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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SYNTHETIC DETAILS

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

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)Cl₂·CH₂Cl₂ (56.6 mg, 69.3 μmol) were suspended in THF (dry, 20 mL) in a microwave vial, purged with N₂ 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%). 1H NMR (500 MHz, CDCl₃) δ/ppm 7.83 (ddd, J = 1.9, 1.2, 0.6 Hz, 1H, H²), 7.64 (dt, J = 7.3, 1.2 Hz, 1H, H⁶), 7.50 (ddd, J = 7.9, 2.3, 1.3 Hz, 1H, H⁴), 7.31 (ddd, J = 7.9, 7.2, 0.6 Hz, 1H, H⁵), 1.35 (s, 12H, HBO₂C₂(CH₃)₄), 1.35 (s, 9H, HtBu). 13C{¹H} NMR (126 MHz, CDCl₃) δ/ppm 150.4 (C₃), 132.2 (C⁶), 131.5 (C²), 128.5 (C⁴), 127.6 (C⁵), 83.8 (CBO₂C₂(CH₃)₄), 34.8 (C(C(CH₃))₂), 31.6 (C(C(CH₃))₂), 25.0 (CBO₂C₂(CH₃)₄). The signal for C¹ was not resolved. ¹¹B NMR (160 MHz, CDCl₃) δ/ppm 31.25. ¹H and ¹³C{¹H} NMR spectroscopic data matched those reported in the literature.

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

The synthesis of 2-(3-(tert-butyl)phenyl)pyridine (tppy) has been previously reported, 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), PdCl₂(PPh₃)₂ (23.1 mg, 32.9 μmol), 2-bromopyridine (63 μL, 104 mg, 0.658 mmol) and Na₂CO₃ (210 mg, 1.98 mmol) were suspended in THF (5 mL) and H₂O (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 H₂O (100 mL) and extracted with CH₂Cl₂ (3 × 60 mL). The combined organic layers were dried over Na₂SO₄ 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%). ¹H NMR spectroscopic data matched those reported in the literature.⁷

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

[Ir(tppy)₂Cl]₂, [Ir(piq)₂Cl]₂, [Ir(ppz)₂Cl]₂ and [Ir(pbtz)₂Cl]₂ were synthesized according to the standard method.⁸,⁹ The cyclometallating ligand was suspended in a mixture of 2-ethoxyethanol and H₂O (3:1) and purged with N₂. IrCl₃·xH₂O 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 Et₂O and dried. The dimers were characterized by ¹H NMR spectroscopy and used for subsequent reactions without further purification.

**[Ir(tppy)₂Cl]₂**

![Image of [Ir(tppy)₂Cl]₂](image1.png)

IrCl₃·xH₂O (ca. 82% IrCl₃, 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)₂Cl]₂ was isolated as a yellow powder (905 mg, 1.06 mmol, 65.9%). ¹H NMR (400 MHz, CDCl₃) 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)₂Cl]₂**

![Image of [Ir(piq)₂Cl]₂](image2.png)

IrCl₃·xH₂O (ca. 82% IrCl₃, 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)₂Cl]₂ was isolated as a dark red powder (532 mg, 610 µmol, 68.5%). ¹H NMR (400 MHz, CDCl₃) 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). ¹H NMR spectroscopic data matched those reported in the literature.¹⁰

[Ir(ppz)₂Cl]₂

IrCl₃·xH₂O (ca. 82% IrCl₃, 564 mg, 1.55 mmol, 1.0 eq.) and 1-phenyl-1H-pyrazole (ppz) (447 mg, 3.10 mmol, 2.0 eq.) in 28 mL solvent. [Ir(ppz)₂Cl]₂ was isolated as an off-white powder (733 mg, 775 µmol, 92.0%). ¹H NMR (400 MHz, acetone-d₆) δ/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 (dd, 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)₂Cl]₂

