Intramolecular excimers based on rigidly-linked platinum(II) complexes: intense deep-red triplet luminescence in solution[†]

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By linking together two cyclometallated, N \wedge C \wedge N-coordinated platinum(II) complexes through a xanthene core, intense luminescence in the red region of the spectrum is achieved in solution at room temperature ($\lambda_{max} = 690$ nm, $\Phi_{lum} = 0.20$, $\tau = 1.7$ µs in CH₂Cl₂) due to the efficient formation of an intramolecular excimer.

The luminescence quantum yields of compounds that emit from triplet states in the deep red and near infra-red region of the spectrum are generally low. The lower the energy, E, of an electronic excited state, the more rapidly it typically undergoes non-radiative decay through energy transfer to vibrational motions. Meanwhile, the coefficient of spontaneous emission varies with E^3 , such that radiative rate constants tend to fall off at long wavelengths. Nevertheless, compounds that emit efficiently in the region 700-900 nm are particularly attractive in biosensing and bioimaging applications, owing to the relative transparency of tissue to such wavelengths.1 In the case of triplet emitters, a further attraction is that their longer luminescence lifetimes (often > 100 ns) may allow time-resolved detection procedures to be employed to discriminate from scattering and background fluorescence (< 10 ns).² Red triplet emitters are also under intensive investigation as phosphors for organic light emitting devices (OLEDs), to trap and promote light emission from the triplet excitons formed upon charge recombination.3

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The formally forbidden radiative decay of triplet states of conjugated organic ligands can be promoted by coordination to metal ions with high spin-orbit coupling constants. A large range of luminescent complexes of 3rd row metals, particularly Os(II), Ir(III) and Pt(II), have been reported over the past few years.⁴ We have been exploring the chemistry and applications of a family of brightly emissive cyclometallated platinum(II) compounds incorporating NACAN-coordinating tridentate ligands based on 1,3-di(2-pyridyl)benzene (dpybH). These complexes emit from triplet states with high luminescence quantum yields {e.g. for Pt(dpyb)Cl, Scheme 1, $\Phi_{lum} = 0.6$,⁵ and function efficiently in OLEDs.6 At elevated concentrations in solution, they form highly emissive excimers, giving rise to an additional band in the emission spectrum centred at around 700 nm ($\Phi_{lum} \sim 0.3$). The effect is also observed in polymer matrices and in neat thin films, offering a strategy for creating single-dopant, white-light emitting devices and near-IR OLEDs respectively.7

We reasoned that a molecular structure in which two Pt(dpyb)Cl units were locked rigidly together in a face-to-face manner might offer uniquely excimeric emission, providing a novel route to high efficiency, deep-red triplet emitters in solution. Tanaka *et al.* have shown that a 4,5-disubstituted xanthene skeleton can be used to bring together two metal-terpyridyl complexes in such a way (*e.g.* mixed Ru, Pt derivatives were prepared), with interplanar separations of the terpyridyl units that could be appropriate for the present objective.⁸ The compound L(PtCl)₂ (Scheme 1) was therefore targeted. 1,3-Di(2-pyridyl)benzene-5-boronic acid (dpybH-B), obtained from the corresponding bromo derivative, was subjected to a palladium-catalysed cross-coupling reaction with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (Br-xnth-Br), in the molar ratio 2:1.[†] The cross-coupling of the



Scheme 1 The structures of the complexes investigated and the synthetic route employed.

first equivalent of dpybH-B took place readily under standard conditions, but hydrodebromination of the xanthene proved to be competitive with the introduction of the second dpyb unit, such that the major product was H-xnth-dpybH. The use of an excess of dpybH-B (4 equiv.) allowed the desired product, xnth-(dpybH)₂ = H₂L, to be obtained. The mono- and dinuclear platinum(II) complexes of the ligand were isolated upon treatment with K₂PtCl₄ in acetonitrile–water (3 : 1 v/v). The introduction of the second platinum(II) ion proved to be much slower than the first: thus HLPtCl was isolated in 80% yield after 3 d, whereas conversion to L(PtCl)₂ required a total of 11 d at reflux.

Photophysical data for HLPtCl and L(PtCl)₂ are compiled in Table 1, together with corresponding values for the parent complex Pt(dpyb)Cl for comparison. The absorption spectrum of L(PtCl)₂ (Fig. 1) is similar to that of Pt(dpyb)Cl in the near-UV/visible region (350–450 nm), with bands in this region attributed to charge-transfer transitions involving the metal and halide coligand, whilst the absorbance at shorter wavelengths is increased due to the superposition of π – π * transitions associated with the xanthene moiety. A very weak absorption band centred at 496 nm is attributed to the spin-forbidden S₀ \rightarrow T₁ transition, enhanced by the large spin–orbit coupling constant of the Pt(II) ion.



