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

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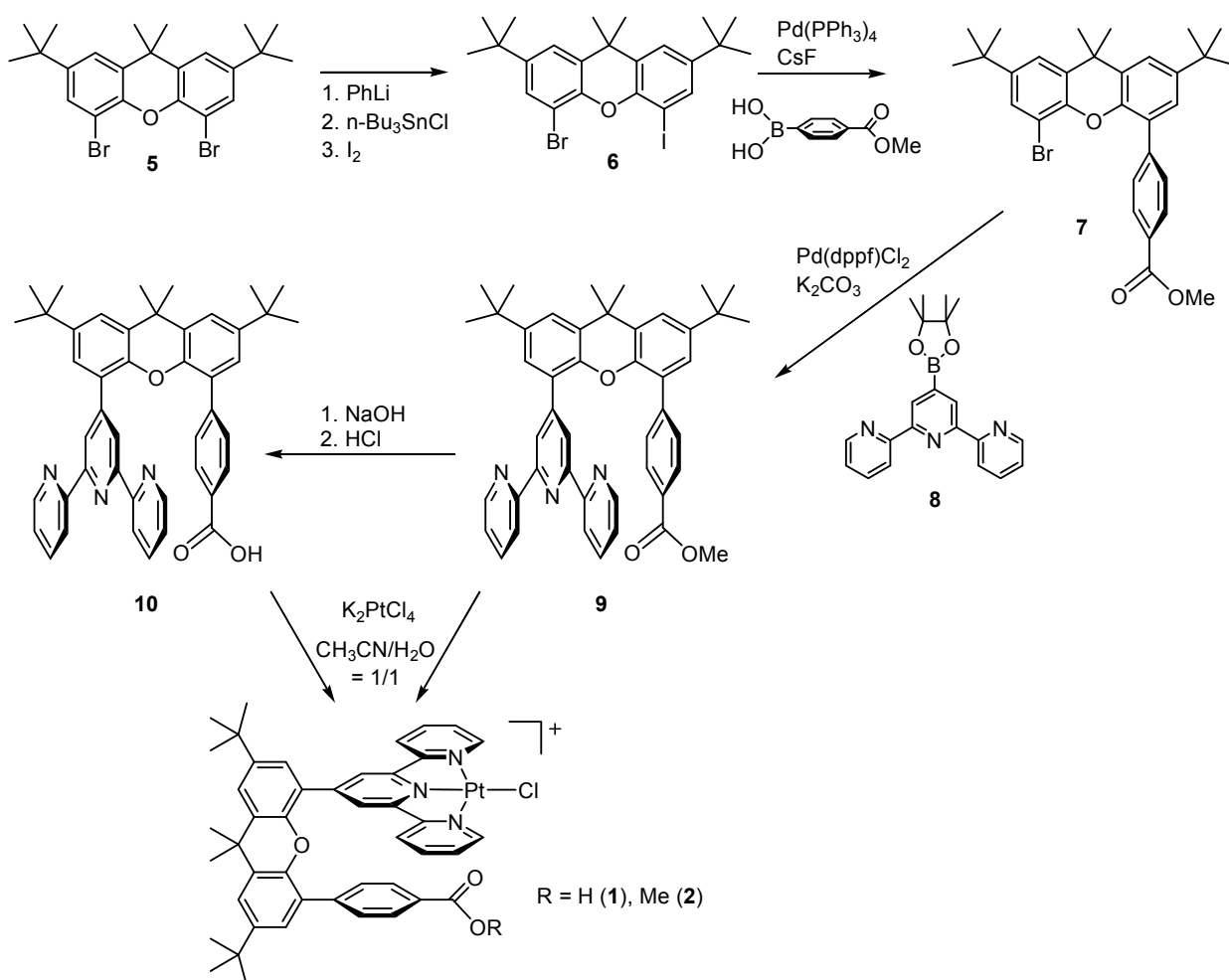
Experimental details and characterization data for functionalized terpyridine ligands and **1–4**; 77 K glass and solid-state emission data for **1–4**; absorption and solution emission spectra of **1** and **2** in CH₂Cl₂ and CH₃CN at 298 K.

