Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Ambient Temperature Liquid Salt Electrolytes

Sourav Bhowmick[a], Mukhtiar Ahmed[a], Andrei Filippov[a], Laura C. Loaiza[b],
Faiz Ullah Shah[a], and Patrik Johansson[b,c]

[a]Chemistry of Interfaces, Luleå University of Technology,
SE-971 87 Luleå, Sweden
[b]Materials Physics, Department of Physics, Chalmers University of Technology,
SE-412 96 Gothenburg, Sweden
[c]ALISTORE-European Research Institute, CNRS FR 3104, Hub de l'Energie,
80039 Amiens, France

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Experimental

Chemicals

Phosphorus(V) oxychloride (99 % purity, Sigma Aldrich), triethylene glycol monomethyl ether (95 % purity, Sigma Aldrich), di(ethylene glycol) ethyl ether (99 % purity, Sigma Aldrich), lithium iodide (98% purity, Sigma Aldrich), sodium iodide (99% purity, Acros Organics), potassium iodide (99 % purity, Sigma Aldrich), sodium sulfate (99% purity, Sigma Aldrich), ethyl acetate (99.5 % purity, Sigma Aldrich) and hexane (99 % purity, Sigma Aldrich) were all used without further purification.

General procedure for the synthesis of TMOP and TEOP

Phosphorus(V)oxychloride (20.00 g, 0.13 mol) was added to a round bottom flask followed by slowly addition of the respective alcohol (0.39 mol). This reaction was carried out without any solvent. The reaction mixture was stirred for 8 hours at ambient temperature. After that the reaction mixture was quenched with $NaHCO_3$ (32.87 gm, 0.39 mol) and stirred for one hour at room temperature. The reaction mixture was extracted with ethyl acetate and washed with brine three times. The organic phase containing the product was dried by sodium sulphate and concentrated using a rotary evaporator to obtain the desired product. A clear liquid was obtained.

TMOP: Yield: 52.5 g, 90%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.11-4.09 (m, 6H), 3.63-3.61 (m, 6H), 3.57-3.55 (m, 6H), 3.49-3.47 (m, 6H), 3.45-3.40 (m, 6H), 1.12-1.09 (t, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -1.14. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 72.02, 70.66, 70.60, 70.46, 70.14, 66.85, 59.10. IR (ATR): 2875.16, 1463.22, 1357.74, 1277.41, 1206.77, 1106.12, 1030.64, 986.12, 853.54 cm^{-1}.

TEOP: Yield: 54.8 g, 94%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.70-3.69 (m, 4H), 3.62-3.59 (m, 24H), 3.51-3.49 (m, 8H), 3.32 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -1.03. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.51, 70.04, 69.83, 66.76, 66.70, 15.16. IR (ATR): 2865.48, 1454.52, 1348.06, 1268.71, 1122.58, 1030.65, 986.13, 840.54, 815.80 cm^{-1}.

Synthesis of LiTEEP and LiDEEP

Trialklyl phosphate (9.32 mmol) and lithium iodide (1.25 g, 9.32 mmol) were taken into a Schlenk flask under nitrogen atmosphere. The reaction mixture was heated at 80 °C under inert atmosphere for 72 hours. After completion, the reaction mixture was extracted with ethyl acetate and water. The desired alkali metal salt was received into water phase. The iodide byproduct was removed by washing the reaction mixture with ethyl acetate for at least three times. The water then was evaporated using rotary evaporator to get the lithium salts. The lithium salts were kept in a vacuum oven at 90 °C for more than one week until the water content was <100 ppm, as determined by Karl Fischer titration using a 917 coulometer (Metrohm) placed inside a glovebox with water and oxygen contents <0.5 ppm. The water contents of all the products were measured thrice (Table S1).

LiTEEP: Yield: 3.5 g, 95%. ^{1}H NMR (400 MHz, CDCl3): δ 4.06-4.05 (m, 4H), 3.68-3.65 (m, 16H), 3.58-3.56 (m, 4H), 3.40 (s, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 0.56. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 71.69, 71.08, 71.01, 70.27, 70.24, 70.16, 64.86, 64.81, 59.10. IR (ATR): 2878.06, 1463.23, 1366.45, 1251.29, 1065.48, 968.71, 817.74 cm^{-1}.

