

Cationic, luminescent cyclometalated iridium(III) complexes based on substituted 2-phenylthiazole ligands

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Electronic Supplementary Information

Additional details of synthesis

Ethyl-4-methyl-2-phenylthiazole-5-carboxylate (emptzH)¹

Thiobenzamide (2.000 g, 14.57 mmol) and ethyl 4-chloroacetoacetate (2.380 g, 14.46 mmol) in ethanol (30 mL) were heated at reflux for 4 h. After cooling, the solvent was removed *in vacuo*. The crude product was extracted into CH₂Cl₂, washed with aqueous NaHCO₃ solution and water, and then dried over MgSO₄. After removal of solvent, the residue was recrystallised from hot methanol. Yield: 2.45 g, 68 %. ¹H NMR (400 MHz, CDCl₃): δ_H = 7.90-7.88 (2H, m), 7.39-7.37 (3H, m), 4.29 (2H, q, ³J_{HH} = 7.1 Hz, CH₂CH₃), 2.71 (3H, s, CCH₃), 1.32 (3H, t, ³J_{HH} = 7.1 Hz, CH₂CH₃) ppm. UV-Vis (CH₃CN) λ_{max}/nm (ε/M⁻¹cm⁻¹) = 310 (18300), 225 (12500). IR (solid): ν 1711 (C=O), 1263 (C-O) cm⁻¹.

Ethyl-dipyrido[3,2-a:2',3'-c]phenazine-11-carboxylate (edppz)²

1,10-Phenanthroline-5,6-dione (0.224 g, 1.06 mmol) was dissolved in ethanol (10 mL), ethyl-1,2-phenylenediamine-4-carboxylate (0.19 mL, 1.13 mmol) and acetic acid (approx. 3 drops) were added and the solution stirred at 80°C for 24 h under a N₂ atmosphere. The solvent was removed *in vacuo*, the resulting solid dissolved in CHCl₃ and the product precipitated by slow addition of petroleum ether to give a pale brown solid. Yield: 0.220 g, 59%. ¹H NMR (250 MHz, CDCl₃): δ_H = 9.50 (2H, dd, J_{HH} = 8.1, 1.7 Hz), 9.22-9.19 (2H, m), 8.95 (1H, app d, ³J_{HH} = 1.8 Hz, NCCHC), 8.41 (1H, dd, J_{HH} = 8.9, 1.8 Hz), 8.26 (1H, d, ³J_{HH} = 8.9 Hz), 7.72 (2H, dd, ³J_{HH} = 8.1, 4.5 Hz, NCHCH), 4.47 (2H, q, ³J_{HH} = 7.1 Hz, OCH₂CH₃), 1.46 (3H, t, ³J_{HH} = 7.1 Hz, OCH₂CH₃) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/M⁻¹cm⁻¹) = 385 (13800), 367 (13500), 275 (57700).

Ethyl-3,6-dimethyl-dipyrido[3,2-a:2',3'-c]phenazine-11-carboxylate (edmdppz)

Prepared similarly to edppz, but using 2,9-dimethyl-1,10-phenanthroline-5,6-dione (0.301 g, 1.26 mmol) and ethyl-1,2-phenylenediamine-4-carboxylate (0.231 g, 1.28 mmol) to give a pale brown solid. Yield: 0.145 g, 30%. ¹H NMR (250 MHz, CDCl₃): δ_H = 9.42 (2H, d, ³J_{HH} = 8.3 Hz), 9.00 (1H, app. d, ³J_{HH} = 1.4 Hz), 8.40 (1H, app. dd, J_{HH} = 8.9, 1.8 Hz), 8.26 (1H, d, ³J_{HH} = 9.0 Hz), 7.59 (2H, d, ³J_{HH} = 8.2 Hz), 4.46 (2H, q, ³J_{HH} = 7.1 Hz, OCH₂CH₃), 2.92 (6H, s, CH₃), 1.45 (3H, t, ³J_{HH} = 7.1 Hz, OCH₂CH₃) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/M⁻¹cm⁻¹) = 390 (11800), 371 (11300), 278 (41800). IR (solid): ν 1717 (C=O), 1271 (C-O) cm⁻¹.

Pyridylimidazo[4,5-f][1,10]phenanthroline (pipphen)³

1,10-phenanthroline-5,6-dione (0.814 g, 3.96 mmol) and ammonium acetate (9.411 g, 122 mmol) were heated to 70 °C in AcOH (40 mL) under a N₂ atmosphere. 4-pyridine carboxaldehyde (0.36 mL, 3.82 mmol) in AcOH (20 mL) was added and the solution stirred at 70-80 °C for 2 h. The reaction was then cooled to room temperature, neutralised with NaOH (1M) and extracted with CH₂Cl₂. The organic layer was dried over MgSO₄ and the solvent was removed *in vacuo* to give the crude product. Recrystallisation from CH₂Cl₂ and Et₂O gave the product as a brown solid. Yield: 0.602g, 52%. ¹H NMR (400 MHz, CDCl₃): δ_H = 9.21-9.19 (2H, m, NCH), 8.89 (1H, dd, J_{HH} = 8.1, 1.8 Hz), 8.84 (2H, dd, J_{HH} = 4.5, 1.6 Hz), 8.65 (1H, dd, J_{HH} = 8.2, 1.7 Hz), 8.15 (2H, dd, ³J_{HH} = 4.5, 1.6 Hz), 7.76-7.72 (2H, m, NCHCH) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/M⁻¹cm⁻¹) = 322 (12700), 271 (27200).

