Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Ionic liquids with trichloride anions for oxidative dissolution of metals and alloys

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1. Experimental section

1.1 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) that can adjust the pressure between 0.3 and 3 bar for outgoing gases. The chlorine flow meter with a range of flow rate between 2.1 and 21 g/h at 2 bar was ordered from Brooks Instrument (The Netherlands), and was built with chlorine-compatible materials. All the chloride ILs shown in Table 1 in the main text were purchased from Iolitec (>95%, Canada). Sodium hydroxide (pearl, 99%) and potassium iodide (99%) were purchased from Sigma-Aldrich (Belgium). Information of the metals and alloys is shown in Table S1, including their suppliers, purities and physical state.

Table S1. Information of the employed metals and alloys.

Metals	Physical state	Purity (%)	Supplier
Fe	powder (<325 mesh)	97	Sigma-Aldrich
Cu	powder (<200 mesh)	99	Sigma-Aldrich
In	powder (–[a])	99.999	Janssen
Ge	powder (<100 mesh)	99.999	Alfa Aesar
Sb	powder (<200 mesh)	99.999	Alfa Aesar
Ta	powder (<100 mesh)	99.98	Alfa Aesar
Zn	granular (<30 mesh)	–	Acros Organics
Ga	foil (<1mm thick)	99.99	Acros Organics
GaSb	pieces (<6 mm)	99.999	Alfa Aesar
InSb	pieces (<1 mm)	99	Alfa Aesar
Sm	pieces (<6 mm)	99.9	Alfa Aesar
Dy	pieces (<6 mm)	99.9	Alfa Aesar
Au	wire (ø 1 mm)	99.997	Sigma-Aldrich
Pt	wire (ø 0.5 mm)	99.9	Sigma-Aldrich

[a] no information available

1.2 Synthesis of trichloride ionic liquids (ILs)

1.2.1 Safety issues

Before introducing the synthetic method, it is important to emphasise the safety issue of chlorine gas. Chlorine is a toxic, corrosive and dangerous gas at room temperature and atmospheric pressure, and the threshold limit value of chlorine is 0.5 ppm. Therefore, several actions were taken to ensure the safety of working with chlorine: (1) the synthesis setup was built in a fume hood; (2) a portable chlorine detector was placed next to the setup; (3) a full-face mask was prepared in case of leakage; (4) four washing bottles were connected to the system, including three NaOH solutions (10 wt%) and one KI solution (10 wt%). The NaOH solutions were used to destroy the excess of chlorine and the KI solution was an indicator for the saturation of NaOH solutions.

1.2.2 Synthetic procedures

A photograph and scheme of the setup for synthesis of trichloride ILs are shown in Fig. S1 and S2. The setup consists of two gas cylinders (Cl_2 and N_2 gas), one reaction flask and four washing bottles. Before reaction, the starting material chloride IL (5–20 g) in a 100 mL round bottom flask was dried under vacuum at 50 °C for 24 h to remove the water. After tightly connecting the flask to the Cl_2 setup, N_2 gas was purged into the system to remove all the moisture at a flow rate of 20 g/h and 2 bar for 30 min. When large amount of N_2 bubbles could be observed in the last washing bottle, which indicates the absence of leaks in the connections of the system, chlorine gas was purged into the flask at the minimum flow rate (2.1 g/h) at 2 bar to allow the maximum contact time between chlorine gas and the chloride IL. After the desired amount of Cl_2 had been added to the reaction flask, N_2 gas was purged into the system again to remove the remaining Cl_2 in the system first at 2.1 g/h for 30 min and then at 20 g/h for 10 min. The excess of Cl_2 was destroyed by reacting with the 10 wt% NaOH solutions. A 10 wt% KI solution was used as an indicator for the saturation of the NaOH solution in the second washing bottle by Cl_2.

Fig. S1 Photograph of the setup for synthesis of trichloride ILs.

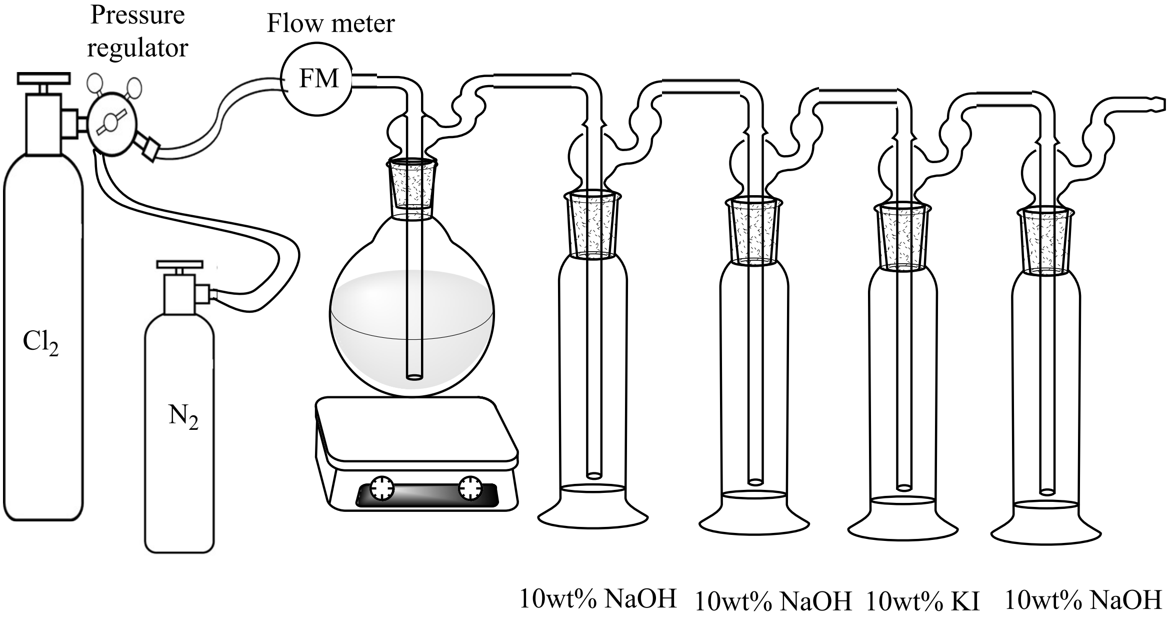


Fig. S2 Scheme of the setup for synthesis of trichloride ILs.

1.3 Analysis

^{1}H NMR, ^{13}C NMR and ^{31}P NMR of the chloride and trichloride ILs were recorded on a Bruker Ascend 400 MHz NMR spectrometer (operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C 162 MHz for ^{31}P). All samples were diluted in DMSO-d_6 using tetramethylsilane as the reference compound. Raman spectra were measured on a Bruker Vertex 70 spectrometer with RAMII Raman module laser (1064 nm), at a power of 500 mW. Melting points and glass transition temperatures were determined on a Mettler-Toledo DSC 1 instrument, using a heating rate of 10 °C/min under a helium atmosphere. The densities were measured with an Anton–Paar DMA 4500 M density meter. Viscosities were measured by an Anton–Paar LOVIS 2000 ME Micro viscometer (falling-ball viscometer), and by a certified calibrated Ubbelohde glass capillary viscometer (40–800 mm^2/s) from SI analytics in a Lauda thermostatted water bath. The elemental analysis of carbon, hydrogen and nitrogen (CHN analysis) was performed on a flash 2000 Elemental analyzer of Thermo Scientific Interscience. Low-resolution mass spectra were recorded on a Thermo Finnigan LCQ Advantage instrument (ESI mode) where 1mg/mL trichloride ILs were diluted in acetonitrile.

A Bruker S2 Picofox total reflection X-ray fluorescence (TXRF) spectrometer was used to determine the metal concentrations in the leachate. A 5 µL drop of the samples (leachate diluted 50 times with ethanol) was dispensed on a quartz sample carrier which was pretreated with a SERVA® silicone solution in isopropanol (30 µL) by drying at 60 °C for 30 min. The sample carriers were dried at 60 °C for 30 min before analysis. Mn, Ga, Au and Ga were used as internal standards for Sm, Dy, Pt and Ta, respectively.

Extended X-ray Absorption Fine Structure (EXAFS) spectra of the K-edge of the metals were collected at the Dutch-Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The measurements were done in transmission mode using Ar/He gas filled ionisation chambers. A brass sample holder with Kapton® windows and a flexible polymeric spacer (VITON®) with a thickness of 2 mm was used as a sample holder.

Standard procedures were used for pre-edge subtraction and data normalization in order to isolate the EXAFS function (χ). The isolated EXAFS oscillations, accomplished by a smoothing spline as realized in the program VIPER,[1] were k^4 – weighted and Fourier transformed over the k-range using a Gaussian Rounded end window function. The data were fitted using the *ab initio* code FEFF 7.0,[2] which was used to calculate the theoretical phase and amplitude functions that subsequently were used in the non-linear least-squares refinement of the experimental data. Fitting of the data with the model was performed in R-space. Estimated standard errors are shown between parentheses in Table 2 in the main text and calculated by VIPER. S_0 was fixed for all fits at 0.95.

2. Results

2.1 IL Characterisation

2.1.1 ^{1}H NMR data

Table S2. ^{1}H NMR data for trichloride ILs and the unit of the coupling constant (*J*) is Hertz

ILs	Chemical shift (ppm)
$[P_{666,14}][Cl_3]$	2.21 (m, 8H, 4 CH_2), 1.10-1.65 (m, 48H, 24 CH_2), 0.86 (m, 12H, 4 CH_3)
$[P_{4444}][Cl_3]$	2.24 (m, 8H, 4 CH_2), 1.42 (m, 16H, 8 CH_2), 0.92 (t, 12H, *J*=6.9, 4 CH_3)
$[P_{444,14}][Cl_3]$	2.22 (m, 8H, 4 CH_2), 1.15-1.55 (m, 36H, 18 CH_2), 0.92 (t, 9H, *J*=7.1, 3 CH_3), 0.86 (t, 3H, *J*=6.8, CH_3)
$[BPy][Cl_3]$	9.33 (d, 2H, *J*=5.8, 2 CH), 8.66 (t, 1H, *J*=7.7, CH), 8.21 (t, 2H, *J*=6.8, 2 CH), 4.73 (t, 2H, *J*=7.4, CH_2), 2.01-1.82 (m, 2H, CH_2) 1.38-1.21 (m, 2H, CH_2), 0.92 (t, 3H, *J*=7.3, CH_3)
$[N_{1888}][Cl_3]$	3.22 (m, 6H, 3 CH_2), 2.96 (s, 3H, CH_3), 1.61 (m, 6H, 3 CH_2), 1.27 (m, 30H, 15 CH_2), 0.87 (t, 9H, *J*=6.3, 3 CH_3)
$[BMPyrr][Cl_3]$	3.51 (m, 4H, 2 CH_2), 3.37 (m, 2H, CH_2), 3.02 (s, 3H, CH_3), 2.08 (m, 4H, 2 CH_2), 1.68 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 0.93 (t, 3H, *J*=7.3, CH_3)
$[2\text{-}MBPy][Cl_3]$	9.20 (d, 1H, *J*=6.1, CH), 8.51 (t, 1H, *J*=7.8, CH), 8.12 (d, 1H, *J*=7.9, CH), 8.01 (t, 1H, *J*=6.8, CH), 4.63 (t, 3H, *J*=7.8, CH_3), 2.89 (s, 3H, CH_3), 1.93-1.72 (m, 2H, CH_2), 1.49-1.27 (m, 2H, CH_2), 0.94 (t, 3H, *J*=7.3, CH_3)
$[BMPip][Cl_3]$	3.53-3.26 (m, 6H, 3 CH_2), 3.05 (s, 3H, CH_3), 1.79 (m, 4H, 2 CH_2), 1.65 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 0.94 (t, 3H, *J*=7.4, CH_3)
$[4\text{-}MBPy][Cl_3]$	9.15 (d, 2H, *J*=6.1, 2 CH), 8.04 (d, 2H, *J*=6.1, 2 CH), 4.65 (t, 2H, *J*=7.4, CH_2), 2.63 (s, 3H, CH_3), 1.89 (m, 2H, CH_2), 1.29 (m, 2H, CH_2), 0.91 (t, 3H, *J*=7.4, CH_3)
$[HPy][Cl_3]$	9.29 (d, 2H, *J* = 5.9, 2 CH), 8.65 (t, 1H, *J*=7.7, CH), 8.21 (t, 2H, *J*=6.8, 2 CH), 4.70 (t, 2H, *J*=7.4, CH_2), 1.94 (m, 2H, CH_2), 1.28 (m, 6H, 3 CH_2), 0.85 (t, 3H, *J*=6.3, CH_3)