LiDEEP: Yield: 3.45 g, 92%. ^{1}H NMR (400 MHz, CDCl3): δ 4.06-4.05 (m, 4H), 3.68-3.67 (m, 8H), 3.60-3.59 (m, 4H), 3.57-3.52 (m, 4H), 1.23-1.20 (m, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 0.19. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 71.04, 70.97, 70.36, 69.66, 66.86, 64.76, 15.17. IR (ATR): 2869.35, 1463.22, 1366.45, 1251.29, 1110.15, 1056.77, 959.03, 817.74 cm^{-1}.

Synthesis of NaTEEP and NaDEEP

Trialklyl phosphate (9.32 mmol) and sodium iodide (1.40 g, 9.32 mmol) were added to Schlenk flask under nitrogen atmosphere and the same procedure was followed as for the lithium salts.

NaTEEP: Yield: 3.4 g, 89%. ^{1}H NMR (400 MHz, CDCl3): δ 4.02-4.01 (m, 4H), 3.67-3.59 (m, 16H), 3.58-3.56 (m, 4H), 3.39 (s, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 1.58. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 71.72, 71.16, 71.09, 70.22, 70.12, 70.09, 64.52, 64.47, 59.07. IR (ATR): 2878.06, 1454.51, 1251.29, 1065.48, 950.32, 791.61 cm^{-1}.

NaDEEP: Yield: 3.65 g, 92%. ^{1}H NMR (400 MHz, CDCl3): δ 4.03-4.02 (m, 4H), 3.68-3.64 (m, 8H), 3.62-3.59 (m, 4H), 3.58-3.54 (m, 4H), 1.24-1.20 (m, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 1.82. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.10, 70.04, 70.32, 69.38, 66.76, 64.75, 64.69, 15.07. IR (ATR): 2869.35, 1454.52, 1357.74, 1242.58, 1110.05, 1065.48, 959.03, 796.45 cm^{-1}.

Synthesis of KTEEP and KDEEP

Trialklyl phosphate (9.32 mmol) and potassium iodide (1.55 g, 9.32 mmol) were taken in schlenk flask under nitrogen atmosphere and the same procedure was followed as for the lithium salts.

KTEEP: Yield: 3.7 g, 93%. ^{1}H NMR (400 MHz, CDCl3): δ 4.04-4.03 (m, 4H), 3.68-3.65 (m, 16H), 3.58-3.57 (m, 4H), 3.41 (s, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 0.30. ^{13}C NMR

($CDCl_3$, 100 MHz): δ 71.71, 71.04, 70.97, 70.16, 70.09, 69.97, 64.56, 64.51, 59.11. IR (ATR): 2878.06, 1454.51, 1348.06, 1251.29, 1065.48, 950.32, 791.61 cm^{-1}.

KDEEP: Yield: 3.6 g, 87%. ^{1}H NMR (400 MHz, CDCl3): δ 4.03-4.02 (m, 4H), 3.67-3.63 (m, 8H), 3.62-3.61 (m, 4H), 3.58-3.53 (m, 4H), 1.24-1.21 (m, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 0.12. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.90, 70.82, 70.29, 69.55, 66.66, 64.68, 64.63, 15.19. IR (ATR): 2878.06, 1463.22, 1348.06, 1251.29, 1110.45, 1048.06, 956.13, 800.32 cm^{-1}.

Structural characterization

A Bruker Ascend Aeon WB 400 (Bruker BioSpin AG, Fällanden, Switzerland) nuclear magnetic resonance (NMR) spectrometer was used to confirm purity of the intermediate compounds and the final products. $CDCl_3$ was used as a solvent in all the experiments for purity confirmation. The ^{7}Li, ^{23}Na and ^{31}P NMR spectra of the neat salts as a function of temperature were recorded by placing the samples in a 5 mm standard NMR tube. The ^{7}Li, ^{23}Na and ^{31}P NMR spectra were referenced to 1.0 M $LiCl_{(aq)}$, 0.1 M NaCl and H_3PO_4, respectively. The working frequencies were 400.21 MHz for ^{1}H, 100.64 MHz for ^{13}C, 155.53 MHz for ^{7}Li, 105.808 MHz for ^{23}Na and 162.01 MHz for ^{31}P. Data were processed using Bruker Topspin 3.5 software. The ESI-MS analysis was performed using a Bruker Impact ESI-Q-TOF system.

