Imidodiphosphinate ligands as antenna units in luminescent lanthanide complexes

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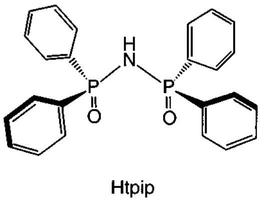
Imidodiphosphinate ligands form a hydrophobic shell around terbium and europium ions leading to long-lived, highly luminescent complexes.

The design of miniature 'antenna' systems based on lanthanides for collecting light and converting it to a different frequency has important applications in the development of photonic devices and sensors.[1] Europium and terbium ions are attractive luminescent centers due to their visible, long-lived emission. A breakthrough in lanthanide chemistry came with the design of cryptand ligands that encapsulate the lanthanide ion, protecting it from coordinating solvent molecules that quench its emission. [2] When the arms of the cryptand are light-harvesting units they act as an antenna for collecting light and transferring the energy to the lanthanide.[1,3] Research efforts have focused on the development of ligand systems for lanthanides based on podand-type structures,[3,4] calixarenes[5] or helicates.[6] We are interested in the development of neutral lanthanide complexes with ligands that completely encapsulate the ion forming a hydrophobic shell around the metal ion. Rather than using a highly designed cryptate ligand we aim to use simple lanthanide complexation principles to govern the formation of such species. In order to achieve this, we need strong binding sites that coordinate to the lanthanide and bulky aromatic units that are 'independent/remote' from the binding site and which form the hydrophobic shell. By using remote light-harvesters (rather than harvesters that are themselves the binding units, *e.g.* polypyridines) we can optimize the ion emission by choosing the best sensitizer, aromatic unit, for the ion; this is important as it is rare to find systems that are ideal both for europium and terbium emission. While remote harvesting units have previously been successfully employed in macrocyclic supramolecular structures to enhance the lanthanide emission,[7,8] using lanthanide complexation principles should allow less synthetically challenging open chain ligands to be used.

We have chosen tetraphenyl imidodiphosphinate (tpip) as an ideal ligand with which to test our design.[9] The imidodiphosphinate binding site can chelate to the lanthanide and does not contain any O–H, C–H or N–H bonds in the binding site that can contribute to the quenching of the lanthanide emission.[10] Attached to each of these binding units are four phenyl groups that (i) play the role of remote light-harvesting units and (ii) form a hydrophobic shell around the ion. We wish now to report our studies on the europium and terbium complexes of tpip which demonstrate that the ligands act as light-collector units forming a hydrophobic shell around the ion resulting in highly luminescent europium and terbium complexes. The chemistry contrasts with the analogous lanthanide β-diketonates where the binding site is surrounded by two rather than four aryl units and short lifetimes result from lack of protection of the lanthanide from the water (which limits their applications as sensors or biolabels). [11]



Htpip

Reaction of K(tpip) with $EuCl_3$ or $TbCl_3$, in 3:1 molar ratio, leads to the formation of the neutral complexes [Eu(tpip)$_3$] and [Tb(tpip)$_3$], respectively. The complexes have been fully characterized and analysed by spectroscopic methods.† X-Ray quality crystals of [Tb(tpip)$_3$] were obtained by slow evaporation from chloroform. The crystal structure (Fig. 1)‡ shows that the twelve phenyl groups surround the lanthanide ion, forming a hydrophobic cage leading to a six-coordinate terbium ion. Two molecules in the unit cell which are different in the symmetry around terbium are observed; **1** being a distorted octahedron and **2** trigonal prismatic. Edge-to-face π stacking is present in both structures with C–H to centroid distance of *ca.* 3.0 Å of two phenyl groups in different ligands. Although there is no water coordinated to terbium, in contrast with the praseodymium crystal structure, there is a short van der Waals contact, observed only in **2**, between the terbium ion and a water molecule situated at the top of the trigonal prism with a Tb–O distance of 3.85 Å (expected van der Waals 4.08 Å). The [Eu(tpip)$_3$] crystal structure is similar to the terbium one with three molecules in the unit cell, in two of which the symmetry around europium is trigonal prismatic and the other one is a

