A simple, general synthesis of mixed d–f complexes containing both {Re(CO)₃Cl(diimine)} and lanthanide-tris(β-diketonate) luminophores linked by bis-diimine bridging ligands

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Reaction of the mononuclear 'complex ligands' [Re(CO)₃Cl(L)] [L = 2,2′-bipyrimidine (bpym) or 2,3-bis-(2-pyridyl)pyrazine (bppz)] with a Ln(β-diketonate)₃ unit affords the heterodinuclear complexes [Re(CO)₃Cl-(μ-bpym)Ln(fod)₃] and [Re(CO)₃Cl(μ-bppz)Ln(tta)₃]; one member of each series has been structurally characterised.

The study of photoinduced processes (energy- or electron-transfer) in multi-chromophoric complexes remains one of the most fruitful and intensely studied areas of inorganic chemistry.[1] Precise control of the movement of excitation energy or of excited electrons in complicated multi-component systems is of particular interest both for understanding and mimicking natural photosynthetic processes, and for making artificial molecules which exploit light in a similar manner for applications ranging from medicine to materials science.[1]

The vast majority of such multi-chromophoric metal complexes are based on well-known d-block transition metal fragments such as [Re(bpy)(CO)₃Cl], [Ru(bpy)₃]²⁺, [Os(bpy)₃]²⁺ (bpy = 2,2′-bipyridine).[1] This is largely for reasons of synthetic convenience. Linking metal complex components together requires a suitable bridging ligand, and the chemistry of bpy- and terpy-based ligands (terpy = 2,2′:6′,2″-terpyridine) which allows several such binding sites to be connected together is very well developed.[2] In contrast to this, photophysical studies on lanthanide complexes have been confined largely to mononuclear species. Luminescent lanthanide complexes have many emission characteristics (high intensity; sharp, line-like emission; long luminescence lifetimes; a range of emission maxima spanning the visible and near-IR regions of the electromagnetic spectrum) which make them suitable for an exceptionally wide variety of applications as diverse as lighting and display devices,[3] fluoroimmunoassay,[4] biomedical imaging,[5] and telecommunications.[6] Despite this, the use of lanthanide luminophores as components of heteropolynuclear photo-active assemblies – in the same way as is commonplace for d-block luminophores – is virtually unknown, despite the fact that many mixed d/f complexes have been studied in other contexts, principally for their magnetic properties.[7,8]

This anomaly arises principally from the synthetic difficulties involved in preparing an asymmetric bridging ligand containing a polypyridyl site for a typical d-block luminophore, and a polyaminocarboxylate site for a lanthanide. There are a few relevant papers in the recent literature, as follows: (i) Yam and Kai described [Ru(bpy)₃]²⁺ derivatives with pendant imino-diacetic acid groups, which bind lanthanides (albeit weakly) at the peripheral site;[9] (ii) van Veggel and co-workers reported sensitised near-IR emission from Nd or Yb centres at a poly-carboxylate binding site, following energy-transfer from a covalently-linked [Ru(bpy)₃]²⁺ antenna;[10] (iii) Beeby and Parker prepared covalently linked dyads in which a Pd(II)-porphyrin unit is attached to a lanthanide complex (M = Nd, Yb) of a macrocyclic amino-carboxylate ligand, such that Pd→M energy-transfer gave sensitised near-IR emission from the lanthanide centre;[11] and (iv) Eu(III)→Cr(III) energy-transfer,

resulting in sensitised emission from Cr(III) in a heterodinuclear Eu(III)/Cr(III) triple helicate, has been reported by Piguet.[12] It will be apparent that, notwithstanding the interesting properties of these complexes, the labour involved in synthesising these elaborate bridging ligands is substantial, and that a general study of the photophysical properties of multinuclear complexes in which d- and f-block chromophores are combined is therefore difficult.

We describe here a simple, general method for the preparation of dinuclear complexes which combine d-block and f-block luminophores *via* compartmental bis-diimine bridging ligands of the sort which are so prevalent in d-block chemistry, *viz.* 2,2′-bipyrimidine (bpym) and 2,3-bis(2-pyridyl)pyrazine (bppz). It has been known for many years that reaction of 6-coordinate Ln(dik)₃ complexes (Ln = a lanthanide ion; dik = a β-diketonate) with a diimine (NN) unit such as phen or bpy results in rapid formation of the adduct [M(dik)₃(NN)];[13] the association constant for this process is typically 10⁷ M⁻¹ in CH₂Cl₂ and 10⁸ M⁻¹ in benzene.[14] We have exploited this by preparing mononuclear complexes containing a d-block luminophore with a vacant NN-donor coordination site (the 'complexes as ligands' principle) and then attaching the Ln(dik)₃ unit at the second coordination site (Scheme 1).