2.1.2 Comparison of the ^{1}H NMR spectra of chloride and trichloride ILs based on imidazolium cations

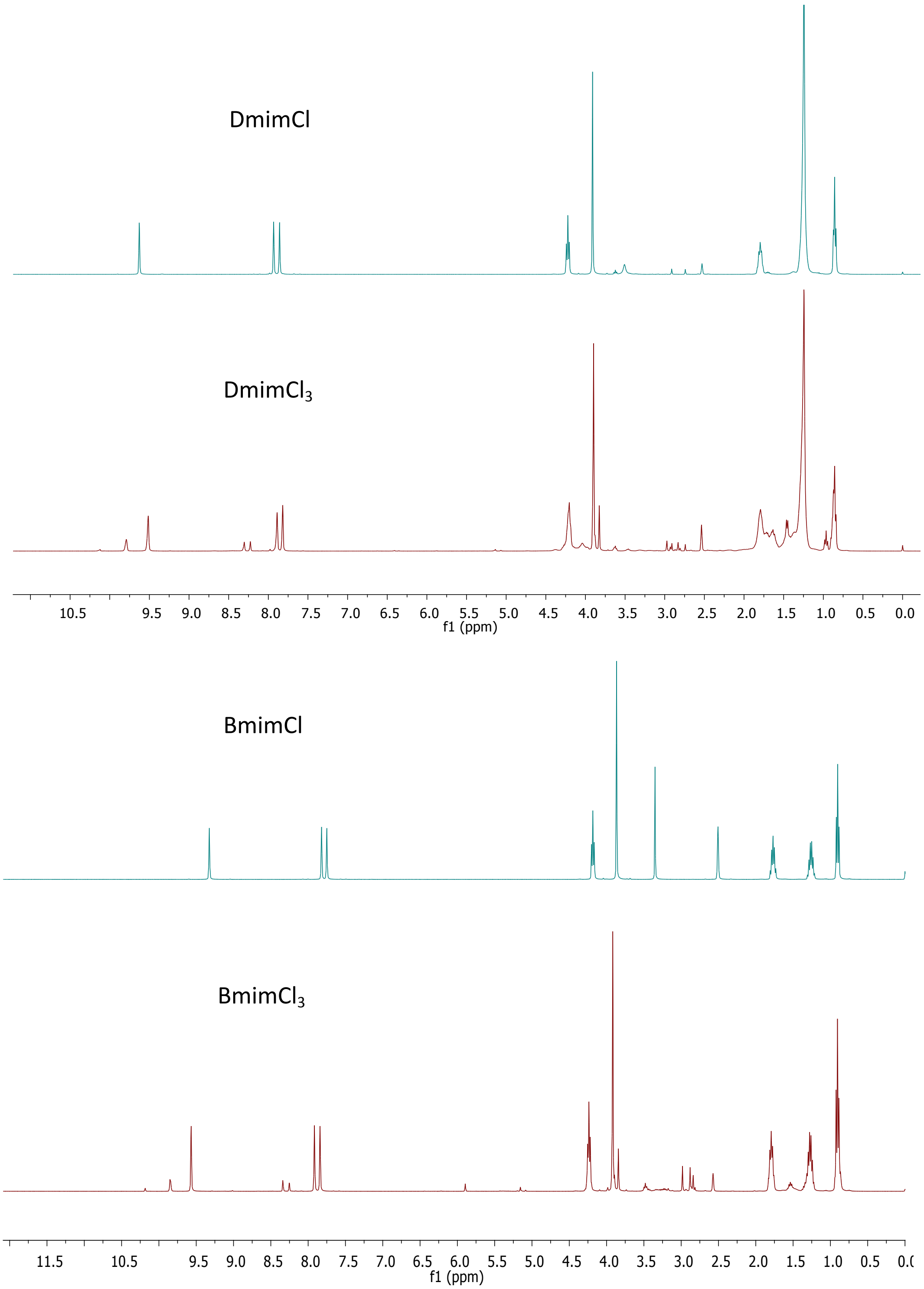
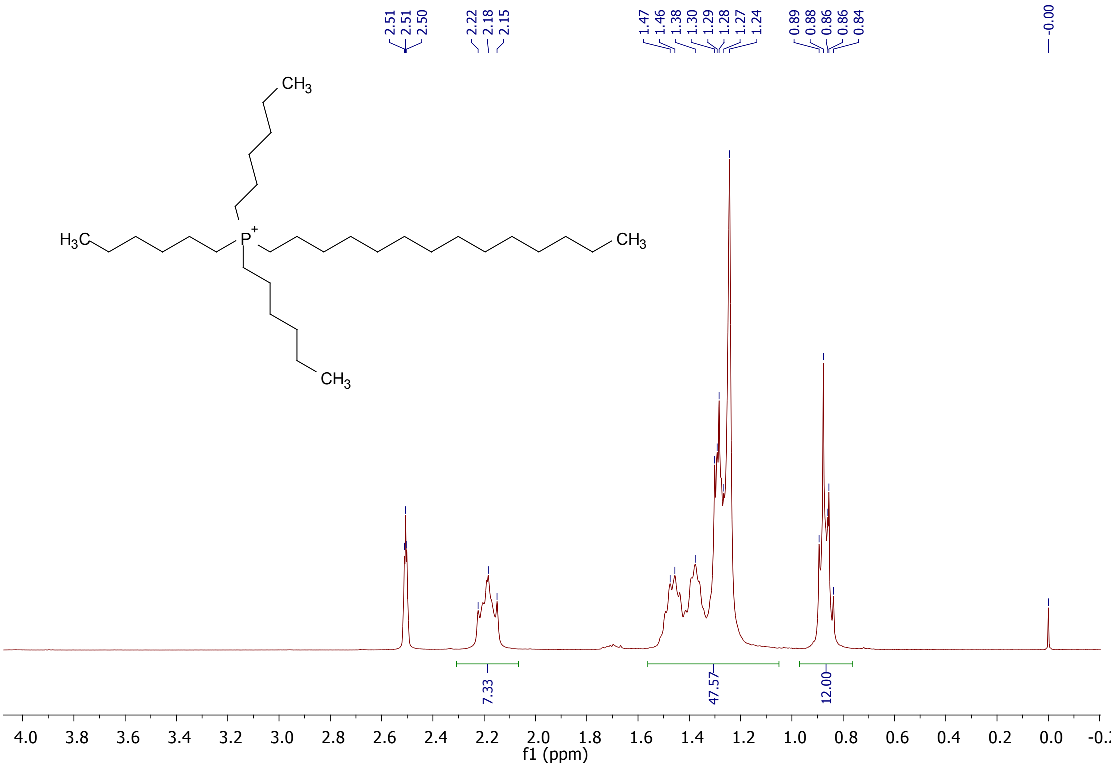


Fig. S3 Comparison of the ^{1}H NMR spectra between [Dmim]Cl and [Dmim][Cl$_3$], and between [Bmim]Cl and [Bmim][Cl$_3$].

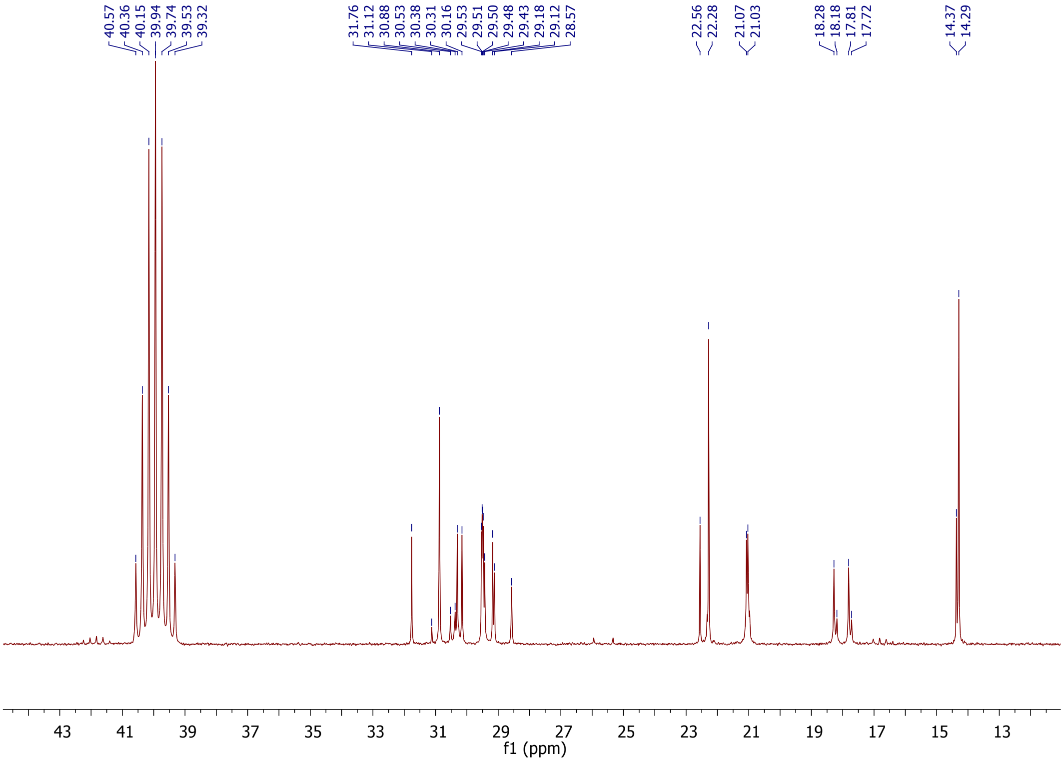
2.1.3 ^{1}H, ^{13}C and ^{31}P NMR spectra of the studied trichloride ILs

2.1.3.1 [$P_{666,14}$][Cl_3]

