

Supplementary Material (ESI) for Chemical Communications

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**Luminescent Metallogel of Platinum(II) Terpyridyl Complexes: Interplay of Metal···Metal,  $\pi$ — $\pi$   
and Hydrophobic—Hydrophobic Interactions on Gel Formation**

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### **Supplementary Information**

### Experimental Procedures:

**Synthesis of 1-OTf:** [Pt(tpy)Cl]OTf<sup>2b,d</sup> with 3,4,5-tri(dodecyloxy)phenylacetylene<sup>7</sup> in the presence of a catalytic amount of CuI in degassed DMF and NEt<sub>3</sub>. The resultant mixture was stirred overnight at room temperature. Upon addition of CH<sub>3</sub>CN, the solution was stirred for further 10 minutes. The precipitate formed was filtered. Subsequent purification by the slow vapour diffusion of diethyl ether into a dichloromethane solution of 1-OTf yielded the pure form of the product as a red solid. **1-OTf:** Yield = 244 mg (40 %). <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-DMSO, 353 K, δ/ppm): δ 9.25 (d, *J* = 4.7 Hz, 2H, terpyridyl H), 8.64-8.57 (m, 5H, terpyridyl H), 8.51-8.47 (dt, *J* = 1.4, 7.9 Hz, 2H, terpyridyl H), 7.96-7.92 (dt, *J* = 1.4, 7.1 Hz, 2H, terpyridyl H), 6.74 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 4.03-4.00 (t, *J* = 6.4 Hz, 4H, -OCH<sub>2</sub>-), 3.94-3.91 (t, *J* = 6.4 Hz, 2H, -OCH<sub>2</sub>-), 1.77-1.68 (m, 6H, -CH<sub>2</sub>-), 1.51-1.47 (m, 6H, -CH<sub>2</sub>-), 1.29-1.27 (m, 48H, -CH<sub>2</sub>-), 0.89-0.85 (m, 9H, -CH<sub>3</sub>); IR (Nujol, ν/cm<sup>-1</sup>): 2115 (w) ν(C≡C), 1164 (s) ν(S=O); Positive-ion FAB-MS: *m/z* 1082 [M - OTf]<sup>+</sup>; elemental analysis calcd (%) for C<sub>60</sub>H<sub>88</sub>N<sub>3</sub>F<sub>3</sub>O<sub>6</sub>SPt·CH<sub>3</sub>CN·3CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>: C 60.09, H 8.16, N 4.33; found: C 59.89, H 7.79, N 3.91.

**1-PF<sub>6</sub>:** Yield = 162 mg (27 %). <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-DMSO, 353 K, δ/ppm): δ 9.22 (d, *J* = 4.7 Hz, 2H, terpyridyl H), 8.62-8.55 (m, 5H, terpyridyl H), 8.50-8.45 (dt, *J* = 1.4, 7.9 Hz, 2H, terpyridyl H), 7.94-7.90 (dt, *J* = 1.4, 7.9 Hz, 2H, terpyridyl H), 6.73 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 4.02-3.99 (t, *J* = 6.3 Hz, 4H, -OCH<sub>2</sub>), 3.92-3.89 (t, *J* = 6.3 Hz, 2H, -OCH<sub>2</sub>), 1.77-1.64 (m, 6H, -CH<sub>2</sub>-), 1.51-1.41 (m, 6H, -CH<sub>2</sub>-), 1.38-1.26 (m, 48H, -CH<sub>2</sub>-), 0.88-0.83 (m, 9H, -CH<sub>3</sub>); IR (Nujol, ν/cm<sup>-1</sup>): 2122 (w) ν(C≡C), 751 (s) ν(P - F); Positive-ion FAB-MS: *m/z* 1082 [M - PF<sub>6</sub>]<sup>+</sup>; elemental analysis calcd (%) for C<sub>59</sub>H<sub>88</sub>N<sub>3</sub>F<sub>6</sub>O<sub>3</sub>PPt·1.5H<sub>2</sub>O: C 57.31, H 7.26, N 3.40; found: C 57.25, H 7.20, N 3.58.

