Electronic Supporting Information

Homogeneous liquid-liquid extraction of metal ions with non-fluorinated bis(2-ethylhexyl)phosphate ionic liquids having a lower critical solution temperature in combination with water

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Experimental Section

Chemicals

Tri-*n*-butylphosphine (97%), 2-chloroethyl methyl ether (98%), bis(2-ethylhexyl)phosphate (97%), chloroform (ACS grade), triethylene glycol monomethyl ether (97%), zinc chloride (reagent grade 98%), cobalt chloride (97%), nickel chloride (98%) and magnesium sulphate hydrate were bought from Sigma-Aldrich (Diegem, Belgium). Heptane (99%) and hydrogen peroxide (35 wt%) were purchased from Chem-Lab (Zedelgem, Belgium). Acetonitrile (HPLC grade), ethanol absolute, dichloromethane (analytical reagent grade) and sodium hydroxide were obtained from Fisher Scientific Limited (Loughborough, UK). Pyridine was acquired from BDH Laboratory Supplies. 2-(2-methoxyethoxy)ethanol (99%), copper chloride (99%) and thionyl chloride (99.7%) were bought from Acros Organics (Geel, Belgium). All chemicals were used without purification.

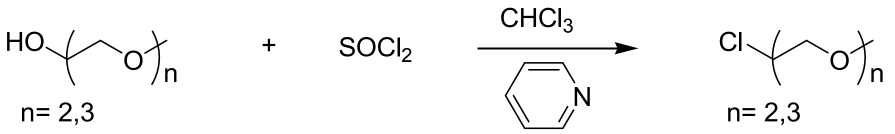
General Techniques

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^{1}H, 75 MHz for ^{13}C). ^{31}P NMR spectra were recorded on a Bruker AMX 400 spectrometer operating at 162 MHz. The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ^{1}H and ^{13}C and to 85% H_3PO_4 for ^{31}P NMR. The coupling constants are given in Hertz. Solutions were made in $CDCl_3$. The spectra were analyzed with SpinWorks software. Fourier transform infrared spectra of the ILs were recorded by a Bruker Vertex 70 spectrometer. The attenuated total reflectance (ATR) technique was used for direct examination of the ionic liquids (Bruker ATR platinum sample holder). OPUS software was used for the analysis. The elemental analysis of carbon, hydrogen and nitrogen was performed on a CE-instruments EA-1110 elemental analyzer. The water content was determined by coulometric Karl Fischer titration using a Mettler-Toledo DL39 titrator. The viscosity of the ionic liquids was measured using an automatic Brookfield plate cone viscometer, Model LVDV-II CP (Brookfield Engineering Laboratories, USA). ESI-MS was performed on a Thermo Electron LCQ Advantage ion trap mass spectrometer connected to Agilent 1100 HPLC system coupled to Xcalibur data system. Extraction experiments were performed in a TMS-200 thermoshaker (Nemux Life). Extraction mixtures were centrifuged using a Heraeus Labofuge 200. A Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal concentrations in both aqueous and organic (ionic liquid) phase as well as for the determination of the chloride content of the ionic liquids. For the sample preparation, plastic microtubes were filled with a small amount of aqueous solution (100 mg) or IL sample (10−50 mg), gallium as internal standard (100 or 50 mg) and water or ethanol (800 µL). The microtubes were then vigorously shaken on a vibrating plate (IKA MS 3 basic). Finally, a 5 µL drop of this solution was put on a quartz plate, previously treated with a silicone/isopropanol solution (Serva®) to avoid spreading of the sample droplet on the quartz plate. The quartz plates were then dried for 30 min at 60 °C prior to analysis. Each sample was measured for 200 s.

Synthesis

Precursor synthesis

Triethylene glycol monomethylether or 2-(2-methoxyethoxy)ethanol were used in the synthesis of the chloride precursors, a literature procedure was followed (Scheme S1).[1,2] A solution of thionyl chloride (1.5 mol eq., 75 mmol) in 10 mL of chloroform was added slowly to a stirred solution of triethylene glycol monomethylether or 2-(2-methoxyethoxy)ethanol (1 mol eq., 50 mmol) and pyridine (1 mol eq., 50 mmol) in 20 mL of chloroform under argon atmosphere. The mixture was refluxed at 60 °C for four hours and then washed four times with water. The organic layer was dried with $MgSO_4$, filtered and the solvent was evaporated. The product was fully dried at the Schlenk line.



