

Supporting Information:

Deep red luminescence and efficient singlet oxygen generation by cyclometalated platinum (II) complexes with 8-hydroxyquinolines and quinoline-8-thiol

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Experimental

Abbreviations used in the text: thpy - 2-(2-thienyl)-pyridine; ppy - 2-phenylpyridine; dba - N,N-dimethylbenzylamine; r.t. – room temperature; br Pt sat – broad ¹⁹⁵Pt-¹H satellites in the ¹H NMR spectra.

All ligands were commercially available. In-house facilities were used to acquire CHN and MALDI MS (CH₂Cl₂, DCTB matrix) data. ¹H NMR spectra were recorded on a Bruker 250 MHz instrument and are presented as δ in ppm and *J* in Hz.

All reactions were carried out in darkness under N₂ using general grade solvents that were degassed by bubbling with N₂ for 10 min. Purification, crystal growth and handling of all compounds were carried out under air with a minimum exposure to light. All products were air- and moisture-stable solids which were stored in the dark when not used.

Synthesis of (Bu₄N)₂PtCl₄. The reaction can be performed under air. K₂PtCl₄ (0.5 g, 1.2 mmol) in water (10 ml) was extracted with (Bu₄N)Cl (0.7 g, 2.52 mmol, small excess) in CH₂Cl₂ (30 ml) to give colourless aqueous layer and orange organic layer. The organic layer was washed with water (10 ml), dried (MgSO₄) and evaporated to give the product in quantitative yield as orange solid.

Synthesis of dimer [(thpy)PtCl]₂. (Bu₄N)₂PtCl₄ (1.2 mmol, prepared from 0.5 g of K₂PtCl₄) in CH₂Cl₂ (20 ml) was mixed with 2-(2-thienyl)-pyridine (0.2 g, 1.24 mmol, excess) in CH₃OH (10 ml) and stirred under N₂ in the dark at 40^oC for 3 days to give dark red solution and yellow precipitate. The reaction mixture was evaporated to dryness and re-dissolved in CH₃OH (10 ml, the solution might be cloudy). Gradual addition of water (90 ml) gave orange or brown precipitate of crude product that was filtered and washed with water and ether. The crude product was suspended in CH₂Cl₂ (10 ml) and CH₃OH (5 ml) and sonicated to give yellow precipitate of pure product that was filtered and washed with ether. The dark red filtrate from the previous step contains monomer Bu₄N[(thpy)PtCl₂] that could be converted to dimer by repeating the purification steps (evaporation to dryness, dissolution in CH₃OH, precipitation with water and sonication in CH₂Cl₂/CH₃OH). Yield – 0.235-0.307 g (0.3-0.39 mmol, 50-65%); C₁₈H₁₂Cl₂N₂Pt₂S₂; M.W. 781.49; insoluble in CH₃OH, CH₂Cl₂ and water.

Synthesis of dimer [(ppy)PtCl]₂. (Bu₄N)₂PtCl₄ (1.2 mmol, prepared from 0.5 g of K₂PtCl₄) in ethanol (20 ml) was mixed with 2-phenylpyridine (0.19 g, 1.22 mmol, small excess) in CH₂Cl₂ (5 ml) and stirred under N₂ in the dark at 30⁰C for 7 days to give yellow solution. Black precipitate was formed if reaction was performed at temperatures >30⁰C. The reaction mixture was evaporated to 10 ml. Addition of water (70 ml) gave yellow precipitate of crude product that was filtered, washed with water and ether and re-dissolved in CH₂Cl₂ (10 ml). Addition of methanol (20 ml) and sonication gave pure product as bright yellow solid. The filtrate from the previous step contains monomer Bu₄N[(ppy)PtCl₂] that could be converted to dimer by repeating the purification steps (evaporation to dryness, dissolution in CH₃OH, precipitation with water and sonication in CH₂Cl₂/CH₃OH). Yield – 0.115 g (0.15 mmol, 25%); C₂₂H₁₆Cl₂N₂Pt₂; M.W. 769.44; insoluble in CH₃OH, CH₂Cl₂ and water.

