Supporting information

Separation of Cobalt and Nickel by Solvent Extraction with

Two Mutually Immiscible Ionic Liquids

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Supplementary ^{1}H NMR data

Solubility of [C$_2$mim]Cl in the [P$_{66614}$][R$_2$POO] phase:

The [P$_{66614}$][R$_2$POO] phase was analyzed by ^{1}H NMR. By comparing the phosphonium multiplet (8H) at 2.4-2.5 ppm with the imidazolium peak at 11.6 ppm (1H), the solubility of [C$_2$mim]Cl in the upper phase ([P$_{66614}$][R$_2$POO]) was determined (Figure S1).
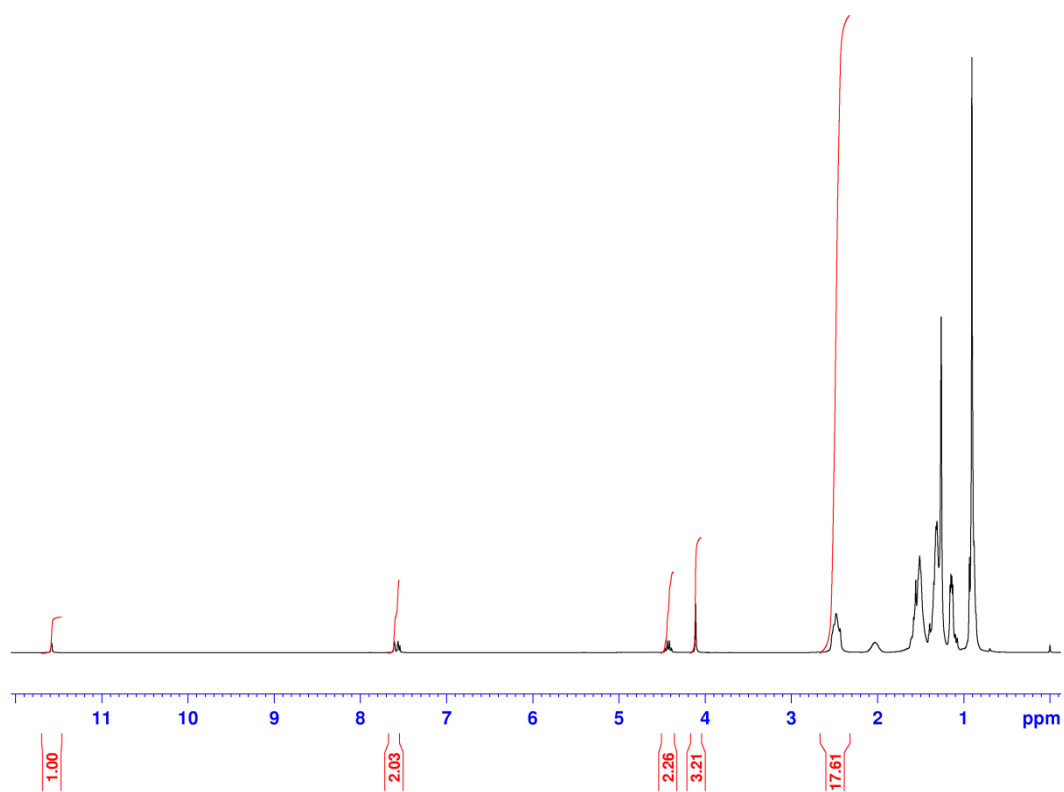
Figure S1: ^{1}H NMR spectrum of [P$_{66614}$][R$_2$POO] after mixing with the [C$_2$mim]Cl phase.

Solubility of $P_{66614}R_2POO$ in the $[C_2mim]Cl$ phase:

