Sensitised near infrared emission from lanthanides *via* anion-templated assembly of d–f heteronuclear [2]pseudorotaxanes†

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The first example of assembling novel heteronuclear lanthanide–transition metal pseudorotaxanes where interpenetration of the lanthanide stoppered thread into the transition metal sensitiser containing macrocycle is signalled *via* sensitised near-infrared (NIR) lanthanide luminescence is described.

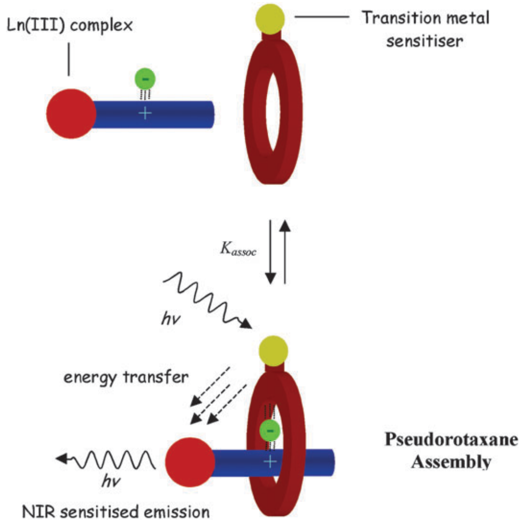
Stimulated by potential applications in diagnostic medical imaging and optical telecommunications there is intense current interest being shown in the design of lanthanide complexes that exhibit near-infrared (NIR) luminescence.[1] The low extinction coefficients of the Laporte forbidden f–f transitions of lanthanides necessitates the use of sensitised energy transfer from a suitable strongly absorbing chromophore to effect lanthanide luminescence.[2] This antenna effect has been successfully exploited using various organic based sensitisers and transition metal fragments covalently linked to lanthanide complexes.[3]

We have recently reported the use of an anion templation strategy for the assembly of a range of [2]pseudorotaxanes, [2]rotaxanes and a [2]catenane.[4] The assembly process is based on coupling anion recognition with ion-pairing where in non-competitive solvent media a coordinatively unsaturated chloride anion of a tight-ion pair threading component facilitates the interpenetration of a pyridinium, imidazolium or guanidinium thread through the annulus of an isophthalamide macrocycle. Herein we describe a novel application of this anion templation methodology to the anion directed assembly of heteronuclear lanthanide–transition metal [2]pseudorotaxanes where pseudorotaxane formation is signaled *via* sensitized NIR lanthanide emission. The strategy employed for assembling a heteronuclear lanthanide–transition metal [2]pseudorotaxane is shown in Scheme 1 where a positively charged ion-pair threading component, stoppered with a lanthanide complex, interpenetrates a macrocycle containing a transition metal sensitiser motif *via* anion template.

Macrocycle **1**, containing a rhenium(I) bipyridyl group as the transition metal sensitiser in combination with an amide cleft for anion recognition and electron rich hydroquinone groups for potential favorable π–π stacking interactions, was prepared according to a synthetic procedure described in the ESI.† The reaction of 5-bromo-methyl-2,2′-bipyridine with benzimidazole and imidazole sodium salts followed by the appropriate alkylating compound, anion exchange and complexation with $\mathrm{Ln[TTA_3]\cdot 2H_2O}$[5] (Ln = Gd, Nd, Yb) produced the potential lanthanide bipyridyl appended imidazolium threading components **2** and **3** (Fig. 1).

We have previously reported that a macrocyclic rhenium(I) bipyridyl amide derivative strongly binds halide anions and forms pseudorotaxanes with pyridinium and imidazolium threading components *via* halide anion templation in polar organic solvents as evidenced by ^{1}H NMR and luminescence.[6] Titration of tetrabutyl ammonium (TBA) chloride into a dichloromethane solution of macrocycle **1** revealed, as expected, an increase in luminescent emission[7] after excitation at the MLCT absorption maximum (440 nm) as a result of halide anion binding at the macrocycle's amide cleft. A 1 : 1 association constant was determined using Specfit analysis[8] to be log 4.72 (±10%).

