# Supporting Information

# Metal recovery from spent samarium-cobalt magnets using a trichloride ionic liquid

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## Materials

The lecture bottle of liquefied chlorine (1 kg, 4.9 bar at 15 °C, > 99.5%) was purchased from Air Liquide (Belgium), together with a pressure regulator (DIM 200-3-5 T purge type). The chlorine flow meter was ordered from Brooks Instrument (The Netherlands). Cyphos IL 101 ($[P_{666,14}][Cl]$, > 95%) was purchased from Cytec Industries Inc. (Niagara Falls, Ontario, Canada). Samarium pieces (99.9%) were ordered from Alfa Aesar (Geel, Belgium). Nitric acid (65 wt%), ammonia solution (25 wt%) and $CoCl_2$ (97%) were ordered from Sigma-Aldrich (Diegem, Belgium). NaCl (99.5%) was purchased from Fisher Chemicals (Aalst, Belgium). $FeCl_3$ (98%) and $CuCl_2$ (99%) were ordered from Acros Organics (Geel, Belgium). $SmCl_3 \cdot 6H_2O$ (99.9%) was purchased from Strem Chemicals (Kehl, Germany). The silicone solution in isopropanol from SERVA Electrophoresis (Heidelberg, Germany) and standard solutions of Ga, Sm, Co, Cu, Fe and Zr were from Chem-Lab (Zedelgem, Belgium). All chemicals were used as received without any further purification. SmCo magnets were kindly provided by Magneti Ljubljana, d.d. (Ljubljana, Slovenia).

## Instrumentation

A Seifert 3003 T/T device was used to record the diffractogram of the crystalline structure of the milled, unsieved SmCo powder, using the following parameters: $2\theta = 10°–70°$, radiation = CuKα, acceleration voltage = 40 kV, acceleration current = 40 mA, a step size of 0.020° and a counting time of 1 s per step, spin mode. The data were elaborated by comparison with the ICDD (International Centre for Diffraction Data) through the X'Pert HighScore software.

A Speedwave Xpert microwave digester, (Berghof, Germany) was used to decompose the ionic

liquid prior to elemental analysis. Ionic liquid leachates (10-60 mg) were weighed and mixed

with 7 mL of 65 wt% $HNO_3$ in a DAP-40 pressure vessel. The digestion program regarding to

temperature and pressure is presented in Table S1.

Table S1. Microwave digestion program with DAP 40 vessels

|  | Temperature (°C) | Pressure (bar) | Ramp (min) | Hold (min) | Magneton Power (%) |
|---|---|---|---|---|---|
| 1 | 145 | 30 | 10 | 10 | 60 |
| 2 | 170 | 30 | 5 | 10 | 70 |
| 3 | 200 | 30 | 5 | 10 | 80 |
| 4 | 50 | 20 | 5 | 20 | 0 |
| 5 | 50 | 15 | 0 | 0 | 0 |

Inductively-coupled plasma optical emission spectrometry (ICP-OES, Optima 8300,

PerkinElmer) was used to measure the metal contents in the aqueous and digested samples. A

series of standard solutions containing samarium, cobalt, copper, iron and zirconium were

analyzed to obtain calibration curves for sample analysis. Gallium was used as internal standard

to track the performance of the analysis. The uncertainty of ICP-OES analysis is ± 5%.

A Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to

determine the metal concentrations in the aqueous and ionic liquid phases after stripping with

$NH_3$ solutions. The samples were diluted 50 times with water containing 5% Triton X-100 for

the aqueous samples and with ethanol for the ionic liquid samples. Gallium was added as the

internal standard. The sample carriers were pretreated with a silicone solution in isopropanol (30 µL) by drying at 60 °C for 30 min, then 5 µL of the diluted samples was dispensed on a quartz and analyzed after drying at 60 °C for 30 min. The uncertainty of TXRF analysis is ± 10%.

