Novel class of functionalized ionic liquids with grafted CMPO-moieties for actinides and rare-earth elements recovery†

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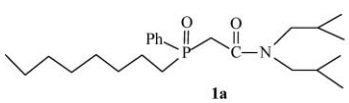
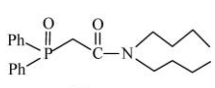
The general approach to a novel class of functionalized ionic liquids **4–6** bearing grafted diphenylcarbamoylmethylphosphine oxide complexing groups in the cation has been elaborated. The synthetic route comprises the preparation of the intermediate (diphenylphosphorylmethylcarbamoyl)propylimidazole **3**, followed by sequential quaternization by alkyl halides (chlorides or bromides) and anionic exchange in the case of ionic liquids bearing the hexafluorophosphate anion. The structures of two ionic liquids were confirmed by X-ray analysis, revealing the strong intramolecular hydrogen bond formed by the acidic protons of the heterocycle and oxygen atom either of the P=O or C=O group, depending on the anion nature. In neutral media, these ionic ligands form complexes ML_2 with europium chloride or europium nitrate *via* an O,O-bidentate mode similar to known neutral CMPO compounds. The solid phase extractants prepared by immobilization of these FILs on solid matrixes possess sorption activity towards actinides and rare-earth elements in nitric acid solutions.

Introduction

Ionic liquids (ILs) are extensively studied nowadays, and have found applications in catalysis,[1] analytical chemistry,[2] and as promoting and recyclable reaction media in different synthetic procedures.[3] The critical review of Seddon and Plechkova demonstrated the parallel and collaborative exchanges between research and industrial developments, dealing both with nitrogen and phosphonium ionic liquids.[4] Notably, hydrophobic ionic liquids themselves have been considered as an alternative for the organic phase in liquid–liquid solvent extraction systems, *e.g.*, for the separation of *f*-elements.[5–7] Indeed, the imidazolium ionic liquids are relatively radiation resistant and do not undergo significant decomposition by radiolysis upon exposure to high radiation doses.[8] In this context, it should be taken into account that due to the ionic nature of ILs, the partitioning equilibria in solvent extraction systems involving ionic liquids are not necessarily identical to those involving conventional organic solvents. The equilibria often involve cation or anion exchange between the aqueous phase and the ionic liquid phase, and the contamination of the aqueous phase by the components of the ionic liquid is a problem for the applicability of ionic liquids in solvent extraction systems. Moreover, the coordination environment of the metal ions in ionic liquids can differ from what is observed in other organic solvents.[6] Over the extraction, cationic or anionic metal species become part of the ionic liquid itself, while the original liquid is destroyed. It should be noted that, as many ionic liquids contain weakly coordinating anions, it will, in general, not be possible to extract metal ions from an aqueous phase to the ionic liquid phase in the absence of extractants.[6] Among the typical extractants for the processing of accumulated liquid acidic radioactive wastes, bidentate carbamoylmethylphosphine oxides (CMPO), *e.g.*, (*N*,*N*-diisobutylcarbamoylmethyl)octylphenylphosphine oxide **1a**[9] or *N*,*N*-dibutylcarbamoylmethyldiphenylphosphine oxide **1b**,[10] are known to be preferable from cost and effectiveness of extraction points of view. It was demonstrated that CMPO dissolved in [bmim]PF_6 can extract lanthanide nitrates from deionized water, and the presence of ionic liquid improved the extractability as well the selectivity of CMPO.[11]



1a



1b

Recently, the development of functionalized ionic liquids (FILs) (also referred to as task-specific ionic liquids (TSILs)) have received much attention due to their potential to impart on the liquid specific chemical and/or physical properties.[12] Therefore, new ILs are being introduced in which a functional group is incorporated as a part of the cation or anion structure. These functional groups can impart a particular reactivity pattern to the IL, enhancing its capacity for interaction with specific solute types. There have been recent developments in functionalized imidazolium salts, which can be used for specific tasks ranging from catalyst recycling, supports for organic synthesis, catalysis, separation of specific metal ions from aqueous solution, and

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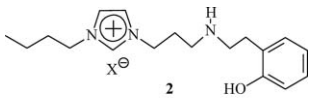
construction of nanostructures and ion-conductive materials.[12] For example, ILs with thioether, thiourea, and urea functional groups capable of complexation and incorporated in the alkyl chains of the imidazolium cations have been prepared and used, in combination with the PF_6^- anion, alone or in a mixture with [C_4mim][PF_6], for Hg^{2+} and Cd^{2+} extraction in liquid–liquid separations.[13] Furthermore, the salicylaldehyde-derived imidazolium salts were suggested to extract Ni^{2+} ions from aqueous solutions,[14] and those with phosphoramide-functionalized imidazolium[14] or ammonium cations[7c] for recovery of actinides from aqueous solutions.

The extractant molecules serve to dehydrate the metal ions and offer a more hydrophobic environment that enables their transport to the extracting phase. Attaching a metal ion coordinating group directly to the imidazolium cation makes the extractant an integral part of the hydrophobic phase and greatly diminishes the chance of loss to the aqueous phase. That prompts the investigation of the functionalized ionic liquid concept for metal ion extraction in ILs.

Upon grafting of such bidentate complexing substructures onto the organic cation of RTILs, the resulting FILs could combine the useful properties both of the IL and the extracting agent, suppressing the problems encountered through extractant/solvent miscibility and facilitating actinide recovery. Thus, Ouadi and co-workers designed task-specific ionic liquids **2** for the extraction of trivalent americium, which contained the 2-hydroxybenzylamine moiety attached to the 1-butylimidazolium core and either hexafluorophosphate (PF_6) or bis(trifluoromethylsulfonyl)imide (Tf_2N) counteranions.[15] These ionic liquids act as extractants and were used in pure form or diluted in another ionic liquid for the extraction of americium from the aqueous to the ionic liquid phase under basic conditions. Americium could be stripped from the ionic liquid phase by washing with an acidic aqueous solution.



2

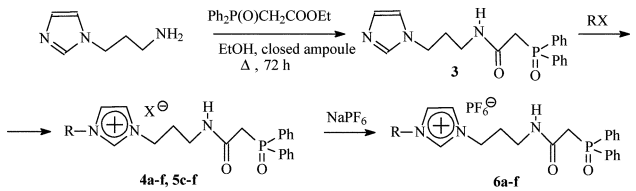
X = PF_6, Tf_2N

In this paper, we report on the synthesis and characterization of a novel type of imidazolium FILs bearing CMPO moieties in alkyl chain, along with their application as active agents for solid phase extractants' preparation for the recovery of actinides and rare earth elements from nitric acid solutions.

Results and discussion

Synthesis of CMPO-modified ionic liquids

The general approach to the synthesis of the desired FILs is based on the quaternization of (phosphorylmethylcarbamoyl)propyl-substituted imidazole **3** by different alkyl halides, namely bromides or chlorides. The alkylation performed in acetonitrile solution presents a rather sluggish reaction; however, the final compounds were obtained as white crystalline compounds in high yields and in high purity after a simple work-up (see experimental). The subsequent anion exchange reaction under the treatment with sodium hexafluorophosphate afforded the FILs with the hexafluorophosphate anion (Scheme 1). The starting CMPO-functionalized imidazole **3** was, in turn, obtained *via* the direct



X = Br (**4**), Cl (**5**)

R=Et (**4a**, **6a**), Bu (**4b**, **6b**), n-Hex (**4c**, 5c, **6c**), n-C_8H_{17} (**4d**, 5d, **6d**), $C_{14}H_{29}$ (**4e**, 5e, **6e**), $C_{16}H_{33}$ (**4f**, 5f, **6f**)

Scheme 1 Synthesis of CMPO-modified ionic liquids **4–6**.

amidation of diphenylphosphorylacetic acid ethyl ester with 3-aminopropylimidazole in ethanol solution according the procedure reported by us recently.[16]

