

## Supporting Information

### Exploring the effect of the cyclometallating ligand in 2-(pyridine-2-yl)benzo[*d*]thiazole-containing iridium(III) complexes for stable light-emitting electrochemical cells

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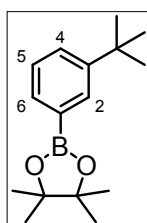
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## SYNTHETIC DETAILS

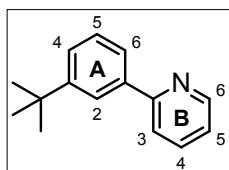
1-Phenylisoquinoline (piq) was synthesized according to a literature procedure<sup>1</sup> and the <sup>1</sup>H NMR spectroscopic data matched those reported. Adaptation of the reported synthesis of 2-(pyridin-2-yl)benzo[*d*]thiazole (btzpy)<sup>2</sup> gave 2-phenylbenzo[*d*]thiazole (pbtz)<sup>3</sup> and <sup>1</sup>H NMR spectroscopic data were compared to those described in the literature. 1-Phenyl-1*H*-pyrazole (ppz) was synthesized adapting a literature procedure;<sup>4</sup> <sup>1</sup>H NMR spectroscopic data matched those reported.<sup>5</sup>

### 2-(3-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



1-Bromo-3-*tert*-butylbenzene (0.24 mL, 300 mg, 1.38 mmol), bis(pinacolato)diboron (712 mg, 2.78 mmol), KOAc (406 mg, 4.14 mmol) and Pd(dppf)<sub>2</sub>Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (56.6 mg, 69.3 μmol) were suspended in THF (dry, 20 mL) in a microwave vial, purged with N<sub>2</sub> and the reaction mixture heated at 90 °C for 1 h in a microwave reactor (4 bar). The resulting mixture was filtered over celite, washed with EtOAc (100 mL) and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane–5% EtOAc) to yield 2-(3-(*tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a yellow oil which solidified upon standing (258 mg, 0.992 mmol, 71.9%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ/ppm 7.83 (ddd, *J* = 1.9, 1.2, 0.6 Hz, 1H, H<sup>2</sup>), 7.64 (dt, *J* = 7.3, 1.2 Hz, 1H, H<sup>6</sup>), 7.50 (ddd, *J* = 7.9, 2.3, 1.3 Hz, 1H, H<sup>4</sup>), 7.31 (ddd, *J* = 7.9, 7.2, 0.6 Hz, 1H, H<sup>5</sup>), 1.35 (s, 12H, H<sup>BO2C2(CH3)4</sup>), 1.35 (s, 9H, H<sup>*t*Bu</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ/ppm 150.4 (C<sup>3</sup>), 132.2 (C<sup>6</sup>), 131.5 (C<sup>2</sup>), 128.5 (C<sup>4</sup>), 127.6 (C<sup>5</sup>), 83.8 (C<sup>BO2C2(CH3)4</sup>), 34.8 (C<sup>C(CH3)3</sup>), 31.6 (C<sup>C(CH3)3</sup>), 25.0 (C<sup>BO2C2(CH3)4</sup>). The signal for C<sup>1</sup> was not resolved. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ/ppm 31.25. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic data matched those reported in the literature.<sup>6</sup>

### 2-(3-(*tert*-Butyl)phenyl)pyridine (tppy)



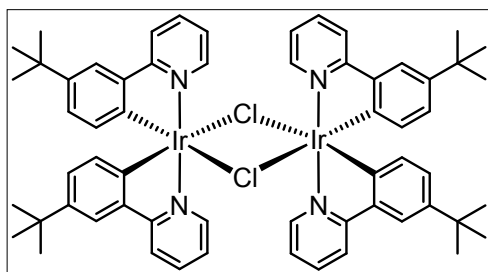
The synthesis of 2-(3-(*tert*-butyl)phenyl)pyridine (tppy) has been previously reported,<sup>7</sup> but the following procedure gives a higher yield. 2-(3-(*tert*-Butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (205 mg, 0.788 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (23.1 mg, 32.9 μmol), 2-bromopyridine (63 μL, 104 mg, 0.658 mmol) and Na<sub>2</sub>CO<sub>3</sub> (210 mg, 1.98 mmol) were suspended in THF (5 mL) and H<sub>2</sub>O (5 mL) in a microwave vial. The mixture was heated at 100 °C for 30 min in

a microwave reactor (7 bar), then poured into H<sub>2</sub>O (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 60 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane–5% EtOAc) to yield 2-(3-(*tert*-butyl)phenyl)pyridine (tppy) as a colourless oil (127 mg, 0.601 mmol, 91.3%). <sup>1</sup>H NMR spectroscopic data matched those reported in the literature.<sup>7</sup>

### General procedure for the synthesis of chlorido-bridged iridium(III) dimers

[Ir(tppy)<sub>2</sub>Cl]<sub>2</sub>, [Ir(piq)<sub>2</sub>Cl]<sub>2</sub>, [Ir(ppz)<sub>2</sub>Cl]<sub>2</sub> and [Ir(pbtz)<sub>2</sub>Cl]<sub>2</sub> were synthesized according to the standard method.<sup>8,9</sup> The cyclometallating ligand was suspended in a mixture of 2-ethoxyethanol and H<sub>2</sub>O (3:1) and purged with N<sub>2</sub>. IrCl<sub>3</sub>·xH<sub>2</sub>O was added and the reaction mixture was heated at reflux overnight. After letting the mixture cool to room temperature, the precipitation was collected, washed with EtOH and Et<sub>2</sub>O and dried. The dimers were characterized by <sup>1</sup>H NMR spectroscopy and used for subsequent reactions without further purification.

