Electronic Supplementary Information for Dalton Transactions

Supporting Information

Blue-Emitting Ir(III) Phosphors with Ancillary 4,6-Difluorobenzyl diphenylphosphine Based Cyclometalate

Jui-Yi Hung,[a] Yun Chi,*[,a] I-Hsuan Pai,[a] Ya-Chien Yu,[b] Gene-Hsiang Lee,[b] Pi-Tai Chou,*[,b] Ken-Tsung Wong,[b] Chung-Chia Chen,[c] Chung-Chih Wu,*[,c]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan, Fax: (+886) 3 572 0864; E-mail: ychi@mx.nthu.edu.tw*

[b] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Fax: (+886) 2 2369 5208; E-mail: chop@ntu.edu.tw*

[c] *Department of Electrical Engineering and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei 106, Taiwan, Fax: (+886) 2 2367 1909; E-mail: chungwu@cc.ee.ntu.edu.tw*

General procedures: All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV_{254}). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

Synthesis of *trans*-(N_{py},N_{py})-[Ir(dfppy)$_2$(dfbdp)Cl] (1). (2,4-difluorobenzyl) diphenylphosphine (dfbdpH, 69 mg, 0.22 mmol) and [(dfppy)$_2$Ir(μ-Cl)]$_2$ (122 mg, 0.1 mmol) were added in anhydrous CH_2Cl_2 (20 mL) and the mixture was stirred at room temperature for 12 hours. After removal of solvent *in vacuo*, the residue was subjected to silica gel column chromatography using a 1:1 mixture of ethyl acetate and hexane as the eluent. The pale yellow crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at RT (137 mg, 0.15 mmol, 74%).

Spectra data of 1: MS (FAB): *m*/*z* 885 ($M–Cl^+$). ^{1}H NMR (400 MHz, $CDCl_3$, 294K): δ 9.36 (d, *J* = 6.0 Hz, 1H), 9.14 (d, *J* = 5.6 Hz, 1H), 8.37 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.25 ~ 7.30 (m, 3H), 7.18 ~ 7.22 (m, 1H), 7.01 ~ 7.07 (m, 6H), 6.96 (t, *J* = 6.8 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 6.57 ~ 6.62 (m, 1H), 6.33 ~ 6.46 (m, 3H), 6.22 (td, *J* = 10.4 Hz, 2.4 Hz, 1H), 5.70 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.27 (td, *J* = 7.2 Hz, 2.4 Hz, 1H) 3.74 (dd, *J* = 16.0, 5.2 Hz, 1H), 3.66 (dd, *J* = 15.6, 4.8 Hz, 1H). $^{19}F–\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 294K): δ −107.30 (dd, *J* = 9.8, 7.5 Hz, 1F), −108.25 (d, *J* = 10.5 Hz, 1F), −109.70 (t, *J* = 9.8 Hz, 1F), −110.12 (d, *J* = 10.5 Hz, 1F), −110.57 (d, *J* = 7.5 Hz, 1F), −111.84 (dd, *J* = 7.5, 4.5 Hz, 1F). $^{31}P–\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 294K): δ −3.41 (s, 1P). Anal. calcd. For $C_{41}H_{27}ClF_6IrN_2P$: N, 3.04; C, 53.51; H, 2.96. Found: N,

3.02; C, 53.50; H, 2.78.

Selected crystal data of **1**: $C_{41}H_{27}ClF_6IrN_2P$, M = 920.27, monoclinic, space group P2(1)/c, T = 150(2) K, a = 10.9279(6), b = 9.5832(6), c = 34.0479(19) Å, β = 94.773(1)°, V = 3553.3(4) Å^3, Z = 4, ρ_{calcd} = 1.720 Mg/m^3, F(000) = 1800, λ(Mo-K$_\alpha$) = 0.7107 Å, μ = 3.943 mm^{-1}, crystal size = 0.42 × 0.12 × 0.06 mm^3, 8038 independent reflections collected (R_{int} = 0.0457), GOF = 1.167, final $R_1[I > 2\sigma(I)]$ = 0.0411, wR_2(all data) = 0.0843, and D-map, max./min. = 1.788/−1.844 e/Å^3.

Synthesis of *cis*-(N_{py},N_{py})-[Ir(dfppy)$_2$(dfbdp)Cl] (2). (2,4-difluorobenzyl) diphenylphosphine (dfbdpH, 69 mg, 0.22 mmol) and [(dfppy)$_2$Ir(μ-Cl)]$_2$ (122 mg, 0.1 mmol) were added in decahydronaphthalene (30 mL) and the mixture was refluxed for 8 hour. After cooling to RT and removal of solvent, the residue was subjected to silica gel column chromatography using a 1:3 mixture of ethyl acetate and hexane as the eluent. The pale yellow crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at RT (94 mg, 0.1 mmol, 51%).