Thus, reaction of bpym or bppz (L) with [Re(CO)₅Cl] afforded the (known)[15,16] mononuclear complexes [Re(CO)₃-Cl(L)], in each of which there is vacant NN-donor coordination site. Reaction of these with various Ln(dik)₃ species in CH₂Cl₂ (1 : 1 stoichiometry) resulted in an immediate deepening of the orange-yellow colour of the Re chromophore; addition of hexane and reduction in volume of the solution resulted in precipitation of the adducts [Re(CO)₃Cl(μ-L)Ln(dik)₃] in good yield,† all of which are air- and moisture-stable. When L = bpym, the lanthanide species [Ln(fod)₃] [Hfod = CF₃CF₂CF₂-C(O)CH₂C(O)ᵗBu; Ln = Eu, Gd, Er, Yb] were used as the second component; with bppz as bridging ligand, the lanthanide species [Ln(tta)₃] (Htta = thienyl-trifluoroacetylacetone; Ln = Nd, Er, Yb, Gd) were used (Scheme 1). Crystal structures of a representative member of each series, *viz.* [Re(CO)₃Cl(μ-bpym)Er(fod)₃] and [Re(CO)₃Cl(μ-bppz)Nd(tta)₃], are shown in Figs. 1 and 2 respectively. ‡ In each case the lanthanide centre is 8-coordinate with a distorted geometry best described as square antiprismatic; for [Re(CO)₃Cl(μ-bpym)Er(fod)₃] the two (crude) square planes consist of N(11)/N(21)/O(54)/O(56) and O(34)/O(36)/O(44)/O(46), and for [Re(CO)₃Cl(μ-bppz)Nd(tta)₃] they are N(11)/N(21)/O(44)/O(41) and O(51)/O(61)/O(64)/O(54). The two metal centres are connected by the diazine unit(s) of the bridging ligands; the Re · · · Er and Re · · · Nd separations are 6.23 and 7.47 Å respectively. For [Re(CO)₃Cl(μ-bpym)-Er(fod)₃] the bridging bipyrimidine ligand is approximately planar, whereas in [Re(CO)₃Cl(μ-bppz)Nd(tta)₃] the bppz ligand is considerably distorted from planarity with pyridyl rings N(11)–C(16) and N(31)–C(36) being twisted from the mean plane of the central pyrazine ring by 36.5 and 22.1° respectively.