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**,² (Scheme S2): **11**,³ (Scheme S3): **14**.⁴

Scheme S1



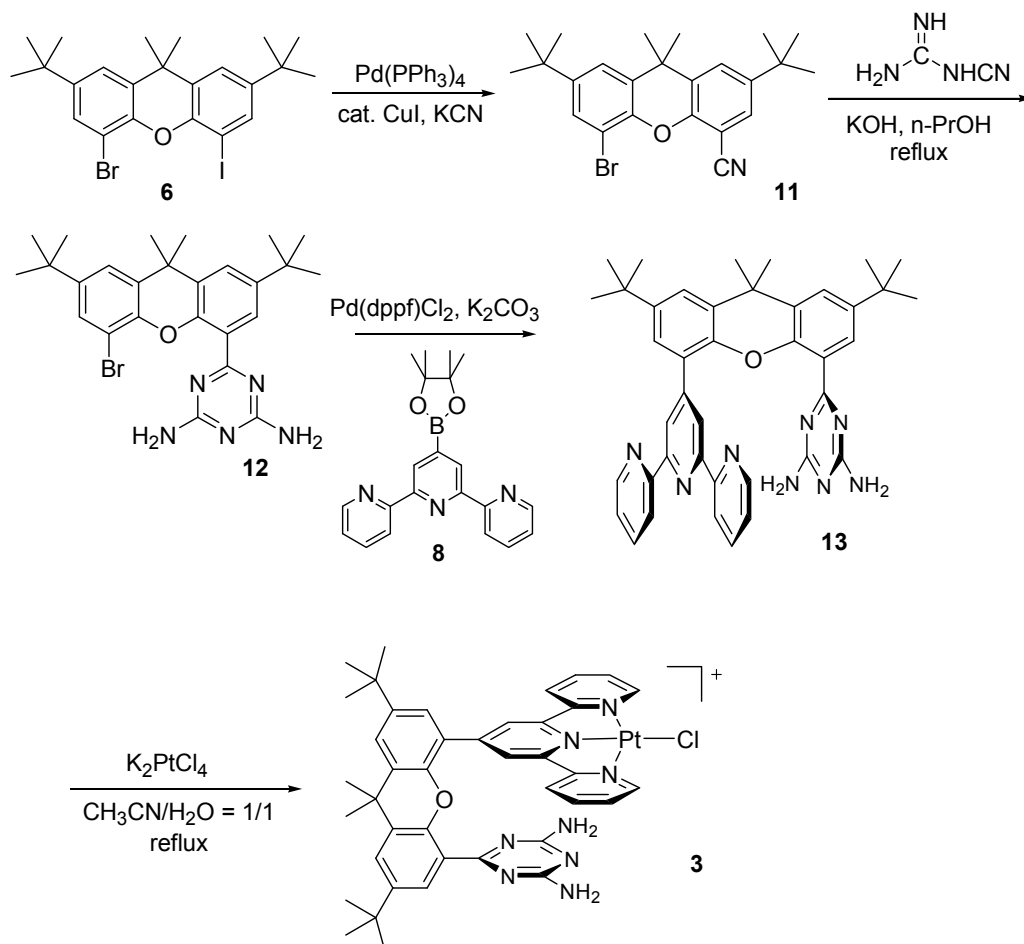
9: To a two-necked flask were added **7** (0.10 g, 0.186 mmol), **8** (0.094 g, 0.260 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (CH_2Cl_2 adduct, 0.017 g, 0.0186 mmol) and K_2CO_3 (0.13 g, 0.928 mmol). The flask

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), 1.77 (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**[PF₆] was afforded by anion metathesis using KPF₆ in CH₃CN. Like **2**[ClO₄], **2**[Cl] and **2**[PF₆] were recrystallized by vapour diffusion of diethyl ether into a CH₂Cl₂/CH₃CN solution to give analytically pure yellow to yellow-orange crystalline solids.