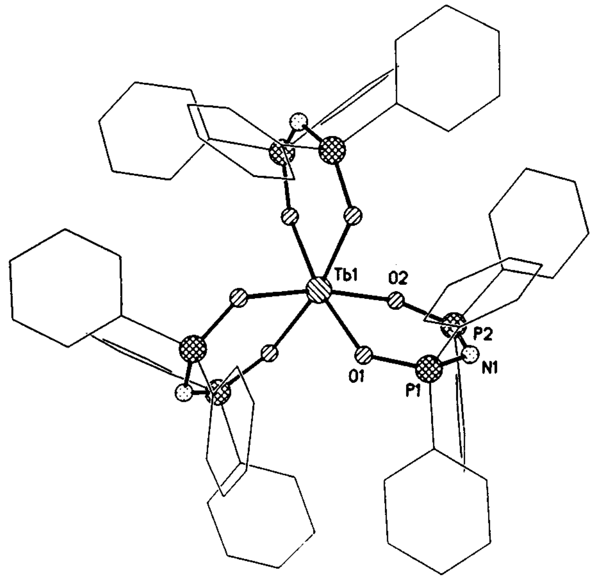


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Fig. 1 Crystal structure of [Tb(tpip)$_3$].

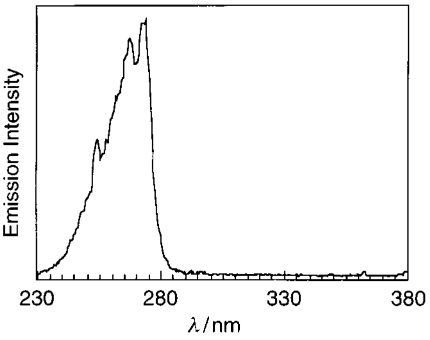

Fig. 2 Excitation spectrum of [Eu(tpip)$_3$] in CHCl$_3$, λ_{em} = 620 nm.

distorted octahedron. The short water van der Waals distance is again observed only in the trigonal prismatic molecules. The low coordination numbers of europium and terbium are attributed to the bulkiness of the ligands, with the twelve phenyl groups forming a cage around the ion.

Upon excitation at 273 nm (ε = 5,000 dm^3 mol^{-1} cm^{-1}) the [Eu(tpip)$_3$] and [Tb(tpip)$_3$] complexes exhibit strong emission, red and green respectively, characteristic of the ion. The excitation spectra of the complexes show a band centered at 270 nm, characteristic of the absorption of the ligand confirming that the emission of the complex is due to energy transfer from the ligand to the lanthanide luminescent center (Fig. 2).

Both europium and terbium complexes exhibit long lifetimes in solution compared with previously reported antenna complexes where lifetimes are optimized either for europium or for terbium. The emission lifetimes were found to be 1.8 ms for [Eu(tpip)$_3$] and 2.8 ms for [Tb(tpip)$_3$] in dry acetonitrile. Although there is no evidence of water coordination in the crystal structure, addition of water in the acetonitrile solution of [Tb(tpip)$_3$] and [Eu(tpip)$_3$] leads to shortening of the emission lifetime by 25 and 43%, respectively. The shortening in the lifetime indicates some involvement of the water molecules in the coordination sphere of the lanthanide. It may be attributed to a twist of the complex conformation in solution to fit the water molecule and agrees with the observed short water van der Waals contacts. The larger effect of water quenching in europium complexes has been well documented.[12]

The quantum yields of the complexes were measured in dry acetonitrile and determined using the method established by Haas and Stein, using [Ru(bipy)$_3$]Cl$_2$ (Φ = 0.028 in water) and quinine sulfate (Φ = 0.546 in 0.5 M H$_2$SO$_4$) as standards for the europium and terbium complex, respectively, taking into account the different excitation wavelength correction.[13] The values obtained are 1.3% for [Eu(tpip)$_3$] and 20% for [Tb(tpip)$_3$]. We postulate that the quenching of the europium emission *via* an LMCT state is not as effective as in the case of calixarene complexes where the quantum yields of the europium and terbium complexes can differ by more than three orders of magnitude.[5] Further photophysical experiments are currently underway to obtain more information about the mechanism of the energy transfer. The lack of any back energy transfer processes observed when bipyridine ligands are employed in terbium complexes leads to a high quantum yield for terbium.

