Table of Contents

S1 Numbering Schemes

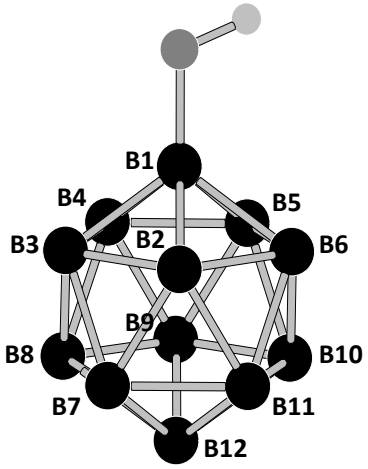

Figure S1: Numbering scheme for a $[B_{12}X_{11}OR]^-$ anion according to IUPAC

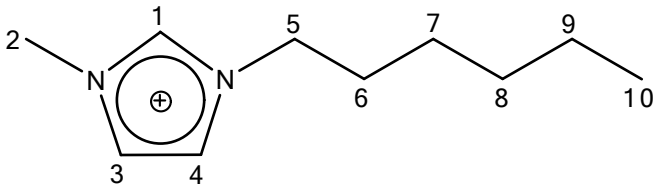

Figure S2: Numbering of the protons of the $[C_6mim]^+$ cation

S2 Experimental Details and Spectroscopic Data

General remarks. IR spectra were measured on a Bruker ALPHA P FT-IR spectrometer equipped with a diamond ATR attachment. Raman spectra of samples in flame-sealed capillaries were recorded using a Bruker Equinox 55 FRA 106/S FT-Raman spectrometer equipped with a highly sensitive Ge detector and a Nd:YAG-Laser (1064 nm). NMR spectra were measured on a Bruker Avance 400 and a Bruker AvanceIII 600 spectrometer in 5 mm NMR tubes at room temperature. Chemical shifts are given with respect to Me_4Si (^1H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). Two dimensional NMR experiments (HSQC (Heteronuclear Single Quantum Coherence), HMBC (Heteronuclear Multiple Bond Correlation) and COSY(Correlated Spectroscopy)) were performed to assist the assignment of the spectra. Electrospray ionization (ESI) mass spectra were recorded using a Bruker micrOTOF instrument. Thermoanalytical measurements were done with a Mettler Toledo TGA/DSC 1

LSTAR System. The coupled thermo gravimetric / mass spectrometric measurements were carried out with a Mettler Toledo TGA/DSC 1 LSTAR System connected to a Pfeiffer Vacuum Thermostar Gas Analysis System and a Gas Controller GC 200.

S2.1 Synthetic Details and Spectroscopic Data for $M_2[B_{12}H_{11}OH]^{2-}$ (M = Na, K)

In the following the synthesis is described exemplarily for $K_2[B_{12}H_{11}OH]$. In a 500 ml three necked round flask 5.0 g (22.7 mmol) of $K_2[B_{12}H_{12}]$ were dissolved in 220 ml of water. In the next step 148 ml of H_2SO_4 (96 %) were slowly dropped into the solution (1 – 2 drops per second). Over the whole time the solution was cooled with an ice/water mixture. After the adding of the sulfuric acid the cooling was removed and the reaction mixture was heated to 90 °C, which was checked by a thermal measurement in the flask. After 120 minutes the reaction was stopped and the solution was transferred into a 1 l Erlenmeyer flask. The solution was neutralized with solid NaOH. Precipitating potassium- and sodium sulfate were removed by filtration several times throughout the whole neutralization process. After finishing the clear and colorless solution was directly used for next step. The product contained small amounts of unreacted $[B_{12}H_{12}]^{2-}$ and also twofold hydroxylated clusters, because the reaction was controlled by time.

^{11}B {^{1}H} NMR (128.38 MHz, D_2O, 298 K): δ = 0.67 (s, 1B, *B*1-O), -19.1 (s, 5B, *B*(2-6)-Cl), -17.8 (s, 5B, *B*(7-11)-Cl), -22.7 (s, 1B, *B*1-Cl)).

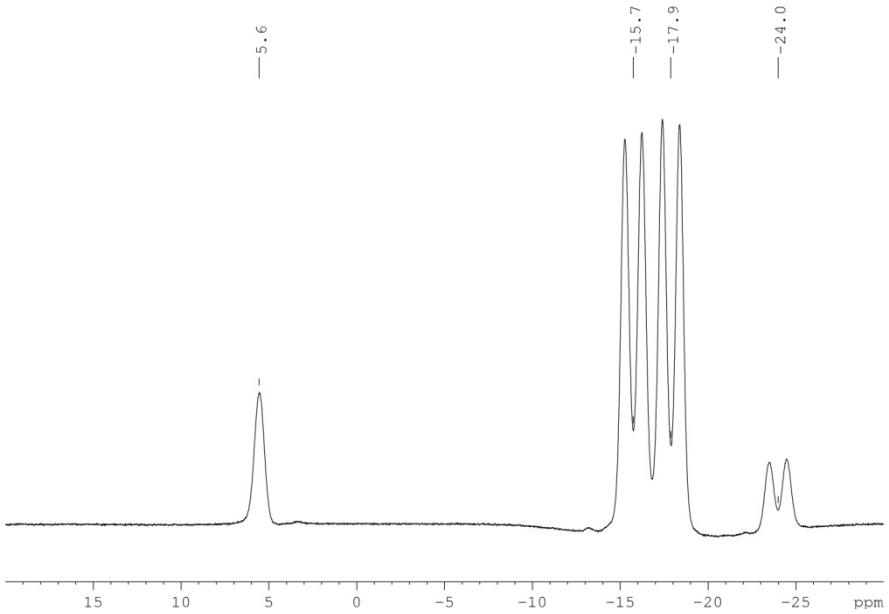

Figure S3: ^{11}B NMR spectrum (128.39 MHz) of $[NBu_4]_2[B_{12}H_{11}OH]$ in CD_3CN at 298 K

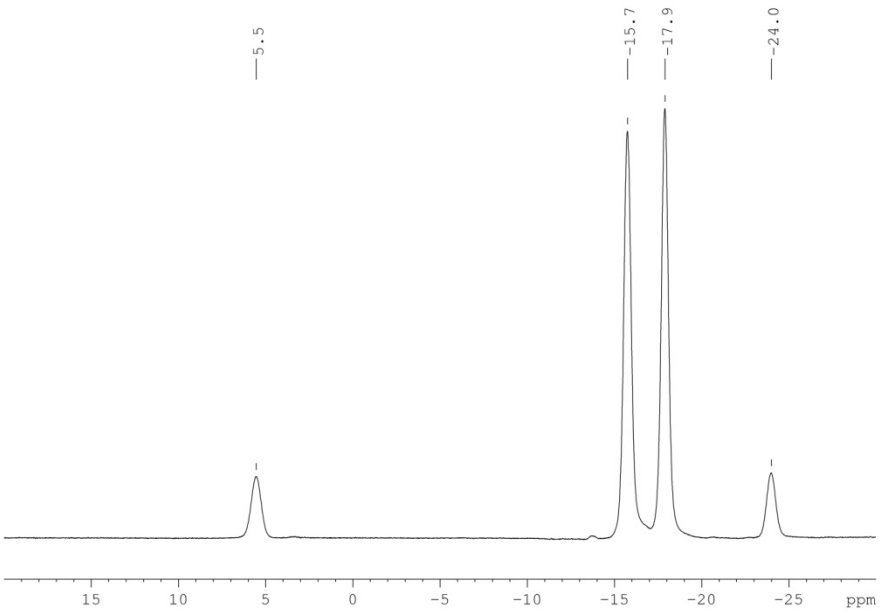

Figure S4: ^{11}B {^{1}H} NMR spectrum (128.39 MHz) of $[NBu_4]_2[B_{12}H_{11}OH]$ in CD_3CN at 298 K

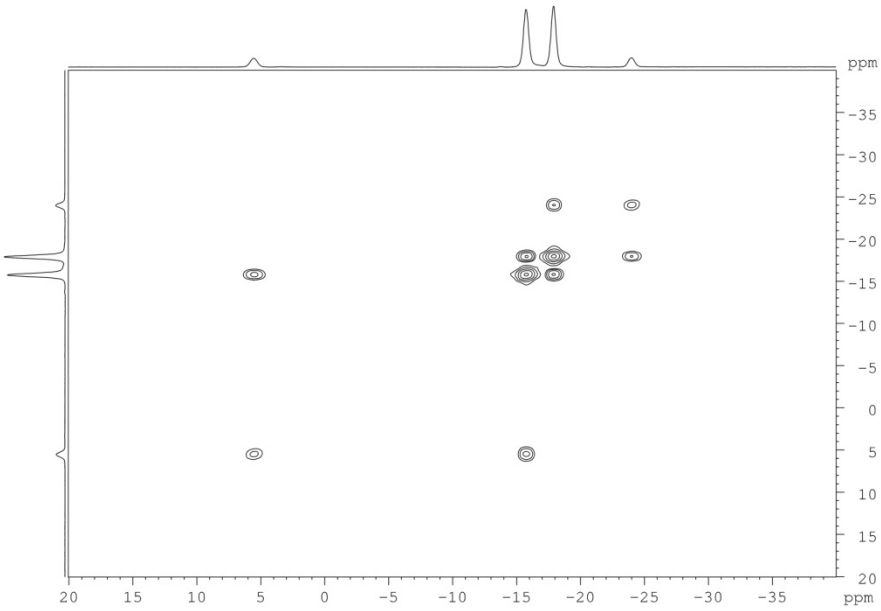

Figure S5: ^{11}B-^{11}B-COSY NMR spectrum (128.38 MHz) of $[NBu_4]_2[B_{12}H_{11}OH]$ in CD_3CN at 298 K

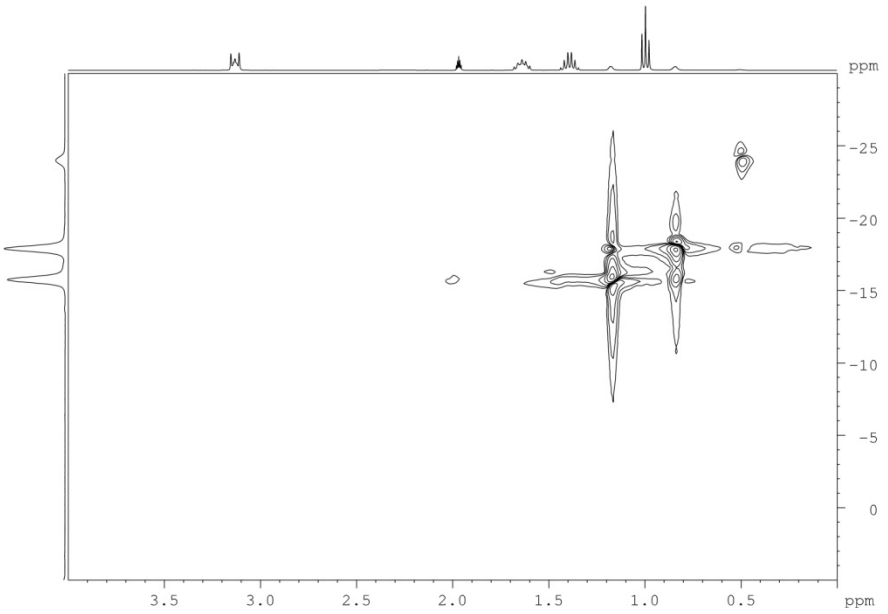

Figure S6: $^{1}H,^{11}B$ correlation (400.13 MHz, HSQC (Heteronuclear Single Quantum Coherence spectrum, optimized for J_{BH} = 100 Hz) of $[NBu_4]_2[B_{12}H_{11}OH]$ in CD_3CN at 298 K

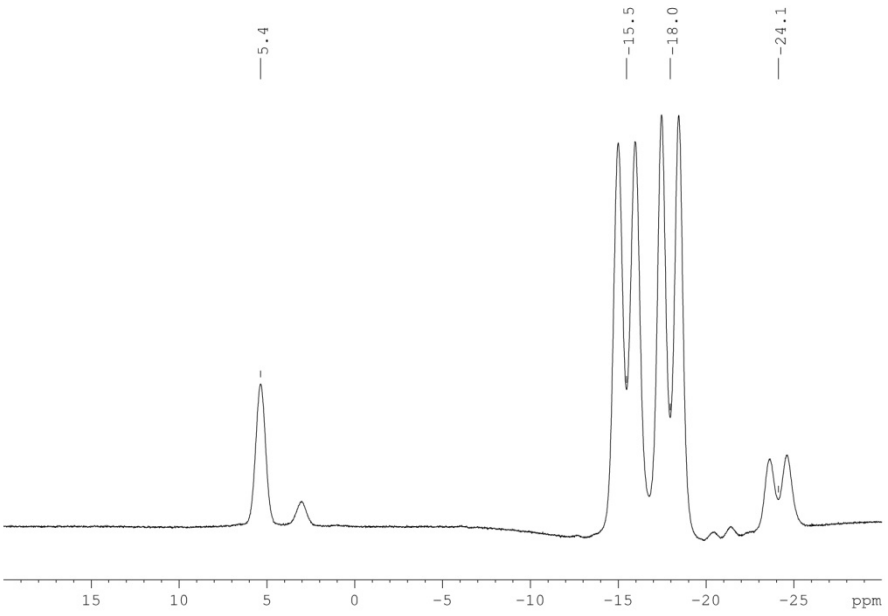

Figure S7: ^{11}B NMR spectrum (128.39 MHz) of $Na_2[B_{12}H_{11}OH]$ in D_2O at 298 K

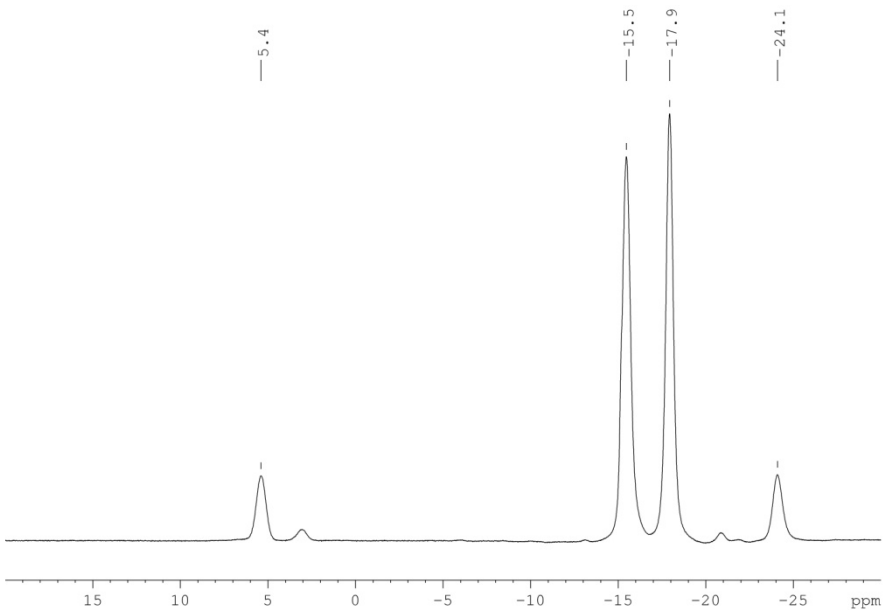

Figure S8: ^{11}B $\{^{1}H\}$ NMR spectrum (128.39 MHz) of $Na_2[B_{12}H_{11}OH]$ in D_2O at 298 K

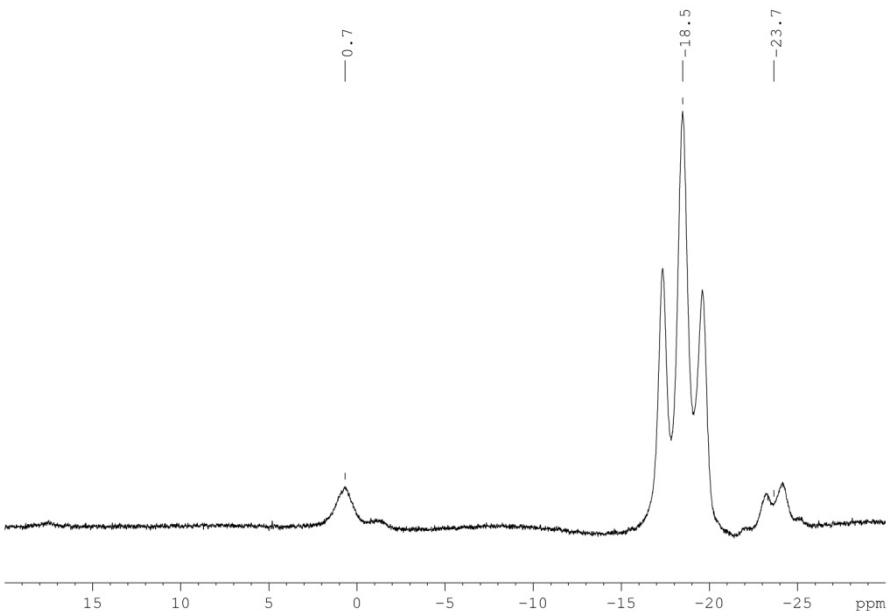

Figure S9: ^{11}B NMR spectrum (128.39 MHz) of $Na_2[B_{12}H_{11}OH]$ in D_2O (pH = 1) at 298 K

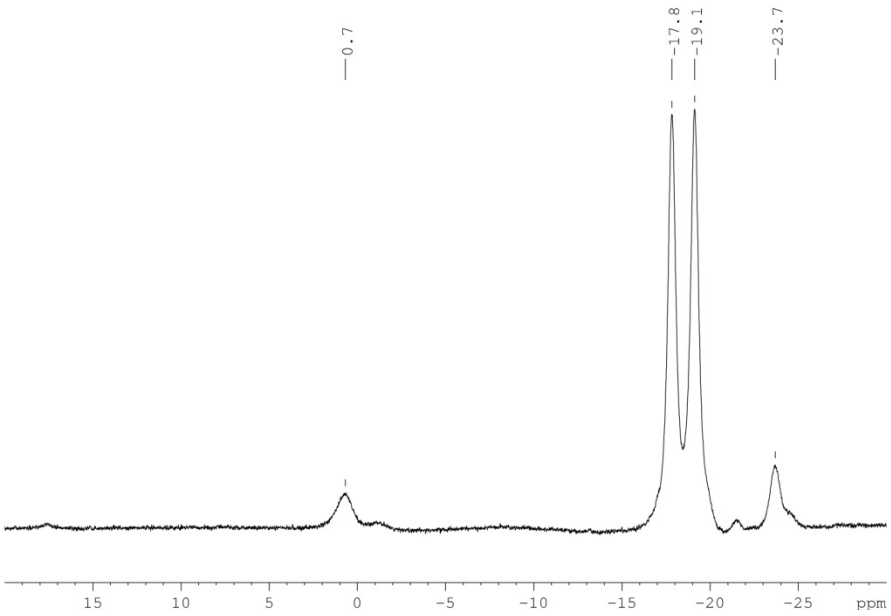

Figure S10: ^{11}B {^{1}H} NMR spectrum (128.39 MHz) of $Na_2[B_{12}H_{11}OH]$ in D_2O (pH = 1) at 298 K

S2.2 Synthetic Details and Spectroscopic Data for $Na_2[B_{12}Cl_{11}OH]$

Chlorine gas was bubbled through a solution of $M_2[B_{12}H_{11}OH]$ (prepared in the previous step) for 24 h while heating the reaction mixture to reflux. The progress of the chlorination reaction was checked by ^{11}B and $^{11}B\{^{1}H\}$ NMR spectroscopy. When the chlorination was completed the solution was cooled down to room temperature and triethylamine was added. The pH value was checked to be weakly acid (~ 3). The mixture was stirred for a few hours to dissolve all of the triethylamine. The white precipitate was removed by filtration, washed with cold water, and dried at 110 °C under reduced pressure. The solid was transferred to a Teflon beaker and two equivalents of solid NaOH dissolved in water were added. The completeness of the metathesis reaction was checked by ^{1}H NMR spectroscopy (absence of any triethylamine traces). The water was removed by heating and the product was obtained as a colorless solid 8.14 g (13.96 mmol, 62%, based on 5.00 g $Na_2[B_{12}H_{12}]$).

^{11}B {^{1}H} NMR (128.38 MHz, D_2O, 298 K): δ = -7.4 (s, 1B, *B*1-O), –13,9 (s, 10B, *B*(2-11)-Cl), –15.8 (s, 1B, *B*12-Cl)). IR (ATR): $\tilde{\nu}$ = 3597 (w, sh), 2291 (vw), 2080 (vw), 1980 (vw), 1607 (vw), 1316 (vw), 1249 (w), 1211 (w), 1089 (m, sh), 1029 (s, sh), 794 (vw), 743 (vw), 711 (vw), 585 (m, sh), 545 (s, sh), 534 (vw), 456 (vw), 427 (w). Raman: $\tilde{\nu}$ = 1624 (vw), 1153 (vw), 994 (m), 409 (w), 317 (m), 301 (vs), 132 (s) cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 268 $[B_{12}Cl_{11}OH]^{2-}$, 559 $[B_{12}Cl_{11}OH + Na]^{-}$.

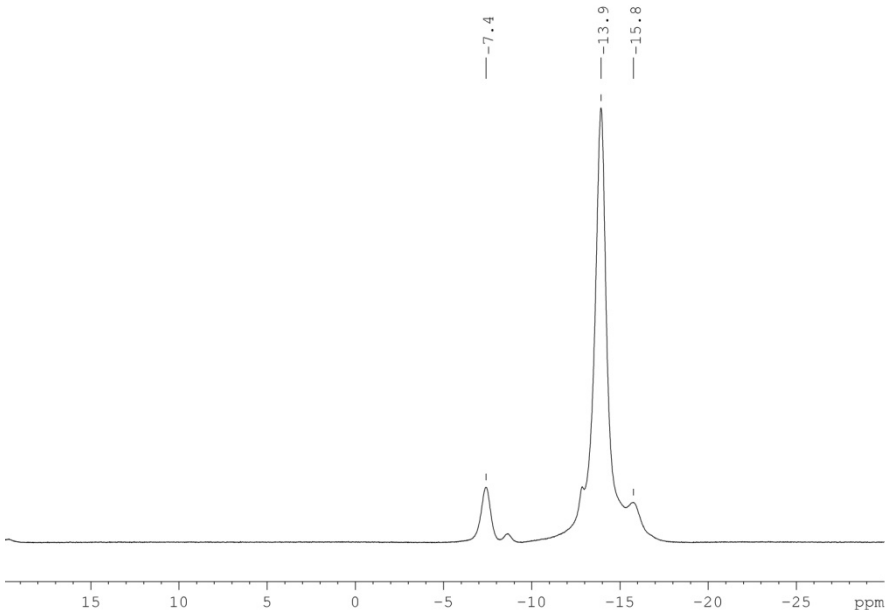

Figure S11: ^{11}B NMR spectrum (128.39 MHz) of $Na_2[B_{12}Cl_{11}OH]$ in D_2O at 298 K

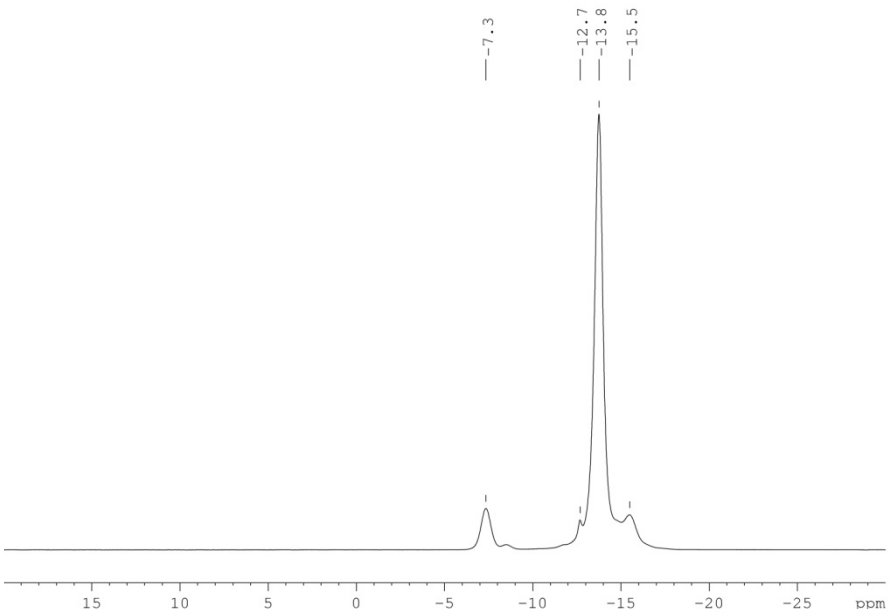

Figure S12: ^{11}B NMR spectrum (128.39 MHz) of $Na_2[B_{12}Cl_{11}OH]$ in CD_3CN at 298 K

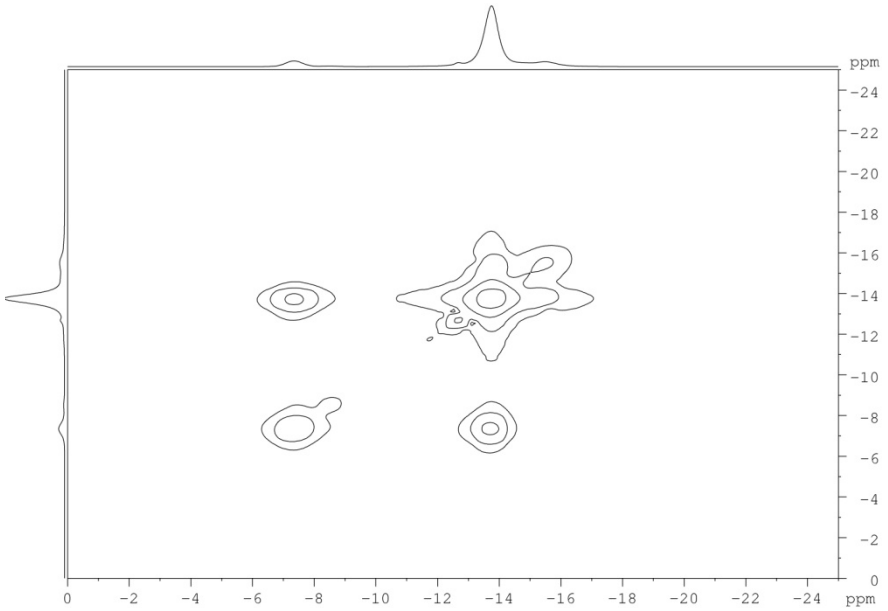

Figure S13: ^{11}B-^{11}B-COSY NMR spectrum (128.38 MHz) of $Na_2[B_{12}Cl_{11}OH]$ in CD_3CN at 298 K

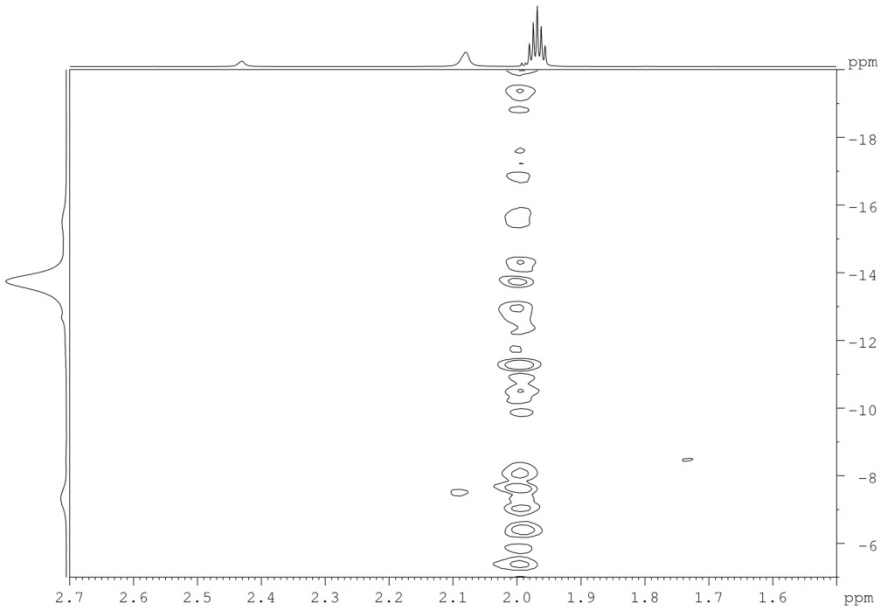

Figure S14: ^{1}H,^{11}B correlation (400.13 MHz) of $Na_2[B_{12}Cl_{11}OH]$ in CD_3CN at 298 K. The resonance in the 11B NMR spectrum at -7.4 ppm shows a cross peak to a broad resonance (the hydroxo group on the boron cluster) at 2.09 ppm in the 1H NMR spectrum.

Figure S15: Negative ESI MS spectrum of the $[B_{12}Cl_{11}OH]^{2-}$ anion

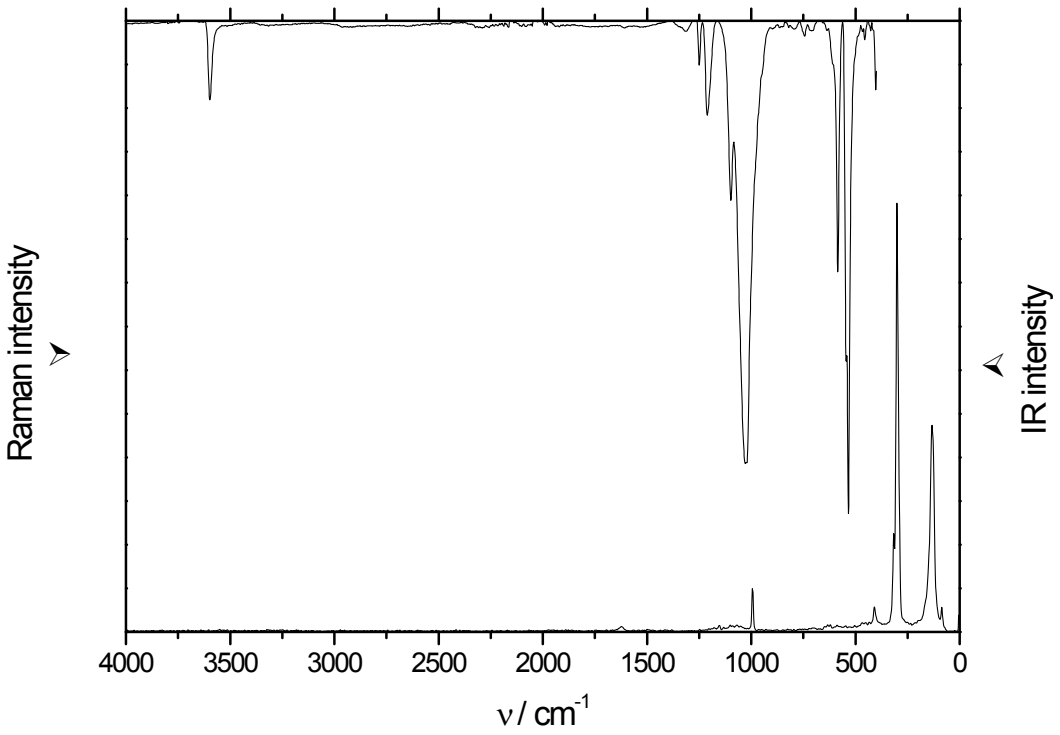

Figure S16: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Cl_{11}OH]$

S2.3 Synthetic Details and Spectroscopic Data for $Na_2[B_{12}Br_{11}OH]$

Methanol (approximately the same volume) was added to a solution of $K_2[B_{12}H_{11}OH]$ prepared in the previous step. Potassium- and sodium sulfate precipitated and were removed by filtration. To the solution 30 ml of bromine were added dropwise and subsequently the reaction mixture was heated to reflux. Another 30 ml of bromine were added to the refluxing solution and the progress of the bromination reaction was checked by ^{11}B and $^{11}B\{^1H\}$ NMR spectroscopy. After 24 h the solution was cooled down to room temperature and all volatiles were removed under reduced pressure. The residue was dissolved in water and the solution was acidified by adding HCl. Triethylamine was added to the solution and the pH value was checked to be still weakly acid (~ 3). The mixture was stirred for a few hours to dissolve all of the triethylamine. The white precipitate was removed by filtration, washed with cold water, and dried at 110 °C under reduced pressure. The solid was transferred to a Teflon beaker and two equivalents of solid NaOH dissolved in water were added. The absence of any traces of triethylamine was checked by ^1H NMR spectroscopy. The water was removed by heating and the product was obtained as a colorless solid 13.49 g (12.59 mmol, 55%, based on 5.00 g $Na_2[B_{12}H_{12}]$).