Compounds **4–6** were isolated as off-white hygroscopic solids with melting points mostly in the range of 57–129 °C, excluding compounds **4c**, **5c**, and **6c** (R = Hex) which possessed the highest melting points in the range of 154–161 °C. The structures of the intermediate imidazole **3** as well as ionic liquids **4–6** were unambiguously confirmed by the multinuclear NMR data and elemental analysis data. The IR spectra of all compounds (KBr pellets or nujol for **6a–f** bearing the weakly coordinating PF_6 anion) show characteristic absorption bands at 1649–1664 cm^{-1} (C=O) and 1163–1197 cm^{-1} (P=O). Usually, the band characteristic to the P=O group has two maxima, suggesting the partial formation of a hydrogen bond P=O···H. The absorption of the NH group appears as a broad band at 3159–3256 cm^{-1} (NH stretching vibrations) and bands at 1550–1591 cm^{-1} (combined frequencies of NH bending vibrations and C–N vibrations). The CH_2 bending vibrations are observed at 1437–1468 cm^{-1}. The ^{31}P NMR spectra show singlets at *ca.* 30 ppm, *i.e.*, these signals appear in the region characteristic of this type of environment of the phosphorus atom.[9,10,16] The ^1H NMR spectra are consistent with the structures of the resulting compounds and have, along with characteristic signals for the hydrogen atoms in the substituents at the phosphorus and heterocyclic nitrogen atom, the characteristic doublet for the protons of the PCH_2 group at 3.45–3.90, with the spin–spin coupling constant of 12.8–13.7 Hz. It should be noted that the signal assigned to the acidic CH-proton of the imidazolium ring located at 10.05–10.35 ppm for ionic liquids **4a–f** and **5c–f** with halide anions was upfield shifted to 8.81–9.18 ppm for their analogues **6a–f** bearing the hexafluorophosphate anion. The presence of only one singlet characteristic for the proton of the N–CH–N moiety in the ^1H NMR spectra of ligands **6a–f** along with the elemental analysis data provided evidence that these ILs are free from halide impurities. Similarly, the ^{13}C NMR spectra fit well the depicted structures.

To obtain additional data on the structure of these CMPO-modified ILs, the molecular structures of bromide **4d** and hexafluorophosphate **6c** were established by X-ray diffraction. The general views of these compounds (with solvated molecules excluded) are shown in Fig. 1 and 2, respectively. Selected bond lengths and angles are given in Table S1 in the ESI.† In general, the presence of the more elongated octyl group at the heterocyclic nitrogen atom and the bromine anion in **4d** lead to a molecular conformation and cation–anion interactions that are totally different compared with those in **6c** bearing the PF_6 anion. Thus, in crystal structure **6c**, the acidic proton H(2A) in the heterocycle binds to the

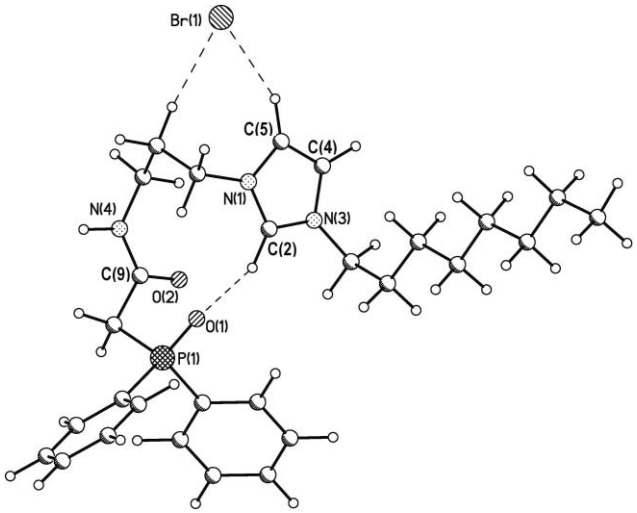


Fig. 1 General view of **4d**.

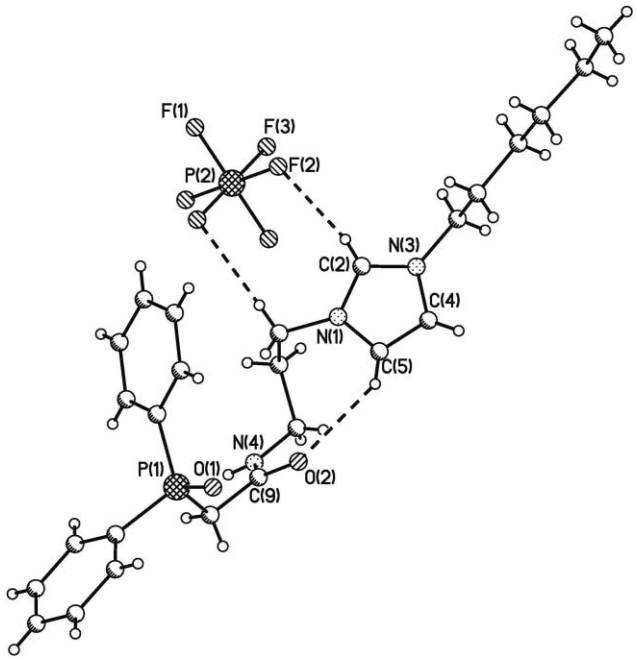


Fig. 2 General view of **6c**.

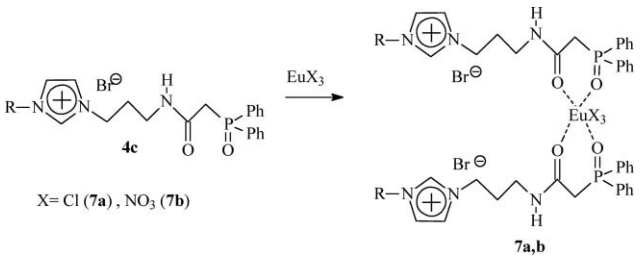
hexafluorophosphate moiety (C···F 3.238(4) Å, CHF 168(1)°), as is typical in the case for most ILs.[17] In bromine salt **4d**, this hydrogen atom does not interact with the anion. In contrast, it forms a strong intramolecular hydrogen bond with the oxygen atom of the phosphoryl group. The reasons for this difference in proton acceptors are as follows.

When the IL cations are isolated from the surroundings, hydrogen bonds are most likely to occur between the NH and PO groups. Indeed, in IL **6c**, the expected intramolecular N–H···O=P bond (N···O 2.876(5) Å, NHO 164(1)°) is observed. As the C=O group and the rest of the hydrogen atoms of imidazole are second in line, there is a weaker C(4)–H(4A)···F interaction with the PF_6^- anion and an additional C(5)–H(5A)···O bond with the carboxyl group. The corresponding geometrical parameters are: C···F 3.511(4) Å, CHF 163(1)° and C···O 3.208(5) Å, CHO 139(1)°.

In the crystal of **4d**, the amide group binds to the bromide anion (N···Br 3.349(3) Å, NHBr 156(1)°), which is a more effective proton acceptor. Therefore, the C(2)–H(2A)···O bond (C···O 3.127(4) Å, CHO 154(1)°) is formed with the phosphoryl moiety. The protons H(4A) and H(5A) of the heterocycle interact with the carbonyl group (C···O 3.109(4) Å, CHO 162(1)°) and bromine anion (C···Br 3.693(3) Å, CHBr 149(1)°), respectively.

As a result, the counteranion causes the marked difference in intermolecular and intramolecular binding in these CMPO-modified ILs that is responsible for stabilizing different molecular conformations.

In model experiments, using compound **4c** as a representative example, we demonstrated that the CMPO-modified ionic ligands readily form stable complexes of ML_2 composition with europium trichloride and europium nitrate in neutral medium (ethanolic solutions) (Scheme 2).



Scheme 2 Synthesis of europium complexes **7a,b**.