We have introduced the imidodiphosphinate ligands as successful ‘antenna’ ligands for sensitizing both europium and terbium emission. The crystal structures of the complexes show unusual six-coordinate lanthanide ions where the ligands form a hydrophobic cage around the ion. We are currently further investigating the formation of these encapsulated lanthanide complexes based on these design principles.

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Notes and references

† *Selected spectroscopic data* [Tb(tpip)$_3$]: ^{1}H NMR (360 MHz, CDCl$_3$, 25 °C, TMS) δ 7.97 (24H, Ar), 7.35 (12H, *p*-Ar), 6.28 (24H, Ar); ^{31}P{^{1}H} NMR (146 MHz, CDCl$_3$, 25 °C, 85% H$_3$PO$_4$) δ 200.7(s); MS (FAB$^+$ in *m*-NBA) *m/z* 1408 (MH$^+$), 991 (M^+ − tpip). [Eu(tpip)$_3$]: ^{1}H NMR (360 MHz, CDCl$_3$, 25 °C, TMS) δ 7.48–7.54 (m, 24H, *o*-Ar), 7.21 [t, ^3J (HH) 7.4 Hz, 12H, *p*-Ar], 6.95–6.99 (m, 24H, *m*-Ar); ^{31}P{^{1}H} NMR (146 MHz, CDCl$_3$, 25 °C, 85% H$_3$PO$_4$) δ 37.7(s); MS (FAB$^+$ in *m*-NBA) *m/z* 1400 (MH$^+$), 983 (M^+ − tpip). The ^{31}P and ^{1}H NMR spectra at low temperature in deuterated dichloromethane or acetone reveal only one solution species which contains only one ligand environment. The lifetime measurements are mono-exponential. The paramagnetic shifts on ^{31}P confirm the metal coordination. From these observations, we can conclude that (i) there is only one solution species (ii) all three ligands are in identical environments (iii) the ligand is bound to the metal centre. We believe that the only formulation that satisfies all these requirements is [ML$_3$] similar to that observed in the solid state.

‡ *Crystal data* [Tb(tpip)$_3$]·$0.7\underline{5}$ H$_2$O: $C_{72}H_{61.50}TbN_3O_{6.75}P_6$, M = 1421.48, rhombohedral, space group $R3$, Z = 12, a = 23.372(4), c = 42.956(8) Å, U = 20320(6) Å^3, T = 220 K, μ = 1.240 mm^{-1}, final R = 0.0624 [based on F and 5674 data with $F > 4\sigma(F)$], wR_2 = 0.1744 (based on F^2 and all 7979 unique data used in refinement) for 535 parameters. The structure was solved by direct methods (SIR 92) and refined by full-matrix least-squares procedures on F^2 (SHELXL-97).[14]

[Eu(tpip)$_3$]·$\underline{0}.67$H$_2$O: $C_{72}H_{61.33}EuN_3O_{6.67}P_6$, M = 1411.75, trigonal, space group $P3$, Z = 6, a = 23.418(2), c = 21.185(3) Å, U = 10061.4(19) Å^3, T = 220 K, μ = 1.13 mm^{-1}; final R = 0.0426 and R_w = 0.0418 [both based on 8591 out of 11861 unique data with $F > 4\sigma(F)$], for 800 parameters. The structure was solved by Patterson methods (DIRDIF) and refined by full-matrix least-squares procedures on F (CRYSTALS).[15] CCDC 182/1097. See http://www.rsc.org/suppdata/cc/1999/61/ for crystallographic files in .cif format.

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