Synthesis of monomer Bu₄N[(C[^]N)PtCl]₂. The reaction can be performed under air. [(C[^]N)PtCl]₂ and Bu₄NCl in 1:2 molar ratio were sonicated in alcohols, CH₂Cl₂ or CH₃CN (10 ml) at r.t. until complete dissolution of [(C[^]N)PtCl]₂ (*ca* 5 min). The resulting solution of Bu₄N[(C[^]N)PtCl₂] was used directly in further synthesis or it was evaporated to dryness to give the product as orange solid.

Synthesis of Pt(dba)Cl(DMSO). PtCl₂(DMSO)₂ (200 mg, 0.47 mmol), N,N-dimethylbenzylamine (64 mg, 0.47 mmol) and sodium acetate (39 mg, 0.47 mmol, base) were refluxed in CH₃OH (20 ml) for 24 hr to give pale yellow solution that was evaporated to dryness and dissolved in CH₂Cl₂ (20 ml). The solution was washed with water, dried (MgSO₄), filtered and evaporated to 5 ml. Addition of hexane (75 ml) gave product as a white solid. Yield – 170 mg (0.38 mmol, 82%); C₁₁H₁₈ClNOPtS; M.W. 442.86. ¹H NMR (CDCl₃): 2.92 (s, *J*_{Pt-H} 35, 6H), 3.54 (s, *J*_{Pt-H} 25, 6H), 3.99 (s, *J*_{Pt-H} 40, 2H), 6.98-7.10 (m, 3H), 7.94 (dd, *J* 7.3, 1.5, br Pt sat, 1H).

Synthesis of Pt(C[^]N) complexes with 8-hydroxyquinolines, 1-R, 2-R and 3-R. Pt(C[^]N) precursor, 8-hydroxyquinoline and excess of Na₂CO₃ (base) were stirred in 2-methoxyethanol (10 ml) at 100⁰C for 24 hr. The dark red reaction mixture was evaporated to dryness and purified by column chromatography (silica, CH₂Cl₂ or acetone/CH₂Cl₂) to give main orange or red fraction that was reduced to 5 ml. Addition of hexane (50 ml) and sonication precipitated the product that was filtered, washed with hexane and dried in vacuum. The products of dark red (**1-R** and **2-R**) or orange (**3-R**) colour were generally insoluble in alkanes and ether, had low solubility in CH₃OH and acetone and were soluble in CH₂Cl₂ and DMSO. Their solubility in CH₂Cl₂ varied in the order **3-R** > **1-R**, **2-R** and in the order **1-CH₃** > **1-H** > **1-Cl**.

1-H. [(thpy)PtCl]₂ (115 mg, 0.15 mmol), 8-hydroxyquinoline (43 mg, 0.30 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 108 mg (0.22 mmol, 72%) of the product. Calc. for C₁₈H₁₂N₂OPtS (M.W. 499.44): C, 43.29; H, 2.42; N, 5.61. Found: C, 43.37; H, 2.51; N, 5.44. MALDI MS *m/z*: 500 (100%, M⁺). ¹H NMR (CD₂Cl₂): 6.95 (dd, *J* 8.0, 0.9, 1H), 7.00-7.09 (m, 2H), 7.31-7.54 (m, 4H), 7.59 (d, *J* 4.9, 1H, br Pt sat), 7.75 (td, *J* 8.0, 1.6, 1H), 8.37 (dd, *J* 8.3, 1.2, 1H), 9.16 (d, *J* 5.8, 1H, br Pt sat), 9.31 (dd, *J* 5.2, 1.2, 1H, br Pt sat).