IrCl₃·xH₂O (ca. 82% IrCl₃, 221 mg, 606 µmol, 1.0 eq.) and 2-phenylbenzo[d]thiazole (pbtz) (256 mg, 1.21 mmol, 2.0 eq.) in 10 mL solvent. [Ir(pbtz)₂Cl]₂ was isolated as an orange powder (323 mg, 249 µmol, 82.2%). ¹H NMR (400 MHz, CDCl₃) δ/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, 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 AgPF₆ 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 [Ir(C^N)₂(MeOH)₂][PF₆] 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 CH₂Cl₂ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica) and solvent removed. The residue was dissolved in little CH₂Cl₂ and precipitated with Et₂O and/or n-hexane. When necessary, the complex was dissolved in little
CH₂Cl₂, 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)₂(btzpy)][PF₆]**

- [Ir(tppy)₂Cl]₂ (151 mg, 0.116 mmol) and AgPF₆ (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, CH₂Cl₂ changing to CH₂Cl₂–2% MeOH) and precipitation with Et₂O/n-hexane. [Ir(tppy)₂(btzpy)][PF₆] was isolated as a red solid (180 mg, 0.186 mmol, 80.0%).

1H NMR (500 MHz, CD₂Cl₂) δ/ppm 8.43 (pseudo-dt, J = 8.0, 1.1 Hz, 1H, H₃E), 8.19 (pseudo-td, J = 7.9, 1.5 Hz, 1H, H₄E), 8.06 (pseudo-dt, J = 8.4, 0.8 Hz, 1H, H₅T), 8.02–7.98 (overlapping m, 2H, H₃B₃+E₆), 7.93 (pseudo-dt, J = 8.3, 1.0 Hz, 1H, H₆D), 7.83–7.71 (overlapping m, 4H, H₃A₃+B₄+C₃+D₄), 7.61 (ddd, J = 5.8, 1.6, 0.8 Hz, 1H, H₅B₆), 7.57–7.49 (overlapping m, 2H, H₃E₅+F₆), 7.47 (pseudo-dt, J = 5.8, 1.2 Hz, 1H, H₆D), 7.16 (ddd, J = 8.4, 7.1, 1.2 Hz, 1H, H₃F₅), 7.12 (dd, J = 8.0, 2.1 Hz, 1H, H₅C₅), 7.07 (dd, J = 8.0, 2.1 Hz, 1H, H₆A₅), 6.99 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H, H₃F₃), 6.93 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H, H₆B₅), 6.79 (dd, J = 8.5, 0.8 Hz, 1H, H₄F₄), 6.35 (d, J = 8.0 Hz, 1H, H₅C₆), 6.20 (d, J = 8.0 Hz, 1H, H₆A₆), 1.38 (s, 9H, H₃C₄-tBu), 1.35 (s, 9H, H₃A₄-tBu).