The considerable upfield shift of the signals of europium complexes **7a**,**b** in the ^{31}P NMR spectra compared to the signal of the free ligand **4c** provide convincing evidence for the participation of the phosphine oxide group in the coordination. The IR spectra of solid-state complexes **7a**,**b** exhibit no absorption bands characteristic of the free P=O and C=O groups. Instead, the spectrum contains bands at 1161 (**7a**) and 1162 cm^{-1} (coordinated P=O group) and at 1628 and 1629 cm^{-1} (coordinated C=O group). In complex **7b**, the nitrate groups coordinated in a bidentate manner absorb at 1470 (ν(N=O)), 1317 ($\nu_{as}(NO_2)$), and 1031 cm^{-1} ($\nu_s(NO_2)$). The absence of the absorption band at ~1380 cm^{-1} (free nitrate group) suggests that all of the nitrate groups in complexes **7b** are coordinated by the metal in a bidentate fashion. These data allow one to assume that the CMPO-modified ionic ligands under investigation act as O,O-bidentate ligands towards *f*-elements, similar to known neutral CMPO ligands.[18]

Application of CMPO-modified ionic liquids for the preparation of solid phase extractants

It seems reasonable to estimate the possibility of using these FILs for the extraction of *f*-elements. However, the highest extent of trivalent actinide separation from nitric acid media is achieved using high concentrations of CMPO in organic phase, while the sorption procedures using solid extractants prepared by non-covalent fixing of such ligands on different matrixes are more effective for recovery of trivalent actinides.[19] Moreover, the possibilities of ionic liquids to be kept on solid surfaces and to possess ion exchange and complexing properties give them potential for the preparation of solid phase extractants. Thus,

previously we demonstrated the possibility to fix phosphonium-type ionic liquids in a mixture with CMPO ligand **1b** on the polyacrylonitrile (PAN) fiber, and solid phase extractants prepared in this way were successfully used for actinides recovery from nitric and hydrochloric acid solutions.[20]

In the present study for the preparation of sorbents, we used PAN fiber, acrylate resin Amberlit XAD-7®, hyper-cross-linked polystyrene and multi-walled carbon nanotubes (Taunit®) as solid supports. For the preparation of sorbents, these solid matrixes were treated with solutions of FILs in dichloroethane or ethanol (on the basis of 0.003 mmol g^{-1}) followed by air drying. As the most selective preconcentration of lanthanides and actinides is usually performed from high acid solutions, in which they exist as anionic complexes, in the experiments model nitric acid solutions (3 M HNO_3) of Pu(IV) and Eu(III) were used.

The nature of the cation (the length of the alkyl group *R*) and anion in the FILs **4–6**, as well as the type of solid support, were found to be important for effective sorption of metal cations. The sorbents on the base of hydrophilic polyacrilonitrile fiber and other hydrophilic matrixes were effective for plutonium recovery from nitric acid solutions (3 M HNO_3) (Table 1). The sorbents prepared using FILs **4c** and **5c** with short hexyl radicals and halide anions were less effective compared to that based on FIL **6c** having the same cation but the hydrophobic hexafluorophosphate anion. Vice versa, among the sorbents impregnated by FILs **4d**, **5d** or **6d**, with octyl group *R* at the nitrogen atom, the effectiveness of sorption decreased in the series Cl > Br > PF_6, while in the case of sorbents impregnated by ionic liquids **4f**, **5f** or **6f** with the longest hexadecyl group, the anion nature did not significantly influence the recovery extent (91, 92 and 94%, respectively). However, under other conditions being equal, the same sorbents were unsuitable for Eu(III) recovery (11–74%), and in this case, the sorbents impregnated with chlorides **5d** and **5f** provided better results (74 and 58%, respectively).

At the same time, the sorbent based on hydrophobic multi-walled carbon nanotubes (Taunite®) in combination with hydrophobic FIL **6f** with the hexafluorophosphate anion resulted in 97% recovery of Pu(IV) and a drastic increase of recovery for trivalent actinides (87 and 89% recovery of Eu(III) and Am(III), respectively) from nitric acid solutions (3 M HNO_3), with excellent sorption properties towards U(VI) (99% recovery) as well. Table 1 summarizes the results presented.

Table 1 Extraction degree (%) of Pu(IV) and Eu(III) by "solid-phase extractants" on the base of PAN-fiber and carbon nanotubes. 3 M HNO_3; content of reagent 0.003 mM g^{-1}, 2 h, V : m = 100 : 1; 2h

Run	Cmpd	Matrix	*R*	Anion	Pu(IV)	Eu(III)
1	**5c**	PAN-fiber	C_6H_{13}	Cl	60	11
2	**4c**	PAN-fiber	C_6H_{13}	Br	62	22
3	**6c**	PAN-fiber	C_6H_{13}	PF_6	87	20
4	**5d**	PAN-fiber	C_8H_{17}	Cl	95	74
5	**4d**	PAN-fiber	C_8H_{17}	Br	83	10
6	**6d**	PAN-fiber	C_8H_{17}	PF_6	79	21
7	**5f**	PAN-fiber	$C_{16}H_{33}$	Cl	92	58
8	**4f**	PAN-fiber	$C_{16}H_{33}$	Br	91	11
9	**6f**	PAN-fiber	$C_{16}H_{33}$	PF_6	94	33
10[a]	**6f**	carbon nanotubes	$C_{16}H_{33}$	PF_6	97	87

[a] Sorption of U(IV): 99%, Am(III): 89%

It should be mentioned that ionic liquids with the hexafluorophosphate anion are believed to be unstable to hydrolysis, especially in acidic media. Using the compound **6c** with *R* = Hex as a representative example, in a special experiment we estimated its hydrolytic stability in 3 M nitric acid. After 2 h of intensive stirring, *i.e.*, the period of time used in sorption experiments, acetonitrile was added to the two-phase system for the formation of a clear solution. The ^{31}P NMR spectrum of the sample did not reveal formation of fluorophosphate or phosphate anions, and no presence of HF was observed in the corresponding ^{19}F spectrum. These data indicate relatively high hydrolytic stability of the reported FILs with the [PF_6] anion.

Although complexes obtained in model experiments in neutral media often differ from complexes produced in an organic phase during real extraction or sorption from acidic media, the fact that CMPO-modified ionic liquids form complexes with *f*-elements similar to other CMPO ligands, *i.e., via O,O*-bidentate chelate mode, allows us to suggest that the mechanism of sorption comprises the formation of complexes of such type, in which nitrate anions may be included into the coordination sphere of the metal. The difference in trivalent actinides' sorption depending on the solid support in use is apparently connected with the mode of bonding of these ionic ligands on the surface of the matrix, and extraction conditions as well. In other words, non-covalent fixing of a ligand on the surface of hydrophilic matrixes, realized through the hydrophilic NH-groups, may prevent effective complexation with metal cations, while on the surface of hydrophobic carbon nanotubes the ligand may be bound *via* the hydrophobic imidazolium moiety giving, in turn, better possibilities for bidentate complexation typical for CMPO-ligands.

These preliminary experiments have shown that a novel class of functionalized ILs with grafted CMPO-moieties possess promising properties for actinide and rare-earth elements recovery from acidic solutions. In this paper, we only outlined the prospects of this area and our further study will comprise investigation of the acid nature influence and that of pH of an aqueous phase on the effectiveness of sorption along with estimation of the reversibility of metal sorption.

Conclusion

In conclusion, we have reported an efficient way to synthesize a new class of FILs bearing a bidentate CMPO complexing moiety in the pendant arm of the cation. The preliminary results described here show that high separation of Pu(IV), Am(III), Eu(III), and U(VI) can be achieved using these ILs as active agents of solid phase sorbents based on carbon nanotubes. The nanostructure features and large surface of the carbon nanotubes determine their high sorption ability and further wide possibilities for creation of solid phase extractants on their base. Ionic liquids possess negligible flammability and volatility and, therefore, represent a new class of "green" solvents. In this sense, further studies will include further improvements of the structure and detailed investigation of the influence of its nature on sorption and extraction properties.

Experimental

Materials and methods

The NMR spectra were recorded on a Bruker AMX-300 and a Bruker AMX-400 instruments in $CDCl_3$ and DMSO-d_6 solutions. The chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{19}F chemical shifts were determined with $CFCl_3$ as an external standard. The ^{13}C NMR spectra were registered using the JMODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. IR spectra were recorded on a Magna-IR 750 FTIR-spectrometer (Nicolet Co., resolution 2 cm^{-1}, scan number 128, KBr pellets or nujol). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and were uncorrected.