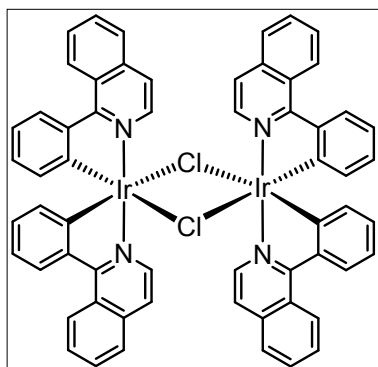
#### [Ir(tppy)<sub>2</sub>Cl]<sub>2</sub>



IrCl<sub>3</sub>·xH<sub>2</sub>O (ca. 82% IrCl<sub>3</sub>, 772 mg, 2.12 mmol, 1.0 eq.) and 2-(3-(*tert*-butyl)phenyl)pyridine (tppy) (894 mg, 4.23 mmol, 2.0 eq.) in 40 mL solvent. [Ir(tppy)<sub>2</sub>Cl]<sub>2</sub> was isolated as a yellow powder (905 mg, 1.06 mmol, 65.9%). <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>) δ/ppm 9.17 (ddd, *J* = 5.8, 1.7, 0.7 Hz, 4H), 7.89–7.84 (m, 4H), 7.71 (ddd, *J* = 8.1, 7.4, 1.6 Hz, 4H), 7.48 (d, *J* = 2.2 Hz, 4H), 6.73 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 4H), 6.64 (dd, *J* = 8.2, 2.2 Hz, 4H), 5.93 (d, *J* = 8.2 Hz, 4H), 1.17 (s, 36H).

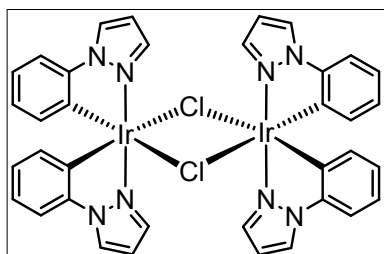
#### [Ir(piq)<sub>2</sub>Cl]<sub>2</sub>



IrCl<sub>3</sub>·xH<sub>2</sub>O (ca. 82% IrCl<sub>3</sub>, 444 mg, 1.22 mmol, 1.0 eq.) and 1-phenylisoquinoline (piq) (501 mg, 2.44 mmol, 2.0 eq.) in 20 mL solvent. [Ir(piq)<sub>2</sub>Cl]<sub>2</sub> was isolated as a dark red powder (532 mg, 610 μmol, 68.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm 9.05 (d, *J* = 6.4 Hz, 4H), 8.99–8.95 (m, 4H), 8.15–8.11 (m, 4H), 7.88–7.80 (overlapping m, 8H), 7.76 (ddd, *J* = 8.4,

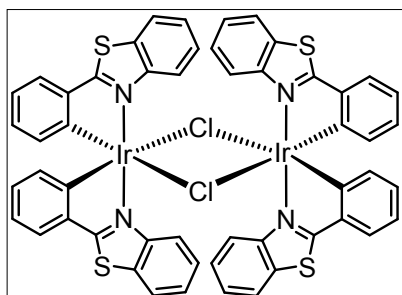
6.4, 2.0 Hz, 4H), 6.81 (ddd,  $J = 8.2, 7.1, 1.3$  Hz, 4H), 6.55 (dd,  $J = 6.5, 0.8$  Hz, 4H), 6.50 (ddd,  $J = 8.3, 7.1, 1.3$  Hz, 4H), 6.03 (dd,  $J = 7.9, 1.2$  Hz, 4H).  $^1\text{H}$  NMR spectroscopic data matched those reported in the literature.<sup>10</sup>

### **[Ir(ppz)<sub>2</sub>Cl]<sub>2</sub>**



$\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  (ca. 82%  $\text{IrCl}_3$ , 564 mg, 1.55 mmol, 1.0 eq.) and 1-phenyl-1*H*-pyrazole (ppz) (447 mg, 3.10 mmol, 2.0 eq.) in 28 mL solvent.  $[\text{Ir}(\text{ppz})_2\text{Cl}]_2$  was isolated as an off-white powder (733 mg, 775  $\mu\text{mol}$ , 92.0%).  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$ /ppm 8.71 (dd,  $J = 2.9, 0.7$  Hz, 4H), 7.81 (dd,  $J = 2.1, 0.7$  Hz, 4H), 7.40 (dd,  $J = 7.9, 1.3$  Hz, 4H), 6.87 (dd,  $J = 2.9, 2.2$  Hz, 4H), 6.75 (ddd,  $J = 7.8, 7.3, 1.3$  Hz, 4H), 6.48 (*pseudo*-td,  $J = 7.5, 1.3$  Hz, 4H), 5.94 (dd,  $J = 7.6, 1.3$  Hz, 4H).

### **[Ir(pbtz)<sub>2</sub>Cl]<sub>2</sub>**



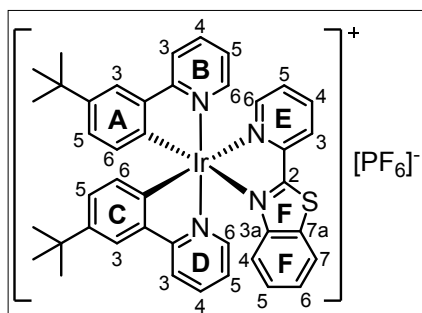
$\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  (ca. 82%  $\text{IrCl}_3$ , 221 mg, 606  $\mu\text{mol}$ , 1.0 eq.) and 2-phenylbenzo[*d*]thiazole (pbtz) (256 mg, 1.21 mmol, 2.0 eq.) in 10 mL solvent.  $[\text{Ir}(\text{pbtz})_2\text{Cl}]_2$  was isolated as an orange powder (323 mg, 249  $\mu\text{mol}$ , 82.2%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm 8.76 (dd,  $J = 7.8, 1.7$  Hz, 4H), 7.53 (dd,  $J = 7.6, 1.5$  Hz, 4H), 7.43–7.39 (m, 4H), 7.10–7.01 (overlapping m, 8H), 6.75 (*pseudo*-td,  $J = 7.4, 1.2$  Hz, 4H), 6.42 (*pseudo*-td,  $J = 7.6, 1.5$  Hz, 4H), 5.99 (d,  $J = 7.7$  Hz, 4H).