1-CH₃. [(thpy)PtCl]₂ (110 mg, 0.14 mmol), 5,7-dimethyl-8-hydroxyquinoline (49 mg, 0.28 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 116 mg (0.22 mmol, 79%) of the product. Calc. for C₂₀H₁₆N₂OPtS (M.W. 527.50): C, 45.54; H, 3.06; N, 5.31. Found: C, 45.65; H, 2.93; N, 5.23. MALDI MS *m/z*: 527 (100%, M⁺). ¹H NMR (CDCl₃): 2.59 (s, 3H), 2.60 (s, 3H), 7.03 (dd, *J* 7.3, 5.8, 1.2, 1H), 7.28 (s,

1H), 7.31-7.42 (m, 3H), 7.56 (d, *J* 4.9, 1H), 7.72 (td, *J* 7.6, 1.5, 1H), 8.43 (dd, *J* 8.6, 1.2, 1H), 9.29 (dd, *J* 5.8, 1.5, 0.6, 1H, br Pt sat), 9.35 (dd, *J* 5.5, 1.5, 1H, br Pt sat).

1-Cl. [(thpy)PtCl]₂ (110 mg, 0.14 mmol), 5-chloro-8-hydroxyquinoline (51 mg, 0.28 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 110 mg (0.21 mmol, 74%) of the product. Calc. for C₁₈H₁₁ClN₂O₂PtS (M.W. 533.89): C, 40.49; H, 2.08; N, 5.25. Found: C, 40.18; H, 2.0; N, 5.1. MALDI MS *m/z*: 534 (100%, M⁺). ¹H NMR (CDCl₃): 6.95-7.08 (m, 2H), 7.33 (d, *J* 5.2, 1H), 7.39 (d, *J* 7.9, 1H), 7.48-7.61 (m, 3H), 7.74 (td, *J* 8.0, 1.5, 1H), 8.7 (dd, *J* 8.6, 1.2, 1H), 9.15 (dd, *J* 5.8, 1.5, 0.9, 1H, br Pt sat), 9.38 (dd, *J* 4.9, 1.2, 1H, br Pt sat).

2-H. [(ppy)PtCl]₂ (110 mg, 0.145 mmol), 8-hydroxyquinoline (41 mg, 0.28 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 58 mg (0.12 mmol, 42%) of the product. Calc. for C₂₀H₁₄N₂O₂Pt (M.W. 493.42): C, 48.68; H, 2.86; N, 5.68. Found: C, 48.73; H, 2.75; N, 5.74. MALDI MS *m/z*: 493 (100%, M⁺). ¹H NMR (CDCl₃): 6.95 (dd, *J* 7.9, 0.9, 1H), 7.11-7.34 (m, 4H), 7.41-7.74 (m, 5H), 7.85 (td, *J* 8.2, 1.5, 1H), 8.34 (dd, *J* 8.3, 1.2, 1H), 9.26 (dd, *J* 5.2, 1.2, br Pt sat, 1H), 9.43 (dd, *J* 6.1, 1.9, 0.9, br Pt sat, 1H).

2-CH₃. [(ppy)PtCl]₂ (110 mg, 0.145 mmol), 5,7-dimethyl-8-hydroxyquinoline (50 mg, 0.29 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 74 mg (0.142 mmol, 49%) of the product. Calc. for C₂₂H₁₈N₂O₂Pt (M.W. 521.47): C, 50.67; H, 3.48; N, 5.37. Found: C, 50.5; H, 3.18; N, 5.51. MALDI MS *m/z*: 521 (100%, M⁺). ¹H NMR (CDCl₃): 2.59 (s, 3H), 2.6 (s, 3H), 7.12-7.34 (m, 4H), 7.41 (dd, *J* 8.3, 5.2, 1H), 7.56 (dd, *J* 7.3, 1.2, 1H), 7.64-7.72 (m, 2H), 7.85 (td, *J* 8.0, 7.3, 1.5, 1H), 8.43 (dd, *J* 8.6, 1.2, 1H), 9.27 (dd, *J* 5.2, 1.2, br Pt sat, 1H), 9.52 (dd, *J* 5.8, 1.8, 0.9, br Pt sat, 1H).