Scheme S1. Synthesis of chloride precursors.

These compounds have been described previously and the spectral data are matching with our findings.

1-(2-methoxyethoxy)-2-chloroethane (E_2Cl)

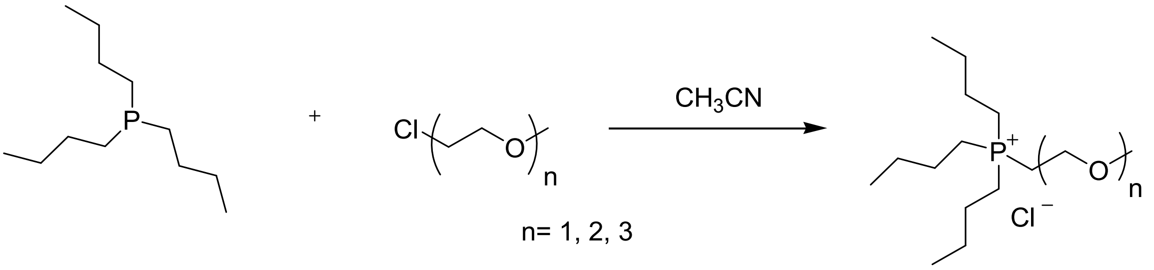
Light brown liquid (2.611 g , 18.84 mmol, 38%). ^1H NMR (300 MHz, δ, $CDCl_3$): 3.79-3.74 (2H, m, CH_2), 3.69-3.63 (4H, m, 2 CH_2), 3.58-3.55 (2H, m, CH_2), 3.40 (3H, s, CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 71.94 (CH_2), 71.37 (CH_2), 70.67 (CH_2), 70.62 (CH_2), 70.61 (CH_2), 59.06 (CH_3), 42.71 (CH_2-Cl). FTIR-ATR: (ν/cm^{-1}): 2877, 1455, 1353, 1200, 1103, 850, 745, 665. CHN analysis: (calculated for $C_5H_{11}ClO_2$): C 43.82% (43.33%), H 8.30% (8.00%), N 0% (0%).

2-[2-(2-methoxyethoxy)ethoxy]ethylchloride (E_3Cl)

Yellow liquid (6.303 g, 34.5 mmol, 69%). ^1H NMR (300 MHz, δ, $CDCl_3$): 3.78 (2H, t, 6.0 Hz, CH_2), 3.68 (8H, m, 4 CH_2), 3.57 (2H, m, CH_2), 3.39 (3H, s, CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 71.94 (CH_2), 71.37 (CH_2), 70.67 (CH_2), 70.62 (CH_2), 70.61 (CH_2), 59.06 (CH_3), 42.71 (CH_2-Cl). FTIR-ATR: (ν/cm^{-1}): 2874, 1455, 1353, 1200, 1103, 850, 745, 665. CHN analysis: (calculated for $C_7H_{15}ClO_3$): C 45.67% (46.03%), H 9.93% (8.28%), N 0% (0%).

Ether-functionalised IL synthesis

Ether-functionalisation was incorporated in the phosphonium ionic liquids according to literature procedures.[1,3,4] Tri-*n*-butyl phosphine was reacted with the organic halide containing the desired ether functional group (Scheme S2). A mixture of tri-*n*-butyl phosphine (1 mol eq., 10 mmol) and oligo ethylene oxide chloride precursor (1 mol eq., 10 mmol) in 15 mL of acetonitrile was refluxed for 48 h. On completion, the acetonitrile was evaporated under reduced pressure at 60 °C. The product was washed with 10 mL of heptane under reflux for 1 h. The upper heptane phase was decanted and the process was repeated four times. The product was fully dried at the Schlenk line.



Scheme S2. Synthesis of ether-functionalised ionic liquids.

These compounds have been described previously and the spectral data are matching with our findings.