### **General procedure for the synthesis of iridium(III) complexes**

The iridium dimer and  $\text{AgPF}_6$  were suspended in MeOH (20–25 mL) and stirred at room temperature for 2.5–4 h. The mixture was filtered through Celite® and washed with MeOH. The filtrate was concentrated under reduced pressure to yield  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{MeOH})_2][\text{PF}_6]$  which was neither purified nor characterized. Ancillary ligand and MeOH (2–10 mL) were added immediately to the solvento intermediate and the mixture stirred at room temperature overnight. The resulting orange-red precipitate was filtered off, redissolved in  $\text{CH}_2\text{Cl}_2$  and concentrated under reduced pressure. The crude product was purified by column chromatography (silica) and solvent removed. The residue was dissolved in little  $\text{CH}_2\text{Cl}_2$  and precipitated with  $\text{Et}_2\text{O}$  and/or *n*-hexane. When necessary, the complex was dissolved in little

CH<sub>2</sub>Cl<sub>2</sub>, layered with toluene and *n*-hexane and kept in the refrigerator overnight. The resulting precipitation was filtered off and dried under vacuum. The reported yields (over two steps) were calculated based on the iridium dimer starting material.

### Complex 1 – [Ir(tppy)<sub>2</sub>(btzpy)][PF<sub>6</sub>]

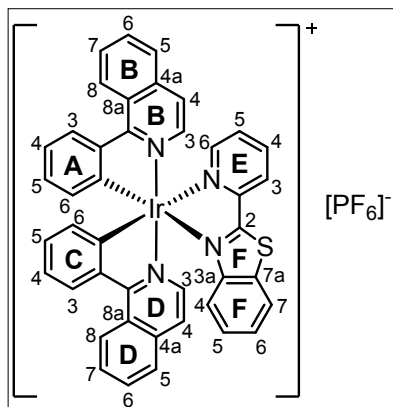


[Ir(tppy)<sub>2</sub>Cl]<sub>2</sub> (151 mg, 0.116 mmol) and AgPF<sub>6</sub> (83.3 mg, 0.329 mmol) in MeOH (25 mL), 3.5 h at room temperature. Addition of 2-(pyridin-2-yl)benzo[*d*]thiazole (btzpy) (49.3 mg, 0.232 mmol) and MeOH (5 mL). Purification by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub> changing to CH<sub>2</sub>Cl<sub>2</sub>–2% MeOH) and precipitation with

Et<sub>2</sub>O/*n*-hexane. [Ir(tppy)<sub>2</sub>(btzpy)][PF<sub>6</sub>] was isolated as a red solid (180 mg, 0.186 mmol, 80.0%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ/ppm 8.43 (*pseudo*-dt, *J* = 8.0, 1.1 Hz, 1H, H<sup>E3</sup>), 8.19 (*pseudo*-td, *J* = 7.9, 1.5 Hz, 1H, H<sup>E4</sup>), 8.06 (*pseudo*-dt, *J* = 8.4, 0.8 Hz, 1H, H<sup>F7</sup>), 8.02–7.98 (overlapping m, 2H, H<sup>B3+E6</sup>), 7.93 (*pseudo*-dt, *J* = 8.3, 1.0 Hz, 1H, H<sup>D3</sup>), 7.83–7.71 (overlapping m, 4H, H<sup>A3+B4+C3+D4</sup>), 7.61 (ddd, *J* = 5.8, 1.6, 0.8 Hz, 1H, H<sup>B6</sup>), 7.57–7.49 (overlapping m, 2H, H<sup>E5+F6</sup>), 7.47 (*pseudo*-dt, *J* = 5.8, 1.2 Hz, 1H, H<sup>D6</sup>), 7.16 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H, H<sup>F5</sup>), 7.12 (dd, *J* = 8.0, 2.1 Hz, 1H, H<sup>C5</sup>), 7.07 (dd, *J* = 8.0, 2.1 Hz, 1H, H<sup>A5</sup>), 6.99 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H, H<sup>D5</sup>), 6.93 (ddd, *J* = 7.3, 5.8, 1.4 Hz, 1H, H<sup>B5</sup>), 6.79 (dd, *J* = 8.5, 0.8 Hz, 1H, H<sup>F4</sup>), 6.35 (d, *J* = 8.0 Hz, 1H, H<sup>C6</sup>), 6.20 (d, *J* = 8.0 Hz, 1H, H<sup>A6</sup>), 1.38 (s, 9H, H<sup>C4-*t*Bu</sup>), 1.35 (s, 9H, H<sup>A4-*t*Bu</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ/ppm 170.0 (C<sup>F2</sup>), 168.8 (C<sup>D2</sup>), 168.2 (C<sup>B2</sup>), 152.3 (C<sup>E2</sup>), 151.5 (C<sup>E6</sup>), 151.2 (C<sup>F3a</sup>), 150.3 (C<sup>B6</sup>), 149.2 (C<sup>D6</sup>), 146.8 (C<sup>C4</sup>), 146.6 (C<sup>A4</sup>), 144.5 (C<sup>C2</sup>), 143.8 (C<sup>C1</sup>), 143.7 (C<sup>A2</sup>), 143.6 (C<sup>A1</sup>), 140.4 (C<sup>E4</sup>), 138.7 (C<sup>B4/D4</sup>), 138.6 (C<sup>B4/D4</sup>), 134.9 (C<sup>F7a</sup>), 132.6 (C<sup>C6</sup>), 131.3 (C<sup>A6</sup>), 129.9 (C<sup>E5</sup>), 129.10 (C<sup>A5/F5</sup>), 129.08 (C<sup>A5/F5</sup>), 128.9 (C<sup>F6</sup>), 128.6 (C<sup>C5</sup>), 126.8 (C<sup>E3</sup>), 123.9 (C<sup>B5</sup>), 123.8 (C<sup>D5</sup>), 123.6 (C<sup>F7</sup>), 123.4 (C<sup>F4</sup>), 122.4 (C<sup>A3</sup>), 122.2 (C<sup>C3</sup>), 120.4 (C<sup>B3</sup>), 120.2 (C<sup>D3</sup>), 34.84 (C<sup>C4-C(CH3)3</sup>), 34.80 (C<sup>A4-C(CH3)3</sup>), 31.8 (C<sup>C4-C(CH3)3</sup>), 31.7 (C<sup>A4-C(CH3)3</sup>). IR (solid,  $\tilde{\nu}$ /cm<sup>-1</sup>) 2953 (w), 2865 (w), 1608 (w), 1561 (w), 1537 (w), 1479 (m), 1429 (m), 1362 (w), 1323 (w), 1297 (w), 1269 (w), 1254 (m), 1202 (w), 1161 (w), 1114 (w), 1070 (w), 1029 (w), 1007 (w), 876 (w), 834 (s), 780 (s), 754 (s), 729 (m), 709 (m), 644 (m), 623 (m), 556 (s), 477 (w), 436 (w), 416 (w). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>, 1.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>) λ/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 257 (47 000), 270 sh (44 000), 335 (24 000), 350 sh (19 000), 387 (9200), 412 (7400). Emission (CH<sub>2</sub>Cl<sub>2</sub>, 1.0 ×