3-H. Pt(dba)Cl(DMSO) (130 mg, 0.29 mmol), 8-hydroxyquinoline (42.6 mg, 0.29 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 108 mg (0.23 mmol, 79%) of the product. Calc. for C₁₈H₁₈N₂O₂Pt (M.W. 473.43): C, 45.67; H, 3.83; N, 5.92. Found: C, 45.35; H, 3.68; N, 5.85. MALDI MS *m/z*: 473 (100%, M⁺). ¹H NMR (CDCl₃): 3.1 (s, *J*_{Pt-H} 35, 6H), 4.07 (s, *J*_{Pt-H} 43, 2H), 6.88 (dd, *J* 8.0, 0.9, 1H), 6.99-7.18 (m, 4H), 7.29-7.39 (m, 2H), 7.46 (t, *J* 8.0, 1H), 8.25 (dd, *J* 8.3, 1.2, 1H), 8.95 (d, br, *J* 5.2, br Pt sat, 1H).

3-CH₃. Pt(dba)Cl(DMSO) (130 mg, 0.29 mmol), 5,7-dimethyl-8-hydroxyquinoline (50.8 mg, 0.29 mmol) and Na₂CO₃ (50 mg, 0.47 mmol, excess) gave 76 mg (0.15 mmol, 52%) of the product that was soluble in alkanes and arenes. Calc. for C₂₀H₂₂N₂O₂Pt (M.W. 501.48): C, 47.9; H, 4.42; N, 5.59. Found: C, 47.61; H, 4.46; N, 5.51. MALDI MS *m/z*: 501 (100%, M⁺). ¹H NMR (CDCl₃): 2.49 (s, 3H), 2.55 (s, 3H), 3.11 (s, *J*_{Pt-H} 34, 6H), 4.07 (s, *J*_{Pt-H} 42, 2H), 7.0-7.16 (m, 3H), 7.2-7.32 (m, 2H), 7.38 (d, *J* 7.0, br Pt sat, 1H), 8.33 (dd, *J* 8.6, 1.5, 1H), 8.94 (d, *J* 4.9, br Pt sat, 1H).

Synthesis of Pt(C[^]N) complexes with quinoline-8-thiol, 1-S and 2-S.

Bu₄N[(C[^]N)PtCl₂] (prepared in situ from [(C[^]N)PtCl]₂ and (Bu₄N)Cl as described above), quinoline-8-thiol hydrochloride and ^tBuOK (base) were stirred in CH₃CN (20 ml) at r.t. for 48 hr with occasional sonication. The brownish-red reaction mixture was evaporated to dryness and purified by column chromatography (silica, CH₂Cl₂) to give main red fraction that was reduced to 5 ml. Addition of hexane (50 ml) and sonication precipitated the product that was filtered, washed with hexane and dried in vacuum. The brown-red products were insoluble in alkanes and ether, had low solubility in CH₃OH and acetone and were soluble in CH₂Cl₂ and DMSO.

1-S. [(thpy)PtCl]₂ (100 mg, 0.13 mmol), (Bu₄N)Cl (71 mg, 0.26 mmol), 8-quinolinethiol hydrochloride (51 mg, 0.26 mmol) and ^tBuOK (58 mg, 0.52 mmol) gave 37 mg (0.072 mmol, 28%) of the product. Calc. for C₁₈H₁₂N₂PtS₂ (M.W. 515.51): C, 41.94; H, 2.35; N, 5.43. Found: C, 41.8; H, 2.25; N, 5.38. MALDI MS *m/z*: 515 (100%, M⁺). ¹H NMR (CDCl₃): 7.11 (td, *J* 7.3, 5.8, 1.5, 1H), 7.27-7.51 (m, 5H), 7.56 (dd, *J* 8.3, 5.2, 1H), 7.78 (td, *J* 7.9, 7.3, 1.5, 1H), 7.95 (dd, *J* 7.3, 1.2, 1H), 8.35 (dd, *J* 8.3, 1.5, 1H), 8.58 (d, *J* 5.8, *J*_{Pt-H} 25, 1H), 9.12 (dd, *J* 5.2, 1.2, br Pt sat, 1H).