^{11}B NMR (128.38 MHz, CD_3CN, 298 K): δ = -4.2 (s, 1B, *B*1-O), –14.1 (s, 10B, *B*(2-11)-Cl), –16.6 (s, 1B, *B*12-Cl)). IR (ATR): $\tilde{\nu}$ = 3674 (w, sh), 3342 (vw), 3115 (vw), 2447 (vw), 2284 (vw), 2162 (vw) , 2050 (vw), 1988 (vw), 1925 (vw), 1792 (vw), 1559 (vw), 1435 (vw), 1315 (vw), 1266 (vw), 1233 (vw), 1197 (m, sh), 1095 (s, sh), 1000 (s, sh), 989 (vs, sh), 909 (vw), 880 (vw), 728 (vw), 676 (vw), 582 (w), 536 (s, sh), 448 (vs, sh), 413 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 539 (vw), 351 (w), 196 (vs) cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 512 $[B_{12}Br_{11}OH]^{2-}$.

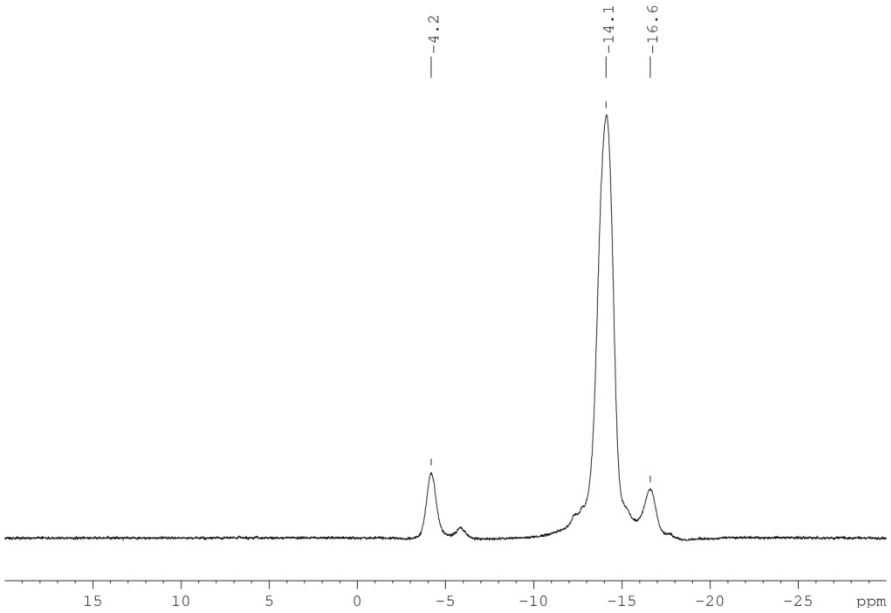

Figure S17: ^{11}B NMR spectrum (128.39 MHz) of $[NEt_3H]_2[B_{12}Br_{11}OH]$ in CD_3CN at 298 K

Figure S18: Negative ESI MS spectrum of the $[B_{12}Br_{11}OH]^{2-}$ anion

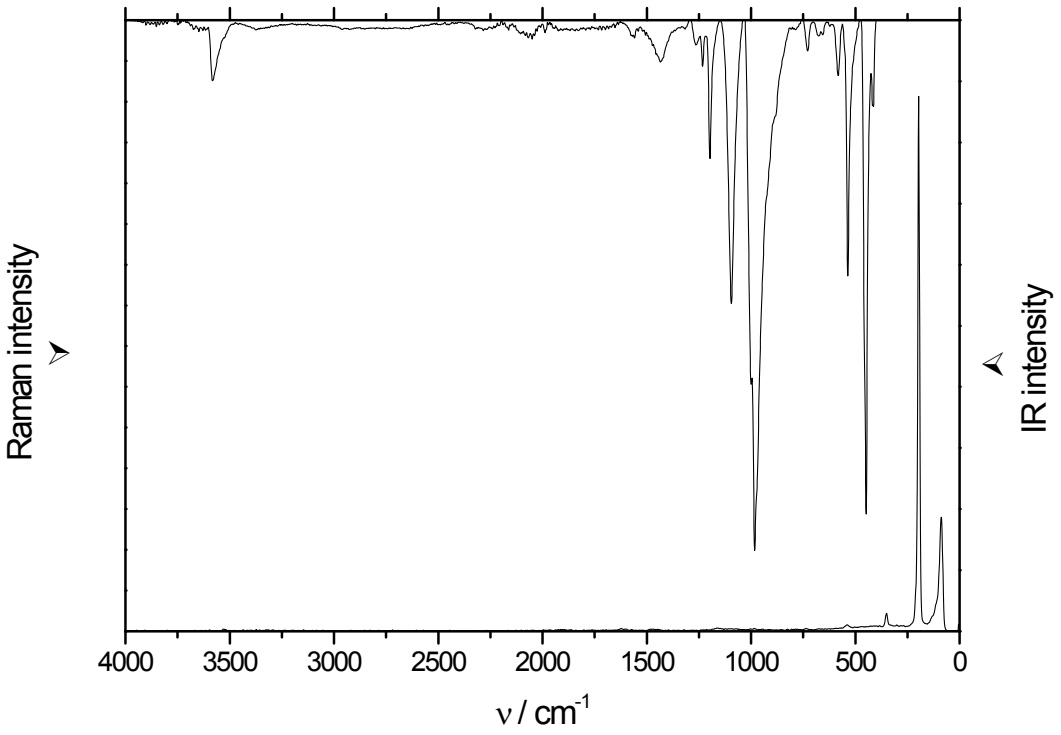

Figure S19: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Br_{11}OH]$

S2.4 Spectroscopic Data for the salts containing the $[B_{12}Cl_{11}O\text{-propyl}]^{2-}$ anion

A general synthetic procedure is described in the main paper. The yields given in the supplementary information refer to the amounts given in the general procedure in the main paper.

Sodium salt: (0.87 g, 1.39 mmol, 81 %) as a colorless solid. ^{1}H NMR (400.13 MHz, D_2O, 298 K): δ = 0.86 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$), 1.57 (tq, $^{3}J_{HH}$ = 7.4 Hz, 2H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$), 3.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$). ^{11}B NMR (128.38 MHz, D_2O, 298 K): δ = –15.7 (s, 1B, *B*1-Cl), –14.0 (s, 10B, *B*(2-11)-Cl), –7.4 (s, 1B, *B*12-O)). ^{13}C{^{1}H} NMR (100.61 MHz, D_2O, 298 K): δ = 11.3 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 26.8 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 70.9 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$. IR (ATR): $\tilde{\nu}$ = 3011 (vw), 2970 (vw), 2937 (vw), 2878 (vw), 1461 (vw), 1435 (vw), 1403 (vw), 1318 (vw), 1264 (w, br), 1199 (vw), 1155 (m, br), 1024 (w), 957 (vs), 908 (vw), 749 (vw), 712 (vw), 624 (w), 575 (w), 540 (m, sh), 475 (vw), 462 (vw), 408 (vw) cm^{-1}. Raman: $\tilde{\nu}$ = 3009, 2920, 2875, 1449, 1415, 1307, 1027, 960, 712, 680, 388, 299, 238, 129 cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 289 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 601 $[B_{12}Cl_{11}OCH_2CH_2CH_3 + Na]^{-}$.

Tetrabutylammonium salt: (0.42 g, 0.04 mmol, 24 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.89 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, $[B_{12}Cl_{11}O(CH_2)_2CH_3]^{2-}$), 1.00 (t, $^{3}J_{HH}$ = 7.4 Hz, 24H, $[N((CH_2)_3CH_3)_4]^{+}$), 1.38 (tq, $^{3}J_{HH}$ = 7.4 Hz, 16H, $[N((CH_2)_2(CH_2)CH_3)_4]^{+}$), 1.50 (tq, $^{3}J_{HH}$ = 7.4 Hz, 2H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$), 1.63 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 3.11 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 3.93 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 10.8 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 13.8 $[N((CH_2)_3CH_3)_4]^{+}$, 20.3 $[N((CH_2)_2CH_2CH_3)_4]^{+}$, 24.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 26.6 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 59.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 68.3 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$.

[C_6mim] salt: (0.35 g, 0.04 mmol, 23 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $[B_{12}Cl_{11}O(CH_2)_2CH_3]^{2-}$), 0.92 (t, $^{3}J_{HH}$ = 6.7 Hz, 3H, *H*10), 1.28-1.40 (m, 6H, *H*7-9), 1.49 (m, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$), 1.85 (m, 2H, *H*6), 3.85 (s, 3H, *H*2), 3.93 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$), 4.14 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, *H*5), 7.37 (m, 2H, *H*3-4), 8.42 (s, 1H, *H*1). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 10.8 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 14.2 [*C*10], 23.1 [*C*9], 26.4 [*C*8], 26.6

$[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 30.6 [*C*7], 31.8 [*C*6], 36.9 [*C*2], 50.6 [*C*5], 68.3 $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$, 123.3 [*C*4], 126.6 [*C*3], 136.8 [*C*1].

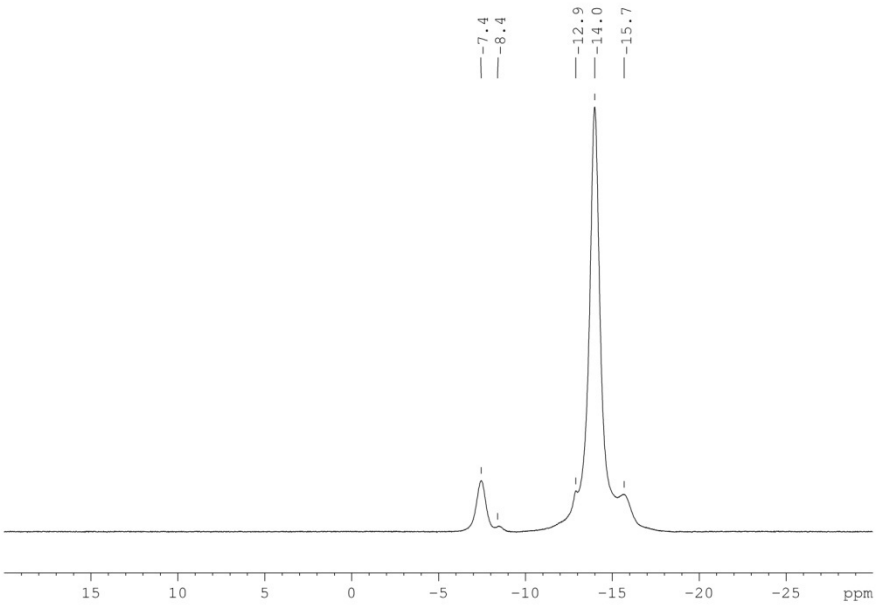

Figure S20: ^{11}B NMR spectrum (128.39 MHz) of $Na_2[B_{12}Cl_{11}O\text{-propyl}]$ D_2O at 298 K

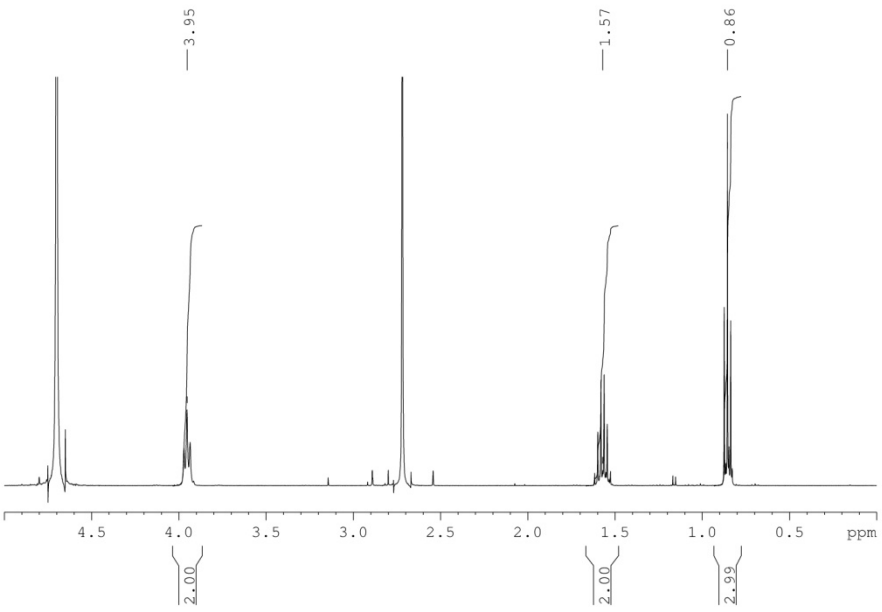

Figure S21: ^{1}H NMR spectrum (400.13 MHz) of $Na_2[B_{12}Cl_{11}O\text{-propyl}]$ in D_2O at 298 K

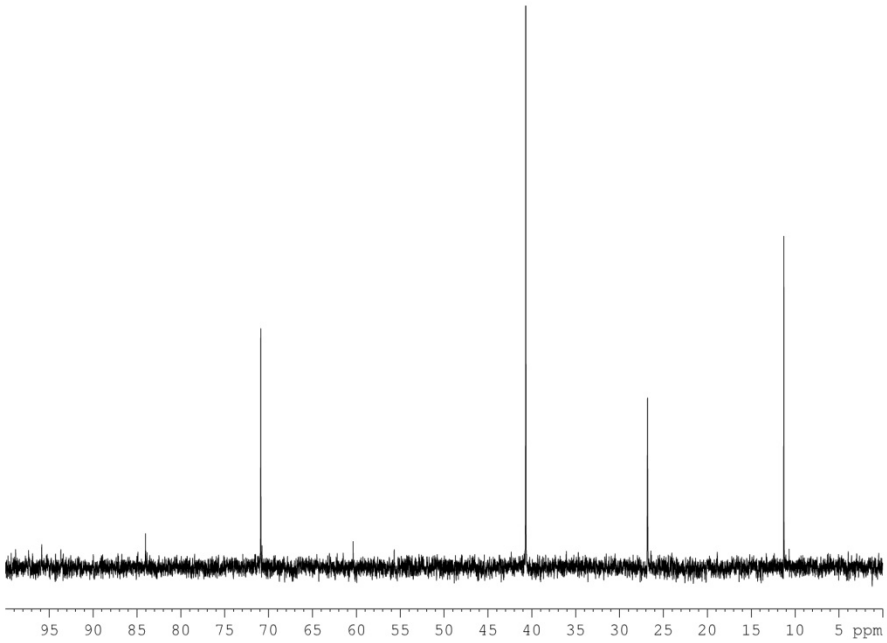

Figure S22: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of $Na_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

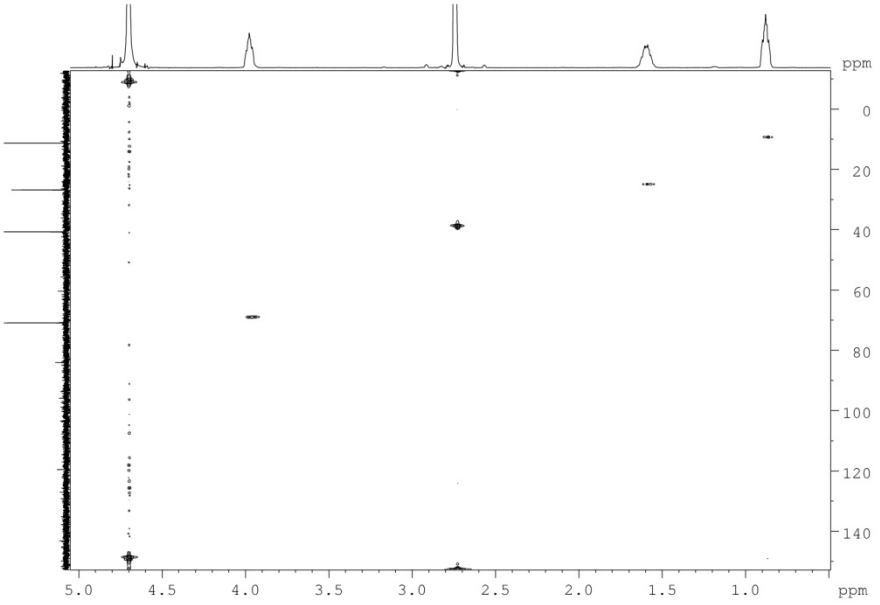

Figure S23: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $Na_2[B_{12}Cl_{11}O\text{-propyl}]$ in D_2O at 298 K

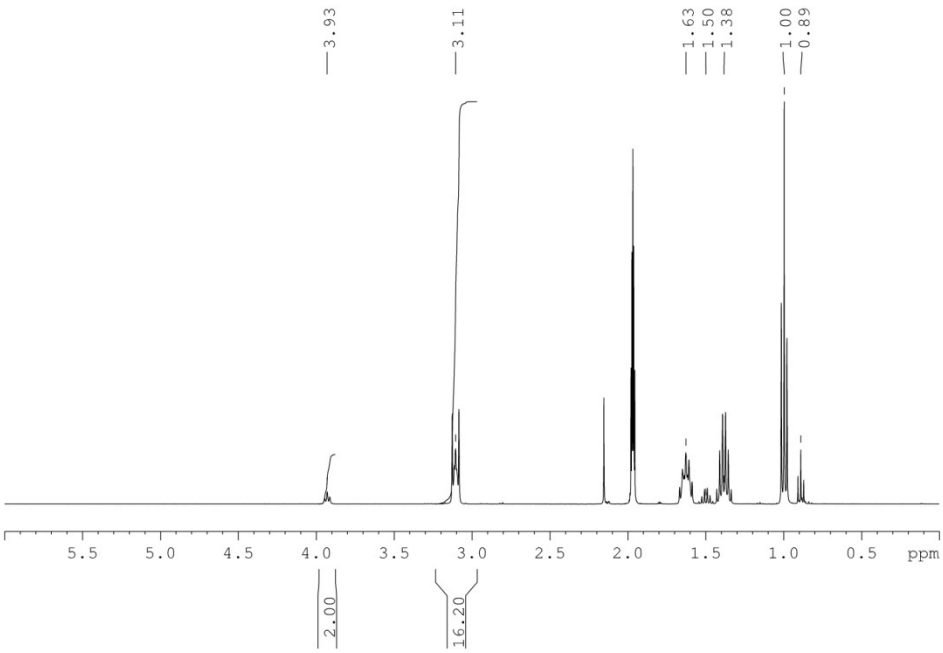

Figure S24: ^{1}H NMR spectrum (400.13 MHz) of $[NBu_4]_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

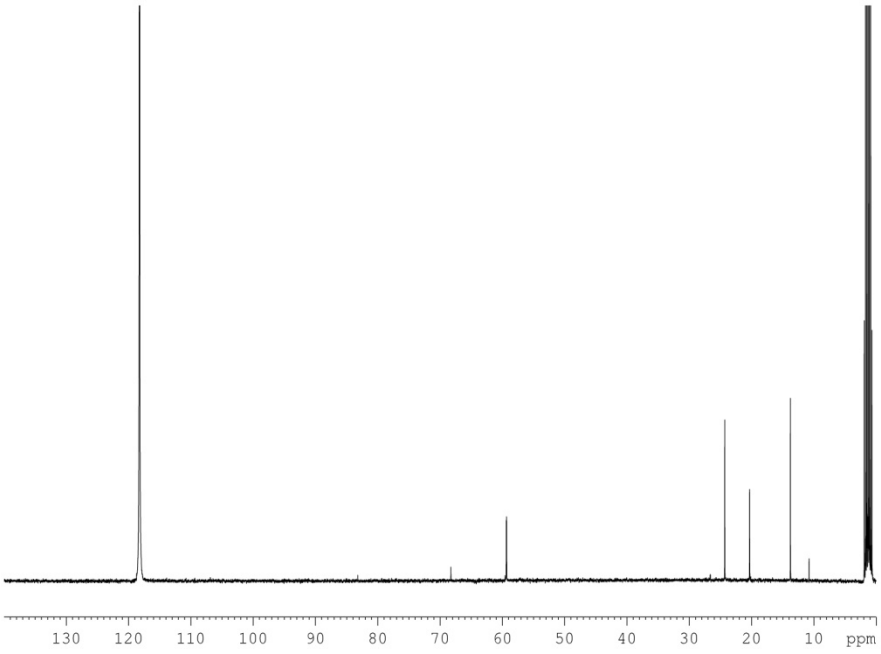

Figure S25: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of $[NBu_4]_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

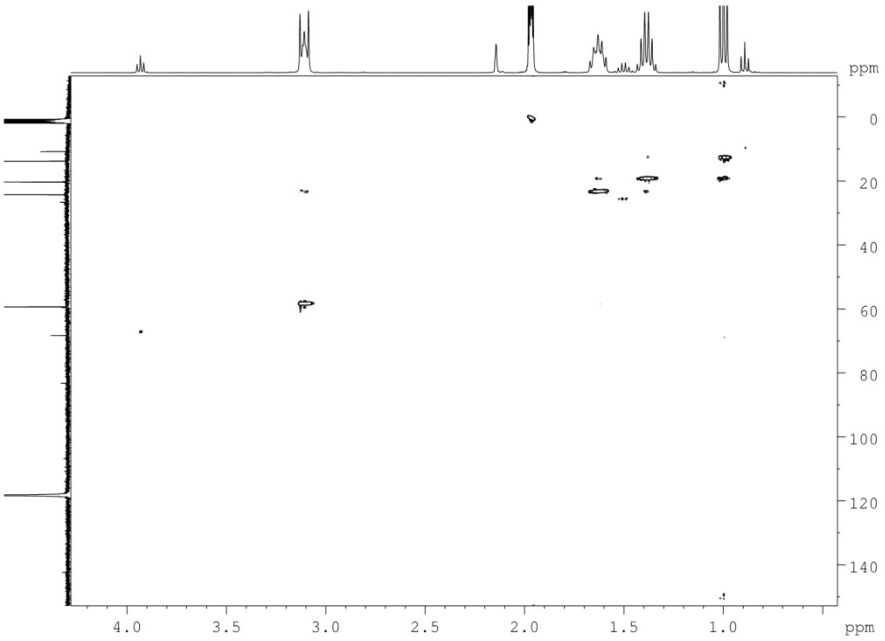

Figure S26: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[NBu_2]_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

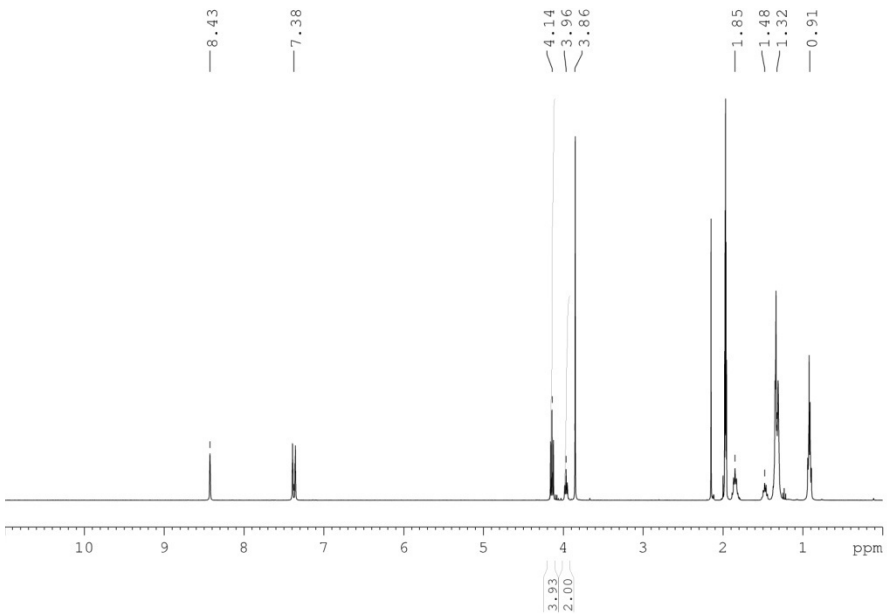

Figure S27: ^{1}H NMR spectrum (400.13 MHz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

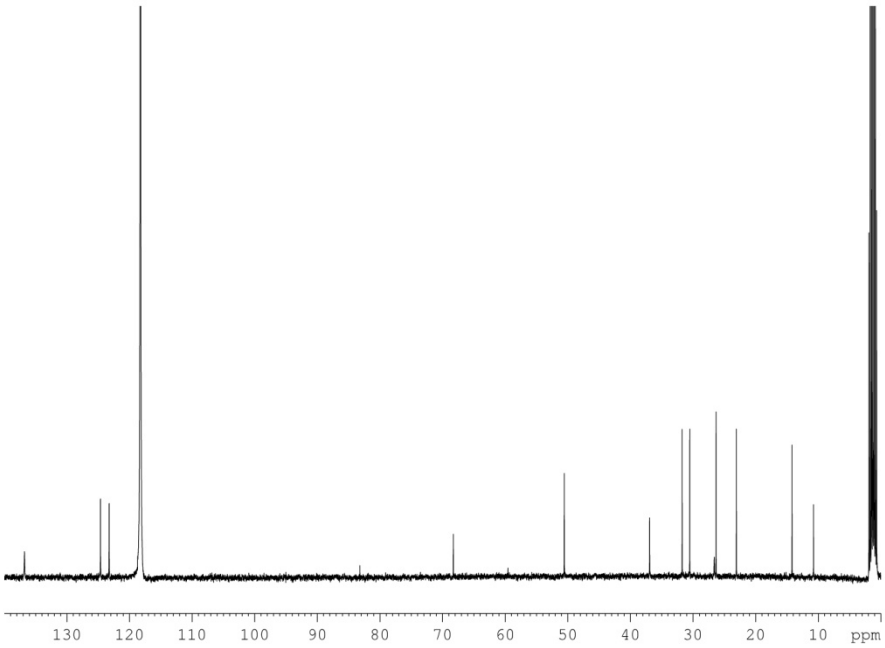

Figure S28: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

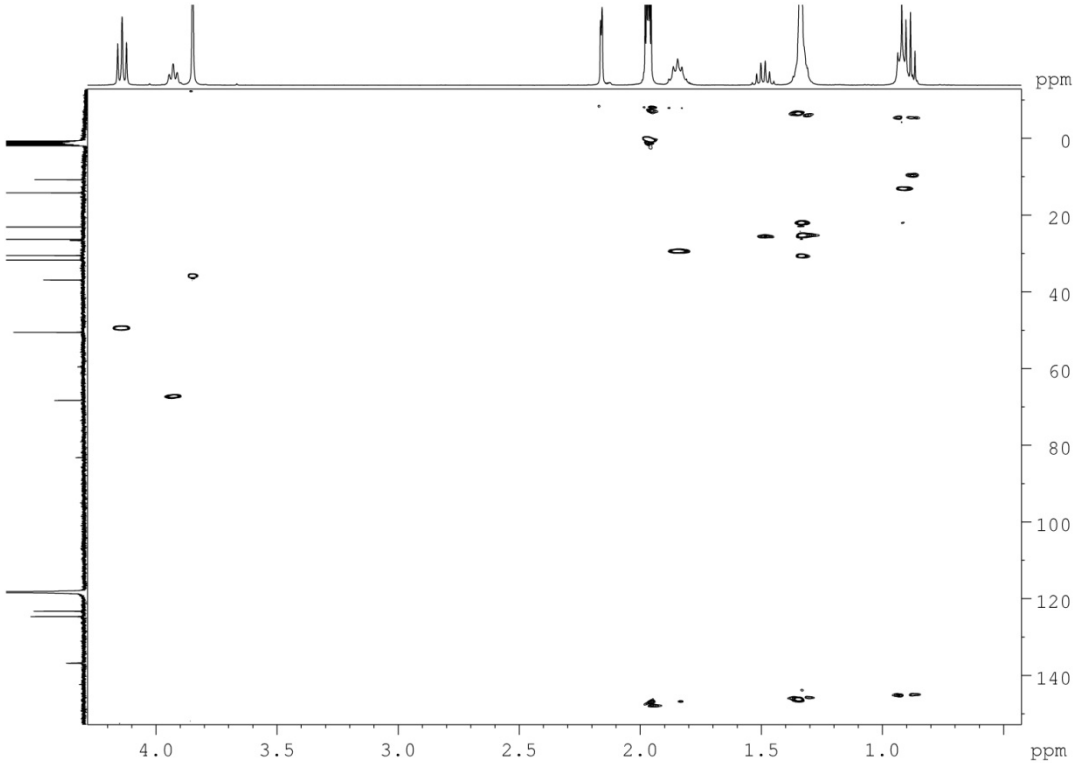

Figure S29: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ in CD_3CN at 298 K

Figure S30: Negative ESI MS spectrum of the $[B_{12}Cl_{11}O\text{-propyl}]^{2-}$ anion

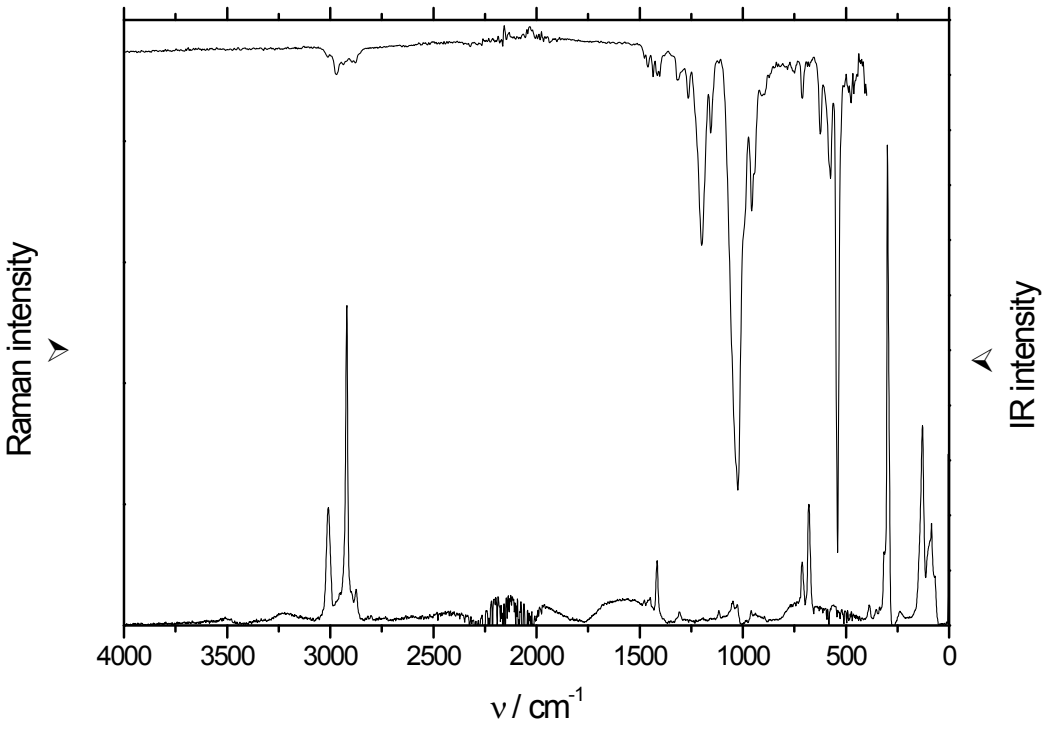

Figure S31: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Cl_{11}O\text{-propyl}]$

S2.5 Spectroscopic Data for the salts containing the $[B_{12}Cl_{11}O\text{-octyl}]^{2-}$ anion

A general synthetic procedure is described in the main paper. The yields given in the supplementary information refer to the amounts given in the general procedure in the main paper.

