Diplatinum alkynyl chromophores as sensitisers for lanthanide luminescence in Pt_2Ln_2 and Pt_2Ln_4 (Ln = Eu, Nd, Yb) arrays with acetylide-functionalized bipyridine/phenanthroline†

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Incorporation of diplatinum complex $Pt_2(\mu\text{-dppm})_2(bpyC{\equiv}C)_4$ or $Pt_2(\mu\text{-dppm})_2(phenC{\equiv}C)_4$ with $Ln(hfac)_3(H_2O)_2$ (Ln = Nd, Eu, Yb) gave a series of Pt_2Ln_2 and Pt_2Ln_4 bimetallic arrays, in which the excitation of d(Pt) → π*(R–C≡C) MLCT absorption induces sensitisation of lanthanide luminescence through efficient d → f energy transfer from Pt^{II} alkynyl chromophores.

Because of the weak absorption of forbidden f–f transitions, luminescence from lanthanides is usually sensitised by the excitation of strongly absorbing organic antenna chromophores.[1] More recently, attention has been focused on the use of d-block metal chromophores as sensitisers for near-infrared (NIR) emission from lanthanides.[2,3] In order for the d-block chromophores to be connected to the lanthanide luminophores, the design of bifunctional bridging ligands with suitable bonding sites for d-block and f-block metals is critical to achieve NIR emitting sensitisation from lanthanides through d → f energy transfer.[2–12] The bridging ligands exploited to date include cyanide,[3e,3f,7] oxalate,[12] tetrazine,[3a–3d] and functionalized oligopyridine[2,4–6,9–11] or porphyrin[8] *etc.*

As bifunctional bridging ligands, acetylide-functionalized diimines have been used widely in the design of multi-component transition metal complexes composed of discrete redox and/or photoactive sub-units.[13,14] It is anticipated that they are ideal bridging ligands for the design of d–f bimetallic arrays by introducing d-block chromophores and f-block luminophores bound to acetylide and bipyridine/phenanthroline, respectively. Furthermore, such heterometallic arrays would allow d → f energy transfer to occur from transition metal alkynyl chromophores to f-block luminophores, thus emitting NIR lanthanide luminescence by excitation of the charge-transfer absorption in the organometallic energy donors.

As shown in Scheme 1, reaction of ligand L_1[15] with $PtCl_2(dppm)$ in the presence of KF and CuI led to binuclear Pt^{II} alkynyl complex **1** being prepared *via* fluoride-catalyzed desilylation. Addition of excess $Ln(hfac)_3(H_2O)_2$ into CH_2Cl_2 solutions of **1**, following crystallization by layering with *n*-hexane, gave Pt_2Ln_2 complexes as yellow crystals. Formation of the Pt_2Ln_2 arrays instead of the desired Pt_2Ln_4 complexes is probably induced by steric effects as well as hydrogen bonding interactions between the

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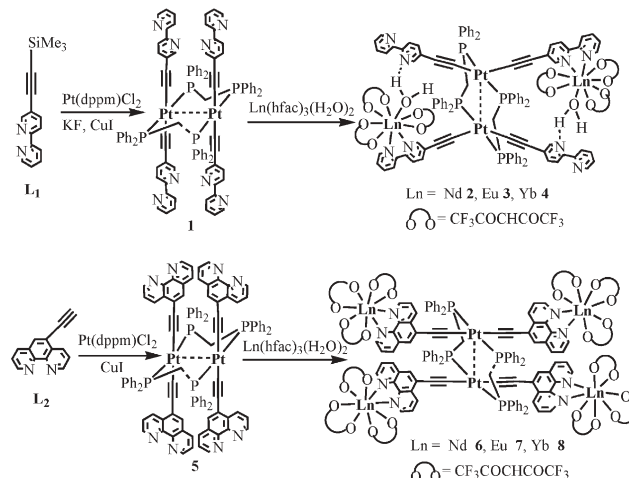
Scheme 1 Synthetic routes to the $Pt^{II}_2Ln^{III}_2$ and $Pt^{II}_2Ln^{III}_4$ complexes.