Tri-*n*-butyl-2-methoxyethylphosphonium chloride

[$P_{444}E_1$][Cl]

Colorless viscous liquid (65%). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.85 (2H, m, CH_2), 3.35 (3H, s, CH_3), 3.00 (2H, m, CH_2), 2.43 (6H, m, 3 CH_2), 1.54 (12H, m, 6 CH_2), 0.98 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 65.96 (CH_2), 65.86 (CH_2), 58.97 (CH_3), 24.11 (CH_2), 21.51 (CH_2), 20.84 (CH_2), 20.04 (CH_2), 19.42 (CH_2), 13.49 (CH_3). ^{31}P NMR (162 MHz, δ, $CDCl_3$): 34.27. FTIR-ATR: (ν/cm^{-1}): 2958, 2931, 2872, 1722, 1463, 1381, 1235, 1189, 1097, 958, 917, 812, 723. CHN analysis: (calculated for $C_{15}H_{34}ClOP{\cdot}H_2O$): C 57.22% (57.00%), H 11.93% (11.52%), N 0% (0%).

Tri-*n*-butyl[2-(2-methoxyethoxy)ethyl]phosphonium chloride

[$P_{444}E_2$][Cl]

Light brown viscous liquid (69%). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.90 (2H, m, CH_2), 3.62 (2H, m, CH_2), 3.49 (2H, m, CH_2), 3.34 (3H, s, CH_3), 3.06 (2H, m, CH_2), 2.44 (6H, m, 3 CH_2), 1.53 (12H, m, 6 CH_2), 0.98 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 71.40 (CH_2), 70.20 (CH_2), 58.95 (CH_3), 24.00 (CH_2), 19.49 (CH_2), 13.67 (CH_3). ^{31}P NMR (162 MHz, δ, $CDCl_3$): 34.22. FTIR-ATR: (ν/cm^{-1}): 2958, 2931, 2872, 1722, 1464, 1381, 1238, 1198, 1098, 970, 906, 809, 741. CHN analysis: (calculated for $C_{17}H_{38}ClO_2P$): C 59.15% (59.89%), H 11.42% (11.24%), N 0% (0%).

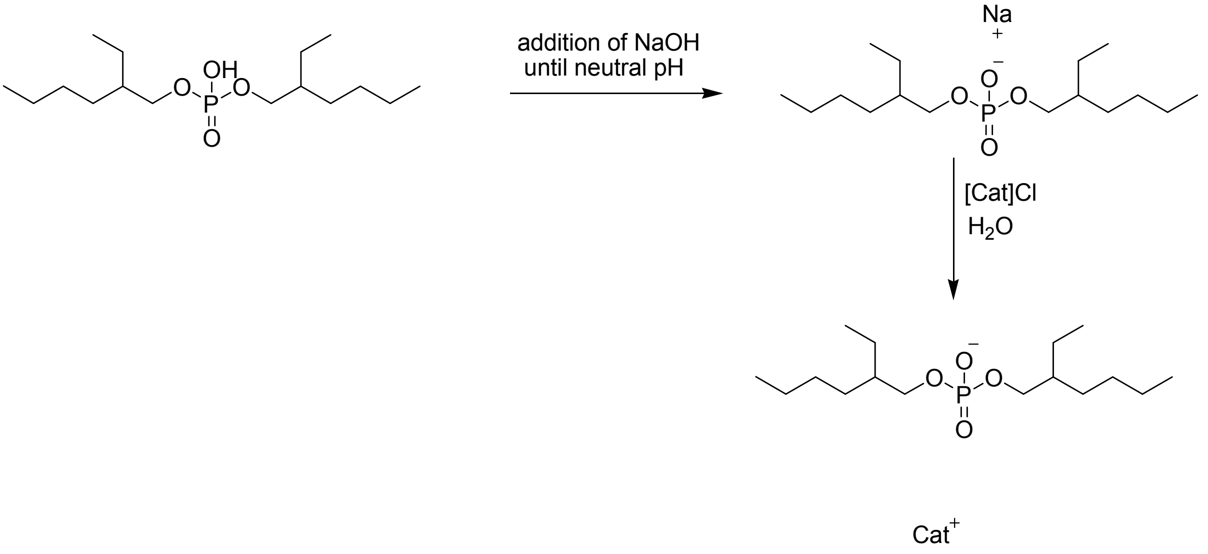
Tri-*n*-butyl-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphonium chloride

[$P_{444}E_3$][Cl]