Diphenylphosphoryl acetic acid was obtained *via* the known procedure,[21] other reagents were used without further purification as purchased (Acros). For full details concerning the synthetic procedures and characterization of the precursor **3**, see the ESI.†

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-alkyl-1*H*-imidazol-3-ium bromides 4a–f (*general procedure*)

To a solution of 3-(1*H*-imidazol-1-yl)-1-propanamine **3** (1 equiv.) in anhydrous CH_3CN (10 mL), the corresponding alkyl bromide (1.2 equiv.) was added dropwise at 0 °C under argon. The mixture was stirred at r.t. for 12 h followed by stirring at 80–85 °C for 70 h. Then the solvent was evaporated under vacuum and the resulting solid residue was washed with Et_2O (2 × 10 mL). The residual ether was removed under reduced pressure and the solid residue was dried under vacuum (2 mm Hg) at 55 °C for 7 h.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-ethyl-1*H*-imidazol-3-ium bromide (4a). Yield: 76%. M.p. 85-87 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 33.99. ^1H NMR (300 MHz, $CDCl_3$): δ 1.60 (t, 3H, CH_3CH_2–N, $^3J_{H-H}$ = 7.3 Hz); 2.11 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 5.4 Hz); 3.14 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 5.3 Hz); 3.90 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.0 Hz); 4.29-4.39 (m, 4H, $CH_2CH_2CH_2NHC(O)$+CH_3CH_2-N); 7.36 (br. s, 1H, C^5H in Im); 7.51-7.62 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.84 (br. s, 1H, C^4H in Im); 7.91-7.98 (m, 4H, *O*-H in C_6H_5P); 8.98 (br. t, 1H, NH, $^3J_{H-H}$ = 5.9 Hz); 10.17 (br. s, 1H, N=CH–N). IR (KBr): 509 (m), 523 (m), 696 (w), 730 (m), 1120 (w), 1164 & 1185 (s, $\nu_{P=O}$), 1308 (w), 1437 (m, ν_{CH_2}), 1555 (s, ν_{NH}), 1663 (s, $\nu_{C=O}$), 2985 (m), 3053(s), 3233 (m) cm^{-1}. Anal. calcd for $C_{22}H_{27}BrN_3O_2P{\cdot}2H_2O$: C, 51.57; H, 6.10; N, 8.20. Found: C, 51.14; H, 5.41; N, 8.21.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-butyl-1*H*-imidazol-3-ium bromide (4b). Yield: 93%. M.p. 79-81 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 34.14. ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, 3H, $CH_3(CH_2)_2CH_2$–N, $^3J_{H-H}$ = 7.1 Hz); 1.35 (sextet, 2H, $CH_3CH_2CH_2CH_2$–N, $^3J_{H-H}$ = 7.1 Hz); 1.87 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.1 Hz); 1.99-2.18 (m, 2H, $CH_3CH_2CH_2CH_2$–N); 3.02-3.21 (m, 2H, $CH_2NHC(O)$); 3.81 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.2 Hz); 4.23 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.1 Hz); 4.30 (t, 2H, $CH_3(CH_2)_2CH_2$–N, $^3J_{H-H}$=5.9); 7.24 (br. s, 1H, C^5H in Im); 7.42-7.58 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.77 (br.s, 1H, C^4H in Im); 7.86-7.93 (m, 4H, *O*-H in C_6H_5P); 8.90 (br. s, 1H, NH); 10.14 (br. s, 1H, N=CH–N). IR (KBr): 510 (w), 525 (m), 732 (m), 1120 (w), 1166 & 1186 (s, $\nu_{P=O}$), 1308 (br, w), 1437 (m, ν_{CH_2}), 1559 (s, ν_{NH}), 1664 (s, $\nu_{C=O}$), 2987 (m), 3054 (s), 3238 (m) cm^{-1}. Anal. calcd for $C_{24}H_{31}BrN_3O_2P{\cdot}1H_2O$: C, 55.18; H, 6.37; N, 8.04. Found: C, 55.11; H, 6.21; N, 8.07.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-hexyl-1*H*-imidazol-3-ium bromide (4c). Yield: 81%. M.p. 157-158 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.80. ^1H NMR (400 MHz, $CDCl_3$): 0.85 (t, 3H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 6.8 Hz); 1.24-1.28 (m, 6H, $CH_3(CH_2)_3CH_2CH_2$–N); 1.85 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 6.5 Hz); 2.06 (appeared quintet, 2H, $CH_3(CH_2)_3CH_2CH_2$–N, $^3J_{H-H}$ = 6.0 Hz); 3.08 (appeared q, 2H, $CH_2NHC(O)$,$^3J_{H-H}$ = 5.8 Hz); 3.71 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.0 Hz); 4.19 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.8 Hz); 4.28 (t, 2H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 6.3 Hz); 7.21 (t, 1H, C^5H in Im, $^3J_{H-H}$ = 1.7 Hz); 7.42-7.52 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.70 (t, 1H, C^4H in Im, $^3J_{H-H}$ = 1.8 Hz); 7.82-7.88 (m, 4H, *O*–H C_6H_5P); 8.79 (br. t, 1H, NH, $^3J_{H-H}$ = 4.8 Hz); 10.11 (br. s, 1H, N=CH–N). IR (KBr): 509 (m), 522 (m), 1166 & 1184 (s, $\nu_{P=O}$), 1440 (m, ν_{CH_2}), 1551 & 1566 (ν_{NH}), 1650 (s, $\nu_{C=O}$), 2933 (s), 3070 (s), 3088 (s), 3208 (m) cm^{-1}. Anal. calcd for $C_{26}H_{35}BrN_3O_2P$: C, 58.65; H, 6.63; N, 7.89; P, 5.82. Found: C, 58.47; H, 6.61; N, 7.91; P, 5.81.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-octyl-1*H*-imidazol-3-ium bromide (4d). Yield: 84%. M.p. 100-101 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 31.21. ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, 3H, $CH_3(CH_2)_6CH_2$–N, $^3J_{H-H}$ = 6.9 Hz); 1.19-1.38 (m, 10H, $CH_3(CH_2)_5CH_2CH_2$–N); 1.74-1.92 (m, 2H, $CH_2CH_2NHC(O)$); 2.01-2.13 (m, 2H, $CH_3(CH_2)_5CH_2CH_2$–N); 3.09 (appeared q, 2H, $CH_2NHC(O)$,$^3J_{H-H}$ = 5.1 Hz); 3.72 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.0 Hz); 4.19 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.6 Hz); 4.29 (t, 2H, $CH_3(CH_2)_6CH_2$–N, $^3J_{H-H}$ = 6.4 Hz); 7.20 (br. s, 1H, C^5H in Im); 7.43-7.53 (m, 6H, *m*-, *p*-C_6H_5P); 7.68 (br. s, 1H, C^4H in Im); 7.82-7.89 (m, 4H, *O*–H in C_6H_5P); 8.80 (br. t, 1H, NH, $^3J_{H-H}$ = 5.4 Hz); 10.12 (br. s, 1H, N=CH–N). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 13.46 (CH_3), 21.93, 25.83, 28.28, 28.39, 28.89, and 29.54 (six s, CH_2 in octyl), 31.03 (CH_2CH_2N), 34.39 ($NHCH_2$), 39.80 (d, PCH_2, $^1J_{PC}$ = 65.3 Hz), 45.77 (N_{Im}–CH_2), 49.43 (N_{Im}–CH_2), 121.57 (C^4(Im)), 122.40 (C^5(Im)), 128.10 (d, *m*-C in C_6H_5, $^3J_{PC}$ = 12.1 Hz), 130.53 (d, *o*-C in C_6H_5, $^2J_{PC}$ = 9.9 Hz), 131.45 (*p*-C in C_6H_5), 131.66 (d, *ipso*-C in C_6H_5, $^1J_{PC}$ = 103.2 Hz), 136.46 (C^2(Im)), 165.12 (d, C(O), $^2J_{PC}$ = 5.5 Hz). IR (KBr): 513 (w), 521 (w), 701 (w), 727 (m), 747 (m), 1120 (m), 1166 & 1187 (s, $\nu_{P=O}$), 1308 (br), 1437 (m, ν_{CH_2}), 1553 & 1564 (s, ν_{NH}), 1649 (s, $\nu_{C=O}$), 2855 (s), 2929 (s), 3054 (s), 3138 (s), 3208 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{28}H_{39}BrN_3O_2P{\cdot}^1/_3CHCl_3$: C, 56.69; H, 6.60; N, 7.00; P, 5.16. Found: C, 56.85; H, 6.91; N, 7.21; P, 4.80.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-tetradecyl-1*H*-imidazol-3-ium bromide (4e). Yield: 94%. Mp 72-73 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.37. ^1H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, 3H, $CH_3(CH_2)_{12}CH_2$–N, $^3J_{H-H}$ = 6.9 Hz); 1.18-1.29 (m, 22H, $CH_3(CH_2)_{11}CH_2CH_2$–N); 1.82 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 5.9 Hz); 2.04 (appeared quintet, 2H, $CH_3(CH_2)_{11}CH_2CH_2$–N, $^3J_{H-H}$ = 5.4 Hz); 3.07 (appeared q, 2H, $CH_2NHC(O)$,$^3J_{H-H}$ = 6.5 Hz); 3.69 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.1 Hz); 4.16 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.7 Hz); 4.26 (t, 2H, $CH_3(CH_2)_{12}CH_2$–N, $^3J_{H-H}$ = 6.1 Hz); 7.23 (br. s, 1H, C^5H in Im); 7.40-7.48 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.75 (br. s, 1H, C^4H in Im);