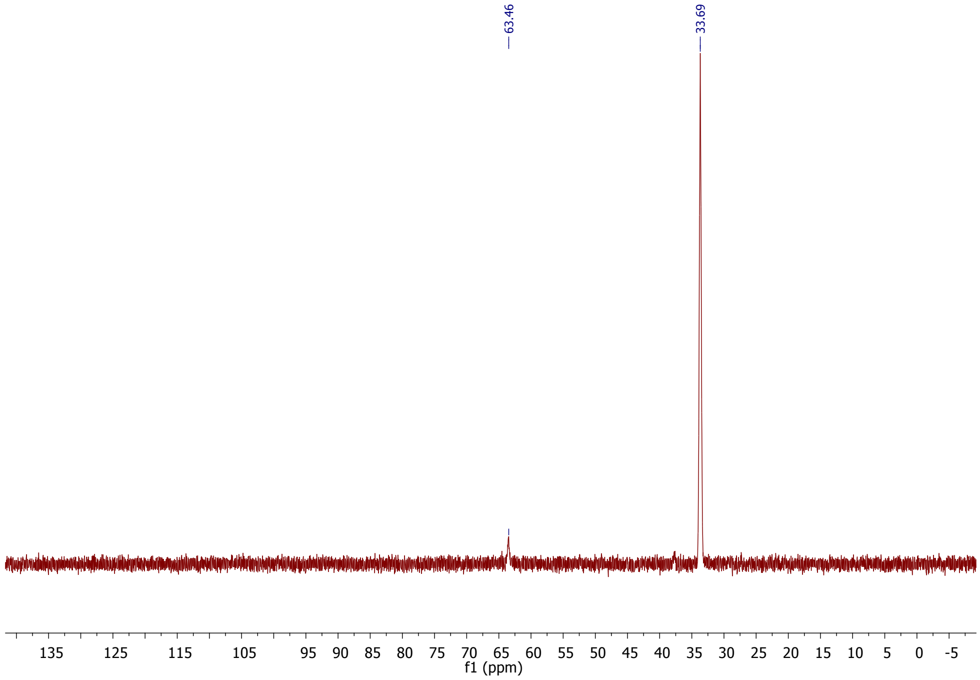
(1) ^{1}H NMR



(2) ^{13}C NMR

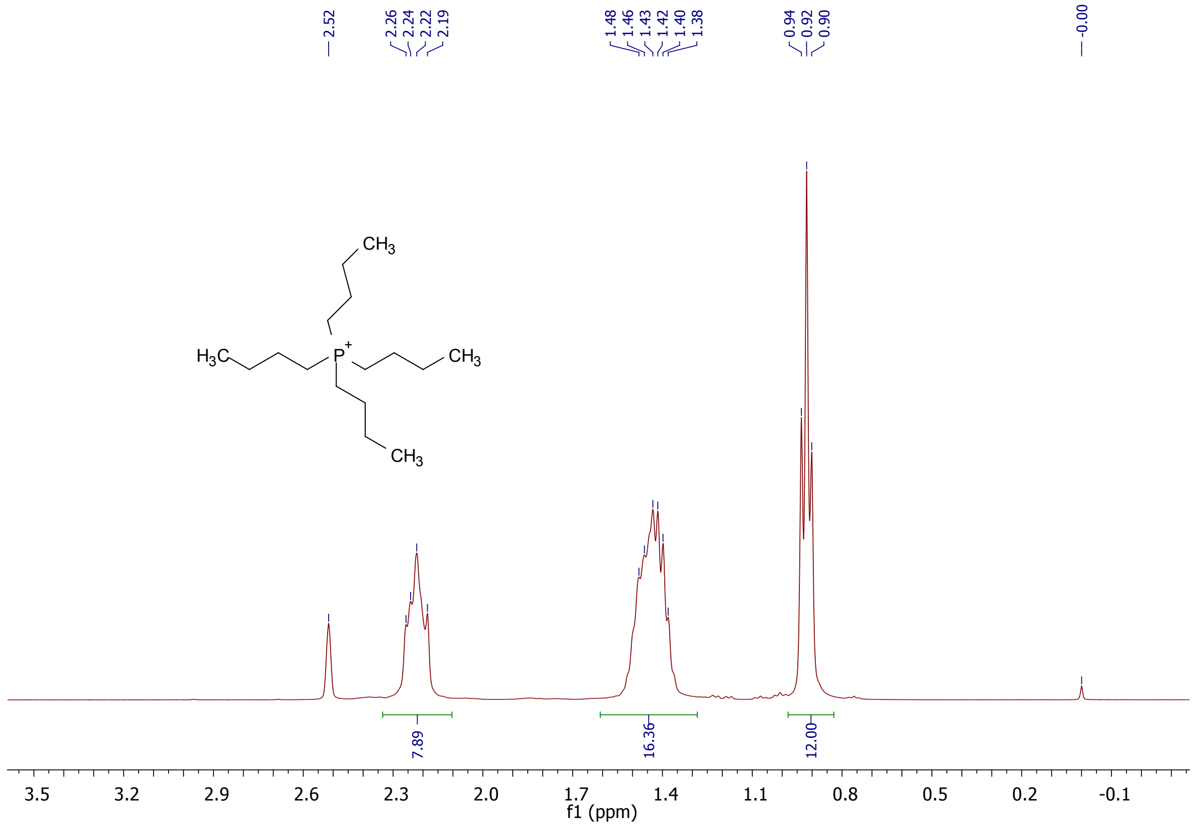


(3) ^{31}P NMR (the peak at 64 ppm is from the impurity of $[P_{666,14}]Cl$)

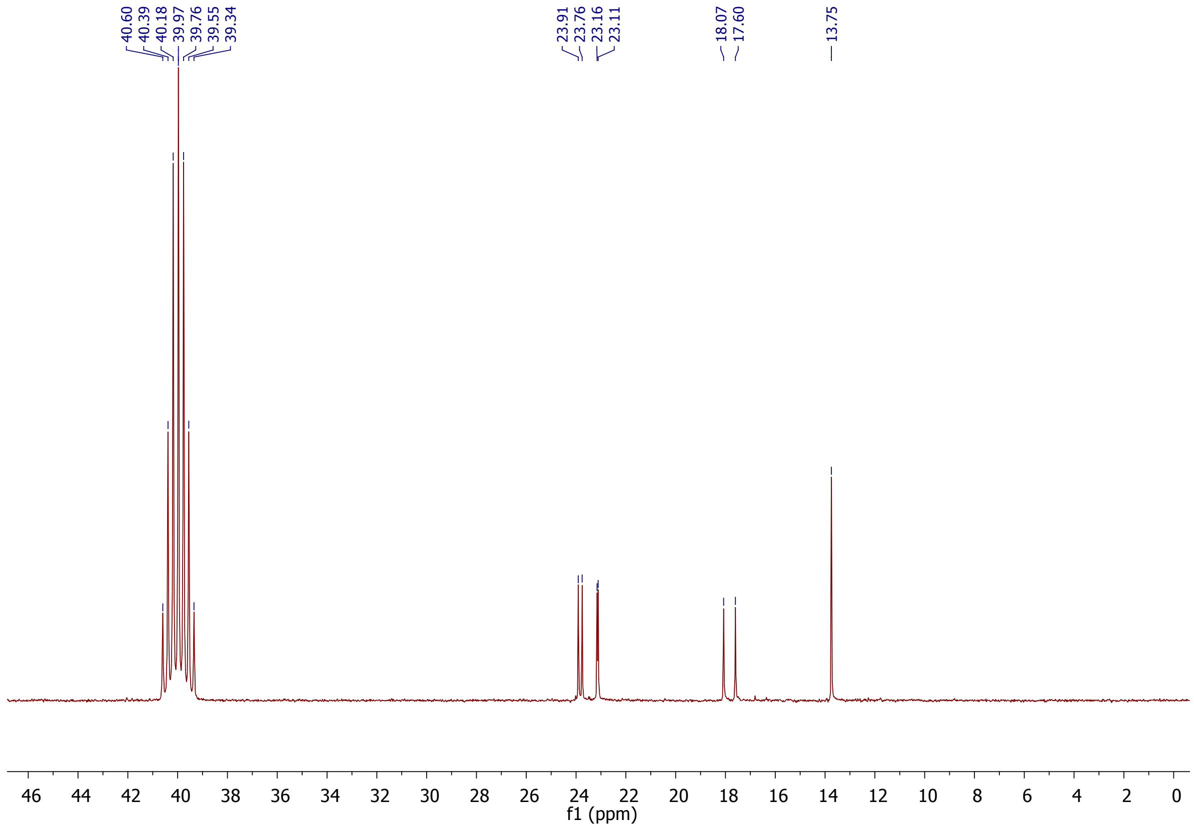


2.1.3.2 $[P_{4444}][Cl_3]$

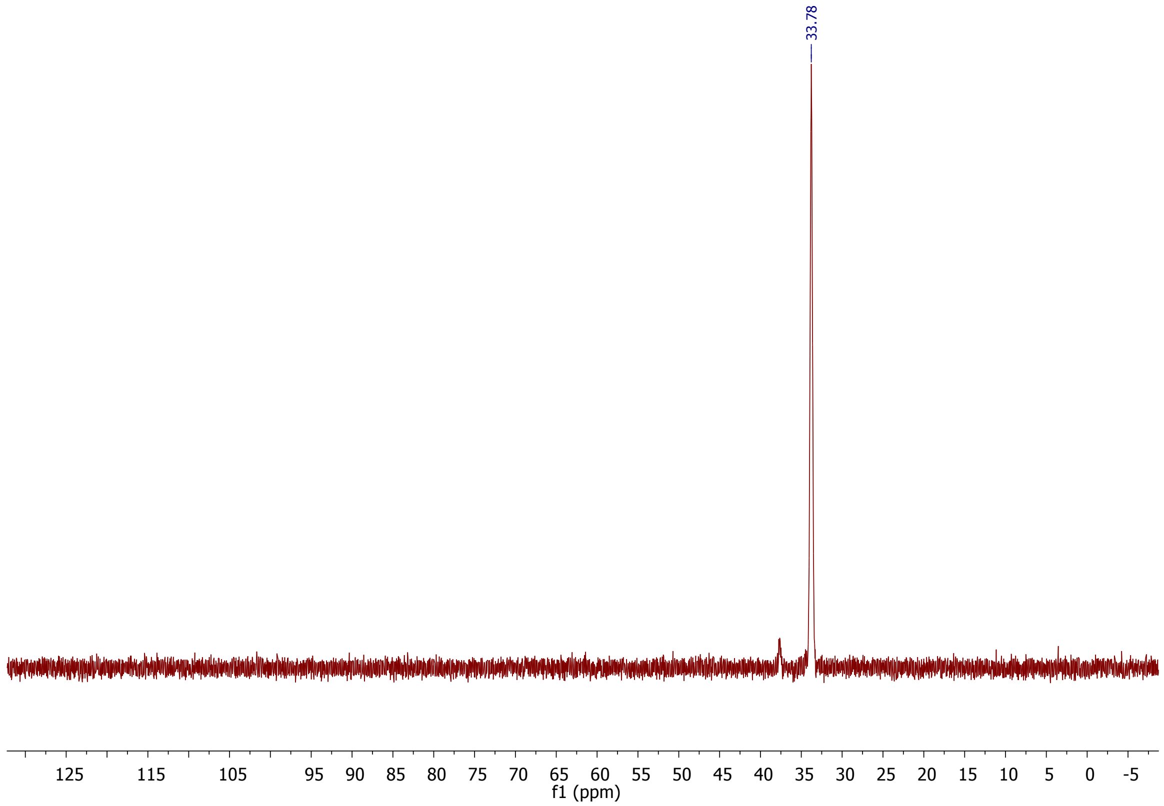
(1) ^{1}H NMR



(2) ^{13}C NMR

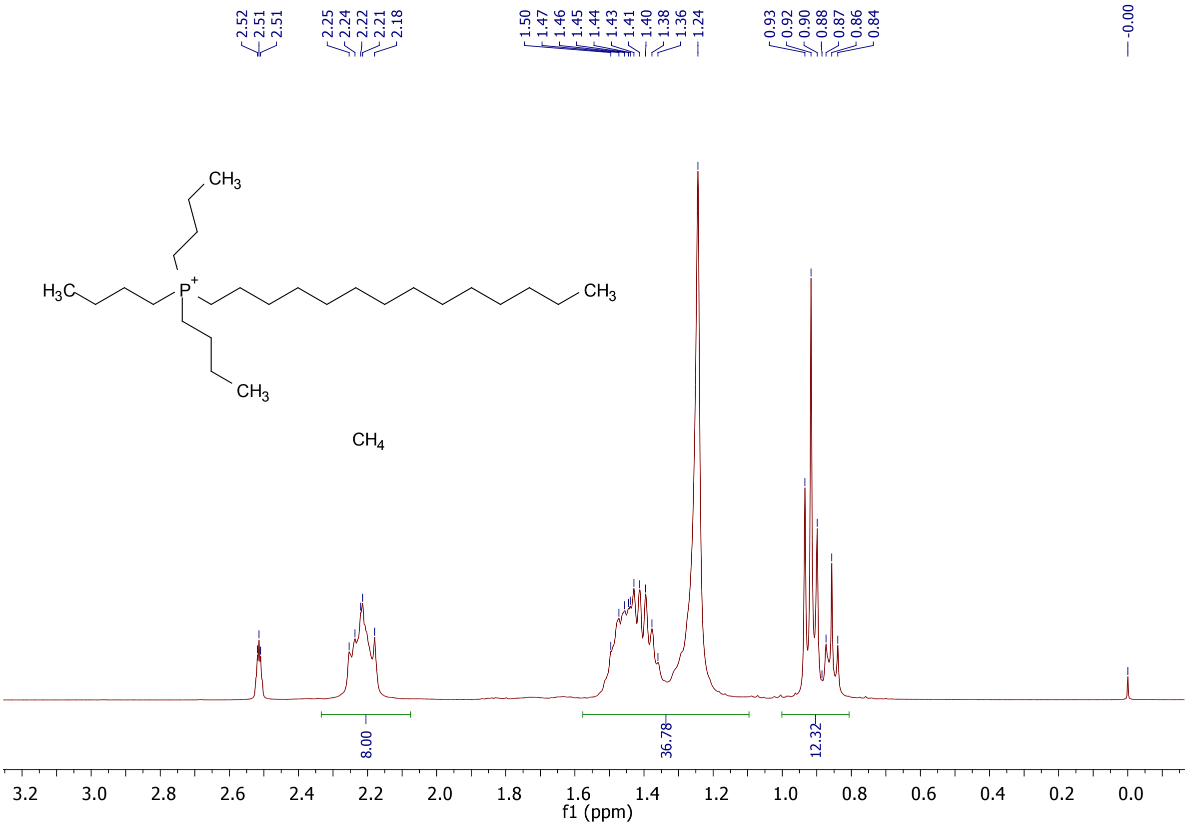


(3) ^{31}P NMR (the peak at 37 ppm is from the impurity of [$P_{444,14}$]Cl)