Fig. 1 Absorption (blue line) and emission spectrum (red, $\lambda_{ex} = 420$ nm) of L(PtCl)₂, at a concentration of 10^{-6} M in degassed CH₂Cl₂ at 298 K. The emission spectra of Pt(dpyb)Cl at 10^{-6} M and 2×10^{-4} M (green solid and dashed lines respectively) are also shown.

Upon excitation at 420 nm, L(PtCl)₂ displays intense luminescence centred at 690 nm (Fig. 1), with a luminescence quantum yield, Φ_{lum} , of 0.20 (± 0.04). The emission spectrum has a broad, unstructured profile which is *independent of the concentration* (the range 2 × 10⁻⁷–5 × 10⁻⁴ M was investigated). The band closely

resembles that displayed by the parent complex Pt(dpyb)Cl at elevated concentrations, which arises from the diffusion-controlled formation of intermolecular excimers. In that case, however, the excimer band is always accompanied by structured emission from isolated molecules ($\lambda_{max} = 490$ nm) and, at lower concentrations, the monomeric emission is exclusively observed (Fig. 1). Thus, the emission from L(PtCl)₂ is attributed to very rapid formation of intramolecular excimers following absorption of light, at a rate that precludes any significant emission from the monomeric excited state. The luminescence of L(PtCl)₂ decays mono-exponentially with a long lifetime of 1.7 µs, indicative of an emitting state of triplet character. Notably, the grow-in of the emission was too fast to be resolved on the nanosecond timescale following pulsed laser diode excitation (using equipment with a response function \sim 0.5 ns). This contrasts with the inter-molecular excimer emission displayed by Pt(dpyb)Cl, whose growth is characterised by a much slower time-constant of the order of 1 µs.5 The difference is readily interpreted in terms of the diffusion-controlled nature of excimer formation in the intermolecular case, whereas in L(PtCl)₂, the two units are held in close proximity.

Such a description inevitably raises the question whether there is already, in the ground state of L(PtCl)₂, some interaction between the two $Pt(N \land C \land N)$ units. Indeed, many examples of platinum(II) complexes are known that display Pt-Pt interactions in the ground state, through overlap of cofacial d₂ orbitals. Such interactions may lead to low-energy emission spectra, as in the many examples of excited states designated MMLCT {metal-metal-bond-toligand charge transfer, or $d\sigma^*(Pt_2) \rightarrow \pi^*(L)$.⁹⁻¹¹ Two pieces of experimental data suggest to us that there is no significant groundstate interaction in L(PtCl)₂, and that an excimeric description is the more appropriate. Firstly, for aggregate species involving a Pt-Pt d σ^* HOMO, a low-energy band in the absorption/excitation spectrum would be anticipated. No such band is detectable in the spectra of L(PtCl)₂: the lowest-energy absorption band at 495 nm corresponds to the $S_0 \rightarrow T_1$ transition at 485 nm in the mononuclear Pt(dpyb)Cl {indeed, a more appropriate model is arguably the 4methyl-substituted analogue of Pt(dpyb)Cl, for which the value of 495 nm is identical to that of $L(PtCl)_2$. Secondly, ground-state Pt-Pt interactions are stabilised with decrease in temperature, leading to well-documented red-shifts in the corresponding absorption and emission bands.¹² In the case of L(PtCl)₂, no such shift is seen as the temperature is lowered in fluid solution. On the contrary, in a rigid glass at 77 K, exclusively monomer-like emission is observed (Fig. 2). This striking observation strongly suggests

Table 1 Photophysical data for the new complexes L(PtCl)₂ and HLPtCl, and for the parent complex Pt(dpyb)Cl for comparison⁴

Complex	$\lambda_{\max}^{abs} b/nm (\varepsilon/M^{-1} cm^{-1})$	λ_{\max}^{em}/nm	$arPsi_{ ext{lum}}$	$\tau_0^{c,d}/\mu s$	$k_{sq}^{c}/10^{9} \text{ M}^{-1} \text{ s}^{-1}$	$k_{\rm Q}^{{ m O2}e}/10^8~{ m M}^{-1}~{ m s}^{-1}$	$\lambda_{\max}^{em} f/nm$ (77 K)	$\tau_0^{f}/\mu s (77 \text{ K})$
Pt(dpyb)Clg	332 (6510), 380 (8690), 401 (7010), 485 (240)	491, 524, 562	0.60 ^h	7.2 (0.50)	5.3	8.5	487, 521, 558	6.1
HLPtCl	386 (7950), 416 (5300), 495 (200)	510, 542, 588sh	0.40 ^h	8.8 (0.55)	1.1	7.7	505, 543, 583	9.0
L(PtCl) ₂	386 (14650), 412 (9940), 495sh (350)	690	0.20 ^{<i>i</i>}	1.7 (0.25)	0.16	16	504, 540, 580	7.6