13C{¹H} NMR (126 MHz, CD₂Cl₂) δ/ppm 170.0 (C₃F₂), 168.8 (C₄D₂), 168.2 (C₅D₂), 152.3 (C₆E₂), 152.5 (C₇E₂), 151.5 (C₈E₂), 151.2 (C₉E₂), 150.3 (C₁₀B₆), 149.2 (C₁₁D₆), 146.8 (C₁₂C₄), 146.6 (C₁₃A₄), 144.5 (C₁₄C₂), 143.8 (C₁₅C₁), 143.7 (C₁₆A₂), 143.6 (C₁₇A₁), 140.4 (C₁₈E₄), 138.7 (C₁₉B₄D₄), 138.6 (C₂₀B₄D₄), 134.9 (C₂₁F₇), 132.6 (C₂₂C₆), 131.3 (C₂₃A₆), 129.9 (C₂₄E₅), 129.10 (C₂₅A₅/F₅), 129.08 (C₂₆A₅/F₅), 128.9 (C₂₇F₆), 128.6 (C₂₈C₅), 126.8 (C₂₉E₃), 123.9 (C₃₀B₅), 123.8 (C₃₁D₅), 123.6 (C₃₂F₇), 123.4 (C₃₃E₄), 122.4 (C₃₄A₃), 122.2 (C₃₅C₃), 120.4 (C₃₆B₃), 120.2 (CD₃), 34.84 (CC₄-C(CH₃)₃), 34.80 (Ca₄-C(CH₃)₃), 31.8 (CC₄-C(CH₃)₃), 31.7 (Ca₄-C(CH₃)₃). IR (solid, ν/cm⁻¹) 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 (CH₂Cl₂, 1.0 × 10⁻⁵ mol dm⁻³) λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 257 (47 000), 270 sh (44 000), 335 (24 000), 350 sh (19 000), 387 (9200), 412 (7400). Emission (CH₂Cl₂, 1.0 × 10⁻⁵ mol dm⁻³) λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 257 (47 000), 270 sh (44 000), 335 (24 000), 350 sh (19 000), 387 (9200), 412 (7400).
10⁻⁵ mol dm⁻³, \( \lambda_{\text{exc}} = 268 \text{ nm} \) \( \lambda_{\text{em}}^\text{max} = 660 \text{ nm} \). ESI-MS m/z 825.2 [M–PF₆]⁺ (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 – [Ir(piq)₂(btzpy)][PF₆]**

[Ir(piq)₂Cl₂] (151 mg, 0.119 mmol) and AgPF₆ (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, CH₂Cl₂ changing to CH₂Cl₂–2% MeOH), layering with toluene/n-hexane and subsequent precipitation with n-hexane from a CH₂Cl₂ solution. [Ir(piq)₂(btzpy)][PF₆] was isolated as a dark orange solid (180 mg, 0.188 mmol, 78.9%).

\(^1\)H NMR (500 MHz, CD₂Cl₂) δ/ppm 9.04–8.97 (overlapping m, 1H, H^8), 8.94 (pseudo-dt, \( J = 7.1, 3.5 \text{ Hz}, 1\text{H}, \text{H}^8 \)), 8.49 (d, \( J = 7.9 \text{ Hz}, 1\text{H}, \text{H}^E3 \)), 8.36 (pseudo-dt, \( J = 8.2, 1.5 \text{ Hz}, 2\text{H}, \text{H}^{A3+C3} \)), 8.19 (pseudo-dt, \( J = 8.2, 1.5 \text{ Hz}, 2\text{H}, \text{H}^{A3+C3} \)), 8.18 (s, 2H, H^D3+D4), 8.06 (dd, \( J = 8.3, 0.9 \text{ Hz}, 1\text{H}, \text{H}^F7 \)), 7.95–7.88 (overlapping m, 2H, H^B5+D5), 7.54 (d, \( J = 6.4 \text{ Hz}, 1\text{H}, \text{H}^B3 \)), 7.52–7.47 (overlapping m, 2H, H^E5+F6), 7.37 (s, 2H, H^D3+D4), 7.25 (ddd, \( J = 8.2, 7.3, 1.3 \text{ Hz}, 1\text{H}, \text{H}^C4 \)), 7.22–7.16 (overlapping m, 2H, H^A4+F5), 7.00–6.90 (overlapping m, 2H, H^A5+C5), 6.68 (d, \( J = 8.4 \text{ Hz}, 1\text{H}, \text{H}^F4 \)), 6.43 (dd, \( J = 7.8, 1.2 \text{ Hz}, 1\text{H}, \text{H}^E6 \)), 6.27 (dd, \( J = 7.6, 1.2 \text{ Hz}, 1\text{H}, \text{H}^A6 \)). \(^{13}\)C{\(^1\)H} NMR (126 MHz, CD₂Cl₂) δ/ppm 170.0 (C^F2), 169.6 (C^D1), 169.0 (C^B1), 152.1 (C^E2), 151.5 (C^E6), 151.1 (C^F3a), 150.9 (C^C1), 150.8 (C^A1), 146.7 (C^C2), 146.0 (C^A2), 141.8 (C^B3), 140.7 (C^D3), 140.5 (C^E4), 137.7 (C^B4a), 137.6 (C^D4a), 134.8 (C^F7a), 133.3 (C^C6), 132.54 (C^B6), 132.45 (C^D6), 132.2 (C^A6), 131.5 (C^A5), 131.42 (C^A3/C3), 131.39 (C^A3/C3), 131.0 (C^C5), 129.9 (C^E5), 129.6 (C^B7), 129.4 (C^D7), 129.2 (C^F5), 128.9 (C^E6), 128.1 (C^B5), 128.0 (C^D5), 127.4 (C^D8), 127.3 (C^B8), 126.99 (C^B8a), 126.95 (C^E3), 126.8 (C^D8a), 123.7 (C^F7), 123.4 (C^A4), 123.2 (C^F4), 123.1 (C^C4), 122.8 (C^B4), 122.5 (C^D4). 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), 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 (CH₂Cl₂, 1.0 × 10⁻⁵ mol dm⁻³) \( \lambda_{\text{nm}} (\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \) 293 (46 000), 335 (35 000), 350 (sh 31 000), 380 (sh 14 000), 433 (8900),
465 sh (4600). Emission (CH$_2$Cl$_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$, $\lambda_{exc}$ = 293 nm) $\lambda_{em}^{max}$ = 642 nm. ESI-MS m/z 813.1 [M–PF$_6$]$^+$ (calc. 813.2). HRMS m/z 813.1665 (calc. 813.1658). Found C 50.71, H 3.52, N 5.82; C$_{42}$H$_{28}$F$_6$IrN$_4$PS·2H$_2$O requires C 50.75, H 3.25, N 5.64%.