Thermal Analysis

A PerkinElmer 8000 TGA instrument was used for the thermogravimetric analysis (TGA). The temperature range was 303−873 K at 10 K min^{-1} under nitrogen as an inert atmosphere. The Pyris software was used to analyse the onset of decomposition temperature, T_{onset}, by taking the intersection of the baseline representing the weight loss and the tangent of the weight vs temperature curve.[1,2]

Differential scanning calorimetry (DSC) was performed using Perkin Elmer DSC 6000 instrument. About 5 mg of the sample was placed in an aluminium pan and data were recorded during both cooling and heating traces from −100 °C to 100 °C, with a scanning rate of 5 °C min^{-1}. The glass transition temperatures, T_g, were determined as the onset of the transition. An inert nitrogen gas was supplied to the instrument with a constant flow rate of 20 mL min^{-1} in order to avoid air and moisture inside the sample chamber.

NMR Diffusometry

Pulsed gradient spin echo-nuclear magnetic resonance (PGSE-NMR) measurements were performed on a Bruker Ascend Aeon WB 400 (Bruker BioSpin AG,) NMR spectrometer using a Bruker PGSE-NMR probe Diff50. Prior to measurements, the sample were equilibrated at a specific temperature for 30 min. The diffusional decays (DD) were recorded using the stimulated echo (StE) pulse train. For single-component diffusion, the form of the DD can be described as:[3]

$$A(\tau,\tau_1,g,\delta) \propto \exp\left(-\frac{2\tau}{T_2}-\frac{\tau_1}{T_1}\right)\exp\left(-\gamma^2\delta^2g^2Dt_d\right)$$

Here, A is the integral intensity of the NMR signal, τ is the time interval between first and second radiofrequency pulses, τ_1 is the time interval between second and third radiofrequency pulses. γ is the gyromagnetic ratio for the magnetic nuclei (^{1}H and ^{7}Li); g and δ are the amplitude and the duration of the gradient pulse; $t_d = (\Delta - \delta / 3)$ is the diffusion time; Δ is the time interval between two identical gradient pulses. D is the diffusion coefficient. In the measurements, the duration of the 90° pulse was 7 µs, δ was in the range of (0.5 – 2) ms, τ was in the range of (3 – 5) ms, and g was varied from 0.06 up to the maximum of the gradient amplitude, 29.73 T m^{-1}. Diffusion time t_d was varied from 4 to 100 ms for the ^{1}H diffusion and in the range 3–6 ms for ^{7}Li diffusion. The repetition time during accumulation of signal transients was 3.5 s.

An Arrhenius equation, which described the temperature dependence of D_s is:

$$D(T) = D_0 \cdot \exp\left(\frac{-E_D}{RT}\right)$$

where D_0 is a parameter that is independent of temperature, E_D is the molar activation energy of diffusion and R is a gas constant. The VFT fittings parameters for diffusivity as a function of temperature are shown in Table S4.

Infrared Spectroscopy

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectra of the intermediate products and the final alkali metals salts were recorded using a Bruker IFS 80v spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and diamond ATR accessory. All the experiments were performed at room-temperature (~22°C) using the double side forward-backward acquisition mode. 256 scans were co-added and signal-averaged at an optical resolution of 4 cm^{-1} for each experiment.

