# Supporting Information

### Phosphorescent Platinum(II) Complexes Bearing

### Pentafluorosulfanyl Substituted Cyclometalating

## Ligands

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#### **Experimental Section**

General Synthetic Procedures. Commercial chemicals were used as supplied. Ligands L1 and L2 were synthesized using our previously reported method.<sup>1</sup> All reactions were performed using standard Schlenk techniques under inert (N<sub>2</sub>) atmosphere with reagent grade solvents. Flash column chromatography was performed using silica gel (60 Å, 40-63 µm). Analytical thin layer chromatography (TLC) was performed using silica plates with aluminum backings (250 µm with indicator F-254). Compounds were visualized under UV light. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on a Bruker Avance spectrometer at 400 MHz, 126 MHz and 376 MHz respectively. The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "p" for pentet and "m" for multiplet. Deuterated chloroform  $(CDCl_3)$  and deuterated dichloromethane  $(CD_3Cl_3)$  were used as the solvents of record. <sup>1</sup>H NMR spectra were referenced to the solvent peak. High-resolution mass spectra were recorded at the EPSRC UK National Mass Spectrometry Facility at Swansea University on a quadrupole time-of-flight (ESI-Q-TOF), model ABSciex 5600 Triple TOF in positive electrospray ionization mode and spectra were recorded using sodium formate solution as the calibrant. Elemental analyses were performed by Mr. Stephen Boyer, London Metropolitan University.

#### Synthesis of Platinum(II) Complexes

To a round bottom flask containing K<sub>2</sub>PtCl<sub>4</sub> (1.0 equiv.) and C<sup>N</sup> ligand (1.1 equiv.) was added 2methoxyethanol to give a suspension ( $1.26 \times 10^{-3}$  moles in 10 mL) with a concentration of ca. 0.1 M. The mixture was degassed via bubbling with N<sub>2</sub> for 20 minutes, before the reaction vessel was sealed. The reaction mixture was heated to 100 °C for 19 h. Over the course of the reaction the mixture everything dissolved to give yellow to pale-yellow solutions. The solution was cooled to room temperature, and the solvent evaporated. At this stage, some decomposition (mixture turning black due to formation of colloidal platinum) was observed. To the residue was added 2,2',6,6' -tetramethylheptane-3,5-dione (3.0 equiv.) and a mixture of DCM/MeOH (1:1 v/v) to give a concentration of ca. 01 M. The suspension was stirred at room temperature for 3 h, before the solvent was removed. The mixture was filtered through a silica plug (hexanes/DCM 1:1) to remove the colloidal platinum, and the solvent was evaporated. Hexanes were added and the yellow suspension was stirred, before filtering and drying to give the pure product. Platinum (II) [2-(phenyl)-pyridinato-*N*,*C*<sup>2'</sup>]-(2,2,6,6-tetramethyl-3,5-heptanedionate): [Pt(ppy)(pivacac)].



Yellow solid (0.134 g). Yield: 43%. Mp: 174 – 175 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 8.99 (ddd, J = 5.8, 1.5, 0.7 Hz, 1H), 7.84 (ddd, J = 8.1, 7.5, 1.6 Hz, 1H), 7.69 – 7.56 (m, Hz, 2H), 7.51 – 7.44 (m, 1H), 7.22 – 7.05 (m, 3H), 5.84 (s, 1H), 1.28 (s, 9H), 1.27 (s, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 195.2, 193.8, 168.6, 147.2, 144.8, 140.2, 138.1, 131.1, 129.4, 123.5, 123.1, 121.6, 118.5, 93.9, 41.7, 41.2, 28.8, 28.5. HR-MS (FTMS<sup>+</sup>): [M + H]<sup>+</sup> Calculated: (C<sub>22</sub>H<sub>27</sub>NO<sub>2</sub>PtH) 533.1765; Found: 533.1772. Anal. Calcd for C<sub>22</sub>H<sub>27</sub>NO<sub>2</sub>Pt (MW 532.55): C, 49.62; H, 5.11; N, 2.63. Found: C, 49.71; H, 5.23; N, 2.55 (average of two runs). The characterisation matches that previously reported.<sup>2</sup>



Figure S1. <sup>1</sup>H NMR spectrum of Platinum (II) [2-(phenyl)-pyridinato-*N*,*C*<sup>2'</sup>]-(2,2,6,6-

tetramethyl-3,5-heptanedionate), [Pt(ppy)(pivacac)], in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S2. <sup>13</sup>C NMR spectrum of Platinum (II) [2-(phenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(ppy)(pivacac)], in CDCl<sub>3</sub>.

