Localised to intraligand charge-transfer states in cyclometalated platinum complexes: an experimental and theoretical study into the influence of electron-rich pendants and modulation of excited states by ion binding

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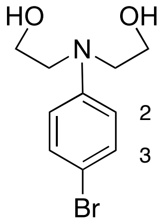
Additional synthetic details – preparation of 4-Bromophenyl-N-monoaza-15-crown-5

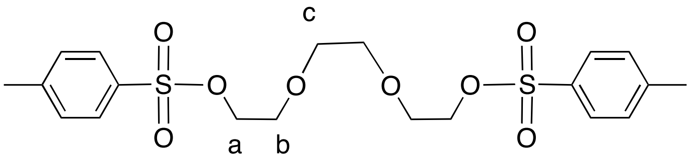
The preparation was based on previously reported cyclisation procedures used to prepare related compounds with other substituents in the aromatic ring.[1,2]

Step 1: 4-Bromo-N,N-bis(2-hydroxyethyl)aniline.



4-Bromoaniline (4.16 g, 0.024 mol), sodium carbonate (3.06 g, 0.029 mol) and 2-chloroethanol (10 ml, 0.149 mol) were stirred at reflux (129 °C) for 4½ h. The mixture was allowed to cool to ambient temperature and separated between DCM (150 mL) and water (100 mL). The organic layer was extracted and reduced *in vacuo* yielding a dark brown solid. Separation was performed by chromatography on silica gel, elution with DCM, followed by a second column on silica gel, elution gradient 100% hexane to 100% diethyl ether. The product was isolated as a colourless solid (2.29 g, 37%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.28 (2H, d, ^3J 9.0, H^3), 6.55 (2H, d, ^3J 9.0, H^2), 3.81 (4H, t, ^3J 5.0, $-CH_2O-$), 3.53 (6H, m, $-NCH_2-$, -OH). MS (ES$^+$): *m/z* 282 [M + Na$^+$]. Anal. Calcd. for $C_{10}H_{14}BrNO_2$: C, 46.17; H, 5.42; N, 5.38. Found: C, 46.15; H, 5.41; N, 5.25%.

Step 2: Tri(ethyleneglycol) di-*p*-toluenesulfonate



Sodium hydroxide (5.60 g, 0.14 mol) was dissolved in water (30 mL) and cooled to 0°C in a salt/ice bath. Tri(ethyleneglycol) (6.68 mL, 50.0 mmol) was dissolved in a mixture of THF (40 mL) and water (10 mL) and added to the reaction, which was allowed to cool back to below 0°C. *p*-Toluenesulfonylchloride (10.8 g, 52.9 mmol) dissolved in THF (40 mL) was added dropwise to the reaction over 4 h. The mixture was then stirred for a further 3 h with the temperature maintained at 0°C, or below, for the entire reaction. The progress of the reaction was monitored by thin layer

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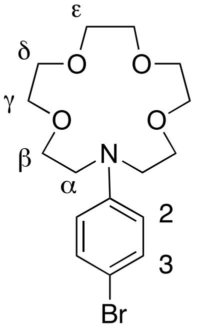
chromatography to confirm the complete consumption of the starting material *p*-toluenesulfonylchloride. The mixture was diluted with water (50 mL), ice (50 g) and toluene (50 mL) and the two phases were separated once the ice had thawed. The organic layer was washed with water (2 x 50 mL), dried over a large quantity of $CaCl_2$, stirred vigorously, filtered and dried *in vacuo* yielding a colourless solid (16.6 g, 73%). At this stage the product was observed to contain minor quantities (< 5%) of the mono-substituted tri(ethylene glycol product), which could easily be removed by chromatography on silica gel, elution gradient 100% hexane to 100% diethyl ether ($R_f = 0.8$ in diethyl ether). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.79 (4H, d, ^3J 8.0, H^2), 7.34 (4H, d, ^3J 8.0, H^3), 4.14 (4H, t, ^3J 4.5, H^a), 3.65 (4H, t, ^3J 4.5, H^b), 3.52 (4H, s, H^c), 2.47 (6H, s, CH_3). MS (ES$^+$): *m/z* 481 [M + Na]$^+$. Anal. Calcd. for $C_{20}H_{26}O_8S_2$: C, 52.39; H, 5.72. Found: C, 55.22; H 5.74%.