1-Phenylpyridylimidazo[4,5-f][1,10]phenanthroline (ppiphen)

Adapted from literature, but using 1,10-phenanthroline-5,6-dione (0.203 g, 0.96 mmol), 4-pyridine carboxaldehyde (0.1 mL, 1.06 mmol), aniline (0.1 mL, 1.10 mmol) and ammonium acetate (0.739 g, 9.59 mmol) were stirred in AcOH (5 mL) at 125°C for 4 h under an N₂ atmosphere. The reaction was cooled, poured over ice water and neutralised with NaOH (approx. 10%). Hypochlorite solution (approx. 15%) was added to remove impurities and the product extracted into CH₂Cl₂. The combined organic phases were dried over MgSO₄ and the solvent removed *in vacuo* to give a dark yellow oil. The crude product was recrystallised from MeCN to give a pale brown solid. Yield: 0.125 g, 35%. ¹H NMR (250 MHz, CDCl₃): δ_H = 9.07 (1H, dd, J_{HH} = 8.1, 1.8 Hz), 9.01 (2H, dd, J_{HH} = 4.3, 1.6 Hz), 8.51 (2H, dd, J_{HH} = 4.6, 1.6 Hz), 7.74-7.62 (5H, m), 7.53-7.50 (2H, m), 7.42-7.36 (3H, m) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/M⁻¹cm⁻¹) = 275 (42200), 243 (29800). IR (solid): ν 3036 (C-H), 1593 (C=C), 700 (=C-H) cm⁻¹.

1-(4-*t*-Butyl)-phenylpyridylimidazo[4,5-f][1,10]phenanthroline (bpiphen)

Prepared similarly to **ppiphen**, but using 1,10-phenanthroline-5,6-dione (0.504 g, 2.40 mmol), 4-pyridine carboxaldehyde (0.22 mL, 2.34 mmol), 4-*t*-butyl-aniline (0.38 mL, 2.39 mmol) and ammonium acetate (1.873 g, 24.3 mmol) in AcOH (10 mL) to give the product as a pale brown solid. Yield: 0.039 g, 32%. ¹H NMR (250 MHz, CDCl₃): δ_H 9.13 (1H, dd, J_{HH} = 4.4, 1.7 Hz), 9.05 (1H, dd, J_{HH} = 8.1, 1.8 Hz), 9.00 (1H, dd, J_{HH} = 4.3, 1.6 Hz), 8.50-8.47 (2H, m), 7.70 (1H, dd, ³J_{HH} = 8.1, 4.4 Hz), 7.65-7.61 (2H, m), 7.41-7.37 (5H, m), 7.25 (1H, dd, J_{HH} = 8.4, 4.3 Hz), 1.42 (9H, s, CH₃) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/M⁻¹cm⁻¹) = 274 (42200), 243 (35500). IR (solid): ν 2963 (C-H), 745, 677 (=C-H) cm⁻¹.

Table S1 . Crystal data and structure refinement details.

	[Ir(emptz)₂(dpphen)](PF₆)
Empirical formula	C ₅₁ H _{42.5} F ₆ IrN ₄ O _{4.25} PS ₂
Formula weight	1180.68
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	16.3828(11)
<i>b</i> / Å	16.9146(11)
<i>c</i> / Å	18.4938(13)
α / °	87.307(5)
β / °	74.660(5)
γ / °	77.226(5)
<i>V</i> / Å³	4819.5(6)
<i>T</i> / K	100(2)
Density (calculated) / Mg / m³	1.627
Absorption coefficient / mm⁻¹	2.964
<i>F</i>(000)	2354
Crystal shape	Needle
Colour	Orange
Crystal size / m³	0.100 × 0.010 × 0.010 mm ³
<i>Z</i>	4
θ range for data collection	3.038 – 27.471°
Index ranges	-20 ≤ <i>h</i> ≤ 21, -21 ≤ <i>k</i> ≤ 21, -23 ≤ <i>l</i> ≤ 23
Reflections collected	59802
Independent reflections	21687 [<i>R</i> _{int} = 0.0918]
Completeness to $\theta = 25.242^\circ$	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.788
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	21687 / 1367 / 1288
Goodness-of-fit on <i>F</i>²	1.075
Final <i>R</i> indices [<i>F</i>² > 2σ(<i>F</i>²)]	<i>R</i> 1 = 0.0646, <i>wR</i> 2 = 0.1074
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1322, <i>wR</i> 2 = 0.1316
Largest diff. peak and hole	3.442 and -1.770 e Å ⁻³