A nuclear magnetic resonance (NMR) spectrometer (Bruker Ascend, 400 MHz) operating at 400 MHz for $^1$H, 100 MHz for $^{13}$C and 162 MHz for $^{31}$P was used to record NMR spectra of the ionic liquids All samples were dissolved in DMSO-$d_6$ using tetramethylsilane as an internal reference compound for $^1$H and $^{13}$C NMR. Raman spectra were measured on a Bruker Vertex 70 spectrometer with RAMII Raman module laser (1064 nm), at a power of 500 mW.
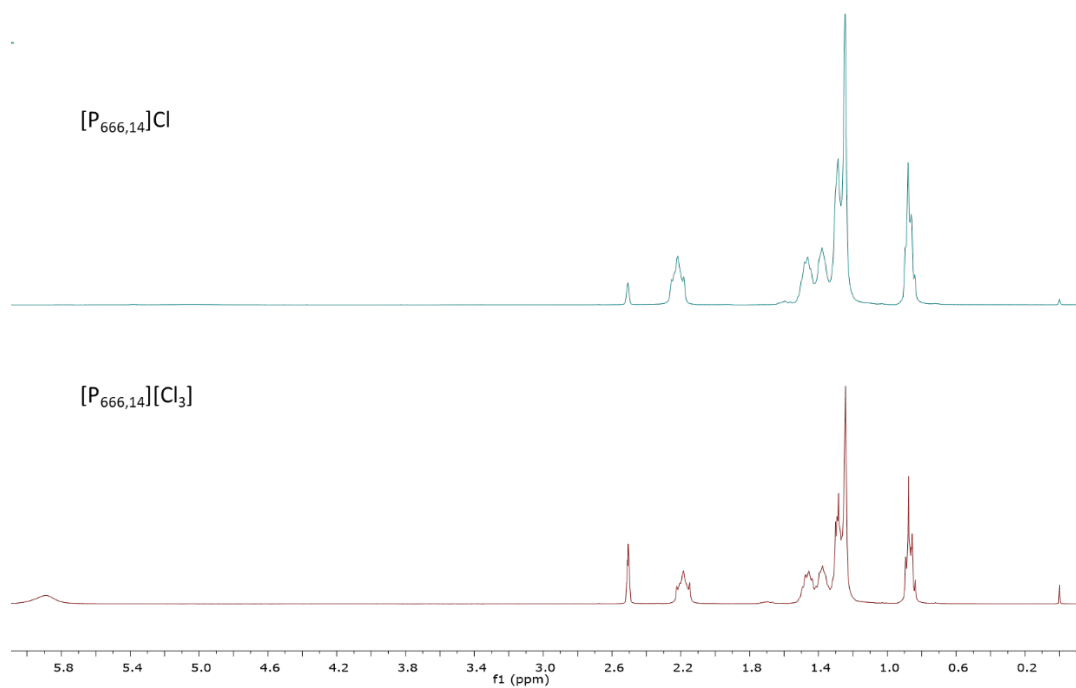


Figure S1. $^1$H NMR spectra of the ionic liquids [P$_{666,14}$][Cl$_3$] and [P$_{666,14}$]Cl.
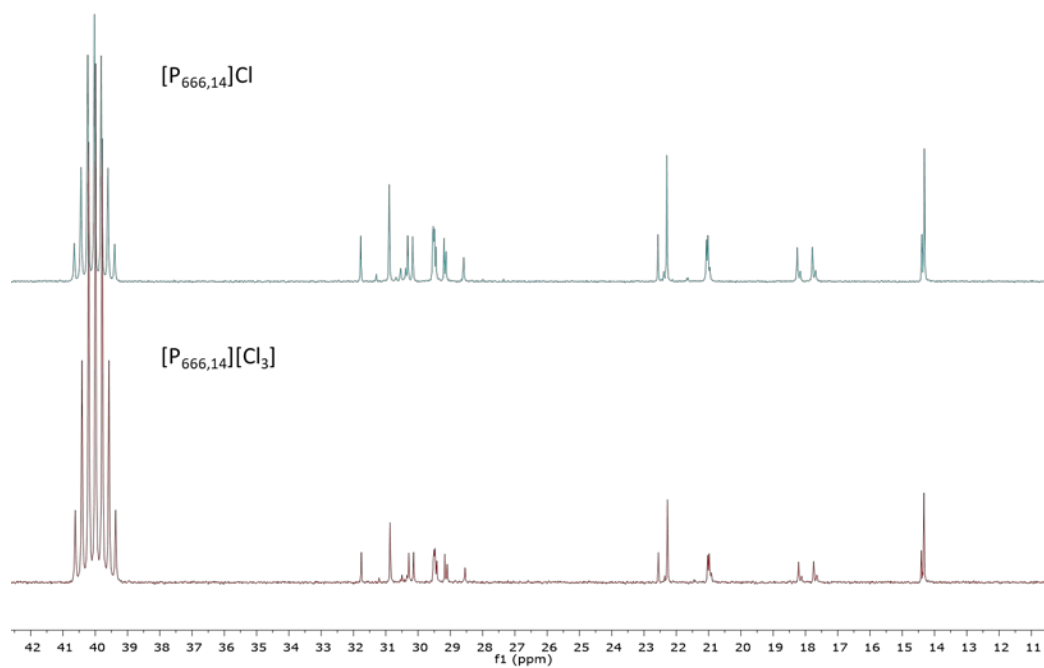
Figure S2. $^{13}$C NMR spectra of the ionic liquids [P$_{666,14}$][Cl$_3$] and [P$_{666,14}$]Cl.
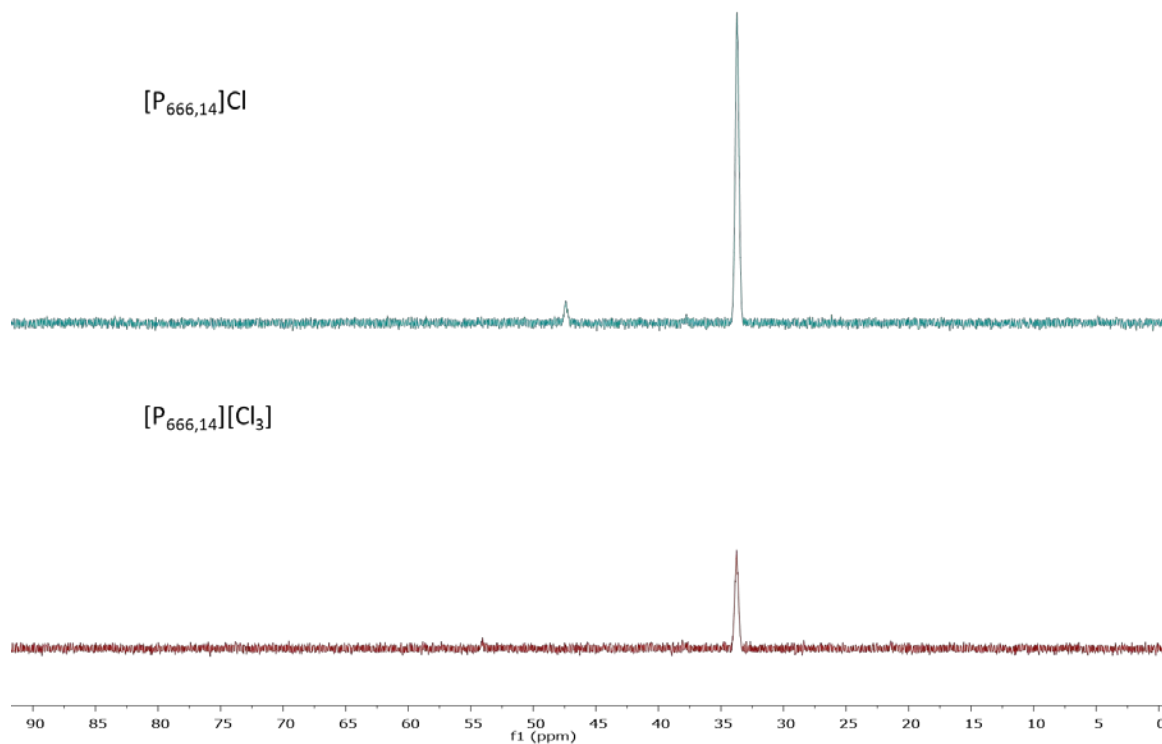


