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COMMUNICATION

Phosphine oxide functionalised imidazolium ionic liquids as tuneable ligands for lanthanide complexation[†][‡]

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A series of novel, phosphine oxide functionalised ionic liquids have been synthesised and their application as tuneable lanthanide complexing agents is demonstrated.

Selective extraction of metal ions from aqueous solutions is a major challenge in mining, nuclear fuel recycling and in sustainable metal waste recovery.¹ Ionic liquids have been described for a number of applications in the separation and extraction of specific metal ions from aqueous solution.²⁻⁵ Davis and Rogers et al. introduced the concept of functionalised ("task-specific") ionic liquids designed for the extraction of heavy metal ions.^{6,7} Functional groups selective towards metal complexation can be tethered covalently either to the cation (such as thioether, thiourea, nitriles,⁸ carboxylic acids⁹) or the anion (β-diketonates^{2,10}). Davis reported on phosphoramidefunctionalised imidazolium ionic liquids for the extraction of actinides.¹¹ Odinets et al. reported on bidentate carbamovlmethylphosphine oxide (CMPO) functionalised ionic liquids for the actinide and rare earth metal recovery.¹² Ionic liquids based on quaternary ammonium cations bearing phosphoryl moieties and their application in the liquid-liquid extraction of U(vi) were reported by Ouadi et al.13 Synthesis of a P=O functionalised imidazolium salt as an intermediate towards carbene-phosphine complexes has been reported by Tsoureas et al.¹⁴

Besides metal extraction, ionic liquids have been used as solvents for lanthanide spectroscopy, giving high luminescence quantum yields and an extraordinary photostability compared to organic solvents. These can be incorporated as components of lanthanide containing hybrid materials, like luminescent polymer films or ionogels.^{15–17} Phosphine oxides are generally well-known complexing ligands for lanthanides^{18–20} due to their ability to remove coordinating water molecules from the first coordination sphere and thereby avoiding vibronic O–H luminescence quenching in optical applications.

In this communication, we report on the synthesis of the first diphenyl phosphine oxide-functionalised ionic liquids (POFILs) and their tuneable ability to complex lanthanides. These POFILs were synthesised in two steps by reacting alkyl bromide-functionalised 1,2-dimethyl-imidazolium ionic liquids with $[Tf_2N]^-$ or $[PF_6]^-$ anions and potassium diphenylphosphine (Scheme 1). The resulting phosphine functionalised ionic liquid was then oxidised using hydrogen peroxide. The synthesis delivered clean products in fairly good yields (around 70%); all ionic liquids have been characterised using ¹H, ¹³C, ³¹P NMR and IR spectroscopy, and ESI mass spectrometry (see ESI \pm).

The P=O stretching vibration in IR was not greatly affected by the length of the $-(CH_2)_n - (n = 2, 3, 4, 6, 8)$ spacer unit, whereas the ³¹P NMR chemical shift increased with the increasing spacer length. The phase transitions for the ionic liquids were determined by Differential Scanning Calorimetry (DSC) and are shown in Table 1. All of the bistriflimide ionic liquids were liquids at RT, except for **1C**, which exhibits a melting point.

All compounds had well defined glass transitions, ranging from -24.9 °C to -5.8 °C (see Table 1). [DMImC₃P(O)Ph₂][PF₆] (2) was expected to have a higher melting point, allowing for crystallisation and the determination of the crystal structure. Fig. 1 shows the cation of the crystal structure of 2 in



Scheme 1 Reaction scheme and structures of the ionic liquids 1-alkyl-diphenylphosphine-oxide-2,3-dimethylimidazolium-cations $[DMImC_nP(O)Ph_2]^+$ and the anions $[A]^-$ bis(trifluoromethylsulfonyl)imide, $[Tf_2N]^-$ (chain length n = 2, 3, 4, 6, 8; 1A-1E) and $[PF_6]^-$ (chain length n = 3, 2).

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 Table 1
 Properties of the phosphine oxide functionalised ionic liquids

Ionic liquid	Phase transition/°C	$\frac{\nu(\mathbf{P}\underline{=}\mathbf{O})/}{\mathrm{cm}^{-1}}$	³¹ P NMR shift/ppm
$[DMImC_2P(O)Ph_2][Tf_2N]$ (1A)	$-5.79(T_{\rm g})$	1179	32.67
$[DMImC_3P(O)Ph_2][Tf_2N]$ (1B)	$-8.25(T_{g})$	1181	37.39
$[DMImC_4P(O)Ph_2][Tf_2N]$ (1C)	$-8.97 (T_{g})/$	1177	37.81
	96.4 (m.p.)		
$[DMImC_6P(O)Ph_2][Tf_2N]$ (1D)	$-20.24(T_{g})$	1177	38.22
$[DMImC_8P(O)Ph_2][Tf_2N]$ (1E)	$-24.87 (T_{g})$	1179	38.28



Fig. 1 Cation in the crystal structure of 1-propyl-diphenylphosphineoxide–2,3-dimethylimidazolium $[PF_6]^-$ showing an O···H contact to an adjacent cation. O1' is at (x - 1, y, z) and H8A" is at (1 + x, y, z). The ellipsoids are shown at 50% probability. Anions are not shown for clarity.

the presence of a P=O···H contact between the phosphine oxide functionality and protons on the α -carbon to phosphorus of an adjacent cation, with a C8–H8A···O1' separation of 2.58 Å [with O1' at (x - 1, y, z)] and a C8–H8A···O1' angle of 158°.

