpic)$	$(HFP)_2Ir(fptz)$
Td (℃) (5% weight loss)	366	368	355