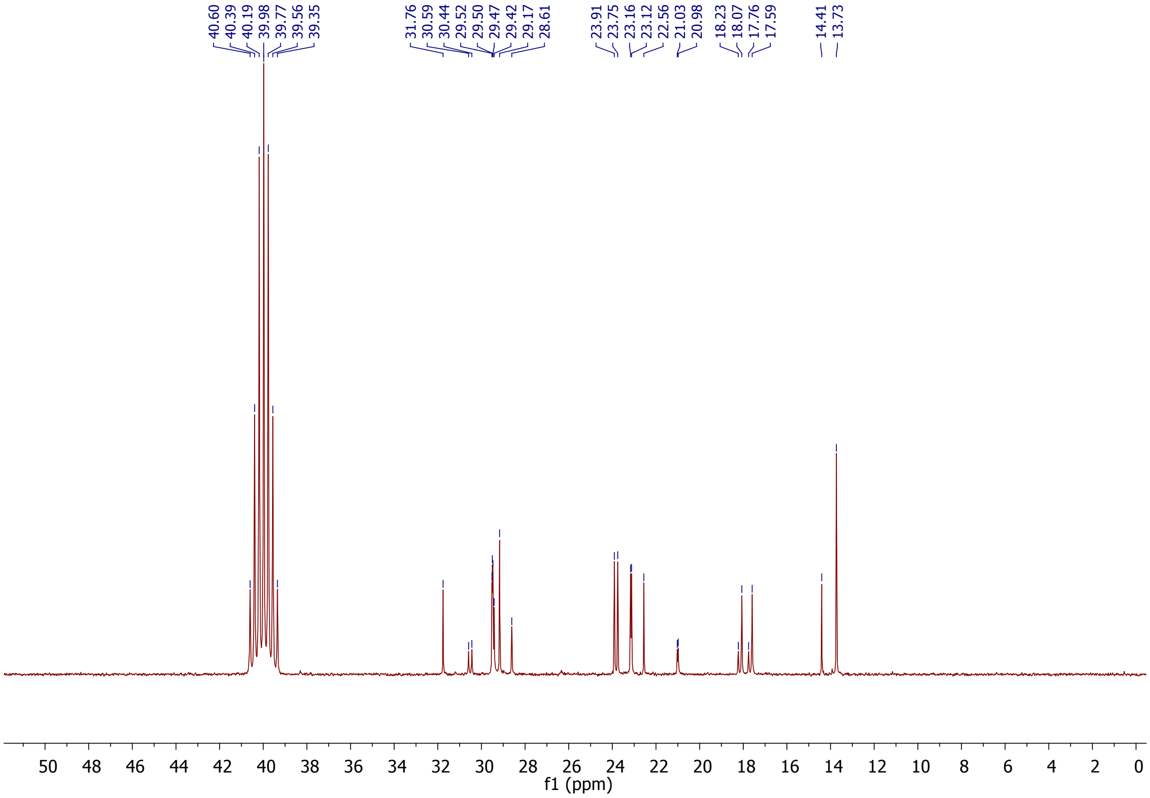


2.1.3.3 $[P_{444,14}][Cl_3]$

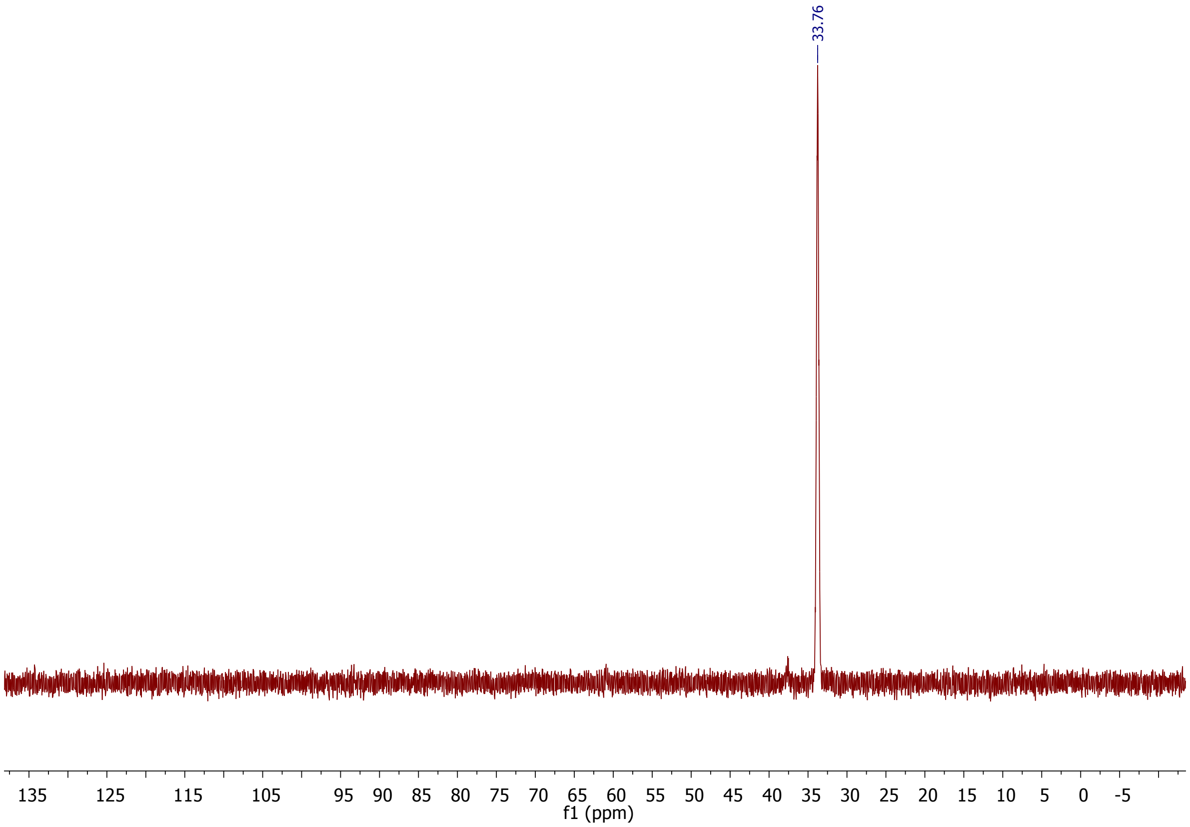
(1) ^{1}H NMR



(2) ^{13}C NMR

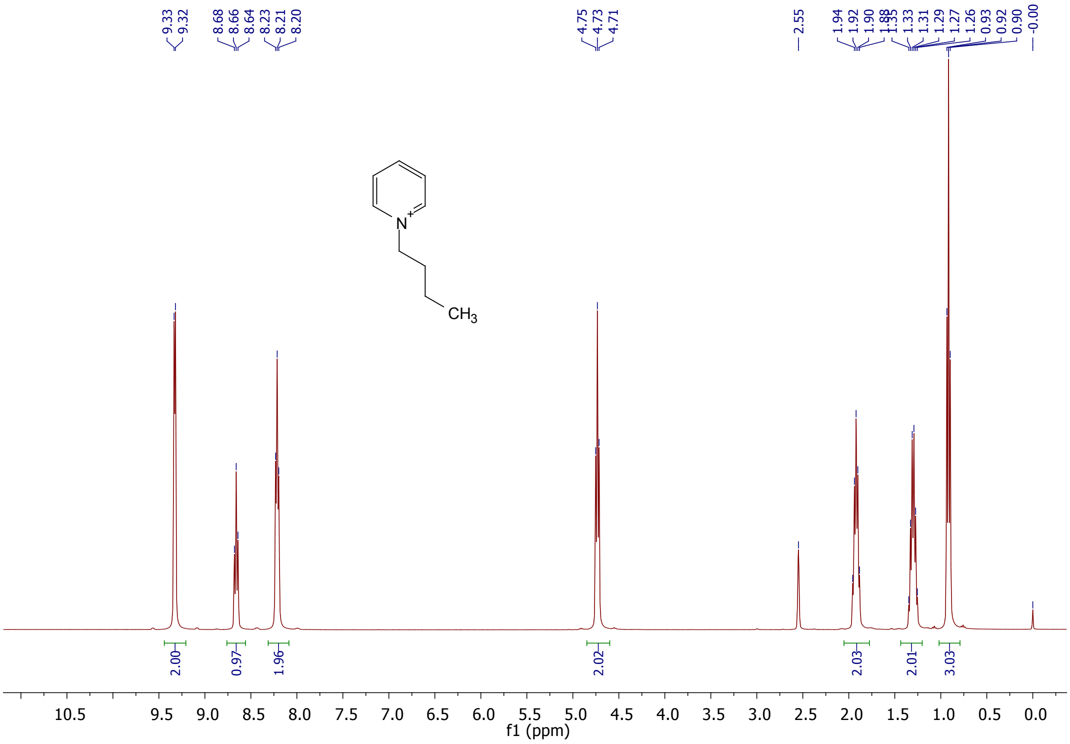


(3) ^{31}P NMR (the peak at 37 ppm is from the impurity of $[P_{4444}]Cl$)

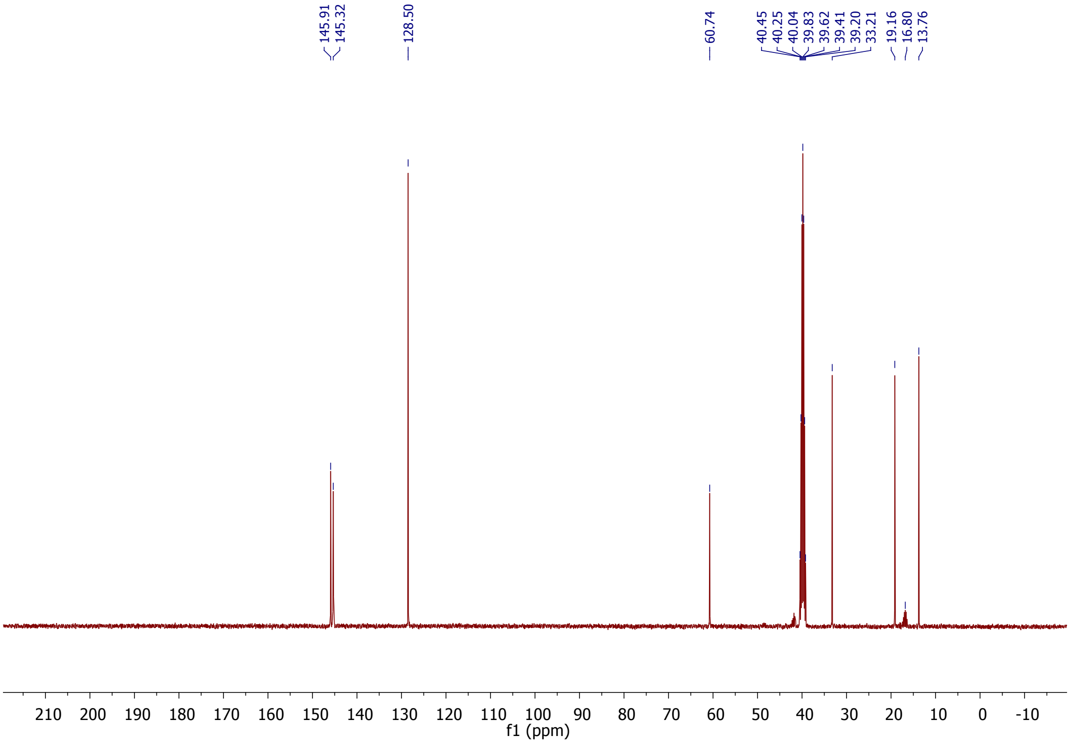


2.1.3.4 [BPy][Cl_3]