Sodium salt: (1.01 g, 1.45 mmol, 84 %) as a colorless solid. ^{1}H NMR (400.13 MHz, D_2O, 298 K): δ = 0.86 (t, $^{3}J_{HH}$ = 8.2 Hz, 3H, $[B_{12}Cl_{11}O(CH)_7CH_3]^{2-}$), 1.30 (m, 10H, $[B_{12}Cl_{11}O(CH_2)_2(CH)_5CH_3]^{2-}$, 1.58 (m, 2H, $[B_{12}Cl_{11}OCH_2CH_2(CH_2)_5CH_3]^{2-}$), 4.01 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, $[B_{12}Cl_{11}OCH_2(CH_2)_6CH_3]^{2-}$). ^{11}B NMR (128.38 MHz, D_2O, 298 K): δ = –15.7 (s, 1B, *B*1-Cl), –14.0 (s, 10B, *B*(2-11)-Cl), –7.4 (s, 1B, *B*12-O)). ^{13}C{^{1}H} NMR (100.61 MHz, D_2O, 298 K): δ = 15.4 $[B_{12}Cl_{11}O(CH)_7CH_3]^{2-}$, 69.3 $[B_{12}Cl_{11}OCH_2(CH_2)_6CH_3]^{2-}$. IR (ATR): $\tilde{\nu}$ = 2956 (vw), 2927 (vw), 2856 (vw), 2162 (vw), 1464 (vw), 1432 (vw), 1307 (vw), 1202 (w), 1179 (w), 1038 (m, br), 960 (w), 893 (vw), 816 (vw), 753 (vw), 712 (vw), 625 (vw), 580 (vw), 541 (m, sh), 470 (vw), 457 (vw) cm^{-1}. Raman: $\tilde{\nu}$ = 3005, 2916, 2860, 1444, 1416, 1307, 1038, 960, 713, 676, 556, 502, 492, 343, 297, 128, cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 324 $[B_{12}Cl_{11}O(CH_2)_7CH_3]^{2-}$, 688 $[B_{12}Cl_{11}O(CH_2)_7CH_3 + K]^{-}$.

Tetrabutylammonium salt: (0.42 g, 0.04 mmol, 24 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.91 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, $[B_{12}Cl_{11}O(CH_2)_7CH_3]^{2-}$), 0.99 (t, $^{3}J_{HH}$ = 7.4 Hz, 24H, $[N((CH_2)_3CH_3)_4]^{2-}$), 1.31 (m, 10H, $[B_{12}Cl_{11}O(CH_2)_2(CH_2)_5CH_3]^{2-}$), 1.39 (m, 16H, $[N((CH_2)_2(CH_2)CH_3)_4]^{2-}$), 1.48 (m, 2H, $[B_{12}Cl_{11}OCH_2CH_2(CH_2)_5CH_3]^{2-}$), 1.63 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{2-}$), 3.11 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{2-}$), 3.97 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H, $[B_{12}Cl_{11}OCH_2(CH_2)_6CH_3]^{2-}$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 13.8 $[N((CH_2)_3CH_3)_4]^{+}$, 14.4 $[B_{12}Cl_{11}O(CH)_7CH_3]^{2-}$, 20.3 $[N((CH_2)_2CH_2CH_3)_4]^{+}$, 24.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 59.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 66.6 $[B_{12}Cl_{11}OCH_2(CH_2)_6CH_3]^{2-}$.

[C_6mim] salt: (0.35 g, 0.04 mmol, 23 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, $[B_{12}Cl_{11}O(CH_2)_2CH_3]^{2-}$), 0.92 (t, $^{3}J_{HH}$ = 6.7 Hz, 3H, *H*10), 1.28-1.40 (m, 10H $[B_{12}Cl_{11}O\text{-}(CH_2)_2(CH_2)_5CH_3]^{2-}$), 1.28-1.40 (m, 6H, *H*7-9), 1.49 (m, $[B_{12}Cl_{11}OCH_2CH_2(CH_2)_5CH_3]^{2-}$), 1.85 (m, 2H, *H*5), 3.85 (s, 3H, *H*2), 3.93 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Cl_{11}OCH_2CH_2CH_3]^{2-}$), 4.14 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, *H*5), 7.37 (m, 2H, *H*3-4), 8.42 (s, 1H, *H*1). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 14.2 [*C*10], 14.4 $[B_{12}Cl_{11}O(CH)_7CH_3]^{2-}$, 23.1 [*C*9], 26.4 [*C*8], 30.6 [*C*7], 31.8 [*C*6], 36.9 [*C*2], 50.6 [*C*5], 66.7 $[B_{12}Cl_{11}OCH_2(CH_2)_6CH_3]^{2-}$, 123.3 [*C*4], 126.6 [*C*3], 136.8 [*C*1].

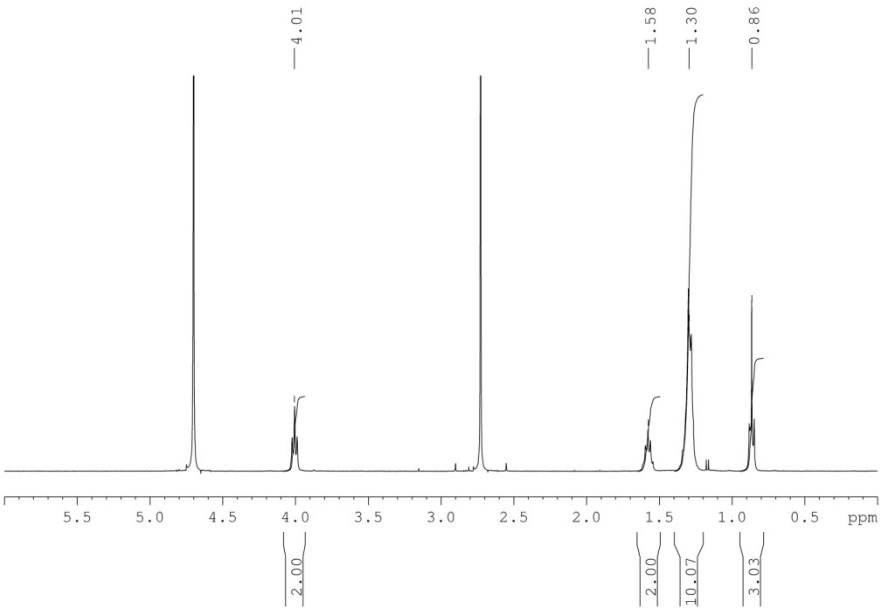

Figure S32: ^{1}H NMR spectrum (400.13 MHz) of $Na_2[B_{12}Cl_{11}O\text{-octyl}]$ in D_2O at 298 K

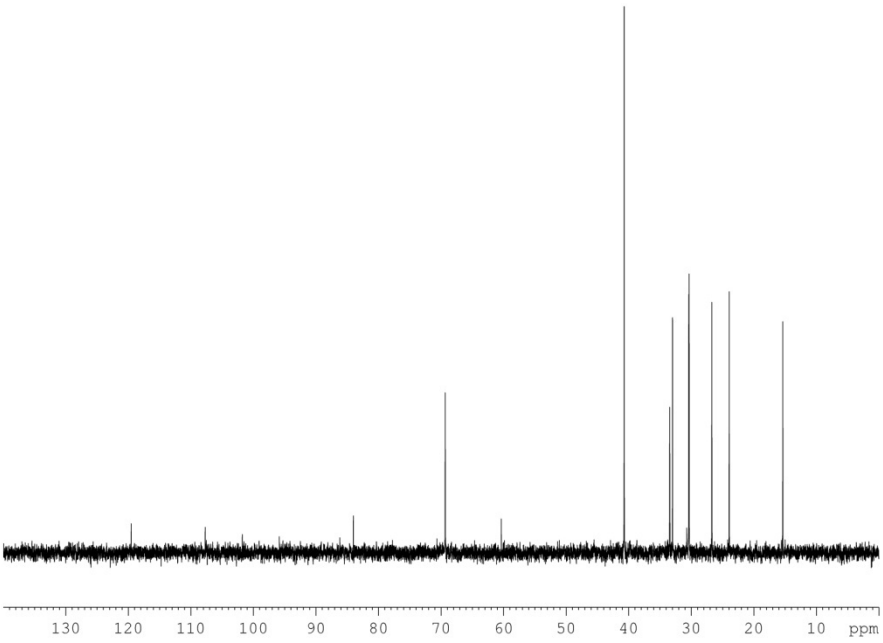

Figure S33: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of $Na_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

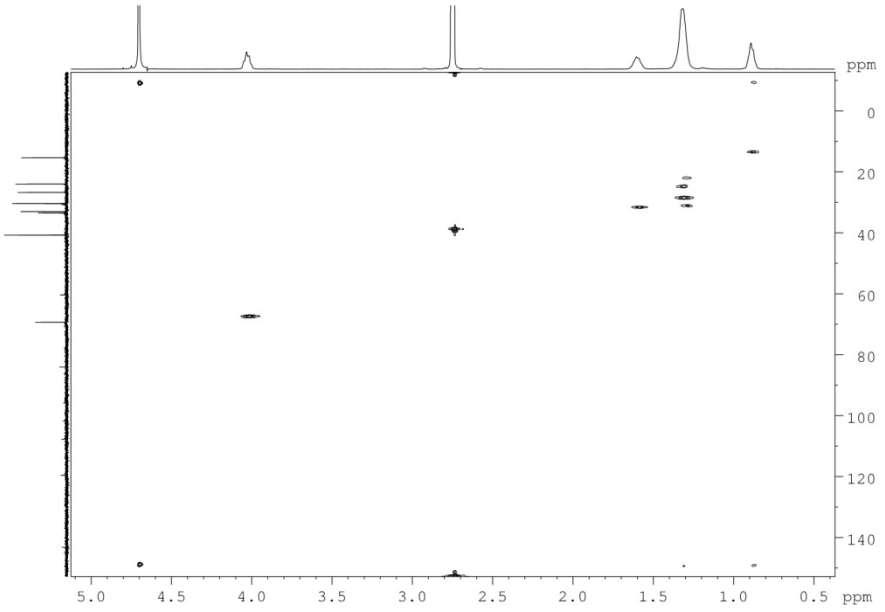

Figure S34: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $Na_2[B_{12}Cl_{11}O\text{-octyl}]$ in D_2O at 298 K

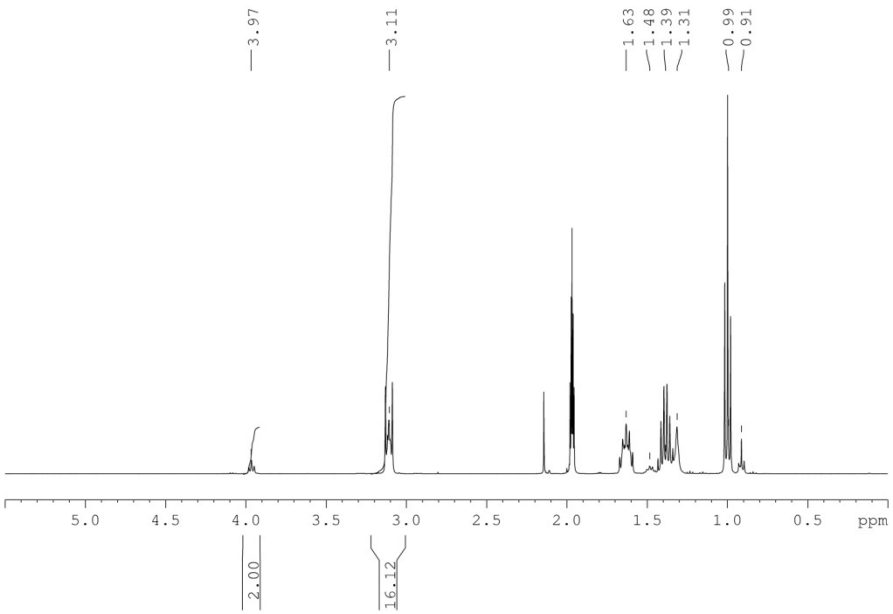

Figure S35: ^{1}H NMR spectrum (400.13 MHz) of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

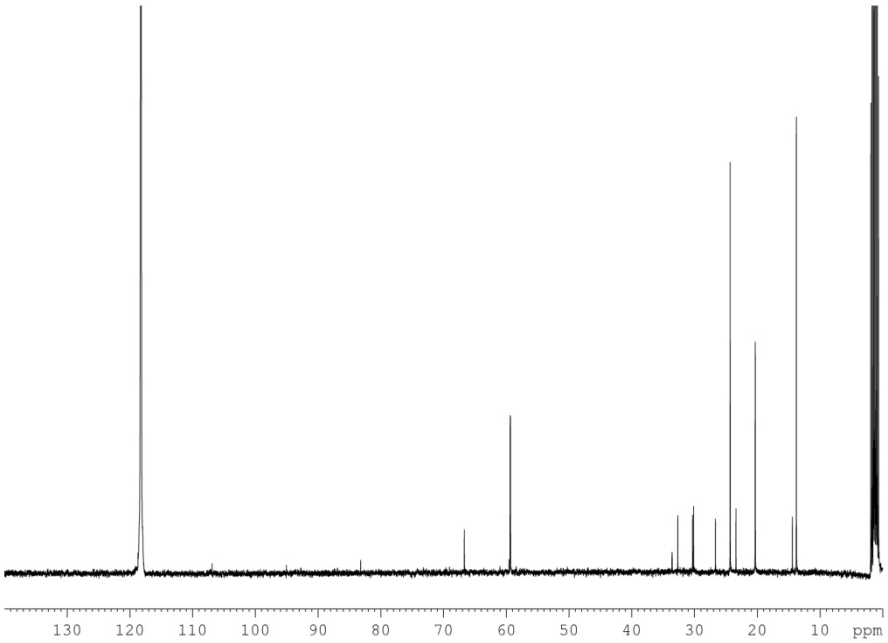

Figure S36: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

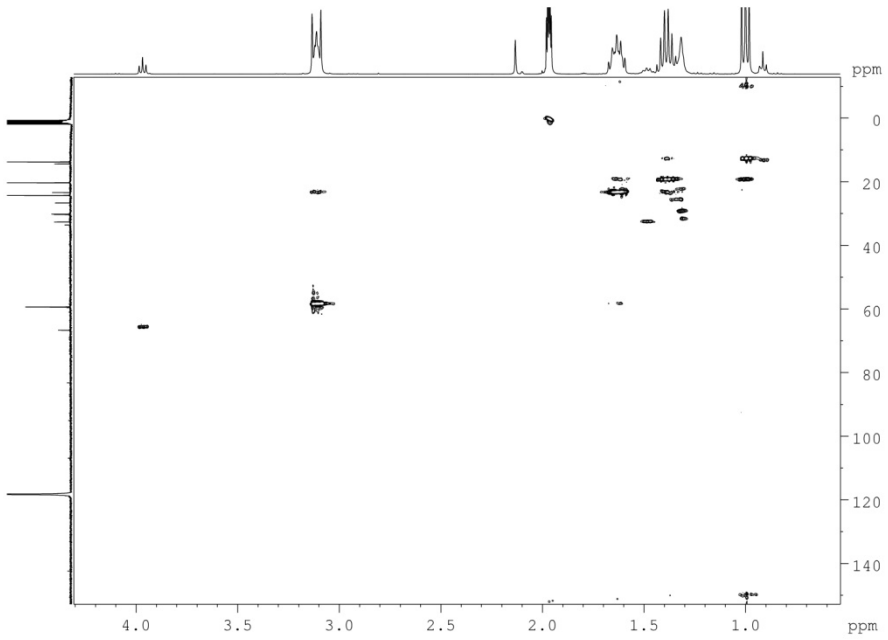

Figure S37: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

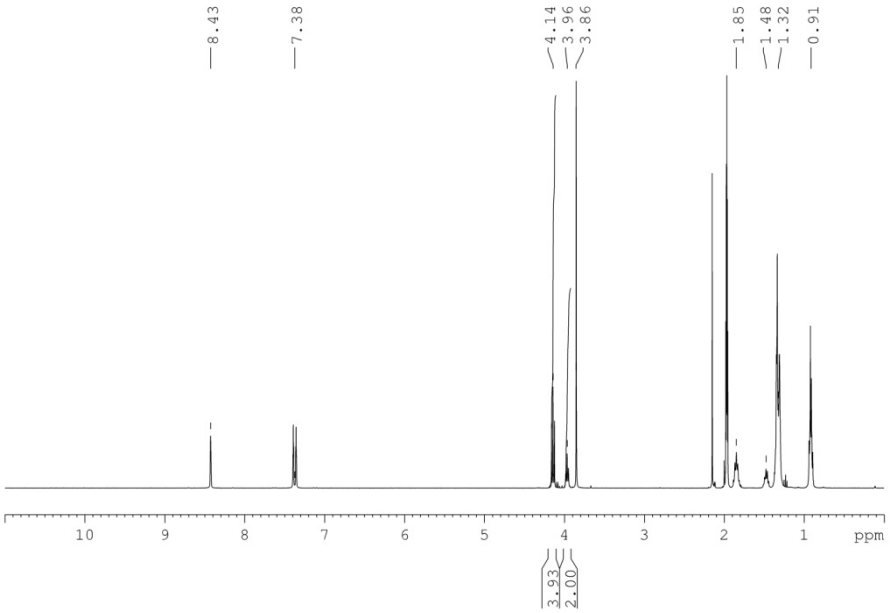

Figure S38: ^{1}H NMR spectrum (400.13 MHz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

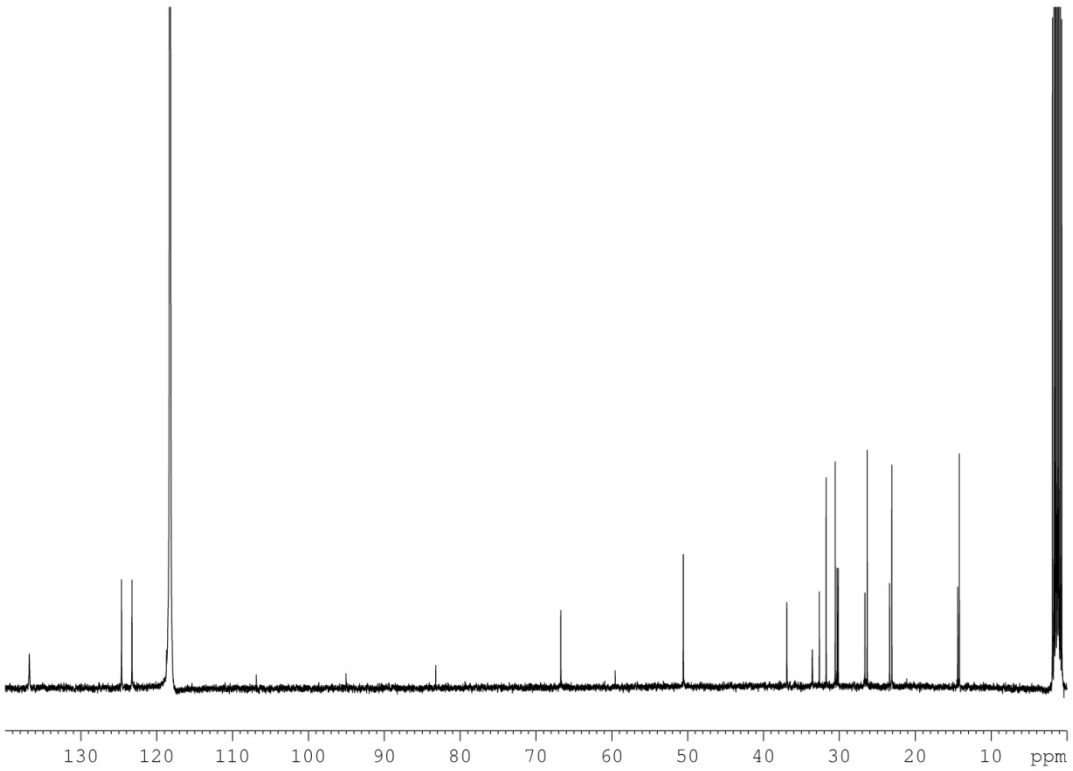

Figure S39: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

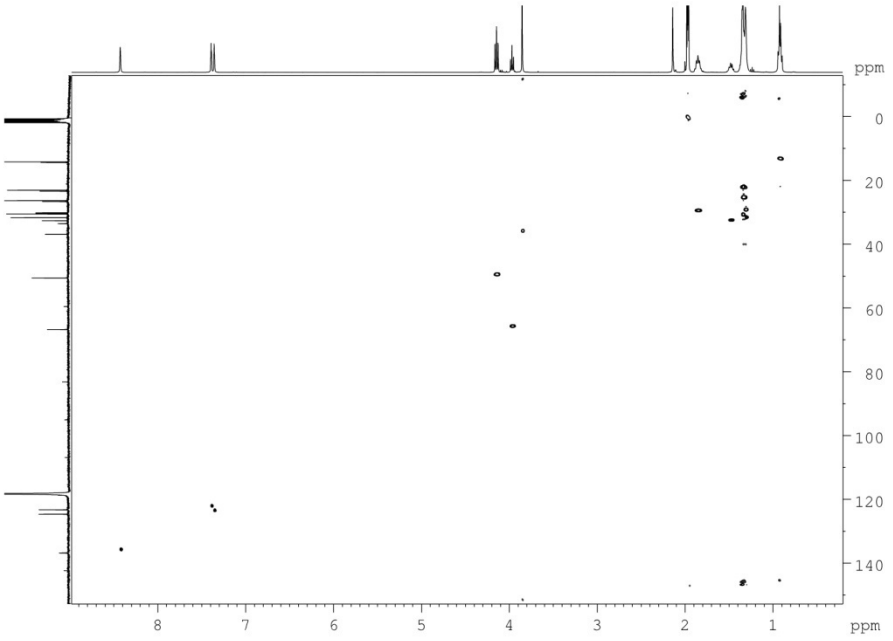

Figure S40: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CD_3CN at 298 K

Figure S41: Negative ESI MS spectrum of the $[B_{12}Cl_{11}O\text{-octyl}]^{2-}$ anion

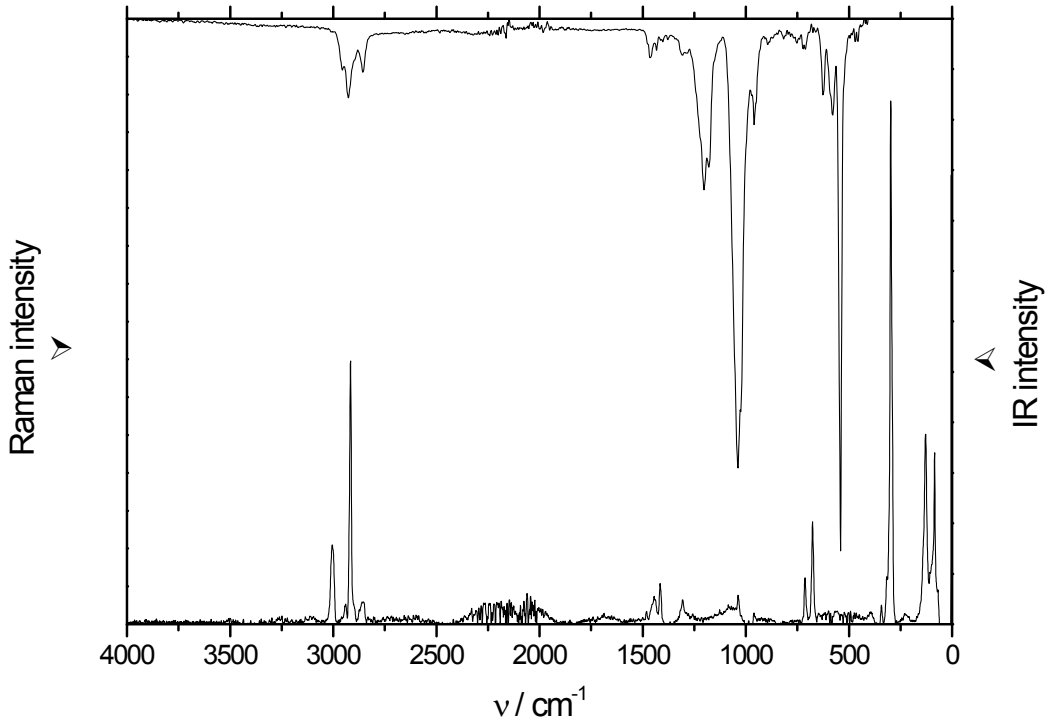

Figure S42: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Cl_{11}O\text{-octyl}]$

S2.6 Spectroscopic Data of the salts containing the $[B_{12}Cl_{11}O\text{-dodecyl}]^{2-}$ anion

A general synthetic procedure is described in the main paper. The yields given in the supplementary information refer to the amounts given in the general procedure in the main paper.

Sodium salt: (1.22 g, 1.62 mmol, 94 %) as a colorless solid. ^{1}H NMR (400.13 MHz, D_2O, 298 K): δ = 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $[B_{12}Cl_{11}O(CH_2)_{11}CH_3]^{2-}$), 1.30 (m, 18H, $[B_{12}Cl_{11}O(CH_2)_2(CH_2)_9CH_3]^{2-}$), 1.61 (m, 2H, $[B_{12}Cl_{11}OCH_2CH_2(CH_2)_9CH_3]^{2-}$), 4.03 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $[B_{12}Cl_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$). ^{11}B NMR (128.38 MHz, D_2O, 298 K): δ = –15.7 (s, 1B, *B*1-Cl), –14.0 (s, 10B, *B*(2-11)-Cl), –7.4 (s, 1B, *B*12-O)). ^{13}C{^{1}H} NMR (100.61 MHz, D_2O, 298 K): δ = 15.4 $[B_{12}Cl_{11}O(CH_2)_{11}CH_3]^{2-}$, 68.8 $[B_{12}Cl_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$. IR (ATR): $\tilde{\nu}$ = 2923 (w), 2853 (vw), 2162 (vw), 1464 (vw), 1432 (vw), 1401 (vw), 1377 (vw), 1315 (vw), 1202 (w, br), 1024 (m, br), 951 (w), 896 (vw), 708 (vw), 622 (vw), 579 (vw), 539 (m, sh), 504 (vw), 473 (vw), 418 (vw) cm^{-1}. Raman: $\tilde{\nu}$ = 3005, 2918, 2846, 1438, 1416, 1302, 1063, 958, 711, 677, 387, 298, 130 cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 352 $[B_{12}Cl_{11}O(CH_2)_{11}CH_3]^{2-}$, 743 $[B_{12}Cl_{11}O(CH_2)_{11}CH_3 + K]^-$.

Tetrabutylammonium salt: (0.42 g, 0.04 mmol, 24 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.92 (t, $^{3}J_{HH}$ = 6.5 Hz, 3H, $[B_{12}Cl_{11}O(CH_2)_{11}CH_3]^{2-}$), 1.00 (t, $^{3}J_{HH}$ = 7.4 Hz, 24H, $[N((CH_2)_3CH_3)_4]^{+}$), 1.27-1.33 (m, 18H, $[B_{12}Cl_{11}O(CH_2)_2(CH_2)_9CH_3]^{2-}$), 1.39 (m, $^{3}J_{HH}$ = 7.4 Hz, 16H, $[N((CH_2)_2(CH_2)CH_3)_4]^{+}$), 1.45-1.52 (m, 2H, $[B_{12}Cl_{11}OCH_2CH_2(CH_2)_9CH_3]^{2-}$), 1.63 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 3.11 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 3,97 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Cl_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, CD_3CN, 298 K): δ = 14.1 $[N((CH_2)_3CH_3)_4]^{+}$, 14.4 $[B_{12}Cl_{11}O(CH_2)_{11}CH_3]^{2-}$, 20.3 $[N((CH_2)_2CH_2CH_3)_4]^{+}$, 24.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 59.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 66.7 $[B_{12}Cl_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$.

[C_6mim] salt: (0.39 g, 0.04 mmol, 28 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (m, 3H, $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$), 0.92 (m, 3H, *H*10) 1.27-1.32 (m, 18H, $[B_{12}Br_{11}O(CH_2)_2(CH_2)_9CH_3]^{2-}$), 1.32-1.38 (m, 6H, *H*7-9), 1.48 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2(CH_2)_9CH_3]^{2-}$), 1.85 (m, 2H, *H*6), 3.85 (s, 3H, *H*2), 3.97 (t, $^{3}J_{HH}$ = 6.3 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$), 4.14 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, *H*5), 7.37 (m, 2H, *H*3-4), 8.42 (s, 1H, *H*1). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, CD_3CN, 298 K): δ = 13.1 [*C*10], 14.4 $[B_{12}Cl_{11}O(CH_2)_{11}CH_3]^{2-}$, 23.1 [*C*9], 26.4 [*C*8], 30.6 [*C*7], 31.8 [*C*6], 36.9 [*C*2], 50.6 [*C*5], 68.3 $[B_{12}Cl_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$, 123.3 [*C*4], 126.6 [*C*3], 136.8 [*C*1].

