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Re(I) sensitised near-infrared lanthanide luminescence from a hetero-trinuclear Re_2Ln array†

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Received (in Cambridge, UK) 13th February 2004, Accepted 27th April 2004
First published as an Advance Article on the web 21st May 2004

The trinuclear complexes Re_2Ln (Ln = Nd, Yb or Er) contain two Re^I tricarbonyl units linked to a DTPA binding site *via* 2,2′-bipyridyl ligands; Ln^{III}-centred emission is sensitised by the Re^I MLCT excited states.

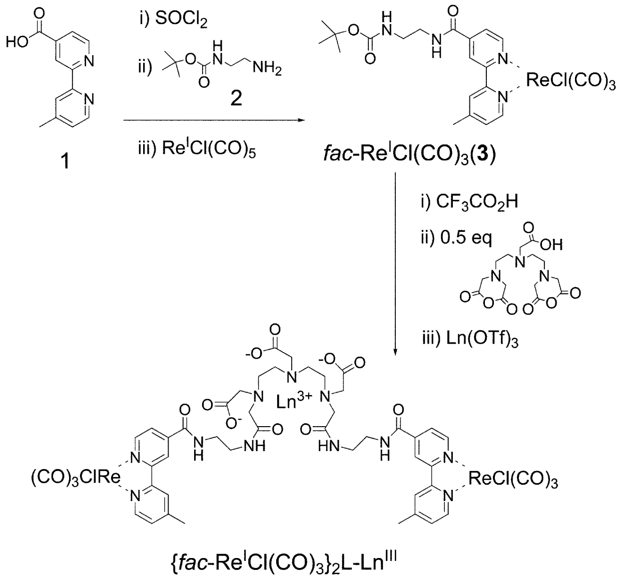
The synthesis and photophysical investigation of multi-chromophoric, often luminescent, metal complexes is an area of intense current activity.[1] Such studies have been dominated by bipyridyl complexes of d-block metal ions such as Ru^{II}, Os^{II} and Re^I. However, interest in luminescence from lanthanide complexes has grown considerably, particularly due to applications in time-resolved immunoassays.[2] The long-lived emissions associated with lanthanide luminescence can be used to improve the sensitivity of assays or imaging experiments.[3]

Lanthanides such as neodymium,[4] ytterbium[5] and erbium,[6] which emit near-IR light outside the range of biological absorption, can be sensitised by well-chosen d-block complexes. The literature contains a few examples of such an approach: notably using $[Ru^{II}(2,2'\text{-bipyridyl})_3]^{2+}$,[7] Pt^{II},[8] ferrocenyl[7] and Pd^{II}-porphyrin[9] complexes as sensitising chromophores in covalently-linked d–f hybrids that are stable in protic solvents. The use of Re^I complexes as lanthanide sensitisers *via* bridging ligands has also been demonstrated, but these species dissociate in protic solvents, and their application to assays is thus severely restricted.[10] Helicates have also been used to form d–f hybrids, most notably in the case of a heterobinuclear Cr^{III}–Nd assembly,[11] in which rate-determining energy transfer prolongs the luminescence lifetime of the Nd-centred emission by several orders of magnitude.

We now report the synthesis of a kinetically stable complex incorporating two Re^I ions and one Ln^{III} ion. In $\{fac\text{-}Re^ICl(CO)_3\}_2L–Ln^{III}$, the Ln^{III} ion is bound in a diethylenetriamine pentaacetic acid (DTPA)-derived coordination environment with the Re^I tricarbonyl moieties held in close proximity. Our synthetic approach (Scheme 1) utilises kinetically stable complexes in combination with orthogonal protecting groups, and builds on our recent application of such methodologies to the formation of heteronuclear f–f hybrids.[12] Treatment of 4′-methyl-2,2′-bipyridyl-4-carboxylic acid (**1**) with thionyl chloride in dichloromethane yields the corresponding acid chloride, which is used without further purification. Subsequent reaction with **2**, affords the functionalised 2,2′-bipyridyl ligand **3**, which is purified by column chromatography on silica [dichloromethane/methanol (95:5)]. Attempted deprotection of **3** with trifluoroacetic acid (TFA) results in unacceptably low product yields and very long reaction times. However, reaction of **3** with $Re^ICl(CO)_5$ in chloroform under reflux gives the complex $fac\text{-}Re^ICl(CO)_3(\mathbf{3})$. Cleavage of the BOC protecting group is then accomplished using TFA at room temperature, with the reaction proceeding to completion within 30 minutes. Treatment of the deprotected complex with 0.5 equivalents of DTPA dianhydride at room temperature in the presence of triethylamine yields the dinuclear complex $\{fac\text{-}Re^ICl(CO)_3\}_2L$.