Representative electronic spectra (Fig. 3) show how (i) the Re-diimine MLCT transition at *ca.* 400 nm in the mononuclear
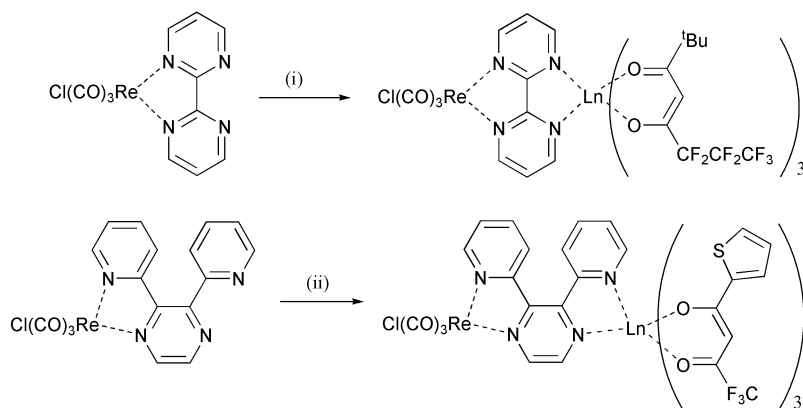
Scheme 1 (i) Ln(fod)$_3$, CH$_2$Cl$_2$; (ii) Ln(tta)$_3$, CH$_2$Cl$_2$.
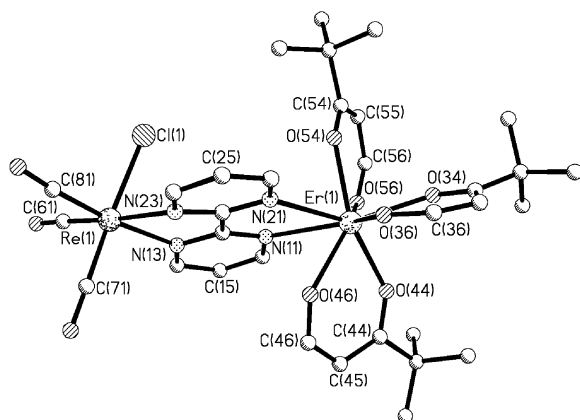
Fig. 1 Structure of [Re(CO)$_3$Cl(μ-bpym)Er(fod)$_3$] (with the CF$_2$CF$_2$-CF$_3$ side-chains of the fod ligands omitted for clarity). Selected bond distances (Å): Er(1)–O(44) 2.250(7), Er(1)–O(54) 2.251(7), Er(1)–O(36) 2.257(7), Er(1)–O(34) 2.276(7), Er(1)–O(46) 2.294(7), Er(1)–O(56) 2.306(7), Er(1)–N(11) 2.526(9), Er(1)–N(21) 2.579(8), Re(1)–C(71) 1.852(14), Re(1)–C(61) 1.898(14), Re(1)–C(81) 1.902(13), Re(1)–N(23) 2.161(9), Re(1)–N(13) 2.166(9), Re(1)–Cl(1) 2.456(3).
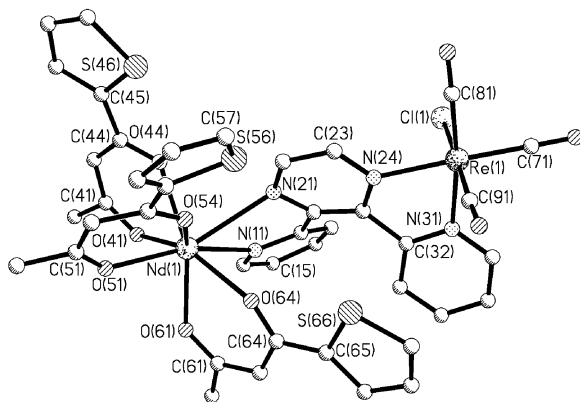

Fig. 2 Structure of [Re(CO)$_3$Cl(μ-bppz)Nd(tta)$_3$] (with the F atoms of the CF$_3$ groups on the tta ligands omitted for clarity). Selected bond distances (Å): Nd(1)–O(51) 2.343(6), Nd(1)–O(44) 2.386(6), Nd(1)–O(41) 2.392(6), Nd(1)–O(64) 2.399(6), Nd(1)–O(61) 2.427(6), Nd(1)–O(54) 2.436(6), Nd(1)–N(11) 2.622(7), Nd(1)–N(21) 2.721(7), Re(1)–C(81) 1.908(10), Re(1)–C(71) 1.916(9), Re(1)–C(91) 1.928(10), Re(1)–N(31) 2.177(7), Re(1)–N(24) 2.181(7), Re(1)–Cl(1) 2.462(2).

Fig. 3 Electronic spectra of (a) [Re(CO)$_3$Cl(μ-bppz)Yb(tta)$_3$] (—), together with spectra of the component parts [Re(CO)$_3$Cl(bppz)] (- - -) and Yb(tta)$_3$ (· · ·); (b) [Re(CO)$_3$Cl(μ-bpym)Yb(fod)$_3$] (—), together with spectra of the component parts [Re(CO)$_3$Cl(bpm)] (- - -) and Yb(fod)$_3$ (· · ·).

Re complexes is red-shifted by coordination of the lanthanide fragment to the secondary binding site; and (ii) this Re-based MLCT transition is an area of the spectrum (400–500 nm) where the Ln(dik)$_3$ unit does not absorb, such that selective Re-centred excitation is possible. Given the precedents that have been established for energy-transfer between d- and f-block chromophores mentioned earlier, the photophysical properties
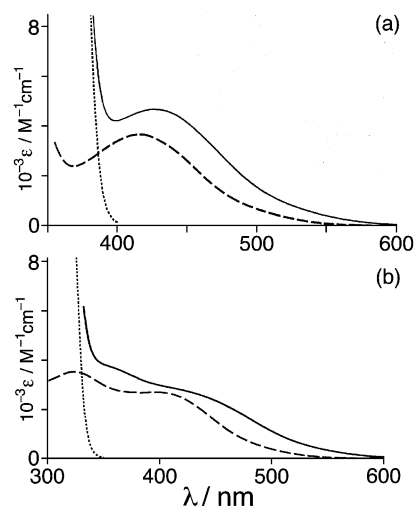
of these complexes should prove to be of considerable interest. Preliminary steady-state luminescence studies show that the ^{3}MLCT emission of [Re(CO)$_3$Cl(bppz)] at 650 nm is quenched when Yb(tta)$_3$, Nd(tta)$_3$ or Er(tta)$_3$ units are attached to the second site; all of these are capable in principle of acting as energy-transfer acceptors from the Re fragment due to the low energy (NIR region) of their emissive excited states.