The $[C_2mim]Cl$ phase was analyzed by ^1H NMR. By comparing the phosphonium multiplet (8H) at 2.4-2.5 ppm with the imidazolium peaks at 10.5 ppm (1H), there was tried to quantify the $[P_{66614}]$ cation concentration in $[C_2mim]Cl$ (Figure S2). The integration values are too low to obtain reliable data for the solubility. However only measuring the solubility of the cation is not sufficient since anions can exchange with each other as well, where phosphinate anions then replaces chlorides. The peaks due to the methyl groups on the branched alkyl chains of the phosphinate anion situated in the ^1H NMR spectra at 0.89 can be detected. The solubility of about 1000 ppm was found. Since the process is used for extraction of cobalt, which has a high affinity for phosphinate ligands, after mixing the phases the phosphinate concentration is expected to be even lower.
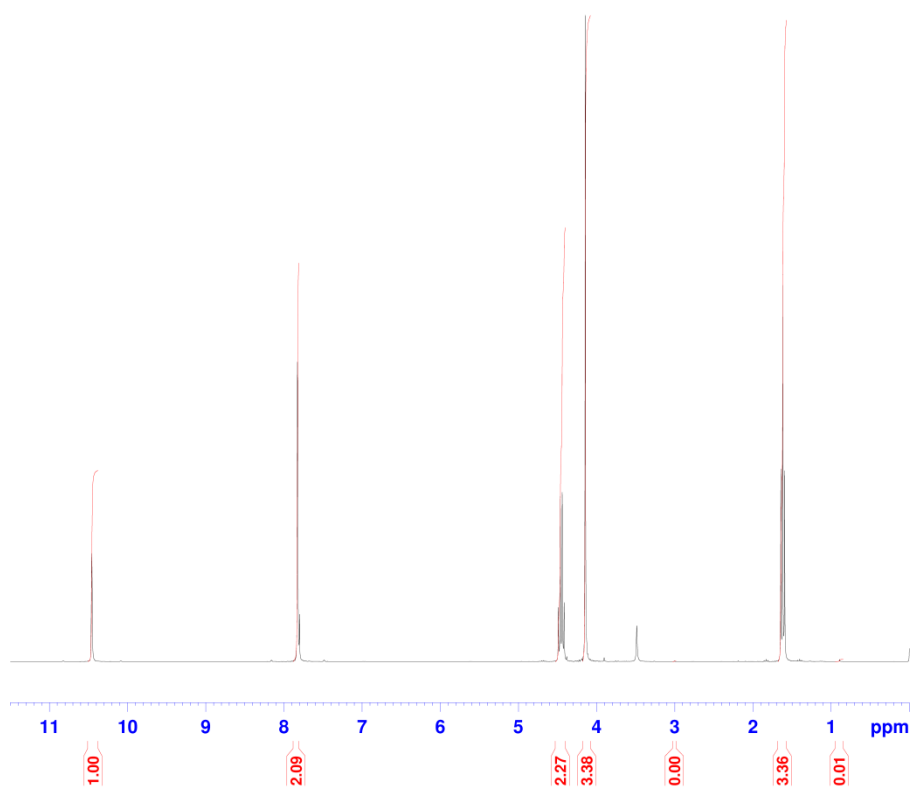
Figure S2: ^{1}H NMR spectrum of the [C$_2$mim]Cl phase after mixing with [P$_{66614}$][R$_2$POO]

Solubility of [C$_2$mim]Cl in [P$_{66614}$][R$_2$POO] after the washing step

To quantify the concentration of [C$_2$mim]Cl in the [P$_{66614}$][R$_2$POO] phase after the washing step, a ^{1}H NMR spectrum of the extraction phase was recorded after washing. By comparing the phosphonium multiplet (8H) at 2.4–2.5 ppm with the imidazolium peak at 11.6 ppm (1H), the solubility of [C$_2$mim]Cl in [P$_{66614}$][R$_2$POO] was determined.
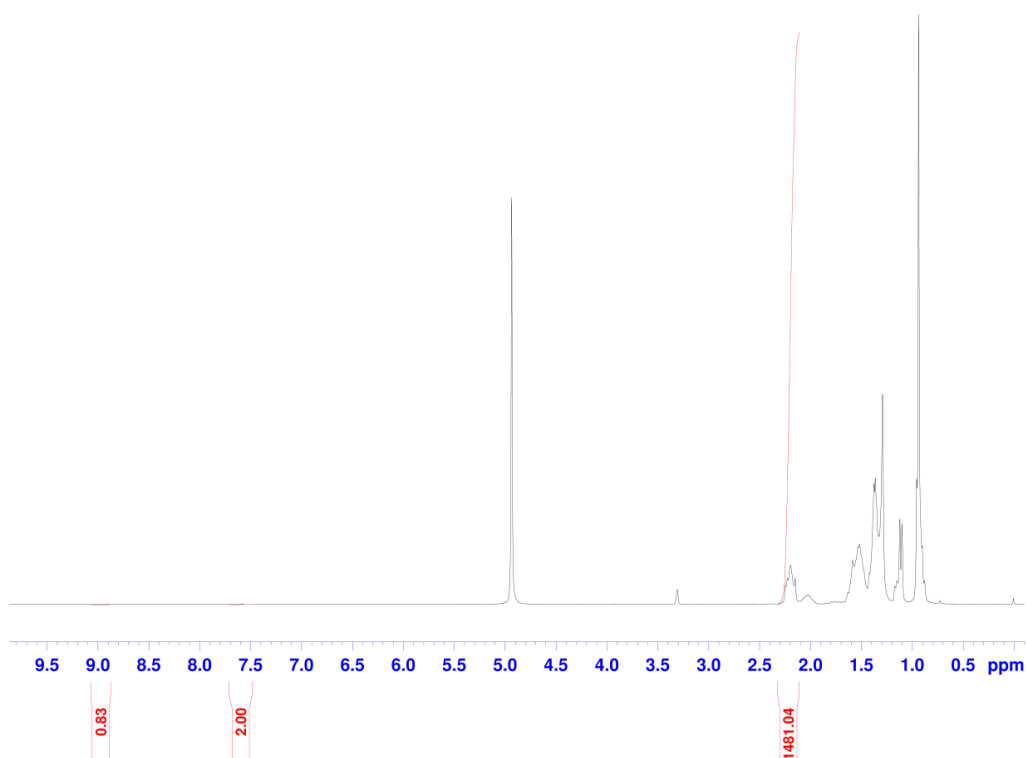
Figure S3: ^{1}H NMR spectrum of [P$_{66614}$][R$_2$POO] after washing.