free bipyridyl N atom and the coordinated H_2O (*vide infra*). Compared to 2,2′-bipyridine, 1,10-phenanthroline is more rigid and has a stronger affinity for Ln^{III} ions. The 1,10-phenanthroline-containing ligand L_2[15] was utilized to prepare binuclear Pt^{II} alkynyl complex **5**. Incorporating **5** with $Ln(hfac)_3(H_2O)_2$ indeed afforded the desired Pt_2Ln_4 complexes. The compounds were all characterized by microanalysis and spectroscopic measurements (ESI†). The structures of **2**, **3** and **7** were determined by X-ray crystallography.‡

The Pt_2Ln_2 array is composed of $Pt_2(\mu\text{-dppm})_2(bpyC{\equiv}C)_4$ units, incorporating $Ln(hfac)_3$ components through 2,2′-bipyridyl chelating, which are stabilized by strong intramolecular hydrogen bonding interactions (Fig. 1a) between the coordinated H_2O and the free bipyridyl N atom, O7···N3A being *ca.* 2.70 Å. The diplatinum unit $Pt_2(\mu\text{-dppm})_2(bpyC{\equiv}C)_4$ displays a face-to-face conformation.[16,17] The *trans*-oriented array C≡C–Pt–C≡C deviates obviously from linearity, with the angles C≡C–Pt and C–Pt–C being 167.9(8)–172.3(6)° and *ca.* 167.7(2)°, respectively. The Pt–Pt distances are *ca.* 3.25 Å, implying the presence of metal–metal contacts.[16,17] The dihedral angles between the bonding and free bipyridyl are 65.3° for **2** and 67.4° for **3**. The Ln^{III} center is nine-coordinated with N_2O_7 donors to form a distorted capped square antiprism. The Pt^{II} center exhibits a square-planar geometry built from *trans*-oriented N_2P_2 donors. The intramolecular Pt···Ln separation through bridging L_1 is *ca.* 8.8 Å.

Pt_2Eu_4 compound **7** (Fig. 1b) is formed from the linkage of four $Eu(hfac)_3$ with $Pt_2(\mu\text{-dppm})_2(phenC{\equiv}C)_4$ through 1,
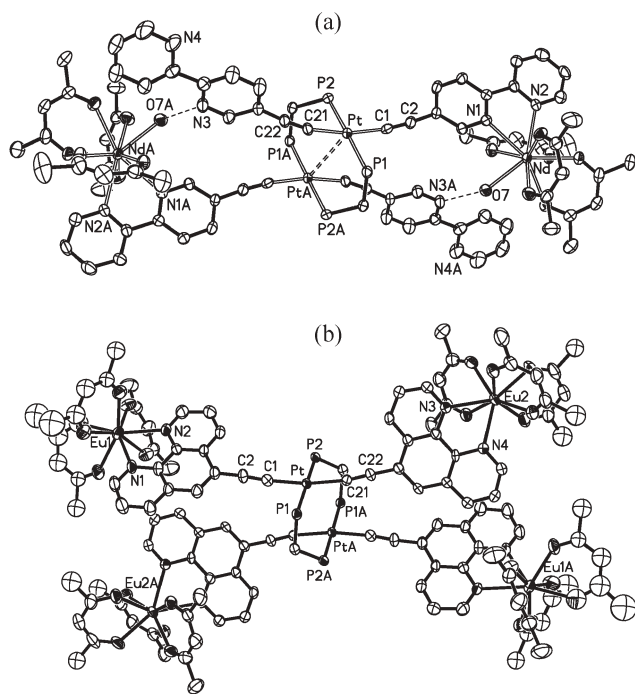
Fig. 1 ORTEP drawing of compounds (a) **2** and (b) **7** with their atom labelling schemes showing 30% thermal ellipsoids. Phenyl rings and F atoms are omitted for clarity.