In conclusion, this simple, modular synthetic method will allow the well-known d-block polypyridyl chromophores to be connected *via* an extensive range of bis-diimine bridging ligands to any desired Ln(dik)$_3$ unit in an almost combinatorial manner, thereby permitting lanthanide chromophores to be incorporated into heteropolynuclear luminescent assemblies in the way that has become commonplace for d-block fragments.

Notes and references

† General procedure for preparation of [Re(CO)$_3$Cl(μ-bpym)Ln(fod)$_3$]. To a solution of [Re(CO)$_3$Cl(bpym)] (30 mg, 65 μmol) in CH$_2$Cl$_2$ (15 cm^3) was added the appropriate Ln(fod)$_3$ complex (65 μmol); the reaction mixture immediately changed from yellow to orange-red. The solution was stirred for 10 minutes, after which time hexane (15 cm^3) was added and the mixture was concentrated *in vacuo*, resulting in precipitation of the orange-red dinuclear complex which was filtered off, washed with hexane, and dried (yield: 65–77%). Large needle-like crystals were grown by slow evaporation from CH$_2$Cl$_2$/hexane. Characterisation data follow for Ln = Er. Anal. calcd. for C$_{41}$H$_{36}$ClErF$_{21}$-N$_4$O$_9$Re: C, 32.5; H, 2.4; N, 3.7%. Found: C, 32.4; H, 2.1; N, 3.9%. IR (CH$_2$Cl$_2$), cm^{-1}: 2033, 1936, 1915. A similar method was used for

preparation of [Re(CO)$_3$Cl(μ-bppz)Nd(tta)$_3$], starting from [Re(CO)$_3$-Cl(bppz)] and [Ln(tta)$_3$]·2H$_2$O, the only difference being that slow evaporation (3–5 days) of the CH$_2$Cl$_2$/hexane solution was necessary to give a crystalline product. These complexes were isolated in 64–72% yield. Characterisation data follow for Ln = Nd. Anal. calcd. for C$_{41}$H$_{22}$ClF$_9$N$_4$NdO$_9$ReS$_3$: C, 36.5; H, 1.7; N, 4.2%. Found: C, 36.4; H, 1.4; N, 4.1%. IR (CH$_2$Cl$_2$), cm^{-1}: 2028, 1932, 1908.

‡ Crystal data for [Re(CO)$_3$Cl(μ-bpym)Er(fod)$_3$]: C$_{41}$H$_{36}$ClErF$_{21}$N$_4$-O$_9$Re, M = 1516.65, triclinic, space group $P\bar{1}$, a = 11.756(4), b = 12.029(3), c = 18.647(5) Å, $α$ = 81.475(17), $β$ = 88.39(2), $γ$ = 83.33(2)°, U = 2589.9(13) Å^3, Z = 2, D_c = 1.945 Mg m^{-3}, $μ$(Mo-Kα) = 4.126 mm^{-1}, T = 173 K, 9114 independent reflections (R_{int} = 0.1108) with $2θ ≤ 50°$. Refinement of 698 parameters converged at final R1 [for selected data with $I > 2σ(I)$] = 0.0565, wR2 (all data) = 0.1227. Crystal data for [Re(CO)$_3$Cl(μ-bppz)Nd(tta)$_3$]: C$_{41}$H$_{22}$ClF$_9$N$_4$NdO$_9$ReS$_3$, M = 1347.70, monoclinic, space group P2$_1$/c, a = 8.800(3), b = 38.712(8), c = 13.527(3) Å, $β$ = 100.45(2)°, U = 4532(2) Å^3, Z = 4, D_c = 1.975 Mg m^{-3}, $μ$(Mo-Kα) = 4.095 mm^{-1}, T = 173 K, 7988 independent reflections (R_{int} = 0.0903) with $2θ ≤ 50°$. Refinement of 622 parameters converged at final R1 [for selected data with $I > 2σ(I)$] = 0.0471, wR2 (all data) = 0.0989. CCDC reference numbers 191575 and 191576. See http://www.rsc.org/suppdata/dt/b2/b207832e/ for crystallographic data in CIF or other electronic format.

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