Temperature dependence of the solubility of phosphinate anions and cobalt(II) phosphinate complexes in [C$_2$mim]Cl

It was observed that the distribution ratio for cobalt decreased as a function of temperature (see Figure 3 in main text). This behavior can be explained by the increase in solubility of the phosphinate anion in the ionic liquid [C$_2$mim]Cl with temperature. The solubility of [R$_2$POO]$^-$ in [C$_2$mim]Cl was quantified at 140 °C, by ^{1}H NMR measurement after bringing the two ionic liquids in contact by stirring their mixture for 10 minutes (Figure S4).
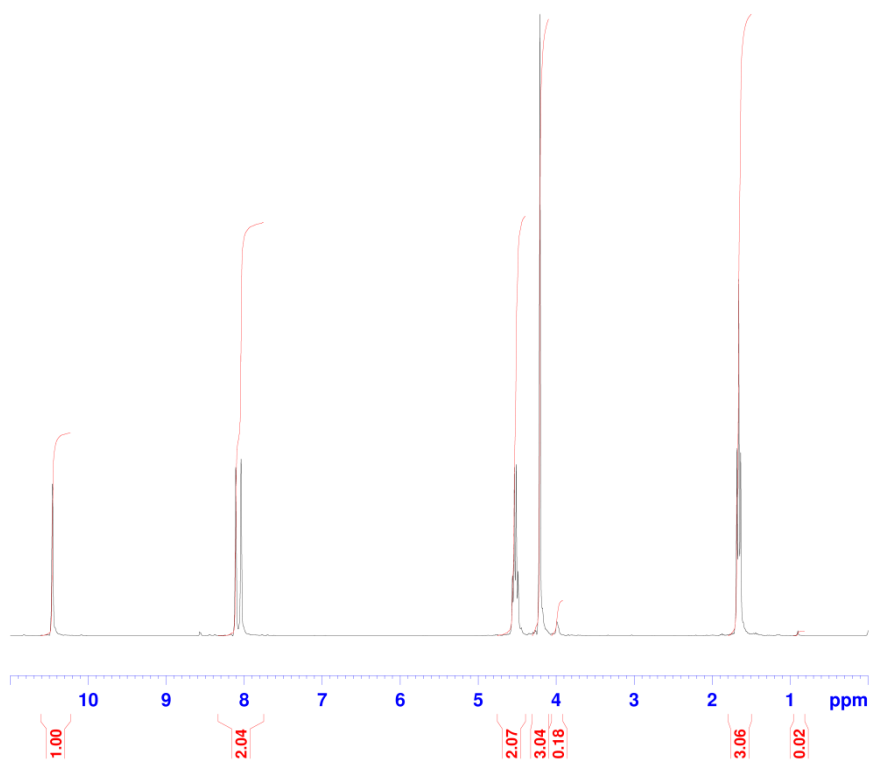
Figure S4: ^{1}H NMR spectra of [C$_2$mim]Cl after extraction at 140 °C.
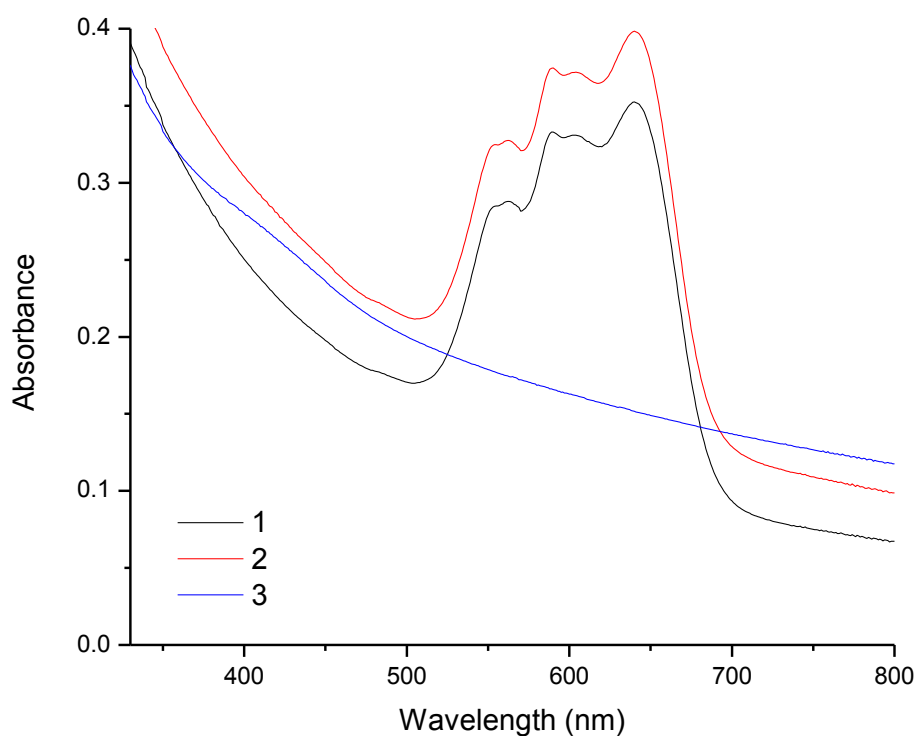
UV-Vis Absorption spectra