Platinum (II) [2-(4-pentafluorosulfanylphenyl)-pyridinato-*N*,*C*<sup>2'</sup>]-(2,2,6,6-tetramethyl-3,5-heptanedionate): [Pt(4-SF<sub>5</sub>ppy)(pivacac)].



Yellow powder (0.080 g). Yield: 35%. Mp: 241 – 246 °C (decomposition). <sup>1</sup>H {<sup>19</sup>F} (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 9.04 (ddd, J = 5.8, 1.6, 0.8 Hz, 1H), 8.01 (d, J = 2.3 Hz, 1H), 7.98 – 7.89 (m, 1H), 7.76 – 7.69 (m, 1H), 7.59 – 7.45 (m, 2H), 7.29 (ddd, J = 7.4, 5.8, 1.4 Hz, 1H), 5.87 (s, 1H) 1.29 (s, 9H), 1.28 (s, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 195.6, 194.3, 166.4, 153.8, 147.7, 141.1, 138.6, 128.6, 127.4, 122.8, 121.0, 119.5, 93.7, 41.7, 41.1, 28.7, 28.5. <sup>19</sup>F {<sup>1</sup>H} NMR (371 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 85.70 (p, J = 148.90 Hz, 1F), 61.94 (d, J = 148.90 Hz, 4F). HR-MS (FTMS<sup>+</sup>): [M + H]<sup>+</sup> Calculated: (C<sub>22</sub>H<sub>26</sub>F<sub>5</sub>NO<sub>2</sub>PtSH) 659.1327; Found: 659.1332. Anal. Calcd for C<sub>22</sub>H<sub>26</sub>F<sub>5</sub>NO<sub>2</sub>PtS (MW 658.59): C, 40.72; H, 3.88; N, 2.63 Found: C, 40.60; H, 4.09; N, 2.41 (average of two runs).



Figure S3. <sup>1</sup>H NMR spectrum of Platinum (II) [2-(4-pentafluorosulfanylphenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(4-SF<sub>5</sub>ppy)(pivacac)], in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S4. <sup>13</sup>C NMR spectrum of Platinum (II) [2-(4-pentafluorosulfanylphenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(4-SF<sub>5</sub>ppy)(pivacac)], in CDCl<sub>3</sub>.



Figure S5. <sup>19</sup>F NMR spectrum of Platinum (II) [2-(4-pentafluorosulfanylphenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(4-SF<sub>5</sub>ppy)(pivacac)], in CD<sub>2</sub>Cl<sub>2</sub>.

Platinum (II) [2-(5-pentafluorosunfanylphenyl)-pyridinato-N,C<sup>2'</sup>]-(2,2,6,6-tetramethyl-3,5-heptanedionate): [Pt(5-SF<sub>5</sub>ppy)(pivacac)].



