Cyclometallated platinum(II) complexes incorporating ethynyl–flavone ligands: switching between triplet and singlet emission induced by selective binding of Pb^{2+} ions†

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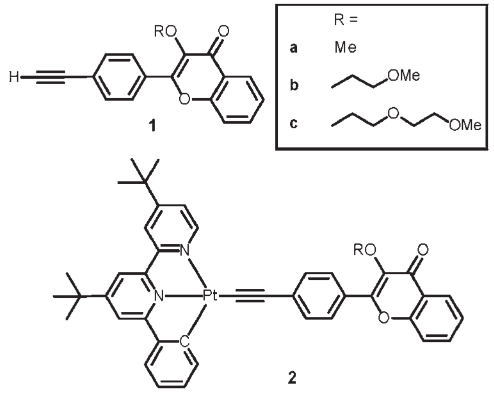
Platinum–ethynylflavone complexes featuring various polyether arms display ^{3}IL phosphorescence associated with the appended flavone perturbed by the platinum centre ($\tau \sim 20$ μs), but switch dramatically to flavone-localised ^{1}IL fluorescence ($\tau \sim 2$ ns) upon selective binding of Pb^{2+}.

The design and study of luminescent transition metal complexes has been the subject of extensive research.[1] In the context of optical chemosensors, square-planar platinum(II) complexes are of particular interest owing to their rich photophysical properties, including high luminescence quantum yields and long excited state lifetimes under ambient conditions.[2] Due to the sensitivity of their excited state energies, platinum–alkynyl complexes[3–5] allow the monitoring of chemical environment, and the ion-binding properties[6] of crown ether-containing Pt complexes have been reported. In this context, functionalization of acetylide complexes with host molecular units for heavy metal ions is of particular interest and we turned our attention to cyclometallated platinum(II) complexes featuring an acetylide-linked flavone moiety. Hydroxyflavones and related organometallic derivatives have been reported to complex various metal cations, such as Mg^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+}, leading to distinctive changes in the electronic absorption spectra.[7,8] In the present contribution, we demonstrate a profound influence of the flavone on the emissive properties of the Pt complex. Moreover, by incorporating a suitable polyether chain onto the flavone, selective binding of Pb^{2+} ions can be achieved, which results in a dramatic switch from triplet to singlet emission, allowing optical detection.

The series of flavone-based Pt(II) complexes investigated, [Pt(*C^N^N*-^{t}Bu$_2$-phbpy)(C≡C-FLV-3-OR)], **2a–c**, are shown in Scheme 1 (^{t}Bu$_2$-phbpyH = 4,4′-di(*tert*-butyl)-6-phenyl-2,2′-bipyridine). Use of the monoanionic C^N^N ligand ensures that the final complexes are charge-neutral (advantageous over cationic complexes in terms of affinity for M^{n+} ions), whilst the *tert*-butyl groups sterically inhibit undesirable intermolecular interactions that frequently lead to concentration-dependent self-quenching of the luminescence.[4a] The compounds were prepared as air-stable orange crystals in good yields (60–70%), upon treatment of [Pt(^{t}Bu$_2$-phbpy)Cl] with the appropriate flavone-based alkyne derivative, using standard procedures.[4b] The requisite terminal alkynes **1** were synthesized by a multi-step procedure previously developed in our laboratory.[8]

Single crystals of **2b** were grown upon slow evaporation of a CH$_2$Cl$_2$ solution and analysed by X-ray diffraction.‡ The structural parameters of the "Pt(*C^N^N*)–C≡C–" moiety in **2b** (Fig. 1) are comparable with those reported for related compounds.[4b] The platinum centre adopts a distorted square planar geometry, and neither π–π nor Pt···Pt interactions were observed. The acetylenic moiety deviates from linearity (C25–C26–C27: 175.9(7)° and the pyrone moiety is non-coplanar with the phenylacetylide fragment (dihedral angle C29–C30–C33–O1 30.2(8)°.

The electronic absorption data of compounds **2a–c** in MeCN solution are listed in Table 1, and the spectrum of **2b**, representative of all three complexes, is shown in Fig. 2. The intense bands around 360 nm may be attributed to intraligand π → π* transitions of the phenylbipyridine ligand, as observed for [Pt(phbpy)Cl], for example, but superimposed with transitions



Scheme 1 Flavone-based alkyne ligands HC≡C-FLV-3-OR, **1a–c**, and their respective Pt complexes **2a–c**.

