Interaction between tetrathiafulvalene carboxylic acid and ytterbium DO3A: solution state self-assembly of a ternary complex which is luminescent in the near IR†

Stephen Faulkner,* Benjamin P. Burton-Pye, Tahir Khan, Leigh R. Martin, Steven D. Wray and Peter J. Skabara*

Department of Chemistry, The University of Manchester, Oxford Road, Manchester, UK M13 9PL.
E-mail: Stephen.Faulkner@man.ac.uk; Fax: 44 161 275 4616; Tel: +44 161 4659

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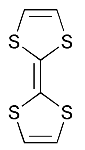
Tetrathiafulvalene carboxylate associates with the charge neutral complex, Yb.DO3A, in methanolic solution to give rise to a novel ternary species; the tetrathiafulvalene unit transfers energy to the lanthanide, causing luminescence from the Yb metal, indicating for the first time that an electron donor chromophore can act as an efficient sensitiser in a self-assembled system containing a lanthanide acceptor.

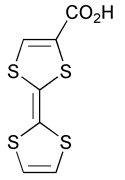
Lanthanide centred luminescence is increasingly used as a tool in assay[1] and imaging,[2] mainly because lanthanide ions have luminescence lifetimes which are usually independent of oxygen concentration and longer than those associated with fluorescence.[3] A number of recent studies has begun to exploit the near-IR luminescence from ions such as ytterbium[4] and neodymium,[5] which offer the potential advantage of allowing excitation of samples outside the range of biological absorption. For ytterbium complexes, the mechanism by which energy is transferred from an antenna chromophore has been the subject of some debate, since ytterbium has only one excited state (centred around 10300 cm^{-1}), which often means that there is negligible overlap with triplet states of sensitising chromophores, implying that other energy transfer pathways involving LMCT states are involved where this is possible.[4b,c,6] We recently published an example of a system where triplet mediated energy transfer occurs only at low pH, while another mechanism, probably involving sequential electron transfer, occurs when the chromophore is deprotonated.[7]

The sulfur-based heterocycle tetrathiafulvalene (TTF) is a highly efficient electron donor which can be oxidised sequentially to the radical cation and dication ($E^{1/2}$ = +0.35 and +0.79 V in CH_2Cl_2/CH_3CN *vs.* Ag/AgCl). Since its discovery in 1970,[8] unceasing effort has been devoted towards the derivatisation of the compound for various materials applications.[9–11] Tetrathiafulvalene carboxylic acid[12] (HL^1) has very similar properties to TTF.

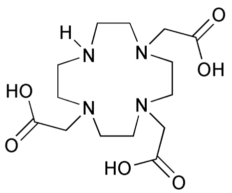
We have now investigated the interaction of L^1 with ytterbium aquo ions and $Yb.L^2$. Since ytterbium has only one excited state, it represents an ideal tool for studying energy transfer from aromatic chromophores. Any emission from the ytterbium centre subsequent to excitation in the visible or UV regions must therefore result from energy transfer from the chromophore. Furthermore, L^1 did not give rise to any near IR emission that could be detected using our spectrometer, meaning that any emission observed from mixtures of L^1 with ytterbium containing systems must result from energy transfer between the two components of the system.



TTF



HL^1



H_3L^2

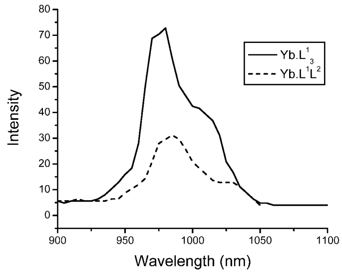


Fig. 1 Uncorrected spectra of $Yb.L^1_3$ and $Yb.L^1L^2$.

The luminescence from mixtures of L^1 with Yb triflate was measured using a pulsed nitrogen laser (337 nm, PTI GL-3301) as a source of coherent radiation, giving rise to excitation at the aromatic chromophore. The steady state spectrum of the mixture is shown in Fig. 1.‡ Time-resolved emission spectra were obtained using the same apparatus by iterative reconvolution of exponential decays with the detector response to obtain the best fit with the observed signal.[7] Fig. 2 shows a typical fitted decay, while the luminescence lifetimes for all the samples studied are shown in Table 1.

The inner sphere solvation number, q, was determined by analysis of the luminescence lifetimes according to eqn. (1):

$$q = A(k_{CH_3OH} - k_{CD_3OD} - B) \qquad (1)$$

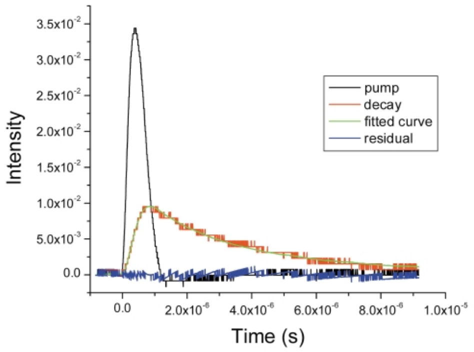


Fig. 2 Fitted time-resolved luminescence profile for $Yb.L^1L^2$ in CD_3OD. The decay is fitted to a luminescence lifetime of 3.49 μs.