Figure S5: Absorption spectra of cobalt(II) and nickel(II) in the $[P_{66614}][R_2POO]$ phase after extraction. With spectrum 1 corresponding to cobalt in $[P_{66614}][R_2POO]$ after extraction; 2 to cobalt and nickel in $[P_{66614}][R_2POO]$ after extraction; and 3 to nickel in $[P_{66614}][R_2POO]$ after extraction
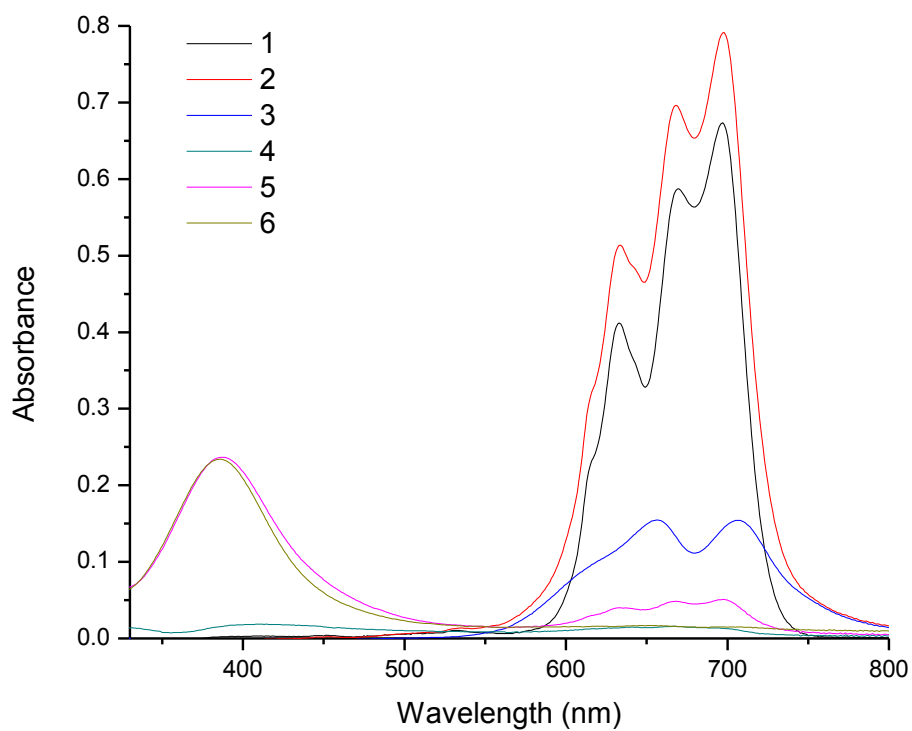
Figure S6: Absorption spectra of cobalt(II) and nickel(II) in the [C_2mimCl] phase before and after extraction. With spectrum 1 corresponding to $CoCl_2$ in [C_2mim]Cl before extraction; 2 to $CoCl_2$ and $NiCl_2$ in [C_2mim]Cl before extraction; 3 to $NiCl_2$ in [C_2mim]Cl before extraction; 4 to cobalt in [C_2mim]Cl after extraction; 5 to cobalt and nickel in [C_2mim]Cl after extraction; and 6 to nickel in [C_2mim]Cl after extraction.