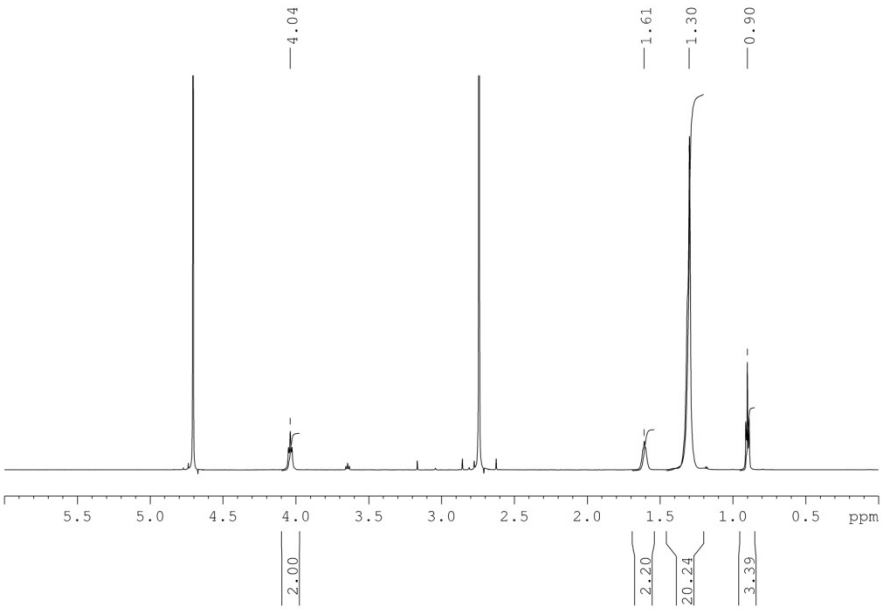

Figure S43: ^{1}H NMR spectrum (400.13 MHz) of $Na_2[B_{12}Cl_{11}O$-dodecyl] in D_2O at 298 K

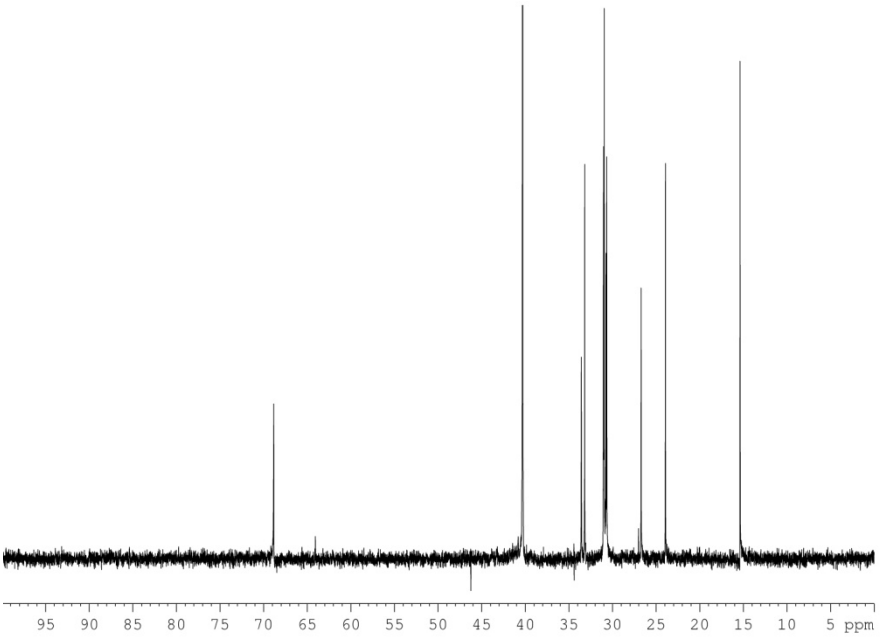

Figure S44: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $Na_2[B_{12}Cl_{11}O$-dodecyl] in D_2O at 298 K

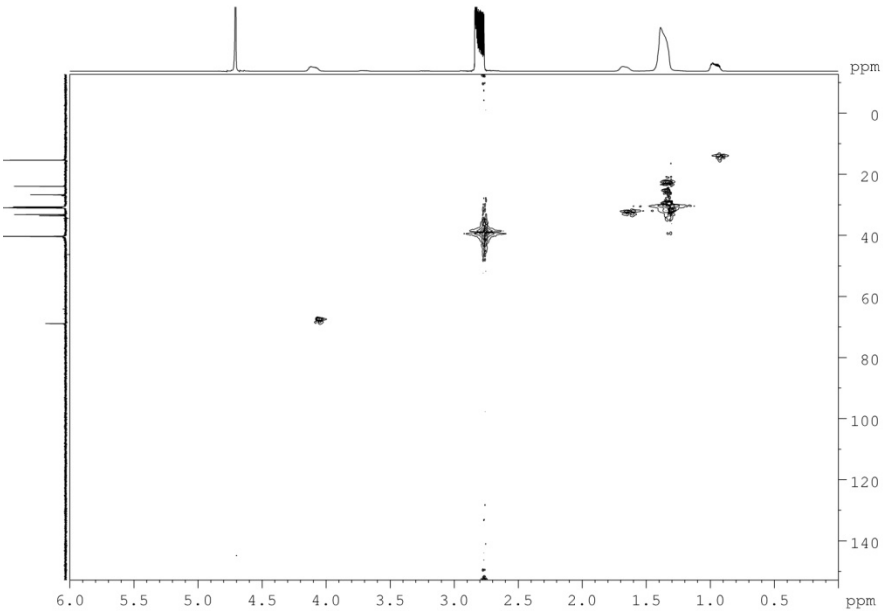

Figure S45: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $Na_2[B_{12}Cl_{11}O$-dodecyl] in D_2O at 298 K

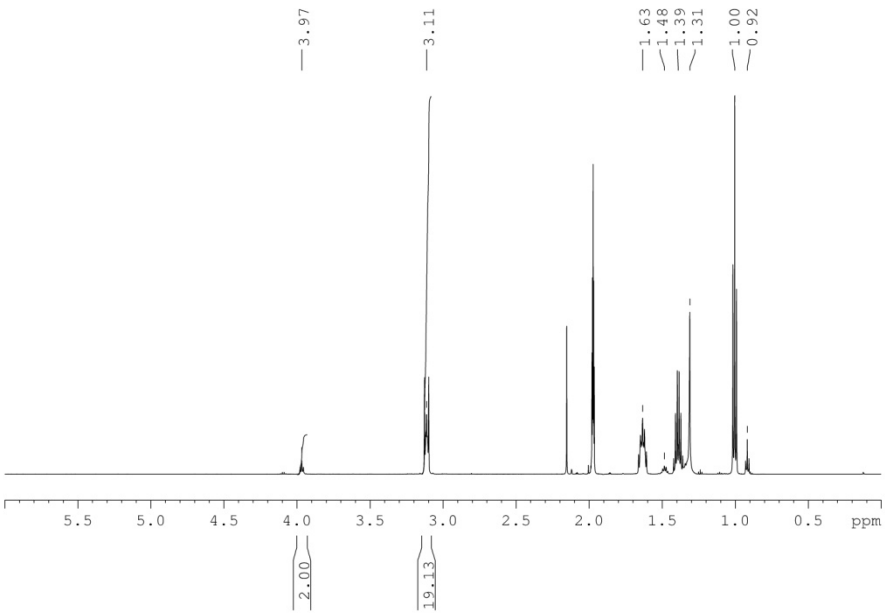

Figure S46: ^{1}H NMR spectrum (400.13 MHz) of $[NBu_4]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

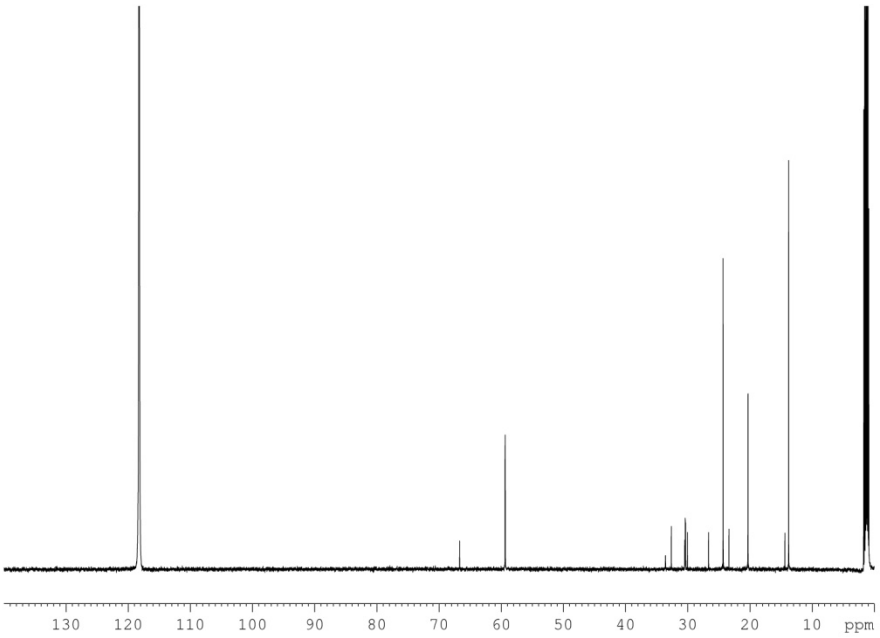

Figure S47: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of of $[NBu_4]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

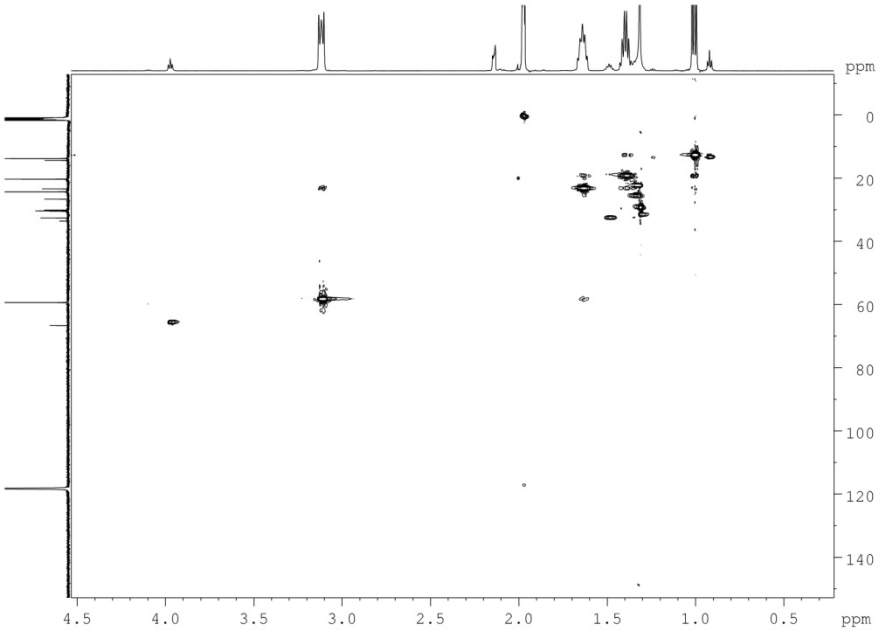

Figure S48: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[NBu_4]_2[B_{12}Cl_{11}O$-dodecyl] in CD_3CN at 298 K

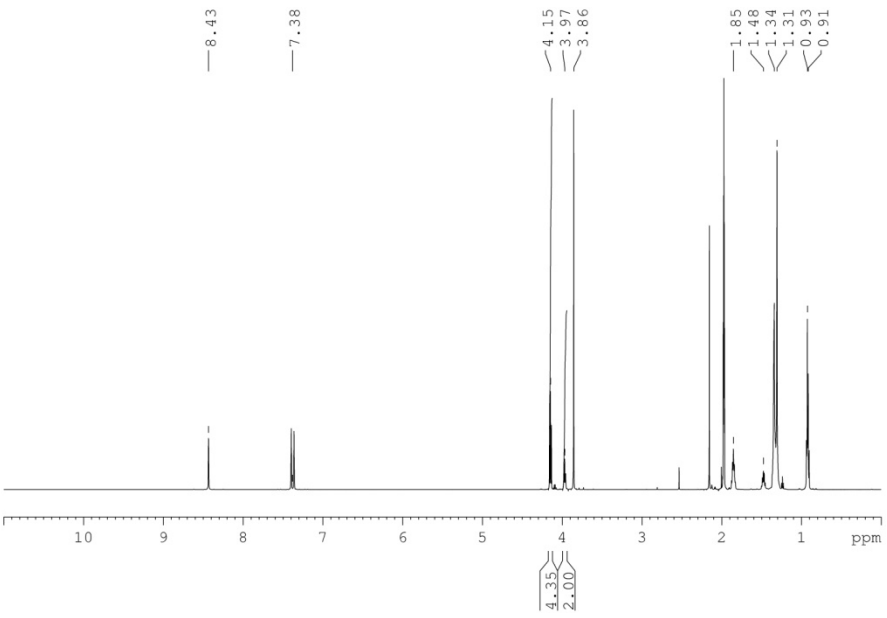

Figure S49: ^{1}H NMR spectrum (400.13 MHz) of $[C_6mim]_2[B_{12}Cl_{11}O$-dodecyl] in CD_3CN at 298 K

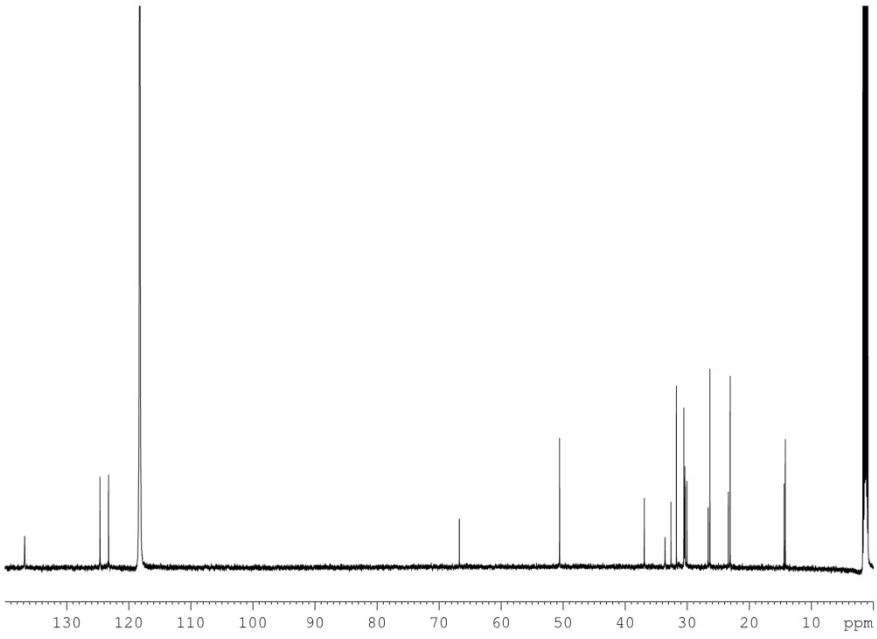

Figure S50: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of of $[C_6mim]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

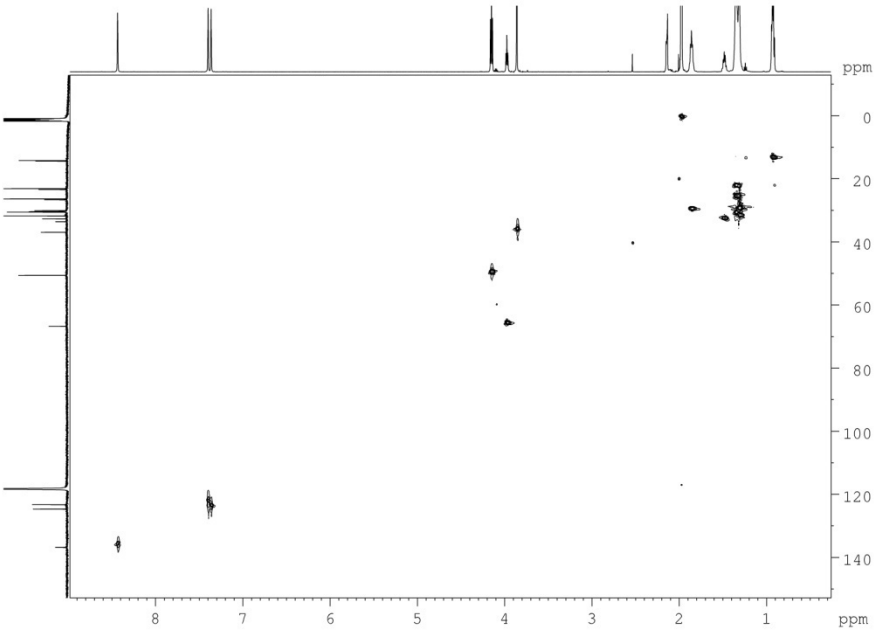

Figure S51: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[C_6mim]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

Figure S52: Negative ESI MS spectrum of the $[B_{12}Cl_{11}O\text{-dodecyl}]^{2-}$ anion

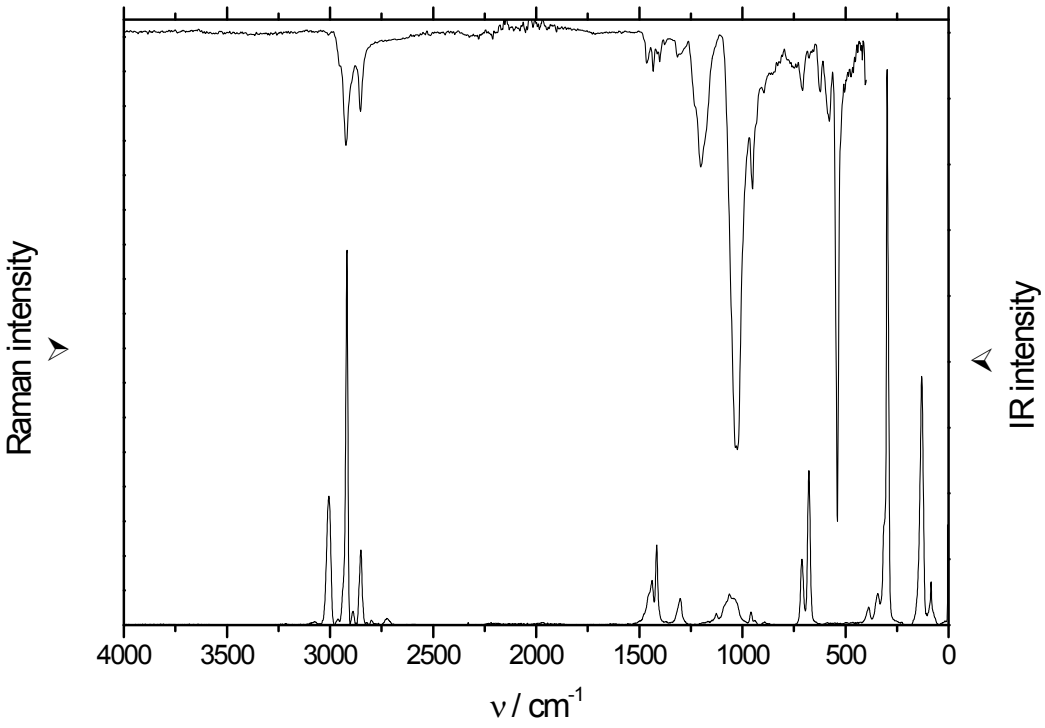

Figure S53: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Cl_{11}O\text{-dodecyl}]$

S2.7 Spectroscopic Data for the salts containing the $[B_{12}Br_{11}O\text{-propyl}]^{2-}$ anion

A general synthetic procedure is described in the main paper. The yields given in the supplementary information refer to the amounts given in the general procedure in the main paper.

Sodium salt: (0.81 g, 0.73 mmol, 78 %) as a colorless solid. ^{1}H NMR (400.13 MHz, D_2O, 298 K): δ = 0.86 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$), 1.60 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$), 4.03 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$); ^{11}B NMR (128.38 MHz, D_2O, 298 K): δ = –16.7 (s, 1B, *B*1-Br), –14.4 (s, 10B, *B*(2-11)-Br), –4.4 (s, 1B, *B*12-O)). ^{13}C{^{1}H} NMR (100.61 MHz, D_2O, 298 K): δ = 11.3 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 27.1 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 70.8 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$. IR (ATR): $\tilde{\nu}$ = 3002 (vw), 2967 (vw), 2323 (vw), 2188 (vw), 2162 (vw), 2090 (vw), 1980 (vw), 1463 (w), 1433 (w,), 1413 (w), 1401 (w), 1315 (w), 1262 (w), 1211 (m, sh), 1189 (w), 1143 (m), 1049 (s, sh), 1020 (s, sh), 1002 (s, sh), 956 (m), 889 (w), 739 (vw), 708 (w), 674 (vw), 556 (vw), 539 (w), 485(w), 453 (m, sh), 432 (vw), 417 (vw) cm^{-1}. Raman: $\tilde{\nu}$ = 3000, 2913, 2745, 1449, 1414, 1313, 1055, 956, 709, 676, 388, 346, 311, 193 cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 534 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$.

Tetrabutylammonium salt: (0.42 g, 0.04 mmol, 24 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_2CH_3]^{2-}$), 1.00 (t, $^{3}J_{HH}$ = 7.4 Hz, 24H, $[N((CH_2)_3CH_3)_4]^{+}$), 1.38 (m, 16H, $[N((CH_2)_2(CH_2)CH_3)_4]^{+}$), 1.50 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$), 1.63 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 3.11 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 4.02 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 10.9 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 13.8 $[N((CH_2)_3CH_3)_4]^{+}$, 20.3 $[N((CH_2)_2CH_2CH_3)_4]^{+}$, 24.3 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 26.6 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 59.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 68.2 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$.

[C_6mim] salt: (0.35 g, 0.04 mmol, 23 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (t, $^{3}J_{HH}$ = 6.7 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_2CH_3]^{2-}$), 0.92 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, *H*10), 1.28-1.40 (m, 6H, *H*7-9), 1.49 (m, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$), 1.85 (m, 2H, *H*6), 3.85 (s, 3H, *H*2), 4.06 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$), 4.14 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, *H*5), 7.37 (m, 2H, *H*3-4), 8.42 (s, 1H, *H*1). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 10.9 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 14.2 [*C*10], 23.1 [*C*9], 26.4 [*C*8], 26.6 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 30.6 [*C*7], 31.8 [*C*6], 36.9 [*C*2], 50.6 [*C*5], 68.1 $[B_{12}Br_{11}OCH_2CH_2CH_3]^{2-}$, 123.3 [*C*4], 126.6 [*C*3], 136.8 [*C*1].

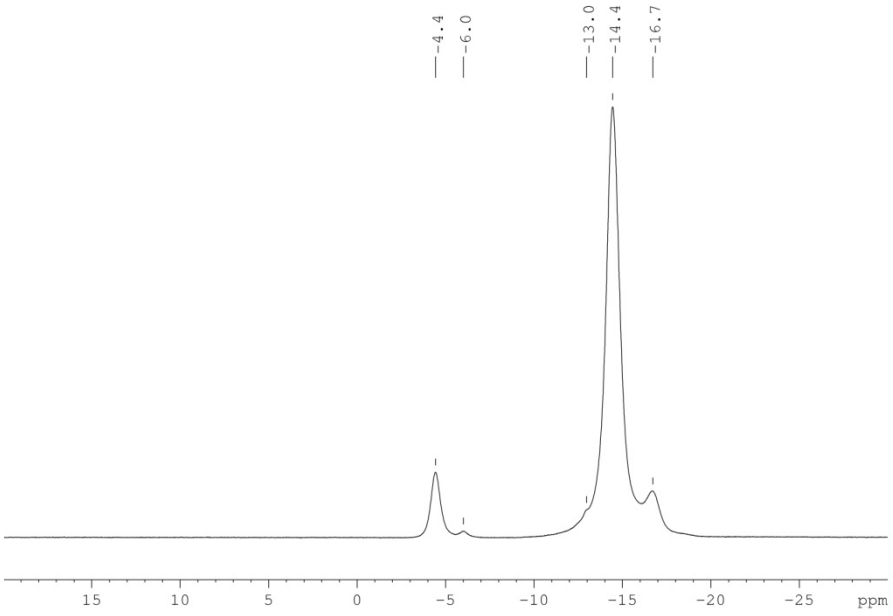

Figure S54: ^{11}B NMR spectrum (128.39 MHz) of $Na_2[B_{12}Br_{11}O\text{-propyl}]$ D_2O at 298 K

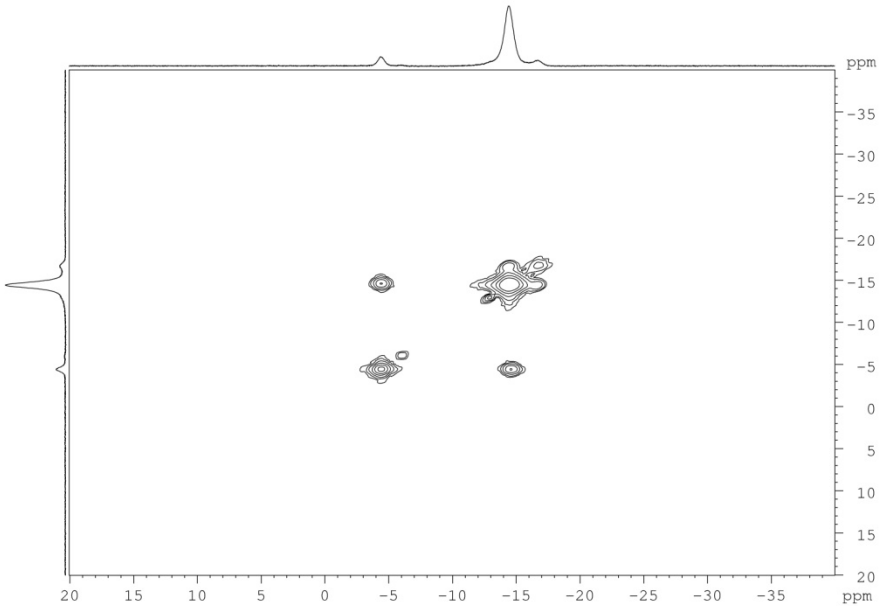

Figure S55: ^{11}B-^{11}B-COSY NMR spectrum (128.38 MHz) of $Na_2[B_{12}Br_{11}O\text{-propyl}]$ in D_2O at 298 K

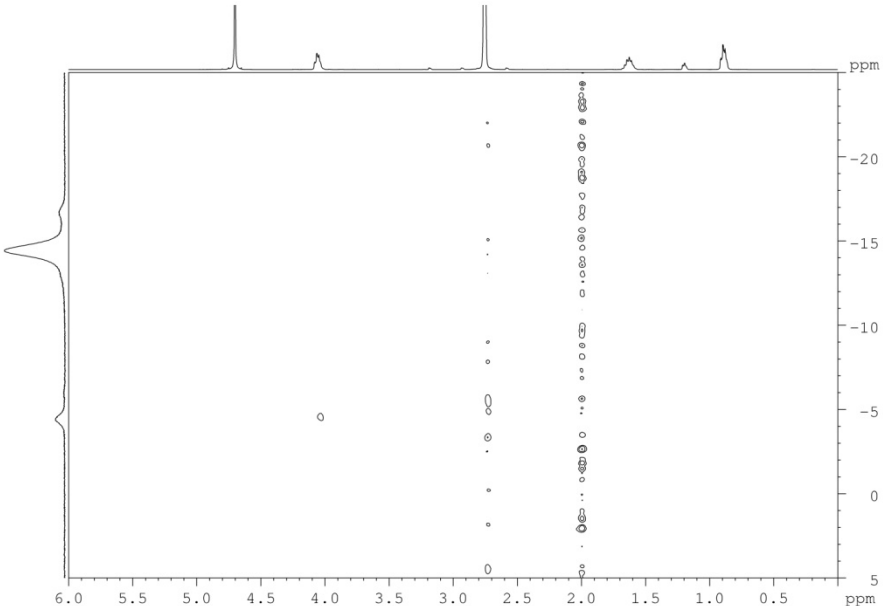

Figure S56: $^{1}H,^{11}B$ correlation (400.13 MHz, HSQC, optimized for J_{BH} = 100 Hz) of $Na_2[B_{12}Br_{11}O\text{-propyl}]$ in D_2O at 298 K

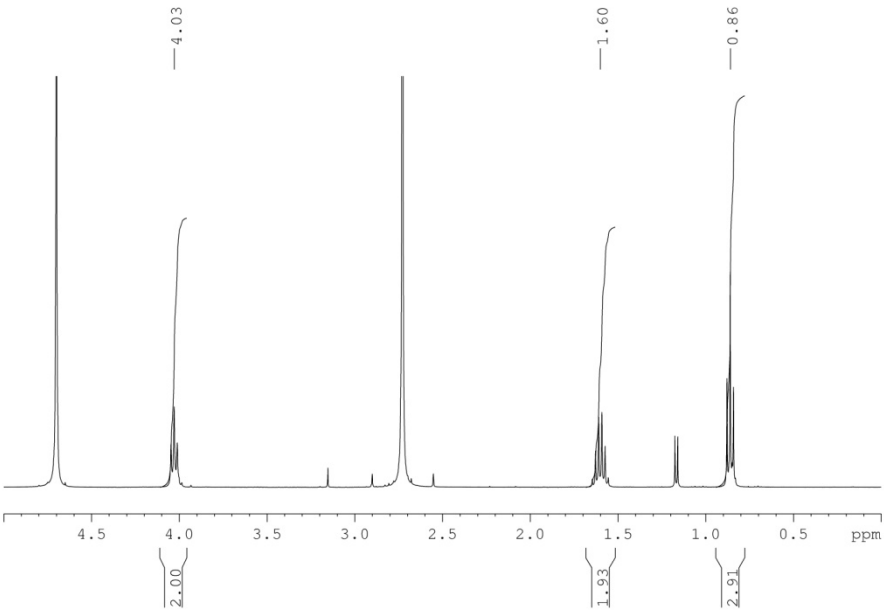

Figure S57: ^{1}H NMR spectrum (400.13 MHz) of $Na_2[B_{12}Br_{11}O\text{-propyl}]$ in D_2O at 298 K

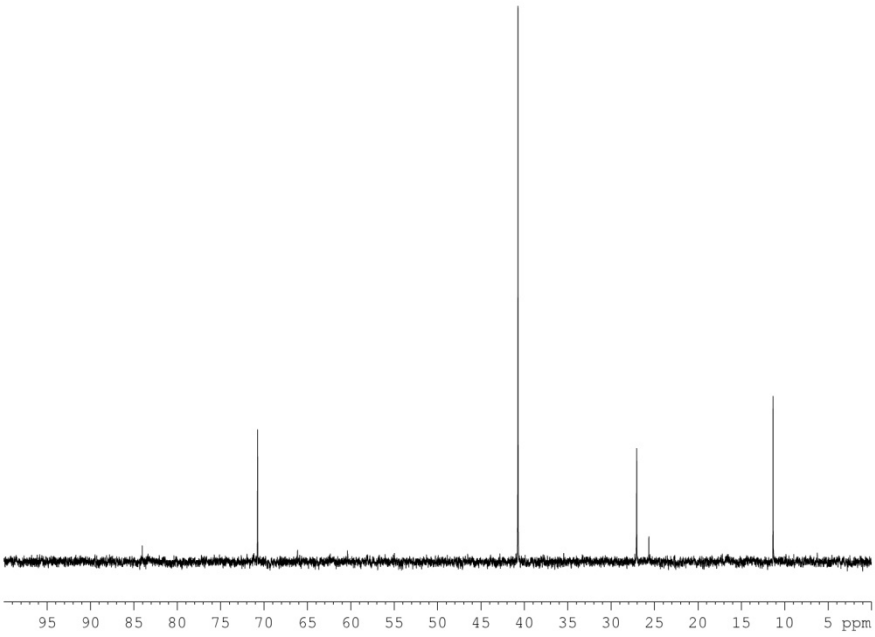

Figure S58: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $Na_2[B_{12}Br_{11}O\text{-propyl}]$ in D_2O at 298 K

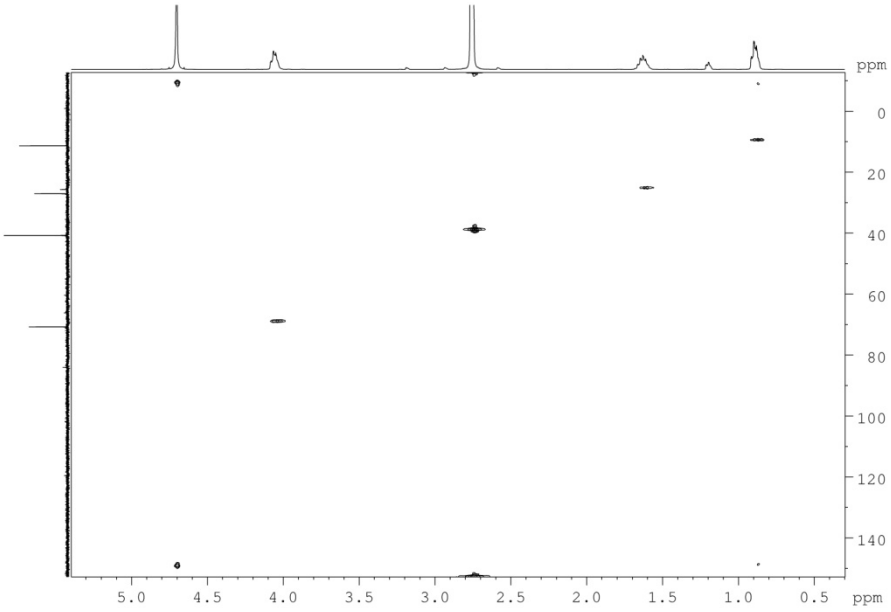

Figure S59: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $Na_2[B_{12}Br_{11}O\text{-propyl}]$ in D_2O at 298 K