Spectra data of 2: MS (FAB): m/z 885 (M–Cl$^+$). ^{1}H NMR (500 MHz, $CDCl_3$, 294K): δ 9.14 (d, J = 5.0 Hz, 1H), 8.24 (d, J = 9.0 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.56 ~ 7.65 (m, 3H), 7.28 ~ 7.32 (m, 3H), 7.16 (t, J = 7.5 Hz, 1H), 7.03 ~ 7.17 (m, 4H), 6.97 (td, J = 7.5 Hz, 2.5 Hz, 2H), 6.93 (t, J = 4.0 Hz, 1H), 6.83 (t, J = 6.0 Hz, 1H), 6.74 (t, J = 7.0 Hz, 1H), 6.60 ~ 6.67 (m, 2H), 6.41 ~ 6.49 (m, 2H), 6.34 (td, J = 11.0, 2.0 Hz, 1H), 6.26 (dd, J = 9.0, 2.0 Hz, 1H), 3.92 (dd, J = 16.0, 8.0 Hz, 1H), 3.31 (dd, J = 15.0, 8.0 Hz, 1H). ^{19}F–{^{1}H} NMR (376 MHz, $CDCl_3$, 294K): δ −107.72 (d, J = 10.2 Hz, 1F), −108.70 (d, J = 9.8 Hz, 1F); −108.99 (d, J = 10.5 Hz, 1F), −109.04 (d, J = 8.3 Hz, 1F), −109.48 (d, J = 10.5 Hz, 1F), −109.48 (dd, J = 7.5, 4.6 Hz, 1F). ^{31}P–{^{1}H} NMR (202 MHz, $CDCl_3$, 294K): δ −6.45 (d, J = 4.6 Hz, 1P). Anal. calcd. For $C_{41}H_{27}ClF_6IrN_2P$: N, 3.04; C, 53.51; H, 2.96. Found: N, 2.96; C, 53.81; H, 3.10.

Selected crystal data of **2**: $C_{41}H_{27}ClF_6IrN_2P$, M = 920.27, monoclinic, space group C2/c, T = 150(2) K, a =34.6365(14), b = 11.3201(5), c = 18.1593(7) Å, β =

107.152(1)°, V = 6803.4(5) Å^3, Z = 8, ρ_{calcd} = 1.797 Mg/m^3, F(000) = 3600, λ(Mo-K$_\alpha$) = 0.7107 Å, μ = 4.118 mm^{-1}, crystal size = 0.26 × 0.20 × 0.05 mm^3, 7813 independent reflections collected (R_{int} = 0.0534), GOF = 1.127, final $R_1[I > 2\sigma(I)]$ = 0.0363, wR_2(all data) = 0.0885, and D-map, max./min. = 1.886/–1.306 e/Å^3.

Synthesis of [Ir(dfppy)$_2$(dfbdp)] (3). (2,4-difluorobenzyl) diphenylphosphine (dfbdpH, 69 mg, 0.22 mmol), [(dfppy)$_2$Ir(μ-Cl)]$_2$ (122 mg, 0.1 mmol) and sodium acetate (82 mg, 1 mmol) were added in degassed decahydronaphthalene (20 mL) and the mixture was refluxed for 26 hours. After cooling to RT and removal of solvent, the residue was subjected to silica gel column chromatography using a 1:1 mixture of ethyl acetate and hexane as the eluent. The pale yellow crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at RT (76 mg, 0.09 mmol, 43%).

Spectra data of 3: MS (FAB): m/z 885 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$, 294K): δ 8.21 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.60 ~ 7.65 (m, 3H), 7.51 (d, J = 5.5 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.29 (t, J = 7.0 Hz, 2H), 7.19 ~ 7.21 (m, 1H), 6.91 (t, J = 7.0 Hz, 1H), 6.85 (t, J = 6.5 Hz, 1H), 6.78 (t, J = 6.0 Hz, 3H), 6.56 ~ 6.62 (m, 3H), 6.33 ~ 6.44 (m, 4H), 5.75 (d, J = 9.0 Hz, 1H), 4.43 (t, J = 15.5 Hz, 1H), 3.94 (dd, J = 17.0, 7.5 Hz, 1H). ^{19}F–{^{1}H} NMR (376 MHz, $CDCl_3$, 294K): δ –109.25 (d, J = 10.5 Hz, 1F), –109.71 ~ –109.79 (m, 4F), –115.50 (d, J = 6.0 Hz, 1F). ^{31}P–{^{1}H} NMR (202 MHz, $CDCl_3$, 294K): δ 14.71 (s, 1P). Anal. calcd. for $C_{41}H_{26}F_6IrN_2P$: N, 3.17; C, 55.72; H, 2.97. Found: N, 3.19; C, 55.49; H, 3.31.