$10^{-5} \text{ mol dm}^{-3}$ ,  $\lambda_{\text{exc}} = 268 \text{ nm}$ )  $\lambda_{\text{em}}^{\text{max}} = 660 \text{ nm}$ . ESI-MS  $m/z$  825.2 [ $M\text{-PF}_6$ ] $^+$  (calc. 825.3). Found C 51.84, H 4.34, N 6.03;  $\text{C}_{42}\text{H}_{40}\text{F}_6\text{IrN}_4\text{PS}$  requires C 52.00, H 4.16, N 5.78%.

### Complex 2 – $[\text{Ir}(\text{piq})_2(\text{btzpy})][\text{PF}_6]$

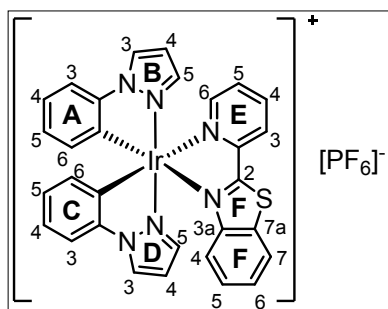


$[\text{Ir}(\text{piq})_2\text{Cl}]_2$  (151 mg, 0.119 mmol) and  $\text{AgPF}_6$  (77.4 mg, 0.306 mmol) in MeOH (25 mL), 3 h at room temperature. Addition of 2-(pyridin-2-yl)benzo[*d*]thiazole (btzpy) (50.8 mg, 0.239 mmol) and MeOH (10 mL). Purification by column chromatography (silica,  $\text{CH}_2\text{Cl}_2$  changing to  $\text{CH}_2\text{Cl}_2$ -2% MeOH), layering with toluene/*n*-hexane and subsequent precipitation with *n*-hexane from a  $\text{CH}_2\text{Cl}_2$  solution.  $[\text{Ir}(\text{piq})_2(\text{btzpy})][\text{PF}_6]$  was isolated as a dark orange