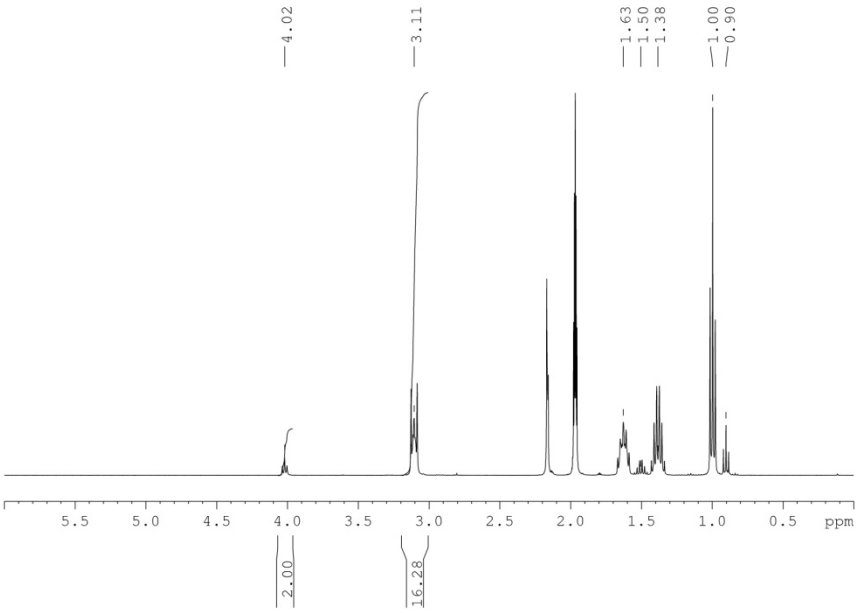

Figure S60: ^{1}H NMR spectrum (400.13 MHz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-propyl}]$ in CD_3CN at 298 K

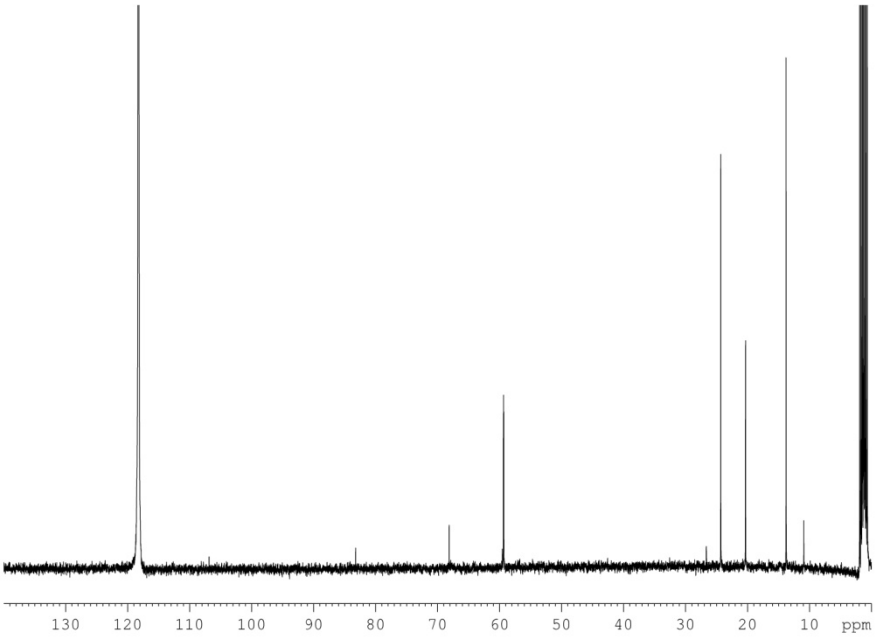

Figure S61: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-propyl}]$ in CD_3CN at 298 K

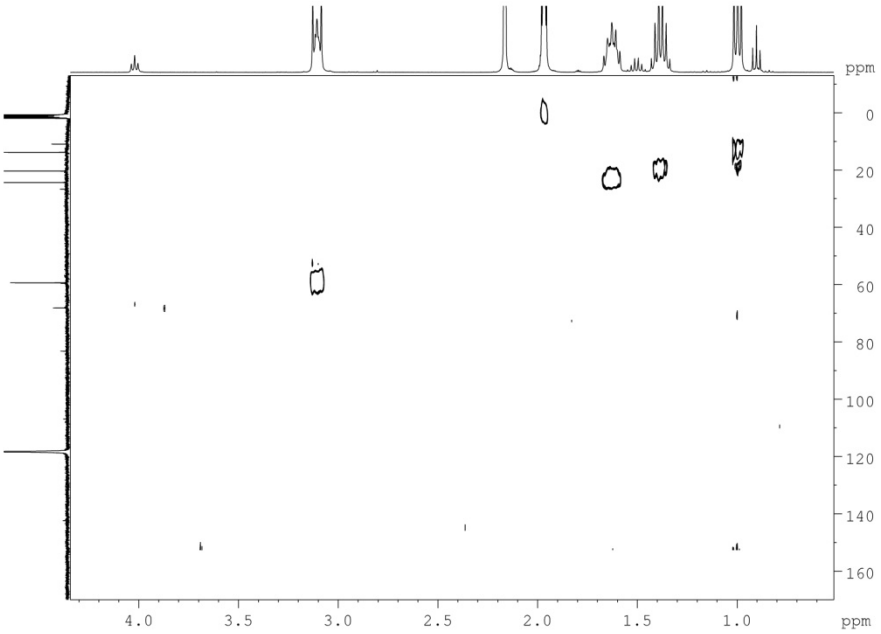

Figure S62: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-propyl}]$ in CD_3CN at 298 K

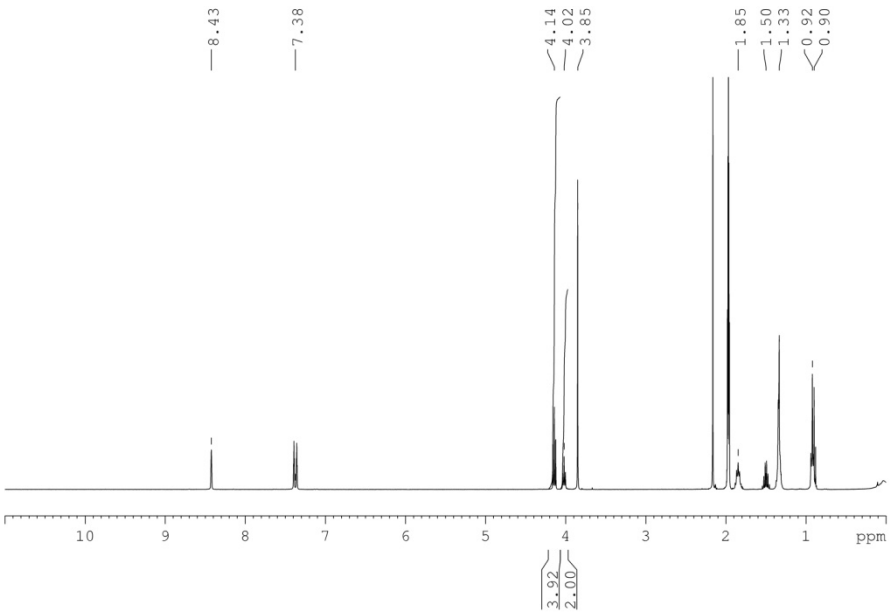

Figure S63: ^{1}H NMR spectrum (400.13 MHz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-propyl}]$ in CD_3CN at 298 K

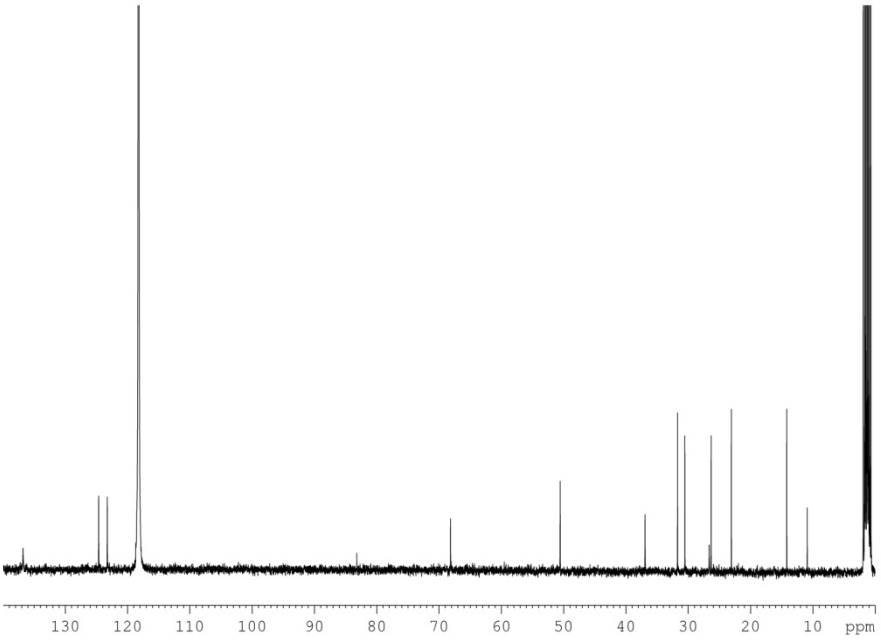

Figure S64: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-propyl}]$ in CD_3CN at 298 K

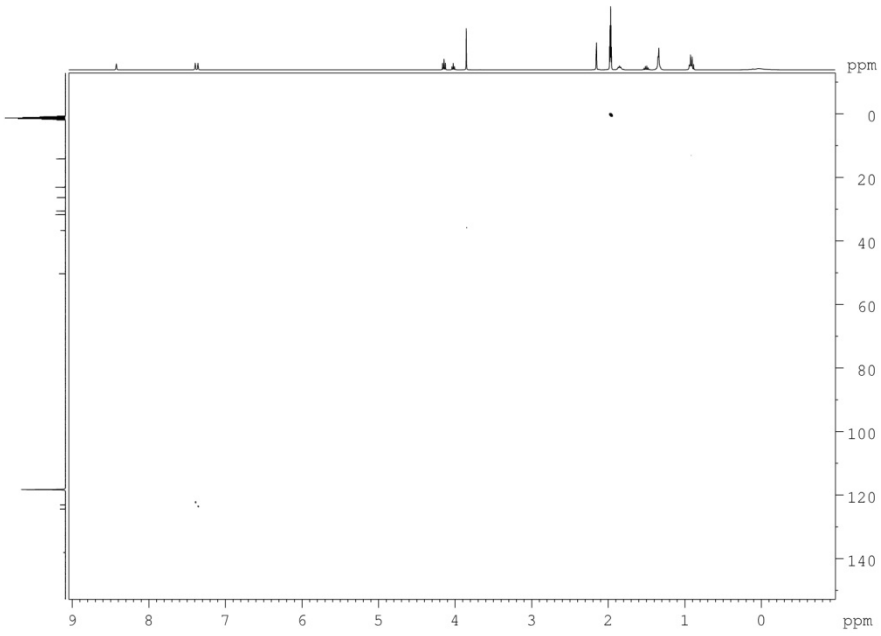

Figure S65: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-propyl}]$ in CD_3CN at 298 K

Figure S66: Negative ESI MS spectrum of the $[B_{12}Br_{11}O\text{-propyl}]^{2-}$ anion

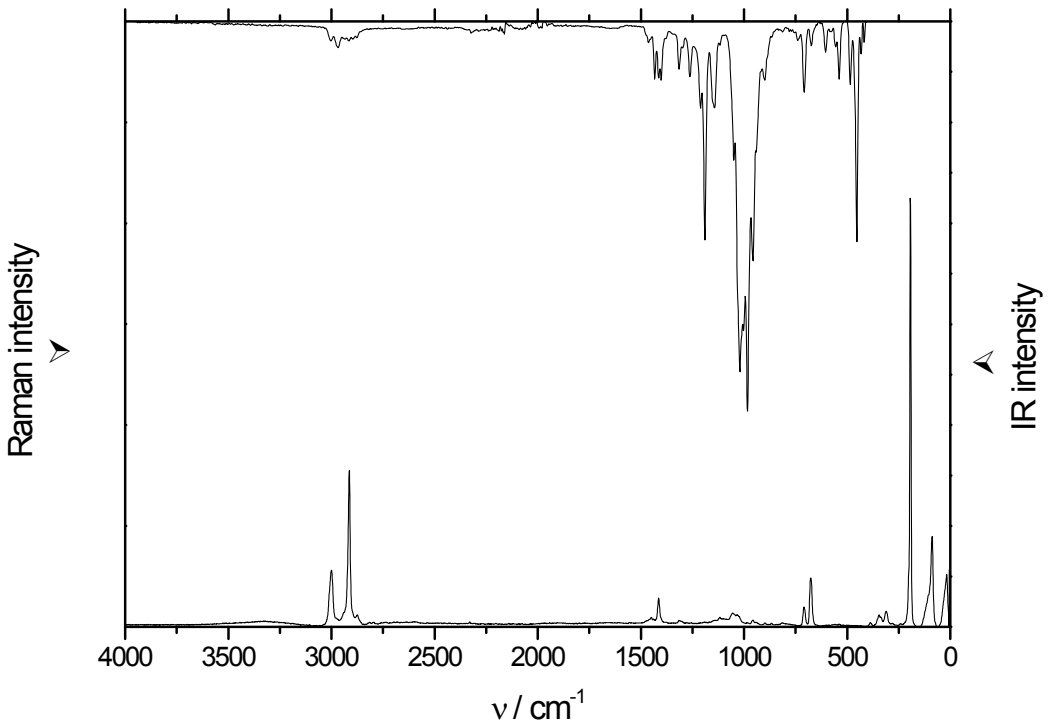

Figure S67: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Br_{11}O\text{-propyl}]$

S2.8 Spectroscopic Data for salts containing the $[B_{12}Br_{11}O\text{-octyl}]^{2-}$ anion

A general synthetic procedure is described in the main paper. The yields given in the supplementary information refer to the amounts given in the general procedure in the main paper.

Sodium salt: (0.87 g, 0.74 mmol, 79 %) as a colorless solid. ^{1}H NMR (400.13 MHz, D_2O, 298 K): δ = 0.86 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_7CH_3]^{2-}$), 1.30 (m, 10H, $[B_{12}Br_{11}O(CH_2)_2(CH_2)_5CH_3]^{2}$), 1.59 (m, 2H, $B_{12}Br_{11}OCH_2CH_2(CH_2)_5CH_3]^{2-}$), 4.07 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_6CH_3]^{2-}$). ^{11}B NMR (128.38 MHz, D_2O, 298 K): δ = –16.7 (s, 1B, *B*1-Br), –14.4 (s, 10B, *B*(2-11)-Br), –4.4 (s, 1B, *B*12-O)). ^{13}C{^{1}H} NMR (100.61 MHz, D_2O, 298 K): δ = 15.5 $[B_{12}Br_{11}O(CH)_7CH_3^{2-}]$, 69.3 $[B_{12}Br_{11}OCH_2(CH_2)_6CH_3^{2-}]$. IR (ATR): $\tilde{\nu}$ = 2925 (m), 2854 (m), 2164 (vw), 2090 (vw), 1987 (vw), 1465 (w), 1433 (w,), 1401 (w), 1316 (w), 1177 (s, sh), 1017 (vs, sh), 1002 (vs, sh), 985 (s, sh), 956 (w), 814 (vw), 712 (w), 673 (vw), 605 (w), 544 (w), 506 (w), 485 (w), 453 (vs, sh), 421 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 3001, 2915, 1438, 1413, 1302, 1040, 956, 711, 676, 347, 311, 196 cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 569 $[B_{12}Br_{11}O(CH_2)_7CH_3]^{2-}$.

Tetrabutylammonium salt: (0.42 g, 0.04 mmol, 24 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.91 (t, $^{3}J_{HH}$ = 6.8 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_7CH_3]^{2-}$), 1.00 (t, $^{3}J_{HH}$ = 7.4 Hz, 24H, $[N((CH_2)_3CH_3)_4]^{2-}$), 1.31 (m, 10H, $[B_{12}Br_{11}O(CH_2)_2(CH_2)_5CH_3]^{2-}$), 1.38 (m, 16H, $[N((CH_2)_2(CH_2)CH_3)_4]^{2-}$), 1.48 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2(CH_2)_5CH_3]^{2-}$), 1.63 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{2-}$), 3.11 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{2-}$), 4.06 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_6CH_3]^{2-}$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 14.4 $[B_{12}Br_{11}O(CH)_7CH_3^{2-}]$, 13.8 $[N((CH_2)_3CH_3)_4]^{+}$, 20.3 $[N((CH_2)_2CH_2CH_3)_4]^{+}$, 24.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 59.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 66.6 $[B_{12}Br_{11}OCH_2(CH_2)_6CH_3]^{2-}$.

[C_6mim] salt: (0.35 g, 0.04 mmol, 23 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_2CH_3]^{2-}$), 0.92 (t, $^{3}J_{HH}$ = 6.7 Hz, 3H, *H*10) 1.28-1.40 (m, 10H $[B_{12}Br_{11}O\text{-}(CH_2)_2(CH_2)_5CH_3]^{2-}$), 1.28-1.40 (m, 6H, *H*7-9), 1.49 (m, $[B_{12}Br_{11}OCH_2CH_2(CH_2)_5CH_3]^{2-}$), 1.85 (m, 2H, *H*6), 3.85 (s, 3H, *H*2), 4.06 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_6CH_3]^{2-}$).4.14 (m, $^{3}J_{HH}$ = 7.3 Hz, 2H, *H*5), 7.37 (m, 2H, *H*3-4), 8.42 (s, 1H, *H*1). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 14.4 $[B_{12}Br_{11}O(CH)_7CH_3^{2-}]$, 14.2 [*C*10], 23.1 [*C*9], 26.4 [*C*8], 30.6 [*C*7], 31.8 [*C*6], 36.9 [*C*2], 50.6 [*C*5], 66.6 $[B_{12}Br_{11}OCH_2(CH_2)_6CH_3]^{2-}$, 123.3 [*C*4], 126.6 [*C*3], 136.8 [*C*1].

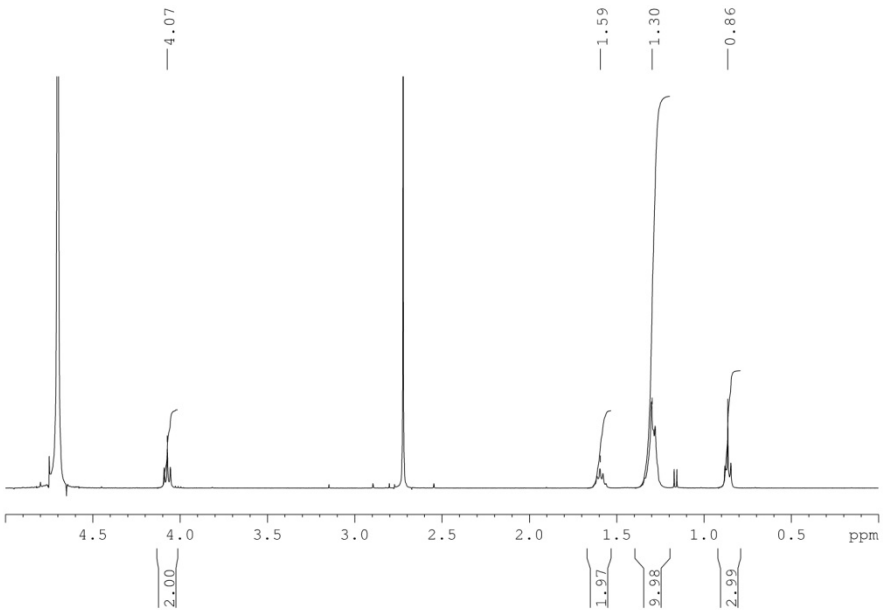

Figure S68: ^{1}H NMR spectrum (400.13 MHz) of $Na_2[B_{12}Br_{11}O\text{-octyl}]$ in D_2O at 298 K

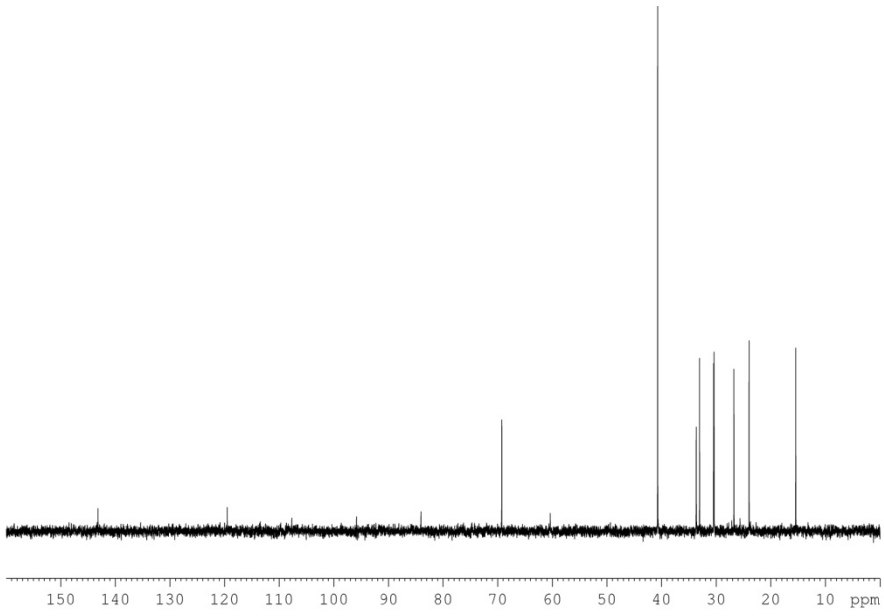

Figure S69: ^{13}C $\{^{1}H\}$ NMR spectrum (100.61 MHz) of $Na_2[B_{12}Br_{11}O\text{-octyl}]$ in D_2O at 298 K

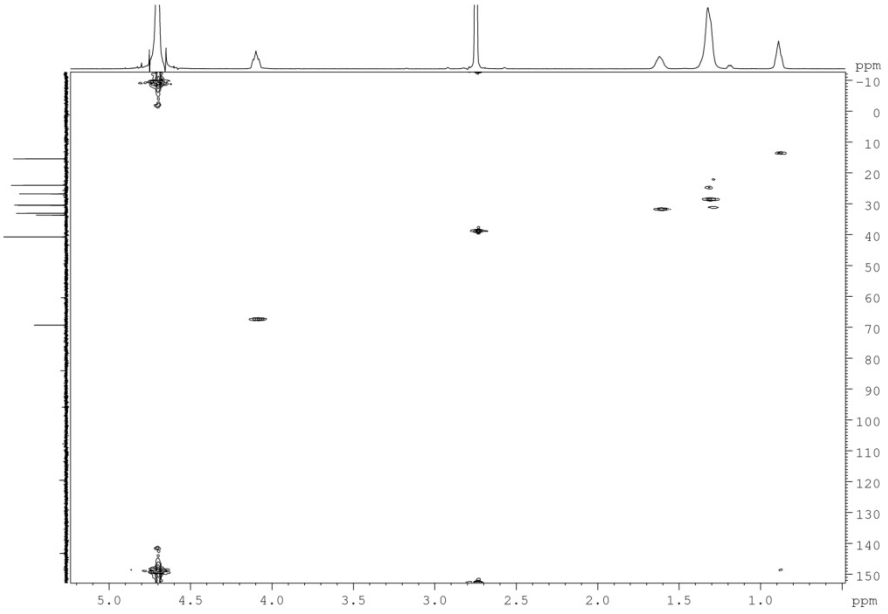

Figure S70: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $Na_2[B_{12}Br_{11}O\text{-octyl}]$ in D_2O at 298 K

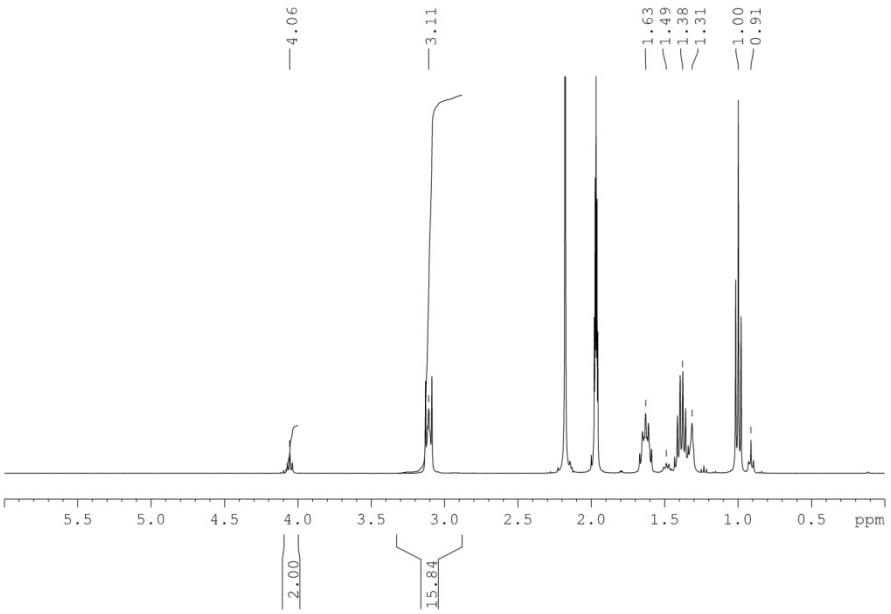

Figure S71: ^{1}H NMR spectrum (400.13 MHz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-octyl}]$ in D_2O at 298 K

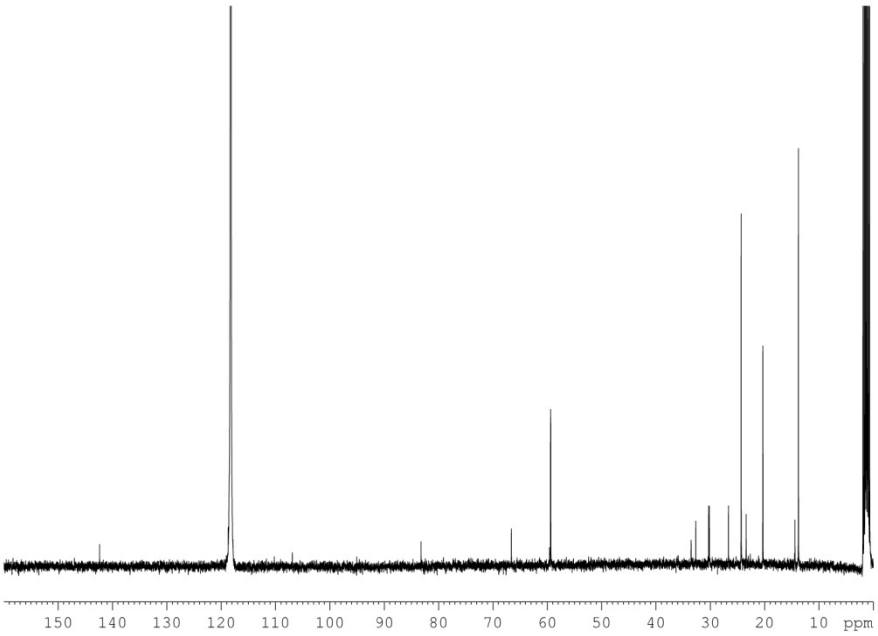

Figure S72: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-octyl}]$ in CD_3CN at 298 K

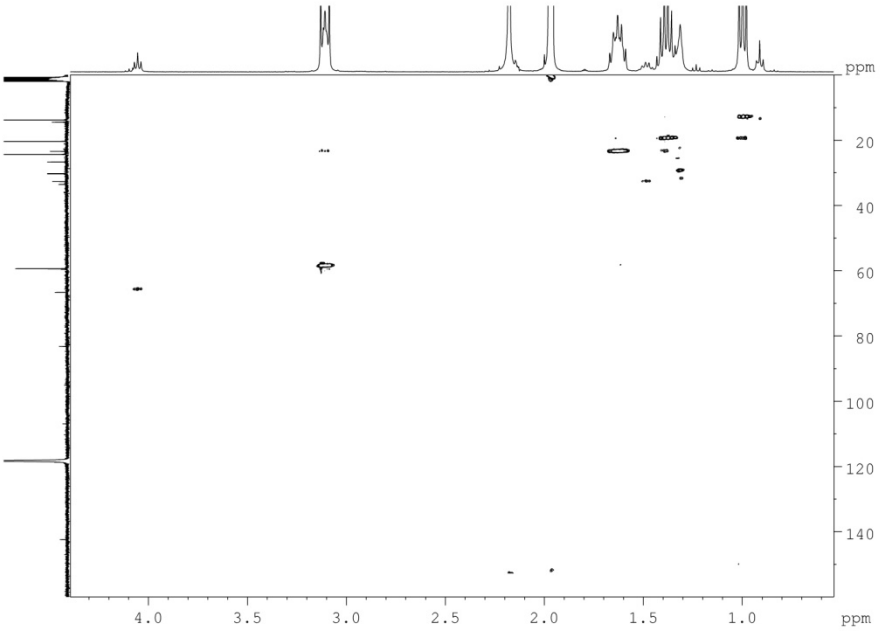

Figure S73: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-octyl}]$ in CD_3CN at 298 K

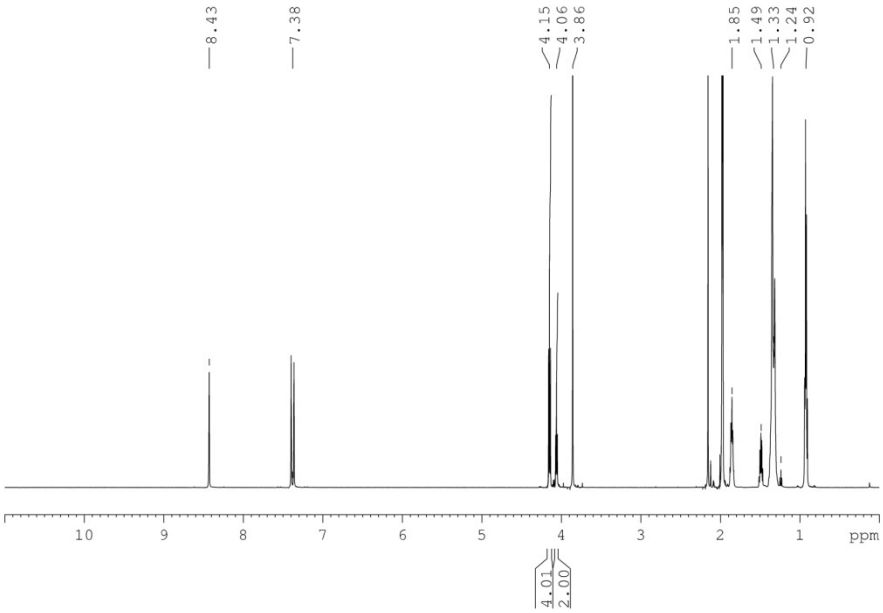

Figure S74: ^{1}H NMR spectrum (400.13 MHz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-octyl}]$ in D_2O at 298 K