(1) ^1H NMR

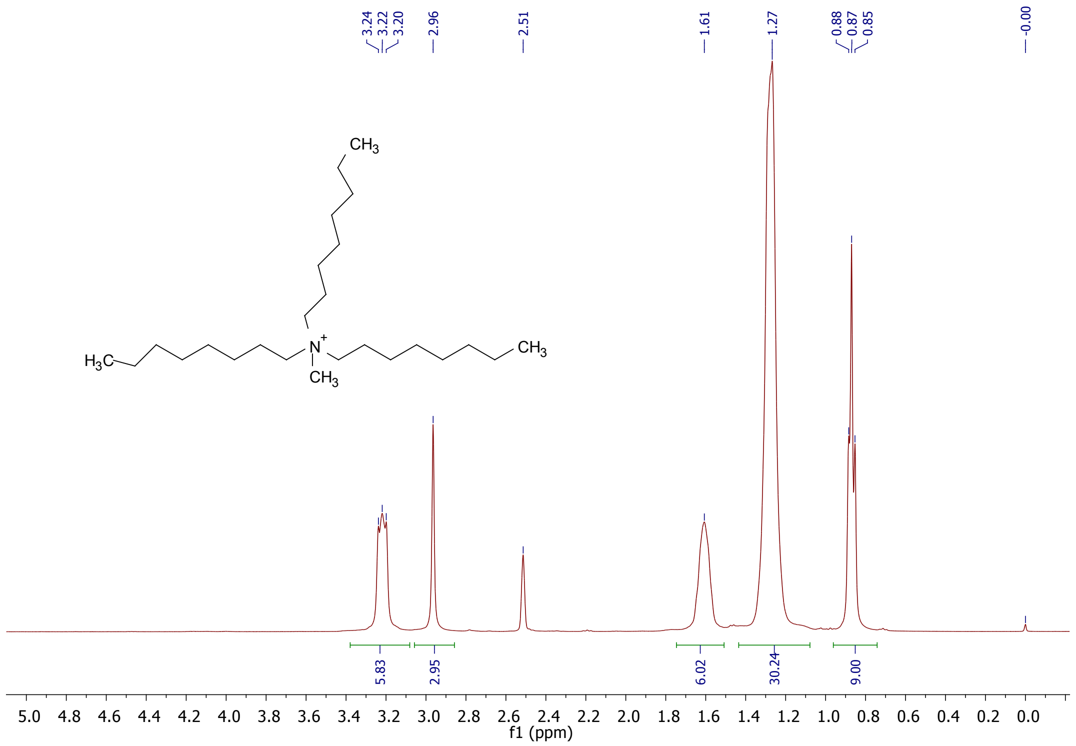


(2) ^{13}C NMR

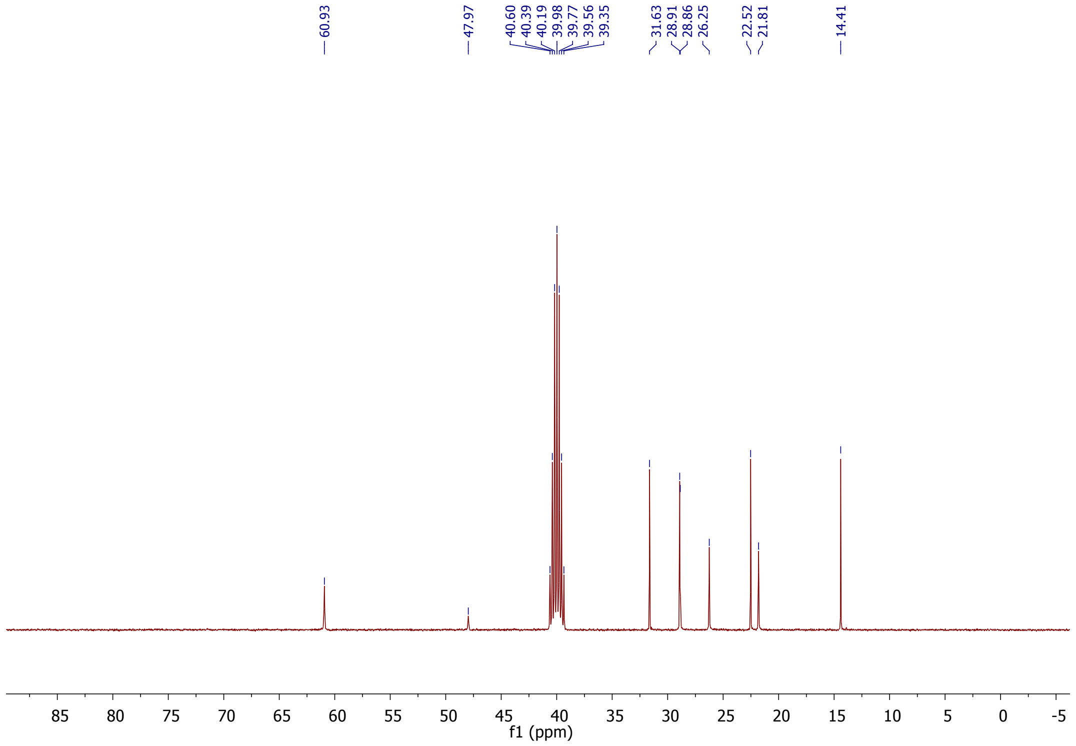


2.1.3.5 [N_{1888}][Cl_3]

(1) ^{1}H NMR

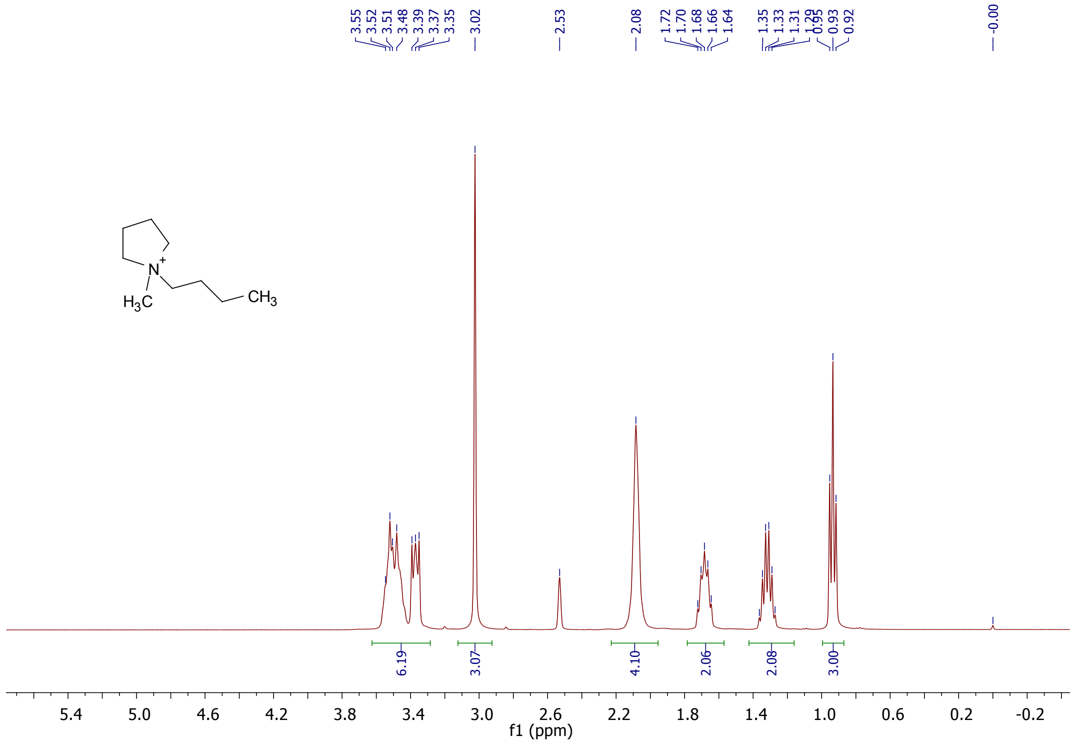


(2) ^{13}C NMR

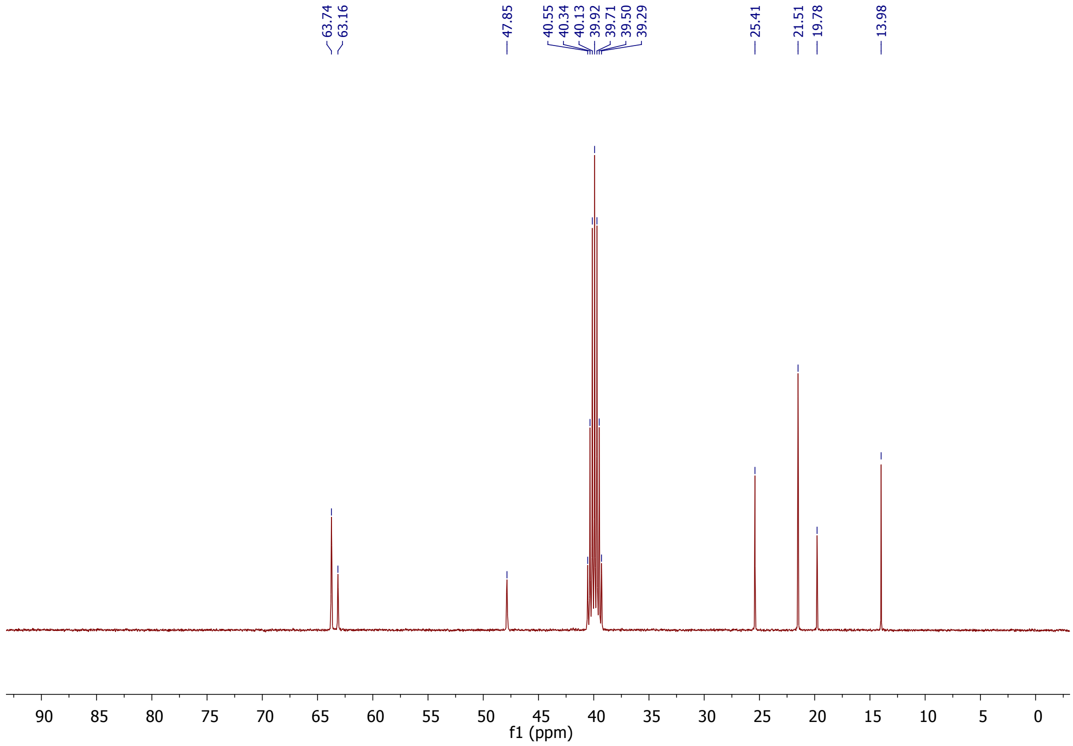


2.1.3.6 [BMPyrr][Cl_3]