**Complex 3 – [Ir(ppz)$_2$(btzpy)][PF$_6$]**

[Ir(ppz)$_2$Cl$_2$] (101 mg, 0.0982 mmol) and 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, CH$_2$Cl$_2$ changing to CH$_2$Cl$_2$–1% MeOH) and precipitation with Et$_2$O. [Ir(ppz)$_2$(btzpy)][PF$_6$] was isolated as an orange solid (79.8 mg, 0.0950 mmol, 48.7%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$/ppm 8.42 (pseudo-dt, $J$ = 8.1, 1.0 Hz, 1H, H$^E_3$), 8.24–8.15 (overlapping m, 3H, H$^B_3$+E$^4$+E$^6$), 8.13 (d, $J$ = 2.9 Hz, 1H, H$^D_3$), 8.08 (dd, $J$ = 8.2, 0.9 Hz, 1H, H$^F_7$), 7.59–7.52 (overlapping m, 2H, H$^E_5$+F$^6$), 7.37 (dd, $J$ = 8.1, 1.1 Hz, 2H, H$^{A_3}$+C$^3$), 7.28 (ddd, $J$ = 8.5, 7.2, 1.2 Hz, 1H, H$^F_5$), 7.18–7.10 (overlapping m, 3H, H$^{A_4}$+C$^4$+F$^4$), 6.99–6.88 (overlapping m, 3H, H$^{A_5}$+B$^5$+C$^5$), 6.87 (d, $J$ = 2.2 Hz, 1H, H$^D_5$), 6.55 (pseudo-t, $J$ = 2.6 Hz, 2H, H$^{B_4}$+D$^4$), 6.38 (dd, $J$ = 7.6, 1.3 Hz, 1H, H$^A_6$).