Analogous luminescent titration experiments with the gadolinium benzimidazolium and imidazolium molecules **2a**



Scheme 1 Strategy for anion-templated assembly of heteronuclear lanthanide–transition metal [2]pseudorotaxanes.

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† Electronic supplementary information (ESI) available: Titration data, selected photophysical experiments and selected experimental information for the preparation of compounds **1** to **3**. See DOI: 10.1039/b601017b

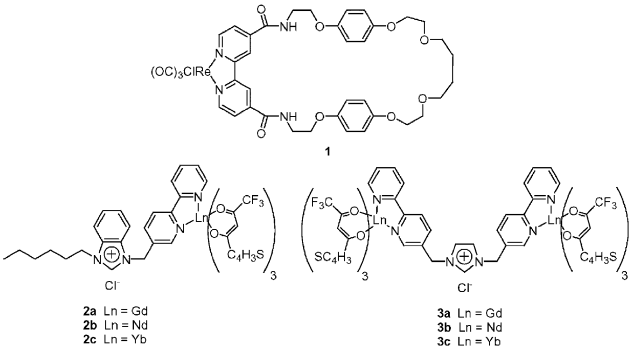

Fig. 1 Macrocycle **1** and lanthanide-containing potential pseudorotaxane threads.

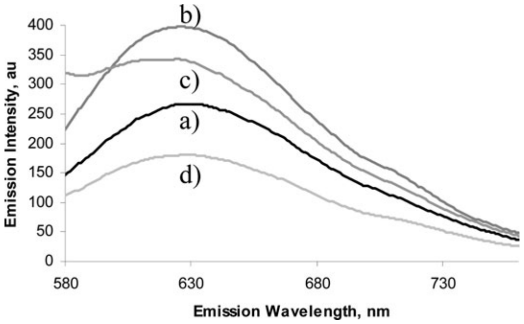

Fig. 2 (a) Observed Re(I) ^{3}MLCT luminescent emission from macrocycle **1** (5.0×10^{-5} M); (b) enhancement of luminescence upon addition of 1 equivalent of tetrabutyl ammonium chloride; (c) enhancement of luminescence upon addition of 1 equivalent of gadolinium thread **3a**; and (d) quenching of luminescence upon addition of 5 equivalents of neodymium thread **3b** (2.5×10^{-4} M) in CH_2Cl_2.

and **3a**, also resulted in an increase in the rhenium ^{3}MLCT emission at 640 nm, indicating the binding of the thread within the cavity. Quantitative titration experiments were carried out and log K_a values of 4.2 (±10%) and 4.8 (±10%) determined for **2a** and **3a**, respectively (see ESI†). Time-resolved spectroscopy‡ also revealed a change in the luminescence lifetime of the rhenium ^{3}MLCT emission upon threading from 31 ns for the free macrocycle to 215 ns. This is strongly suggestive of a decrease in non-radiative quenching due to restriction of mobility in the pseudorotaxane structure.

In contrast, steady state studies with the neodymium containing threads **2b** and **3b** show a significant *quenching* of the rhenium MLCT emission (Fig. 2 and ESI†), while no quenching was observed with the ytterbium threads **2c** and **3c** compared to the unthreaded macrocycle. However, this comparison is false, in that the gadolinium appended thread (the pseudorotaxane in the case of threads **2a** and **3a**) is much more emissive, as mentioned above. This Gd complex is the true standard by which the emission intensity should be measured, and the difference in intensity is indicative of energy transfer taking place to the ytterbium ion. The case for energy transfer to neodymium is even more clear cut, and quenching is apparent compared to both the macrocycle and the pseudorotaxane with a Gd containing thread.

To clarify the situation further, a time-resolved study was carried out to establish the lifetime and nature of the photophysical processes involved. The results are summarized in Table 1 (see also ESI†).