**Synthesis of 2-OTf:** [Pt(<sup>t</sup>Bu<sub>3</sub>tpy)Cl]OTf<sup>2b,d</sup> reacted with 3,4,5-tri(dodecyloxy)phenylacetylene<sup>7</sup> using a procedure similar to that for 1-OTf except that CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent. **2-OTf:** Yield = 253 mg (71 %). <sup>1</sup>H NMR (300 MHz, d<sup>6</sup>-acetone, 298 K, δ/ppm): δ 9.24-9.22 (d, *J* = 6.0 Hz, 2H, terpyridyl H), 8.85 (s, 2H, terpyridyl H), 8.80-8.78 (d, *J* = 1.5 Hz, 2H, terpyridyl H), 7.96-7.93 (dd, *J* = 1.9, 6.0 Hz, 2H, terpyridyl H), 6.75 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 4.04-4.00 (t, *J* = 6.3 Hz, 4H, -OCH<sub>2</sub>-), 3.98-3.94 (t, *J* = 6.3 Hz,

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2H, -OCH<sub>2</sub>-), 1.85-1.70 (m, 6H, -CH<sub>2</sub>-), 1.56-1.52 (m, 9H, -<sup>t</sup>Bu; 6H, -CH<sub>2</sub>-), 1.50 (s, 18H, -<sup>t</sup>Bu), 1.37-1.28 (m, 48H, -CH<sub>2</sub>-), 0.88-0.84 (m, 9H, -CH<sub>3</sub>); IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 2116 (w)  $\nu(\text{C}\equiv\text{C})$ , 1158 (s)  $\nu(\text{S}=\text{O})$ ; Positive-ion FAB-MS:  $m/z$  1250 [ $\text{M} - \text{OTf}$ ]<sup>+</sup>; elemental analysis calcd (%) for C<sub>72</sub>H<sub>112</sub>N<sub>3</sub>F<sub>3</sub>O<sub>6</sub>Spt-CH<sub>3</sub>CN-0.5CH<sub>2</sub>Cl<sub>2</sub>: C 60.32, H 7.88, N 3.78; found: C 60.49, H 8.08, N 3.81.

**Synthesis of *N*-(4-ethynylphenyl)-3,4,5-(trioctyloxy)benzamide:** To a solution of 3,4,5-(trioctyloxy)benzoic acid<sup>6a</sup> dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added dropwise SOCl<sub>2</sub> (2 ml). The resulting mixture was stirred at room temperature for 2 hours under nitrogen atmosphere. The excess SOCl<sub>2</sub> was distilled off under reduced pressure. In a 100-mL 2-necked round-bottomed flask equipped with a dropping funnel, 4-ethynylaniline was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and NEt<sub>3</sub> (2 mL). The acid chloride was transferred into the dropping funnel via cannula and then added dropwise at 0 °C. The mixture was gradually brought to room temperature and stirred for 12 hours. The mixture was washed with water and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel (5 % ethyl acetate in hexane) to give the pure product as a yellow solid (223 mg, 38 %). <sup>1</sup>H NMR (300 MHz, d<sup>1</sup>-chloroform, 298 K,  $\delta/\text{ppm}$ ):  $\delta$  7.83 (s, 1H, -NH), 7.61-7.58 (d,  $J = 9.0$  Hz, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.47-7.44 (d,  $J = 9.0$  Hz, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.02 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 4.00-3.98 (m, 6H, OCH<sub>2</sub>), 3.00 (s, 1H, -C $\equiv$ CH), 1.82-1.72 (m, 6H, -CH<sub>2</sub>-), 1.48-1.45 (m, 6H, -CH<sub>2</sub>-), 1.29-1.23 (m, 24H, -CH<sub>2</sub>-), 0.90-0.85 (m, 9H, -CH<sub>3</sub>); Positive-ion FAB-MS:  $m/z$  606 [ $\text{M} + \text{H}$ ]<sup>+</sup>; elemental analysis calcd (%) for C<sub>39</sub>H<sub>59</sub>NO<sub>4</sub>: C 77.31, H 9.82, N 2.31; found C 77.15, H 9.62, N 2.54.