^{31}P NMR spectra

To proof the phosphonium and phosphinate are still present in a 1:1 ratio after the processing steps, ^{31}P NMR measurements were measured after each step. The ratio between was checked by integration of the phosphonium peak at 38.1 ppm (1P) and phosphinate peak at 43.6 ppm (1P) in the ^{31}P NMR spectra, during the processing steps, which are extraction, washing and recovery. For the stripping step, the ratio between the peaks at 38.1 ppm (1P) and at 54.11 ppm (1P) in the ^{31}P NMR spectra was determined. The latter peak originates from the formation of the phosphinic acid in acidic media. If the peaks are integrated, it can be noticed that more phosphinic acid is present. This is explained by taking into account the impurity of phosphinic acid, which was already present in the ionic liquid before the extraction.
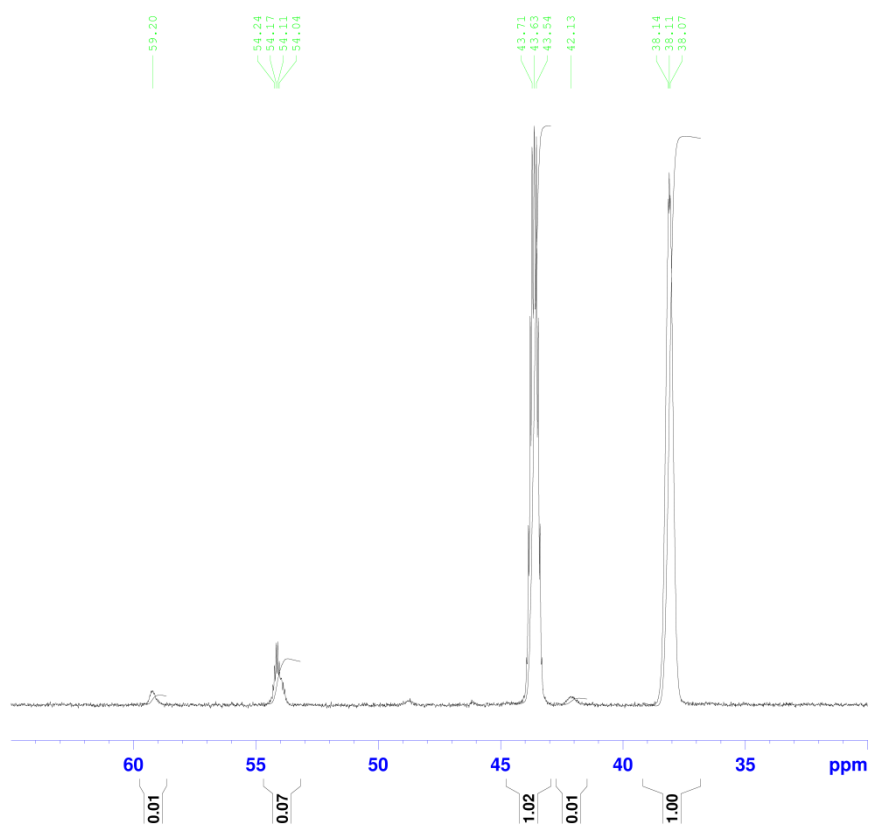

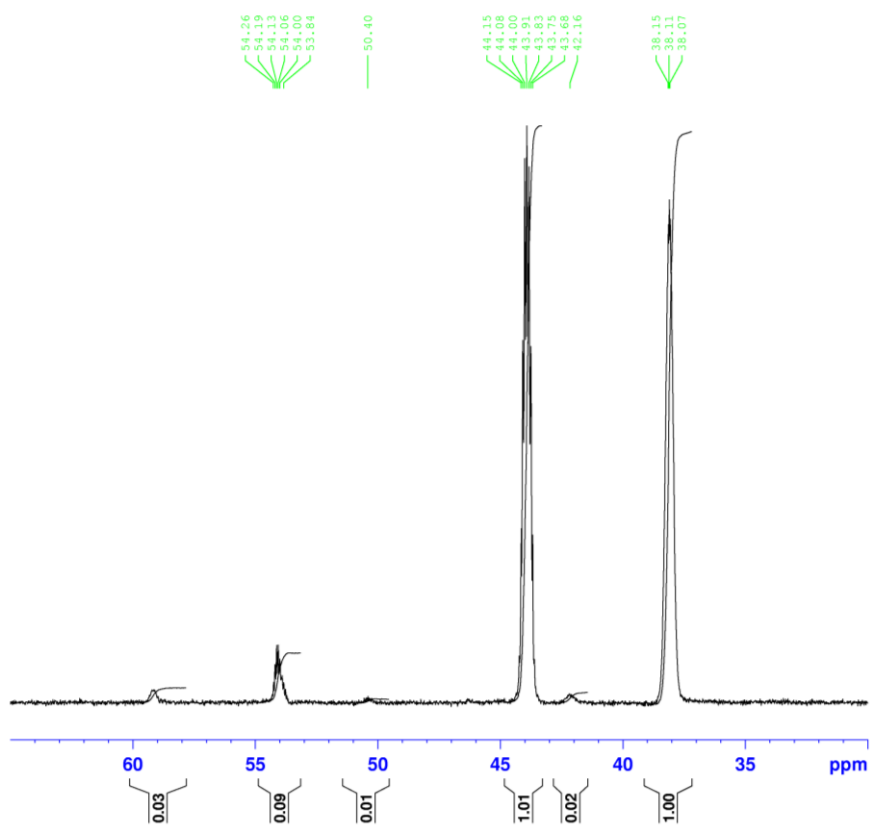Figure S7: ^{31}P NMR spectrum of [P$_{66614}$][R$_2$POO].