(1) ^{1}H NMR

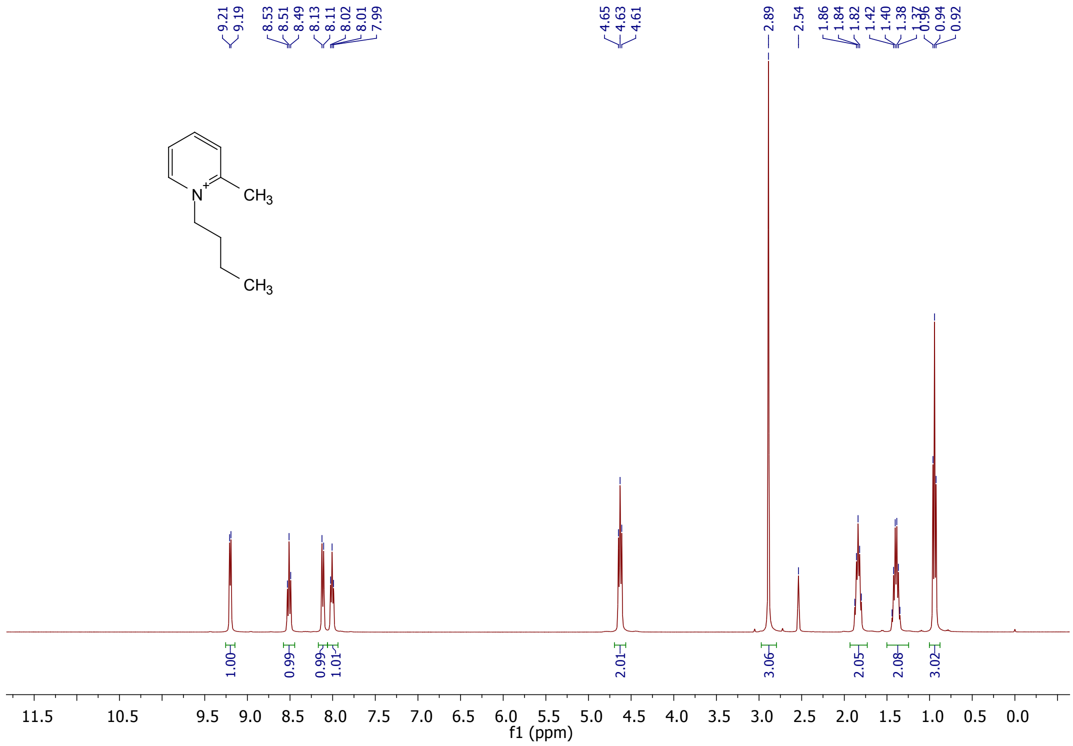


(2) ^{13}C NMR

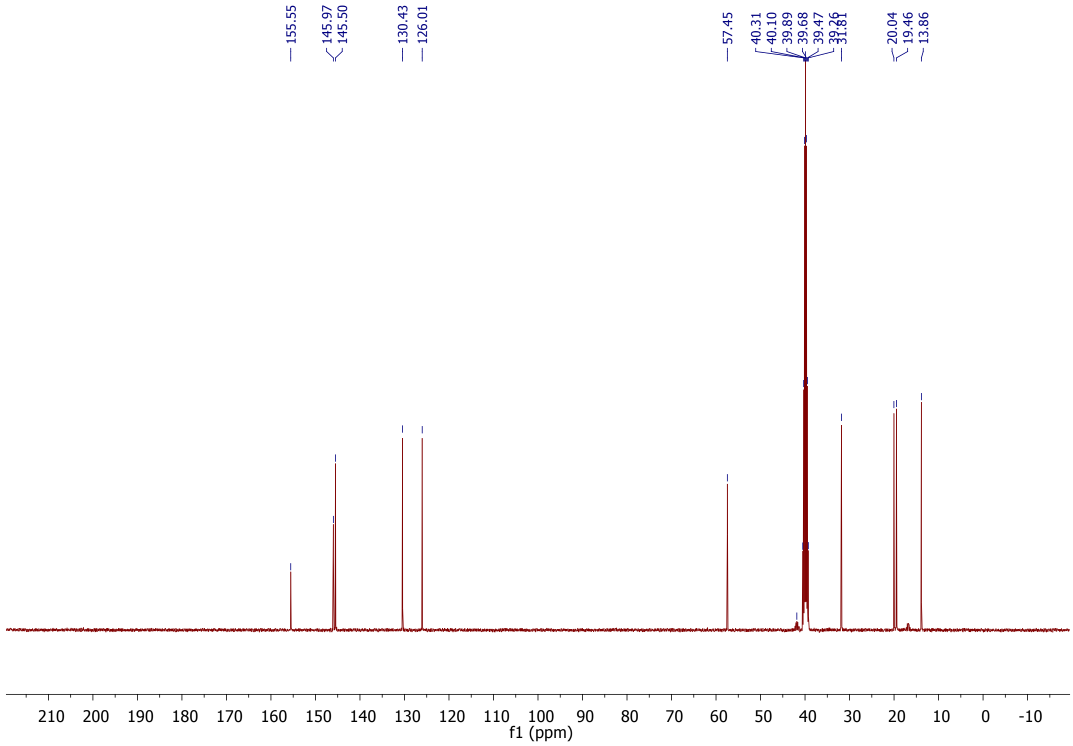


2.1.3.7 [2-MBPy][Cl_3]

(1) ^{1}H NMR

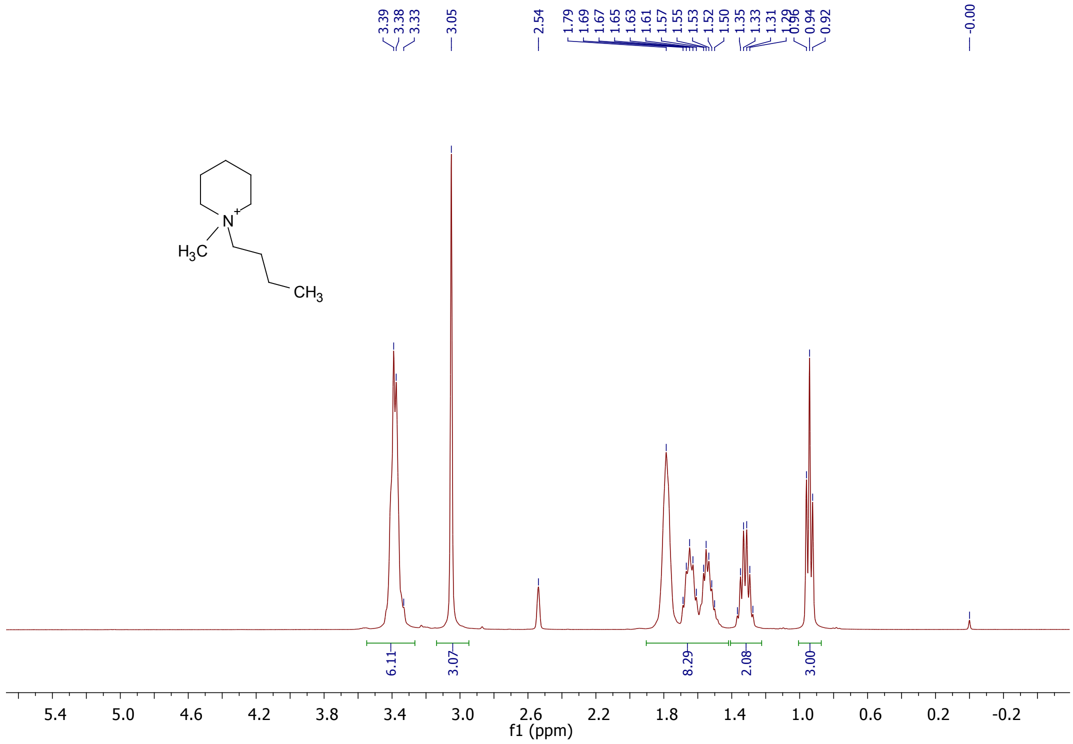


(2) ^{13}C NMR

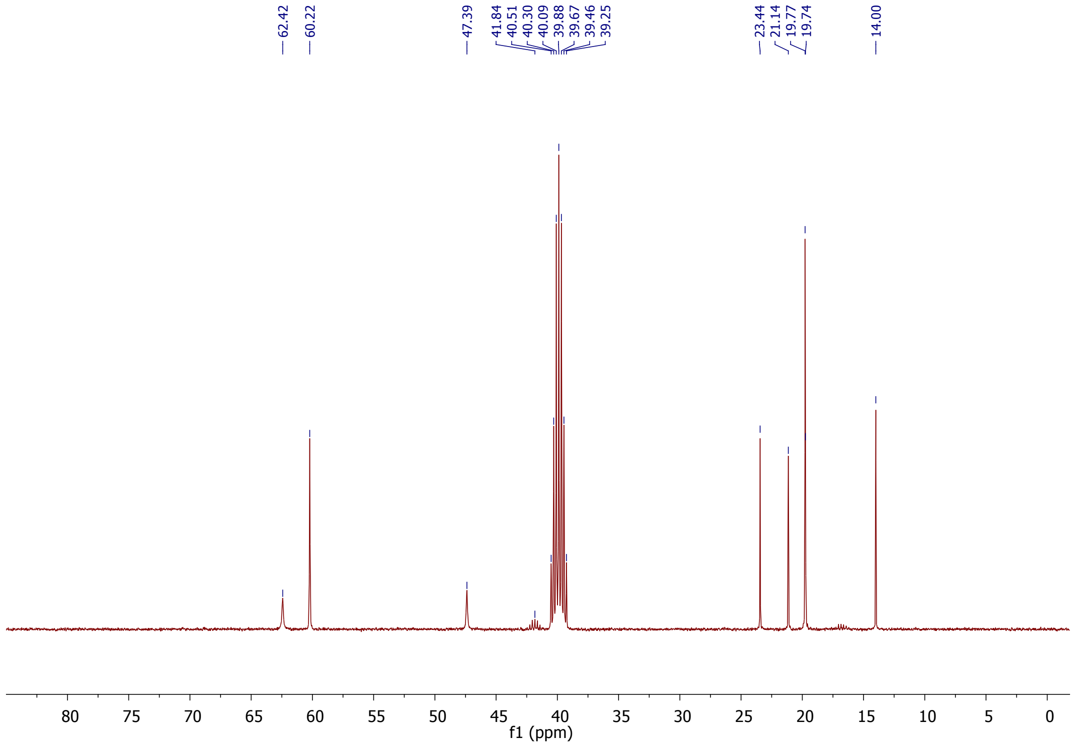


2.1.3.8 [BMPip][Cl_3]

(1) ^{13}H NMR

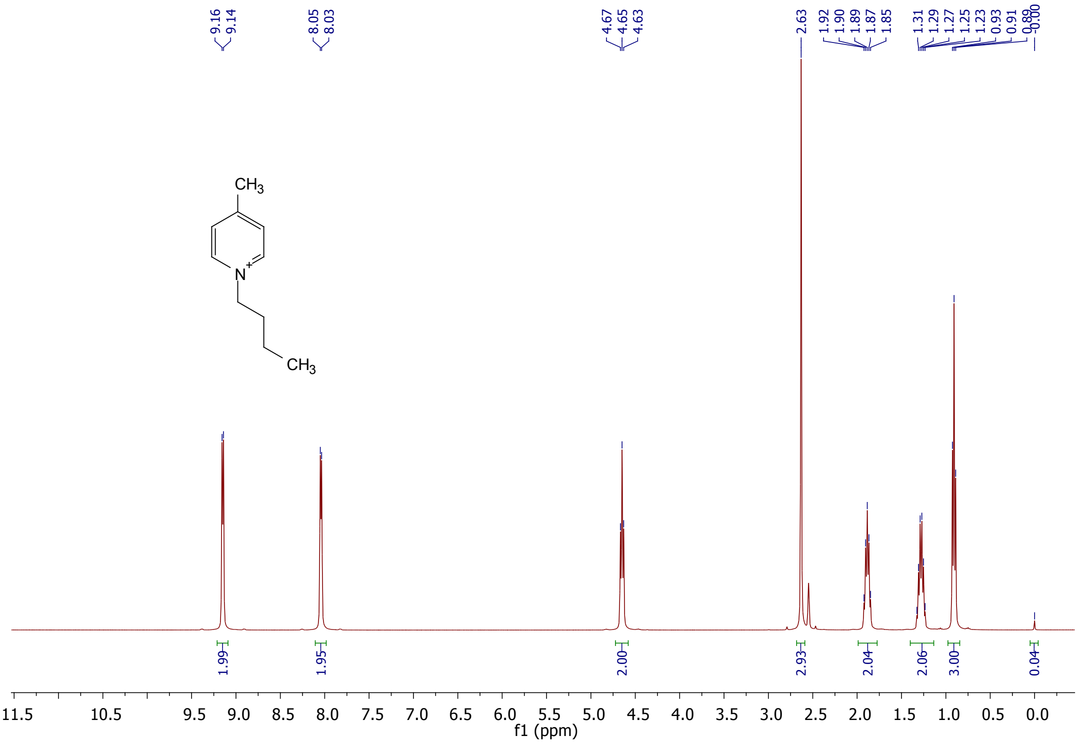


(2) ^{13}C NMR

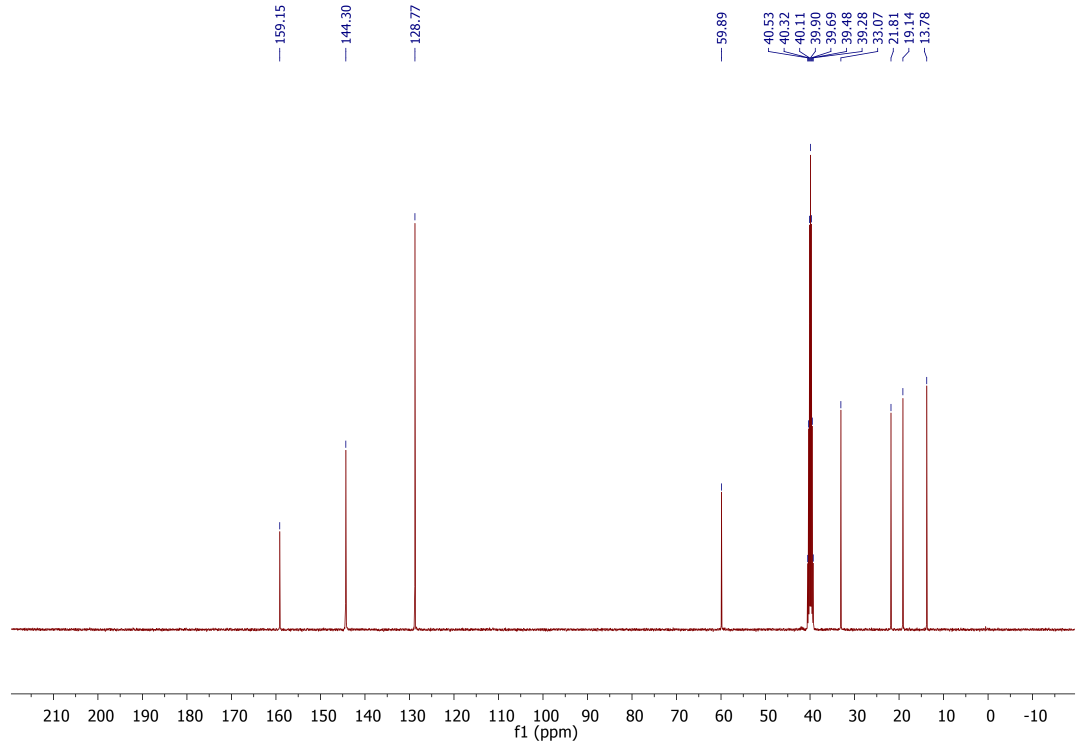


2.1.3.9 [4-MBPy][Cl$_3$]