7.80-7.87 (m, 4H, *O*–H in C_6H_5P); 8.77 (br. t, 1H, NH, $^3J_{H-H}$ = 5.6 Hz); 10.05 (br. s, 1H, N=CH–N). IR (KBr): 509 (m), 523 (m), 695 (m), 728 (m), 745 (m), 1120 (w), 1166 & 1188 (s, $\nu_{P=O}$), 1308 (br), 1437 (m, ν_{CH_2}), 1561 (s, ν_{NH}), 1664 (s, $\nu_{C=O}$), 2853 (m), 2924 (s), 3055 (s), 3235 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{34}H_{51}BrN_3O_2P$: C, 63.35; H, 7.97; N, 6.52; P, 4.80. Found: C, 63.17; H, 8.07; N, 6.49; P, 4.61.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-hexadecyl-1*H*-imidazol-3-ium bromide (4f). Yield: 87%. Mp 67-68 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.92. ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, 3H, $CH_3(CH_2)_{14}CH_2$–N, $^3J_{H-H}$ = 7.0 Hz); 1.17-1.33 (m, 26H, $CH_3(CH_2)_{13}CH_2CH_2$–N); 1.85 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 5.2 Hz); 2.08 (appeared quintet, 2H, $CH_3(CH_2)_{13}CH_2CH_2$–N, $^3J_{H-H}$ = 5.3 Hz); 3.10 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 5.3 Hz); 3.71 (d, 2H, PCH_2, $^2J_{P-H}$ = 12.9 Hz); 4.19 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.5 Hz); 4.30 (t, 2H, $CH_3(CH_2)_{14}CH_2$–N, $^3J_{H-H}$ = 6.6 Hz); 7.18 (br. s, 1H, C^5H in Im); 7.45-7.52 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.65 (br. s, 1H, C^4H in Im); 7.83-7.88 (m, 4H, *O*–C_6H_5P); 8.80 (br. s, 1H, NH); 10.15 (br. s, 1H, N=CH–N). IR (KBr): 509 (m), 523 (m), 695 (m), 728 (m), 1120 (w), 1166 & 1187 (s, $\nu_{P=O}$), 1308 (br), 1437 (s, ν_{CH_2}), 1466 (s), 1561 (s, ν_{NH}), 1664 (s, $\nu_{C=O}$), 2851 (m), 2923 (s), 3053 (s), 3235 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{36}H_{55}BrN_3O_2P$: C, 64.27; H, 8.24; N, 6.25; P, 4.60. Found: C, 64.31; H, 8.29; N, 6.11; P, 4.36.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-alkyl-1*H*-imidazol-3-ium chlorides (5c–f)

A mixture of 3-(1*H*-imidazol-1-yl)-1-propanamine **3** (3.3 mmol) and the corresponding alkyl chloride (3.9 mmol) in 8 mL of anhydrous CH_3CN was heated in a sealed tube on a boiling water bath for 160–170 h. The tube was opened and the solvent was removed *in vacuo*. The crude product was washed with a mixture of Et_2O–EtOH (10 : 1, 2 × 10 mL) and the residual solvent was removed *in vacuo*. Additional Et_2O (30 mL) was added to the crude product and the mixture was kept at −5 °C for 12 h. The obtained residue was filtered, washed with Et_2O (2 × 10 mL) and maintained in vacuum (2 mm Hg) at 40 °C for 2 h.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-hexyl-1*H*-imidazol-3-ium chloride (5c). Yield: 93%. Mp 159-161 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.82. ^1H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 3H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 6.2 Hz); 1.24-1.42 (m, 6H, $CH_3(CH_2)_3CH_2CH_2$–N); 1.82-1.97 (m, 2H, $CH_2CH_2NHC(O)$); 2.03-2.18 (m, 2H, $CH_3(CH_2)_3CH_2CH_2$–N); 3.14 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 3.6 Hz); 3.77 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.0 Hz); 4.26 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.6 Hz); 4.37 (t, 2H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 5.7 Hz); 7.24 (br. s, 1H, C^5H in Im); 7.49-7.56 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.67 (br. s, 1H, C^4H in Im); 7.89-7.95 (m, 4H, *O*-H in C_6H_5P); 9.36 (br. t, 1H, NH, $^3J_{H-H}$=5.0); 10.35 (br. s, 1H, N=CH–N). IR (KBr): 511 (m), 522 (m), 704 (m), 729 (m), 748 (m), 1185 & 1197 (s, $\nu_{P=O}$), 1226 (w), 1310 (br), 1439 (m, ν_{CH2}), 1550 & 1567 (m, ν_{NH}), 1649 (s, $\nu_{C=O}$), 2885 (s), 2950 (s), 3033 (s), 3090 (s), 3140 (s), 3192 (m) cm^{-1}. Anal. calcd for $C_{26}H_{35}ClN_3O_2P$: C, 63.99; H, 7.23; N, 8.61; P, 6.35. Found: C, 63.84; H, 7.24; N, 8.51; P, 6.37.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-octyl-1*H*-imidazol-3-ium chloride (5d). Yield: 84%. Mp 51-52 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.82. ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, 3H, $CH_3(CH_2)_6CH_2$–N, $^3J_{H-H}$ = 6.9 Hz); 1.26-1.39 (m, 10H, $CH_3(CH_2)_5CH_2CH_2$–N); 1.90 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 6.8 Hz); 2.10 (appeared quintet, 2H, $CH_3(CH_2)_5CH_2CH_2$–N, $^3J_{H-H}$ = 4.8 Hz); 3.13 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 5.5 Hz); 3.77 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.2 Hz); 4.26 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.8 Hz); 4.36 (t, 2H, $CH_3(CH_2)_6CH_2$–N, $^3J_{H-H}$ = 6.2 Hz); 7.24 (br. s, 1H, C^5H in Im); 7.51-7.61 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.69 (br. s, 1H, C^4H in Im); 7.88-7.95 (m, 4H, *O*–H in C_6H_5P); 9.35 (br. s, 1H, NH); 10.33 (br. s, 1H, N=CH–N). IR (KBr): 510 (m), 523 (m), 696 (m), 729 (m), 747 (m), 1120 (m), 1163 & 1189 (s, $\nu_{P=O}$), 1309 (m, br), 1437 (m, ν_{CH_2}), 1560 (s, ν_{NH}), 1663 (s, $\nu_{C=O}$), 2855 (s), 2927 (s), 2923 (s), 3054 (s), 3235 (br, ν_{NH}) cm^{-1}. Anal. calcd for $C_{28}H_{39}ClN_3O_2P$: C, 65.17; H, 7.62; N, 8.14; P, 6.00. Found: C, 64.71; H, 7.95; N, 8.14; P, 5.90.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-tetradecyl-1*H*-imidazol-3-ium chloride (5e). Yield: 87%. highly hygroscopic material. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.36. ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, 3H, $CH_3(CH_2)_{12}CH_2$–N, $^3J_{H-H}$ = 6.4 Hz); 1.19-1.39 (m, 22H, $CH_3(CH_2)_{11}CH_2CH_2$–N); 1.88 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 6.3 Hz); 2.06 (appeared quintet, 2H, $CH_3(CH_2)_{11}CH_2CH_2$–N, $^3J_{H-H}$ = 5.3 Hz); 3.10 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 4.8 Hz); 3.76 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.0 Hz); 4.22 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.5 Hz); 4.33 (t, 2H, $CH_3(CH_2)_{12}CH_2$–N, $^3J_{H-H}$ = 5.9 Hz); 7.29 (br. s, 1H, C^5H in Im); 7.46-7.56 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.81 (br. s, 1H, C^4H in Im); 7.88-7.94 (m, 4H, *O*–H in C_6H_5P); 9.33 (br. t, 1H, NH, $^3J_{H-H}$ = 5.0 Hz); 10.25 (br. s, 1H, N=CH–N). IR (KBr): 509 (m), 524 (m), 696 (m), 729 (m), 746 (m), 1121 (m), 1167 & 1186 (s, $\nu_{P=O}$), 1310 (m, br), 1437 & 1466 (m, ν_{CH_2}), 1562 (s, ν_{NH}), 1664 (s, $\nu_{C=O}$), 2853 (s), 2924 (s), 3056 (s), 3245 (m, ν_{NH}), 3412 (br, H_2O) cm^{-1}. Anal. calcd for $C_{34}H_{51}ClN_3O_2P{\cdot}1H_2O$: C, 66.05; H, 8.64; N, 6.80; P, 5.01. Found: C, 66.82; H, 8.83; N, 7.10; P, 5.14.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-hexadecyl-1*H*-imidazol-3-ium chloride (5f). Yield: 91%. Mp 59-60 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.53. ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, 3H, $CH_3(CH_2)_{14}CH_2$–N, $^3J_{H-H}$ = 7.1 Hz); 1.21-1.41 (m, 26H, $CH_3(CH_2)_{13}CH_2CH_2$–N); 1.89 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 5.9 Hz); 2.08 (appeared quintet, 2H, $CH_3(CH_2)_{13}CH_2CH_2$–N, $^3J_{H-H}$ = 5.5 Hz); 3.12 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 5.1 Hz); 3.77 (d, 2H, PCH_2, $^2J_{P-H}$ = 13.0 Hz); 4.24 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.5 Hz); 4.35 (t, 2H, $CH_3(CH_2)_{14}CH_2$–N, $^3J_{H-H}$ = 6.2 Hz); 7.26 (br. s, 1H, C^5H in Im); 7.47-7.55 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.75 (br. s, 1H, C^4H in Im); 7.88-7.95 (m, 4H, *O*–H in C_6H_5P); 9.36 (br. t, 1H, NH, $^3J_{H-H}$ = 5.4 Hz); 10.31 (br. s, 1H, N=CH–N). IR (KBr): 510 (m), 524 (m), 696 (m), 729 (m), 745 (m), 1104 (w), 1121 (w), 1167 & 1187 (s, $\nu_{P=O}$), 1310 (br), 1437 & 1466 (m, ν_{CH_2}), 1561 (s, ν_{NH}), 1663 (s, $\nu_{C=O}$), 2853 (s), 2927 (s), 2931 (s), 3060 (s), 3239 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{36}H_{55}ClN_3O_2P$: C, 68.82; H, 8.82; N, 6.69; P, 4.93. Found: C, 68.69; H, 8.91; N, 6.78; P, 4.87.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-alkyl-1*H*-imidazol-3-ium hexafluorophosphates (6a–f) (*general procedure*)