Figure S3. $^{31}$P NMR spectra of the ionic liquids [P$_{666,14}$][Cl$_3$] and [P$_{666,14}$]Cl.
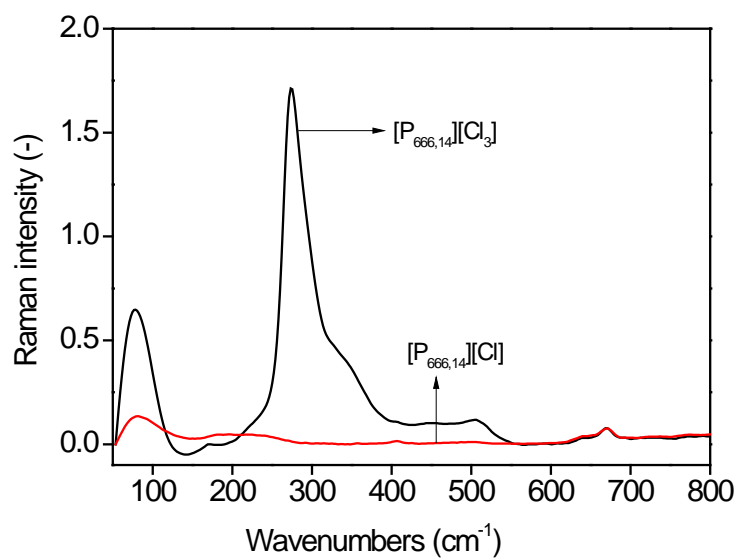
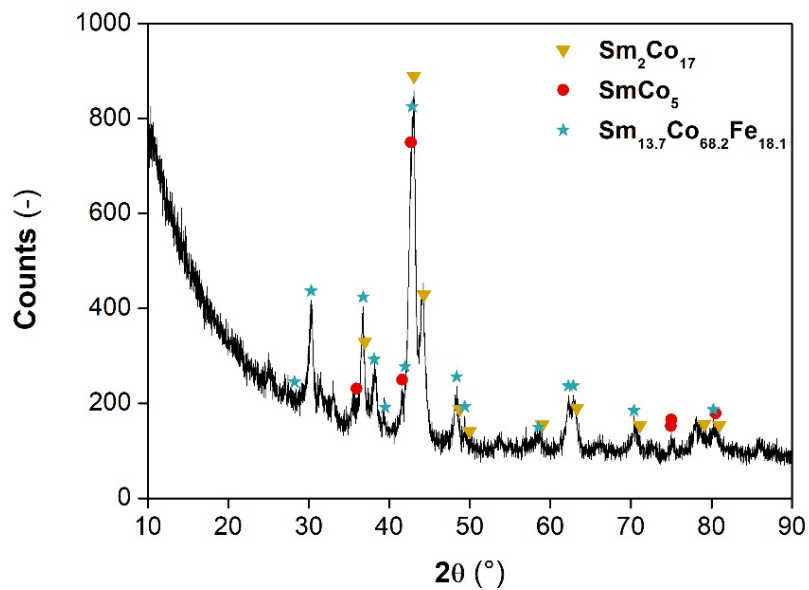Figure S4. Raman spectra of the ionic liquids [P$_{666,14}$][Cl$_3$] and [P$_{666,14}$]Cl.
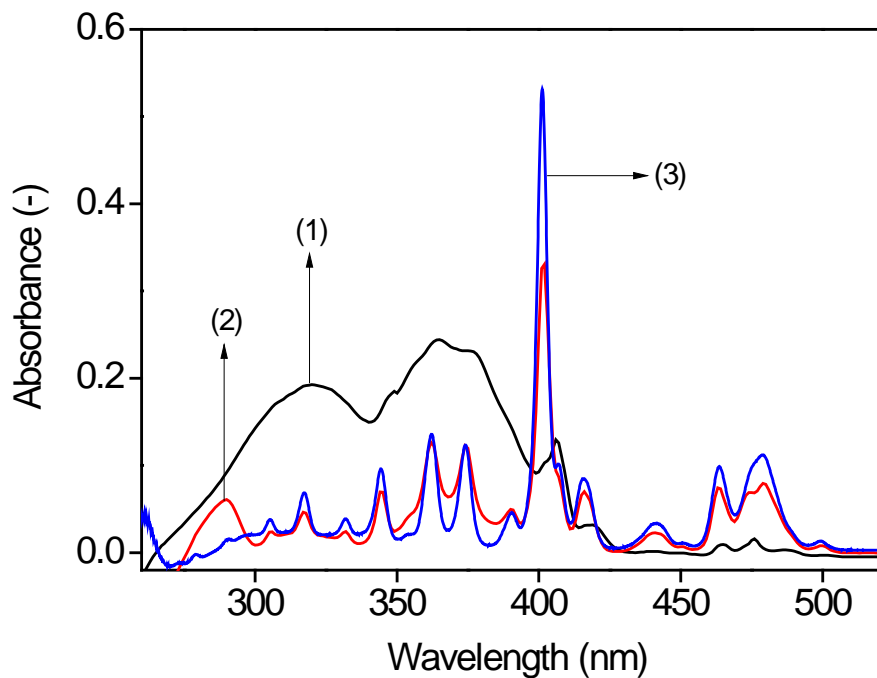
Figure S5. X-ray diffractogram of milled SmCo magnet.