(1) ^{1}H NMR

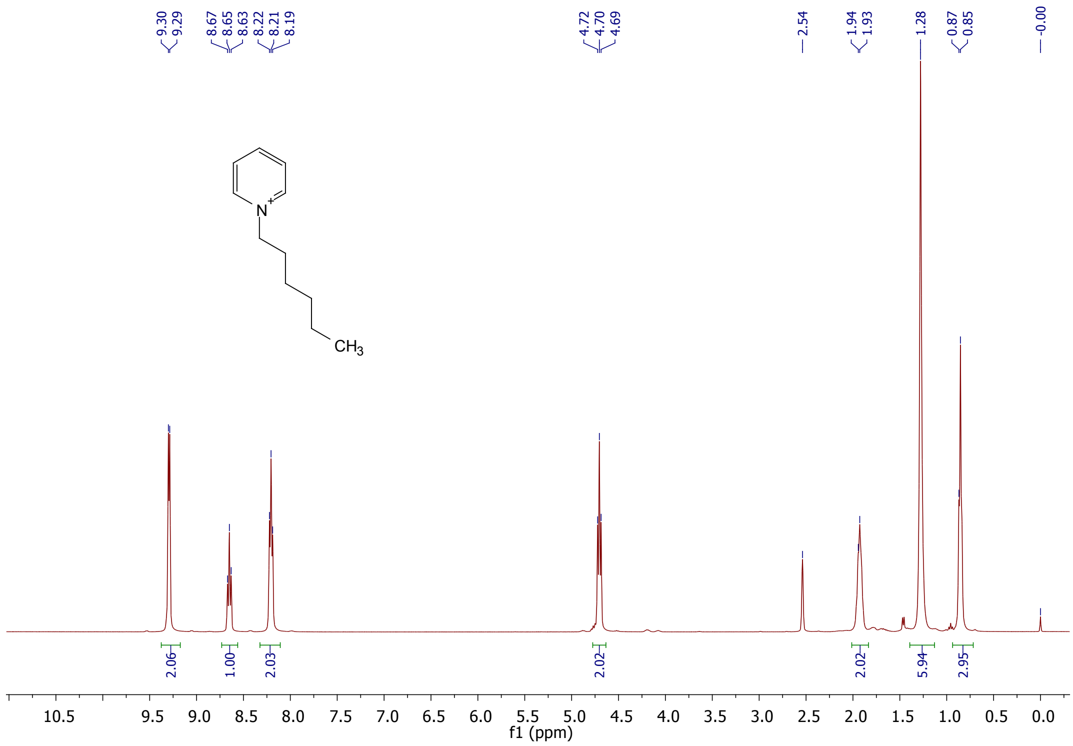


(2) ^{13}C NMR

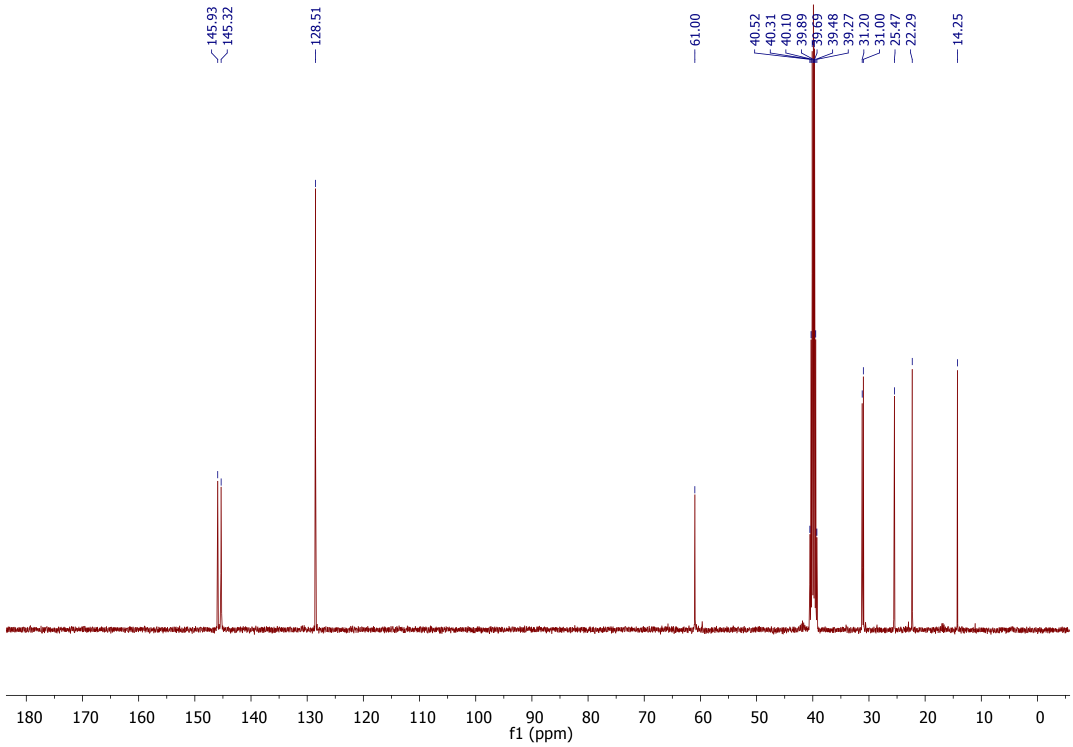


2.1.3.10 [HPy][Cl$_3$]

(1) ^{1}H NMR



(2) ^{13}C NMR



2.1.4 CHN analysis

Table S3. Results of CHN analysis for trichloride ILs

ILs	Molecular formula	Calculated (%)			Found (%)		
		N	C	H	N	C	H
$[P_{666,14}][Cl_3]$	$C_{32}H_{68}PCl_3$	0.0	65.1	11.6	0.7	64.9	11.6
$[P_{4444}][Cl_3]$	$C_{16}H_{36}PCl_3$	0.0	52.5	9.9	0.7	53.1	10.2
$[P_{444,14}][Cl_3]$	$C_{26}H_{56}PCl_3$	0.0	61.7	11.2	1.1	62.1	11.4
$[BPy][Cl_3]$	$C_9H_{14}NCl_3$	5.8	44.6	5.8	7.2	46.9	6.3
$[N_{1888}][Cl_3]$	$C_{25}H_{54}NCl_3$	2.9	63.2	11.5	3.6	63.2	11.4
$[BMPyrr][Cl_3]$	$C_9H_{20}NCl_3$	5.6	43.5	8.1	5.9	43.8	8.2
$[2\text{-}MBPy][Cl_3]$	$C_{10}H_{16}NCl_3$	5.5	46.8	6.3	6.1	47.7	6.5
$[BMPip][Cl_3]$	$C_{10}H_{22}NCl_3$	5.3	45.7	8.4	5.9	46.0	8.7
$[4\text{-}MBPy][Cl_3]$	$C_{10}H_{16}NCl_3$	5.5	46.8	6.3	6.2	47.5	6.4
$[HPy][Cl_3]$	$C_{11}H_{18}NCl_3$	5.2	48.8	6.7	6.0	50.2	7.0

2.1.5 ESI-MS analysis

Table S4. Results of ESI-MS analysis for the cationic species of trichloride ILs

ILs	Found m/z
$[P_{666,14}][Cl_3]$	484 : $[P_{666,14}]^+$
$[P_{4444}][Cl_3]$	259 : $[P_{4444}]^+$, 553 : $[[P_{4444}]_2Cl]^+$
$[P_{444,14}][Cl_3]$	400 : $[P_{444,14}]^+$, 434 : $[[P_{444,14}]Cl - H]^+$, 834 : $[[P_{444,14}]_2Cl]^+$
$[BPy][Cl_3]$	136 : $[BPy]^+$, 307 : $[[BPy]_2Cl]^+$
$[N_{1888}][Cl_3]$	369 : $[N_{1888}]^+$, 771 : $[[N_{1888}]_2Cl]^+$
$[BMPyrr][Cl_3]$	142 : $[BMPyrr]^+$, 319 : $[[BMPyrr]_2Cl]^+$
$[2\text{-}MBPy][Cl_3]$	150 : $[2\text{-}MBPy]^+$, 335: $[[2\text{-}MBPy]_2Cl]^+$
$[BMPip][Cl_3]$	156 : $[BMPip]^+$, 347 : $[[BMPip]_2Cl]^+$
$[4\text{-}MBPy][Cl_3]$	150 : $[4\text{-}MBPy]^+$, 335: $[[4\text{-}MBPy]_2Cl]^+$
$[HPy][Cl_3]$	164 : $[HPy]^+$, 363 : $[[HPy]_2Cl]^+$

2.2 Raman spectra

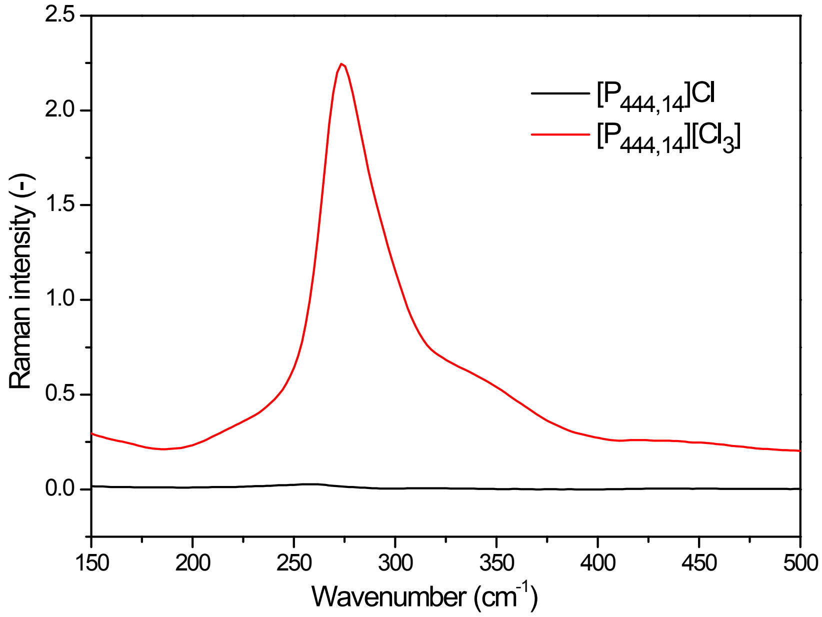


Fig. S4 Raman spectra of [$P_{444,14}$]Cl and [$P_{444,14}$][Cl_3]

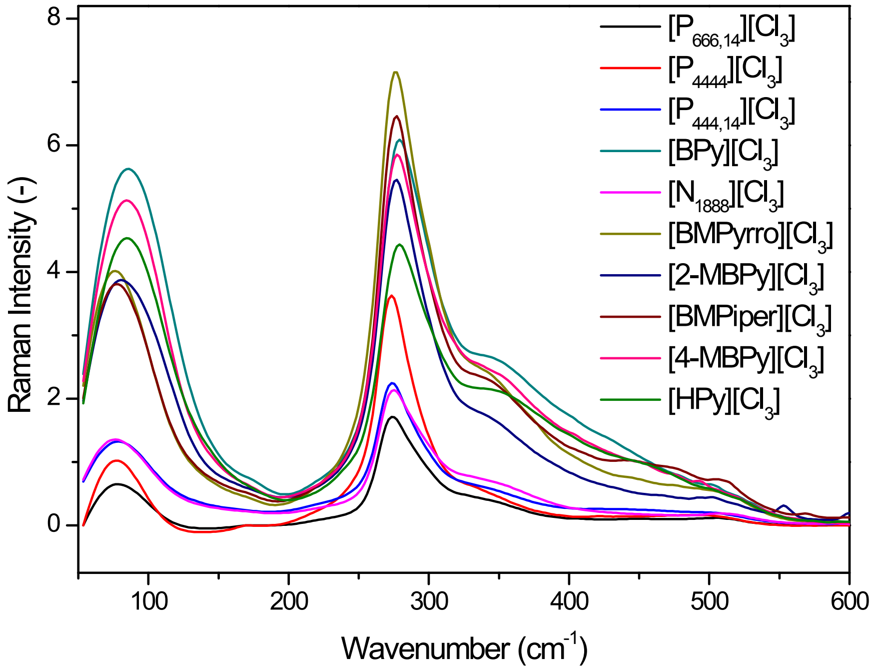


Fig. S5 Raman spectra of the trichloride ILs.