solid (180 mg, 0.188 mmol, 78.9%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ /ppm 9.04–8.97 (overlapping m, 1H,  $\text{H}^{\text{B}8}$ ), 8.94 (*pseudo*-dt,  $J = 7.1, 3.5 \text{ Hz}$ , 1H,  $\text{H}^{\text{D}8}$ ), 8.49 (d,  $J = 7.9 \text{ Hz}$ , 1H,  $\text{H}^{\text{E}3}$ ), 8.36 (*pseudo*-dt,  $J = 8.2, 1.5 \text{ Hz}$ , 2H,  $\text{H}^{\text{A}3+\text{C}3}$ ), 8.19 (*pseudo*-td,  $J = 7.9, 1.5 \text{ Hz}$ , 1H,  $\text{H}^{\text{E}4}$ ), 8.06 (dd,  $J = 8.3, 0.9 \text{ Hz}$ , 1H,  $\text{H}^{\text{F}7}$ ), 7.95–7.88 (overlapping m, 2H,  $\text{H}^{\text{B}5+\text{D}5}$ ), 7.85–7.80 (overlapping m, 3H,  $\text{H}^{\text{B}6+\text{B}7+\text{E}6}$ ), 7.80–7.75 (overlapping m, 2H,  $\text{H}^{\text{D}6+\text{D}7}$ ), 7.54 (d,  $J = 6.4 \text{ Hz}$ , 1H,  $\text{H}^{\text{B}3}$ ), 7.52–7.47 (overlapping m, 2H,  $\text{H}^{\text{E}5+\text{F}6}$ ), 7.37 (s, 2H,  $\text{H}^{\text{D}3+\text{D}4}$ ), 7.32 (d,  $J = 6.4 \text{ Hz}$ , 1H,  $\text{H}^{\text{B}4}$ ), 7.25 (ddd,  $J = 8.2, 7.3, 1.3 \text{ Hz}$ , 1H,  $\text{H}^{\text{C}4}$ ), 7.22–7.16 (overlapping m, 2H,  $\text{H}^{\text{A}4+\text{F}5}$ ), 7.00–6.90 (overlapping m, 2H,  $\text{H}^{\text{A}5+\text{C}5}$ ), 6.68 (d,  $J = 8.4 \text{ Hz}$ , 1H,  $\text{H}^{\text{F}4}$ ), 6.43 (dd,  $J = 7.8, 1.2 \text{ Hz}$ , 1H,  $\text{H}^{\text{C}6}$ ), 6.27 (dd,  $J = 7.6, 1.2 \text{ Hz}$ , 1H,  $\text{H}^{\text{A}6}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ /ppm 170.0 ( $\text{C}^{\text{F}2}$ ), 169.6 ( $\text{C}^{\text{D}1}$ ), 169.0 ( $\text{C}^{\text{B}1}$ ), 152.1 ( $\text{C}^{\text{E}2}$ ), 151.5 ( $\text{C}^{\text{E}6}$ ), 151.1 ( $\text{C}^{\text{F}3\text{a}}$ ), 150.9 ( $\text{C}^{\text{C}1}$ ), 150.8 ( $\text{C}^{\text{A}1}$ ), 146.7 ( $\text{C}^{\text{C}2}$ ), 146.0 ( $\text{C}^{\text{A}2}$ ), 141.8 ( $\text{C}^{\text{B}3}$ ), 140.7 ( $\text{C}^{\text{D}3}$ ), 140.5 ( $\text{C}^{\text{E}4}$ ), 137.7 ( $\text{C}^{\text{B}4\text{a}}$ ), 137.6 ( $\text{C}^{\text{D}4\text{a}}$ ), 134.8 ( $\text{C}^{\text{F}7\text{a}}$ ), 133.3 ( $\text{C}^{\text{C}6}$ ), 132.54 ( $\text{C}^{\text{B}6}$ ), 132.45 ( $\text{C}^{\text{D}6}$ ), 132.2 ( $\text{C}^{\text{A}6}$ ), 131.5 ( $\text{C}^{\text{A}5}$ ), 131.42 ( $\text{C}^{\text{A}3/\text{C}3}$ ), 131.39 ( $\text{C}^{\text{A}3/\text{C}3}$ ), 131.0 ( $\text{C}^{\text{C}5}$ ), 129.9 ( $\text{C}^{\text{E}5}$ ), 129.6 ( $\text{C}^{\text{B}7}$ ), 129.4 ( $\text{C}^{\text{D}7}$ ), 129.2 ( $\text{C}^{\text{F}5}$ ), 128.9 ( $\text{C}^{\text{F}6}$ ), 128.1 ( $\text{C}^{\text{B}5}$ ), 128.0 ( $\text{C}^{\text{D}5}$ ), 127.4 ( $\text{C}^{\text{D}8}$ ), 127.3 ( $\text{C}^{\text{B}8}$ ), 126.99 ( $\text{C}^{\text{B}8\text{a}}$ ), 126.95 ( $\text{C}^{\text{E}3}$ ), 126.8 ( $\text{C}^{\text{D}8\text{a}}$ ), 123.7 ( $\text{C}^{\text{F}7}$ ), 123.4 ( $\text{C}^{\text{A}4}$ ), 123.2 ( $\text{C}^{\text{F}4}$ ), 123.1 ( $\text{C}^{\text{C}4}$ ), 122.8 ( $\text{C}^{\text{B}4}$ ), 122.5 ( $\text{C}^{\text{D}4}$ ). IR (solid,  $\tilde{\nu}/\text{cm}^{-1}$ ) 3046 (w), 1576 (m), 1541 (m), 1502 (w), 1485 (w), 1448 (m), 1434 (m), 1382 (m), 1352 (m), 1324 (m), 1298 (w), 1272 (m), 1159 (m), 1049 (w), 1030 (w), 1009 (w), 836 (s), 757 (s), 741 (s), 731 (s), 712 (m), 676 (m), 664 (m), 628 (m), 581 (m), 556 (s), 516 (m), 499 (m), 481 (w), 439 (m), 407 (m). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ,  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ )  $\lambda/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 293 (46 000), 335 (35 000), 350 sh (31 000), 380 sh (14 000), 433 (8900),

465 sh (4600). Emission ( $\text{CH}_2\text{Cl}_2$ ,  $1.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ,  $\lambda_{\text{exc}} = 293$  nm)  $\lambda_{\text{em}}^{\text{max}} = 642$  nm. ESI-MS  $m/z$  813.1  $[\text{M}-\text{PF}_6]^+$  (calc. 813.2). HRMS  $m/z$  813.1665 (calc. 813.1658). Found C 50.71, H 3.52, N 5.82;  $\text{C}_{42}\text{H}_{28}\text{F}_6\text{IrN}_4\text{PS} \cdot 2\text{H}_2\text{O}$  requires C 50.75, H 3.25, N 5.64%.

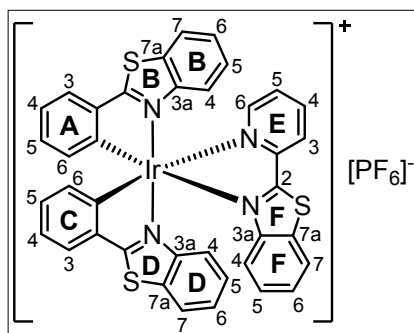
### Complex 3 – $[\text{Ir}(\text{ppz})_2(\text{btzpy})][\text{PF}_6]$



$[\text{Ir}(\text{ppz})_2\text{Cl}]_2$  (101 mg, 0.0982 mmol) and  $\text{AgPF}_6$  (57.6 mg, 0.228 mmol) in MeOH (20 mL), 4 h at room temperature. Addition of 2-(pyridin-2-yl)benzo[d]thiazole (btzpy) (31.0 mg, 0.198 mmol) and MeOH (2 mL). Purification by column chromatography (silica,  $\text{CH}_2\text{Cl}_2$  changing to  $\text{CH}_2\text{Cl}_2$ -1% MeOH) and precipitation with  $\text{Et}_2\text{O}$ .  $[\text{Ir}(\text{ppz})_2(\text{btzpy})][\text{PF}_6]$