10-phenanthroline chelation. The *trans*-situated array C≡C–Pt–C≡C is a little more linear than in the Pt_2Ln_2 complexes **2** and **3** with 2,2′-bipyridyl-5-acetylide. The Pt^{II} center exhibits an approximately square-planar geometry with *trans*-oriented C_2P_2 donors, whereas the Eu^{III} center is eight-coordinated with the N_2O_6 chromophore to form a distorted square-antiprism. The dihedral angle between the 1,10-phenanthrolines bound to Eu1 and Eu2 is 38.9°. The Pt–Pt distance (3.298(8) Å) is a little longer than those (3.246–3.251 Å) in Pt_2Ln_2 complexes **2** and **3**. The intramolecular Pt···Eu separation through bridging L_2 is *ca.* 10.2 Å.

The UV-vis spectra of diplatinum compounds **1** and **5** in CH_2Cl_2 display a dppm-centered absorption band at *ca.* 230–270 nm together with two low energy bands at 348 and 392 nm for **1**, and at 345 and 378 nm for **5**, most likely originating from metal-perturbed $\pi \rightarrow \pi^*(C{\equiv}C)$ and $d(Pt) \rightarrow \pi^*(R{-}C{\equiv}C)$ metal-to-ligand charge transfer (MLCT) transitions,[17] respectively. Upon formation of the Pt_2Ln_2 or Pt_2Ln_4 assemblies, the two low energy bands show *ca.* 10–20 nm bathochromic shifts relative to those of the Pt_2 precursor compounds **1** or **5**. By addition of portions of $Eu(hfac)_3(H_2O)_2$ to a CH_2Cl_2 solution of **1**, the MLCT bands show a red shift from 348 and 392 nm to 366 and 405 nm, which is responsible for the color deepening during the reaction. The dependence of the absorbance at a selected wavelength on the amount of $Eu(hfac)_3(H_2O)_2$ added reveals a 1 : 2 ratio between the Pt_2 and $Eu(hfac)_3$ components in the produced Pt_2Eu_2 array. The calculated association constant for the binding of the Ln^{III} fragment to the bipyridyl sites is *ca.* 3×10^7 for Pt_2Eu_2 complex **3**. Similarly, titration of a CH_2Cl_2 solution of **5** by addition of an increasing amount of $Nd(hfac)_3(H_2O)_2$ reveals a 1 : 4 ratio between the Pt_2 and $Nd(hfac)_3$ units in the produced Pt_2Nd_4 complex.

With excitation wavelength $\lambda_{ex} > 340$ nm, both solid and solution (CH_2Cl_2) samples of diplatinum compounds **1** and **5** luminesce in the range 530–650 cm^{-1} at 298 K. With reference to the emission studies of $[Pt_2(\mu\text{-}dppm)_2(C{\equiv}CR)_4]$ (R = alkyl or aryl),[17] their origin is ascribed tentatively to a $d(Pt_2) \rightarrow \pi^*(R{-}C{\equiv}C)$ [3]MMLCT (metal–metal-to-ligand charge transfer) transition in view of their microsecond range lifetimes at 298 K and their short intramolecular Pt–Pt contacts in the solid state. Additionally, CH_2Cl_2 solutions of **1** and **5** afford intense ligand-centered emission at 375–450 nm due to the intraligand transitions of L_1 or L_2.

