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Controlled assembly of luminescent racks based on heteroleptic dinuclear lanthanide complexes†

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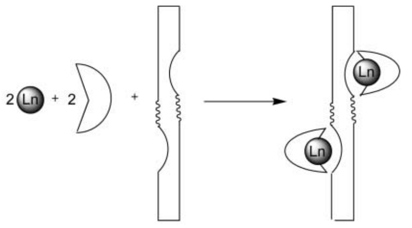
Luminescent lanthanide racks are formed in solution through supramolecular assembly of lanthanide ions with a rigid bis-didentate sensitiser ligand and octadentate aminopolycarboxylate ligands.

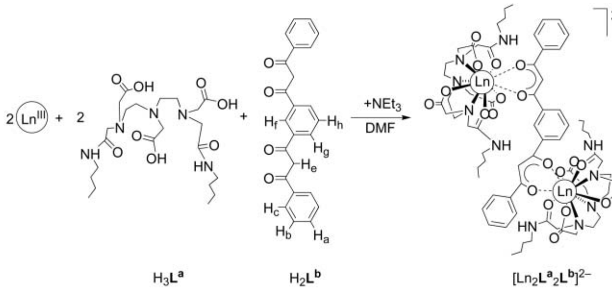
The incorporation of luminescent lanthanide ions in supramolecular architectures can lead to functionality control of rather complex, sophisticated structures.[1] Solution self-assembly of polynuclear luminescent lanthanide complexes[2] is attractive for the development of systems with high light signal output due to the unique photophysical properties of the ions. Although *d*-block self-assembly[3–9] has been mastered by formation of helicates, cylinders, racks, ladders, squares, boxes, triangles, tetrahedrons, catenates or rotaxanes, solution self-assembly of polynuclear lanthanide complexes is rather challenging.[10] This is due to the preference of lanthanides for high coordination numbers and the absence of geometrical and crystal-field type control in lanthanide chemistry. Bi- or tri-nuclear lanthanide helicates and podates are successful examples of assembly strategies where fine-tuning of the binding sites in multidentate ligands allows selective binding of different lanthanides.[11–16] Recent advances include strategies for the assemblies of wheels,[17] hairpin structures[18] and a recent example of a molecular square[19] formed from transition metal complexes together with lanthanides. In this manuscript we wish to report the formation of luminescent dinuclear lanthanide racks by solution self-assembly.

In our approach we use heteroligand assembly controlled by the lanthanide coordination sphere with a multidentate and a bis-didentate ligand. The multidentate ligand is designed to wrap around the lanthanide ion leaving free sites available for the binding of the didentate ligand (Scheme 1). The bis-didentate ligand bears a rigid phenylene spacer in between the two didentate binding sites in order to act as a rack for the attachment of the two lanthanide ions. This ligand is also designed to sensitise lanthanide luminescence upon assembly, thus providing a spectroscopic handle for monitoring the process. We used the bis-*n*-butylamide of diethylene triamino pentaacetic acid, H_3L^a, as an octadentate ligand[20,21] and 1,3-bis(3-phenyl-3-oxopropanoyl)benzene, H_2L^b, as a bis-diketonate ligand[22] (Scheme 2).

Mixing stoichiometric amounts of $LnCl_3$, H_3L^a and $(HNEt_3)_2L^b$ (H_2L^b deprotonated with excess NEt_3) in DMF with 1% H_2O led to the formation of $(HNEt_3)_2[Ln_2L^a{}_2L^b]$. The complex LnL^a could be formed and isolated in an intermediate step, either *in situ* by mixing equivalent amounts of $LnCl_3{\cdot}xH_2O$ (Ln = Eu, La or Y) with H_3L^a or isolated as a powder and independently characterised. Step-wise assembly of LnL^a and $(HNEt_3)_2L^b$ in 2 : 1 stoichiometry gave the same supramolecular complex $(HNEt_3)_2[Ln_2L^a{}_2L^b]$.



Scheme 1



Scheme 2

The formation of the dinuclear heteroleptic rack was confirmed by electrospray mass spectrometry in negative mode. Strong peaks which manifold at 1777 and 888 amu were observed for $(HNEt_3)_2[Eu_2L^a{}_2L^b]$ and at 1750 and 875 amu for $(HNEt_3)_2[La_2L^a{}_2L^b]$. These correspond to $\{M - (HNEt_3)\}^-$ and $\{M - (HNEt_3) - H\}^{2-}$ respectively. To monitor the formation of the dinuclear rack by luminescence spectroscopy, firstly we examined the assembly of LnL^a and H_2L^b to demonstrate the 2 : 1 stoichiometry. The luminescence signal of Eu(III) in EuL^a was monitored upon titration of $(HNEt_3)_2L^b$ (Fig. 1). The luminescence of EuL^a upon excitation at 350 nm is very weak due to the lack of any sensitising groups in the complex. Addition of a strong sensitiser L^b led to a strong signal increase of around 200-fold. In

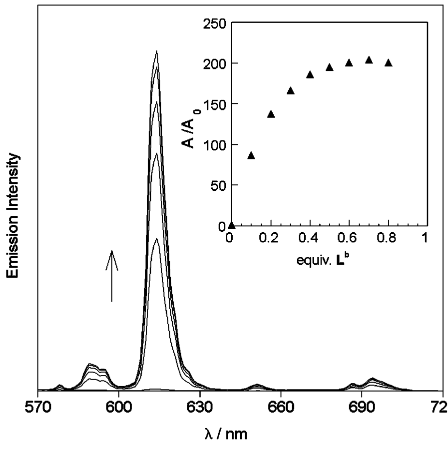


Fig. 1 Emission spectra recorded upon titration of 5 μl increments of $(HNEt_3)_2L^b$ (7.5×10^{-4} mol dm^{-3}) to a solution of EuL^a (1.5×10^{-5} M) in DMF with 1% H_2O. Inset: plot of relative area increase of the 615 nm band *vs.* equivalents of L^b.