Selected crystal data of **3**: $C_{42}H_{28}Cl_2F_6IrN_2P$, M = 968.73, Triclinic, space group P-1, T = 150(2) K, a = 9.7300(5), b = 10.1357(5), c = 18.3439(9) Å, α = 80.580(1)°, β = 80.553(1)°, γ = 80.913(1)°, V = 1744.44(15) Å^3, Z = 2, ρ_{calcd} = 1.844 Mg/m^3, F(000) = 948, λ(Mo-K$_\alpha$) = 0.7107 Å, μ = 4.095 mm^{-1}, crystal size = 0.40 × 0.10 × 0.07 mm^3, 7985 independent reflections collected (R_{int} = 0.0411), GOF = 1.051, final $R_1[I > 2\sigma(I)]$ = 0.0293, wR_2(all data) = 0.0677, and D-map, max./min. = 1.663/ –1.318 e/Å^3.

Synthesis of [Ir(dfpbpy)$_2$(dfbdp)] (4). (2,4-difluorobenzyl) diphenylphosphine (dfbdpH, 69 mg, 0.22 mmol), [(dfpbpy)$_2$Ir(μ-Cl)]$_2$ (144 mg, 0.1 mmol) and sodium acetate (82 mg, 1 mmol) were added in degassed decahydronaphthalene (20 mL) and the mixture was refluxed for 28 hours. After cooling to RT and removal of solvent, the residue was subjected silica gel column chromatography using a 1:1 mixture of ethyl acetate and hexane as the eluent. The pale yellow crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at RT (92 mg, 0.09 mmol, 46%).

Spectra data of 4: MS (FAB): *m*/*z* 996 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$, 294K): δ 8.21 (s, 1H), 8.08 (s, 1H), 7.63 (t, *J* = 8.5 Hz, 2H), 7.36 ~ 7.39 (m, 2H), 7.29 (t, *J* = 6.5 Hz, 2H), 7.13 (dd, *J* = 6.0, 3.5 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 6.75 ~ 6.78 (m, 3H), 6.63 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.57 (t, *J* = 9.0 Hz, 2H), 6.33 ~ 6.44 (m, 4H), 5.75 (dd, *J* = 5.5, 1.5 Hz, 1H), 4.41 (t, *J* = 15.0 Hz, 1H), 3.92 (dd, *J* = 16.0, 7.0 Hz, 1H), 1.28 (s, 9H), 1.23 (s, 9H). ^{19}F–{^{1}H} NMR (376 MHz, $CDCl_3$, 294K): δ −110.06 ~ −110.09 (m, 2F), −110.18 (d, *J* = 9.4 Hz, 1F), −110.22 (d, *J* = 10.2 Hz, 1F), −110.52 (d, *J* = 9.4 Hz, 1F), −115.80 (d, *J* = 5.6 Hz, 1F). ^{31}P–{^{1}H} NMR (202 MHz, $CDCl_3$, 294K): δ 14.83 (s, 1P). Anal. calcd. for $C_{49}H_{42}F_6IrN_2P$: N, 2.81; C, 59.09; H, 4.25. Found: N, 3.19; C, 58.91; H, 4.25

Synthesis of [Ir(dfppy)$_2$(bdp)] (5). Benzyldiphenylphosphine (bdpH, 61 mg, 0.22 mmol), [(dfppy)$_2$Ir(μ-Cl)]$_2$ (122 mg, 0.1 mmol) and sodium acetate (82 mg, 1 mmol) were added in degassed decahydronaphthalene (30 mL) and the mixture was refluxed for 26 hours. After cooling to RT and removal of solvent, the residue was subjected to silica gel column chromatography using a 1:3 mixture of ethyl acetate and hexane as the eluent. The pale yellow crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at RT (70 mg, 0.08 mmol, 41%).