Electrochemical Measurements

The ionic conductivity and linear sweep voltammetry (LSV) were measured using an Autolab PGSTAT302 N electrochemical workstation (FRA32 M module). The TSC 70 closed cell connected to a Microcell HC temperature controller through a Peltier element regulating the temperature from −20 to 100 °C. For ionic conductivity measurements, a two-electrode cell using platinum wire as a working electrode and Pt cup as a counter electrode was used. The impedance spectra were recorded in the frequency range from 0.1 Hz to 1 MHz. The ionic conductivity is analyzed by fitting the data to an empirical Vogel– Fulcher–Tammann equation (VFT):

$$\sigma = \sigma_0 \exp\left(\frac{-B}{(T - T_0)}\right)$$

where σ_0 is a pre-exponential factor, B a factor related to the activation energy and T_0 is the ideal glass transition temperature. Energy of activation for ionic conductivity is related to B as $E_\sigma = B \cdot R$.

The LSV experiments were carried out at 20°C and a scan rate of 1 mV s^{-1}, using a three-electrode system: glassy carbon (GC) and Pt wire as working electrodes (WEs), a Pt cup as a counter electrode (CE), and an Ag wire (coated with AgCl) as a pseudo reference electrode (RE). The electrochemical potentials were recorded with ferrocene as an internal reference and shifted using $E_{\mathrm{Li/Li+}} \approx E_{\mathrm{Fc/Fc+}} + 3.2$ V, $E_{\mathrm{Na/Na+}} \approx E_{\mathrm{Fc/Fc+}} + 3.06$ V and $E_{\mathrm{K/K+}} \approx E_{\mathrm{Fc/Fc+}} + 3.35$ V.[4] The anodic stability limits were determined using a 0.1 mA cm^{-2} as cut-off current density.[5]

LiTEEP was selected for battery preliminary tests. Coin cells were assembled using commercially available LTO (Li_2TiO_3) (Custom cells, 2 mAh/cm^3 areal capacity, coated on Al foil, 90% of active material) and Li foil as CE and RE, respectively. A spacer was placed in between the two electrodes in order to avoid contact and short circuit. The cells were cycled at 60°C using a Biologic VMP3 potentiostat coupled with an intermediate temperature system (ITS) controlling the coin cell temperature by a Peltier element. A charge/discharge current of 0.025 mA was applied between 0.5 – 3.0 V *vs.* Li^+/Li^o.

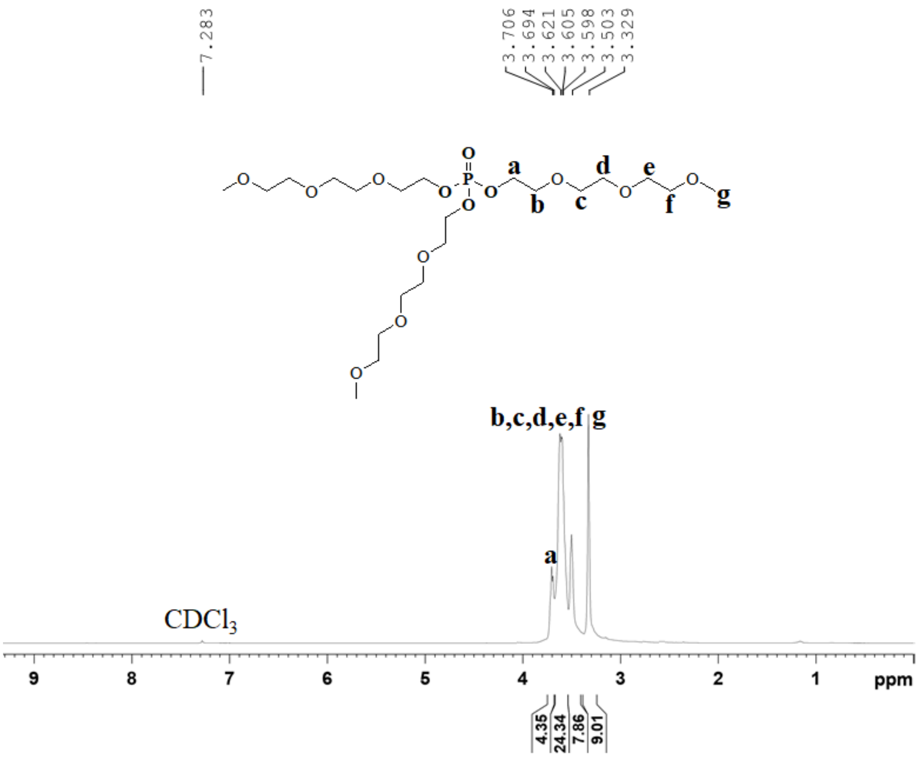

Figure S1. ^{1}H NMR spectrum of TMOP in $CDCl_3$.