By studying the lifetime of the rhenium centered emission, we may use the emissive lifetime of the Gd analogue (in which the metal centered excited state is higher in energy than the MLCT state) to estimate rate constants for energy transfer (ET) in structural analogues containing emissive lanthanide ions.[9] The rate of ET can usually be approximated by using $k(\mathrm{ET}) = 1/\tau2 - 1/\tau1$ (where $\tau1$ is the donor lifetime of the Gd$^{\mathrm{III}}$ complex, and $\tau2$ the donor lifetime of the Ln complex) and the resulting values are reported in Table 1. These suggest that similar rates of energy transfer occur for the ytterbium and neodymium containing systems. That for the neodymium containing system is slightly greater than for ytterbium, consistent with more effective overlap between the donor and acceptor states. There is an apparent contradiction between these values and the apparent difference in the emissive intensity of the ^{3}MLCT state for the steady state spectra, which would imply a change in the effectiveness of energy transfer. However the trend is consistent with comparable efficiencies of the energy transfer in both cases, though both arguments suggest that transfer to Nd is more effective. A more precise treatment would require a better understanding of the radiative lifetime of the ^{3}MLCT state in both cases.

Time resolved emission spectroscopy was also used to characterize the processes occurring. Fig. 3 shows two typical spectra in which it can be noted that the tail of the rhenium emission is superimposed upon the beginning of the lanthanide centered emission. These spectra imply that energy transfer from the chromophore is relatively inefficient as otherwise the MLCT tail would be expected to be quenched completely.

Given the lack of covalent bonding in the pseudorotaxane system, our results imply that Förster energy transfer[10] occurs from the Re ^{3}MLCT donor state (~15 900 cm^{-1}) to the emissive states of the metal (11 360 cm^{-1} for Nd$^{\mathrm{III}}$, 10 300 cm^{-1} for Yb$^{\mathrm{III}}$).[11] The large difference in energy between the donor and acceptor states also precludes back energy transfer,[12] ensuring that the MLCT state is not repopulated. In the case of neodymium, energy transfer into higher energy acceptor states is possible, increasing the overlap integral and hence the efficiency of the process. Ytterbium lacks any higher energy states, and must rely on simple energy transfer direct

Table 1 Photophysical data

Compound	τ_{MLCT}/ns^a	T_{Ln}/ns^b	$(1/\tau2 - 1/\tau1)$/s^{-1}
1	31	—	—
1 · 3a	215	—	—
1 · 3b	52	800	1.46×10^7 ^{c}
1 · 3c	55	11 070	1.35×10^7 ^{c}

^{a} Measured at 700 nm. ^{b} Measured at emission wavelengths 880 nm and 1055 nm for the neodymium complexes, and at 980 nm for the ytterbium complex. In both cases, decays were fitted to a double exponential decay, with the shorter component fixed to the lifetime of the MLCT state obtained at 700 nm, Fitting to two floating exponentials yielded no discernable improvement in fit. ^{c} Calculated from the value of ^{3}MLCT for the isostructural Gd containing system as described in the body of the manuscript. All experiments carried out in CH_2Cl_2 at 293 K.