Spectra data of 5: MS (FAB): *m*/*z* 848 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$, 294K): δ 8.17 (d, *J* = 9.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.55 ~ 7.64 (m, 4H), 7.36 ~ 7.40

(m, 3H), 7.28 (t, *J* = 7.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 6.72 ~ 6.83 (m, 6H), 6.62 ~ 6.66 (m, 3H), 6.38 ~ 6.43 (m, 1H), 6.27 ~ 6.35 (m, 3H), 4.32 (dd, *J* = 15.5, 8.0 Hz, 1H), 4.21 (t, *J* = 15.0, 1H). $^{19}F-\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 294K): δ −110.05 ~ −110.01 (m, 2F), −110.23 (d, *J* = 10.9 Hz, 1F); −110.28 (d, *J* = 9.0 Hz, 1F), $^{31}P-\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 294K): δ 13.34 (s, 1P). Anal. calcd. For $C_{41}H_{28}F_4IrN_2P$: N, 3.30; C, 58.08; H, 3.33. Found: N, 2.96; C, 57.84; H, 3.10.

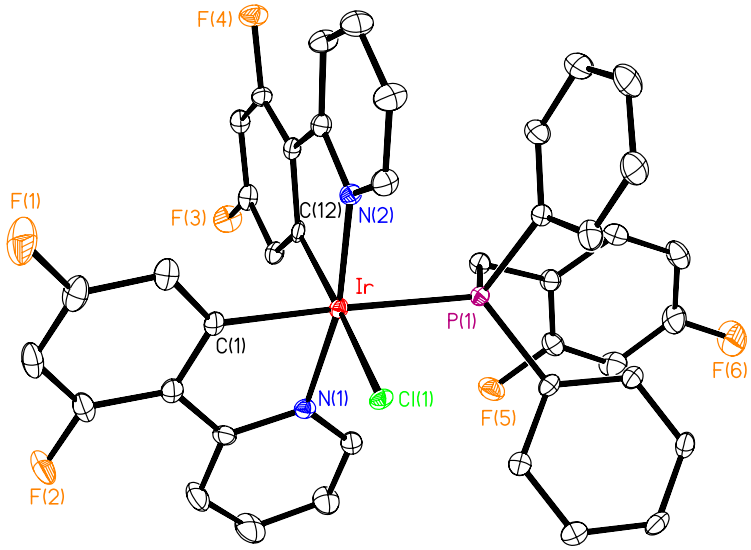

Figure S1. ORTEP diagram of complex **1**; selected bond distances: Ir-C(12) = 2.006(4), Ir-C(1) = 2.035(5), Ir-N(2) = 2.036(4), Ir-N(1) = 2.064(4), Ir-P(1) = 2.391(1), Ir-Cl(1) = 2.487(1) Å.

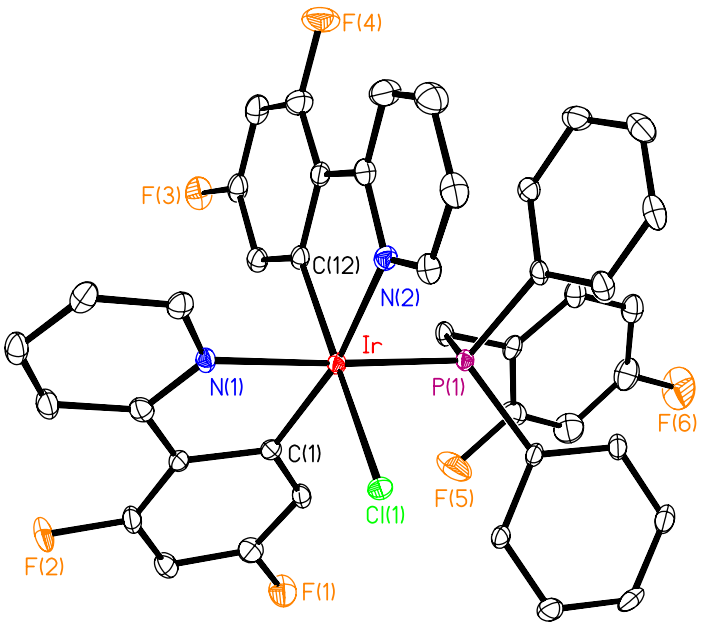

Figure S2. ORTEP diagram of complex **2**; selected bond distances: Ir-C(12) = 2.005(4), Ir-C(1) = 2.039(4), Ir-N(1) = 2.100(3), Ir-N(2) = 2.118(4), Ir-P(1) = 2.288(1), Ir-Cl(1) = 2.481(1) Å.