(3) 4-Bromophenyl-N-monoaza-15-crown-5



All glassware was dried in an oven for 1 day prior to the start of the reaction. While still hot from the oven, the apparatus was evacuated and back-filled with dinitrogen three times. A large excess of sodium hydride (400 mg, 16.7 mmol) was suspended in anhydrous THF (20 mL) and treated with 4-bromo-N,N-bis(2-hydroxyethyl)aniline (525 mg, 2.02 mmol) in anhydrous THF (10 mL), transferred by cannular under positive pressure of dinitrogen. The mixture, stirred at room temperature, was then treated with tri(ethylene glycol)-di-*p*-tolylsulfonate (821 mg, 1.79 mmol) dissolved in anhydrous THF (15 mL), again transferred by cannular. The mixture was then stirred at 40°C for 3 d when complete consumption of the starting materials was observed by GC analysis. The reaction was then taken into DCM (100 mL) and any solid removed by filtration, and the organic solution was evaporated *in vacuo* to a light coloured oil. Purification was performed by chromatography on aluminium oxide; elution gradient 100% hexane to 50:50 hexane:ethyl acetate mix ($R_f = 0.8$ in ethyl acetate). The product was isolated as a colourless solid (256 mg, 34%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (2H, d, ^3J 9.0, H^3), 6.53 (2H, d, ^3J 8.5, H^2), 3.73 (4H, ^3J 6.0, H$^\beta$), 3.66 (8H, m, H$^\gamma$, H$^\delta$), 3.63 (4H, s, H$^\varepsilon$), 3.56 (4H, t, ^3J 6.2, H$^\alpha$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.7 (C^1), 131.9 (C^3), 113.2 (C^2), 107.6 (C^4), 71.4 (C$^\gamma$ or C$^\delta$), 70.3 (C$^\varepsilon$), 70.2 (C$^\delta$ or C$^\gamma$), 68.4 (C$^\beta$), 52.7 (C$^\alpha$). MS (ES$^+$): *m/z* 374 [M + H]$^+$, 396 [M + Na]$^+$. HRMS (ES$^+$): *m/z* 374.09626, [$C_{16}H_{25}O_4N^{79}Br$] requires 374.09615. Anal. Calcd. for $C_{16}H_{24}NO_4Br$: C, 51.35; H, 6.46; N, 3.74. Found: C, 51.38; H 6.55; N, 3.59%.

1. D. Parker, “Macrocycle Synthesis, A Practical Approach”, OUP, Oxford, 1996.
2. C.-T. Chen and W.-P. Huang, *J. Am. Chem. Soc.*, 2002, **124**, 6246.

Table S1 Selected DFT/B3LYP calculated structural data for [PtL^{3}Cl] and [PtL^{6}Cl], with corresponding experimental values determined by X-ray diffraction.

	[PtL^{3}Cl]		[PtL^{6}Cl]	
distances (Å)	calculated	experimental[*a*]	calculated	experimental[*a*]
Pt – N1	2.069	2.044	2.069	2.045
Pt – N2	2.033	2.033	2.069	2.045
Pt – C	1.926	1.908	1.925	1.912
Pt – Cl	2.446	2.406	2.445	2.422
angles (°)				
N1-Pt-N2	160.4	161.5	160.4	161.1

(*a*) data from reference 13

Table S2 TD-DFT B3LYP/CPCM (CH_2Cl_2) singlet excitation energies (eV) for [PtL^{9}Cl] with oscillator strength larger than 0.001, and corresponding experimental values