Scheme S2

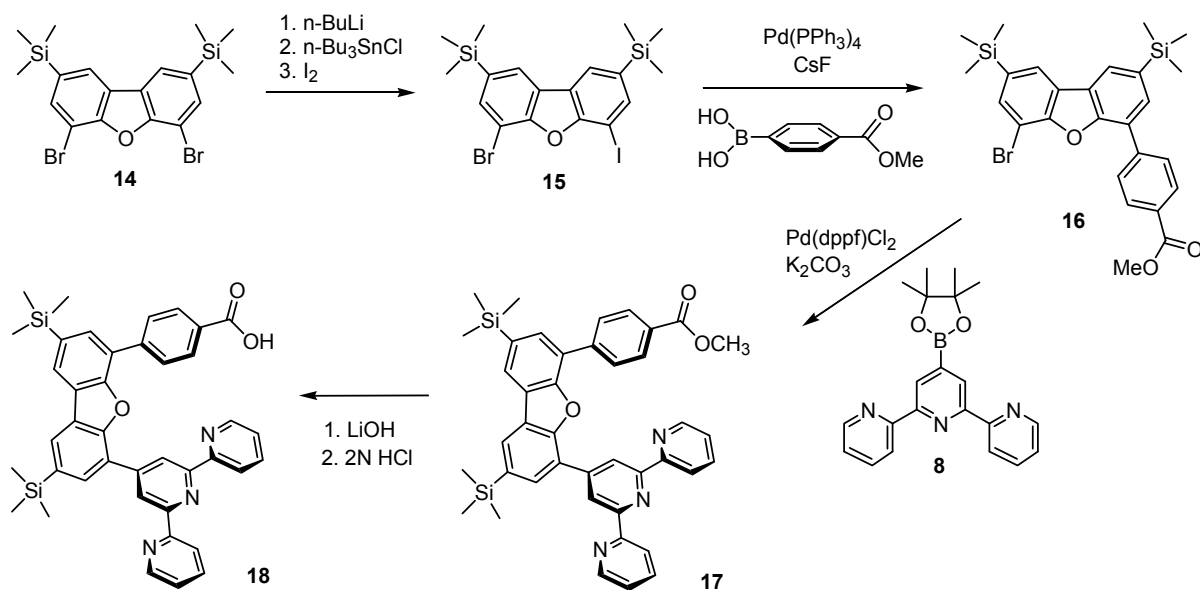


12: To a mixture of **11** (0.237 g, 0.559 mmol), powdered KOH (0.038 g, 0.670 mmol) and dicyandiamide (0.235 g, 2.798 mmol) was added 20 mL of 1-propanol. The reaction mixture was stirred at reflux overnight, then poured into CH_2Cl_2 . The organic layer was washed with water and brine, dried over MgSO_4 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%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 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 $[\text{M} + \text{H}]^+$.

13: Under an inert atmosphere, **12** (0.142 g, 0.278 mmol), **8** (0.100 g, 0.279 mmol), K₂CO₃ (0.192 g, 1.391 mmol) and Pd(dppf)Cl₂ (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 CH₂Cl₂ and filtered through celite. The filtrate was concentrated *in vacuo* and purified by alumina column chromatography (CHCl₃ to 2% MeOH in CHCl₃) to afford **13** as white solid (0.137 g, 75%). ¹H NMR (CDCl₃, 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[ClO₄]: see main paper.