Light yellow viscous liquid (57%). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.55 (2H, m, CH_2), 3.50 (6H, m, 3 CH_2), 3.41 (2H, m, CH_2), 3.24 (3H, s, CH_3), 2.58 (2H, m, CH_2), 2.20 (6H, m, 3 CH_2), 1.53-1.35 (12H, m, 6 CH_2), 0.88 (9H, t, 7.0 Hz, 3 CH_3). ^{13}C NMR (75 MHz, δ, DMSO-d_6): 71.20 (CH_2), 69.42 (CH_2), 58.00 (CH_3), 23.39 (CH_2), 22.63 (CH_2), 18.39 (CH_2), 17.73 (CH_2), 13.17 (CH_3). ^{31}P NMR (162 MHz, δ, $CDCl_3$): 34.22. FTIR-ATR: (ν/cm^{-1}): 2958, 2931, 2872, 1464, 1381, 1350, 1236, 1198, 1101, 1012, 969, 920, 810, 723. CHN analysis: (calculated for $C_{18}H_{40}ClO_3P{\cdot}H_2O$): C 55.41% (55.58%), H 11.23% (10.88%), N 0% (0%).

Bis(2-ethylhexyl)phosphate anion exchange reaction

The synthesis of the ILs was performed by a metathesis reaction in which the chloride anion of the ether-functionalised ILs was exchanged to the bis(2-ethylhexyl)phosphate (Scheme S3). First, the acid form of the phosphate is neutralised by a base, as found in the literature.[5] To bis(2-ethylhexyl)phosphate in ethanol absolute was added a solution of 20 wt% NaOH until neutral pH was reached. The solvent was evaporated and the product dried in the vacuum oven at 60 °C for 2h. The phosphate salt (1 mol eq) and the chloride ionic liquid (1.5 mol eq) were dissolved in water and stirred overnight. Dichloromethane was added and the product was extracted to the organic phase and washed with water to remove NaCl and the excess of ionic liquid. The organic phase was isolated and evaporated.



Scheme S3. Synthesis of dialkylphosphate ILs.

Tri-*n*-butyl-2-methoxyethylphosphonium bis(2-ethylhexyl)phosphate

[$P_{444}E_1$][DEHP]

Colorless liquid (89 %). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 3.87 (2H, m, CH_2), 3.69 (4H, m, 2 CH_2), 3.33 (3H, s, CH_3), 2.98 (2H, m, 2 CH), 2.35 (6H, m, 3 CH_2), 1.52 (18H, m, 6 CH_2 + 2 CH), 1.27 (12H, m, 6 CH_2), 0.97 (9H, t, 3 CH_3)), 0.87 (12H, m, 4 CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 67.27 (CH_2), 66.07 (CH_2), 58.75 (CH_3), 40.56 (CH_2), 30.20 (CH_2), 29.13 (CH_2), 24.12 (CH_2), 23.91 (CH_2), 23.85 (CH_2), 23.78 (CH_2), 23.42 (CH_2), 23.18 (CH_2), 19.75 (CH_2), 19.12 (CH_2), 14.14 (CH_3), 13.47 (CH_3), 11.03 (CH_3). ^{31}P NMR (162 MHz, δ, $CDCl_3$): 33.64, 0.65. FTIR-ATR: (ν/cm^{-1}): 2958, 2928, 2873, 1462, 1380, 1244, 1054, 810, 532. Cl content:

195 ppm. CHN analysis: (calculated for $C_{31}H_{68}O_5P_2 \cdot H_2O$): C 61.91% (61.97%), H 13.27% (11.74%), N 0% (0%). ESI-MS (MeOH): *m/z* 322.5 (DEHP), 263.4 ($P_{444}E_1$).

Tri-*n*-butyl[2-(2-methoxyethoxy)ethyl]phosphonium bis(2-ethylhexyl)phosphate

[$P_{444}E_2$][DEHP]

