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Self-assembly between dicarboxylate ions and a binuclear europium complex: formation of stable adducts and heterometallic lanthanide complexes†

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A binuclear lanthanide complex consisting of two lanthanide binding domains linked by a m-xylyl bridging unit forms very stable 1 : 1 adducts with benzene dicarboxylic acids and their derivatives. The complex with isophthalate derivatives is particularly stable.

The luminescence from lanthanide ions is long-lived, allowing lanthanide-centred signals to be separated from fluorescent backgrounds leading to a range of important biomedical applications, particularly in the areas of time-resolved imaging and assays.1,2

Since the very beginning, bioassays involving lanthanide complexes have exploited self-assembly, both in the immunological part of the assay, and in the self-assembly of brightly emissive lanthanide complexes when the assay is developed.3 More recently, self-assembly at lanthanide centres has been applied to a wide variety of chemical systems. Self-assembled helicates containing lanthanide ions have been prepared and studied in detail,4 and have been shown to be effective cellular imaging agents, while heptadentate lanthanide complexes have been used as responsive probes for a wide variety of anions that can coordinate to the lanthanide centre with associated displacement of water.5 A wide variety of complex architectures can also be formed through self-assembly, including d–f hybrid complexes6 and coordination polymers.7

We have previously utilised the self-assembly between carboxylates and lanthanide complexes of DO3A derivatives to establish energy transfer mechanisms in near IR luminescence,8 and as a rapid and effective means of screening transition metal and aryl chromophores for their suitability as sensitisers of lanthanide emission.9 We have also shown that DO3A derivatives bearing benzoate pendent arms exhibit pH dependent self-assembly that can be exploited in switching their luminescence on and off.10

We now report the results of a study on the self-assembly of ternary complexes between the binuclear lanthanide complex Eu₂·1 and a series of dicarboxylate ions, and illustrate how such an approach can be used to assemble heterometallic lanthanide complexes. We recently reported the synthesis of 1 and its lanthanide complexes,11 which we have found to offer a high degree of kinetic stability, to the point where they are stable even in the conditions required for diazotisation and incorporation into azo dyes.12 This system also contains two lanthanide centres in close proximity, which can potentially bind to two anionic donors to form a chelating ligand, as shown in Scheme 1.

![Scheme 1 Binding of diacids by binuclear lanthanide complex Eu₂·1.](image-url)
2 to [Tb-3]3+ as shown in Scheme 2. In such a system, excitation of the benzoate chromophore should only sensitise terbium emission effectively when the bimetallic complex is assembled. Data from a titration of Eu-2 with Tb-3 are shown in Fig. 1. These data cannot be interpreted with a simple binding model. Both complexes are heptadentate and the binding occurs without discrimination as indicated in Scheme 2. The speciation is complicated further by the possibility of both mono- and bi-dentate binding of the carboxylic acid to the lanthanide centre. Thus, a minimum of five species has to be taken into account in the data analysis. From the data presented in Fig. 1 it was not possible to determine which species, if any, dominates. It follows that no binding constants could be determined. However, it is clear from the switching on of the terbium centred luminescence that self-assembly is occurring. It is known that the binding of benzoic acids to lanthanide centres have binding constants in the order of $K \approx 10^4$ M$^{-1}$. For most practical applications this value is too low, as the self-assembled structure will be disassembled by phosphate in aqueous media or serum.

We next chose to study the binuclear system Eu-1-3 and its binding of phthalic acids. In this system, two carboxylate groups can bind to a metal centre and the electron deficient aromatic ring of the phthalate may dock with the electron rich aniline ring linking the two metal ligands. While Eu-1 is charge neutral, some residual positive charge will reside on the lanthanide centres, meaning that electrostatic effects can still play a role in modulating self-assembly.

We performed a series of binding studies of Eu-1 and benzoic acid (4), phthalic acid (5), isophthalic acid (6) and terephthalic acid (7) to determine the degree of selectivity that could be achieved through self-assembly. Due to low solubility the studies were performed in a mixture of methanol–water. The structures of the acids used are shown in Scheme 3 and the binding constants are tabulated in Table 1. Experimental details and data are given as electronic supporting information.$^\dagger$
to question, though previous reports indicate that each metal centre in Eu₂⁻¹ is bound to one water molecule. Binding of an acid can occur with liberation of the water or by going from an eight-coordinate complex to a coordination number of nine.

The gain of the binding in the bidentate of the complex is evident as K(Eu₂⁻¹:8) = 12 000 M⁻¹ and K(Eu₂⁻¹:7) = 1.9 × 10⁶ M⁻¹. The binding of benzoic acid to Eu₂⁻¹ is 1000 fold weaker than the bidentate binding. This increase alone removes the concern of the possible self-association experienced in Table 1. The binding of the isophthalate motif of Tb⁻¹ gives the answer, as isophthalic acid binds at least 10 times more strongly than the terephthalic acid. In this solvent system isophthalic acid binds to Eu₂⁻¹ with a binding constant larger than we are capable of measuring. Thus the optimal system for self-assembly is a combination of Eu⁻¹ and an isophthalic acid derivative.

We then turned our attention to using isophthalate appended lanthanide complexes in the self-assembly of a heterometallic array. To obviate the problem of self-association experienced with Eu₂⁻¹, we elected to use Tb⁻⁸,¹⁷ which makes use of an octadentate ligand in this phase of the study. Tb⁻⁸ was self-assembled with Eu⁻¹ in two different aqueous buffer systems, namely a competitive phosphate (PBS) and non-competitive ammonium–sulfonate buffer (HEPES). Both buffers were adjusted to pH = 7.4, where the isophthalate is fully deprotonated. The self-assembly was followed by emission spectroscopy. The titrations were performed as described above and in the ESI,¹ but in this case only the terbium emission could be monitored owing to the intense terbium centred emission from the Eu⁻¹: Tb⁻⁸ complex. A typical dataset is shown in Fig. 2. The binding constants were determined from several different datasets and are reported in Table 1. The binding of the isophthalate motif of Tb⁻⁸ in aqueous buffer is a factor of 100 weaker than in the mixed solvent system, but still so strong that there is no difference between the buffers.

Conclusions

In this paper, we have shown how heterometallic lanthanide complexes can be prepared by spatial matching of the interactions between two kinetically stable complexes. Furthermore, bidentate donor units such as isophthalate can be exploited to give tightly bound systems that remain assembled even in the presence of competitor ions such as phosphate. This raises a number of exciting possibilities, notably that it may be possible to self-assemble much more complicated lanthanide architectures from well-designed building blocks. We are currently investigating the prospects for such systems.

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**Notes and references**