Scheme S3



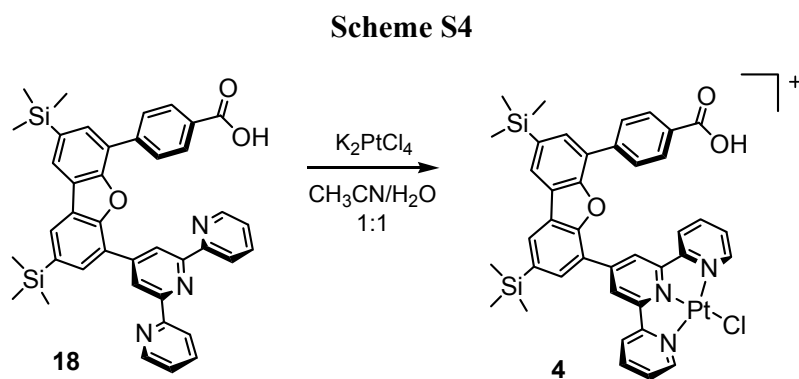
Compounds **15–18** were prepared by modifying the synthetic procedures for **6**, **7**, **9** and **10** respectively.²

15: 53 % yield. ¹H NMR (300 MHz, CDCl₃): δ 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. ¹H NMR (300 MHz, CDCl₃): δ 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. ¹H NMR (300 MHz, CDCl₃): δ 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, 1H), 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).

18: 95 % yield. ^1H NMR (300 MHz, CDCl_3): δ 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 $[\text{M} + \text{H}]^+$.



$4[\text{ClO}_4]$: see main paper.