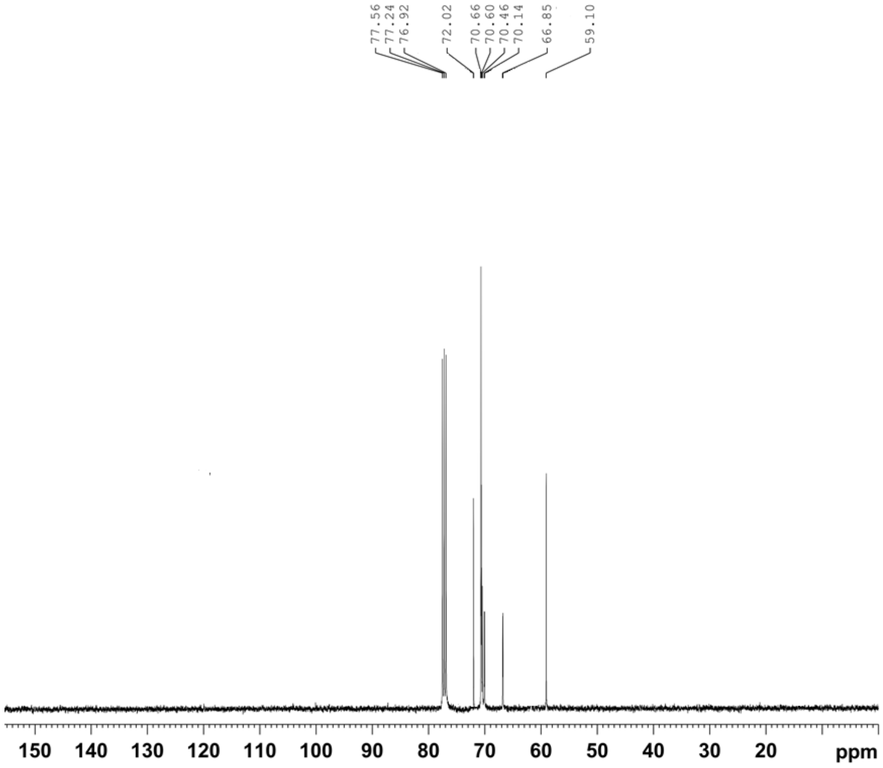

Figure S2. ^{13}C NMR spectrum of TMOP in $CDCl_3$.