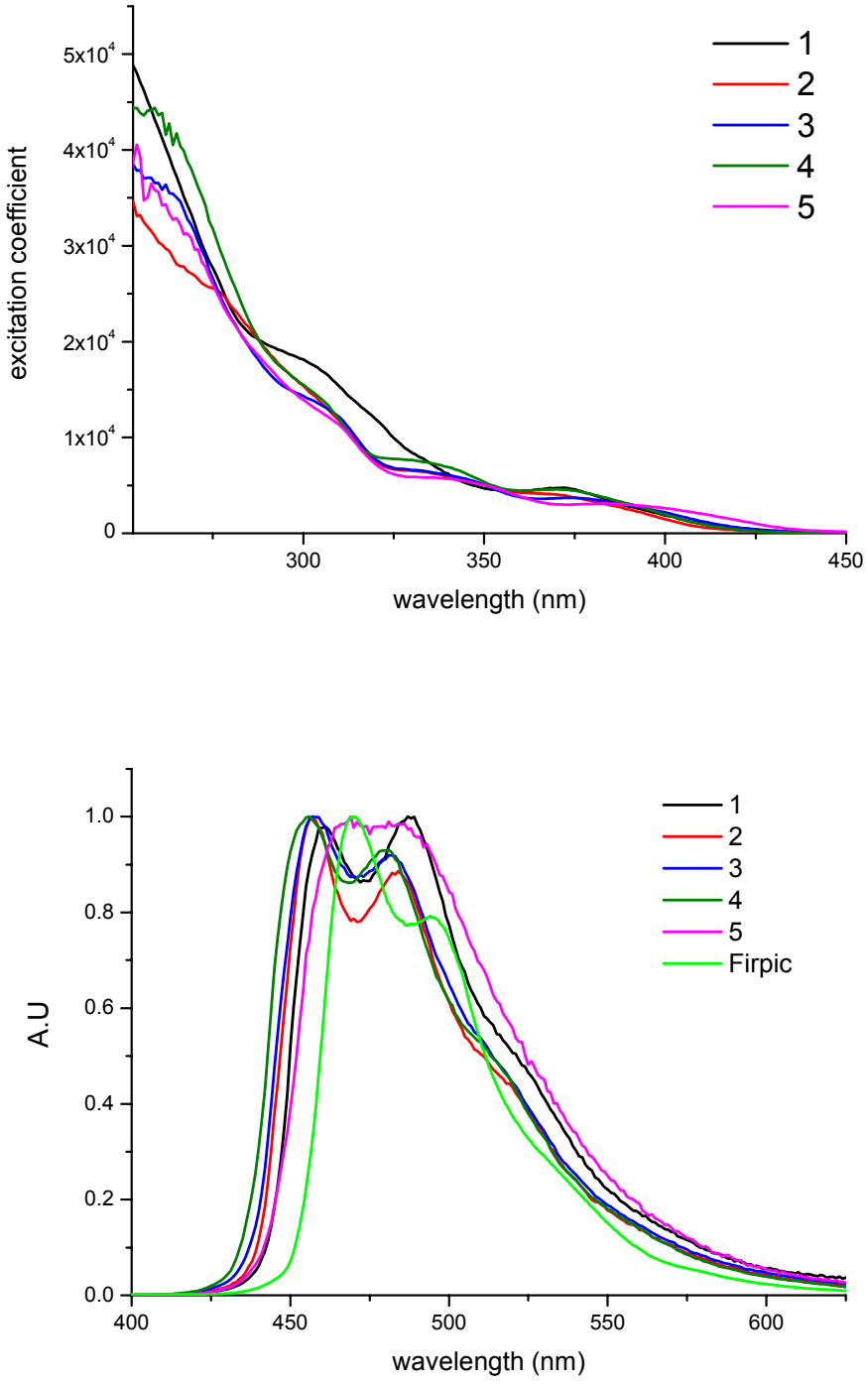

Figure S3. The UV-Vis absorption and emission spectra of Ir(III) complexes **1 ~ 5** and **Firpic** in CH_2Cl_2 at RT.

Table S1. Performance characteristics for the OLEDs based on complexes **4**.

sample		η_{ext} (%)	η_l (cd/A)	η_p (lm/W)	V_{on} (@ 1 cd/m^2)	CIE (x, y) (@ 100 cd/m^2)	Max. Luminance (cd/m^2) (@V)
4	Peak	10.24	15.95	10.07	4.6V	(0.156, 0.199)	9679 (20.0V)
	100 cd/m^2	9.09	14.14	6.17			