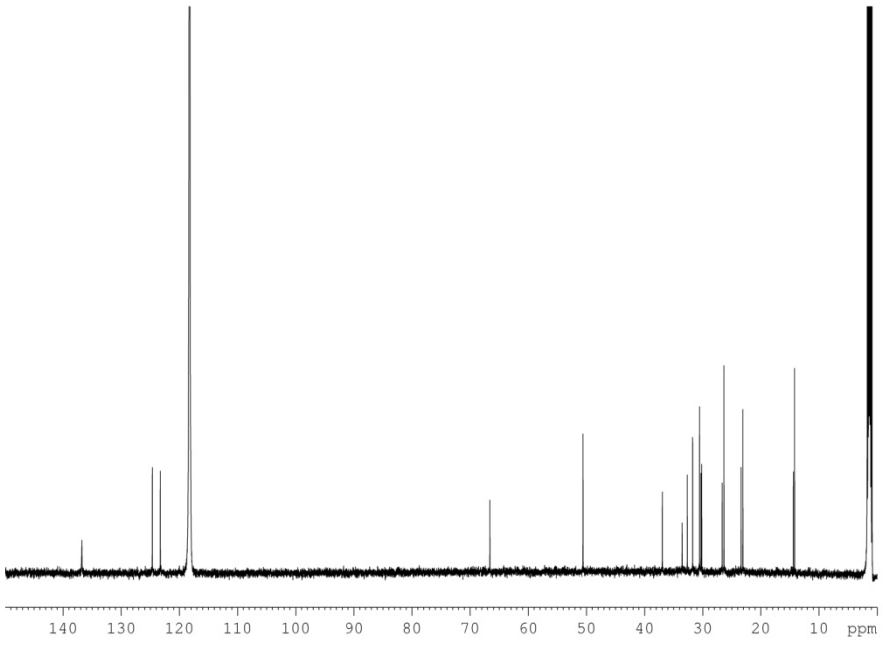

Figure S75: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-octyl}]$ in CD_3CN at 298 K

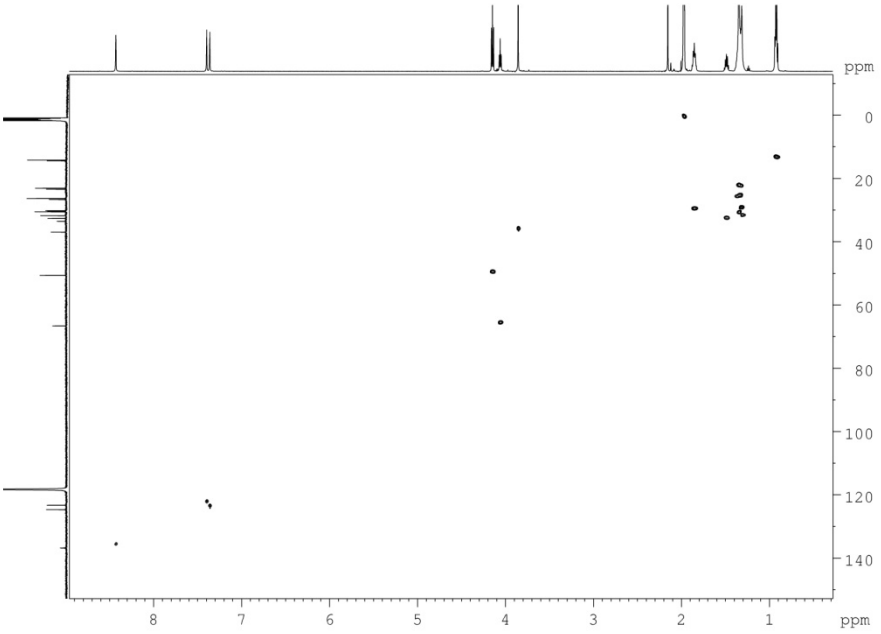

Figure S76: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-octyl}]$ in CD_3CN at 298 K

Figure S77: Negative ESI MS spectrum of the $[B_{12}Br_{11}O\text{-octyl}]^{2-}$ anion

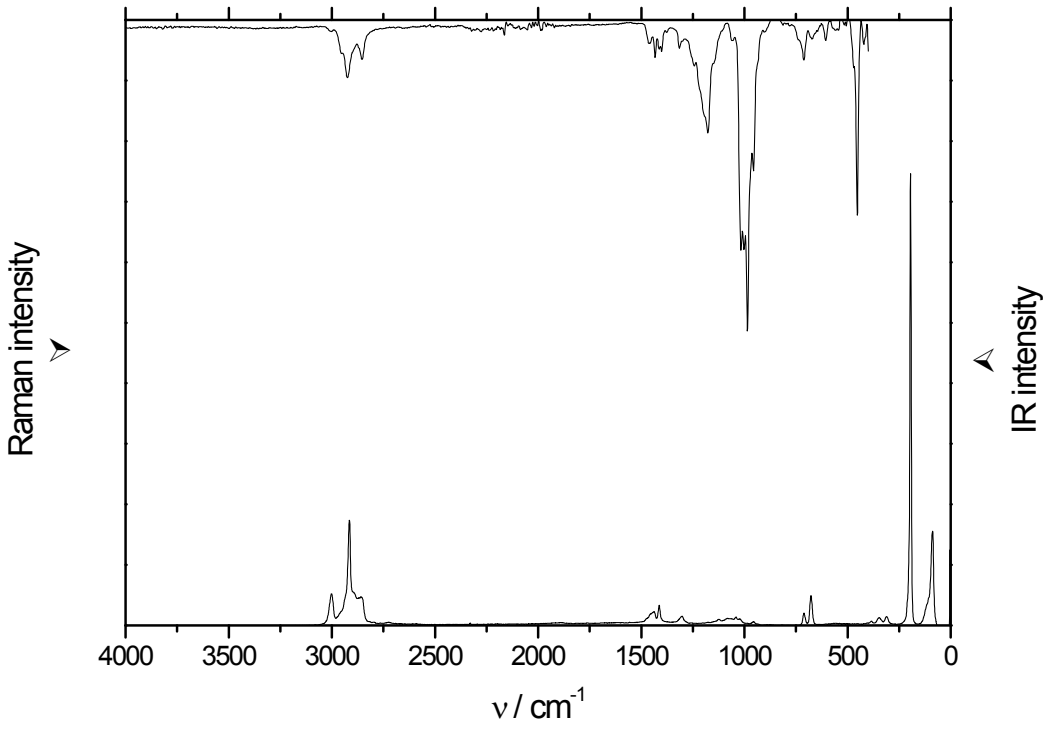

Figure S78: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Br_{11}O\text{-octyl}]$.

S2.9 Spectroscopic Data for salts containing the $[B_{12}Br_{11}O\text{-dodecyl}]^{2-}$ anion

A general synthetic procedure is described in the main paper. The yields given in the supplementary information refer to the amounts given in the general procedure in the main paper.

Sodium salt: (0.95 g, 0.77 mmol, 82 %) as a colorless solid. ^{1}H NMR (400.13 MHz, D_2O, 298 K): δ = 0.91 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$), 1.31 (m, 18H, $[B_{12}Br_{11}O(CH_2)_2(CH_2)_9CH_3]^{2-}$), 1.65 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2(CH_2)_9CH_3]^{2-}$), 4.13 (m, $^3J_{HH}$ = 6.3 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$). ^{11}B NMR (128.38 MHz, D_2O, 298 K): δ = –16.6 (s, 1B, *B*1-Br), –14.4 (s, 10B, *B*(2-11)-Br), –4.4 (s, 1B, *B*12-O)). $^{13}C\{^1H\}$ NMR (100.61 MHz, D_2O, 298 K): δ = 16.1 $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$, 69.3 $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$]. IR (ATR): $\tilde{\nu}$ = 3005 (w), 2923 (m, sh), 2852 (m, sh), 2190 (vw), 2164 (vw), 2050 (vw), 1985 (vw), 1923 (vw), 1464 (w), 1433 (m, sh), 1412 (m), 1401 (m), 1314 (w), 1188 (m, br), 1143 (m), 1001 (s, sh), 984 (vs, sh), 955 (s, sh), 807 (vw), 708 (m, sh), 672 (w), 605 (w), 578 (w), 533 (vw), 503 (vw), 452 (s, sh), 418 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 3000, 2914, 2851, 1440, 1414, 1304, 1055, 958, 709, 676, 343, 309, 194 cm^{-1}. ESI-MS (– mode, D_2O): *m/z*: 597 $[B_{12}Br_{11}O(CH)_{11}CH_3]^{2-}$.

Tetrabutylammonium salt: (0.42 g, 0.04 mmol, 24 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.91 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$), 1.00 (m, 24H, $[N((CH_2)_3CH_3)_4]^{+}$), 1.31 (m, 18H, $[B_{12}Br_{11}O(CH_2)_2(CH_2)_9CH_3]^{2-}$), 1.39 (m, 16H, $[N((CH_2)_2(CH_2)CH_3)_4]^{+}$), 1.49 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2(CH_2)_9CH_3]^{2-}$), 1.63 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 3.11 (m, 16H, $[N(CH_2CH_2CH_2CH_3)_4]^{+}$), 4.06 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 14.4 $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$, 13.8 $[N((CH_2)_3CH_3)_4]^{+}$, 20.3 $[N((CH_2)_2CH_2CH_3)_4]^{+}$, 24.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 59.4 $[N(CH_2CH_2CH_2CH_3)_4]^{+}$, 66.6 $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$.

[C_6mim] salt: (0.39 g, 0.04 mmol, 28 %) as a colorless solid. ^{1}H NMR (400.13 MHz, CD_3CN, 298 K): δ = 0.90 (t, 3H, $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$), 0.92 (m, 3H, *H*10) 1.27-1.32 (m, 18H, $[B_{12}Br_{11}O(CH_2)_2(CH_2)_9CH_3]^{2-}$), 1.32-1.38 (m, 6H, *H*7-9), 1.48 (m, 2H, $[B_{12}Br_{11}OCH_2CH_2(CH_2)_9CH_3]^{2-}$), 1.85 (m, 2H, *H*6), 3.85 (s, 3H, *H*2), 4.05 (t, $^{3}J_{HH}$ = 6.3 Hz, 2H, $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$), 4.14 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, *H*5), 7.37 (m, 2H, *H*3-4), 8.42 (s, 1H, *H*1). ^{13}C{^{1}H} NMR (100.61 MHz, CD_3CN, 298 K): δ = 14.4 $[B_{12}Br_{11}O(CH_2)_{11}CH_3]^{2-}$, 14.2 [*C*10], 23.1 [*C*9], 26.4 [*C*8], 30.6 [*C*7], 31.8 [*C*6], 36.9 [*C*2], 50.6 [*C*5], 66.6 $[B_{12}Br_{11}OCH_2(CH_2)_{10}CH_3]^{2-}$], 123.3 [*C*4], 126.6 [*C*3], 136.8 [*C*1].

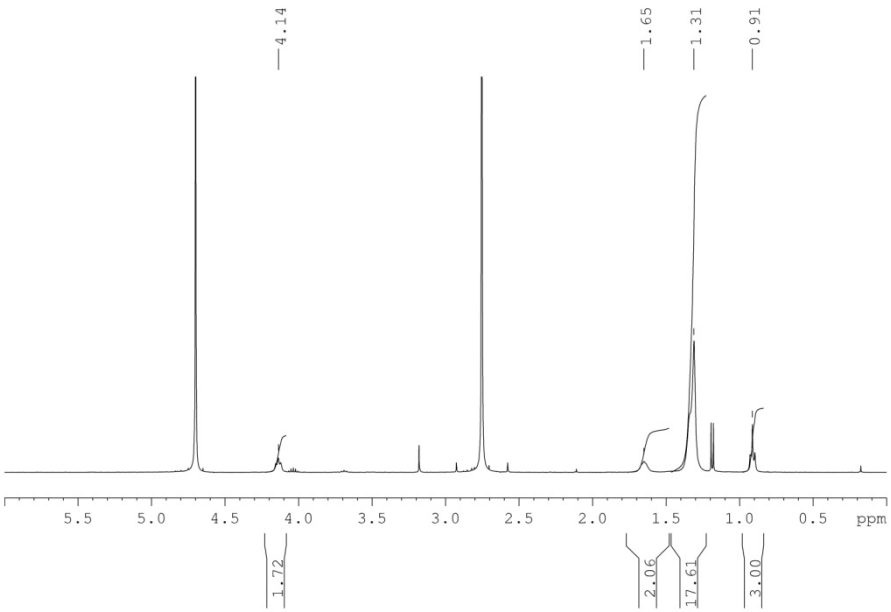

Figure S79: ^{1}H NMR spectrum (400.13 MHz) of $Na_2[B_{12}Br_{11}O$-dodecyl**]** in D_2O at 298 K

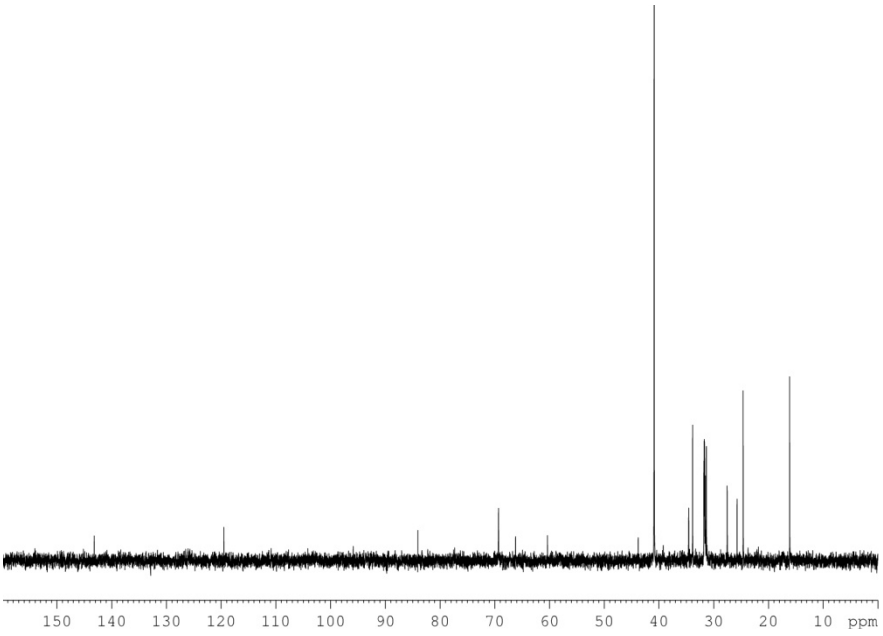

Figure S80: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $Na_2[B_{12}Br_{11}O$-dodecyl] in D_2O at 298 K

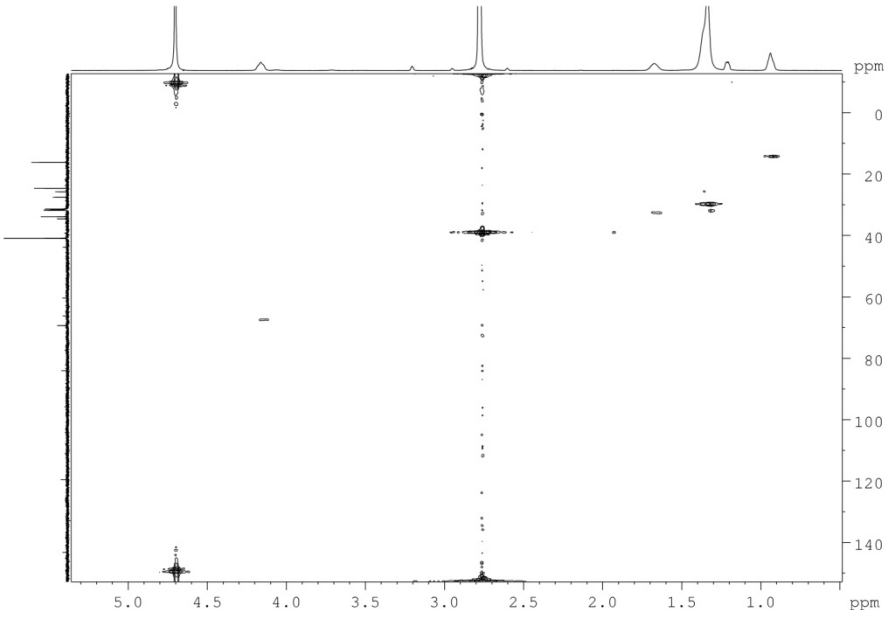

Figure S81: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $Na_2[B_{12}Br_{11}O$-dodecyl] in D_2O at 298 K

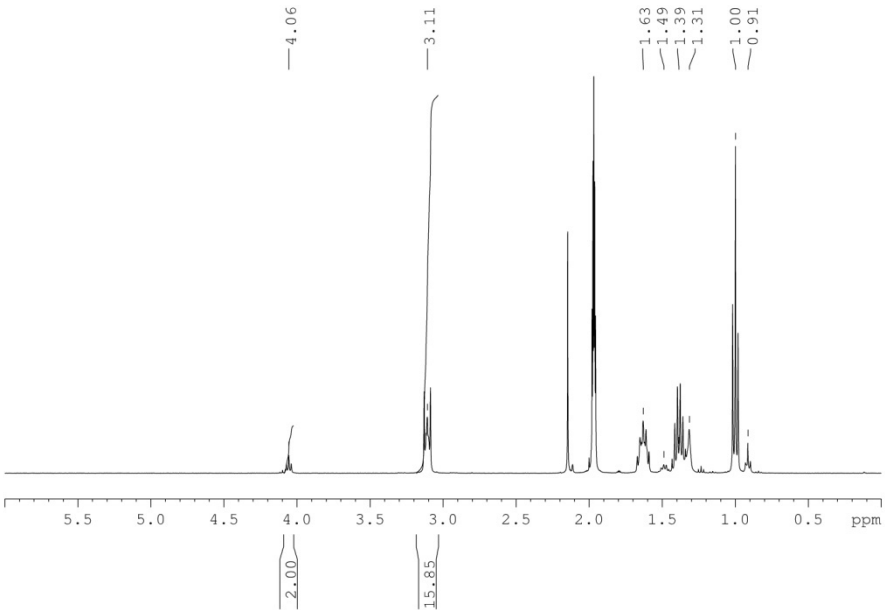

Figure S82: ^{1}H NMR spectrum (400.13 MHz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

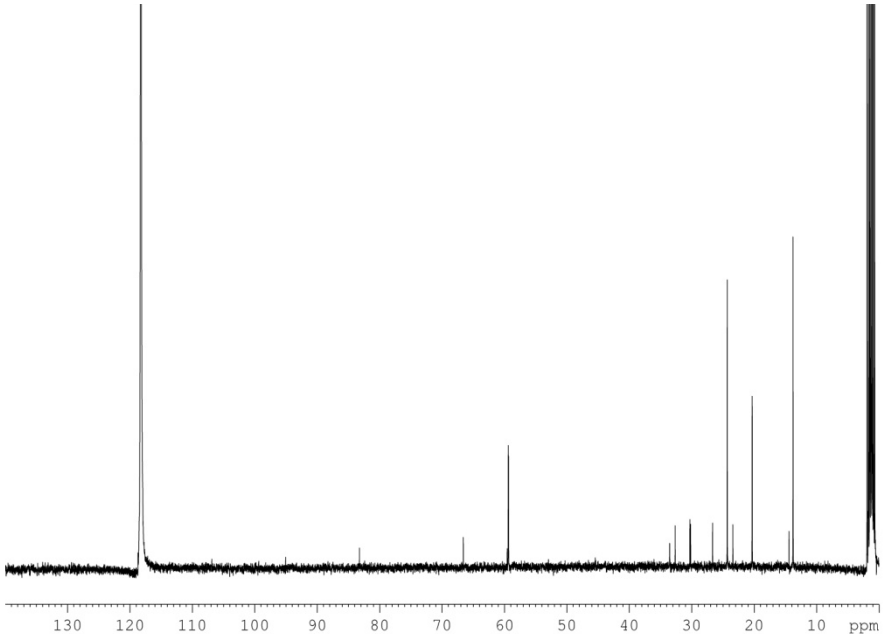

Figure S83: ^{13}C $\{^{1}$H$\}$ NMR spectrum (100.61 MHz) of $[NBu_4]_2[B_{12}Br_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

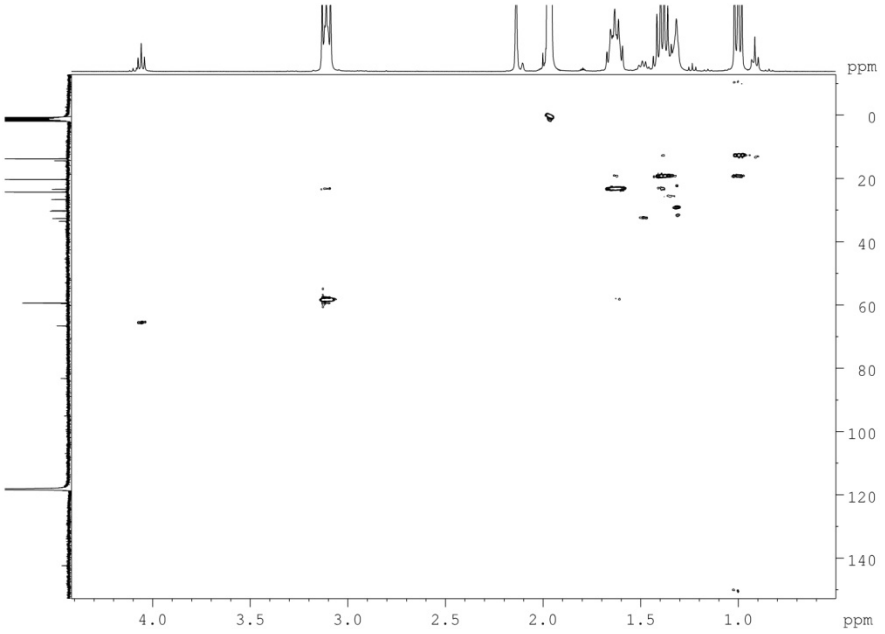

Figure S84: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[NBu_4]_2[B_{12}Br_{11}O$-dodecyl] in CD_3CN at 298 K

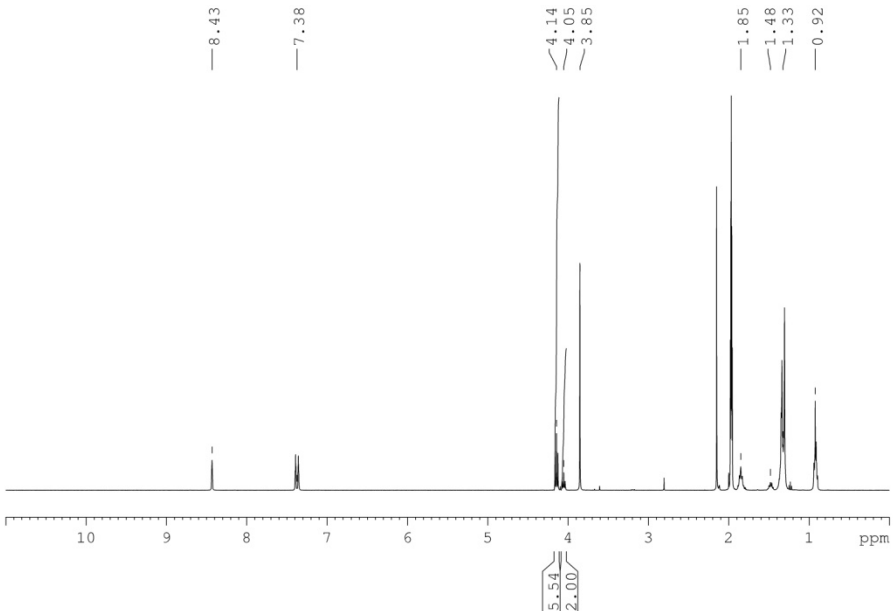

Figure S85: ^{1}H NMR spectrum (400.13 MHz) of $[C_6mim]_2[B_{12}Br_{11}O$-dodecyl] in CD_3CN at 298 K

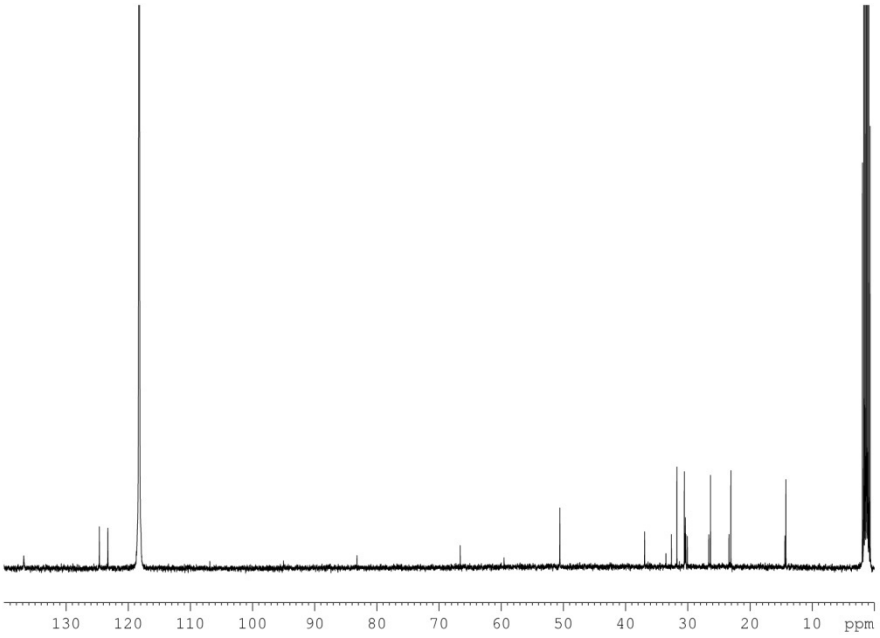

Figure S86: ^{13}C {^{1}H} NMR spectrum (100.61 MHz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

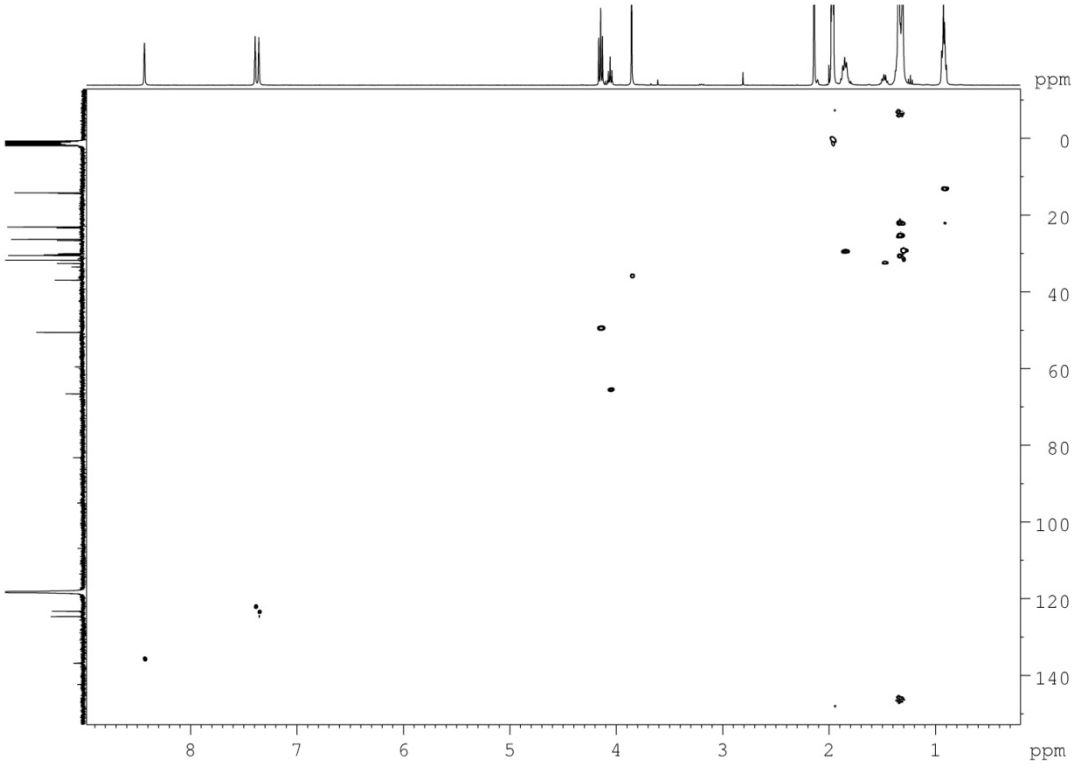

Figure S87: ^{1}H, ^{13}C correlation (400.13 MHz, HSQC, optimized for J_{CH} = 145 Hz) of $[C_6mim]_2[B_{12}Br_{11}O\text{-dodecyl}]$ in CD_3CN at 298 K

Figure S88: Negative ESI MS spectrum of the $[B_{12}Br_{11}O\text{-dodecyl}]^{2-}$ anion

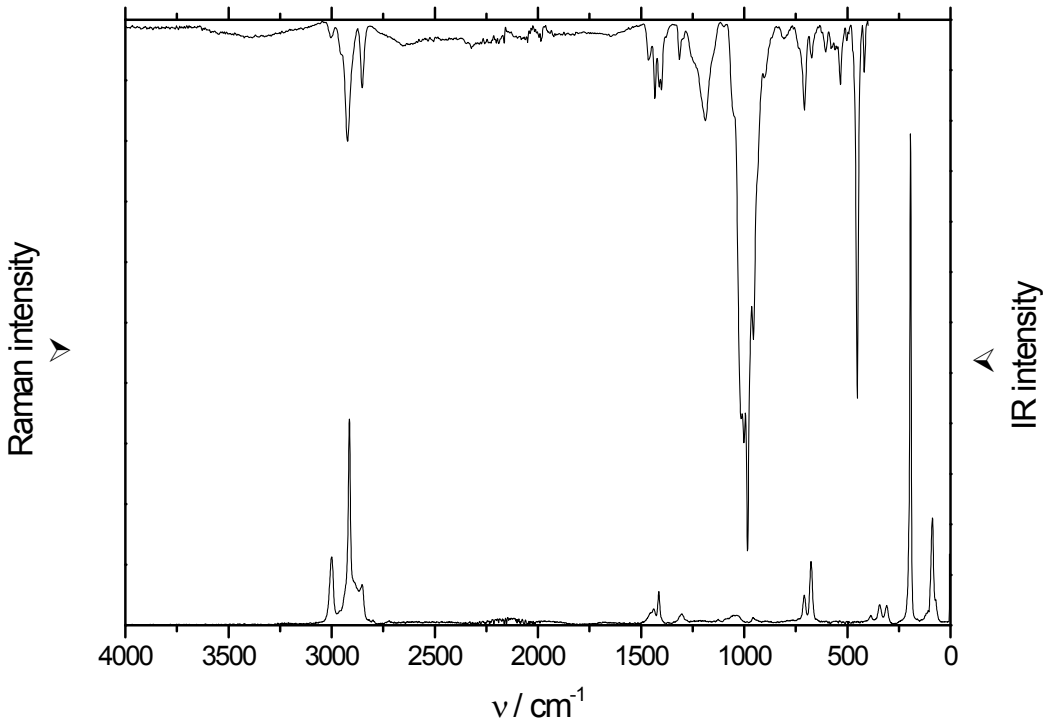

Figure S89: IR (diamond ATR, top) and Raman (1000 scans, 300 mW, bottom) spectra of $Na_2[B_{12}Br_{11}O\text{-dodecyl}]$