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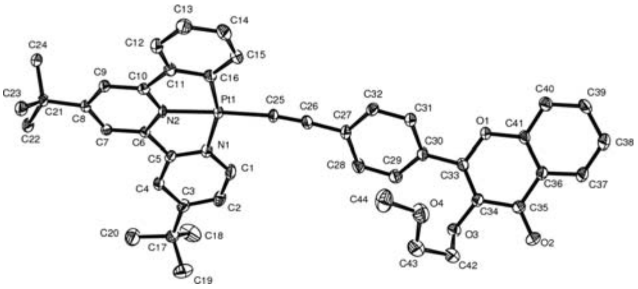

Fig. 1 An ORTEP plot for **2b** drawn with thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. $T = 110$ K.

Table 1 Photophysical data for complexes **2** in acetonitrile solution at 298 K

	λ_{abs}/nm (ε/L mol^{-1} cm^{-1})	$\lambda_{em}{}^{a}$/nm	τ/μs	$\Phi_{em}{}^{ab}$
2a	329 (24 544), 368 (38 296), 420 (14 500)	565	12	0.024
2b	329 (27 900), 368 (37 096), 420 (15 800)	567	18	0.027
2c	329 (23 184), 368 (35 890), 420 (14 521)	570	21	0.032

[a] Data for degassed solutions. [b] Measured using $[Ru(bpy)_3]Cl_2$ in air-equilibrated water as the standard.

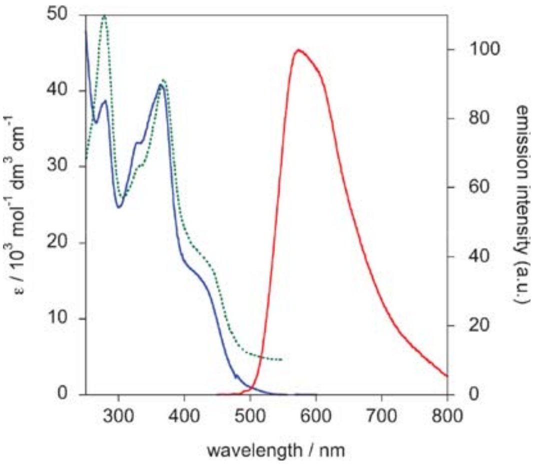

Fig. 2 Absorption (blue), excitation (dashed green, $\lambda_{em} = 570$ nm) and emission (red, $\lambda_{ex} = 420$ nm) spectra of **2b** (10^{-5} M) in CH_3CN at 298 K.

associated with the flavone-acetylide ligand C≡C-FLV-3-OR, since the free ligands **1** also absorb in this region. At lower energy, the moderately intense absorption bands in the 400–510 nm range can be tentatively attributed to dπ(Pt) → π*(phbpy) metal-to-ligand charge transfer (MLCT) transitions, on the basis of previous studies.[4] Predictably, varying the polyether arm does not induce significant differences in the absorption spectra.

All three complexes **2a–c** emit intense luminescence, centred in the range 565–570 nm, in degassed acetonitrile solution, upon excitation into the MLCT band ($\lambda_{exc} = 420$ nm). The observed emission lifetimes of ~20 μs are much longer than those of related complexes without the flavone unit, despite the emission being in the same region; *e.g.* for [Pt(^{t}Bu$_2$-phbpy)(–C≡C–Ph)], **3**, $\tau = 0.8$ μs.[4b] This indicates that the radiative rate constants k_r for **2a–c** are an order of magnitude smaller than for **3**, suggesting that the emissive excited state has substantial ^{3}IL(C≡C-FLV-3-OR) character, with the metal making a smaller contribution to the HOMO than it does in the parent compounds, wherein the emission is normally assigned to a ^{3}MLCT state, d(Pt) → π*(C^N^N).§[4b] The uncomplexed terminal alkyne **1b** displays only fluorescence upon UV excitation at room temperature, centred at 437 nm in MeCN. In a frozen glass at 77 K, however, the fluorescence ($\lambda_{max} = 414$ nm, $\tau = 3.5$ ns) is accompanied by a weaker phosphorescence band centered around 550 nm ($\tau = 130$ ms) (see Fig. S1†). Clearly, the latter corresponds to the emission observed at 298 K in the Pt complexes, where the contribution of the metal—with its high spin–orbit coupling constant—is sufficient to promote intersystem crossing to the triplet and its subsequent formally forbidden radiative decay.