State	Main components (%)	Transition energy[a] / eV (nm)	Oscillator Strength	Experimental Trans. / nm	Extinction coefficient
a ^{3}A	77 (HOMO → LUMO)	2.36 (525)			
b ^{3}A	93 (HOMO → LUMO+1)	2.39 (518)			
a ^{1}A	95 (HOMO → LUMO)	2.65 (467)	0.041	431	8880
b ^{1}A	95 (HOMO → LUMO+1)	2.65 (466)	0.042	380	6410
c ^{1}A	91 (HOMO-1 → LUMO)	3.42 (362)	0.006		
d^{1}A	77 (HOMO-1 → LUMO+1)	3.43 (361)	0.071		
f^{1}A	82 (HOMO → LUMO+2)	3.53 (351)	0.025		
h^{1}A	70 (HOMO-2 → LUMO+1)	4.02 (309)	0.145	312 sh	55000
l^{1}A	90 (HOMO → LUMO+4) (π→π*) ligand	4.16 (298)	1.213	290	76900

[a] wavelength (nm) in parenthesis

Further comments on the assignment of absorption bands with the aid of DFT

TD DFT-calculated charge-transfer transition energies depend on the functional used and are usually underestimated (particularly in the case of pure functional). Moreover, the ratio of calculated oscillator strengths does not always reflect experiment. Here, the lowest lying transitions have mostly intraligand character and TD DFT using hybrid B3LYP or PBE0 functionals with CPCM solvent correction gives reasonable transition energies. In the case of PtL^{1}Cl, we found only one intense transition, HOMO→LUMO+1, but the calculated oscillator strengths of other transitions forming the low energy band could be underestimated. The calculated transition energies and oscillator strength for PtL^{1}Cl describe the experimental spectrum only qualitatively and assignment of the spectra is not unambiguous. The structure of the lowest energy band is not well reproduced, and the triplet transitions also make a significant contribution to the absorption spectrum (see Fig S1 for a possible deonvolution of the spectrum). In the case of PtL^{9}Cl, no transition with low oscillator strength below 2.65 eV was calculated.