Light yellow liquid (97%). ^1H NMR (300 MHz, δ, $CDCl_3$): 3.87 (2H, m, CH_2), 3.69 (4H, m, 2 CH_2), 3.59 (2H, m, CH_2), 3.48 (2H, m, CH_2), 3.34 (3H, s, CH_3), 2.99 (2H, m, 2 CH), 2.35 (6H, m, 3 CH_2), 1.52 (18H, m, 6 CH_2 + 2 CH), 1.29 (12H, m, 6 CH_2), 0.97 (9H, t, 3 CH_3) , 0.87 (12H, m, 4 CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 71.46 (CH_2), 70.09 (CH_2), 67.46 (CH_2), 64.55 (CH_2), 58.72 (CH_3), 40.55 (CH_2), 30.19 (CH_2), 29.12 (CH_2), 24.14 (CH_2), 23.94 (CH_2), 23.85 (CH_2), 23.79 (CH_2), 23.18 (CH_2), 21.20 (CH_2), 19.72 (CH_2), 19.09 (CH_2), 14.15 (CH_3), 13.48 (CH_3), 11.03 (CH_3). ^{31}P NMR (162 MHz, δ $CDCl_3$): 33.56, 0.72. FTIR-ATR: (ν/cm^{-1}): 2958, 2928, 2873, 1462, 1380, 1246, 1053, 809, 554. Cl content: 165 ppm. CHN analysis: (calculated for $C_{33}H_{72}O_6P_2 \cdot 2H_2O$): C 59.78% (59.79%), H 11.44% (11.56%), N 0% (0%). ESI-MS (MeOH): *m/z* 322.5 (DEHP), 307.9 ($P_{444}E_2$).

Tri-*n*-butylephosphonium bis(2-ethylhexyl)phosphate

[$P_{444}E_3$][DEHP]

Light yellow liquid (89 %). ^1H NMR (300 MHz, δ, $CDCl_3$): 3.91 (2H, m, CH_2), 3.69 (4H, m, 2 CH_2), 3.58 (6H, m, 3 CH_2), 3.51 (2H, m, CH_2), 3.36 (3H, s, CH_3), 2.98 (2H, m, CH_2), 2.35 (6H, m, 3 CH_2), 1.49 (18H, m, 6 CH_2 + 2 CH), 1.30 (12H, m, 6 CH_2), 0.97 (9H, t, 3 CH_3), 0.87 (12H, m, 4 CH_3). ^{13}C NMR (75 MHz, δ, $CDCl_3$): 71.95 (CH_2), 70.36 (CH_2), 70.16 (CH_2), 67.50 (CH_2), 58.97 (CH_3), 40.59 (CH_2), 30.23 (CH_2), 29.16 (CH_2), 24.17 (CH_2), 23.96 (CH_2), 23.90 (CH_2), 23.83 (CH_2), 23.46 (CH_2), 23.20 (CH_2), 19.76 (CH_2), 19.13 (CH_2), 14.16 (CH_3), 13.52 (CH_3), 11.05 (CH_3). ^{31}P NMR (162 MHz, δ, $CDCl_3$): 33.55, 0.62. FTIR-ATR: (ν/cm^{-1}): 2957, 2928, 2873, 1462, 1245, 1094, 1053, 810, 530. Cl content: 341 ppm. CHN analysis:

(calculated for $C_{35}H_{76}O_7P_2 \cdot H_2O$): C 59.41% (59.46%), H 11.15% (11.41%), N 0% (0%). ESI-MS (MeOH): *m/z* 322.5 (DEHP), 352.5 ($P_{444}E_3$).

Viscosities of chloride ether-functionalised ILs

Interestingly, for the chloride ionic liquids, a decrease in viscosity with longer oligoethylene chain is seen. Viscosities were listed in Table 1: This is in contrast with the typically found increase in viscosity with increasing alkane chain length in other ionic liquids, which can be explained by a combination increasing intermolecular Van der Waals forces and higher molecular mass, both reducing the ionic mobility.[6] Apparently, the interaction between chains with multiple "oxygen orbitals" is sterically conflicting with close packing, thus reducing intermolecular attraction. This mobility enhancing effect is apparently dominating the mobility reducing effect of increasing mass.

Transmission measurements

A CW 532-nm laser (Samba 100, Cobolt®) was used as probe laser. The transmitted light was collected by a lens and sent to a photodetector (read by an HP34401A multimeter). The sample cell was situated inside an optical cryostat (Optistat-DN-V, Oxford Instruments®), where the temperature could be regulated by an accompanying temperature controller (ITC 503, Oxford Instruments®). In order to account for possible temperature differences between the cold finger and the sample, a resistive PT1000 thermometer, read by a second HP34401A® multimeter, was attached to the sample cuvette, monitoring its temperature nearby the region of the probe beam. In the setup, all the instruments were connected to one PC via GPIB interface.