was isolated as an orange solid (79.8 mg, 0.0950 mmol, 48.7%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta/\text{ppm}$  8.42 (*pseudo*-dt,  $J = 8.1, 1.0$  Hz, 1H,  $\text{H}^{\text{E}3}$ ), 8.24–8.15 (overlapping m, 3H,  $\text{H}^{\text{B}3+\text{E}4+\text{E}6}$ ), 8.13 (d,  $J = 2.9$  Hz, 1H,  $\text{H}^{\text{D}3}$ ), 8.08 (dd,  $J = 8.2, 0.9$  Hz, 1H,  $\text{H}^{\text{F}7}$ ), 7.59–7.52 (overlapping m, 2H,  $\text{H}^{\text{E}5+\text{F}6}$ ), 7.37 (dd,  $J = 8.1, 1.1$  Hz, 2H,  $\text{H}^{\text{A}3+\text{C}3}$ ), 7.28 (ddd,  $J = 8.5, 7.2, 1.2$  Hz, 1H,  $\text{H}^{\text{F}5}$ ), 7.18–7.10 (overlapping m, 3H,  $\text{H}^{\text{A}4+\text{C}4+\text{F}4}$ ), 6.99–6.88 (overlapping m, 3H,  $\text{H}^{\text{A}5+\text{B}5+\text{C}5}$ ), 6.87 (d,  $J = 2.2$  Hz, 1H,  $\text{H}^{\text{D}5}$ ), 6.55 (*pseudo*-t,  $J = 2.6$  Hz, 2H,  $\text{H}^{\text{B}4+\text{D}4}$ ), 6.38 (dd,  $J = 7.6, 1.3$  Hz, 1H,  $\text{H}^{\text{C}6}$ ), 6.28 (dd,  $J = 7.5, 1.3$  Hz, 1H,  $\text{H}^{\text{A}6}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta/\text{ppm}$  170.5 ( $\text{C}^{\text{F}2}$ ), 152.8 ( $\text{C}^{\text{E}2}$ ), 151.9 ( $\text{C}^{\text{F}3\text{a}}$ ), 151.8 ( $\text{C}^{\text{E}6}$ ), 143.6 ( $\text{C}^{\text{C}2}$ ), 143.3 ( $\text{C}^{\text{A}2}$ ), 140.6 ( $\text{C}^{\text{E}4}$ ), 139.8 ( $\text{C}^{\text{B}5}$ ), 138.78 ( $\text{C}^{\text{D}5}$ ), 134.5 ( $\text{C}^{\text{C}6}$ ), 134.3 ( $\text{C}^{\text{F}7\text{a}}$ ), 133.4 ( $\text{C}^{\text{A}6}$ ), 129.8 ( $\text{C}^{\text{A}1}$ ), 129.5 ( $\text{C}^{\text{E}5}$ ), 129.31 ( $\text{C}^{\text{F}5}$ ), 129.28 ( $\text{C}^{\text{C}1}$ ), 129.0 ( $\text{C}^{\text{F}6}$ ), 127.9 ( $\text{C}^{\text{B}3}$ ), 127.7 ( $\text{C}^{\text{D}3}$ ), 127.6 ( $\text{C}^{\text{A}5}$ ), 127.2 ( $\text{C}^{\text{C}5}$ ), 126.5 ( $\text{C}^{\text{E}3}$ ), 124.4 ( $\text{C}^{\text{A}4}$ ), 124.2 ( $\text{C}^{\text{C}4}$ ), 123.7 ( $\text{C}^{\text{F}7}$ ), 123.2 ( $\text{C}^{\text{F}4}$ ), 112.5 ( $\text{C}^{\text{A}3}$ ), 112.4 ( $\text{C}^{\text{C}3}$ ), 109.0 ( $\text{C}^{\text{B}4}$ ), 108.8 ( $\text{C}^{\text{D}4}$ ). IR (solid,  $\tilde{\nu}/\text{cm}^{-1}$ ) 3147 (w), 1589 (w), 1482 (m), 1459 (w), 1446 (m), 1413 (m), 1338 (m), 1325 (m), 1277 (m), 1248 (w), 1163 (w), 1111 (w), 1075 (m), 1058 (m), 1032 (m), 1010 (w), 968 (w), 918 (w), 836 (s), 751 (s), 730 (m), 703 (m), 656 (m), 610 (m), 557 (s), 477 (m), 457 (m), 437 (m). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ,  $1.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$ )  $\lambda/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) 255 (35 000), 330 (23 000), 350 sh (18 000), 380 sh (5500), 410 sh (3000). Emission ( $\text{CH}_2\text{Cl}_2$ ,  $1.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ,  $\lambda_{\text{exc}} = 261$  nm)  $\lambda_{\text{em}}^{\text{max}} = 607$  nm. ESI-MS  $m/z$  691.1  $[\text{M}-\text{PF}_6]^+$  (calc. 691.1). Found C 42.66, H 3.03, N 10.29;  $\text{C}_{30}\text{H}_{22}\text{F}_6\text{IrN}_6\text{PS} \cdot 0.5\text{H}_2\text{O}$  requires C 42.65, H 2.74, N 9.95%.

### Complex 4 – [Ir(pbtz)<sub>2</sub>(btzpy)] [PF<sub>6</sub>]



[Ir(pbtz)<sub>2</sub>Cl]<sub>2</sub> (151 mg, 0.116 mmol) and AgPF<sub>6</sub> (73.8 mg, 0.292 mmol) in MeOH (25 mL), 2.5 h at room temperature. Addition of 2-(pyridin-2-yl)benzo[*d*]thiazole (btzpy) (49.1 mg, 0.134 mmol) and MeOH (10 mL). Purification by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub> changing to CH<sub>2</sub>Cl<sub>2</sub>–2% MeOH) and precipitation with Et<sub>2</sub>O/*n*-hexane. [Ir(pbtz)<sub>2</sub>(btzpy)] [PF<sub>6</sub>] was isolated as a