Figure S1 Attempted deconvolution of the absorption spectrum of PtL^{1}Cl

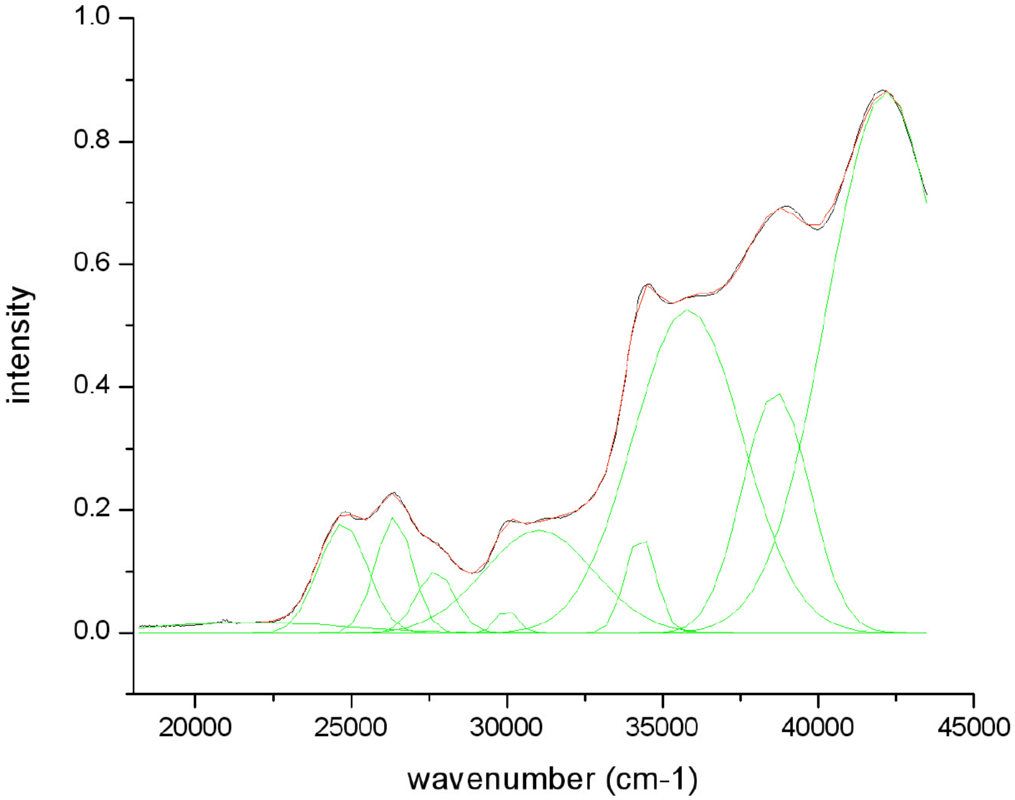


Figure S2 Absorption and emission spectra of the oxo-substituted complexes PtL^{13}Cl (blue), PtL^{14}Cl (red) and PtL^{15}Cl (green) in CH_2Cl_2, together with those of PtL^{1}Cl (black) for comparison.

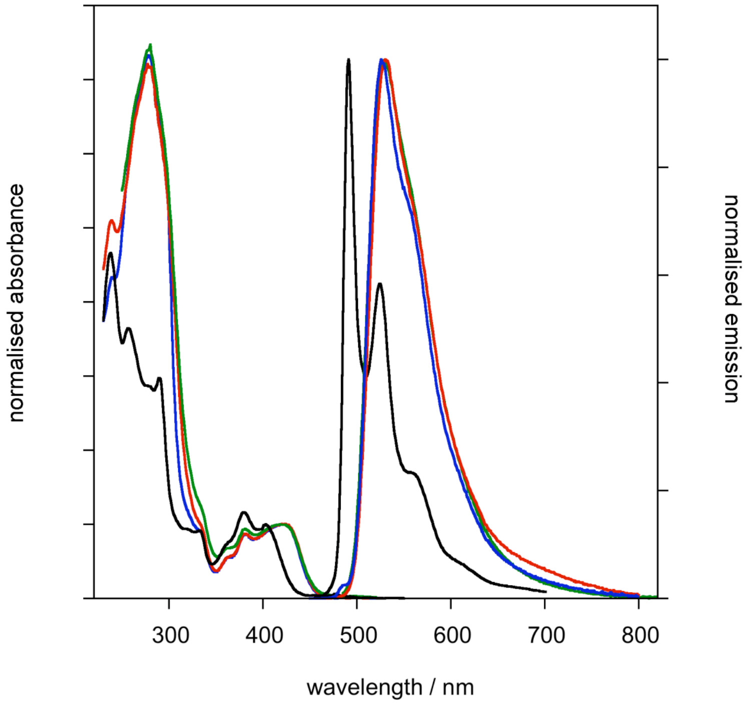


Figure S3 Emission spectra of PtL^{9}Cl in DCM at 298K and in an EPA glass at 77K. The emission spectrum of PtL^{1}Cl at 298K is also shown for comparison.