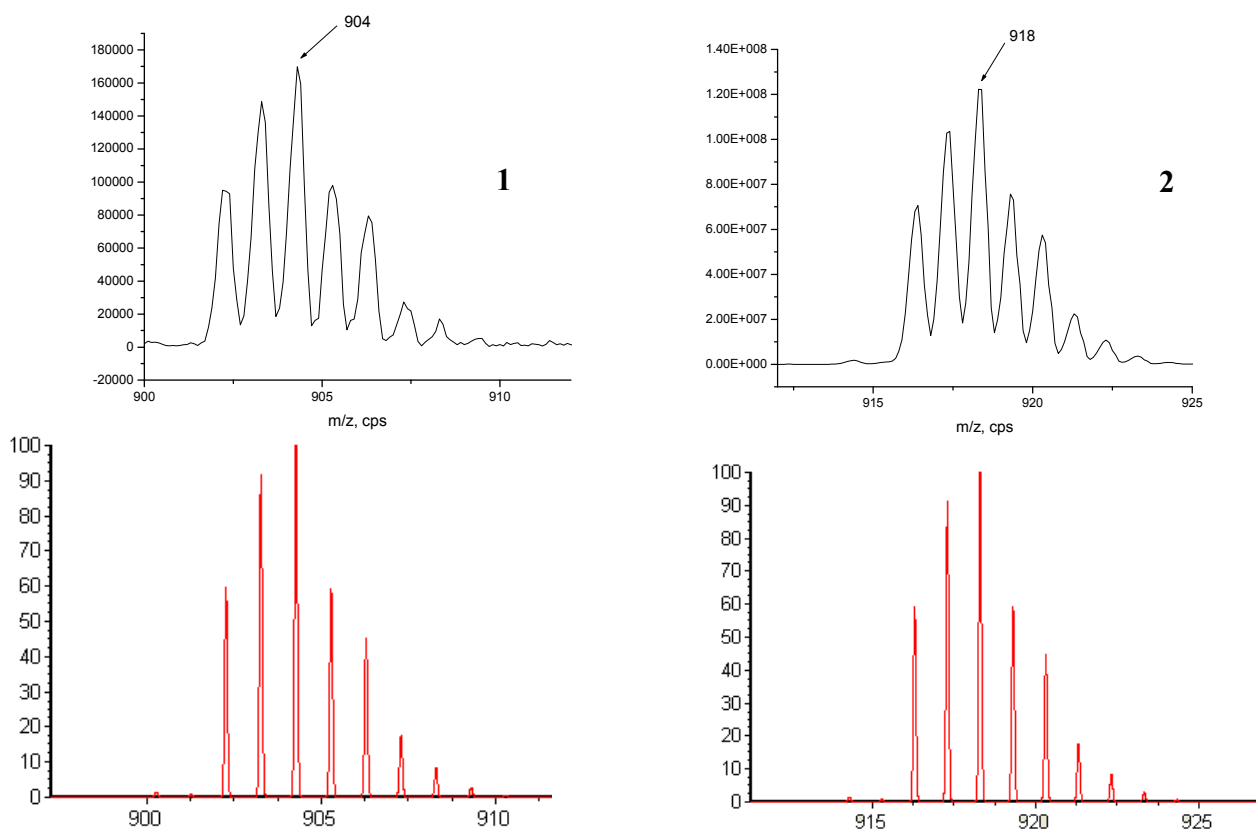


Fig. S1. ESI mass spectra of $[M^+]$ in CH_2Cl_2 (upper) and isotopic distribution simulation (lower) for **1** $[ClO_4]$ (left) and **2** $[ClO_4]$ (right).

Table S1. 77 K glass (10^{-5} M unless specified) and solid-state emission data

Fluid	$\lambda_{\text{ex}}/\text{nm}$	77K: $\lambda_{\text{max}}/\text{nm}$; $\tau/\mu\text{s}$	
1[ClO ₄]	419	520 ^a (max; $\tau = 32$), 554, 598	
2[ClO ₄]	425	520 ^b (max; $\tau = 35$), 555, 610 ^c ($\tau_1 = 3.4$; $\tau_2 = 41$)	
3[ClO ₄]	410	519 ^b (max; $\tau = 29$), 556, 597	
4[ClO ₄]	406	542 ^d (max; $\tau = 11$), 584, 654 ^c ($\tau_1 = 2.1$; $\tau_2 = 9.5$)	

Solid state		298 K: $\lambda_{\text{max}}/\text{nm}$; $\tau/\mu\text{s}$	77K: $\lambda_{\text{max}}/\text{nm}$; $\tau/\mu\text{s}$
1[ClO ₄]	419	518 (max), 548; 1.6	519 (max), 556, 593; 14
2[Cl]	425	552; 1.4	549; 28
2[ClO ₄]	425	585; 0.8	555 (max), 583; 34
2[PF ₆]	420	597; 1.1	574; 36
3[ClO ₄]	430	583; 0.2	547, 601 (max); 15
4[ClO ₄]	406	595; 0.5	537, 624 (max); 11

^a In MeOH:EtOH (1:4). ^b In butyronitrile. ^c Excimeric emission observed at 10^{-3} M.

^d In DMSO.

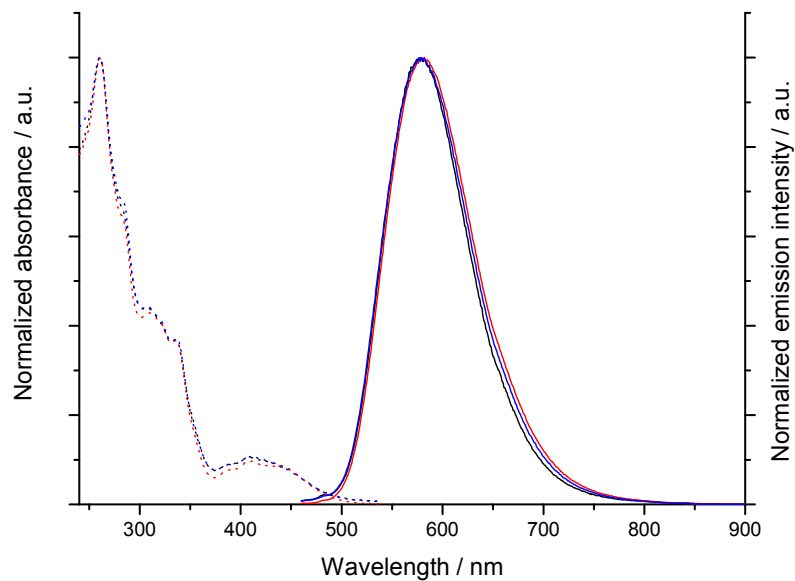


Fig. S2. Absorption (dots) and solution emission (line; λ_{ex} 410 nm) spectra of Cl^- (black), ClO_4^- (red) and PF_6^- (blue) salts of **2** in CH_2Cl_2 (10^{-5} M) at 298 K.