bright orange solid (130 mg, 0.134 mmol, 57.8%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ/ppm 8.40 (*pseudo*-dt, *J* = 8.1, 1.1 Hz, 1H, H<sup>E3</sup>), 8.23 (*pseudo*-td, *J* = 7.8, 1.5 Hz, 1H, H<sup>E4</sup>), 8.11 (*pseudo*-dt, *J* = 5.5, 1.0 Hz, 1H, H<sup>E6</sup>), 8.08 (*pseudo*-dt, *J* = 8.4, 0.9 Hz, 1H, H<sup>F7</sup>), 7.93–7.85 (overlapping m, 4H, H<sup>A3+B7+C3+D7</sup>), 7.64–7.55 (overlapping m, 2H, H<sup>E5+F6</sup>), 7.39–7.32 (overlapping m, 2H, H<sup>B6+D6</sup>), 7.28 (ddd, *J* = 8.5, 7.3, 1.2 Hz, 1H, H<sup>F5</sup>), 7.22–7.14 (overlapping m, 2H, H<sup>A4+C4</sup>), 7.11 (ddd, *J* = 8.5, 7.3, 1.2 Hz, 1H, H<sup>D5</sup>), 7.00–6.89 (overlapping m, 4H, H<sup>A5+B5+C5+F4</sup>), 6.52 (dd, *J* = 7.8, 1.0 Hz, 1H, H<sup>C6</sup>), 6.40–6.33 (overlapping m, 2H, H<sup>A6+B4</sup>), 6.01 (d, *J* = 8.4 Hz, 1H, H<sup>D4</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ/ppm 182.3 (C<sup>D2</sup>), 181.5 (C<sup>B2</sup>), 170.3 (C<sup>F2</sup>), 153.1 (C<sup>E2</sup>), 151.8 (C<sup>E6</sup>), 151.6 (C<sup>F3a</sup>), 149.7 (C<sup>D3a</sup>), 149.5 (C<sup>B3a</sup>), 147.4 (C<sup>C1</sup>), 147.3 (C<sup>A1</sup>), 141.4 (C<sup>C2</sup>), 141.0 (C<sup>E4</sup>), 140.6 (C<sup>A2</sup>), 134.4 (C<sup>F7a</sup>), 134.3 (C<sup>C6</sup>), 133.2 (C<sup>A6</sup>), 132.9 (C<sup>A5</sup>), 132.7 (C<sup>C5</sup>), 132.08 (C<sup>B7a/D7a</sup>), 132.05 (C<sup>B7a/D7a</sup>), 130.1 (C<sup>E5</sup>), 129.7 (C<sup>F5</sup>), 129.2 (C<sup>F6</sup>), 128.72 (C<sup>B5/D5</sup>), 128.69 (C<sup>B5/D5</sup>), 127.37 (C<sup>A3/C3</sup>), 127.36 (C<sup>A3/C3</sup>), 126.73 (C<sup>B6/D6/E3</sup>), 126.69 (C<sup>B6/D6/E3</sup>), 126.5 (C<sup>B6/D6</sup>), 124.3 (C<sup>A4</sup>), 124.2 (C<sup>D7</sup>), 124.14 (C<sup>B7</sup>), 124.08 (C<sup>C4</sup>), 124.0 (C<sup>F7</sup>), 123.1 (C<sup>F4</sup>), 118.3 (C<sup>B4</sup>), 117.7 (C<sup>D4</sup>). IR (solid,  $\tilde{\nu}$ /cm<sup>-1</sup>) 3059 (w), 1581 (w), 1552 (w), 1485 (w), 1470 (w), 1459 (w), 1448 (m), 1439 (m), 1408 (m), 1324 (w), 1299 (w), 1267 (m), 1162 (w), 1126 (w), 1078 (w), 1053 (w), 1028 (w), 997 (w), 836 (s), 754 (s), 741 (m), 725 (m), 712 (m), 685 (w), 657 (w), 646 (w), 583 (w), 557 (s), 509 (w), 480 (w), 449 (m). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>, 1.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>) λ/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 253 (32 000), 270 (28 000), 279 (27 000), 290 (26 000), 324 (46 000), 409 (9200), 435 sh (6300). Emission (CH<sub>2</sub>Cl<sub>2</sub>, 1.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, λ<sub>exc</sub> = 326 nm) λ<sub>em</sub><sup>max</sup> = 600 nm. ESI-MS *m/z* 825.0 [*M*-PF<sub>6</sub>]<sup>+</sup> (calc. 825.1). Found C 46.88, H 2.79, N 6.16; C<sub>38</sub>H<sub>24</sub>F<sub>6</sub>IrN<sub>4</sub>PS<sub>3</sub> requires C 47.05, H 2.49, N 5.78%.

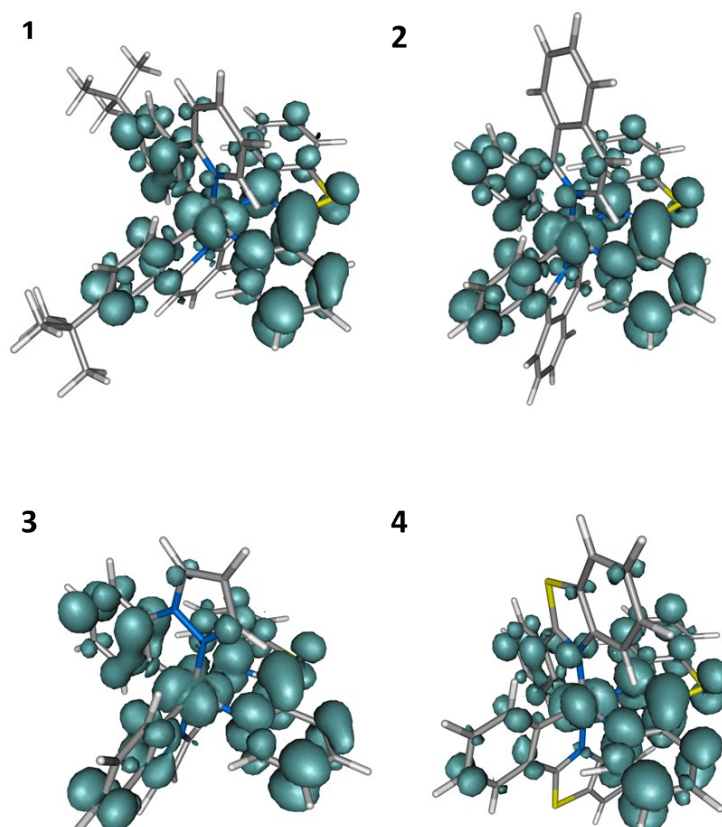


## THEORETICAL CALCULATIONS

**Table S1** Selected bond distances (in Å), bond angles and dihedral angles (in deg.) calculated for complexes **1–4** in the singlet ground state ( $S_0$ ). Calculations were performed at the B3LYP/(6-31G\*\*+LANL2DZ) level in the presence of the solvent ( $\text{CH}_2\text{Cl}_2$ ).