For each sample (1:1weight ratio of IL:water), one temperature scan was performed in steps of 0.1 K. At each temperature 100 pairs of temperature-transmitted light intensity were recorded for averaging. Examples of transmission curves are shown in Figure S1.

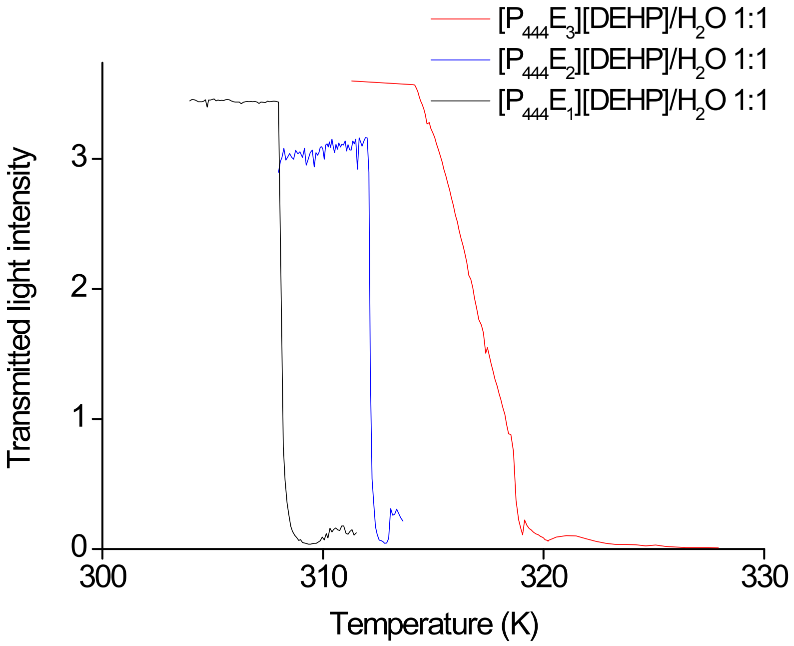


Figure S1. Temperature dependence of transmitted intensity for three binary mixtures of IL and water (1:1 wt/wt).

Quantitative ^1H NMR measurements

The amount of IL that is lost into the IL phase was determined by quantitative ^{1}H-NMR. To 100 mg of the water layer of presaturation of the IL was added 5 mg of pyridine to obtain approximately equimolar concentrations to the aliquot of water presaturated with the IL. Pyridine was chosen as internal standard since there is no overlap with the ^{1}H NMR spectrum of the ionic liquid. The ^{1}H NMR spectrum of the water sample was recorded and the relative concentration versus pyridine and the absolute concentration of $[P_{444}E_3][DEHP]$were calculated by integration of the peaks.

Extraction measurements

In the extraction experiments, 500 mg of the presaturated IL was typically contacted with 500 mg of an aqueous metal solution. The mixtures were cooled in an ice bath for several minutes to reach the homogeneous region. As can be seen in Figure S2, after 5 minutes, no significant changes in the percentage extraction (%*E*) (eq 1) could be observed. Next, the mixtures were left to settle at room temperature for 10 min. A sample was taken from the aqueous layer and analysed for its metal content by TXRF.

$$\%E = \frac{c_{org} \cdot m_{org}}{c_{org} \cdot m_{org} + c_{aq} \cdot m_{aq}} \times 100\% \tag{1}$$

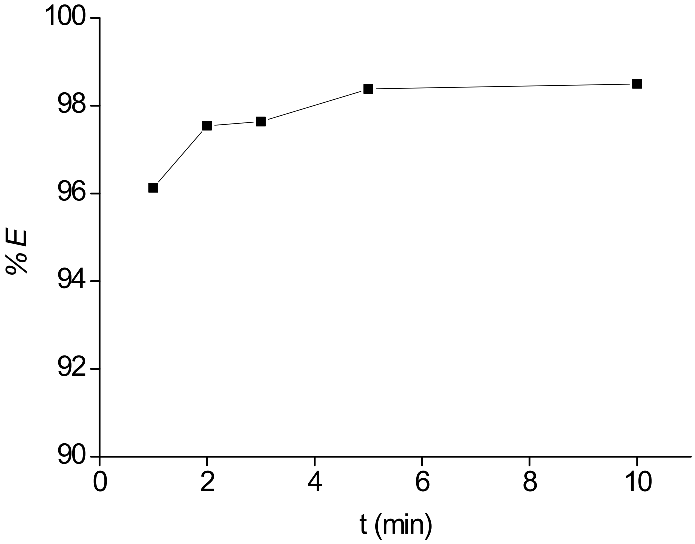


Figure S2. Percentage extraction as a function of time in the ice bath. (Co(II) concentration: 6866 ppm, pH_{eq}= 3.39).