The metal-binding properties of **2a–c** were probed by means of absorption spectroscopy in the first instance, in MeCN solution at 10^{-5} M. A range of metal ions were screened in the form of their perchlorate salts: Mg^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. Compound **2b** displayed a high selectivity for Pb^{2+}: the IL band in the UV region decreases with increasing [Pb^{2+}] (along with a slight hypsochromic shift), while the lower-energy band at 420 nm increases in intensity throughout the addition (Fig. 3). Taking the absorption peak intensity of **2b** and **2b**-Pb^{2+} to be A_0 and A, respectively, a straight line plot of $A_0/(A_0 - A)$ against **2b**/[Pb^{2+}] at 420 nm is depicted in Fig. 3 (inset), supporting a 1 : 1 complexation ratio. Accordingly, the log K was deduced to be 5.0 ± 0.05. This value, two orders of magnitude greater than that of the free terminal ethynylflavone **1b** (log $K = 3.0 \pm 0.02$) illustrates the influence of the "Pt(C^N^N)" organometallic moiety. In contrast to this response to Pb^{2+}, addition of Mg^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}, even in concentrations up to 10^{-3} M, did not lead to any detectable spectral changes.

The influence of lead binding on the photoluminescence properties of **2b** was also investigated. Addition of increasing concentrations of $Pb(ClO_4)_2$ to a 10^{-7} M solution of **2b** in CH_3CN led to the appearance of a new, blue-shifted, structured band centred at *ca.* 450 nm, while the intensity of the initial band centred at 567 nm concomitantly decreased

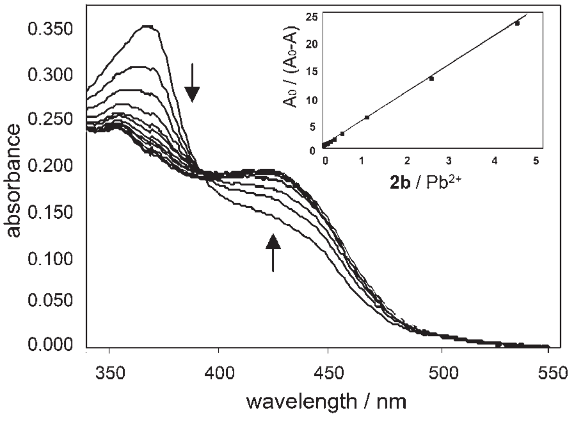

Fig. 3 UV-Vis absorption spectral changes of **2b** (10^{-5} M) in CH_3CN upon addition of $Pb(ClO_4)_2$. The inset shows the plot of $A_0/(A_0 - A)$ against **2b**/[Pb^{2+}] at 420 nm.

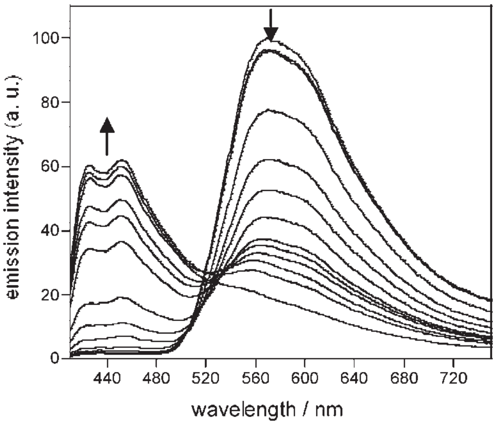

Fig. 4 Luminescence spectral changes of **2b** (10^{-5} M) in CH_3CN upon addition of $Pb(ClO_4)_2$ (λ_{exc} = 393 nm).

