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Synthesis and Spectroscopic Properties of Modular Platinum(II) Terpyridine Phosphorescent Pockets

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Experimental details and characterization data for functionalized terpyridine ligands and 1–4; 77 K glass and solid-state emission data for 1–4; absorption and solution emission spectra of 1 and 2 in CH$_2$Cl$_2$ and CH$_3$CN at 298 K.
Experimental Section

Synthetic Procedures

CAUTION: Perchlorate salts of metal-organic complexes are potentially explosive and should be handled with care and in small amounts. Compound 5 was purchased from Carbocore Inc. (USA). Published procedures or minor modifications thereof were used for the preparation of the following compounds (Scheme S1): 6 and 7, 1 8; 1 (Scheme S2): 11; 3 (Scheme S3): 14. 4

Scheme S1

9: To a two-necked flask were added 7 (0.10 g, 0.186 mmol), 8 (0.094 g, 0.260 mmol), Pd(dppf)Cl₂ (CH₂Cl₂ adduct, 0.017 g, 0.0186 mmol) and K₂CO₃ (0.13 g, 0.928 mmol). The flask
was fitted with a septum, evacuated, and refilled with N₂. A degassed mixture of 1,4-dioxane/DI water (10:1; 5 mL) was added via syringe, and the sealed reaction mixture was stirred at 100 °C for 40 h. The resultant black suspension was diluted with CH₂Cl₂ and filtered with copious washing of CH₂Cl₂. The black filtrate was concentrated *in vacuo* and purified by alumina column chromatography (10 % ethyl acetate in hexane) to afford 9 as a white crystalline solid (0.11 g, 85%). ¹H NMR (300 MHz, CD₂Cl₂): δ 8.63 (d, J = 7.9 Hz, 2H), 8.58 (d, J = 4.0 Hz, 2H), 8.37 (s, 2H), 7.90-7.85 (m, 2H), 7.55 (d, J = 2.3 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 2.2 Hz, 1H), 7.33-7.31 (m, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H), 177 (s, 6H), 1.40 (s, 9H), 1.34 (s, 9H). ES-MS (+ve mode): m/z 689 [M + H]⁺.

10: A mixture of 9 (0.050 g, 0.0734 mmol) and 3.0 M NaOH (0.35 mL, 1.03 mmol) in THF (1 mL) in a round bottom flask was sealed then stirred at 100 °C for 3 hr. The resultant colourless solution was diluted with a mixture of diethyl ether and THF, and the reaction mixture was acidified by 2N HCl. The organic layer was separated and then washed with brine, and dried over MgSO₄. The solvent was evaporated *in vacuo*, and the resultant purple paste was re-dissolved in CH₃CN and filtered to afford 10 as a pale yellow powder (0.030 g, 60%). ¹H NMR (300 MHz, CDCl₃): δ 8.66 (d, J = 5.0 Hz, 2H), 8.65 (d, J = 6.6 Hz, 2H), 8.34 (s, 2H), 7.87-7.81 (m, 2H), 7.51 (d, J = 2.2 Hz, 1H), 7.49 (d, J = 2.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 2.5 Hz, 1H), 7.33-7.29 (m, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 2.2 Hz, 2H), 1.78 (s, 6H), 1.38 (s, 9H), 1.36 (s, 9H). ES-MS (+ve mode): m/z 675 [M + H]⁺.