It has been demonstrated for nitrile functionalised ionic liquids that the length of the spacer chain between the CN group and the positively charged methyl-pyrrolidinium cation has a distinct influence on the electron density of the nitrile functionality and therefore on the donor properties towards metal centres.8 These electron-withdrawing effects were found to have some degree of influence over six CH₂ groups between the positive charge and the CN group. As a measure for the coordinating ability of the phosphine oxide functionalised ionic liquids, a complexometric titration with an increasing amount of La(OTf)₃·6H₂O has been carried out by ³¹P NMR spectroscopy. The ³¹P NMR chemical shifts of the respective $[DMImC_nP(O)Ph_2][Tf_2N]$ ionic liquids (n = 2, 3, 4, 6, 8) with increasing amounts of La(OTf)₃.6H₂O were monitored. Lanthanum has been used, since it is diamagnetic, as opposed to complexes of paramagnetic lanthanides (such as Eu, Tb, Nd). The triflate, [OTf]⁻, has been used, since it is a weakly coordinating anion towards the lanthanides in solution. The results of the NMR titration are shown in Fig. 2.

There is a distinct difference in the ³¹P shifts for the spacer lengths with 2 and 3 CH₂ groups between the cation and the Ph₂P=O group. The effect significantly levels off as the chain length increases beyond 4 or more CH₂ groups. The binding constants were calculated from these ³¹P NMR shifts and range from 23.2 to 140.8, reflecting the ability of increased binding of the lanthanide to the phosphine oxide ligand with increasing lengths of the spacer unit; however, the binding constant of the compound with the shortest spacer is slightly



Fig. 2 ³¹P NMR complexometric titration. The ³¹P chemical shifts of the respective $[DMImC_nP(O)Ph_2][Tf_2N]$ ionic liquids (n = 2, 3, 4, 6, 8) with increasing amounts of La(OTf)₃·6H₂O were monitored.



Fig. 3 Determined binding constants (triangles) and ³¹P NMR shifts (rhombuses) of the $[DMImC_nP(O)Ph_2][Tf_2N]$ ionic liquids (n = 2, 3, 4, 6, 8).

higher (40.8) than for n = 3 (see Fig. 3). ES mass spectra of La(OTf)₃·6H₂O solutions in methanol were obtained in the presence of a 10-fold excess of [DMImC_nP(O)Ph₂][Tf₂N] ionic liquids (n = 2, 3, 4, 6, 8). The expected masses corresponding to lanthanide–ionic liquid complexes such as [La(OTf)_x-(DMImC_nP(O)-Ph₂)_y(Tf₂N)_z]⁺ (x = 1-4; y = 1-6; z = 1-3) were identified to be present in these solutions and a full table with the assigned fragments is shown in the ESI.‡ With increasing spacer length, species with more phosphine oxide ligands were detected, *i.e.* larger values for y (*e.g.* species y = 6 only for n = 6, 8; see ESI‡).

We further examined the possibility of using phosphine functionalised ionic liquids as additional ligands for lanthanide



Fig. 4 Structure of the europium complex Eu(hfa)₄(DMImC₃P(O)Ph₂).



Fig. 5 Crystal structure of the complex $Eu(hfa)_4(DMImC_3P(O)Ph_2)$. The ellipsoids are shown at 40% probability.

 β -diketonate complexes. From a solution of Eu(hfa)₃·6H₂O (hfa = 1,1,1,5,5,5-hexafluoro-acetylacetonate), and the ionic liquid [DMImC₃P(O)Ph₂][Tf₂N] (**1B**) in methanol, an unexpected complex, Eu(hfa)₄(DMImC₃P(O)Ph₂) (**3**), crystallised out (see Fig. 4 and crystal structure in Fig. 5). To our knowledge, there is not a single other tetrakis β -diketonate complex of any lanthanide reported that has an additional ligand coordinating to the metal. Starting from Eu(hfa)₃, the compound can be formed according to the following equation:

 $2\text{Eu}(hfa)_{3} + [DMImC_{3}P(O)Ph_{2}][Tf_{2}N] \rightarrow$ Eu(hfa)_4(DMImC_{3}P(O)Ph_{2})_{cryst} + [Eu(hfa)_{2}][Tf_{2}N]_{sol}

Driving force for the formation of this zwitterionic complex may be the increased stability originating from the ion-pairing between the negatively charged [Eu(hfa)₄]⁻ moiety and the positively charged coordinating cation, $[DMImC_3P(O)Ph_2]^+$. The crystal structure of Eu(hfa)₄(DMImC₃P(O)Ph₂) indicates the presence of four hfa ligands in addition to the coordinating phosphine oxide. The coordination number of the europium complex is nine and forms a distorted tricapped trigonal prism. The shortest Eu–O bond length is found for the oxygen of the P=O ligand, of 2.302(9) Å, whereas the other Eu-O distances range from 2.387(9) to 2.451(6) Å. The length of the P = O bond in the solid state of the complex is 1.51(1) A longer than the P=O distance in the structure of the free ligand of 1.489(2) Å. There is strong C–H···O hydrogen bonding found from the C5 acidic proton of the imidazolium ring to two oxygen atoms of the hfa ligand of an adjacent complex (2.44(1) A and 2.64(8) Å).

In summary, we have synthesised and characterised a new class of phosphine oxide bearing ionic liquids and demonstrated their tuneable metal ligating abilities. Increasing lengths of the spacer unit between cations and the phosphine oxide group appear to increase the binding ability of the ligand towards lanthanide metals. These novel ionic liquids have a great potential for applications in lanthanide, actinide and transition metal separation and extraction, for light emitting devices and for composite materials with diverse polymers. Further investigations, involving simulations, are underway to examine the formation of the europium complex with the unusual coordination geometry, and whether the spacer unit has an influence on a potential ion-pairing effect. We are currently exploring other hydrophobic functionalised cations, like tri-alkyl phosphonium, as well as their luminescence characteristics of lanthanide complexes (Vis and NIR emitters).

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