2-S. [(ppy)PtCl]₂ (120 mg, 0.155 mmol), (Bu₄N)Cl (87 mg, 0.31 mmol), 8-quinolinethiol hydrochloride (62 mg, 0.31 mmol) and ^tBuOK (70 mg, 0.62 mmol) gave 61 mg (0.12 mmol, 39%) of the product. Calc. for C₂₀H₁₄N₂PtS (M.W. 509.48): C, 47.15; H, 2.77; N, 5.50. Found: C, 47.27; H, 2.82; N, 5.44. MALDI MS *m/z*: 509 (100%, M⁺). ¹H NMR (CDCl₃): 7.07-7.16 (m, 2H), 7.24-7.37 (m, 2H), 7.46 (t, *J* 7.6, 1H), 7.53-7.62 (m, 2H), 7.77-8.05 (m, 4H), 8.36 (dd, *J* 8.3, 1.5, 1H), 8.63 (d, *J* 5.8, br Pt sat), 9.04 (d, *J* 5.2, br Pt sat, 1H). The sample contained 5% of an isomer that could not be separated by column chromatography with some ¹H NMR signals at 7.45 (t, *J* 7.6), 8.29 (dd, *J* 8.3, 1.2), 9.48 (dd, *J* 5.2, 1.2).

X-ray crystallography. Single crystals were grown by slow evaporation of mixed CH₂Cl₂/petroleum ether solutions of **1-CH₃** and **2-H**, and CH₂Cl₂/heptane solutions of **3-CH₃**.

Data were collected on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. All reflections were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods and refined by full matrix least squares methods on *F*². Complex scattering factors were taken from the program package SHELXTL [An integrated system for solving and refining crystal structures from diffraction data, Revision 5.1, Bruker AXS LTD] as implemented on an IBM PC. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Data in common: T = 150(2) K, λ = 0.71073 Å.

1-CH₃. C₂₀H₁₆N₂OPtS; M.W. 527.50; red plates; size [mm]: 0.37 x 0.12 x 0.07; triclinic; space group *P*-1 (*C*_i¹, No. 2); *a/b/c* [Å] = 7.866(6) / 9.909(7) / 11.743(8); α/β/γ [°] = 65.319(10) / 89.036(11) / 81.856(11); V = 822.4(10) Å³; Z = 2; ρ_{calc} = 2.130 g cm⁻³; μ = 8.669 mm⁻¹; data/restraints/parameters = 3635 / 0 / 228; R(I > 2σ_I): R1 = 0.0462, wR2 = 0.0981; R(all data): R1 = 0.0621, wR2 = 0.1026.

2-H. C₂₀H₁₄N₂OPt; M.W. 493.42; red needles; size [mm]: 0.28 x 0.08 x 0.08; monoclinic; space group *P*2₁/n (a non-standard setting of *P*2₁/*c* *C*₂⁵ *h*, No. 14); *a/b/c* [Å] = 9.3802(14) / 7.6678(12) / 20.661(3); α/β/γ [°] = 90 / 90.746(2) / 90; V = 1485.9(4) Å³; Z = 4; ρ_{calc} = 2.206 g cm⁻³; μ = 9.452 mm⁻¹; data/restraints/parameters = 2619 / 0 / 217; R(I > 2σ_I): R1 = 0.0255, wR2 = 0.0611; R(all data): R1 = 0.0349, wR2 = 0.0651.