S2.10 Thermal analysis

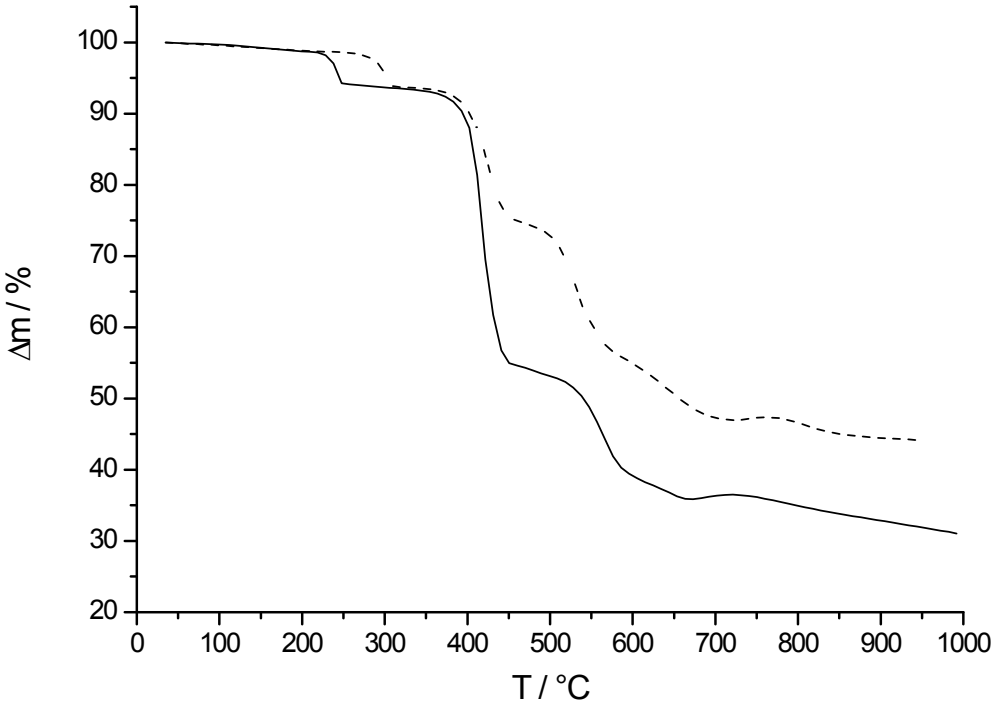

Figure S90: Thermo gravimetrical analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-propyl}]$ (solid graph) and $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$ (dashed graph)

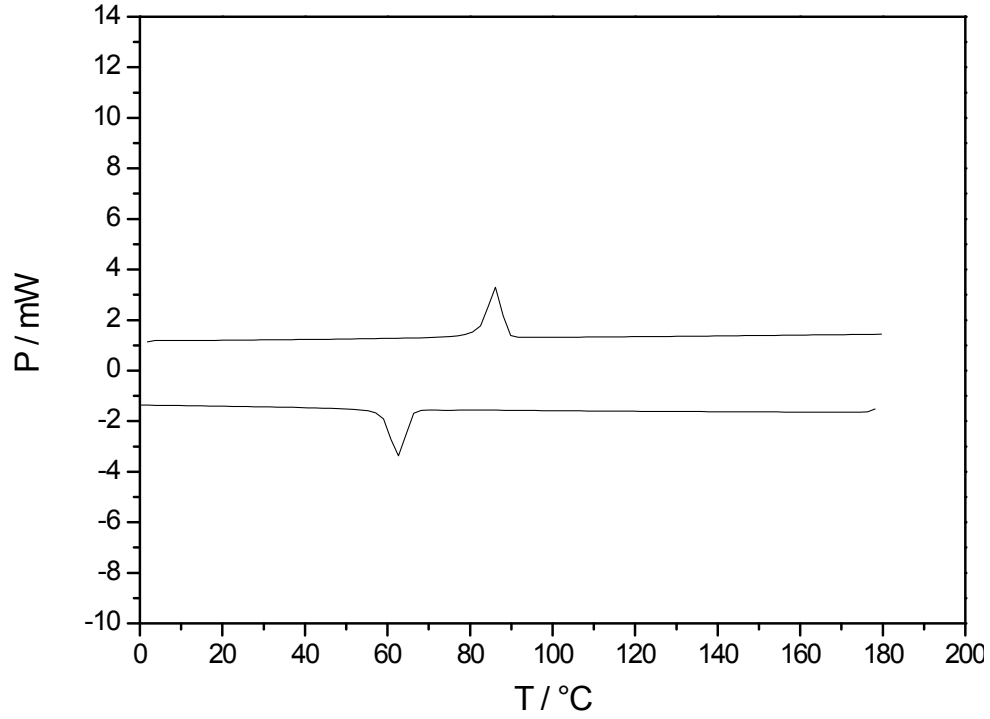

Figure S91: Differential Scanning Calorimetry of $[NBu_4]_2[B_{12}Cl_{11}O\text{-propyl}]$

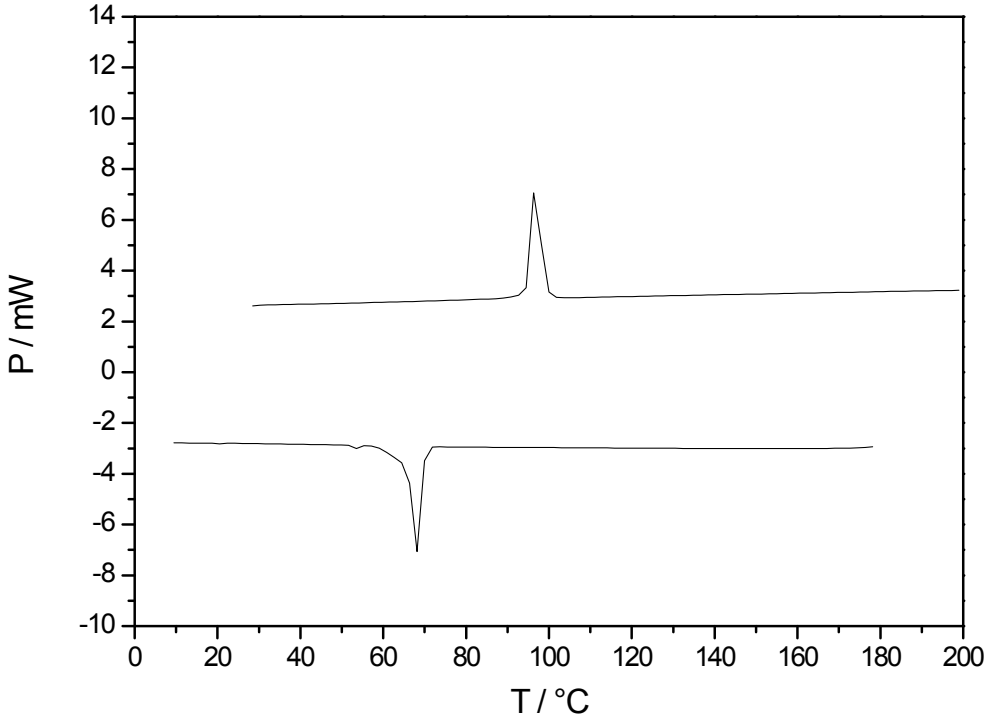

Figure S92: Differential Scanning Calorimetry of $[C_6mim]_2[B_{12}Cl_{11}O\text{-propyl}]$

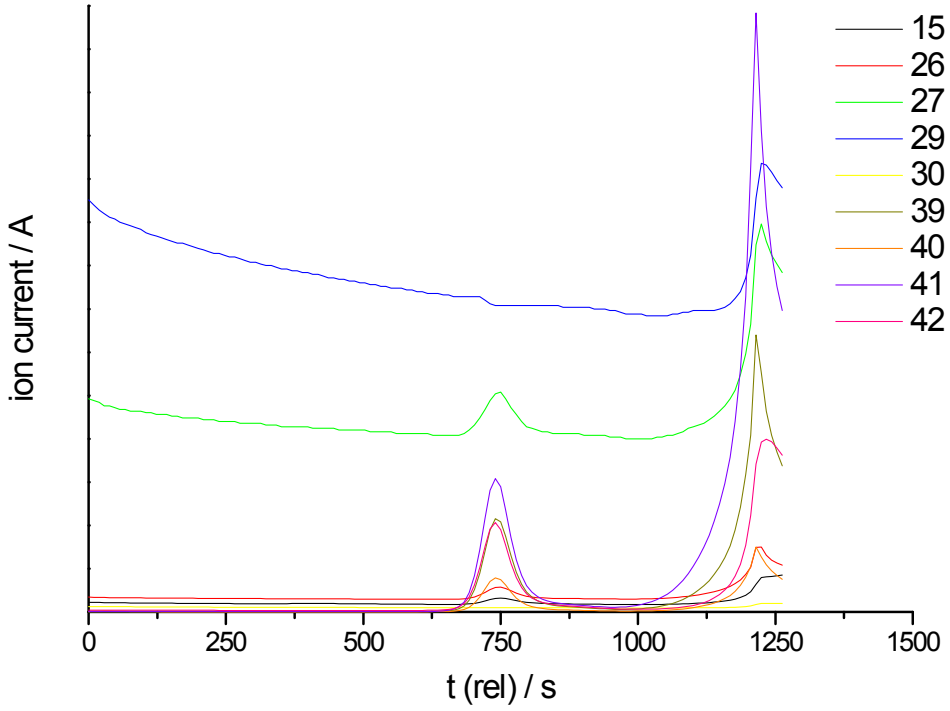

Figure S93: Coupled thermo gravimetric – mass spectrometric analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-propyl}]$ (the first decomposition step belongs to the loss of the alkyl group at 350 °C after 750 s heating with 20 K/min. The second step belongs to both, the decomposition of the cation and the remaining cluster itself)

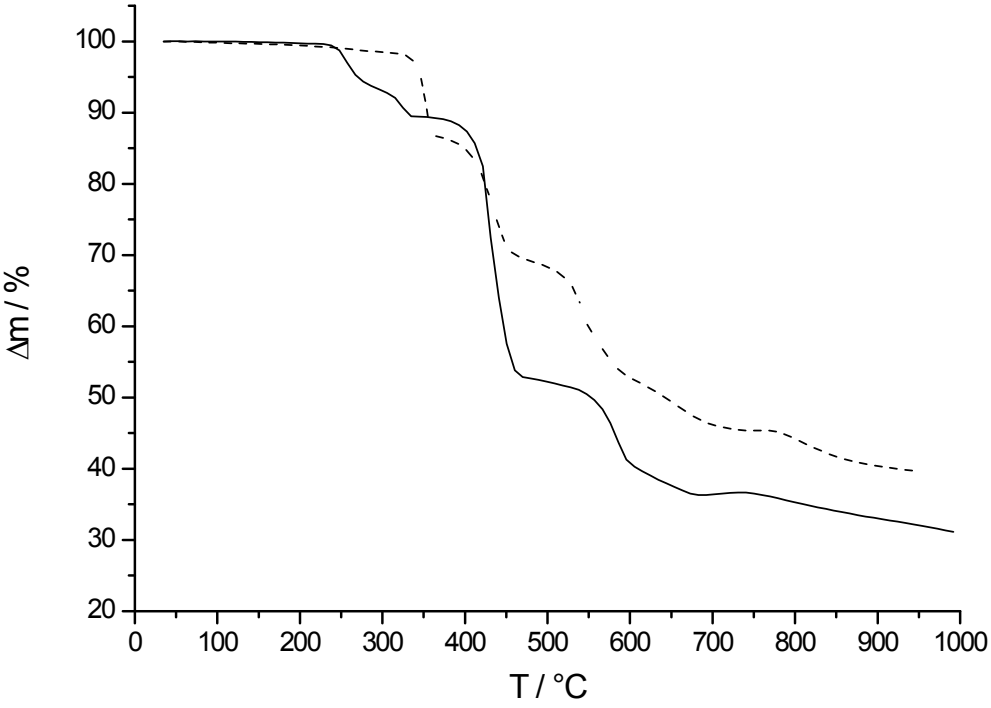

Figure S94: Thermo gravimetrical analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$ (solid graph) and $[C_6mim]_2[B_{12}Cl_{11}O\text{-octyl}]$ (dashed graph)

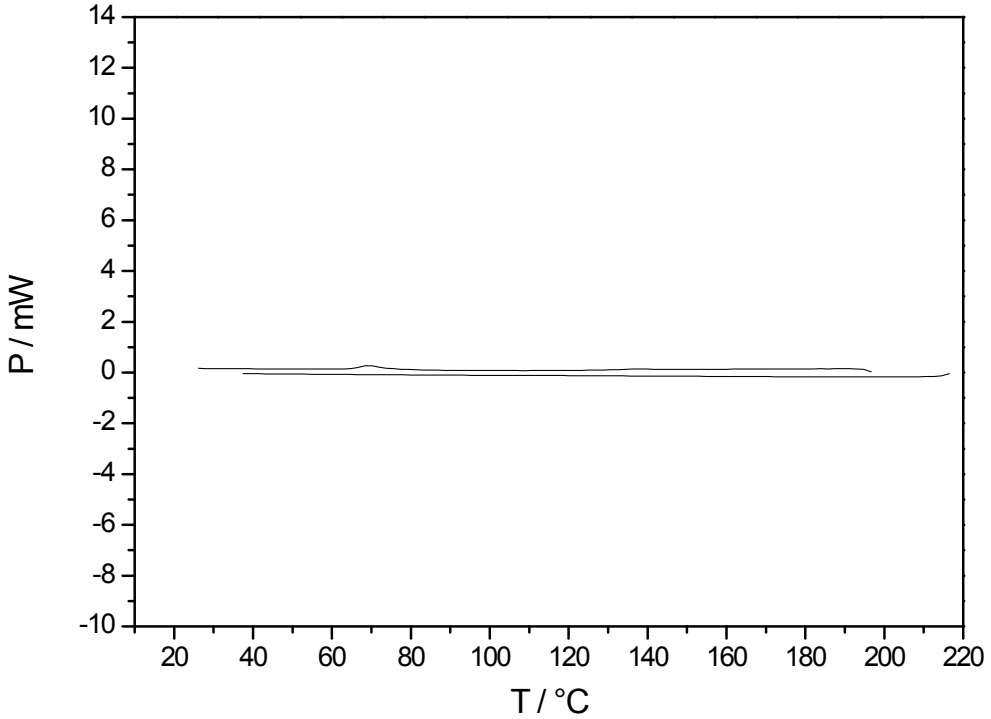

Figure S95: Differential Scanning Calorimetry of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$

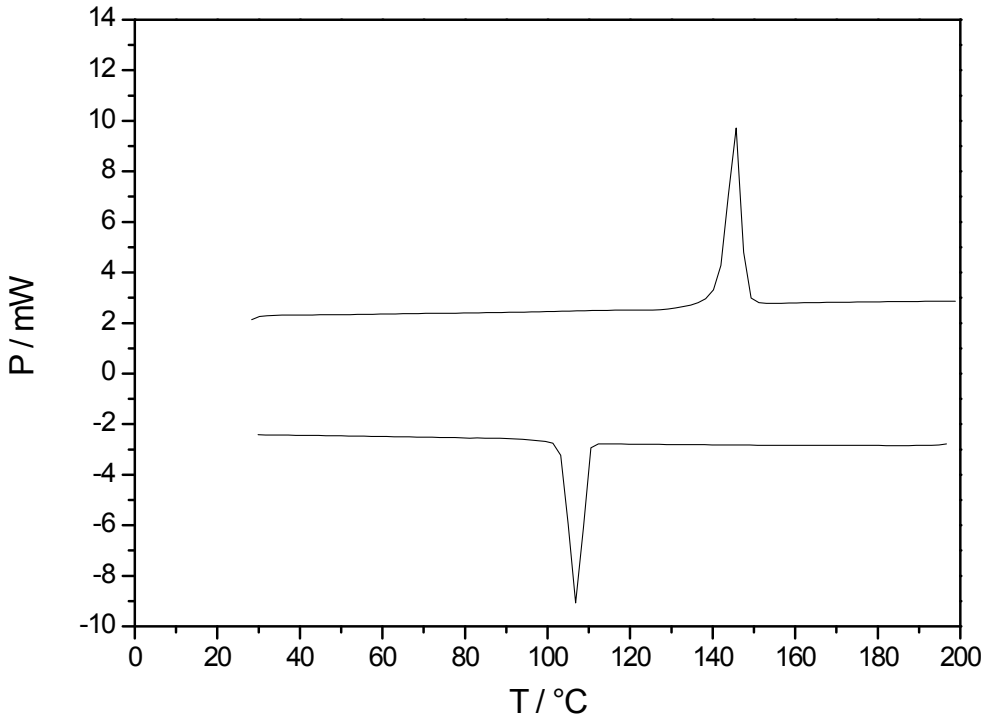

Figure S96: Differential Scanning Calorimetry of $[C_6mim]_2[B_{12}Cl_{11}O\text{-octyl}]$

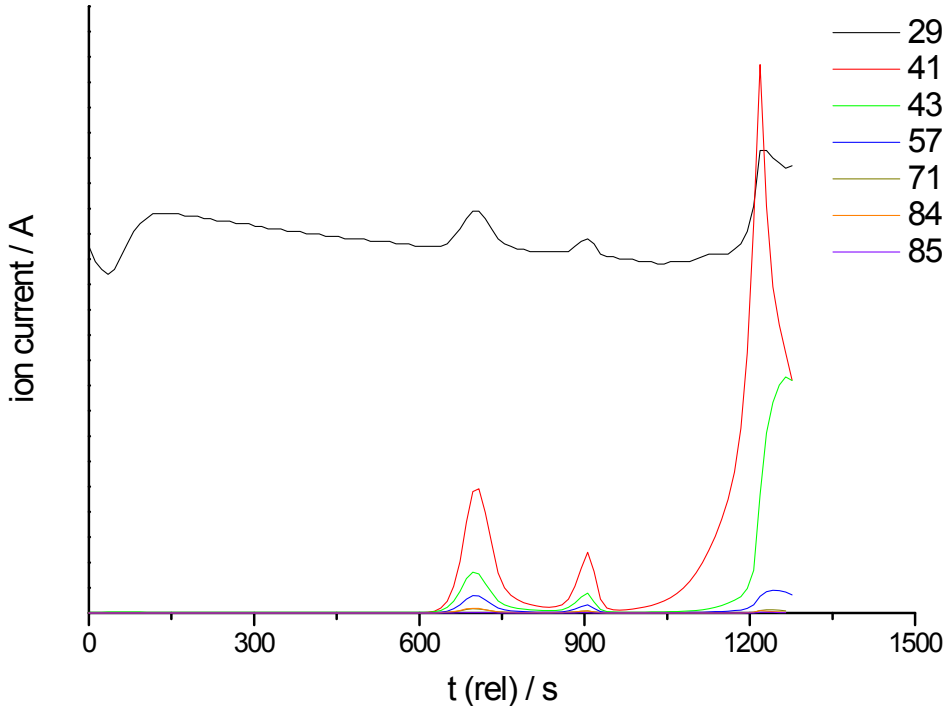

Figure S97: Coupled thermo gravimetric – mass spectrometric analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$ (the first decomposition step belongs to the loss of the alkyl group at 368 °C after 700 s heating with 20 K/min. The second step belongs to both, the decomposition of the cation and the remaining cluster itself)

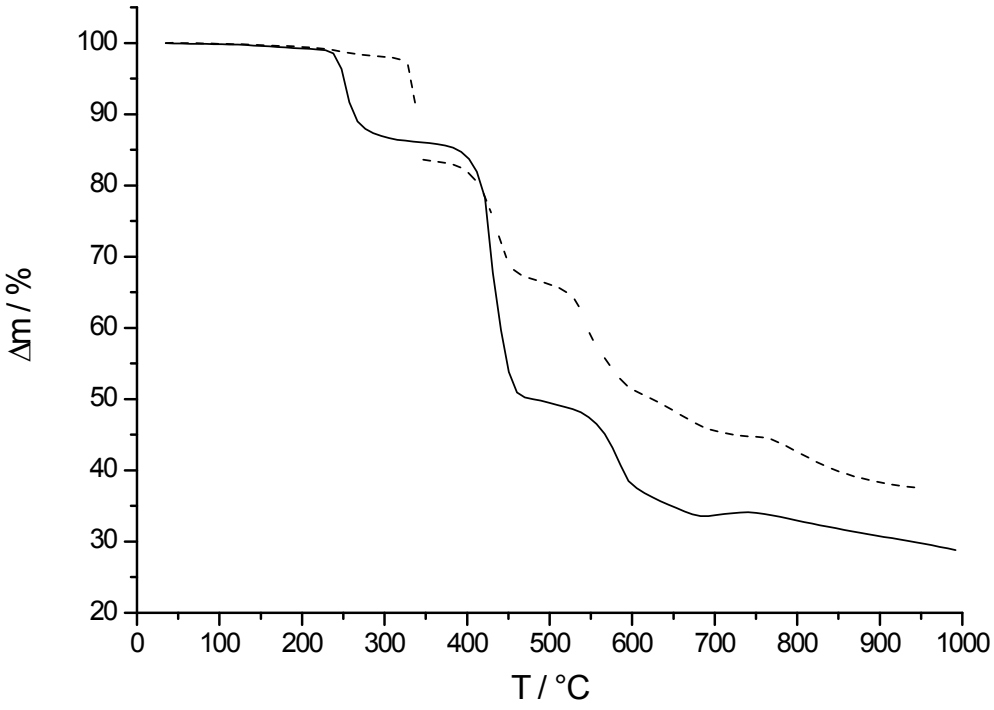

Figure S98: Thermo gravimetrical analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ (solid graph) and $[C_6mim]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ (dashed graph)

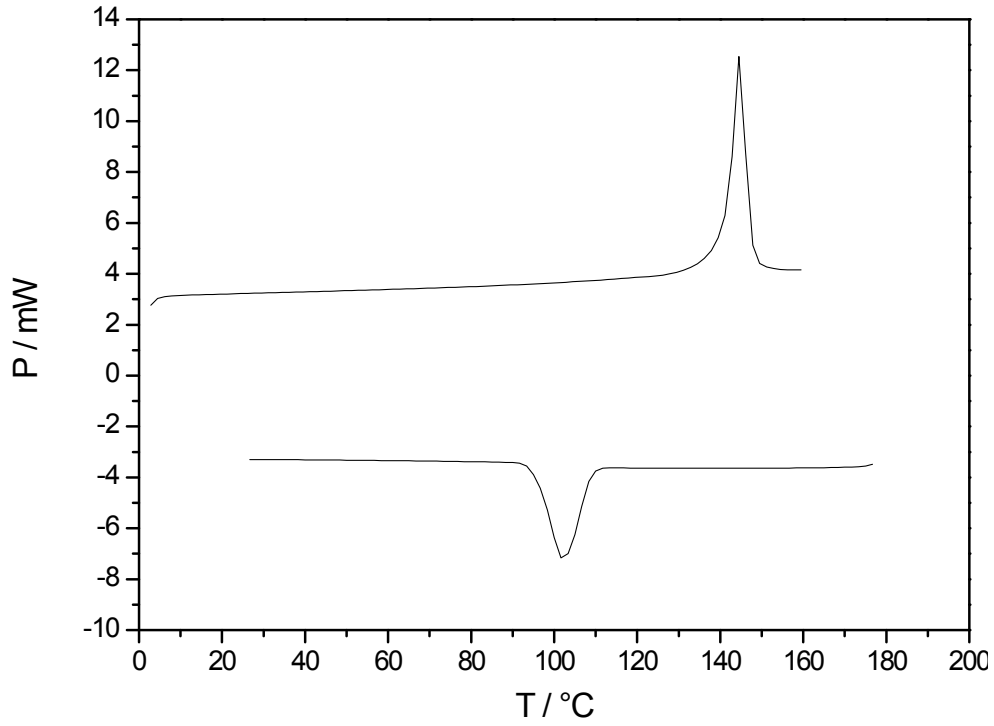

Figure S99: Differential Scanning Calorimetry of $[NBu_4]_2[B_{12}Cl_{11}O\text{-dodecyl}]$

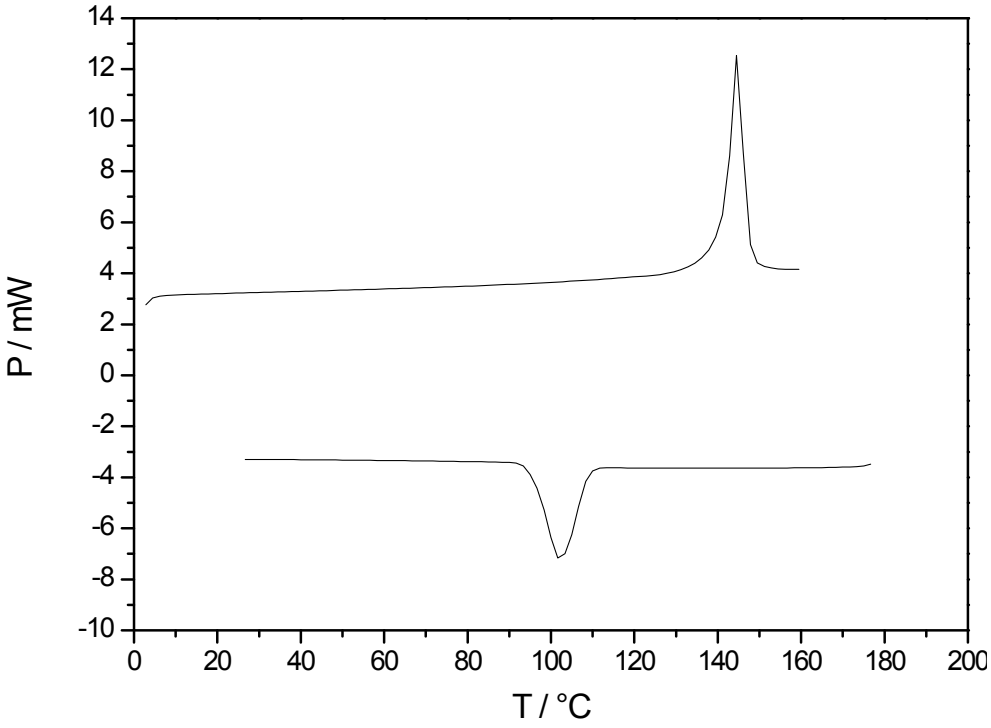

Figure S100: Differential Scanning Calorimetry of $[C_6mim]_2[B_{12}Cl_{11}O\text{-dodecyl}]$

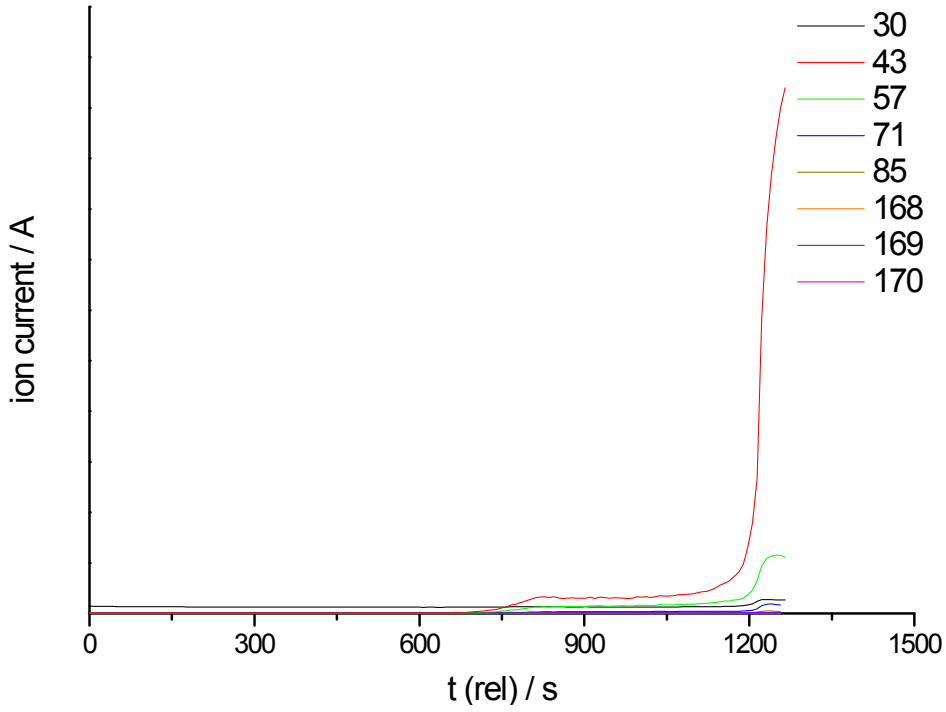

Figure S101: Coupled thermo gravimetric – mass spectrometric analysis of $[NBu_4]_2[B_{12}Cl_{11}O\text{-dodecyl}]$ (the first decomposition step belongs to the loss of the alkyl group at 355 °C after 800 s heating with 20 K/min. The second step belongs to both, the decomposition of the cation and the remaining cluster itself)

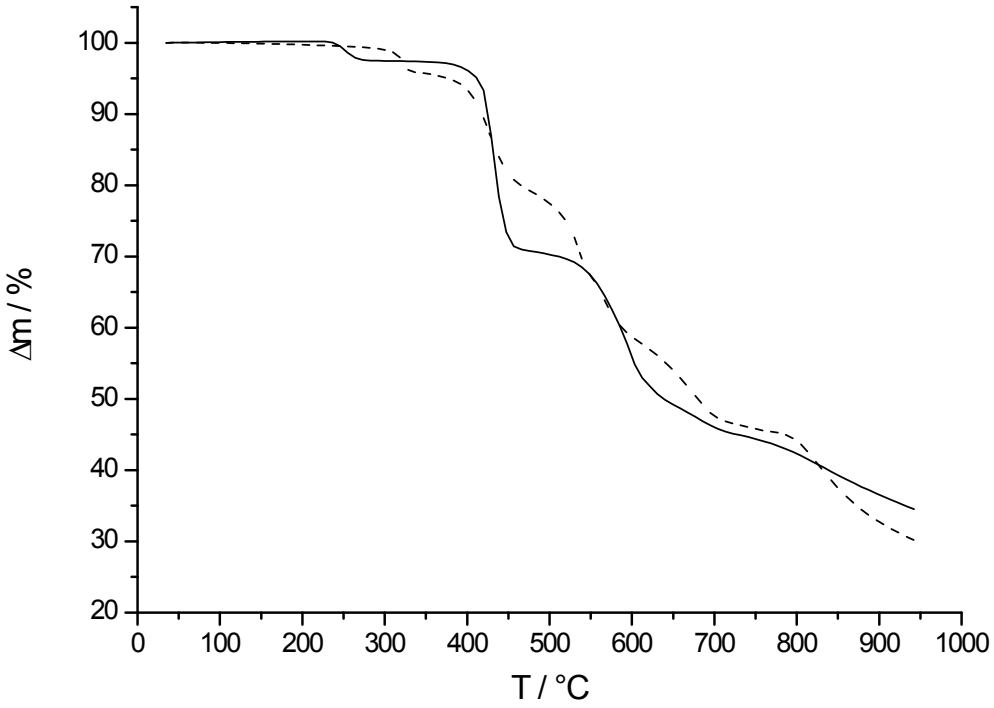

Figure S102: Thermo gravimetrical analysis of $[NBu_4]_2[B_{12}Br_{11}O\text{-propyl}]$ (solid graph) and $[C_6mim]_2[B_{12}Br_{11}O\text{-propyl}]$ (dashed graph)