^{*a*} In deoxygenated CH₂Cl₂ at 298 K except where stated otherwise. ^{*b*} For bands > 300 nm. ^{*c*} τ_0 is the lifetime at infinite dilution and k_{s0} the bimolecular self-quenching rate constant, determined from the *y*-intercept and gradient, respectively, of a plot of τ^{-1} versus concentration. ^{*d*} Values in air-equilibrated solution are given in parentheses. ^{*c*} Bimolecular rate constant of quenching by O₂, estimated from the lifetimes in degassed and air-equilibrated solutions. ^{*f*} In diethyl ether–isopentane–ethanol, 2:2:1 by volume. ^{*g*} Data from ref. 5. ^{*h*} Measured using fluorescein in 0.1 M NaOH as the standard ($\Phi = 0.90$). ^{*i*} Measured using Ru(bpy)₃Cl₂ in air-equilibrated H₂O as the standard ($\Phi = 0.028$). Estimated uncertainty in Φ_{lum} is ±0.04.

that the formation of the emissive state responsible for the red band at 690 nm is a thermally activated process, requiring at least some motion of the two $Pt(N \land C \land N)Cl$ units relative to one another. Although the emitting state might involve Pt-Pt interaction-in which case it could be formulated as an MMLCT state that exists only in the excited state, this is not necessarily the case, since $\pi - \pi^*$ or $d - \pi^*$ interactions could also account for the stabilisation relative to the monomeric excited state.13 In a recent study of structurally related cationic anthraguinonebridged platinum terpyridyl complexes, Pt · · · Pt distances in the most rigid systems (acetylide linkers) are estimated to be up to 11 Å, much longer than that necessary to support MMLCT interactions.14 In the present instance, the charge neutrality of the complexes eliminates the effect of electrostatic repulsion that is expected in the cationic systems, such that closer separations would be anticipated, but distances are still expected to be > 4.5 Å based on the corresponding ligands. In contrast, it should be noted that adoption of angles significantly less than 90° between the xanthene and N \wedge C \wedge N planes will favour close d $-\pi^*$ or π - π^* (but not $Pt \cdots Pt$) interactions.



Fig. 2 Emission spectra of $L(PtCl)_2$ in diethyl ether–isopentane–ethanol (2:2:1) at 77 K (blue) and in CH_2Cl_2 at 298 K (red). The spectrum of HLPtCl in CH_2Cl_2 at 298 K is in green.

Red emission is also observed from the compound in the solid state, although the spectra show some variation according to sample preparation (λ_{max} in the range 670–710 nm, according to the solvent from which the sample is evaporated and the rate of evaporation). This probably reflects subtle differences in intermolecular packing of the molecules, akin to those seen in simple monometallic derivatives of Pt(dpyb)Cl.¹⁵

The singly complexed derivative HLPtCl displays an emission spectrum that resembles the monomer emission of Pt(dpyb)Cl (Fig. 2). At elevated concentrations in solution, only a weak intermolecular excimer band is observed, much less intense than that displayed by Pt(dpyb)Cl at comparable concentrations. This lower propensity of HLPtCl to intermolecular excimer formation can be rationalised in terms of the neighbouring uncomplexed dipyridylbenzene unit offering the Pt(N \wedge C \wedge N) moiety protection from intermolecular interactions, at least from one face, an effect which is also reflected in the smaller self-quenching rate constant k_{sq} (Table 1).

In conclusion, the high luminescence efficiency of $L(PtCl)_2$ is particularly remarkable given the low energy of the emission. Although progress has been made recently in the design of red-emitting Pt(II) complexes,¹⁶ quantum yields remain much lower for diimine complexes, whilst the benchmark platinum porphyrins have Φ_{lum} values in solution of around 0.05.¹⁷ The use of intramolecular excimer formation could open up a powerful new approach to obtaining more efficient red emitters. Recent work has shown that the excimer energies in mononuclear derivatives of Pt(dpyb)Cl can be varied by at least 2000 cm⁻¹ through simple structural modification.¹⁸ Thus the present strategy could prove versatile in the design of bright emitters with tuneable wavelengths across the red and into the NIR.

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