Figure S8: ^{31}P NMR spectrum of [P$_{66614}$][R$_2$POO] after extraction.
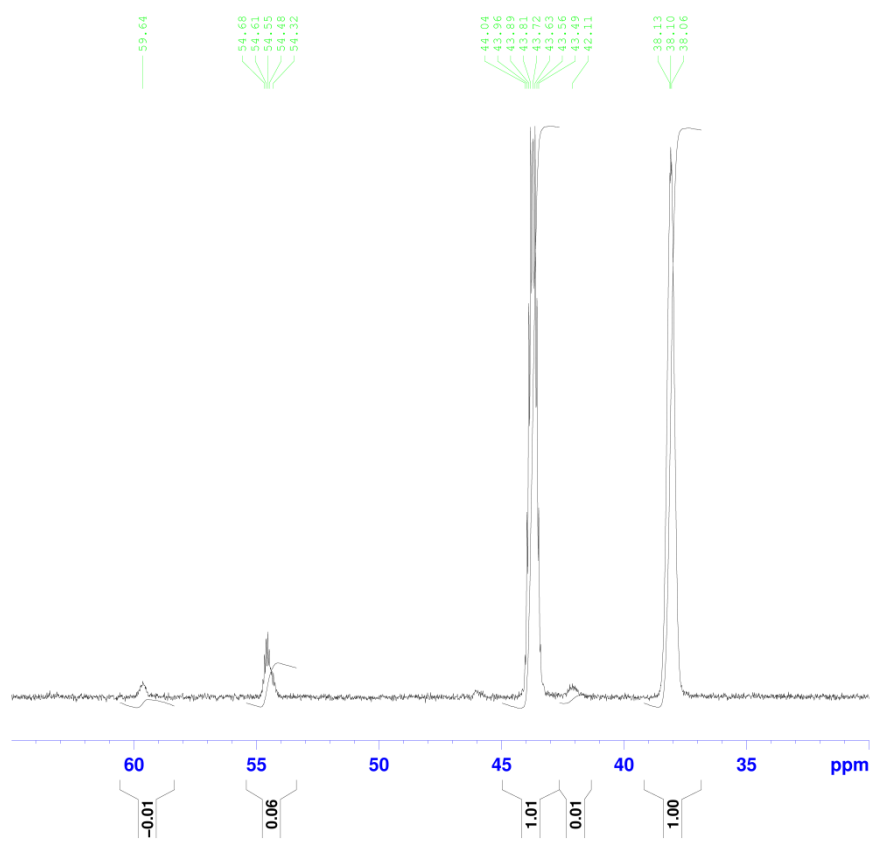
Figure S9: ^{31}P NMR spectrum of [P$_{66614}$][R$_2$POO] after recovery.