$^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$) $\delta$/ppm 170.5 (C$^F_2$), 152.8 (C$^E_2$), 151.9 (C$^{F_3}_a$), 151.8 (C$^{E_6}$), 143.6 (C$^{C_2}$), 143.3 (C$^{A_2}$), 140.6 (C$^{E_4}$), 139.8 (C$^{B_5}$), 138.78 (C$^{D_5}$), 134.5 (C$^{C_6}$), 134.3 (C$^{F_7}_a$), 133.4 (C$^{A_6}$), 129.8 (C$^{A_1}$), 129.5 (C$^{E_5}$), 129.31 (C$^{F_5}$), 129.28 (C$^{C_1}$), 129.0 (C$^{F_6}$), 127.9 (C$^{B_3}$), 127.7 (C$^{D_3}$), 127.6 (C$^{A_5}$), 127.2 (C$^{C_5}$), 126.5 (C$^{E_3}$), 124.4 (C$^{A_4}$), 124.2 (C$^{C_4}$), 123.7 (C$^{F_7}$), 123.2 (C$^{F_4}$), 112.5 (C$^{A_3}$), 112.4 (C$^{C_3}$), 109.0 (C$^{B_4}$), 108.8 (C$^{D_4}$). IR (solid, $\tilde{v}$/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 (CH$_2$Cl$_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$) $\lambda$/nm (e/dm$^3$ mol$^{-1}$ cm$^{-1}$) 255 (35 000), 330 (23 000), 350 sh (18 000), 380 sh (5500), 410 sh (3000). Emission (CH$_2$Cl$_2$, 1.0 × 10$^{-5}$ mol dm$^{-3}$, $\lambda_{exc}$ = 261 nm) $\lambda_{em}^{max}$ = 607 nm. ESI-MS m/z 691.1 [M–PF$_6$]$^+$ (calc. 691.1). Found C 42.66, H 3.03, N 10.29; C$_{30}$H$_{22}$F$_6$IrN$_6$PS·0.5H$_2$O requires C 42.65, H 2.74, N 9.95%.
Complex 4 – [Ir(pbtz)_2(btzpy)][PF_6]

[Ir(pbtz)_2Cl_2] (151 mg, 0.116 mmol) and AgPF_6 (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_2Cl_2 changing to CH_2Cl_2–2% MeOH) and precipitation with Et_2O/n-hexane. [Ir(pbtz)_2(btzpy)][PF_6] was isolated as a bright orange solid (130 mg, 0.134 mmol, 57.8%). \(^1\)H NMR (500 MHz, CD_2Cl_2) δ/ppm 8.40 (pseudo-dt, J = 8.1, 1.1 Hz, 1H, H^E3), 8.23 (pseudo-tdd, J = 7.8, 1.5 Hz, 1H, H^E4), 8.11 (pseudo-dt, J = 5.5, 1.0 Hz, 1H, H^E6), 8.08 (pseudo-dt, J = 8.4, 0.9 Hz, 1H, H^F7), 7.93–7.85 (overlapping m, 4H, H^A3+B7+C3+D7), 7.64–7.55 (overlapping m, 2H, H^E5+F6), 7.39–7.32 (overlapping m, 2H, H^B6+D6), 7.28 (ddd, J = 8.5, 7.3, 1.2 Hz, 1H, H^F3), 7.22–7.14 (overlapping m, 2H, H^A4+C4), 7.11 (ddd, J = 8.5, 7.3, 1.2 Hz, 1H, H^D5), 7.00–6.89 (overlapping m, 4H, H^A5+B5+C5+F4), 6.52 (dd, J = 7.8, 1.0 Hz, 1H, H^C6), 6.40–6.33 (overlapping m, 2H, H^A6+B4), 6.01 (d, J = 8.4 Hz, 1H, H^D4). \(^{13}\)C\(^{1}\)H NMR (126 MHz, CD_2Cl_2) δ/ppm 182.3 (C^D2), 181.5 (C^B2), 170.3 (C^F2), 153.1 (C^E2), 151.8 (C^E6), 151.6 (C^F3a), 149.7 (C^D3a), 149.5 (C^B3a), 147.4 (C^C1), 147.3 (C^A1), 141.4 (C^C2), 141.0 (C^E4), 140.6 (C^A2), 134.4 (C^F7a), 134.3 (C^C6), 133.2 (C^A6), 132.9 (C^A5), 132.7 (C^C5), 132.08 (C^B7a/D7a), 132.05 (C^B7a/D7a), 130.1 (C^E5), 129.7 (C^F5), 129.2 (C^F6), 128.72 (C^B5/D5), 128.69 (C^B5/D5), 127.37 (C^A3/C3), 127.36 (C^A3/C3), 126.73 (C^B6/D6/E3), 126.69 (C^B6/D6/E3), 126.5 (C^B6/D6), 124.3 (C^A4), 124.2 (C^D7), 124.14 (C^B7), 124.08 (C^C4), 124.0 (C^F7), 123.1 (C^F4), 118.3 (C^B4), 117.7 (C^D4). IR (solid, ν/cm\(^{-1}\)) 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_2Cl_2, 1.0 × 10\(^{-5}\) mol dm\(^{-3}\)) λ/νm (ε/dm\(^{3}\) mol\(^{-1}\) cm\(^{-1}\)) 253 (32 000), 270 (28 000), 279 (27 000), 290 (26 000), 324 (46 000), 409 (9200), 435 sh (6300). Emission (CH_2Cl_2, 1.0 × 10\(^{-5}\) mol dm\(^{-3}\)), λ\(_{\text{exc}}\) = 326 nm) λ\(_{\text{em}}\) = 600 nm. ESI-MS m/z 825.0 [M–PF_6]^\text{+} (calc. 825.1). Found C 46.88, H 2.79, N 6.16; C\(_{38}\)H\(_{24}\)F\(_6\)IrN\(_4\)PS\(_3\) 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 (CH\(_2\)Cl\(_2\)).