Figure S6. UV-VIS absorption spectra of samples with the reference of pure $[P_{666,14}]Cl$: (1) $SmCl_3$ in dry $[P_{666,14}]Cl$; (2) $SmCl_3$ in water saturated $[P_{666,14}]Cl$; (3) $SmCl_3$ in water.
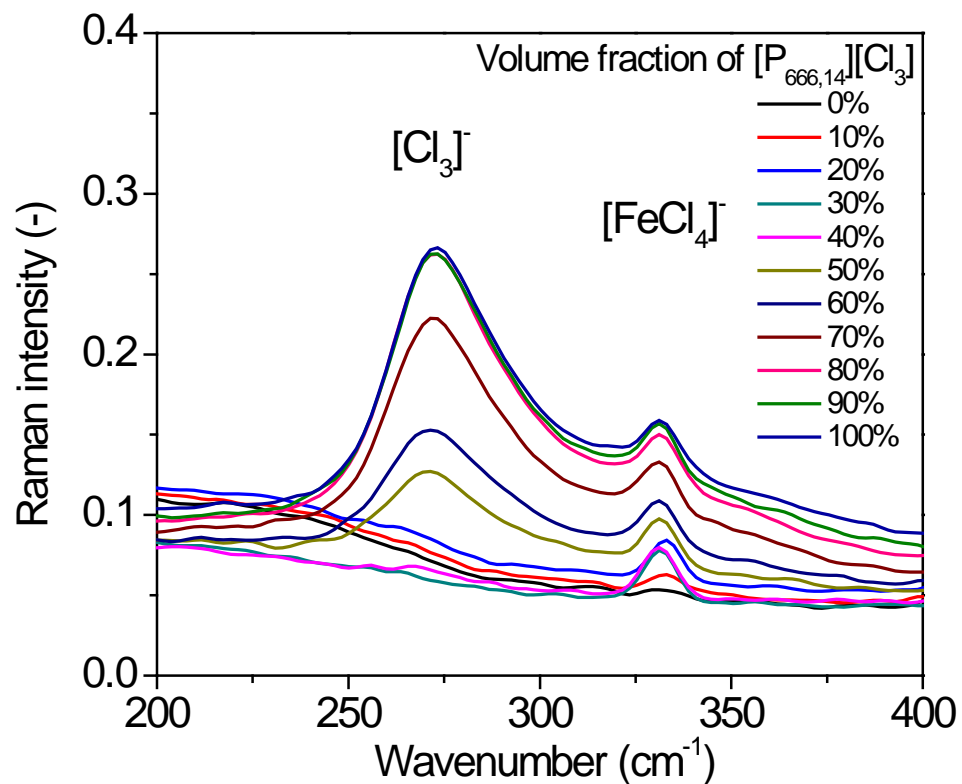
Figure S7. Raman spectra of the loaded ionic liquid after dissolution of SmCo magnets in ionic liquid mixtures with various fraction of $[P_{666,14}][Cl_3]$ in $[P_{666,14}]Cl$ with a solid-to-liquid ratio of 20 g/L at room temperature after 24 h.
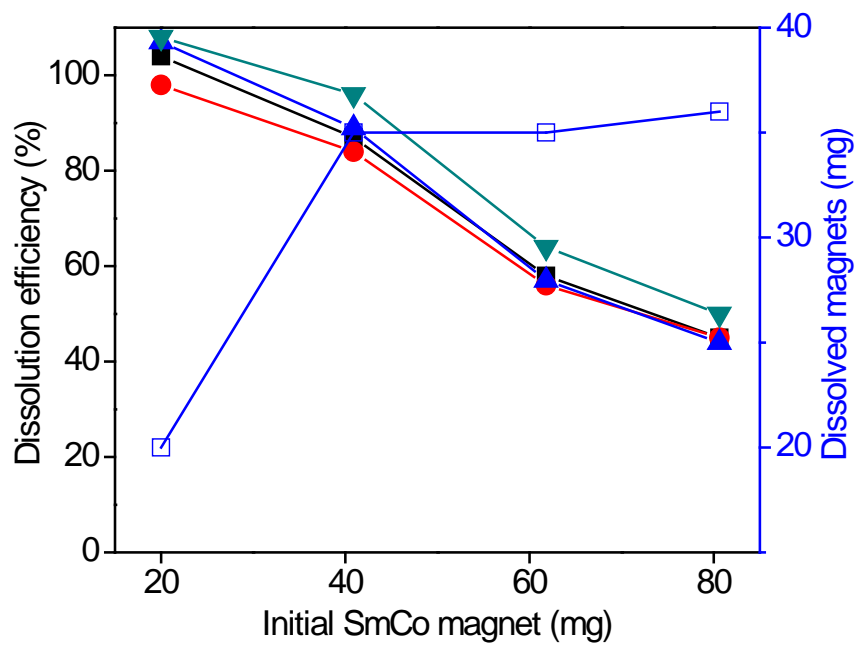
Figure S8. Dissolution of varying amount of SmCo magnet in 1 mL of $[P_{666,14}]_2[Cl_3]Cl$ at room temperature for 24 h. Fe(■), Sm(●), Co(▲), Cu(▼). The amounts of dissolved magnet (□) are shown on the right Y-axis.
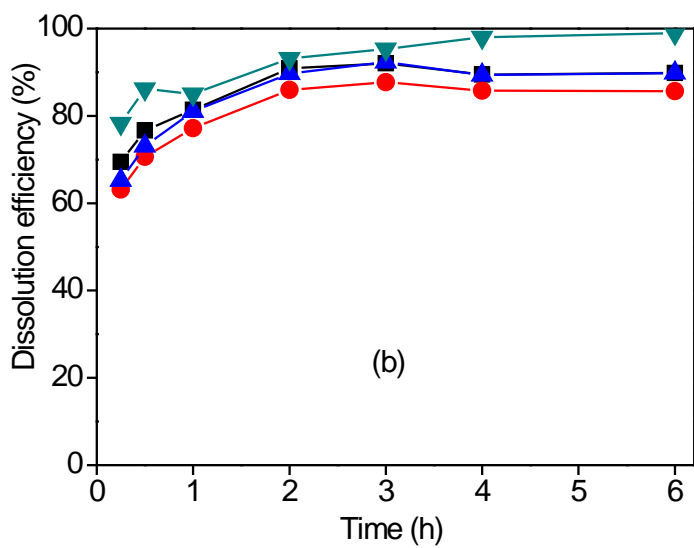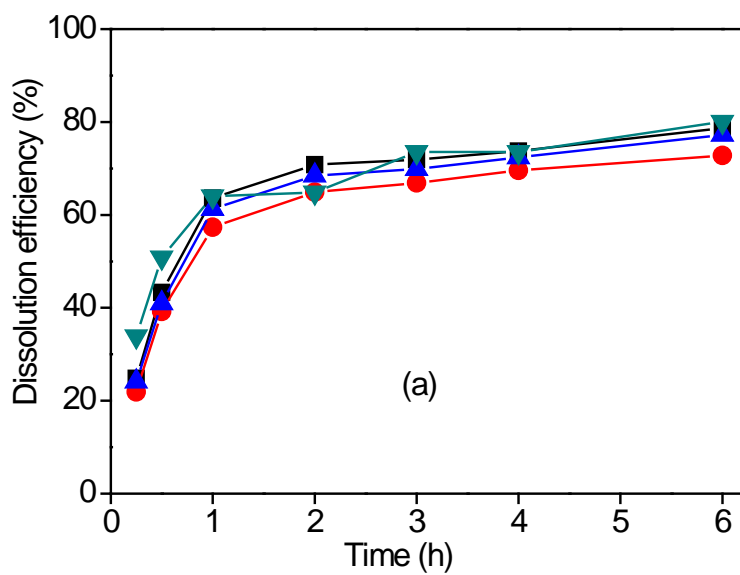
Figure S9. Dissolution of SmCo magnet in $[P_{666,14}]_2[Cl_3]Cl$ with a solid-to-liquid ratio of 40 g/L as a function of time at (a) 25 °C and (b) 50 °C. Fe(■), Sm(●), Co(▲), Cu(▼).
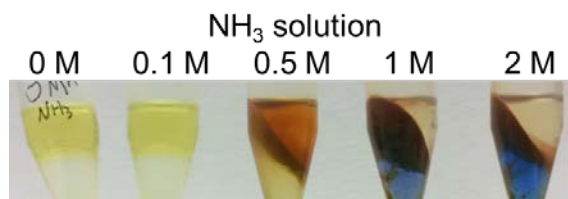
NH₃ solution