To a solution of the corresponding 1-[3-[[(diphenylphosphinyl)acetyl]amino]propyl]-3-alkyl-1*H*-imidazol-3-ium bromide (2 mmol) in anhydrous CH_3CN (7 mL) a solution of $NaPF_6$

(4 mmol) in anhydrous CH_3CN (10 mL) was added. The mixture was stirred at room temperature for 48 h. Then, the solvent was evaporated under reduced pressure and water was added to a solid residue (15 mL). The product was extracted into CH_2Cl_2 (3 × 15 mL) and the organic phase was washed with water (3 × 10 mL). The collected organic layers were dried over $MgSO_4$, filtered and the solvent was removed on a rotary evaporator. The ionic liquid was dried by heating at 55 °C under vacuum (2 mm Hg) for 4 h.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-ethyl-1*H*-imidazol-3-ium hexafluorophosphate (6a). Yield: 43%. Mp 128-129 °C. ^{31}P NMR (121.5 MHz, DMSO-d_6): δ 27.74; -144.09 (quintet, PF_6, $^1J_{P\text{-}F}$ = 710.8 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): δ –70.09 (d, PF_6, $^1J_{P\text{-}F}$ = 711.2 Hz). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.33 (t, 3H, CH_3CH$_2$–N, $^3J_{H\text{-}H}$ = 7.3 Hz); 1.88 (appeared quintet, 2H, CH_2CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 5.9 Hz); 2.98 (appeared q, 2H, CH_2NHC(O), $^3J_{H\text{-}H}$ = 6.4 Hz); 3.57 (d, 2H, PCH$_2$, $^2J_{P\text{-}H}$ = 13.7 Hz); 4.09 (t, 2H, CH_2CH$_2$CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 7.1 Hz); 4.16 (t, 2H, CH$_3$CH_2–N, $^3J_{H\text{-}H}$ = 7.1 Hz); 7.49-7.60 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.75 (br. s, 1H, C^{5}H in Im); 7.78-7.86 (m, 5H, *O*–H in C_6H_5P+C^{4}H in Im); 8.15 (br. t, 1H, NH, $^3J_{H\text{-}H}$ = 5.3 Hz); 9.13 (br. s, 1H, N=CH–N). IR (nujol): 509 (w), 525 (w), 558 (m), 696 (m), 729 (m), 842 (s), 1122 (w), 1166 & 1183 (s, $\nu_{P=O}$), 1439 (m, ν_{CH_2}), 1564 (m, ν_{NH}), 1664 (s, $\nu_{C=O}$), 3252 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{22}H_{27}F_6N_3O_2P_2$: C, 48.81; H, 5.03; N, 7.76; P, 11.44, F, 21.05. Found: C, 48.89; H, 5.07; N, 7.69; P, 11.30, F, 20.94.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-butyl-1*H*-imidazol-3-ium hexafluorophosphate (6b). Yield: 73%. Mp 57-58 °C. ^{31}P NMR (121.5 MHz, DMSO-d_6): δ 27.78; -144.07 (quintet, PF_6, $^1J_{P\text{-}F}$ = 712.8 Hz). ^{19}F NMR (282.4 MHz, DMSO-d_6): δ –70.09 (d, PF_6, $^1J_{P\text{-}F}$ = 711.2 Hz). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.90 (t, 3H, CH_3(CH$_2$)$_2$CH$_2$–N, $^3J_{H\text{-}H}$ = 7.5 Hz); 1.24 (sextet, 2H, CH$_3$CH_2CH$_2$CH$_2$–N); 1.73 (appeared quintet, 2H, CH_2CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 7.3 Hz); 1.93 (appeared quintet, 2H, CH$_3$CH$_2$CH_2CH$_2$–N, $^3J_{H\text{-}H}$ = 6.4 Hz); 3.02 (appeared q, 2H, CH_2NHC(O), $^3J_{H\text{-}H}$ = 6.2 Hz); 3.63 (d, 2H, PCH$_2$, $^2J_{P\text{-}H}$ = 13.7 Hz); 4.11 (t, 2H, CH_2CH$_2$CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 7.1 Hz); 4.22 (t, 2H, CH$_3$(CH$_2$)$_2$CH_2–N, $^3J_{H\text{-}H}$ = 6.6 Hz Hz); 7.54-7.64 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.80-7.90 (m, 6H, *O*–H in C_6H_5P+C^{5}H in Im+C^{4}H in Im); 8.21 (br. t, 1H, NH, $^3J_{H\text{-}H}$ = 5.5 Hz); 9.18 (br. s, 1H, N=CH–N). IR (nujol): 509 (w), 525 (w), 558 (m), 696 (w), 729 (w), 842 (s), 1122 (w), 1166 & 1183 (s, $\nu_{P=O}$), 1439 (m, ν_{CH_2}), 1564 (m, ν_{NH}), 1664 (s, $\nu_{C=O}$), 3252 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{24}H_{31}F_6N_3O_2P_2$: C, 50.62; H, 5.49; N, 7.38; P, 10.88; F, 20.02. Found: C, 50.74; H, 5.39; N, 7.29; P, 10.68; F, 19.87.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-octyl-1*H*-imidazol-3-ium hexafluorophosphate (6d). Yield: 81%. Mp 114-115 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.24; –144.30 (heptet, PF_6, $^1J_{P\text{-}F}$ = 708.8 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ –71.91 (d, PF_6, $^1J_{P\text{-}F}$ = 712.9 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, 3H, CH_3(CH$_2$)$_6$CH$_2$–N, $^3J_{H\text{-}H}$ = 6.8 Hz); 1.17-1.32 (m, 10H, CH$_3$(CH_2)$_5$CH$_2$CH$_2$–N); 1.80 (appeared quintet, 2H, CH_2CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 6.1 Hz); 1.95 (appeared quintet, 2H, CH$_3$(CH$_2$)$_5$CH_2CH$_2$–N, $^3J_{H\text{-}H}$ = 5.8 Hz); 3.11 (appeared q, 2H, CH_2NHC(O), $^3J_{H\text{-}H}$ = 5.8 Hz); 3.46 (d, 2H, PCH$_2$, $^2J_{P\text{-}H}$ = 12.8 Hz); 4.03 (t, 2H, CH_2CH$_2$CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 6.8 Hz); 4.06 (t, 2H, CH$_3$(CH$_2$)$_6$CH_2–N, $^3J_{H\text{-}H}$ = 7.5 Hz); 7.16 (br. s, 1H, C^{5}H in Im); 7.24 (br. s, 1H, NH); 7.36 (br. s, 1H, C^{4}H in Im); 7.46-7.50 (m, 4H, *m*-H in C_6H_5P); 7.52-7.56 (m, 2H, *p*-H in C_6H_5P); 7.72-7.77 (m, 4H, *O*–H in C_6H_5P); 8.81 (br. s, 1H, N=CH–N). IR (nujol): 506 (w), 529 (w), 558 (w), 730 (m), 841 (s), 1168 & 1181 (s, $\nu_{P=O}$), 1321 (m), 1440 (m, ν_{CH_2}), 1564 (m, ν_{NH}), 1659 (s, $\nu_{C=O}$), 3252 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{28}H_{39}F_6N_3O_2P_2\cdot 1H_2O$: C, 52.25; H, 6.42; N, 6.53; F, 17.71 Found: C, 52.72; H, 6.38; N, 6.45; F, 17.44.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-tetradecyl-1*H*-imidazol-3-ium hexafluorophosphate (6e). Yield: 80%. Mp 89-90 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.62; –144.30 (heptet, PF_6, $^1J_{P\text{-}F}$ = 708.5 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ –71.92 (d, PF_6, $^1J_{P\text{-}F}$ = 712.9 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, 3H, CH_3(CH$_2$)$_{12}$CH$_2$–N, $^3J_{H\text{-}H}$ = 7.0 Hz); 1.16-1.35 (m, 22H, CH$_3$(CH_2)$_{11}$CH$_2$CH$_2$–N); 1.71-1.83 (m, 2H, CH_2CH$_2$NHC(O)); 1.88-1.99 (m, 2H, CH$_3$(CH$_2$)$_{11}$CH_2CH$_2$–N); 3.03-3.17 (m, 2H, CH_2NHC(O)); 3.45 (d, 2H, PCH$_2$, $^2J_{P\text{-}H}$ = 12.8 Hz); 3.98-4.09 (m, 4H, CH_2CH$_2$CH$_2$NHC(O)+CH$_3$(CH$_2$)$_{12}$CH_2–N); 7.17 (br. s, 1H, C^{5}H in Im); 7.33 (br. t, 1H, NH, $^3J_{H\text{-}H}$ = 5.6 Hz); 7.36 (br.s, 1H, C^{4}H in Im); 7.41-7.48 (m, 4H, *m*-H in C_6H_5P); 7.49-7.56 (m, 2H, *p*-H in C_6H_5P); 7.71-7.76 (m, 4H, *O*–H in C_6H_5P); 8.82 (br. s, 1H, N=CH–N). IR (nujol): 507 (w), 529 (w), 558 (w), 840 (s), 1169 & 1182 (s, $\nu_{P=O}$), 1439 (m, ν_{CH2}), 1565 (m, ν_{NH}), 1659 (s, $\nu_{C=O}$), 3252 (m, ν_{NH}) cm^{-1}. Anal. calcd for $C_{34}H_{51}F_6N_3O_2P_2$: C, 57.54; H, 7.24; N, 5.92; P, 8.73; F, 16.06. Found: C, 57.31; H, 7.29; N, 5.85; P, 8.65; F, 15.88.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-hexadecyl-1*H*-imidazol-3-ium hexafluorophosphate (6f). Yield: 88%. Mp 96-97 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.71, –144.20 (quintet, PF_6, $^1J_{P\text{-}F}$ = 712.8 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ –72.00 (d, PF_6, $^1J_{P\text{-}F}$ = 712.9 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, 3H, CH_3(CH$_2$)$_{14}$CH$_2$–N, $^3J_{H\text{-}H}$ = 6.9 Hz); 1.21-1.39 (m, 26H, CH$_3$(CH_2)$_{13}$CH$_2$CH$_2$–N); 1.85 (appeared quintet, 2H, CH_2CH$_2$NHC(O), $^3J_{H\text{-}H}$ = 6.2 Hz); 2.01 (appeared quintet, 2H, CH$_3$(CH$_2$)$_{13}$CH_2CH$_2$–N, $^3J_{H\text{-}H}$ = 5.5 Hz); 3.17 (appeared q, 2H, CH_2NHC(O), $^3J_{H\text{-}H}$ = 5.5 Hz); 3.52 (d, 2H, PCH$_2$, $^2J_{P\text{-}H}$ = 13.0 Hz); 4.08-4.13 (m, 4H, CH_2CH$_2$CH$_2$NHC(O)+CH$_3$(CH$_2$)$_{14}$CH_2-N); 7.23 (br. s, 1H, C^{5}H in Im); 7.44 (br. s, 2H, C^{4}H in Im+NH); 7.50-7.62 (m, 6H, *m*-, *p*-H in C_6H_5P); 7.78-7.84 (m, 4H, *O*-H in C_6H_5P); 8.93 (br. s, 1H, N=CH–N). IR (nujol): 508 (w), 529 (w), 558 (m), 695 (w), 730 (w), 742 (w), 838 (s), 857 (s), 1123 (w), 1181 (s, $\nu_{P=O}$), 1439 (m, ν_{CH_2}), 1565 (m, ν_{NH}), 1659 (s, $\nu_{C=O}$), 3256 (m) cm^{-1}. Anal. calcd for $C_{36}H_{55}F_6N_3O_2P_2$: C, 58.61; H, 7.51; N, 5.70; P, 8.40; F, 15.45. Found: C, 59.07; H, 7.79; N, 5.12; P, 7.77; F, 15.27.

1-[3-[[(Diphenylphosphinyl)acetyl]amino]propyl]-3-hexyl-1*H*-imidazol-3-ium hexafluorophosphate (6c). A solution of 1-[3-[[(diphenylphosphinyl)acetyl]amino]propyl]-3-hexyl-1*H*-imidazol-3-ium bromide (2 mmol), $NaPF_6$ (4 mmol) and water (15 mL) was stirred at room temperature for 48 h. The product was extracted into CH_2Cl_2 (3 × 15 mL) and the organic phase was washed with water (3 × 10 mL). The collected organic layers were dried over $MgSO_4$, filtered and the solvent was removed on a rotary evaporator. The ionic liquid was dried by heating at 55 °C under vacuum (2 mm Hg) for 4 h. Yield: 87%. Mp 154-155 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.37; –144.31 (heptet, PF_6, $^1J_{P\text{-}F}$ = 708.7 Hz). ^{19}F NMR (282.4 MHz, $CDCl_3$: δ –72.17 (d, PF_6, $^1J_{P\text{-}F}$ = 712.9 Hz). ^{1}H NMR (400 MHz, $CDCl_3$):