(Fig. 4). This dramatic change in emission was triggered only by Pb^{2+} ions and not by the presence of other cations (Mg^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}). The dramatic and unprecedented change in the emission spectrum of **2b** upon binding of Pb^{2+} must be due to a profound change in the excited state properties of the molecule. A clue to its origin is provided by the observation that the emission in the 400–475 nm region has a lifetime of only 1.7 ± 0.5 ns in degassed solution (compared to 18 μs for the initial luminescence band at 567 nm in the absence of Pb^{2+}), and resembles very closely the emission profile displayed by the free flavone acetylide **1b**. Evidently, the new band is due to fluorescence from the singlet state of the flavone. On the other hand, the temporal decay of the emission registered at 570 nm in the presence of an excess of Pb^{2+} reveals a second, weak component with a lifetime of ~700 ns, superimposed on the tail of the fluorescence, which is not detectable in aerated solution. This component may be due to emission from the ^{3}MLCT state associated with the "Pt(C^N^N)(–C≡C)" moiety, similar to that of parent **3** (τ = 800 ns[4b]). These changes can be tentatively rationalised in terms of binding of Pb^{2+} leading to a decrease in the energy of the highest-occupied flavone-localised orbitals, breaking the partial conjugation with the Pt centre that had previously facilitated formation of the flavone triplet. The result is a decoupling of the flavone orbitals from those of the "Pt(C^N^N)(–C≡C)" unit, leading to fluorescence from the singlet state of the flavone and ^{3}MLCT emission from the Pt centre.

Interestingly, the response to Pb^{2+} is even more striking in *aerated solution*, since the initial long-lived phosphorescence is quenched very efficiently by dissolved molecular oxygen, whereas the flavonol fluorescence is not: the effect of Pb^{2+} is then essentially to "switch on" emission.

The complexation of the metal ion on **2b** might occur *via* the formation of a chelate involving the oxygen atom of the C=O group of the benzopyrone moiety and the terminal oxygen atom of the polyether arm. The participation of the oxygen atom in the 3-position of the flavone, in the binding process, can be ruled out, as demonstrated by our experimental data on **2a** (R = OMe) which displays *no affinity* for any divalent metal ions: no modification of the electronic absorption (10^{-5} M) and luminescence spectra (5×10^{-6} M) of **2a** can be observed upon addition of the same set of metal cations (Mg^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, $Zn^{2+}$and Pb^{2+}; 10^{-2} M) in CH_3CN solution. Conversely, the introduction of additional oxygen atoms onto the polyether arm as in **2c** allows the complexation of a variety of metal ions such as Pb^{2+} ($\log K = 5 \pm 0.1$), Cd^{2+} ($\log K = 2.6 \pm 0.01$) and Ca^{2+} ($\log K = 3.8 \pm 0.06$) and the optical changes observed in the absorption spectrum are similar to those observed for **2b**. Thus, these results demonstrate that the fine-tuning of the cation affinities of the platinum complexes **2** can be achieved through the facile chemical modification of the polyether arm. To our knowledge, this is an unprecedented system that switches from triplet to singlet emission in response to metal binding.

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Notes and references

‡ *Crystal data* for **2b** at 110 K: $C_{45}H_{44}Cl_2N_2O_4Pt$, M_r = 942.81, triclinic, space group $P\bar{1}$, a = 11.4614(8), b = 13.0906(9), c = 13.8985(7) Å, α = 72.550(5), β = 78.944(5), γ = 81.274(6)°, V = 1942.5(2) Å^3, Z = 2, D_c = 1.6121 Mg m^3, crystal size: 0.24 × 0.20 × 0.20 mm^3, $F(000)$ = 944, λ(Mo-Kα) = 0.71073 Å, 13 552 independent reflections (R_{int} = 0.0444). Final R indices: $R1$ = 0.0502 [$I > 2\sigma(I)$] and $wR2$ = 0.1392 (all data).

§ Such a change from ^{3}MLCT to arylacetylide-localised ^{3}IL emission has been proposed: Castellano and co-workers observed long-lived pyrenyl-localised $^3\pi$–π* emission from Pt(^{t}Bu$_2$-bpy)(–C≡C-pyrene)$_2$,[9a] and reported on a solvent-dependent balance between such states in systems incoporating extended acetylides.[9b]

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