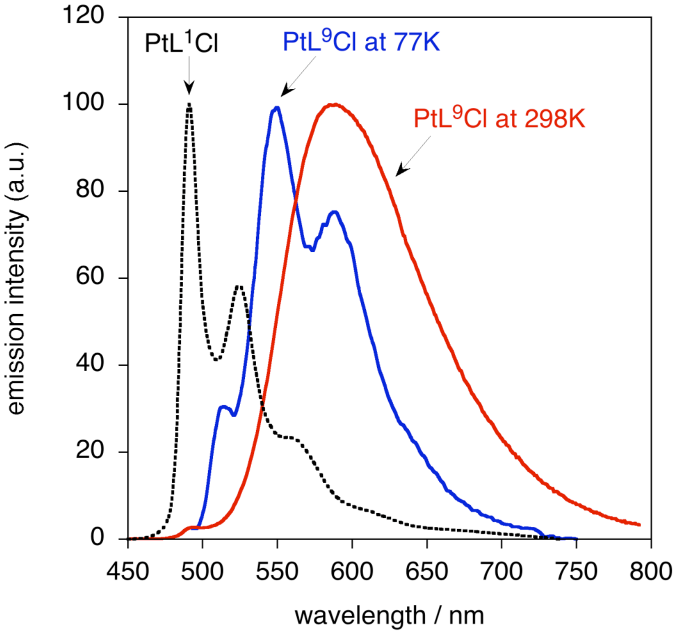


Figure S4 Representative TDCP photoresponse trace for PtL^{9}Cl in toluene at 298K using an applied field of 40 kV cm^{-1} (red line), and fitted curve with $\mu_{ex}{}^2 - \mu_{gd}{}^2$ = 150 Debye^2, τ_{ex} = 12.7 µs, rotational correlation time = 0.25 ns (green line). The laser pulse is also shown (blue dashed line).

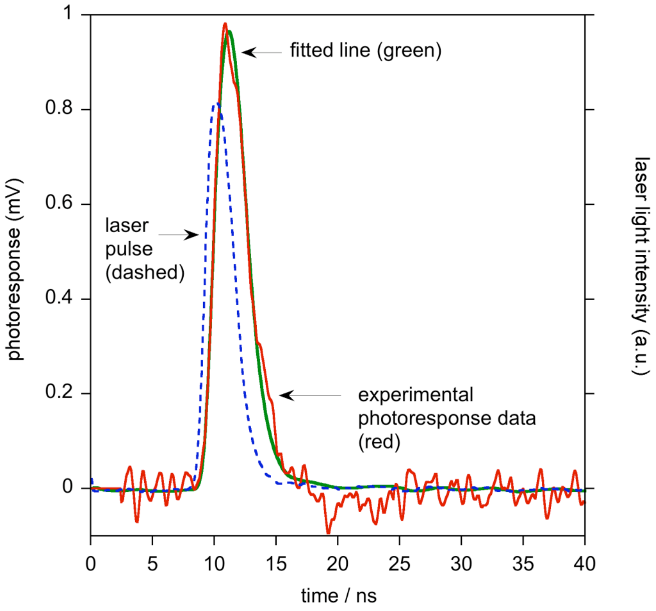


Figure S5 Examples of the determination of singlet oxygen quantum yields. Plot of the integrated intensity of O_2 $^1\Delta_g$ luminescence in the near-IR as a function of incident laser energy for PtL^{1}Cl (black circles), PtL^{11}Cl (green squares), PtL^{12}Cl (blue triangles), and the phenalenone standard (red diamonds), in air-equilibrated CH_2Cl_2 at 298K.

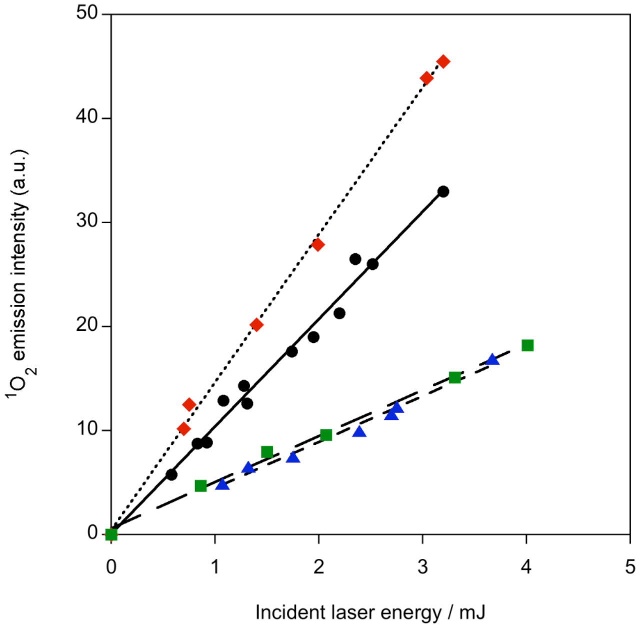


Figure S6 Molecular structure of PtL^{10}Cl in the crystal determined by X-ray diffraction. A full refinement was hampered both by disorder in the diphenylamino pendant and by the occasional presence of a molecule of CH_2Cl_2 in the associated void, but the structure satisfactorily confirms the identity of the complex.