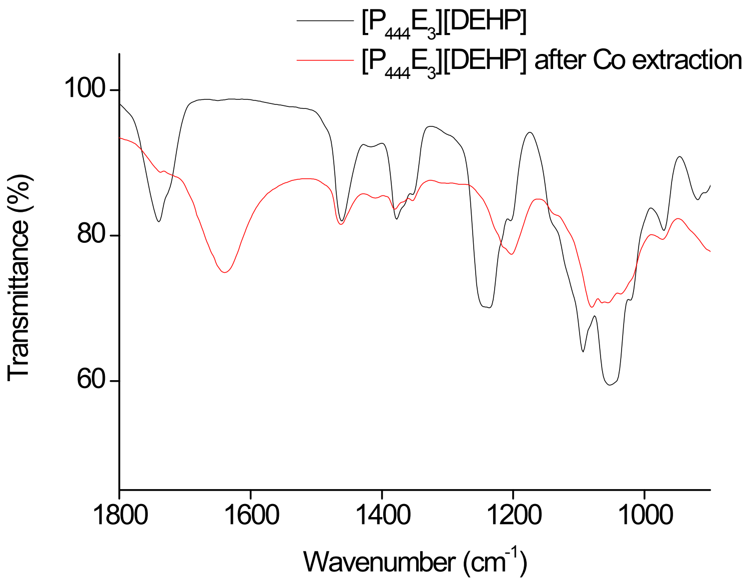


Figure S3. ATR-FTIR spectra of IL [$P_{444}E_3$][DEHP] dry and after extraction of Co(II). For explanation: see main text.

Stripping measurements

In the stripping experiments, equimolar amounts of oxalic acid were added to 500 mg of the loaded IL, and shaken for 30 min at room temperature. The vials were centrifuged to accumulate all precipitate at the bottom (Figure S4). A sample of the IL phase was taken for analysis of its metal content by TXRF.

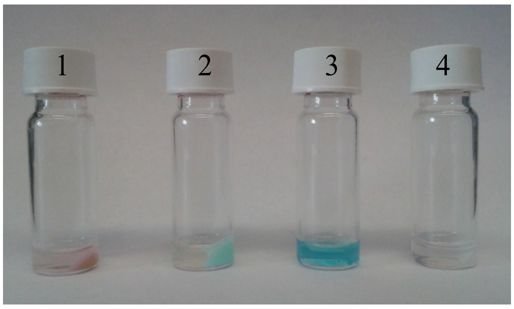


Figure S4. Precipitation of the metal oxalates: 1) CoC_2O_4, 2) NiC_2O_4, 3) Cu: small precipitate CoC_2O_4 and highly coloured IL phase and 4) ZnC_2O_4.

References

(1) G. Cui, C. Wang, J. Zheng, Y. Guo, X. Luo, H. Li, *Chem. Commun.,* 2012**, 48***,* 2633.

(2) V. Gudipati, D. P. Curran, C. S. Wilcox, *J. Org. Chem.,* 2006**, 71***,* 3599.

(3) J. Leicunaite, I. Klimenkovs, J. Kviesis, D. Zacs, J. P. Kreismanis, *C. R. Chimie,* 2010**, 13***,* 1335.

(4) Y. Zhang, S. Zhang, X. Lu, Q. Zhou, W. Fan, X. Zhang, *Chemistry- A European Journal,* 2009**, 15***,* 3003.

(5) D. C. Steytler, D. L. Sargeant, G. E. Welsh, B. H. Robinson, R. K. Heenan, *Langmuir,* 1996**, 12***,* 5312.

(6) J. Leys, M. Wübbenhorst, C. Preethy Menon, R. Rajesh, J. Thoen, C. Glorieux, P. Nockemann, B. Thijs, K. Binnemans, S. Longuemart, *J. Chem. Phys.,* 2008**, 128***,* 064509.