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† Electronic supplementary information (ESI) available: further characterisation data. See http://www.rsc.org/suppdata/cc/b4/b412999g/

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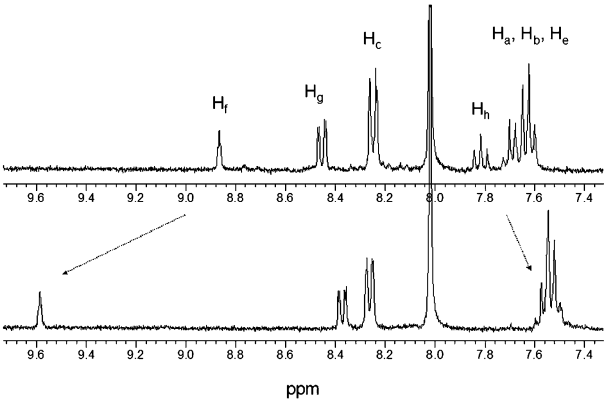

Fig. 2 The aromatic region of the 300 MHz ^{1}H NMR spectra of $(HNEt_3)_2L^b$ (top) and $(HNEt_3)_2[Y_2L^a{}_2L^b]$ (bottom) in d^7-DMF : D_2O, 10 : 1.

the titration 5 μl aliquots of $(HNEt_3)_2L^b$, in DMF were added to a solution of EuL^a in DMF with 1% H_2O (Fig. 1). A saturation point was reached at the addition of 0.5 equivalents of $(HNEt_3)_2L^b$ confirming the 2 : 1 stoichiometry of EuL^a to L^b. A control experiment was performed by addition of dibenzoylmethane to EuL^a under the same conditions to compare the binding event. Dibenzoylmethane, bearing one didentate site was employed to act as effectively "half" of the H_2L^b ligand. The luminescence signal of EuL^a was increased 120-fold upon addition of dibenzoylmethane (deprotonated with NEt_3) and a saturation point was reached at a 1 : 1 ratio of dibenzoylmethide to EuL^a. The formation of mononuclear europium multidentate complexes with dibenzoylmethane in 1 : 1 stoichiometry and the selective Eu(III) sensitisation by dibenzoylmethane has been previously reported.[23,24] To demonstrate the one-pot assembly process, the luminescence spectrum of a solution obtained by mixing stoichiometric amounts of $EuCl_3$, H_3L^a and $(HNEt_3)_2L^b$ was compared under the same experimental conditions with the spectrum of the step-wise assembly of EuL^a and $(HNEt_3)_2L^b$. The luminescence spectrum of the complex from the one-pot assembly was identical (within experimental error) in shape and peak intensities with the spectrum of the step-wise assembly. The same luminescence signal output demonstrates that the sensitisation of both the Eu(III) ions takes place *via* the bound bis-didentate ligand. The sensitisation process of Eu(III) luminescence is attributed to energy transfer from the L^b sensitiser to the Eu(III) ion. This was demonstrated by excitation spectroscopy. Monitoring of the Eu(III) luminescence at 615 nm showed an excitation peak centered at 360 nm in agreement with the absorption peak of the bound L^b ligand.

The formation of $(HNEt_3)_2[Ln_2L^a{}_2L^b]$ was also demonstrated by ^{1}H NMR spectroscopy. Yttrium(III) was employed as a diamagnetic analogue for Eu(III) to avoid the line broadening effects associated with paramagnetic complexes. YL^a also proved more soluble than LaL^a in the conditions of the experiment. The ^{1}H NMR spectrum of $[Y_2L^a{}_2L^b]^{2-}$ (Fig. 2) showed a single set of peaks for L^b in the aromatic region confirming the high symmetry of the resultant species and coordination of both the didentate sites.

The distinct shifts in the aromatic region of the spectrum of $(HNEt_3)_2[Y_2L^a{}_2L^b]$ are characteristic of coordination of L^b to the Y(III) ion. The aliphatic region of the spectrum of $[Y_2L^a{}_2L^b]^{2-}$ remained unchanged when compared with YL^a. The integration of the aliphatic with the aromatic protons agrees with the stoichiometry of L^a to L^b of 2 : 1. The resonance of H_f was shifted from δ 8.9 ppm in $(HNEt_3)_2L^b$ to δ 9.6 ppm in $[Y_2L^a{}_2L^b]^{2-}$. The signals of H_g and H_h in $[Y_2L^a{}_2L^b]^{2-}$ showed upfield shifts of 0.08 and 0.28 ppm respectively. The signal of H_e proton appears below the manifold at δ 7.5 ppm which was shifted 0.13 ppm upfield in the dinuclear rack complex. The observed shifts of the resonances are in agreement with previously reported shifts in dinuclear homoleptic complexes.[22]

The formation of dinuclear lanthanide racks has been demonstrated in this manuscript by the selective assembly of different ligands around the lanthanide centre. This strategy of controlled assembly is expected to lead to even more sophisticated architectures. The application of such structures in the formation of luminescent materials is currently under investigation.

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