<table>
<thead>
<tr>
<th>Geometrical parameter</th>
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<th>2</th>
<th>3</th>
<th>4</th>
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</thead>
<tbody>
<tr>
<td>Ir−N(^{C/N})</td>
<td>2.081</td>
<td>2.084</td>
<td>2.078</td>
<td>2.100</td>
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<tr>
<td>Ir−C(^{C/N})</td>
<td>2.016</td>
<td>2.023</td>
<td>2.016</td>
<td>2.026</td>
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<tr>
<td>Ir−N(^{N/N})</td>
<td>2.230</td>
<td>2.262</td>
<td>2.231</td>
<td>2.216</td>
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<tr>
<td>C(^{C/N})−Ir−N(^{C/N})</td>
<td>80.08</td>
<td>79.93</td>
<td>79.25</td>
<td>79.72</td>
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<tr>
<td>N(^{N/N})−Ir−N(^{N/N})</td>
<td>74.39</td>
<td>74.40</td>
<td>74.85</td>
<td>74.85</td>
</tr>
<tr>
<td>C(^{N}) Inter-ring dihedral angle(^a)</td>
<td>0.98</td>
<td>0.67</td>
<td>16.87</td>
<td>16.74</td>
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<tr>
<td>N(^{N}) Inter-ring dihedral angle(^a)</td>
<td>1.98</td>
<td>2.14</td>
<td>0.68</td>
<td>6.67</td>
</tr>
</tbody>
</table>

\(^a\) 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 CH₂Cl₂ solution and as powder samples. \( \tau_{\text{ave}} \) = average lifetime.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solution(^a,b)</th>
<th>Powder(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_{\text{ave}} ) [ns]</td>
<td>( \tau_1 ) [ns] (A₁)</td>
</tr>
<tr>
<td>1</td>
<td>55</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>380</td>
<td>251 (8009)</td>
</tr>
<tr>
<td>3</td>
<td>459</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>1200</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\) Measured in de-aerated CH₂Cl₂ solution under an atmosphere of argon. \(^b\) \( \lambda_{\text{exc}} = 280 \) nm. Biexponential fits were used for the excited-state lifetime determination of all powder samples and solution samples of 2, according to the equation \( \tau_{\text{ave}} = \sum A_i \tau_i \sum A_i \) (\( A_i \) = 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⁻² (1000 Hz, 50% duty cycle, block wave). Extrapolation in dashed lines.
REFERENCES