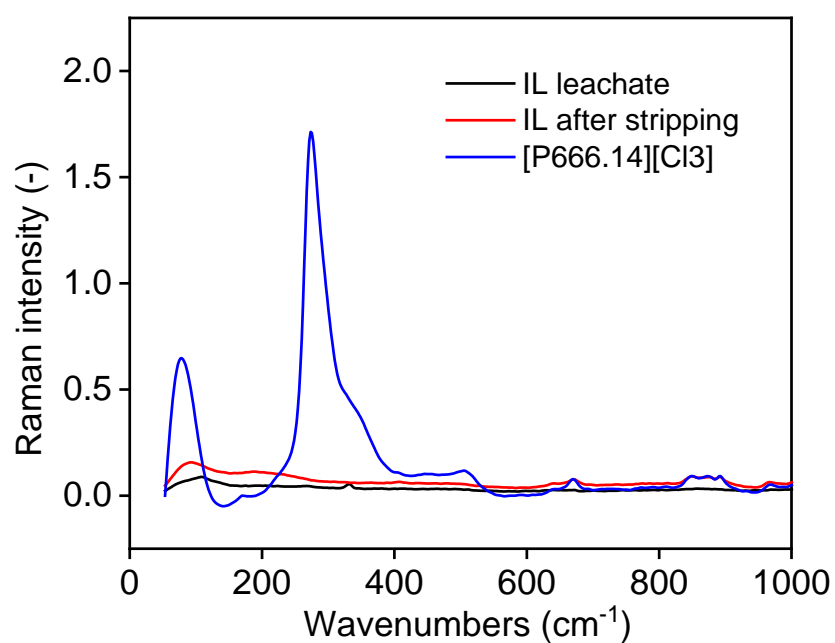Figure S10. Stripping of Fe and Cu from IL-Feed-2 with various NH$_3$ solutions.