**Synthesis of 3-OTf:** [Pt(<sup>t</sup>Bu<sub>3</sub>tpy)Cl]OTf<sup>2b,d</sup> reacted with *N*-(4-ethynylphenyl)-3,4,5-(trioctyloxy)benzamide using a procedure similar to that for **1**-OTf except that CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent. **2**-OTf: Yield = 163 mg (78 %). <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-acetone, 298 K,  $\delta/\text{ppm}$ ):  $\delta$  9.48 (s, 1H, -NH), 9.32-9.31 (d,  $J = 5.9$  Hz, 2H, terpyridyl H), 8.82 (s, 2H, terpyridyl H), 8.77-8.76 (d,  $J = 2.0$  Hz, 2H, terpyridyl H), 8.03-8.01 (dd,  $J = 2.0, 5.9$  Hz, 2H, terpyridyl H), 7.79-7.77 (d,  $J = 8.5$  Hz, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.50-7.48 (d,  $J = 8.5$  Hz, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.31 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 4.11-4.08 (t,  $J = 6.3$  Hz, 4H, -OCH<sub>2</sub>-), 4.05-4.02 (t,  $J = 6.3$  Hz, 2H, -OCH<sub>2</sub>-), 1.88-1.73 (m, 6H, -CH<sub>2</sub>-),

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1.57-1.55 (m, 9H, <sup>t</sup>Bu; 6H, -CH<sub>2</sub>-), 1.50 (s, 18H, <sup>t</sup>Bu), 1.41-1.33 (m, 24H, -CH<sub>2</sub>-), 0.92-0.89 (m, 9H, -CH<sub>3</sub>); IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 2114 (w)  $\nu(\text{C}\equiv\text{C})$ , 1164 (s)  $\nu(\text{S}=\text{O})$ ; Positive-ion FAB-MS:  $m/z$  1202 [M – OTf]<sup>+</sup>; elemental analysis calcd (%) for C<sub>67</sub>H<sub>98</sub>N<sub>4</sub>F<sub>3</sub>O<sub>7</sub>SPt·0.5CH<sub>2</sub>Cl<sub>2</sub>: C 57.98, H 7.14, N 4.01; found: C 57.96, H 6.90, N 4.23.

**Gelation Test:** A weighted amount of the platinum metallogelator was suspended in a measured volume of a particular organic solvent inside a screw-capped sample vial. The suspension was heated until all the solids were dissolved. The sample vial was cooled in air to room temperature and then left to stand for overnight. The gelation properties were evaluated by the “stable-to-inversion of a test tube” method.

Table S1 Photophysical data of **1-OTf**, **1-PF<sub>6</sub>**, **2-OTf** and **3-OTf**

Complex	Medium (T/K)	Absorption Data	Emission
		$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{em}}/\text{nm}$ ( $\tau_0/\mu\text{s}$ )
<b>1-OTf</b>	DMSO (298)	267 (36820), 334 (13280), 349 (12225), 476 (4435)	780 <sup>a</sup> (< 0.1)
	Solid (298)		712 (0.15)
	Solid (77)		650 (2.75)
	Glass <sup>b</sup> (77)		565, 604 (11.00)
<b>1-PF<sub>6</sub></b>	DMSO (298)	274 (37370), 334 (14165), 350 (13415), 470 (4495)	790 <sup>a</sup> (< 0.1)
	Solid (298)		643 (< 0.1)
	Solid (77)		604, 644 (5.60)
	Glass <sup>b</sup> (77)		566, 610 (14.00)
<b>2-OTf</b>	CH <sub>3</sub> CN (298)	268 (36605), 326 (12385), 406 (3340), 454 (3920)	--- <sup>c</sup>
	Solid (298)		566, 607 (0.17)
	Solid (77)		560, 600 (4.80)
	Glass <sup>b</sup> (77)		560, 600 (13.50)
<b>3-OTf</b>	CH <sub>3</sub> CN (298)	288 (22345), 308 (23105), 406 (2600), 454 (3095)	663 (< 0.1)
	Solid (298)		637 (0.20)
	Solid (77)		616 (2.70)
	Glass <sup>b</sup> (77)		554 (10.75)

<sup>a</sup> Emission band can only be observed at concentration  $\geq 10^{-4}$  M.

<sup>b</sup> In butyronitrile glass.

<sup>c</sup> Non-emissive.

