

## Sensitised near-infrared emission from lanthanides using a covalently-attached Pt(II) fragment as an antenna group†

Nail M. Shavaleev,<sup>a</sup> Lucy P. Moorcraft,<sup>a</sup> Simon J. A. Pope,<sup>b</sup> Zöe R. Bell,<sup>b</sup> Stephen Faulkner<sup>\*b</sup> and Michael D. Ward<sup>\*a</sup>

<sup>a</sup> School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS.

E-mail: mike.ward@bristol.ac.uk

<sup>b</sup> Department of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL.

E-mail: stephen.faulkner@man.ac.uk

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In a series of heterodinuclear complexes in which a Pt(PPh<sub>3</sub>)<sub>2</sub>(catechol) chromophore is covalently linked to a lanthanide tris(diketonate) unit, sensitised near-IR emission from Yb(III), Nd(III) and Er(III) occurs on excitation of the Pt(II) chromophore at 520 nm.

There has been considerable recent interest in NIR luminescence from *e.g.* Yb(III), Nd(III), Pr(III) and Er(III) complexes because of its possible applications in (i) biological imaging, where human tissue is relatively transparent to the longer-wavelength radiation, and (ii) telecommunications, where the emission wavelengths of Pr(III) (*ca.* 1330 nm) and Er(III) (*ca.* 1550 nm) closely match the 'windows of transparency' in silica used for fibre-optic data transmission.<sup>1–5</sup>

Unless very intense irradiation is used for direct excitation of the weak (Laporte forbidden) lanthanide f–f transitions, emission has to be sensitised by energy-transfer from a suitable adjacent chromophore, commonly an aromatic unit in a ligand which may be either directly attached to, or just lie close to, the metal. This requires high-energy (UV/blue) excitation for simple aromatic chromophores (*e.g.* pyridine-based ligands). However for NIR-emitting lanthanides, excitation using much lower energy (visible/red) light should be possible. To this end sensitised NIR emission has been detected from various lanthanides using visible-light excitation of a variety of organic chromophores having particularly low energy absorptions, such as fluorescein, eosin, fluorexon,<sup>2</sup> and tetrazine,<sup>5</sup> which have all been incorporated into suitable ligands.

A more appealing and versatile route for low-energy sensitisation of NIR emission from lanthanides is to exploit the light-absorbing properties of transition-metal fragments, for which charge-transfer transitions in particular can be intense and have low energy, and are readily 'tunable'. Such 'd→f' energy-transfer has been demonstrated in some solid-state lattices in which cyanometallate complex anions were crystallised with lanthanide cations.<sup>6</sup> For molecular species, d→f energy-transfer requires the preparation of heterodinuclear complexes in which a d-block chromophore and a lanthanide luminophore are connected by an appropriate bridging ligand; there are few examples of this. Van Veggel and co-workers described recently how emission from Nd(III) and Yb(III) could be sensitised by excitation of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> or ferrocenyl chromophores;<sup>7</sup> Beeby and Parker used a Pd(II)-porphyrin chromophore to sensitise emission from Yb(III) and Nd(III).<sup>8</sup>

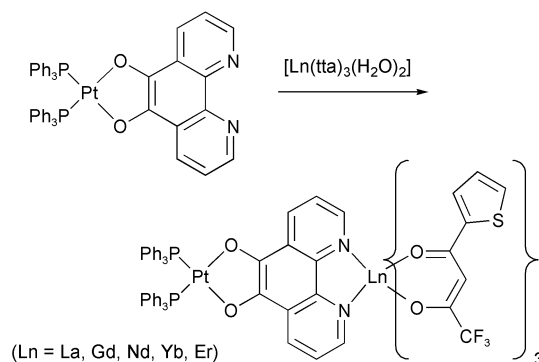
To extend this very limited field we recently reported a simple, general synthesis for a variety of such heterodinuclear complexes, based on the stepwise attachment of a d-block fragment and then a Ln(dik)<sub>3</sub> fragment (where 'dik' denotes a 1,3-diketonate) to the two binding sites of a bis-bidentate bridging ligand.<sup>9</sup> We describe here the preparation and structural characterisation of the series of complexes

[(PPh<sub>3</sub>)<sub>2</sub>Pt(μ-pdo)Ln(tta)<sub>3</sub>] (Scheme 1; H<sub>2</sub>pdo = 5,6-dihydroxy-1,10-phenanthroline; Htta = thenoyltrifluoroacetone), abbreviated hereafter as **Pt–Ln** (Ln = La, Nd, Gd, Er, Yb), together with luminescence measurements on the complexes with Ln = Nd, Er and Yb, which show that sensitised NIR emission from the lanthanides can occur following excitation of the Pt-centred chromophore.