Figure S11. Raman spectra of IL leachate after leaching of SmCo magnet with IL mixture [P$_{666,14}$]$_2$[Cl$_3$][Cl] (solid-to-liquid ratio 40g/L) and IL phase after four stripping steps in the first cycle, compared with the Raman spectra of pure [P$_{666,14}$]$_2$[Cl$_3$].
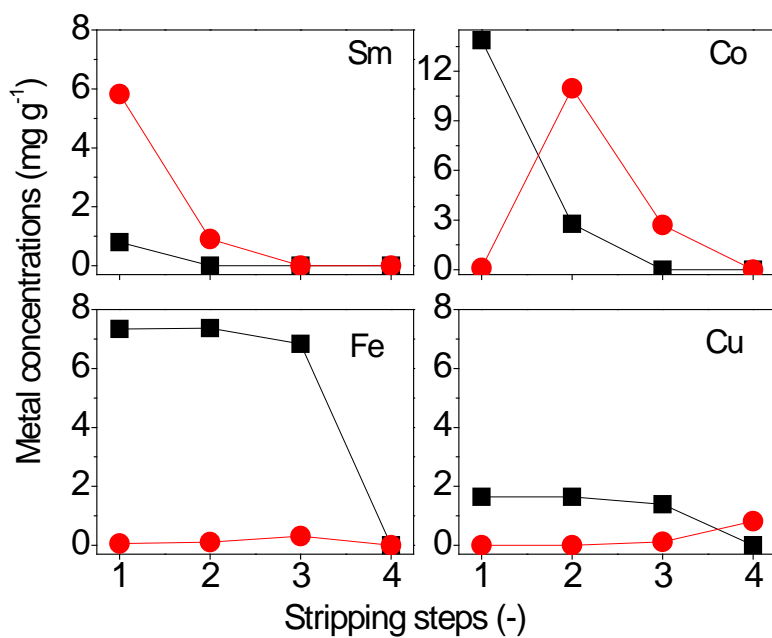
Figure S12. Metal concentrations in the ionic liquid (■) and aqueous phases (●) after each stripping step in the first cycle.