3-CH₃. C₂₀H₂₂N₂OPt; MW = 501.49; yellow blocks; size [mm]: 0.38 x 0.26 x 0.21; triclinic; space group *P*-1 (*C*_i¹, No. 2); *a/b/c* [Å] = 9.0504(9) / 9.3633(9) / 11.0494(11); α/β/γ [°] = 99.431(2) / 96.608(2) / 109.814(2); V = 854.19(15) Å³; Z = 2; ρ_{calc} = 1.950 g cm⁻³; μ = 8.222 mm⁻¹; data/restraints/parameters = 3781 / 0 / 217; R(I > 2σ_I): R1 = 0.0355, wR2 = 0.0883; R(all data): R1 = 0.0385, wR2 = 0.0900.

Spectroscopy. Spectroscopic studies were performed with freshly prepared $(2-5) \cdot 10^{-5}$ M solutions of the complexes. For luminescence studies, the solutions were degassed by three freeze-pump-thaw cycles and kept under dry N_2 (purity - 99.5%; O_2 content - 66 ppm). The dry solvents were obtained from the in-house Grubbs column set-up.

Absorption spectra were recorded with a Cary 50 Bio UV-Visible Spectrophotometer in 1 cm cells.

Luminescence spectra were recorded with a Perkin Elmer LS 50B spectrofluorimeter with the red-sensitive R928 PMT, and were corrected for the instrument sensitivity using the file supplied by manufacturer. Luminescence quantum yields were determined relative to a solution of $Ru(bpy)_3Cl_2$ in air saturated water, $\phi_0 = 2.8\%$, using the equation $\phi_x = (n_x/n_o)^2 \cdot (\phi_0)(1-10^{-A_o})I_x / ((1-10^{-A_x}) \cdot I_o)$, where ϕ is a quantum yield, A – optical density at the excitation wavelength, I - integrated emission, n - refractive index of the solvent and subscripts x/o refer to sample/standard solution. The following conditions were used: optical density at excitation wavelength < 0.15 , excitation and emission slits – 10 and 5 nm, respectively.

Luminescence lifetimes were measured with a Mini- τ fluorimeter (Edinburgh Instrument) which had a picosecond diode laser (410 nm, 80 ps) as an excitation source and allowed to select emission wavelength range by colour filters. The luminescence lifetimes for **1-CH₃**, **2-CH₃** and **3-CH₃** were measured on a home-built set-up comprising Nd:YAG laser as an excitation source (355 nm), red-sensitive Hamamatsu R928 PMT and a Spectra-Physics Monochromator. The emission decay traces were recorded on the Tektronix 3032B oscilloscope. The laser was provided through the EPSRC/RAL laser loan pool scheme.

Experimental uncertainties are estimated to be $\pm 10\%$ for extinction coefficients, ± 2 nm for wavelengths, $\pm 20\%$ for emission quantum yields and $\pm 15\%$ for luminescence lifetimes.

Singlet oxygen measurements. The 1270 nm luminescence of singlet oxygen ($^1\Delta_g O_2$) was produced by photo excitation of metal complexes at r.t. in air saturated CH_2Cl_2 or toluene solution using third harmonic of a Nd:YAG laser (355 nm, 7 ns). The luminescence was detected by a liquid nitrogen cooled Germanium Detector/Amplifier (Applied Detector Corporation 403HS) close-coupled to the laser photolysis cell in right-angle geometry. A 1 mm thick, 20 mm diameter piece of AR-coated silicon (II-IV Inc) was placed between the diode and cell to act as a cut-off filter for light below 1100 nm. The 403HS power supply bias voltage was operated at 450 V. The amplifier output was AC coupled to the digitizer. The output was displayed on a Tektronix TDS 380 digitizing oscilloscope. Data processing was performed on an IBM PC using in-house developed software.