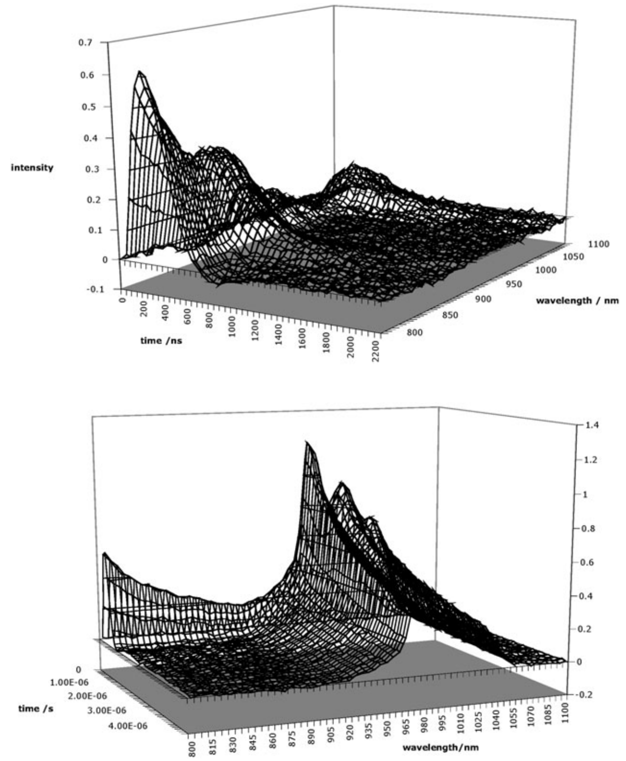

Fig. 3 Top: time-resolved emission spectrum of the pseudorotaxane containing thread **3b** following excitation at 440 nm, showing the tail of the short-lived rhenium MLCT state and the longer-lived neodymium emission at 880 and 1055 nm. Bottom: truncated time-resolved emission spectrum of the pseudorotaxane formed with thread **3c** following excitation at 440 nm, showing the tail of the rhenium MLCT emission and the very long-lived decay of the ytterbium centered emission at 980 nm.

to the emissive state or must be sensitised *via* a sequential electron transfer mechanism.[13] Either of these mechanisms can be used to explain the energy transfer process, and Rehm–Weller treatment suggests that both may be feasible in this system. The efficiency of Förster energy transfer is inversely proportional to the sixth power of the donor–acceptor separation,[14] and the rapid rate constants for energy transfer therefore imply that the observed emission comes from the assembled pseudorotaxane, and that the donor and acceptor are close in space within the system. Fig. 4 shows a cartoon of the energy transfer process, showing that assembly is necessary for sensitised NIR emission.

The anion-templated assembly of d–f heterobimetallic [2]pseudorotaxanes has been demonstrated. Energy transfer between rhenium and neodymium metal fragments leads to sensitized NIR lanthanide emission and indicates the close proximity of the two metals centers in the interpenetrated structure. Such a signaling process may be further exploited in interlocked molecular systems designed to exhibit molecular machine-like behaviour. Ongoing studies are being carried out to determine the nature of the energy transfer process and to further exploit it in self-assembled systems.

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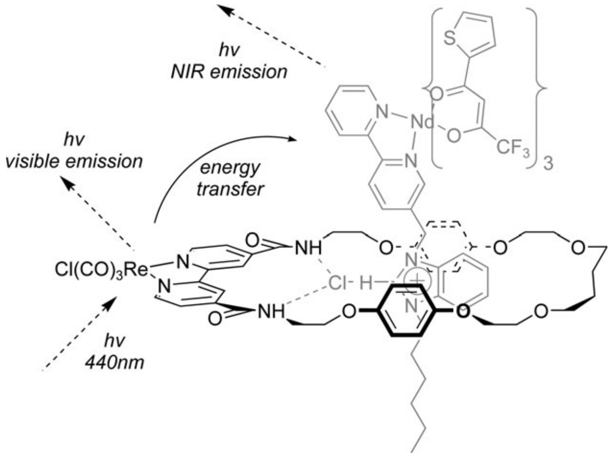

Fig. 4 Proposed interpenetrated [2]pseudorotaxane assembly which facilitates a through space energy transfer mechanism.

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‡ *Typical time-resolved spectroscopy experimental*. In the case of the ytterbium pseudorotaxane complex, **1**·**3c**, the sample was excited using a pulsed nitrogen laser (PTI-3301, 337 nm) or a nitrogen laser pumped dye laser operating at 10 Hz. Light emitted at right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. The growth and decay of the luminescence at selected wavelengths was detected using a germanium photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS220) before being transferred to a PC for analysis. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal centered luminescence, using a spreadsheet running in Microsoft Excel. Further details of this approach can be found in ref. 15.

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