Fresh [P$_{666,14}$]Cl

Recovered [P$_{666,14}$]Cl in cycle 2

Recovered [P$_{666,14}$]Cl in cycle 5

3.6   3.4   3.2   3.0   2.8   2.6   2.4   2.2   2.0   1.8   1.6   1.4   1.2   1.0   0.8   0.6   0.4   0.2   0.0
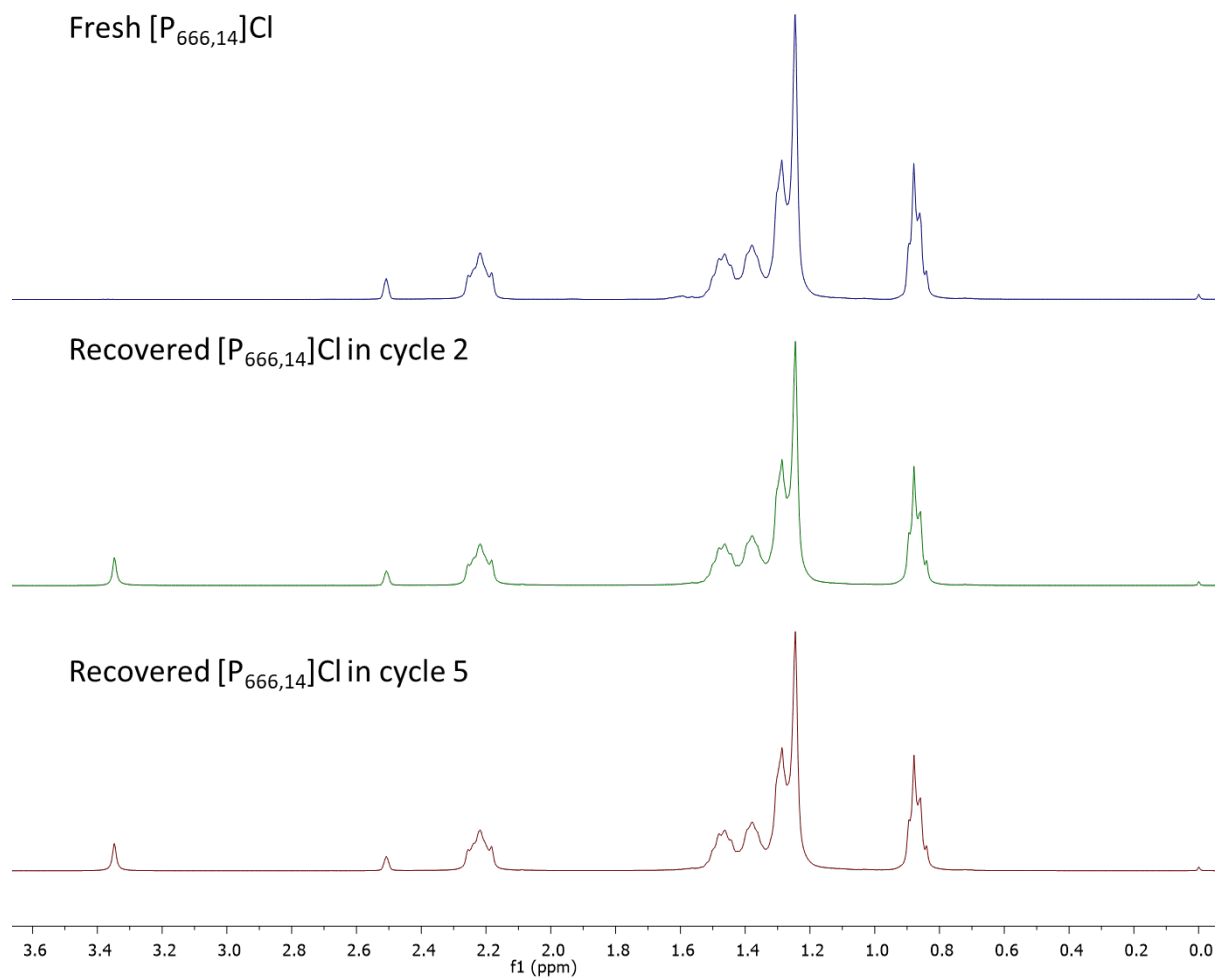f1 (ppm)