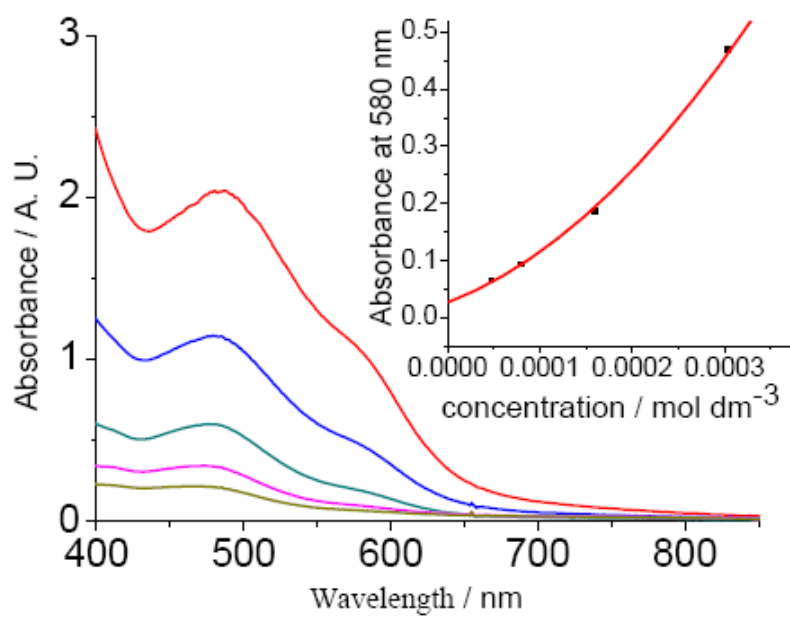


Figure S 1 UV-vis absorption spectral changes of **1-OTf** as concentration increases from  $5 \times 10^{-4}$  to  $4.8 \times 10^{-5}$  M. Inset: plot of the absorbance at 580 nm as a function of concentration.

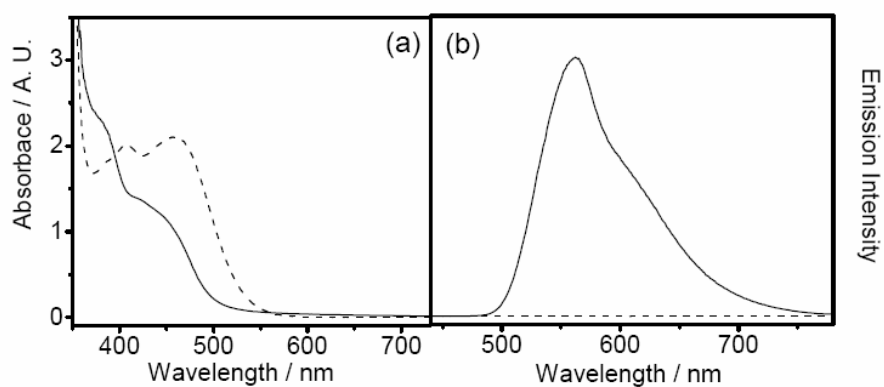


Figure S 2 (a) UV-vis absorption spectra of **2-OTf** at room temperature (—) in gel form and 90 °C (---) in sol form and (b) emission spectra of **2-OTf** at room temperature (—) in gel form and 90 °C (---) in sol form.

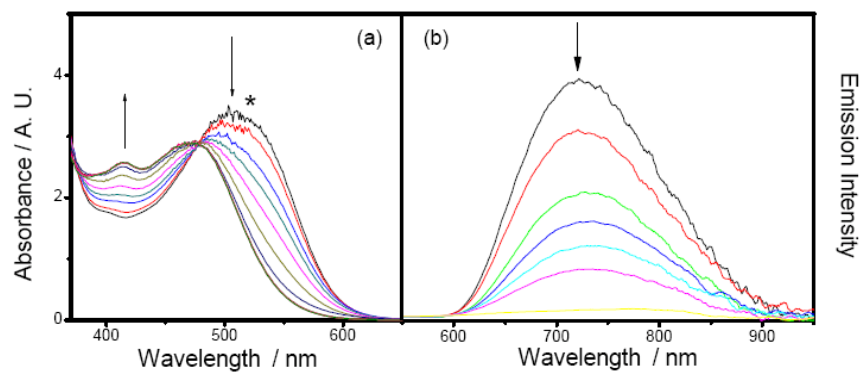


Figure S 3 (a) UV-vis absorption spectra of **1**-PF<sub>6</sub> at various temperatures from 20 to 60 °C (\*Saturation occurs even in 1mm-path length quartz cuvette due to the high concentration required for gelation) and (b) corrected emission spectra of the DMSO gel of **1**-PF<sub>6</sub> at various temperatures in the range of 20-42 °C.