Excitation of $\{fac\text{-}Re^ICl(CO)_3\}_2L$ at 337 nm produces an intense, short-lived (τ_{em} = 13 ns) emission peak at 625 nm, typical of Re^I tricarbonyl 2,2′-bipyridyl complexes. On addition of $Ln^{III}(OTf)_3$, this emission is attenuated by *ca.* 30%, indicative of quenching by the Ln^{III} component in $\{fac\text{-}Re^ICl(CO)_3\}_2L–Ln^{III}$. Furthermore, time-resolved luminescence measurements on the mixed-metal neodymium complex show that the lifetime of the MLCT emission is reduced to *ca.* 10 ns. Whilst such lifetimes are close to the limit of reliability for reconvolution-based methods,[4] the trend upon complexation is clear.

It is reasonable to assume that the observed quenching arises from energy transfer from the Re^I ^3MLCT states to the proximate lanthanides. This conclusion, and the assignment of the structures of the complexes, is borne out by a study of the Ln^{III}-centred emission from $\{fac\text{-}Re^ICl(CO)_3\}_2L–Ln^{III}$ (Ln = Nd, Er, Yb) in CH_3OH and CD_3OD. A typical fitted decay is shown in Fig. 1 and the luminescence lifetimes for the complexes are shown in Table 1. Time-resolved emission spectra (Fig. 2) show the short-lived MLCT emission superimposed on the Ln^{III} spectrum. For the Nd



Scheme 1 Synthesis of $\{fac\text{-}Re^ICl(CO)_3\}_2L–Ln^{III}$ and its precursors.

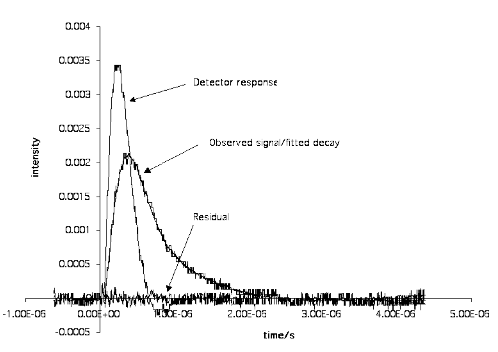


Fig. 1 Fitted decay for $\{fac\text{-}Re^ICl(CO)_3\}_2L–Er^{III}$ in CD_3OD (λ_{ex} = 337 nm, λ_{em} = 1530 nm). The fit was obtained by iterative reconvolution with the detector response by minimisation of residuals squared. The fitted curve and the observed decay are almost exactly superimposed.

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† Electronic supplementary information (ESI) available: experimental protocols and characterisation, time-resolved emission spectra of the heteronuclear complexes, illustrative spectra, showing signal separation by time gating. See http://www.rsc.org/suppdata/cc/b4/b402270j/

DOI: 10.1039/b402270j

Table 1 Photophysical data for the complexes

Compound	$\lambda_{em(Re)}$ (nm)	τ_{Re} (ns)	$\lambda_{em(Ln)}$ (nm)	τ_{CH3OH} (ns)	τ_{CD3OD} (ns)	q
$\{ReCl(CO)_3\}_2L$	625	13		—	—	—
$\{ReCl(CO)_3\}_2L$–Nd	625	10	1340	237	512	0.3
$\{ReCl(CO)_3\}_2L$–Er	625	12	1530	—	540	—
$\{ReCl(CO)_3\}_2L$–Yb	625	13	980	1882	8303	0.7