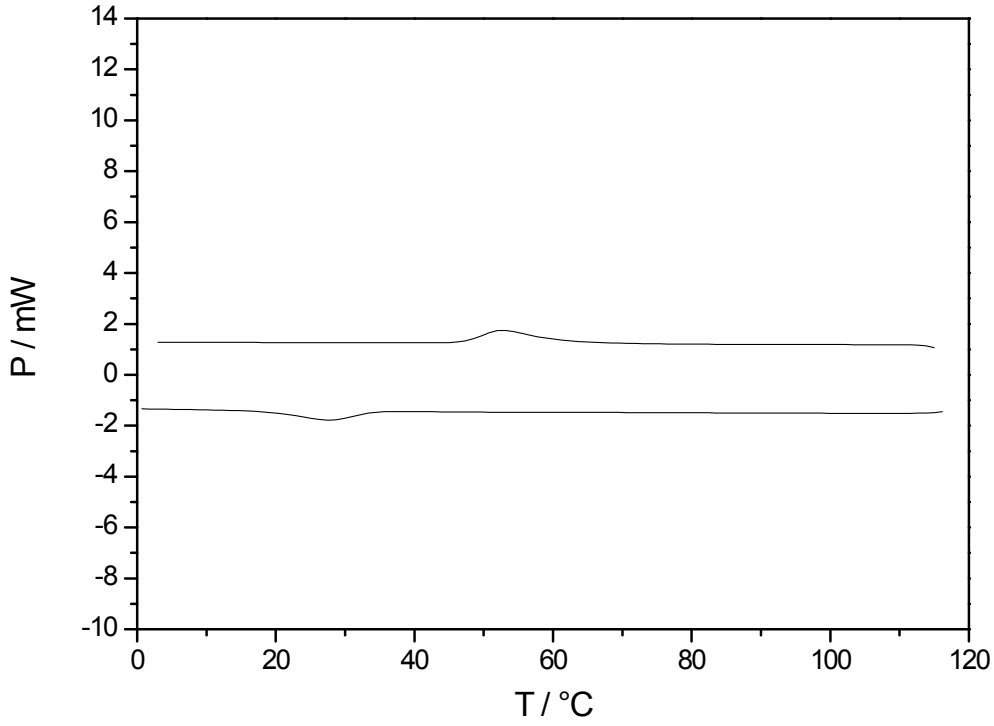

Figure S103: Differential Scanning Calorimetry of $[NBu_4]_2[B_{12}Br_{11}O\text{-propyl}]$

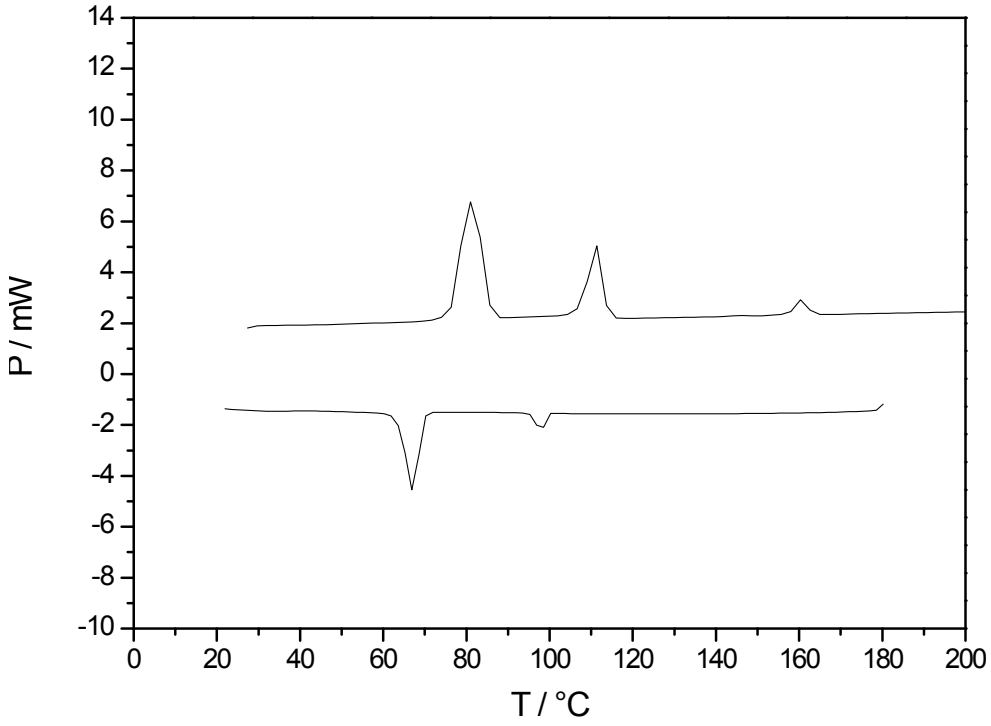

Figure S104: Differential Scanning Calorimetry of $[C_6mim]_2[B_{12}Br_{11}O\text{-propyl}]$. The salt $[C_6mim]_2[B_{12}Br_{11}O\text{-propyl}]^{2-}$ surprisingly shows two phase transitions of much higher intensity than for the melting process. Such a behavior is uncommon but not unknown, as the examples $K[HF_2]$ and $Cs[HF_2]$ have shown (E. F. Westrum Jr, C. P. Landee, Y. Takahashi, M. Chavret, *J. Chem. Thermodyn.* 1978, 10, 835-846).

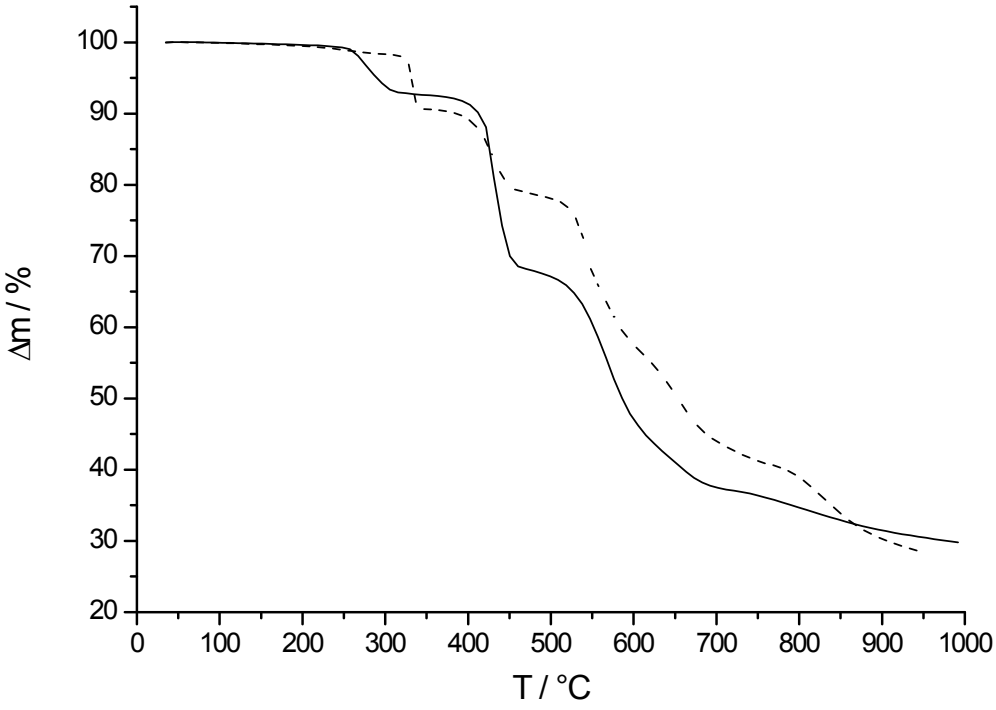

Figure S105: Thermo gravimetrical analysis of $[NBu_4]_2[B_{12}Br_{11}O\text{-octyl}]$ (solid graph) and $[C_6mim]_2[B_{12}Br_{11}O\text{-octyl}]$ (dashed graph)

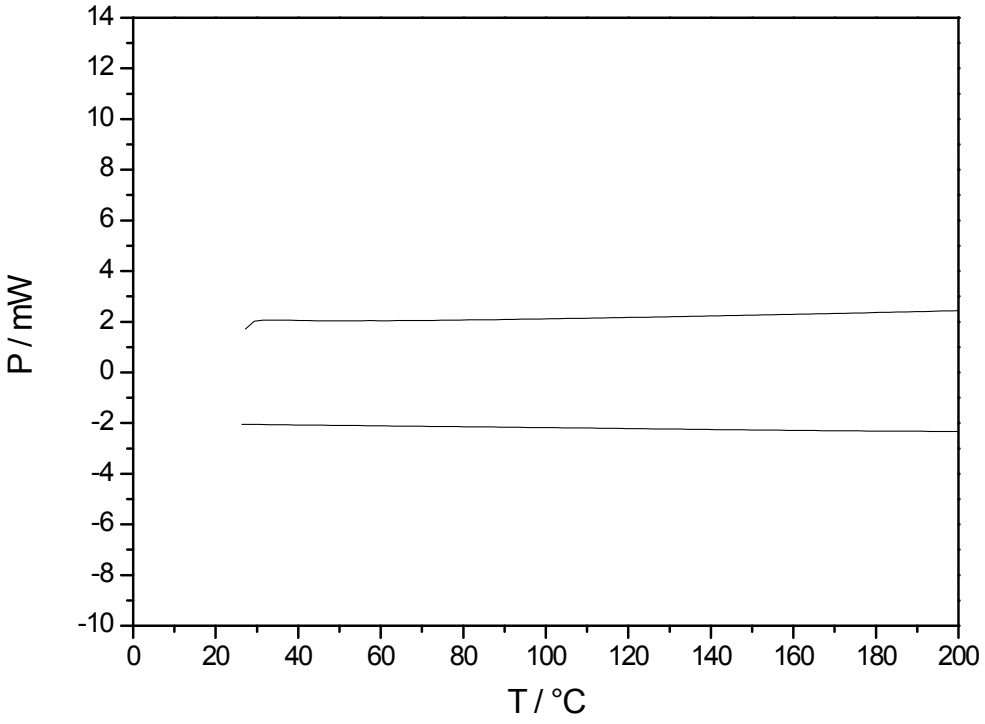

Figure S106: Differential Scanning Calorimetry of $[NBu_4]_2[B_{12}Br_{11}O\text{-octyl}]$

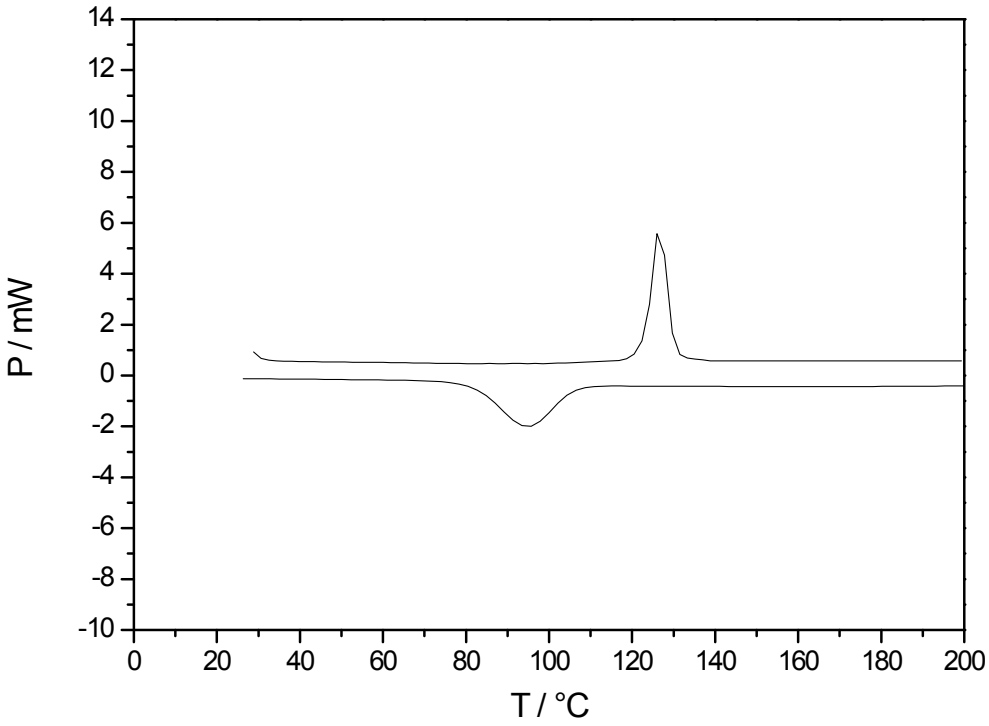

Figure S107: Differential Scanning Calorimetry of $[C_6mim]_2[B_{12}Br_{11}O\text{-octyl}]$

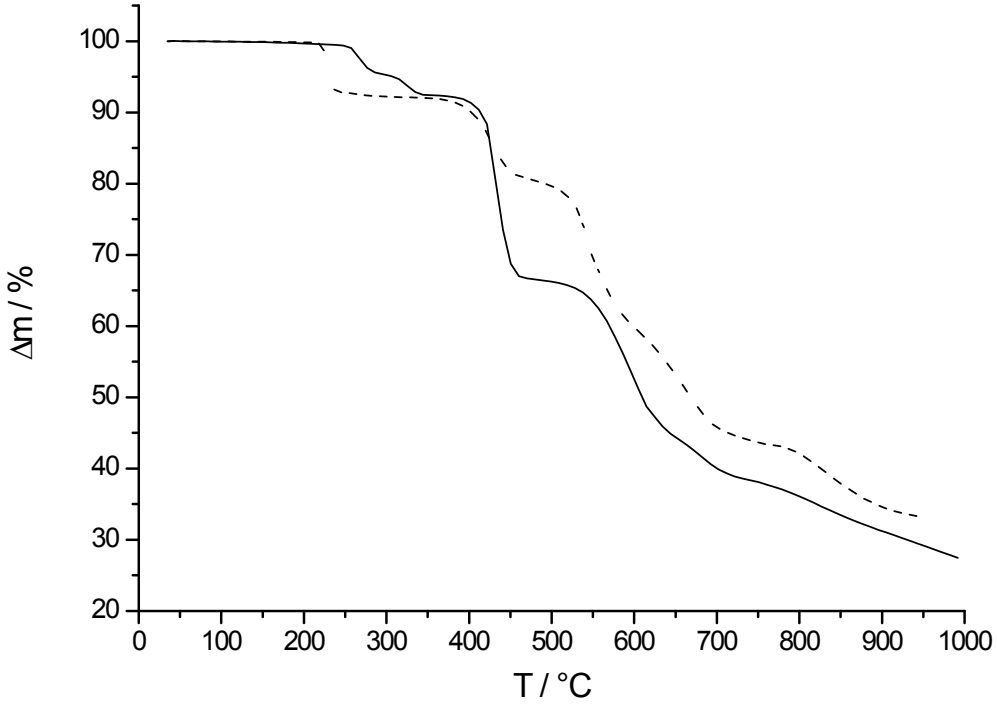

Figure S108: Thermo gravimetrical analysis of $[NBu_4]_2[B_{12}Br_{11}O\text{-dodecyl}]$ (solid graph) and $[C_6mim]_2[B_{12}Br_{11}O\text{-dodecyl}]$ (dashed graph)

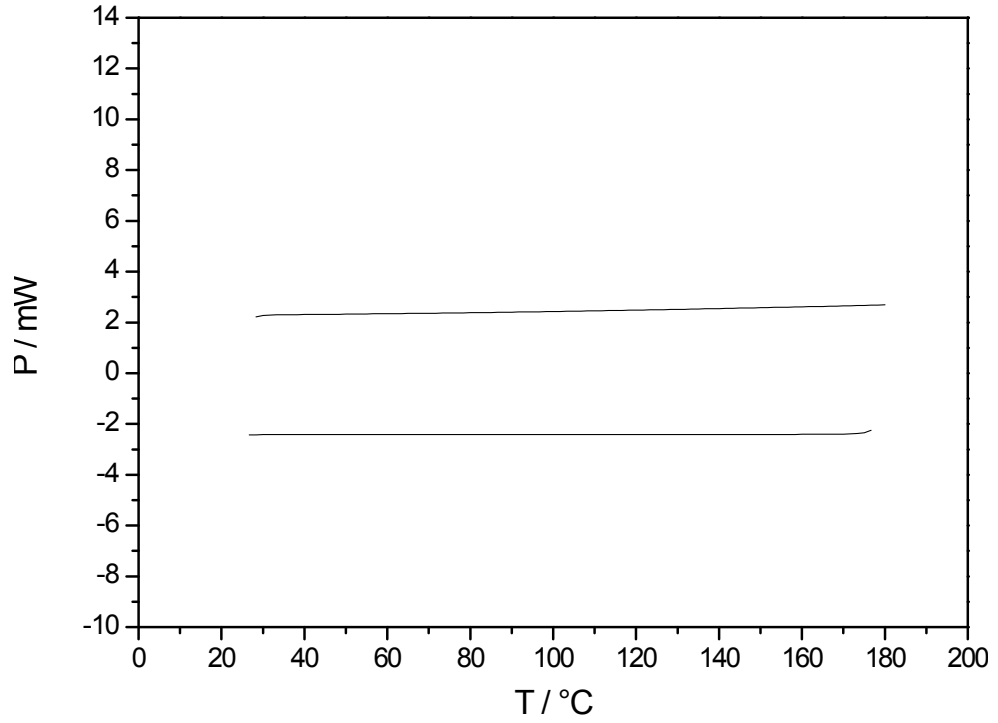

Figure S109: Differential Scanning Calorimetry of $[NBu_4]_2[B_{12}Br_{11}O\text{-dodecyl}]$

S2.11 Cyclic voltammetry

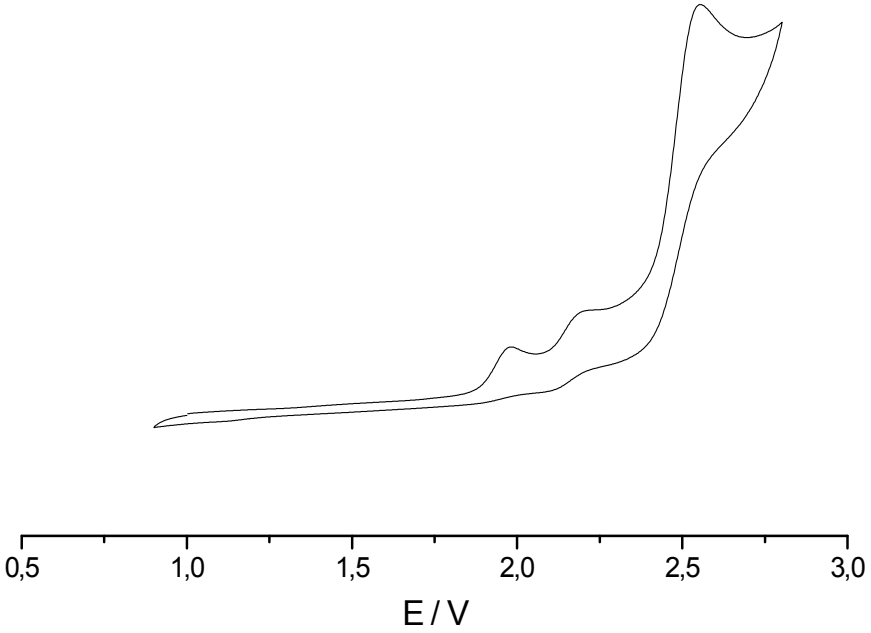

Figure S110: Cyclic voltammogram of $[NBu_4]_2[B_{12}Cl_{11}O\text{-octyl}]$ in CH_3CN at room temperature with 0.1 M $[NBu_4][AsF_6]$ as supporting electrolyte on a Pt-working electrode. This cyclic voltammogram is representative for all $[NBu_4]_2[B_{12}X_{11}OR]$ salts (X = Cl, Br; R = H, propyl, octyl, dodecyl), because all measured compounds showed very similar voltammograms.

S2.12 Crystal structures

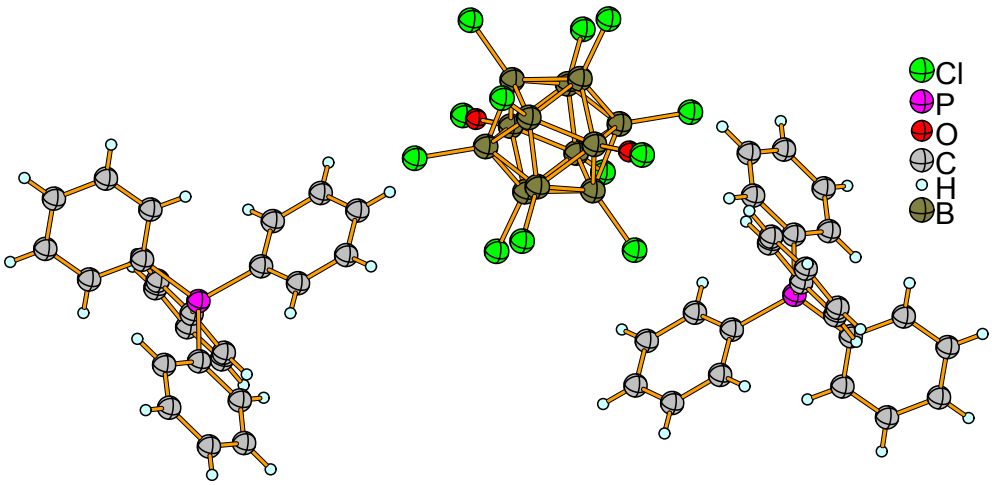

Figure S111: Part of the crystal structure of $[PPh_4]_2[B_{12}Cl_{11}OH]$

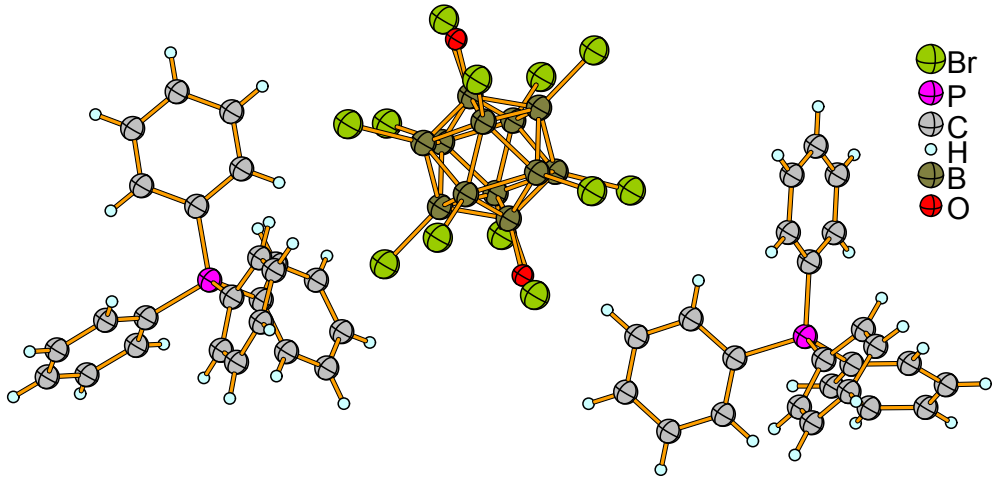

Figure S112: Part of the crystal structure of $[PPh_4]_2[B_{12}Br_{11}OH]$

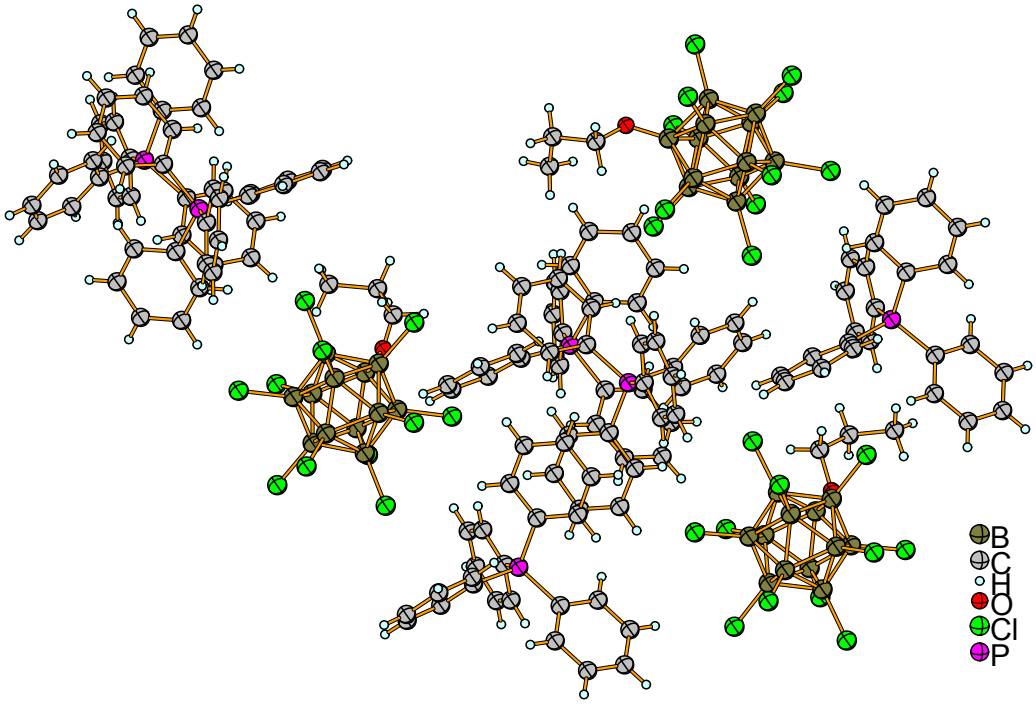

Figure S113: Part of the crystal structure of $[PPh_4]_2[B_{12}Cl_{11}O\text{-propyl}]$

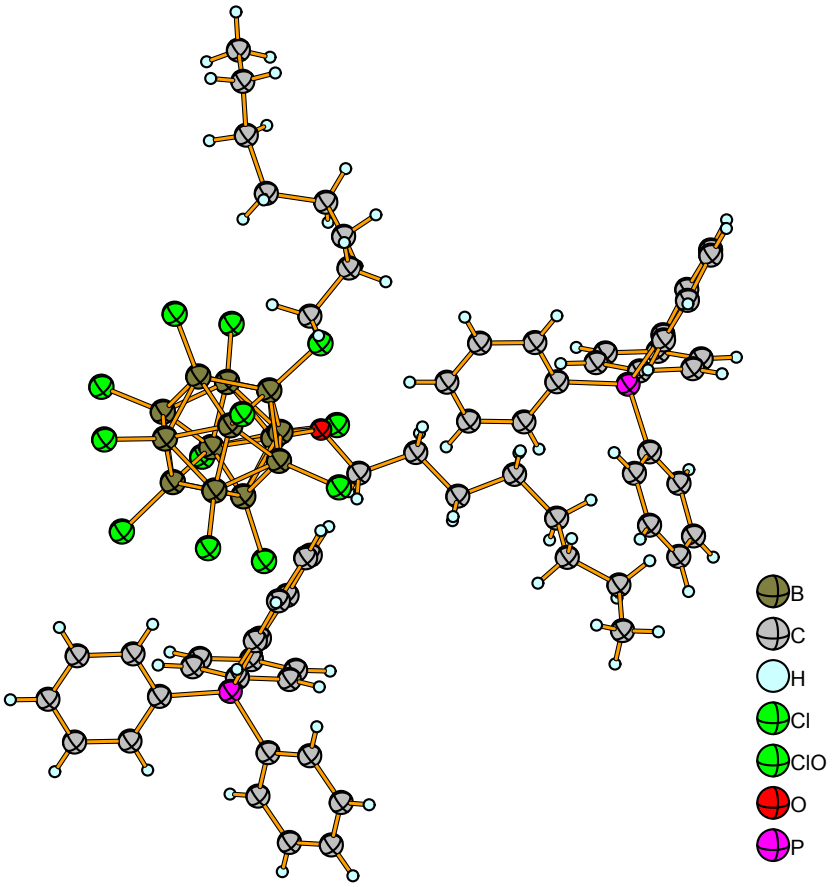

Figure S114: Part of the crystal structure of $[PPh_4]_2[B_{12}Cl_{11}O\text{-octyl}]$. The O-octyl group is disordered over two positions in 70:30 ratios.

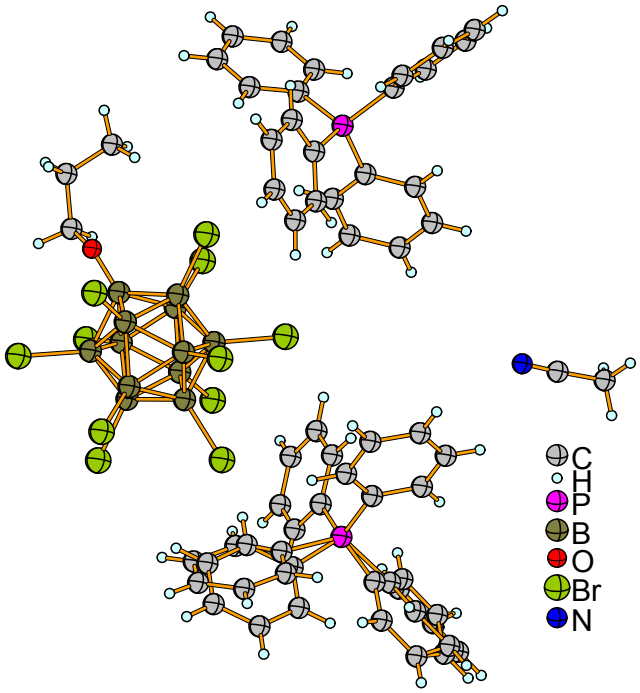

Figure S115: Part of the crystal structure of $[PPh_4]_2[B_{12}Br_{11}O\text{-propyl}]\bullet CH_3CN$

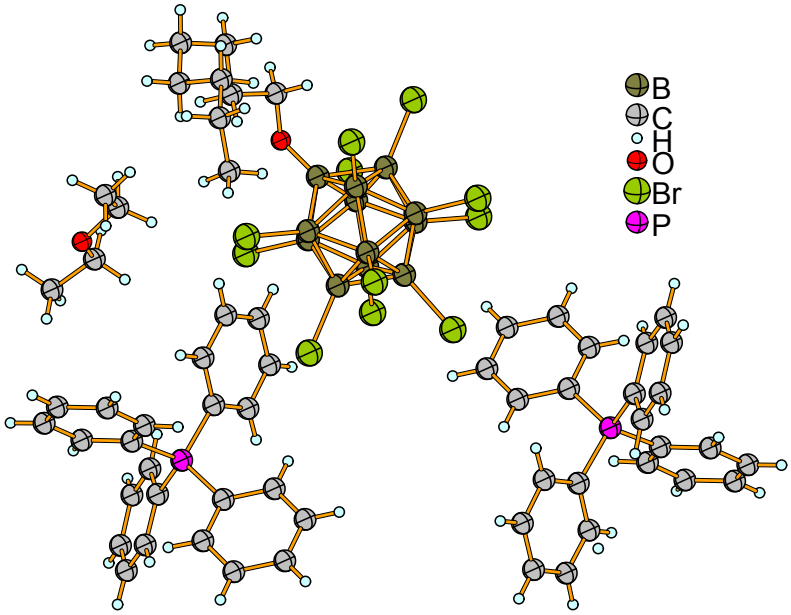

Figure S116: Part of the crystal structure of $[PPh_4]_2[B_{12}Br_{11}O\text{-octyl}]\bullet OEt_2$