Figure S13. $^1$H NMR spectra of fresh [P$_{666,14}$]Cl and the recovered one after cycles 2 and 5. The peak at 3.3 ppm in recovered ionic liquid is from water.
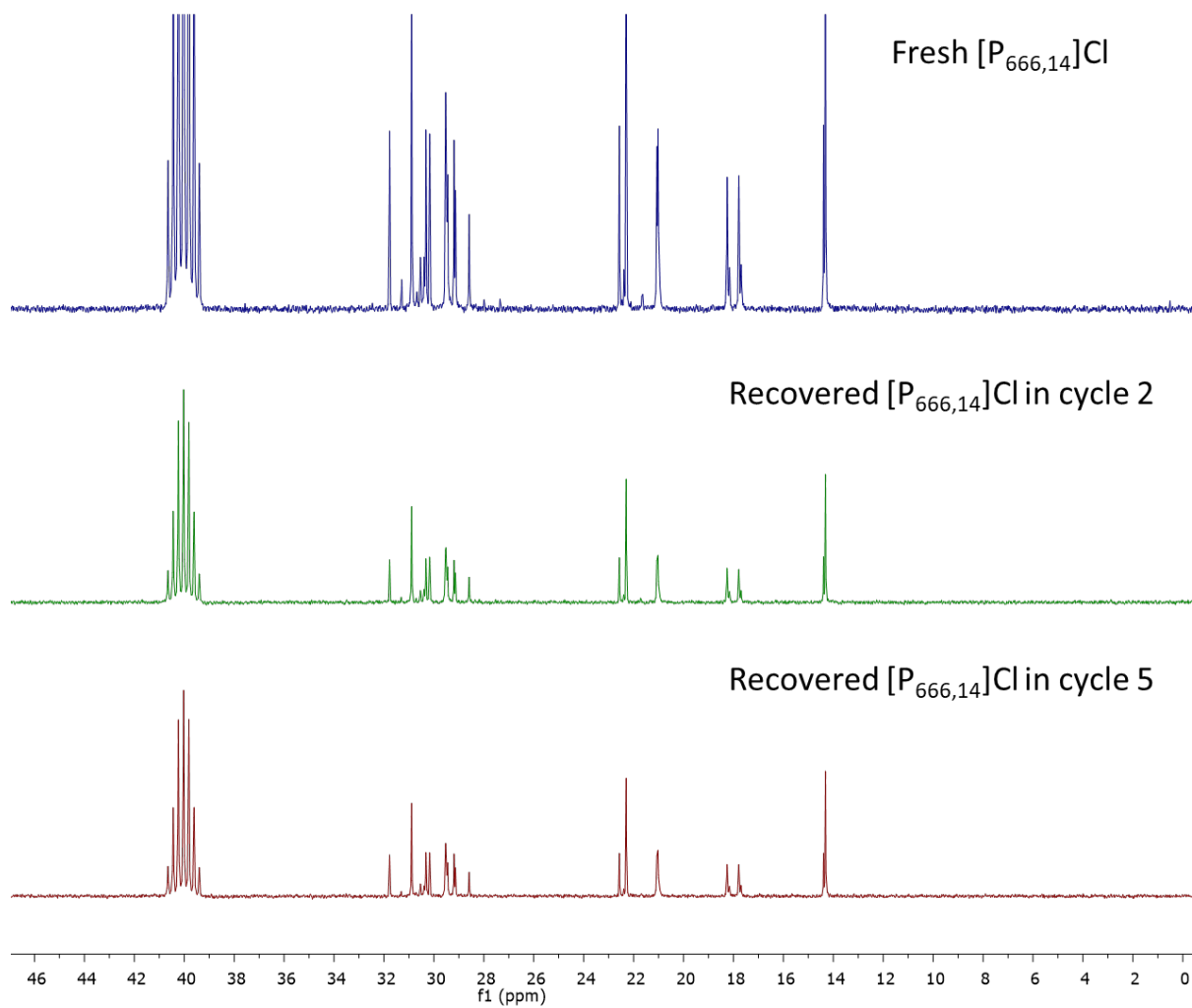
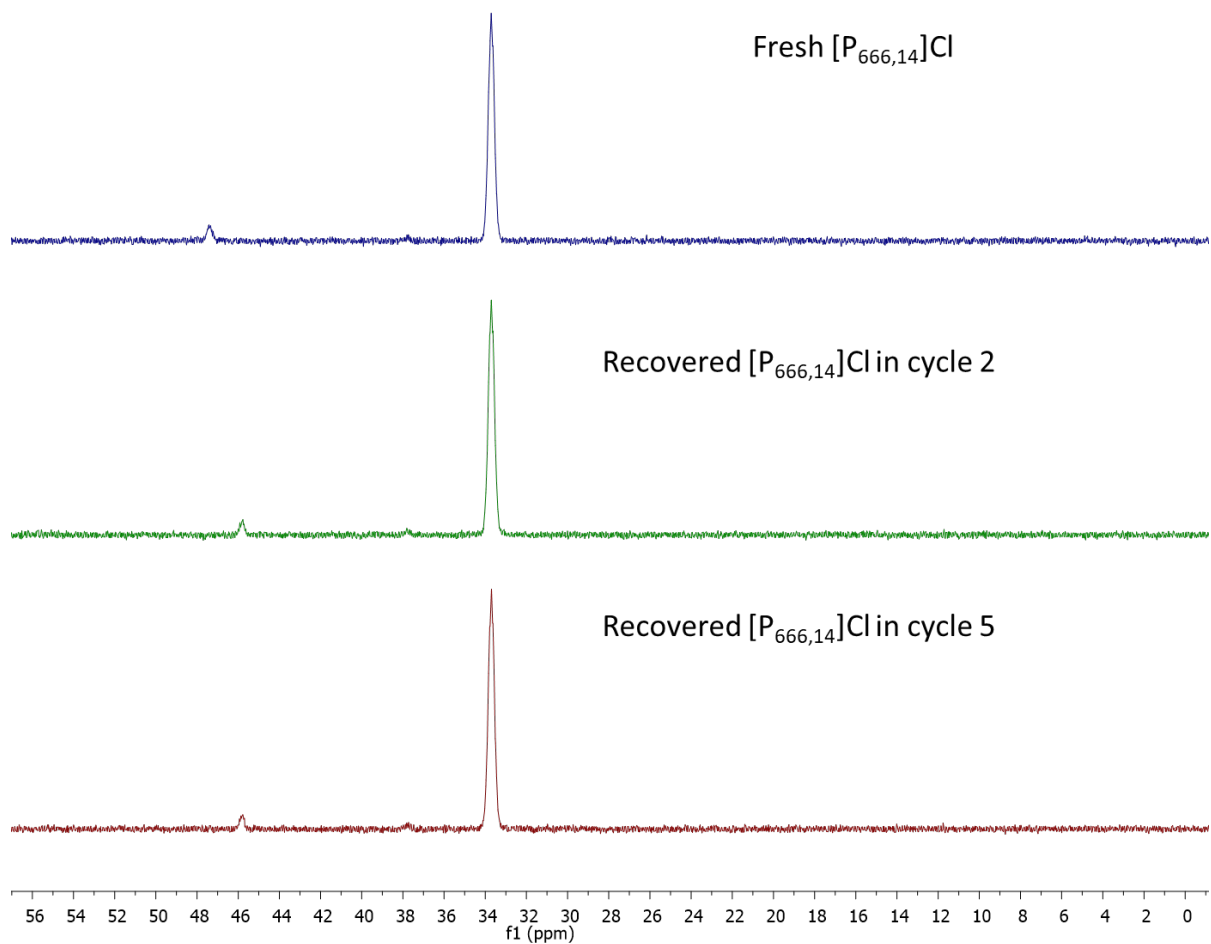Figure S14. $^{13}$C NMR spectra of fresh [P$_{666,14}$]Cl and the recovered one after cycles 2 and 5.

Figure S15. $^{31}$P NMR spectra of fresh [P$_{666,14}$]Cl and the recovered one after cycles 2 and 5. The peaks at 46 and 47 ppm are from impurities phosphine oxides in the starting ionic liquid.