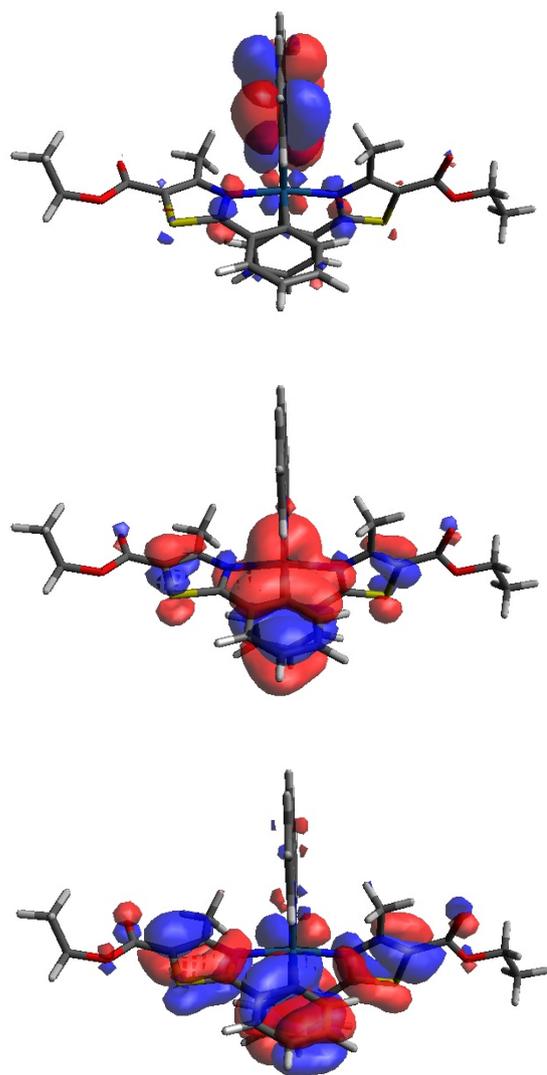


Figure S1 Visual representations of the HOMO-1 (bottom), HOMO (middle) and LUMO (top) for [Ir(emptz)₂(phen)]⁺.

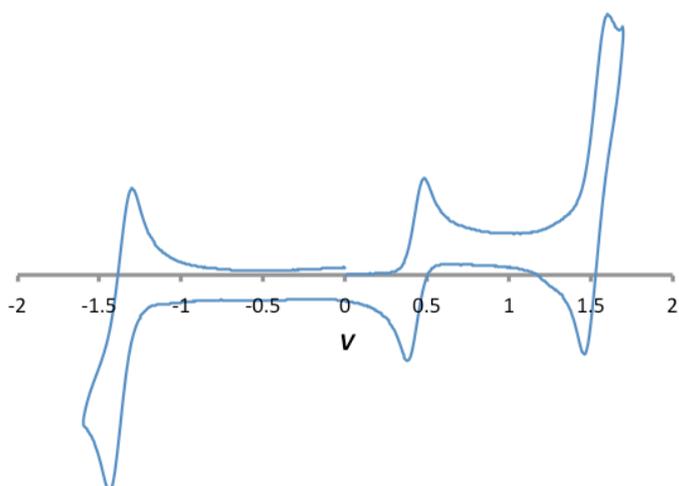


Figure S2. $[\text{Ir}(\text{emptz})_2(\text{bipy})](\text{PF}_6)$ measured in CH_2Cl_2 solutions at 200 mV s^{-1} with $0.1 \text{ M } [\text{NBu}_4][\text{PF}_6]$ as supporting electrolyte calibrated with Fc/Fc^+ .

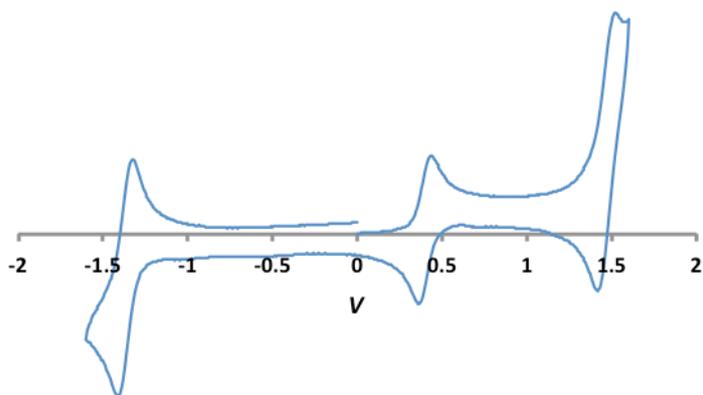


Figure S3. $[\text{Ir}(\text{emptz})_2(\text{dppe})](\text{PF}_6)$ measured in CH_2Cl_2 solutions at 200 mV s^{-1} with $0.1 \text{ M } [\text{NBu}_4][\text{PF}_6]$ as supporting electrolyte calibrated with Fc/Fc^+ .

References

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