The quantum yield of 1O_2 production was determined by comparing the slopes of the linear plots of initial emission intensity vs. laser energy for optically matched solutions (λ_{exc} 355 nm) of the compounds under study and that of the standard (phenalenone, $\phi(^1O_2) = 95\%$).

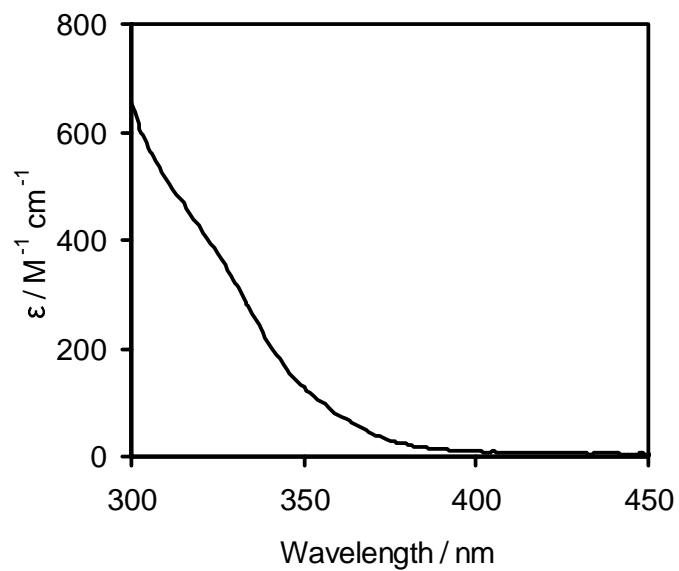


Fig. 1S Absorption spectrum of Pt(dba)Cl(DMSO) in CH₂Cl₂.

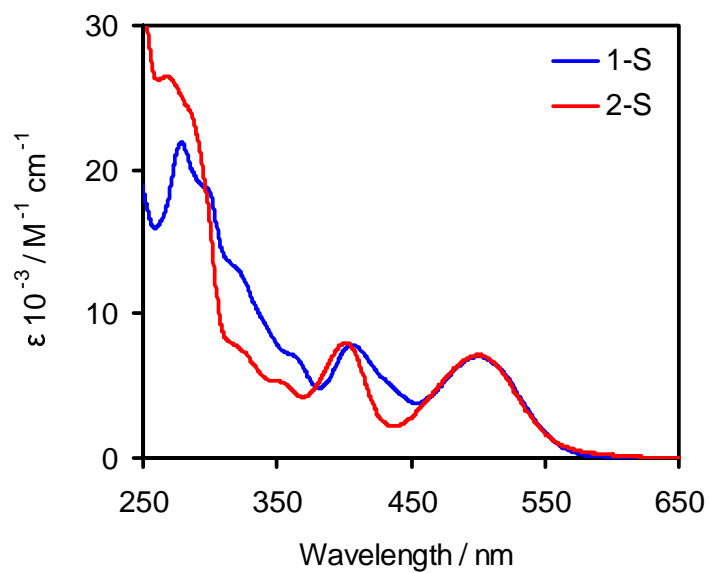


Fig. 2S Absorption spectra of 1-S and 2-S in CH₂Cl₂.