δ 0.86 (t, 3H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 6.8 Hz); 1.24-1.31 (m, 6H, $CH_3(CH_2)_3CH_2CH_2$–N); 1.81 (appeared quintet, 2H, $CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.6 Hz); 1.97 (appeared quintet, 2H, $CH_3(CH_2)_3CH_2CH_2$–N, $^3J_{H-H}$ = 6.4 Hz); 3.13 (appeared q, 2H, $CH_2NHC(O)$, $^3J_{H-H}$ = 5.7 Hz); 3.47 (d, 2H, PCH_2, $^2J_{P-H}$ = 12.8 Hz); 4.04-4.09 (m, 4H, $CH_2CH_2CH_2NHC(O)$ + $CH_3(CH_2)_4CH_2$–N); 7.16 (t, 1H, C^5H in Im, $^3J_{H-H}$ = 1.7 Hz); 7.37 (t, 1H, C^4H in Im, $^3J_{H-H}$ = 1.7 Hz); 7.41 (br. t, 1H, NH, $^3J_{H-H}$ = 5.2 Hz); 7.46-7.50 (m, 4H, *m*-H in C_6H_5P); 7.53-7.57 (m, 2H, *p*-H in C_6H_5P); 7.73-7.78 (m, 4H, *O*–H in C_6H_5P); 8.95 (br. s, 1H, N=CH–N). ^{13}C NMR (100.61 MHz, CD_3CN): δ 13.11 (CH_3), 21.96, 25,25, 29.13, 29.29 (four s, CH_2 in hexyl), 30.62 (CH_2CH_2N), 34.84 ($NHCH_2$), 38.41 (d, PCH_2, $^1J_{PC}$ = 62.4 Hz), 46.01 (N_{Im}–CH_2), 49.42 (N_{Im}–CH_2), 122.06 (C^4(Im)), 122.30 (C^5(Im)), 128.71 (d, *m*-C in C_6H_5, $^3J_{PC}$ = 11.7 Hz), 130.54 (d, *o*-C in C_6H_5, $^2J_{PC}$ = 9.5 Hz), 131.91 (*p*-C in C_6H_5), 132.42 (d, *ipso*-C in C_6H_5, $^1J_{PC}$ = 102.7 Hz), 135.64 (C^2(Im)), 165.07 (d, C(O), $^2J_{PC}$ = 5.9 Hz). IR (nujol): 818 (s), 842 (s), 1171 &1182 (s, $\nu_{P=O}$), 1441 (m, ν_{CH_2}), 1572 (m, ν_{NH}), 1657 (s, $\nu_{C=O}$), 2922, 2959, 3253 cm^{-1}. Anal. calcd for $C_{26}H_{35}F_6N_3O_2P_2$: C, 52.26; H, 5.90; N, 7.03; F, 19.08. Found: C, 52.45; H, 5.85; N, 6.91, F, 18.66.

Preparation of complexes 7a,b

An ethanolic solution (4 mL) of the corresponding metal salt (0.098 mmol) was added dropwise to a solution of the ligand **4c** (119.4 mg, 0.2 mmol) in 4 mL of C_2H_5OH (the ratio L : M = 2 : 1). The resulting mixture was left under ambient conditions for 2 h and evaporated to a volume of ~1 mL. Addition of ether (5 mL) to the reaction solution afforded precipitation of the corresponding complexes which were filtered off, washed with 10 mL of Et_2O and dried in vacuum.

[Eu{bis[1-[3-[[(diphenylphosphinyl)acetyl]amino]propyl]-3-hexyl-1*H*-imidazol-3-ium]}Br_2Cl_3] 7a. Yield: 56% (white solid). Mp 78-81 °C. ^{31}P NMR (121.5 MHz, CD_3OH): δ 3.06. ^{1}H NMR (300 MHz, CD_3OH): 0.99 (t, 3H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 6.8 Hz); 1.37-1.52 (m, 6H, $CH_3(CH_2)_3CH_2CH_2$–N); 2.05 (appeared q, 2H, $CH_3(CH_2)_3CH_2CH_2$–N, $^3J_{H-H}$ = 6.9 Hz); 2.41-2.67 (m, 4H, $CH_2CH_2NHC(O)$ + $CH_2NHC(O)$); 4.08 (br. s, 2H, PCH_2); 4.40 (t, 2H, $CH_2CH_2CH_2NHC(O)$, $^3J_{H-H}$ = 7.3 Hz); 4.86 (t, 2H, $CH_3(CH_2)_4CH_2$–N, $^3J_{H-H}$ = 6.8 Hz); 4.99 (br. s, 1H, NH); 6.73-6.91 (m, 4H, *O*–H in C_6H_5P); 7.24-7.34 (m, 4H, *m*-H in C_6H_5P); 7.52-7.57 (m, 2H, *p*-H in C_6H_5P); 7.87 (br. s, 1H, C^5H in Im); 8.06 (br. s, 1H, C^4H in Im); 9.50 (br. s, 1H, N=CH–N). IR (KBr, cm^{-1}): 507, 528, 694, 735, 1095, 1124, 1161 ($\nu_{P=O}$), 1438 (ν_{CH_2}), 1563 (ν_{NH}), 1588, 1628 ($\nu_{C=O}$), 2858, 2930, 3056, 3205 (ν_{NH}), 3348. Anal. calcd for $C_{52}H_{70}Br_2Cl_3EuN_6O_4P_2$: C, 47.20; H, 5.33; N, 6.35. Found: C, 47.18; H, 5.38; N, 6.41.

[Eu{bis[1-[3-[[(diphenylphosphinyl)acetyl]amino]propyl]-3-hexyl-1*H*-imidazol-3-ium]}$Br_2(NO_3)_3$] 7b. Yield: 78%, white solid, Mp. 87-89 °C. ^{31}P NMR (121.5 MHz, EtOH): δ −12.36. IR (nujol, cm^{-1}): 507 (w), 528 (w), 695 (w), 737 (m), 1031 (w, νas(NO_2)), 1097 (w), 1124, 1138, 1162 (s, $\nu_{P=O}$), 1314 (s, νas(NO_2)), 1438 (s, ν_{CH_2}), 1470 (s, ν(N=O)), 1563 (m, ν_{NH}), 1588, 1628 (s, $\nu_{C=O}$), 3055 (ν_{NH}), 3348. Anal. calcd for $C_{52}H_{70}Br_2Cl_3EuN_6O_4P_2$: C, 47.20; H, 5.33; N, 6.35. Found: C, 47.18; H, 5.38; N, 6.41. Anal. calcd for $C_{52}H_{70}Br_2EuN_9O_{13}P_2$: C, 44.52; H, 5.03; N, 8.99. Found: C, 44.57; H, 5.09; N, 8.79.

Solid-state structures of ionic liquids

Crystals of **4d** and **6c** suitable for X-ray diffraction were grown by recrystallization from EtOAc–Et_2O–EtOH (**4d**) and EtOH (**6c**) at −20 °C. X-Ray diffraction experiments were carried out with a Bruker SMART APEX2 CCD using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 120 K. The structures were solved by direct methods and refined by the full-matrix least-squares against F^2 in anisotropic approximation for no-hydrogen atoms. Hydrogen atoms of NH groups were located from the Fourier density synthesis and refined in isotropic approximation. The H(C) atom positions in these structures were calculated and refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5 $U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are, respectively, the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded. In the case of **4d**, the hydrogen atom of OH group of the solvent ethanol molecule hasn't been localized due to its strong disorder. Crystal data and structure refinement parameters for **4d** and **6c** are given in Table S2 (see ESI†). All calculations were performed using the SHELXTL software.[22] CCDC reference numbers 758107 (**4d**) and 758108 (**6c**). For crystallographic data in CIF format or other electronic formate see the ESI.†

Recovery of actinides and rare-earth elements by solid phase extractants

For the preparation of sorbents, the solid matrixes of polyacrylonitrile fiber (discs, 1 cm diameter, m = 10 g) and multi-walled carbon nanotubes Taunite® (20 mg, Russia) were treated by solutions of FILs (30 mg) in dichloroethane or ethanol (0.5 ml) followed by air drying. In experiments, radio-chemical isotopes ^{239}Pu and $^{152-154}$Eu radionuclides purchased from "Isotop" company (Russia) were used. The experiments were performed under static conditions at the aqueous phase, volume 2 mL (3 M HNO_3). The aqueous solution of the corresponding radionuclide (concentration ranged from 2×10^{-5} to 4×10^{-5} mol L^{-1}) together with a sample of the sorbent was stirred for 2 h. As was found previously, this is a time which is longer than that required for the system to reach equilibrium. The sorption activity was estimated on the basis of radionuclide recovery (%) determined by radioactivity before and after the experiment using an "Alpha Analyst" (Canberra) instrument and radiometer UMF-2000 (Russia). The experiments were done in the radiochemical laboratory of Vernadsky Institute of Geochemistry and Analytical Chemistry RAS having the corresponding license.

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