2.3 Density and viscosity

Table S5. Densities of trichloride ILs at different temperatures

	Density (g·cm^{-3})			
ILs	30 °C	40 °C	50 °C	60 °C
[$P_{666,14}$][Cl_3]	0.9440	0.9378	0.9317	0.9255
[P_{4444}][Cl_3]	1.0368	1.0306	1.0244	1.0181
[$P_{444,14}$][Cl_3]	0.9755	0.9693	0.9630	0.9567
[BPy][Cl_3]	1.2200	1.2131	1.2058	1.1946
[N_{1888}][Cl_3]	0.9585	0.9525	0.9465	0.9404
[BMPyrr][Cl_3]	1.1619	1.1556	1.1492	1.1429
[2-MBPy][Cl_3]	1.2059	1.1993	1.1927	1.1861
[BMPip][Cl_3]	1.1509	1.1447	1.1384	1.1318
[4-MBPy][Cl_3]	1.1826	1.1760	1.1693	1.1627
[HPy][Cl_3]	1.1630	1.1563	1.1495	1.141

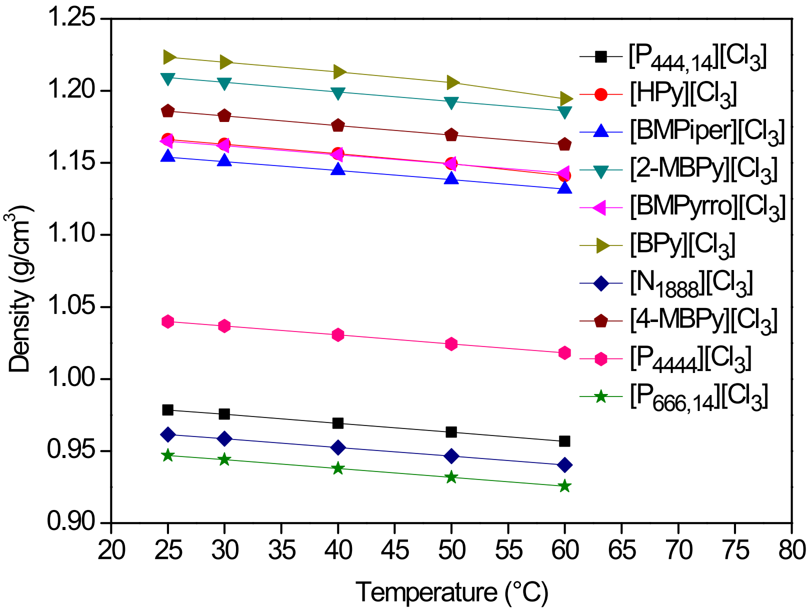


Fig. S6 Densities of trichloride ILs as a function of temperature.

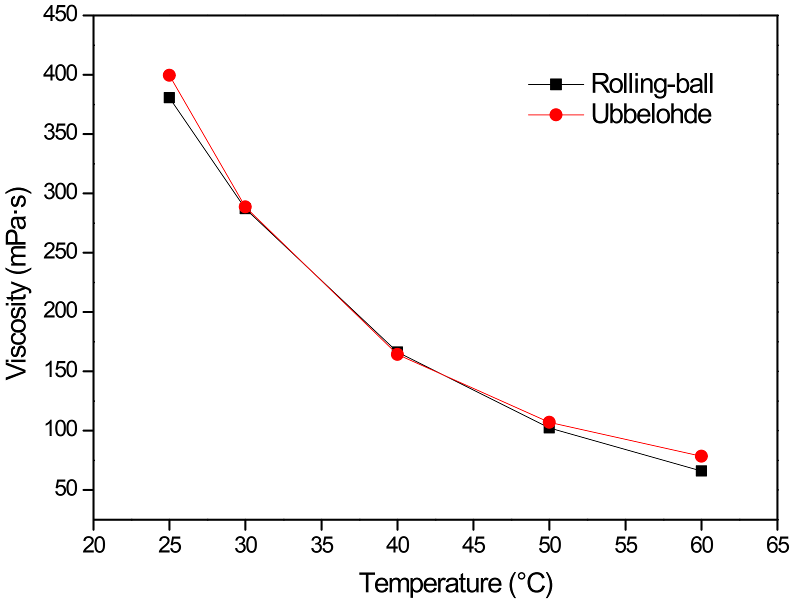


Fig. S7 Viscosity of $[P_{444,14}][Cl_3]$ measured with both a rolling-ball viscometer and an Ubbelohde glass capillary viscometer.

2.4 EXAFS

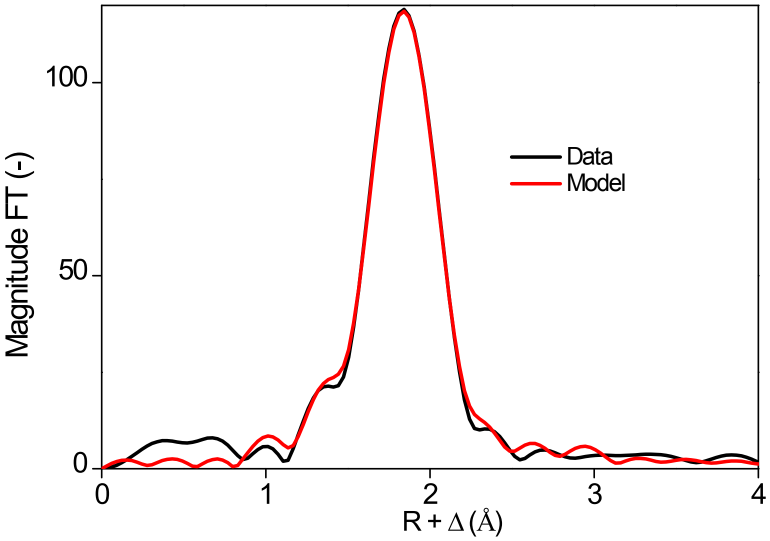


Fig. S8 Fourier transform and fitted model of the EXAFS spectrum of $[CuCl_4]^{2-}$.

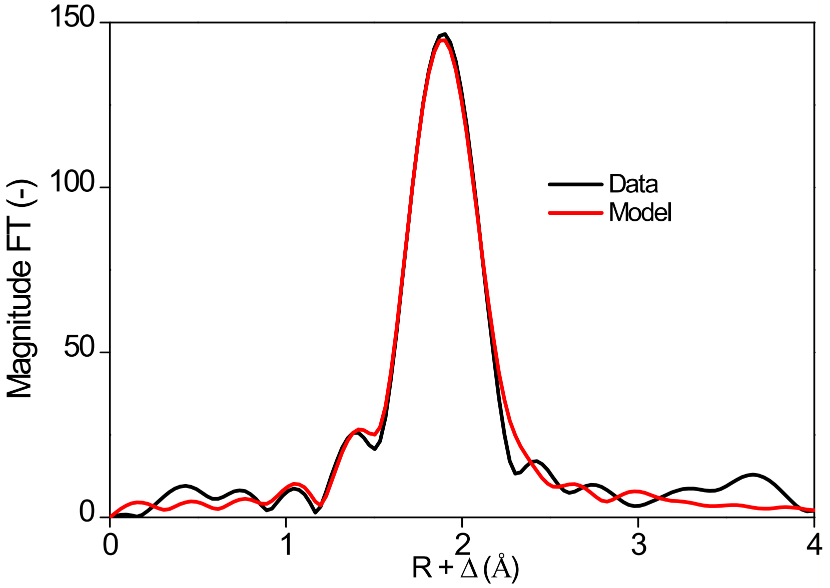


Fig. S9 Fourier transform and fitted model of the EXAFS spectrum of $[ZnCl_4]^{2-}$.

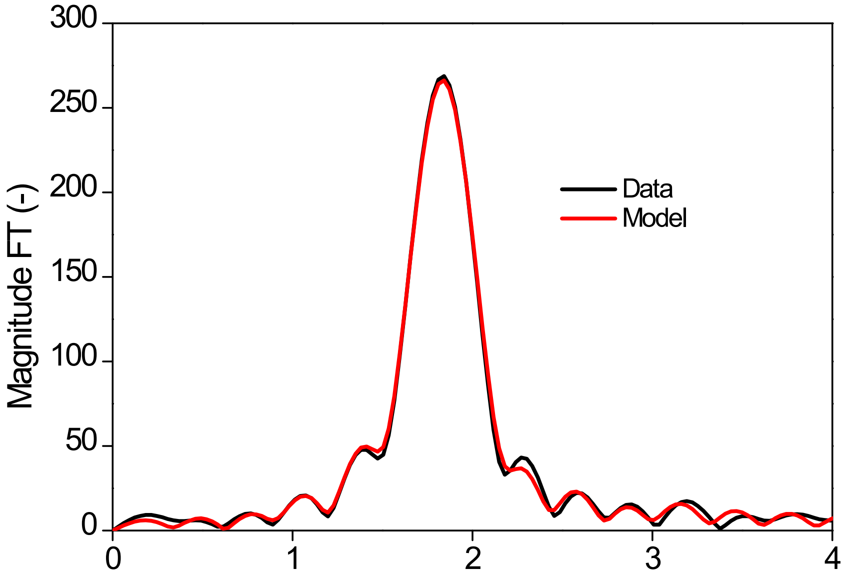


Fig. S10 Fourier transform and fitted model of the EXAFS spectrum of $[GaCl_4]^{-}$.

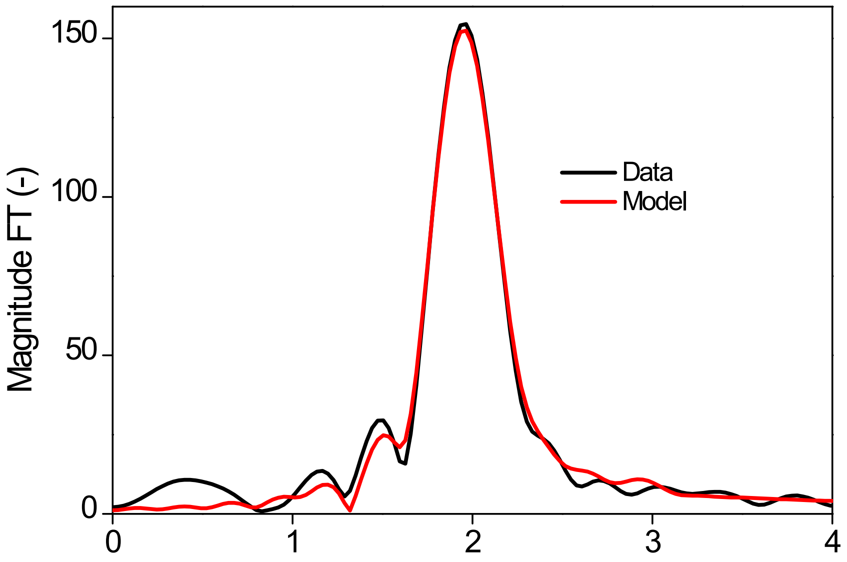


Fig. S11 Fourier transform and fitted model of the EXAFS spectrum of $[InCl_4]^-$.

References

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