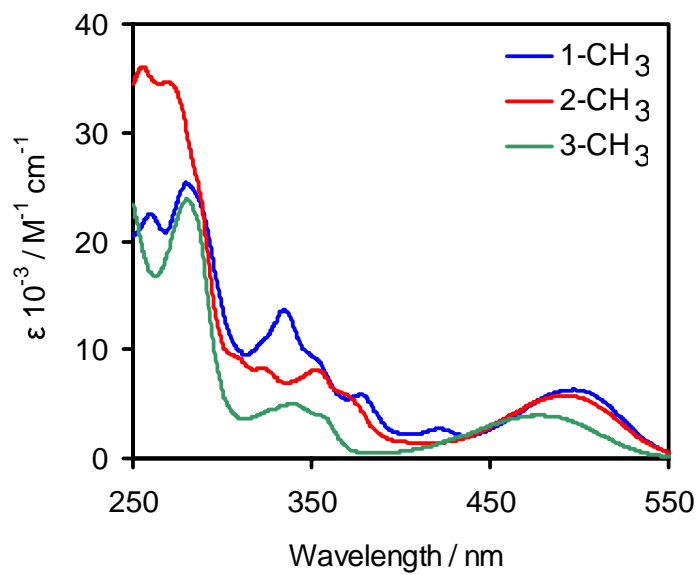


Fig. 3S Absorption spectra of **1-CH₃**, **2-CH₃** and **3-CH₃** in CH₂Cl₂.

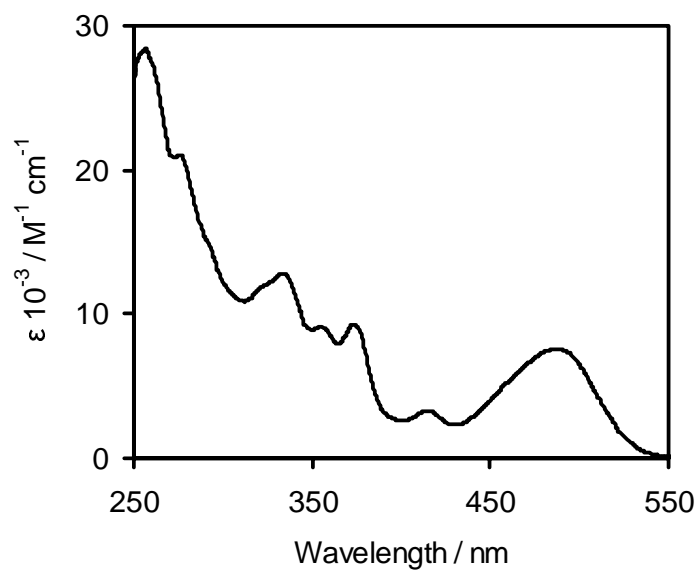


Fig. 4S Absorption spectrum of **1-Cl** in CH₂Cl₂.

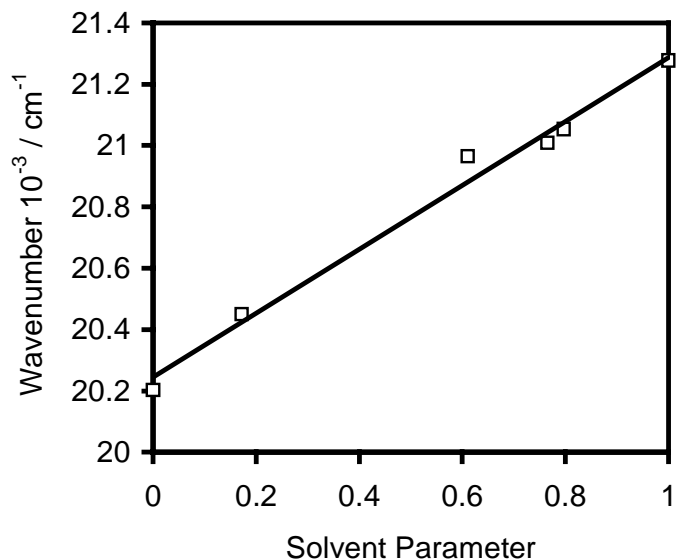


Fig. 5S.

The correlation between absorption energy and the solvent parameter for the complex **1-H**. The slope of the plot gives the value of “solvatochromic shift” of 1040 cm^{-1} (0.13 eV). The solvent parameter / absorption maximum data used in the plot are as follows: CCl_4 (0; 495 nm); toluene (0.172; 489 nm); CHCl_3 (0.61; 477 nm); CH_2Cl_2 (0.765; 476 nm); acetone (0.797; 475 nm); acetonitrile (1; 470 nm). The solvent parameter data were taken from Cummings, S.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949.