Luminescence lifetimes were obtained by iterative reconvolution of the detector response with exponential components for growth and decay of the luminescence. Errors are ±10% for lifetimes and ±20% for calculated inner sphere hydration numbers.

and Er complexes, Ln^{III} emissions dominate the tail of the MLCT emissions (at 1340 and 1530 nm, respectively), and the observed decays exhibit single exponential behaviour, with no improvement in fit on fitting to two or more exponentials.

In contrast, the Yb emission spectrum (and the higher energy bands of the Nd emission spectrum) is itself convoluted with the MLCT emission. In such cases, the luminescence lifetimes for Ln^{III}-centred processes can be obtained by time-gating, or by fitting to a double exponential decay where the decay constant for one, and in each case the shorter, component is defined by the lifetime of the MLCT state.

Differences in the efficiency of non-radiative quenching of Ln^{III} luminescence by O–H and O–D oscillators permit the inner sphere hydration state, q, to be deduced for Yb in methanolic solution using the relation $q = 2(k_{CH3OH} - k_{CD3OD} - 0.05)$ where k_H and k_D are the observed rate constants for luminescence in μs^{-1}, combined with a correction term for outer sphere contributions.[13] In this case the DTPA-like site is expected to be octadentate and previous studies have shown that when bound in this environment the degree of solvation, q, for Yb is approximately zero. The calculated value of q in the Yb complex is slightly higher, but still < 1, possibly indicative of the weakly coordinating amide moieties.

Further structural evidence can be obtained by study of the Nd complex. In this case, the relation between q and the observed rate constants is less well established, owing to the ease of non-radiative quenching of the excited state by C–H oscillators and the consequent dependence of quenching efficiency on ligand structure. However, the relation $q = 290(k_{CH3OH} - k_{CD3OD}) - 0.4$ works well with aminocarboxylate ligands.[14] Application of this equation to our system gives $q = 0.3$ for the Nd complex. This result is entirely consistent with the octadentate coordination environment binding the Nd^{III} ion.

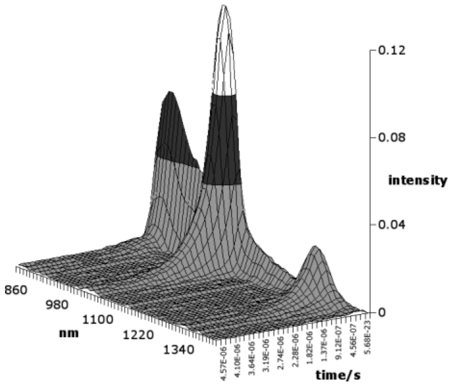

Fig. 2 Time-resolved emission spectrum of $\{fac\text{-}Re^{I}Cl(CO)_3\}_2L\text{–}Nd^{III}$ in CD_3OD ($\lambda_{ex} = 337$ nm).

In the case of Er, quenching by C–H oscillators is even more pronounced and energy matching with O–H oscillators is extremely effective, to the point where the low intensity of the luminescence in CH_3OH precludes analysis of the luminescence lifetime. However, the lifetime of 540 ns obtained in CD_3OD is similar to that of the Nd complex.

As well as confirming the structures of the complexes, time-resolved spectroscopy can be used to assess the effectiveness of the energy transfer processes. In all cases, the rise-time of the Ln^{III}-centred signal is short, suggesting efficient energy transfer from the MLCT state with rate-determining Ln^{III}-centred emission.

In summary, our results show the potential of Re^{I} sensitisers for near-IR luminescence from lanthanide ions. We are currently investigating the utility of these and related systems as biological probes.

The authors wish to acknowledge support from the EPSRC (grant GR/S04949) and the University of Manchester.

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