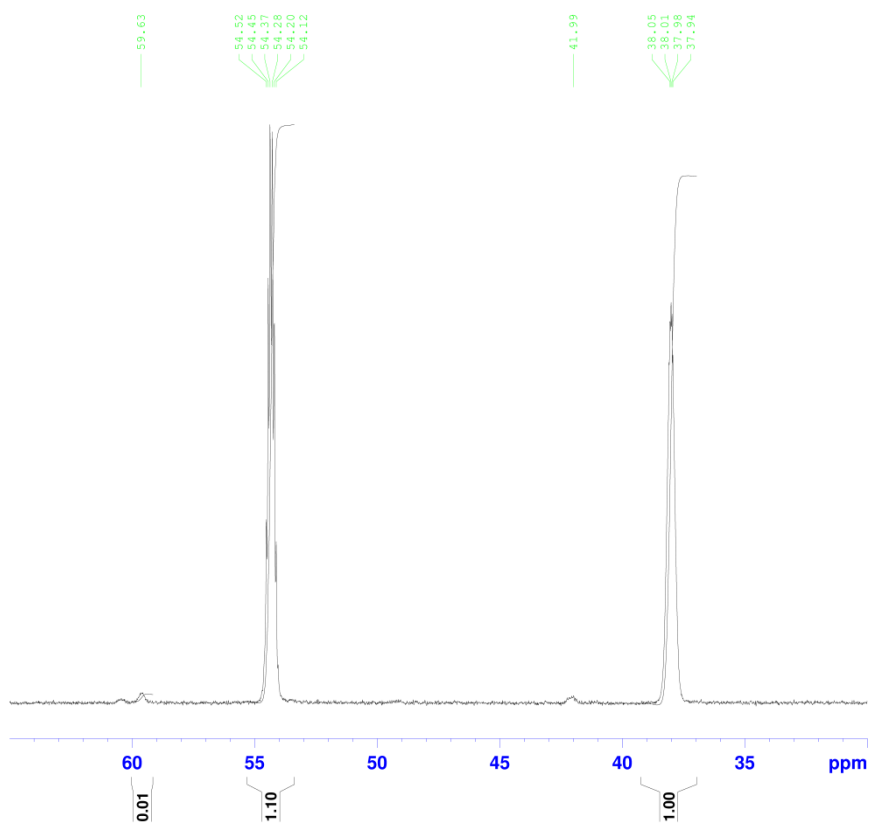
Figure S10: ^{31}P NMR spectrum of [P$_{66614}$][R$_2$POO] after stripping.
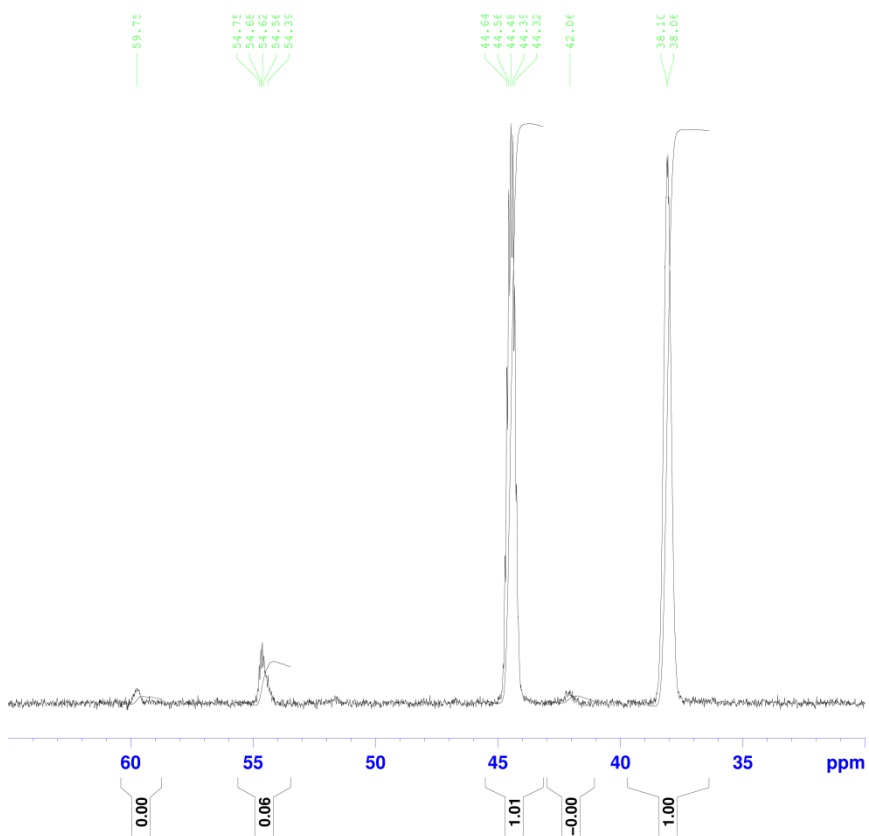
Figure S11: ^{31}P NMR spectrum of [P$_{66614}$][R$_2$POO] after washing.