Yellow crystalline flakes (0.094 g). Yield: 40%. Mp: 206 – 208 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 9.06 (ddd, J = 5.8, 1.5, 0.7 Hz, 1H), 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.82 (d, J = 2.3 Hz, 1H), 7.74 (t, J = 8.5 Hz, 1H), 7.54 (dd, J = 8.5, 2.4 Hz, 2H), 7.28 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H), 5.88 (s, 1H), 1.29 (s, 9H), 1.28 (s, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 195.7, 194.3, 166.8, 150.5, 147.5, 145.9, 144.9, 138.7, 130.9, 126.2, 122.5, 120.1, 119.0, 93.7, 41.7, 41.3, 28.9, 28.5. <sup>19</sup>F {<sup>1</sup>H} NMR (371 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 86.65 (p, J = 149.50 Hz, 1F), 63.29 (d, J = 149.50 Hz, 4F). HR-MS (FTMS+): [M + H]<sup>+</sup> Calculated: (C<sub>22</sub>H<sub>26</sub>F<sub>5</sub>NO<sub>2</sub>PtSH) 659.1327; Found: 659.1337. Anal. Calcd for C<sub>22</sub>H<sub>26</sub>F<sub>5</sub>NO<sub>2</sub>PtS (MW 658.59): C, 40.12; H, 3.98; N, 2.13 Found: C, 40.54; H, 4.11; N, 2.38.



Figure S6. <sup>1</sup>H NMR spectrum of Platinum (II) [2-(5-pentafluorosunfanylphenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(5-SF<sub>5</sub>ppy)(pivacac)], in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S7. <sup>13</sup>C NMR spectrum of Platinum (II) [2-(5-pentafluorosunfanylphenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(5-SF<sub>5</sub>ppy)(pivacac)], in CDCl<sub>3</sub>.



Figure S8. <sup>19</sup>F NMR spectrum of Platinum (II) [2-(5-pentafluorosunfanylphenyl)-pyridinato- $N,C^{2'}$ ]-(2,2,6,6-tetramethyl-3,5-heptanedionate), [Pt(5-SF<sub>5</sub>ppy)(pivacac)], in CD<sub>2</sub>Cl<sub>2</sub>.



Figure **S9**. CV trace of both reduction processes of complex [**Pt(4-SF<sub>5</sub>ppy)(pivacac**)] (2) in MeCN solution, reported versus SCE ( $Fc/Fc^+ = 0.38$  V in MeCN).<sup>3</sup> The cathodic scan was performed at 100 mV s<sup>-1</sup>.



Figure S10. CV trace of both reduction processes of complex [Pt(5-SF<sub>5</sub>ppy)(pivacac)] (3) in MeCN solution, reported versus SCE (Fc/Fc<sup>+</sup> = 0.38 V in MeCN).<sup>3</sup> The cathodic scan was performed at 100 mV s<sup>-1</sup>.



Figure S11. Emission lifetime of neat films of complexes 1 ( $\lambda_{em} = 488 \text{ nm}$ ), 2 ( $\lambda_{em} = 530 \text{ nm}$ ) and 3 ( $\lambda_{em} = 518 \text{ nm}$ ) after excitation at 378 nm.



Figure **S12**. Emission lifetime of neat films of complexes **1** ( $\lambda_{em} = 627 \text{ nm}$ ) and **3** ( $\lambda_{em} = 622 \text{ nm}$ ) after excitation at 378 nm.



Figure **S13**. Photos of powder samples of complexes **1**, **2** and **3** illuminated under UV (365 nm) light before (left) and after (right) grinding.

*Photophysical measurements.* All samples were prepared in HPLC grade acetonitrile (MeCN) with varying concentrations on the order of  $\mu$ M. Absorption spectra were recorded at RT using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least three independent solutions at varying concentrations with absorbance ranging from  $3.23 \times 10^{-4}$  to  $1.82 \times 10^{-5}$  M.

The sample solutions for the emission spectra were degassed by vigorous bubbling. Steadystate emission and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. All samples for steady-state measurements were excited at 360 nm using a xenon lamp, while samples for time-resolved measurements were excited at 378 nm using a PDL 800-D pulsed diode laser. Emission quantum yields were determined using the optically dilute method.<sup>4</sup> A stock solution with absorbance of ca. 0.5 was prepared and then four dilutions were prepared with dilution factors of 5, 6.6, 10 and 20 to obtain solutions with absorbances of ca. 0.1 0.075, 0.05 and 0.025, respectively. The Beer-Lambert law was found to be linear at the concentrations of the solutions. The emission spectra were then measured after the solutions were degassed by nitrogen purging for fifteen minutes per sample prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor  $(R^2)$  for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation  $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$  was used to calculate the relative quantum yield of each of the sample, where  $\Phi_r$  is the absolute quantum yield of the reference, *n* is the refractive index of the solvent, *A* is the absorbance at the excitation wavelength, and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution of quinine sulfate in 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi r = 54.6\%$ ) was used as the external reference.<sup>5</sup>