1[ClO₄] and 2[ClO₄]: see main paper. 2[Cl] was obtained before the anion metathesis procedure. 2[PFO₆] was afforded by anion metathesis using KPF₆ in CH₃CN. Like 2[ClO₄], 2[Cl] and 2[PFO₆] were recrystallized by vapour diffusion of diethyl ether into a CH₂Cl₂/CH₃CN solution to give analytically pure yellow to yellow-orange crystalline solids.
12: To a mixture of 11 (0.237 g, 0.559 mmol), powdered KOH (0.038 g, 0.670 mmol) and dicyanodiamide (0.235 g, 2.798 mmol) was added 20 mL of 1-propanol. The reaction mixture was stirred at reflux overnight, then poured into CH$_2$Cl$_2$. The organic layer was washed with water and brine, dried over MgSO$_4$ and then concentrated in vacuo. The crude product was purified by silica gel column chromatography (chloroform to 10% methanol in chloroform) to afford 12 as white solids (0.182 g, 64%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.51 (d, $J = 2.2$ Hz, 1H), 7.48 (d, $J = 2.5$ Hz, 1H), 7.40 (d, $J = 2.2$ Hz, 1H), 7.31 (d, $J = 2.2$ Hz, 1H), 5.31 (br, s, 4H), 1.64 (s, 6H), 1.34 (s, 9H), 1.30 (s, 9H). ES-MS (+ve mode): m/z 510 [M + H]$^+$. 

S 4
13: Under an inert atmosphere, 12 (0.142 g, 0.278 mmol), 8 (0.100 g, 0.279 mmol), K$_2$CO$_3$ (0.192 g, 1.391 mmol) and Pd(dppf)Cl$_2$ (0.023 g, 0.028 mmol) in dioxane/water (10:1, 10 mL) were added to a reaction flask. The reaction mixture was heated to 100°C, then sealed and stirred at this temperature for 2 d. The crude product was diluted with CH$_2$Cl$_2$ and filtered through celite. The filtrate was concentrated in vacuo and purified by alumina column chromatography (CHCl$_3$ to 2% MeOH in CHCl$_3$) to afford 13 as white solid (0.137 g, 75%). $^1$H NMR (CDCl$_3$, 300 MHz) δ 8.61-8.58 (m, 4H), 8.49 (s, 2H), 7.41 (dd, $J = 7.7$, 7.7 Hz, 2H), 7.50 (d, $J = 2.2$ Hz, 1H), 7.46 (d, $J = 2.2$ Hz, 1H), 7.30 (d, $J = 2.2$ Hz, 1H), 7.27 (d, $J = 2.2$ Hz, 1H), 7.16-7.12 (m, 2H), 5.29 (br, s, 4H), 1.76 (s, 6H), 1.36 (s, 9H), 1.34 (s, 9H). ES-MS (+ve mode): m/z 663 [M + H]$^+$. 

3[ClO$_4$]: see main paper.
Compounds 15–18 were prepared by modifying the synthetic procedures for 6, 7, 9 and 10 respectively.\(^2\)

**15**: 53 % yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 8.03 (d, J = 0.8 Hz, 1H), 8.00 (d, J = 0.8 Hz, 1H), 7.94 (d, J = 0.8 Hz, 1H), 7.73 (d, J = 0.8 Hz, 1H), 0.36 (s, 9H), 0.37 (s, 9H).

**16**: 49 % yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 8.23 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 1.2 Hz, 1H), 8.07 (s, 1H), 8.05 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 1.2 Hz, 1H), 7.73 (s, 1H), 3.99 (s, 3H), 0.41 (s, 9H), 0.38 (s, 9H).

**17**: 83 % yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 9.08 (s, 2H), 8.75 (d, J = 4.8 Hz, 2H), 8.71 (d, J = 7.9 Hz, 2H), 8.26 (s, 1H), 8.21 (s, 1H), 8.12 (d, J = 8.3 Hz, 2H), 8.04 (s, 1 H), 7.93 (t, J = 7.5 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.83 (s, 1H), 7.41 (t, J = 6.1 Hz, 2H), 3.89 (s, 3H), 0.46 (s, 9H), 0.43 (s, 9H).

\(\text{Scheme S3}\)
18: 95 % yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.09 (s, 2H), 8.77 (d, $J$ = 4.1 Hz, 2H), 8.70 (d, $J$ = 7.9 Hz, 2H), 8.26 (d, $J$ = 0.9 Hz, 1H), 8.23 (d, $J$ = 0.9 Hz, 1H), 8.15 (d, $J$ = 8.5 Hz, 2H), 8.05 (d, $J$ = 1.2 Hz, 1H), 7.95 (d, $J$ = 8.5 Hz, 2H), 7.95-7.90 (m, 2H), 7.84 (d, $J$ = 1.2, 1H), 7.43-7.39 (m, 2H), 0.45 (s, 9H), 0.44 (s, 9H). ES-MS (+ve mode): m/z 664 [M + H]$^+$. 