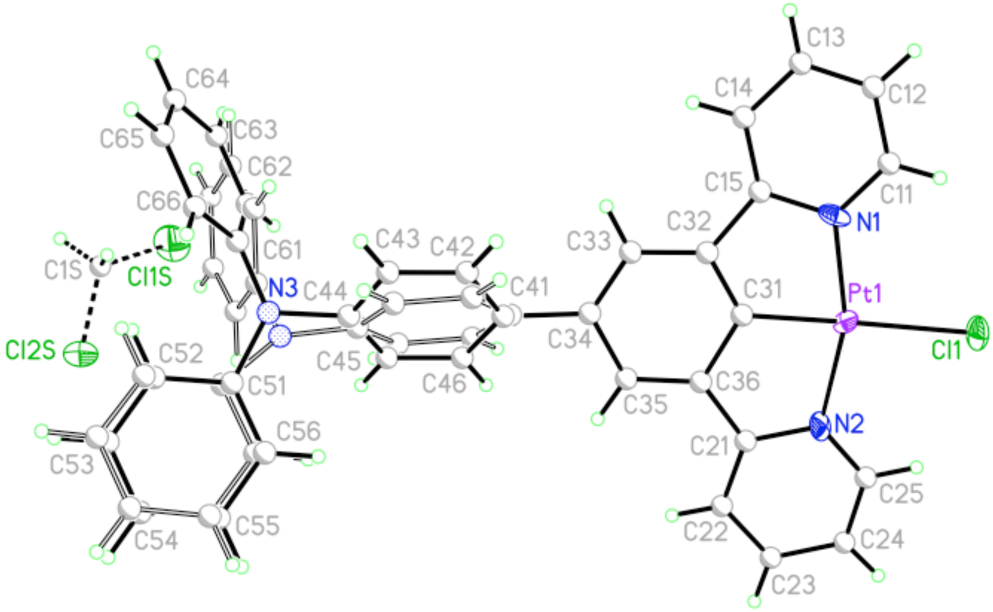
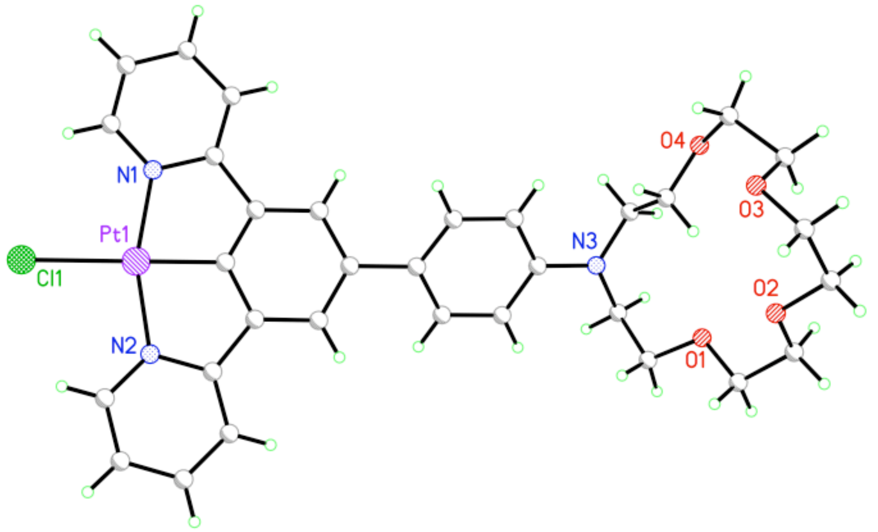


Figure S7 Atomic connectivity of PtL^{12}Cl in the crystalline state determined by X-ray diffraction.



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