The dinuclear complexes were prepared by reaction of the known mononuclear complex [(PPh<sub>3</sub>)<sub>2</sub>Pt(pdo)],<sup>10</sup> in which the {Pt(PPh<sub>3</sub>)<sub>2</sub>}<sup>2+</sup> unit is coordinated to the diolate site of (pdo)<sup>2–</sup> and the phenanthroline site is free, with the appropriate lanthanide complex [Ln(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]. This synthesis is based on the well-known formation of 8-coordinate adducts between {Ln(dik)<sub>3</sub>} units and *N,N*-bidentate chelates such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen).<sup>11</sup> Simply mixing the starting components [(PPh<sub>3</sub>)<sub>2</sub>Pt(pdo)] and [Ln(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] in benzene–heptane (4:1, v/v), and leaving the solution to evaporate slowly for a few days, afforded good yields of the dinuclear adducts as X-ray quality crystals in every case.† All of the complexes gave correct elemental analyses, and the <sup>1</sup>H NMR spectrum of **Pt–La** was exactly in agreement with the expected structure of the complex (see ESI†). We note that use of [(PPh<sub>3</sub>)<sub>2</sub>Pt(pdo)] as a 'bipyridine equivalent' for the formation of heterodinuclear (d–d) complexes has been described by others.<sup>12</sup>

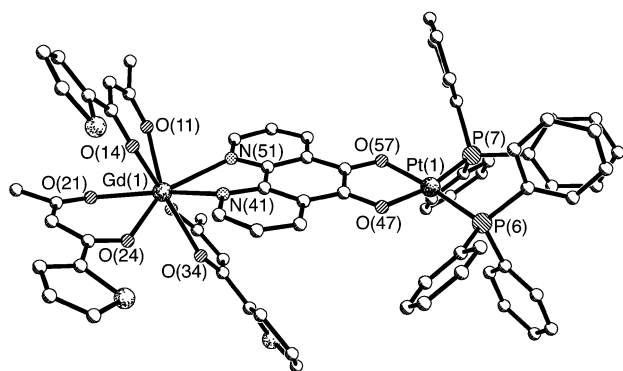
The crystal structure of a representative member of the series (**Pt–Gd**) is in Fig. 1.§ The Pt(II) centre is square planar; the 8-coordinate lanthanide centre has an approximately square-antiprismatic geometry. Bond distances and angles around individual metal centres are unremarkable. The Pt...Gd distance is 8.43 Å. The complexes **Pt–Yb**, **Pt–Er** and **Pt–La** have also been structurally characterised and are isostructural; full details of these will be reported later.

The structural integrity of the complexes in CH<sub>2</sub>Cl<sub>2</sub> solution was confirmed by a UV/Vis spectroscopic titration, in which portions of [Gd(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] were added to a 7.4 × 10<sup>–5</sup> M solution of [(PPh<sub>3</sub>)<sub>2</sub>Pt(pdo)]. It was clear that the association between the [(PPh<sub>3</sub>)<sub>2</sub>Pt(pdo)] and {Gd(tta)<sub>3</sub>} units is at the strong limit at this concentration, implying that *K* ≫ 1.4 × 10<sup>4</sup>



Scheme 1

† Electronic supplementary information (ESI) available: characterisation data and luminescence spectra. See <http://www.rsc.org/suppdata/cc/b3/301878d/>

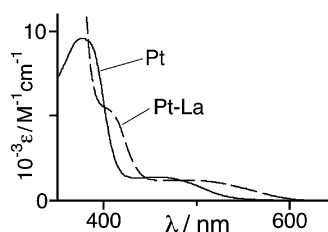


**Fig. 1** Molecular structure of  $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-pdo})\text{Gd}(\text{tta})_3]$ . Selected bond distances ( $\text{\AA}$ ): Gd(1)–O(31) 2.335(5), Gd(1)–O(11) 2.338(5), Gd(1)–O(21) 2.352(5), Gd(1)–O(34) 2.359(5), Gd(1)–O(24) 2.359(5), Gd(1)–O(14) 2.374(5), Gd(1)–N(51) 2.535(6), Gd(1)–N(41) 2.540(6), Pt(1)–O(47) 2.011(5), Pt(1)–O(57) 2.025(4), Pt(1)–P(6) 2.2202(17), Pt(1)–P(7) 2.2211(19).

$\text{M}^{-1}$ , in agreement with the known association constants of ligands such as bpy and phen which are  $\sim 10^7 \text{ M}^{-1}$  in non-polar solvents.<sup>11</sup>

The absorption spectrum of a representative dinuclear **Pt–Ln** complex, and mononuclear  $[(\text{PPh}_3)_2\text{Pt}(\text{pdo})]$ , are shown in Fig. 2.  $[(\text{PPh}_3)_2\text{Pt}(\text{pdo})]$ , which is orange-brown, has its lowest-energy absorption maximum at 460 nm ( $\epsilon = 1,400 \text{ M}^{-1} \text{ cm}^{-1}$ ). In the dinuclear **Pt–Ln** complexes this is red-shifted to 485 nm ( $\epsilon = 1,200 \text{ M}^{-1} \text{ cm}^{-1}$ ) and also develops a low-energy tail which does not decay until *ca.* 650 nm; this results in the colour becoming a much deeper brown. Absorptions in the 400–500 nm region are characteristic of  $[(\text{PPh}_3)_2\text{Pt}(\text{OO})]$  complexes (where ‘OO’ denotes a dianionic *o*-catecholate type donor).<sup>13</sup> Although these spectra have not been analysed in detail, the transitions have been assigned as a combination of catecholate  $\rightarrow$  phosphine LLCT and catecholate  $\rightarrow$  Pt LMCT;<sup>14</sup> some Pt-centred d–d character is also possible. Importantly, the  $\{\text{Ln}(\text{tta})_3\}$  units do not have strong absorptions at wavelengths longer than 400 nm,<sup>5</sup> only very the weak f–f transitions, so use of an excitation wavelength of  $> 400 \text{ nm}$  will result in essentially selective excitation of the Pt-based chromophore.