**Scheme S4**

4[ClO$_4$]: see main paper.
Fig. S1. ESI mass spectra of [M⁻] in CH₂Cl₂ (upper) and isotopic distribution simulation (lower) for 1[ClO₄] (left) and 2[ClO₄] (right).
**Table S1.** 77 K glass (10⁻⁵ M unless specified) and solid-state emission data

<table>
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<tr>
<th>Fluid</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt;/nm</th>
<th>77K: λ&lt;sub&gt;max&lt;/sub&gt;/nm; τ/μs</th>
<th>77K: λ&lt;sub&gt;max&lt;/sub&gt;/nm; τ/μs</th>
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<tbody>
<tr>
<td>1[ClO₄]</td>
<td>419</td>
<td>520&lt;sup&gt;a&lt;/sup&gt; (max; τ = 32), 554, 598</td>
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<tr>
<td>2[ClO₄]</td>
<td>425</td>
<td>520&lt;sup&gt;b&lt;/sup&gt; (max; τ = 35), 555, 610&lt;sup&gt;c&lt;/sup&gt; (τ₁ = 3.4; τ₂ = 41)</td>
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<tr>
<td>3[ClO₄]</td>
<td>410</td>
<td>519&lt;sup&gt;b&lt;/sup&gt; (max; τ = 29), 556, 597</td>
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<tr>
<td>4[ClO₄]</td>
<td>406</td>
<td>542&lt;sup&gt;d&lt;/sup&gt; (max; τ = 11), 584, 654&lt;sup&gt;c&lt;/sup&gt; (τ₁ = 2.1; τ₂ = 9.5)</td>
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<th>Solid state</th>
<th>298 K: λ&lt;sub&gt;max&lt;/sub&gt;/nm; τ/μs</th>
<th>77K: λ&lt;sub&gt;max&lt;/sub&gt;/nm; τ/μs</th>
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<tbody>
<tr>
<td>1[ClO₄]</td>
<td>419</td>
<td>518 (max), 548; 1.6</td>
</tr>
<tr>
<td>2[Cl]</td>
<td>425</td>
<td>552; 1.4</td>
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<tr>
<td>2[ClO₄]</td>
<td>425</td>
<td>585; 0.8</td>
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<tr>
<td>2[PFO₆]</td>
<td>420</td>
<td>597; 1.1</td>
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<tr>
<td>3[ClO₄]</td>
<td>430</td>
<td>583; 0.2</td>
</tr>
<tr>
<td>4[ClO₄]</td>
<td>406</td>
<td>595; 0.5</td>
</tr>
</tbody>
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<sup>a</sup> In MeOH:EtOH (1:4).  <sup>b</sup> In butyronitrile.  <sup>c</sup> Excimeric emission observed at 10⁻³ M.
<sup>d</sup> In DMSO.
**Fig. S2.** Absorption (dots) and solution emission (line; $\lambda_{\text{ex}}$ 410 nm) spectra of Cl$^-$ (black), ClO$_4^-$ (red) and PF$_6^-$ (blue) salts of 2 in CH$_2$Cl$_2$ ($10^{-5}$ M) at 298 K.

**Fig. S3.** Absorption (dots) and solution emission (line; $\lambda_{\text{ex}}$ 410 nm) spectra of 1 in CH$_2$Cl$_2$ (red) and CH$_3$CN (black) ($10^{-5}$ M) at 298 K.
**Fig. S4.** Absorption (dots) and solution emission (line; \( \lambda_{\text{ex}} \) 410 nm) spectra of 2 in CH\(_2\)Cl\(_2\) (red) and CH\(_3\)CN (black) (10\(^{-5}\) M) at 298 K.

**References in ESI**