Samples for solid-state measurements were prepared by spin-coating toluene solutions of each complex (5 mg / 1 mL) onto quartz substrates. Steady-state emission and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. All samples for steady-state measurements were excited at 360 nm xenon lamp while samples for time-resolved measurements were excited at 378 nm using a PDL 800-D pulsed diode laser, and were recorded under air. Photoluminescence quantum yields were measured using an integrating sphere, under a nitrogen atmosphere.

*Electrochemistry measurements.* Cyclic voltammetry (CV) measurements were performed on an Electrochemical Analyzer potentiostat model 600D from CH Instruments. Solutions for cyclic voltammetry were prepared in MeCN and degassed with MeCN-saturated nitrogen bubbling for about 10 min prior to scanning. Tetra(*n*-butyl)ammoniumhexafluorophosphate (TBAPF<sub>6</sub>; ca. 0.1 M in MeCN) was used as the supporting electrolyte. A Pt wire was used as the pseudo-reference electrode; a Pt wire coil was used as the counter electrode and a Pt disk electrode was used for the working electrode. The redox potentials are reported relative to a saturated calomel electrode (SCE) electrode with a ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) redox couple as an internal reference (0.38 V vs SCE).<sup>3</sup>

#### X-ray crystallography

Single crystals of the complexes were grown by vapour diffusion of hexane into concentrated dichloromethane solutions. Data were collected at 173 K by using a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics and Rigaku XtaLAB P200 system, with Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å). A preliminary screen of a crystal of **1** allowed determination of the unit cell, which was in agreement with that of the known structure,<sup>6</sup> which had been determined at ambient temperature. Intensity data for 2 and 3 were collected using  $\omega$  steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using CrystalClear.<sup>7</sup> Structures were solved by Patterson (PATTY)<sup>8</sup> methods and refined by full-matrix least-squares against F<sup>2</sup> (SHELXL-2013).<sup>9</sup> Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure interface.<sup>10</sup> Crystallographic data for complexes 2 and 3 are presented in Table S1. Given that the thermal ellipsoids seen in 2 suggested deviation of parts of the complex away from the crystallographic mirror-plane, the data was also evaluated in the space group  $P2_1$ . While this did not show the exaggerated ellipsoids seen in one of the *t*-butyl groups of 2, it did show a range of unusual bond distances and angles in multiple parts of the structure, a wider range of atoms needing restraint to their thermal parameters, and a Flack parameter of 0.49(2). Further attempts at refinement in PI showed the same pattern of elongated ellipsoids in the same the *t*-butyl group, so the data was left in  $P2_1/m$ .

	2	3
empirical formula	C <sub>22</sub> H <sub>26</sub> F <sub>5</sub> NO <sub>2</sub> PtS	C <sub>22</sub> H <sub>26</sub> F <sub>5</sub> NO <sub>2</sub> PtS
fw	658.59	658.59
crystal description	yellow, needle	colourless, platelet
crystal size [mm <sup>3</sup> ]	0.11×0.03×0.01	0.18×0.12×0.03
temp [K]	173	173
space group	$P2_1/m$ (No. 11)	<i>Pbca</i> (No. 61)
a [Å]	12.916(4)	12.2353(10)
<i>b</i> [Å]	6.8394(18)	13.7645(13)
<i>c</i> [Å]	14.546(5)	28.3482(18)
β [°]	1188.1(6)	4774.2(7)
$\operatorname{vol}\left[\operatorname{\AA}\right]^{3}$	1.841	1.832
Ζ	6.027	5.999
$\rho$ (calc) [g/cm <sup>3</sup> ]	640	2560
$\mu [\mathrm{mm}^{-1}]$	22880	36543
F(000)	2373 (0.1172)	4340 (0.0319)
reflns collected	2373/22/183	4340/0/295
independent reflns ( $R_{int}$ )	1.165	1.072
data/restraints/params	0.0746	0.0167
GOF on $F^2$	0.1994	0.0328
$R_{I}[I > 2\sigma(I)]$	6.31/-0.93	0.41/-0.53
$wR_2$ (all data)	C22H26F5NO2PtS	C <sub>22</sub> H <sub>26</sub> F <sub>5</sub> NO <sub>2</sub> PtS
largest diff. peak/hole [e/Å <sup>3</sup> ]	658.59	658.59