Upon irradiation of the MLCT absorption of the diplatinum alkynyl moiety at $\lambda_{ex} = 350$–450 nm, all of the Pt_2Ln_2 and Pt_2Ln_4 complexes exhibit characteristic emissions for these lanthanide ions with lifetimes in the microsecond range in both the solid state and in CH_2Cl_2 solution at 298 K (Table 1). By contrast, MMLCT and ligand-centered emissions from diplatinum alkynyl chromophores disappeared entirely for all of the Pt–Ln complexes in both the solid state and in CH_2Cl_2 solution, indicating that the Pt-based luminescence is completely quenched because of a quite efficient and fast energy transfer occurring from the d-block chromophores to the f-block luminophores. As anticipated, three emission bands were observed for Pt^{II}–Nd^{III} complexes at *ca.* 865, 1060 and 1330 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}, {}^4I_{11/2}, {}^4I_{13/2}$), four for Pt^{II}–Eu^{III} complexes at *ca.* 595, 615, 650 and 695 nm ($^5D_0 \rightarrow {}^7F_1, {}^7F_2, {}^7F_3, {}^7F_4$), and one for Pt^{II}–Yb^{III} complexes at *ca.* 980 nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) (Fig. 2). It has been suggested that the efficiency of $d \rightarrow f$ energy transfer is principally determined by the conjugacy of the bridging ligand and the distance between transition metal chromophores and lanthanide luminophores.[1,3,5] Because of the short Pt–Ln distances (<10.5 Å) as well as favourable conjugacy in the bridging ligands L_1 or L_2, both Dexter and Förster energy transfer mechanisms are likely to be operative in the Pt–Ln bimetallic complexes.

In summary, an unprecedented synthetic route has been established to prepare a series of Pt^{II}–Ln^{III} bimetallic arrays using acetylide-functionalized bipyridines/phenanthrolines as bridging ligands. Sensitisation of lanthanide luminescence by the $d(Pt_2) \rightarrow \pi^*(R{-}C{\equiv}C)$ [3]MMLCT excited state is achieved through efficient $d \rightarrow f$ energy transfer from the Pt^{II} alkynyl antenna chromophore to the f-block energy acceptor. This synthetic strategy opens up a

Table 1 Luminescence data for compounds **1–8** at 298 K

Compound	Solid λ_{em}/nm ($\tau/\mu s$)[a]	CH_2Cl_2 λ_{em}/nm ($\tau/\mu s$)[a]	$\Phi \times 10^{3b,c}$
1	585 (0.76)	540 (<0.1)	
2	1060 (0.21)	1060 (weak)	0.84
3	615 (16.4)	615 (250.6)	24
4	980 (11.3)	980 (12.2)	5.65
5	566 (0.27)	535 (<0.1)	
6	1060 (0.49)	1060 (weak)	1.96
7	615 (25.2)	615 (33.6)	5.0
8	980 (12.7)	980 (12.9)	6.35

[a] The excitation wavelength in the lifetime measurements is 397 nm. [b] The quantum yields of Nd^{III} and Yb^{III} complexes in the solid state are estimated by the equation $\Phi = \tau_{obs}/\tau_0$, in which τ_{obs} is the observed emission lifetime and τ_0 is the radiative or 'natural' lifetime with $\tau_0 = 0.25$ ms for Nd^{III} and 2 ms for Yb^{III}. [c] The quantum yields of Eu^{III} complexes in de-gassed CH_2Cl_2 are determined relative to that of $Eu(terpy)_3(ClO_4)_3$ ($\Phi = 0.013$)[18] in de-gassed CH_3CN.
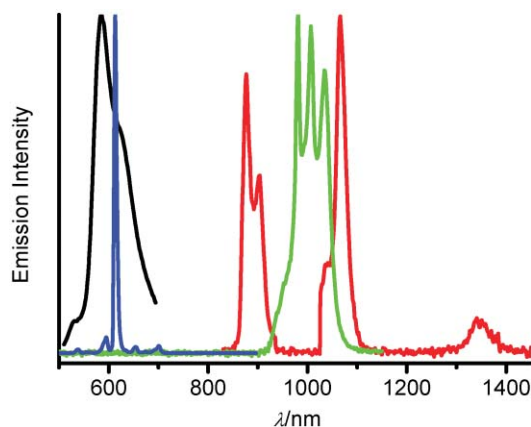
Fig. 2 Emission spectra of **1** (black), **2** (red), **3** (blue) and **4** (green) in CH_2Cl_2 at 298 K.

significant approach for designing d–f bimetallic arrays that emit lanthanide NIR luminescence by d → f energy transfer from metal alkynyl energy donors using an acetylide-functionalized diimine as a connector between the d- and f-block components.

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