Table 1 Luminescence lifetimes[a] and inner sphere solvation numbers for the complexes under study

	τ_{CH_3OH}/μs	τ_{CD_3OD}/μs	q
$Yb.L^1_3$	0.50	3.67	3.25
$Yb.L^2L^1$	2.02	3.49	0.21

[a] Errors in lifetime measurements are ± 10%.

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† Electronic supplementary information (ESI) available: cyclic voltammograms of TTF-YbDO3A and YbDO3A. See http://www.rsc.org/suppdata/cc/b2/b204218e/

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where $A = 2.0$ μs and $B = 0.1$ μs^{-1} for ytterbium complexes in methanol.[6b,13]

In the case of the complex with L^1, the value of $q = 3.25$ implies that there are three bound methanol molecules per ytterbium centre. Given that the nonadentate ytterbium ion is tripositive, while L^1 bears a single carboxylate, this implies that charge neutral ML$_3$ complexes exist on the timescale of the luminescence experiment, possibly as a result of the carboxylate acting as a bidentate ligand. Further evidence for the formation of complexes was provided by studying methanolic solutions containing ytterbium trifluoromethanesulfonate and tetrathiafulvalene (TTF) itself. These mixtures can only give rise to metal centred luminescence as a result of intermolecular, rather than intramolecular, energy transfer. Even at high concentrations, the metal centred luminescence from such mixtures was at least two orders of magnitude less intense, suggesting that association was not occurring in the absence of the carboxylate group, and implying that the carboxylate functionality (rather than the TTF sulfur atoms or some form of π interaction) is involved in coordination.

Having shown that L^1 acts as a sensitiser for Yb^{3+}, we then investigated its interaction with Yb.DO3A (Yb.L^2), a stable charge neutral complex in which the metal binds to two solvent molecules.[14] Although the complex overall is charge neutral, the water molecules can be displaced, giving access to the charged metal centre. When irradiated at 337 nm, the complex showed no metal centred luminescence. Mixtures of the complex with L^1 showed classical ytterbium centred luminescence upon irradiation of **L^1** at 337 nm. Figure 1 shows the luminescence spectra, while Table 1 shows the luminescence lifetimes of the systems studied.

Analysis of the luminescence lifetimes using eqn. (1) gives a value for q of 0.21, suggesting that both inner sphere solvent molecules have been displaced by the chromophore carboxylate group, acting as a bidentate ligand. Self assembled complexes such as this have a number of potential uses, particularly in time-resolved bioassay, where the switching on of the signal is dependent on both the chomophore and the bound metal ion being in the same place.

It remains to discuss the mechanism of energy transfer from the chromophore to the metal. Two mechanisms may occur, involving either mediation of energy transfer by the triplet state, or by electron transfer and back transfer from the ligand to the metal. In both cases, the overlap between the carboxylate triplet and the metal centre is likely to be negligible (E_T = 22000 cm^{-1}),[15] though this does not rule out electron transfer *via* the triplet state in the postulated electron redistribution mechanism. Furthermore, the growth of the luminescence signal is almost instantaneous ($\tau_{growth} < 5$ ns), suggesting that a fully allowed process is occurring. We have previously reported the extension of the Raehm–Weller treatment of exciplexes to energy transfer in lanthanide complexes.[7,16] Applying this treatment, the change in free energy on electron transfer, ΔG_{ET} in eV is approximated by $\Delta G_{ET} = (E_{ox} - E_{red}) - E_s - e_0^2/\varepsilon_a$ where E_{ox} is the oxidation potential of the donor (0.35 V for the complex), E_{red} is the reduction potential of the acceptor (Yb^{3+}; −0.83 V for the ternary complex in DMSO, determined by cyclic voltammetry experiments *vs.* Ag/AgCl (10^{-3} M substrate, 0.1 M TBAPF$_6$ as supporting electrolyte), using glassy carbon and Pt working and counter electrodes, respectively); E_s is the singlet state energy of the donor group (3.4 eV from averaging the longest wavelength absorption maximum and shortest wavelength emission maximum) and e_0^2/ε_a represents the attraction between the resulting radical ion pair. For an exciplex $e_0^2/\varepsilon_a \approx 0.15$ eV. In our case, where a π–π interaction is precluded by the nature of the complex, this value will be smaller, but 0.15 eV serves as a good upper limiting condition.

Thus for a complex in which TTF carboxylic acid acts as the donor, $\Delta G_{ET} \geq (0.35 + 0.83) - 3.4 - 0.15$ eV, *i.e.* $\Delta G_{ET} \geq -2.37$ eV. This implies that the electron redistribution mechanism for energy transfer is likely to be feasible, though the absolute nature of the mechanism depends on the rate of electron transfer relative to transfer from the triplet state.[17]

Taken together, the results above demonstrate that strong electron donors can be used as sensitisers for ytterbium. The nature of the self assembled luminescent system also suggests that this method could be applied to assays and to choosing suitable chromophores for a wide range of lanthanide ions. Results of ultrafast studies on other near-IR emissive lanthanides with a range of donor chromophore and upon termolecular complexes formed from amino carboxamides will be reported in due course.

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Notes and references

‡ Luminescence from the sample was collected at right angles to the incident beam and focused onto the slits of a monochromator (PTI120). The luminescence at selected wavelengths was detected using a germanium photodiode (Edinburgh Instruments, EI-P).

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