 Table S1. Crystal Data and Structure Refinement.

#### **DFT and TD-DFT calculations**

To perform DFT and TD-DFT calculations, we have used the Gaussian program.<sup>11</sup> Our calculations consisted in geometry optimization vibrational spectra determinations and TD-DFT calculations of the different structures. We have applied default procedures, integration grids, algorithms and parameters, except for tighten energy (typically  $10^{-10} a.u.$ ) and internal forces  $(10^{-5} a.u.)$  convergence thresholds and the use of the *ultrafine* integration DFT grid. The groundstate geometrical parameters have been determined with the PBE0 functional.<sup>12</sup> The vibrational spectrum has been subsequently determined analytically at the same level of theory and it has been checked that all structures correspond to true minima of the potential energy surface. At least, the first forty low-lying excited-states have been determined within the vertical TD-DFT approximation using the same functional, that is suited for optical spectra.<sup>13</sup> Phosphorescence was studied by optimizing the lowest triplet excited-state with unrestricted DFT (PBE0 functional). The oxidation and reduction effects have been estimated by computing the radical cation and radical anion forms in the vertical approximation (neutral geometry). For the structural and vibrational calculations, we used the 6-311G(d,p) atomic basis set for all light atoms, whereas during the single-point and TD-DFT steps, a larger basis set, namely 6-311+G(2d,p) was applied). The Pt center was systematically described using the LanL08(f) pseudo-potential and atomic basis set. During all steps, a modeling of bulk solvent effects (here MeCN) through the Polarizable Continuum Model (PCM),<sup>14</sup> using the liner-response approach in its non-equilibrium limit for the TD-DFT part of the calculation. For the optimizations of the excimeric dimer of 2 and 3, we used the same level of theory as above, but for the consideration of dispersion corrections with the D3-BJ approach.<sup>15</sup> We extracted the starting geometries from the XRD data, taking the closest dimer in each case. We first optimized the geometry

considering that the two complexes are in their ground-state structure. Next, starting with this ground-state minimal structure, we replaced one of the two ground-state complex by a tripletoptimized monomer and re-optimized the resulting structure to determine the excimer (triplet) structure. The MOs plot reported below use a contour threshold of 0.04 au, whereas the spin density plots use a contour threshold of 0.002 au.



Figure **S14**. Simulated UV/Vis spectra for the three studied complexes. This corresponds to the TD-DFT vertical transitions (stick) broadened with a Gaussian of FWHM=0.3 eV.

Spin densities for the triplet structures



Figure **S15**. Spin density difference plots of the lowest triplet state at its optimal geometry.

#### Excimeric dimer

By simply taking the difference between the energies of the dimers and the separated monomers, one can roughly estimate the ground-state interaction energies to attain 28 kcal.mol<sup>-1</sup> and 29 kcal.mol<sup>-1</sup> for **2** and **3**, respectively. Though these values that do not account for entropic corrections, are certainly too large, they clearly indicate a similar behaviour for the two systems. When performing the calculations considering one complex in its SO structure and the other in its T1 structure, we obtained, as can be seen in Figure **S16**, excimeric structure, with the spin density almost exclusively localized on one of the two complex. In that case, the interaction energy remains again similar for both **2** and **3** (28 kcal.mol<sup>-1</sup> and 33 kcal.mol<sup>-1</sup>, respectively).



Figure **S16**. Top and side views of the spin density difference for the optimized excimeric dimer.

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