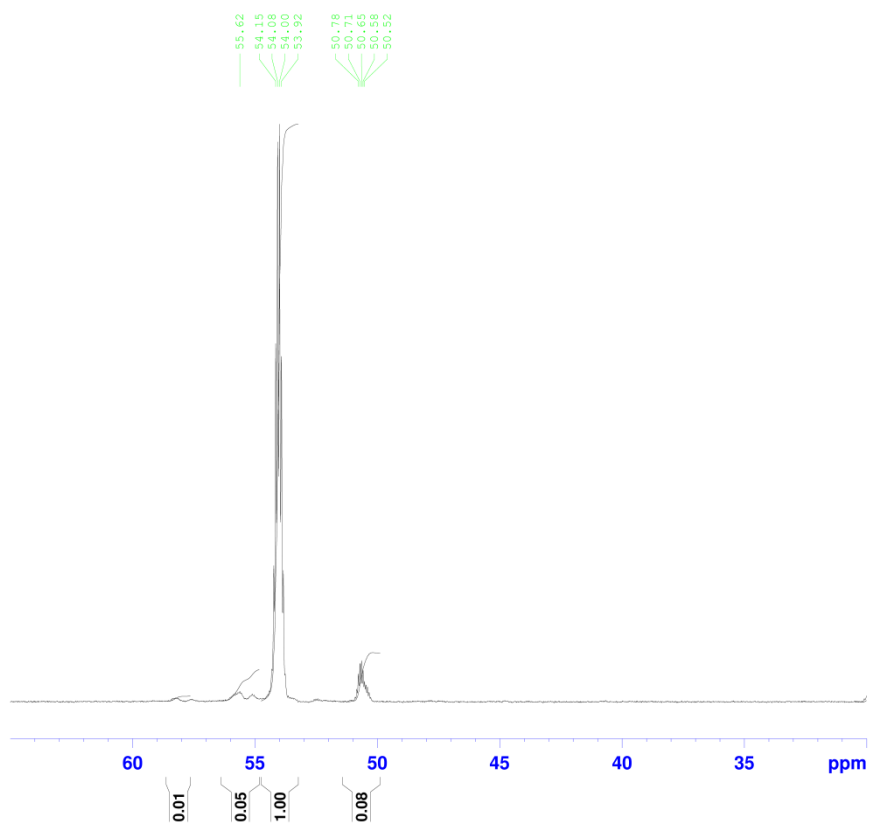
Figure S12: ^{31}P NMR spectrum of Cyanex272.
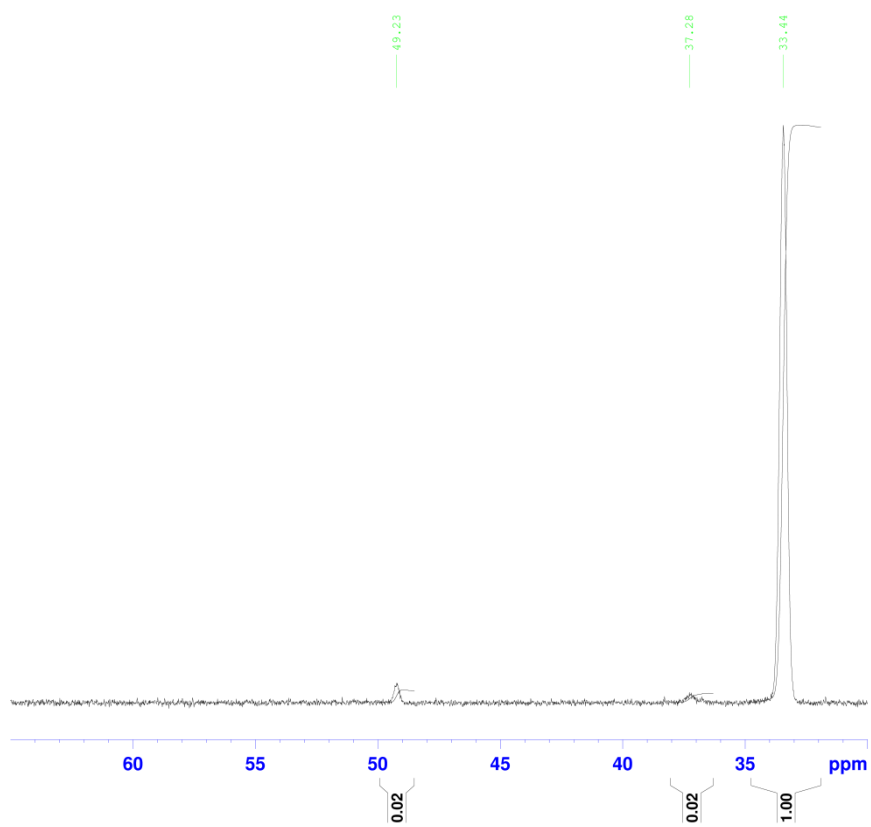
Figure S13: ^{31}P NMR spectrum of P$_{66614}$Cl.