Excitation at 520 nm of both solid and solution ( $\text{CH}_2\text{Cl}_2$ ) samples of these complexes produced in every case the NIR emission characteristic of these lanthanide elements, with lifetimes on the microsecond timescale comparable to those of other NIR-emitting complexes where excitation through a directly-coordinated ligand is used.<sup>1–5,¶</sup> The lifetimes are similar in both the solid state and solution, confirming the integrity of the complexes in solution. The lifetimes and quantum yields are summarised in Table 1. Representative emission spectral profiles are given as ESI.† It is clear from these results that NIR emission from lanthanides can be sensitised using relatively long wavelength (visible-light) excitation of electronic transitions localised on the d-block metal chromophore in these heterodinuclear complexes, followed by metal-to-metal (d  $\rightarrow$  f) energy-transfer. Such heterodinuclear antenna-emitter complexes are readily prepared from d-block complexes having a pendant diimine-type binding site, using the ‘complexes as ligands’ approach.



**Fig. 2** Electronic spectra of mononuclear  $[(\text{PPh}_3)_2\text{Pt}(\text{pdo})]$  (**Pt**) and the dinuclear complex **Pt–La**.

**Table 1** Luminescence data for the complexes

Complex	$\tau/\mu\text{s}$		$\Phi_{\text{Ln}}^a$
	$\text{CH}_2\text{Cl}_2$	Solid	
<b>Pt–Nd</b> <sup>b</sup>	0.99	0.95	$4 \times 10^{-3}$
<b>Pt–Yb</b> <sup>c</sup>	10.6	11.0	$5.3 \times 10^{-3}$
<b>Pt–Er</b> <sup>d</sup>	2.52	1.56	$1.8 \times 10^{-4}$

<sup>a</sup> Quantum yield in  $\text{CH}_2\text{Cl}_2$  solution determined from  $\Phi_{\text{Ln}} = \tau_{\text{obs}}/\tau_0$ , in which  $\tau_{\text{obs}}$  is the observed emission lifetime and  $\tau_0$  is the radiative or ‘natural’ lifetime, *viz.* 14 ms, 2 ms and 0.25 ms for Er(III), Yb(III) and Nd(III) respectively (see ref. 5). These values refer to the metal-based emission process only and do not account for the efficiency of inter-system crossing and energy-transfer processes. <sup>b</sup> Luminescence decay measured at 1055 nm <sup>c</sup> Luminescence decay measured at 980 nm <sup>d</sup> Luminescence decay measured at 1530 nm

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## Notes and references

† A mixture of  $[(\text{PPh}_3)_2\text{Pt}(\text{pdo})]$  (34 mg, 37  $\mu\text{mol}$ ) and the appropriate  $[\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2]$  (37  $\mu\text{mol}$ ) in benzene–heptane (4:1, v/v; 15  $\text{cm}^3$ ) was allowed to slowly evaporate over several days. Dark brown–red crystals formed which were filtered off, washed with hexane and dried to give the **Pt–Ln** complex in 70–85% yield. Satisfactory analytical data were obtained (see ESI†). The complexes are stable to air and moisture.

§ Crystal data for  $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-pdo})\text{Gd}(\text{tta})_3]$ :  $\text{C}_{72}\text{H}_{48}\text{F}_9\text{GdN}_2\text{O}_8\text{P}_2\text{PtS}_3$ ,  $M = 1750.58$ , triclinic, space group  $P\bar{1}$ ,  $a = 15.097(4)$ ,  $b = 16.802(4)$ ,  $c = 18.618(6) \text{ \AA}$ ,  $\alpha = 86.67(2)$ ,  $\beta = 69.923(17)$ ,  $\gamma = 69.81(2)^\circ$ ,  $U = 4153(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.400 \text{ Mg m}^{-3}$ ,  $\mu(\text{Mo–K}\alpha) = 2.655 \text{ mm}^{-1}$ ,  $T = 173 \text{ K}$ , 18951 independent reflections ( $R_{\text{int}} = 0.0753$ ) with  $2\theta \leq 50^\circ$ . Refinement of 884 parameters converged at final  $R1$  [for selected data with  $I > 2\sigma(I)$ ] = 0.0595,  $wR2$  (all data) = 0.1487. There is disorder involving one of the thiophene rings (not shown); a diffuse solvent correction was applied because of severely disordered lattice solvent.

CCDC 204633. See <http://www.rsc.org/suppdata/cc/b3/b301878d/> for crystallographic data in .cif or other electronic format.

¶ For experimental details on the equipment and methods used for the luminescence studies, see refs. 4 and 5.

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