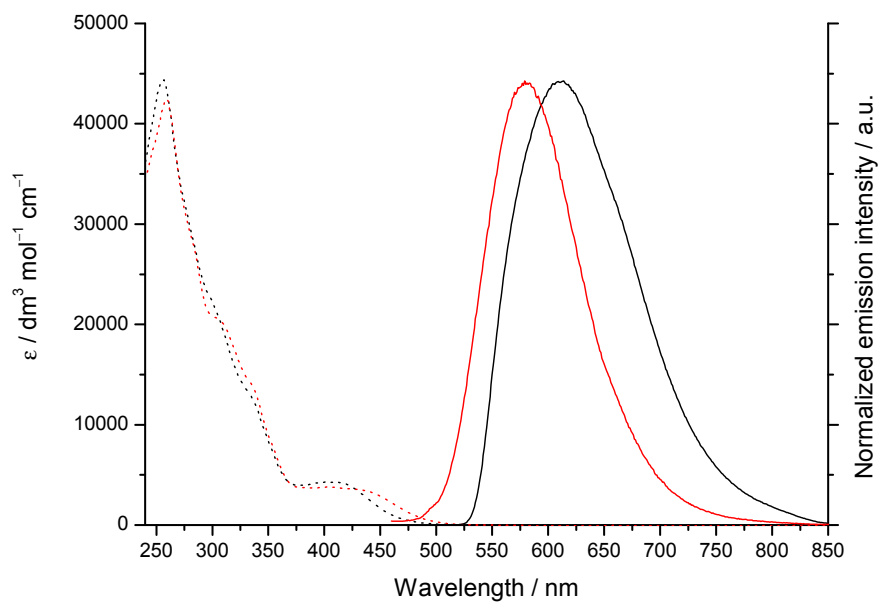


Fig. S3. Absorption (dots) and solution emission (line; λ_{ex} 410 nm) spectra of **1** in CH_2Cl_2 (red) and CH_3CN (black) (10^{-5} M) at 298 K.

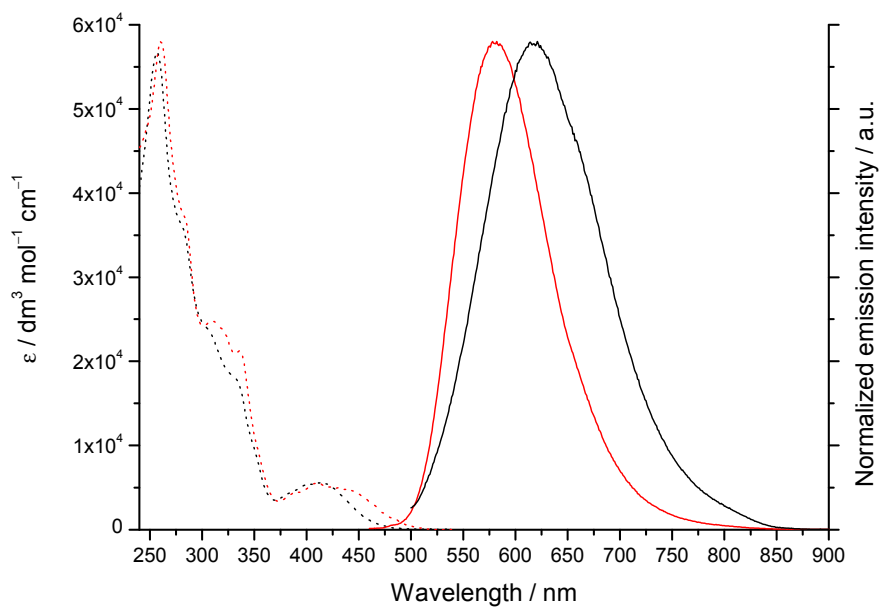


Fig. S4. Absorption (dots) and solution emission (line; λ_{ex} 410 nm) spectra of **2** in CH_2Cl_2 (red) and CH_3CN (black) (10^{-5} M) at 298 K.

References in ESI

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