Geometrical parameter	<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>	
Ir–N <sup>C^N</sup>	2.081	2.084	2.084	2.078	2.052	2.053	2.100	2.108
Ir–C <sup>C^N</sup>	2.016	2.023	2.009	2.016	2.026	2.034	2.022	2.028
Ir–N <sup>N^N</sup>	2.230	2.262	2.231	2.263	2.216	2.249	2.232	2.266
C <sup>C^N</sup> –Ir–N <sup>C^N</sup>	80.08	79.93	79.25	79.42	79.72	79.55	79.76	79.63
N <sup>N^N</sup> –Ir–N <sup>N^N</sup>	74.39		74.40		74.85		74.29	
C <sup>C^N</sup> Inter-ring dihedral angle <sup>a</sup>	0.98	0.67	16.87	16.74	0.35	1.26	1.68	1.03
N <sup>N^N</sup> Inter-ring dihedral angle <sup>a</sup>	1.98		2.14		0.68		6.67	

<sup>a</sup> Dihedral angle formed by the average planes of the two rings of the ligand where the coordinated atoms are located.



**Fig. S1** Unpaired-electron spin-density contours (0.002 a.u.) calculated for fully relaxed  $T_1$  states of complexes **1–4**.

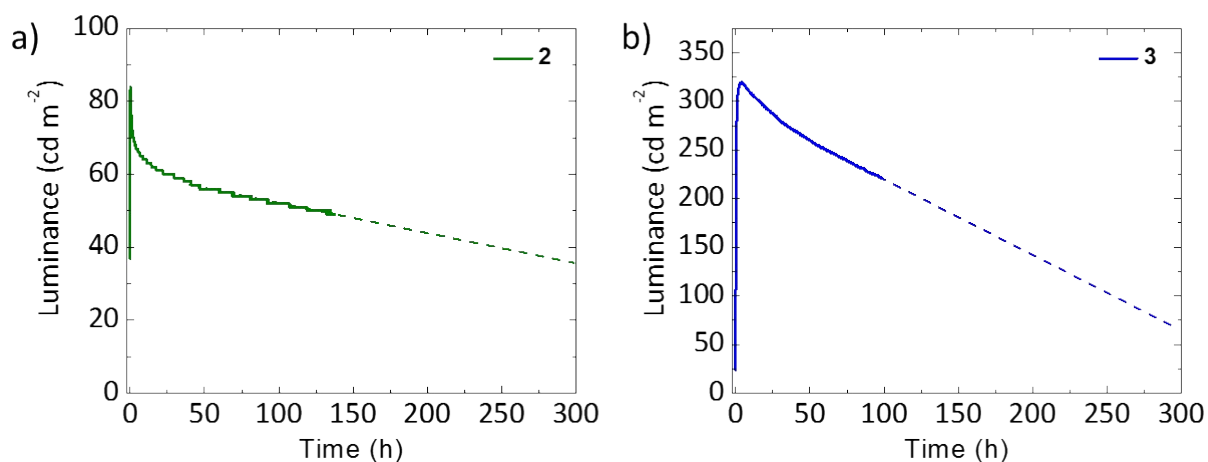
## DETAILED EXCITED-STATE LIFETIME DATA

**Table S2** Detailed excited-state lifetime data of complexes **1–4** in de-aerated CH<sub>2</sub>Cl<sub>2</sub> solution and as powder samples.  $\tau_{\text{ave}}$  = average lifetime.

Complex	Solution <sup>a,b</sup>			Powder <sup>b</sup>		
	$\tau_{\text{ave}}$ [ns]	$\tau_1$ [ns] (A <sub>1</sub> )	$\tau_2$ [ns] (A <sub>2</sub> )	$\tau_{\text{ave}}$ [ns]	$\tau_1$ [ns] (A <sub>1</sub> )	$\tau_2$ [ns] (A <sub>2</sub> )
<b>1</b>	55	---	---	328	175 (5547)	444 (2858)
<b>2</b>	380	251 (8009)	1349 (199)	142	111 (8362)	256 (1006)
<b>3</b>	459	---	---	337	176 (3291)	379 (5783)
<b>4</b>	1200	---	---	730	538 (3936)	808 (6488)

<sup>a</sup> Measured in de-aerated CH<sub>2</sub>Cl<sub>2</sub> solution under an atmosphere of argon. <sup>b</sup>  $\lambda_{\text{exc}} = 280$  nm. Biexponential fits were used for the excited-state lifetime determination of all powder samples and solution samples of **2**, according to the equation  $\tau_{\text{ave}} = \frac{\sum A_i \tau_i}{\sum A_i}$  ( $A_i$  = pre-exponential factor of the lifetime). Monoexponential fits were used for the remaining complexes (no  $\tau_1$  and  $\tau_2$  reported).

## ELECTROLUMINESCENCE DATA



**Fig. S2** Extended luminance vs. time graphs for a) LEC **2** and b) LEC **3**, both operated under an average pulsed current density of 700 A m<sup>-2</sup> (1000 Hz, 50% duty cycle, block wave). Extrapolation in dashed lines.

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