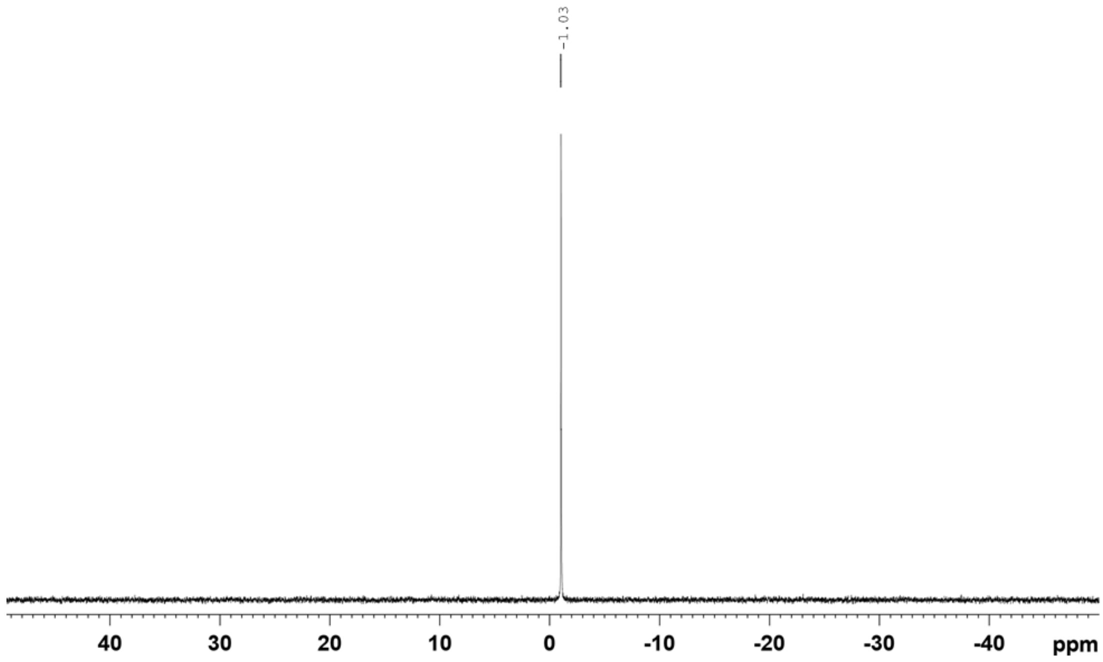

Figure S3. ^{31}P NMR spectrum of TMOP in $CDCl_3$.

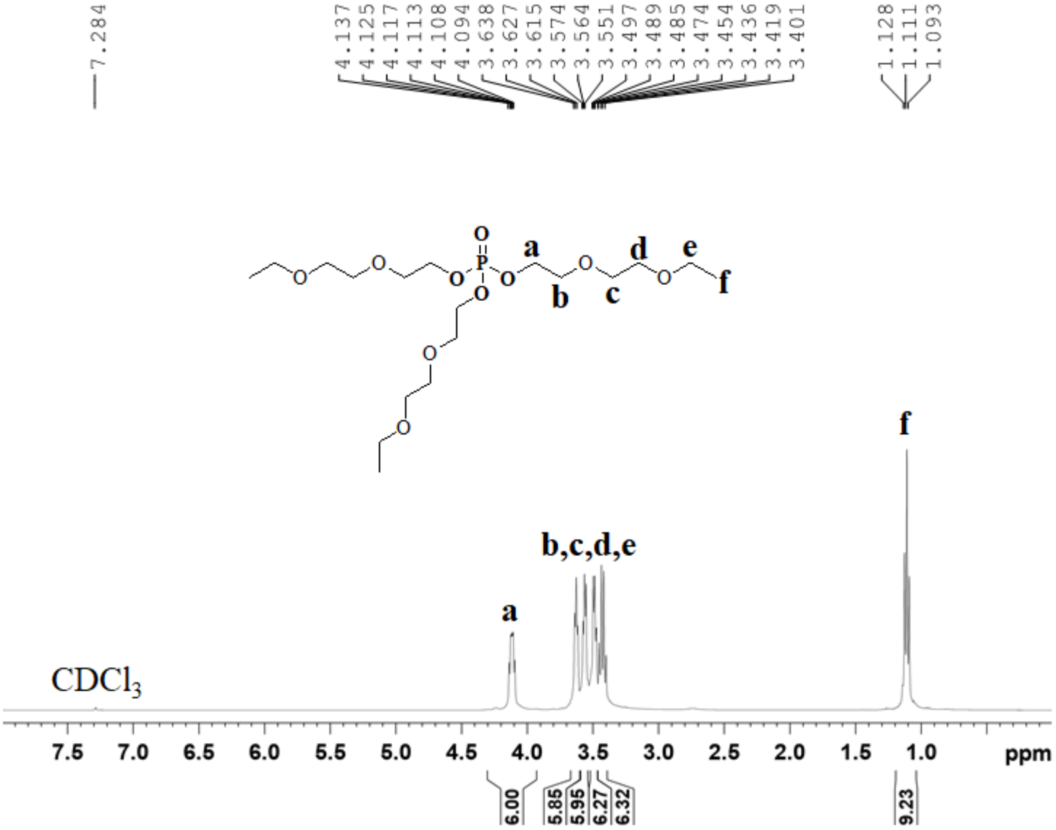

Figure S4. ^{1}H NMR spectrum of TEOP in $CDCl_3$.

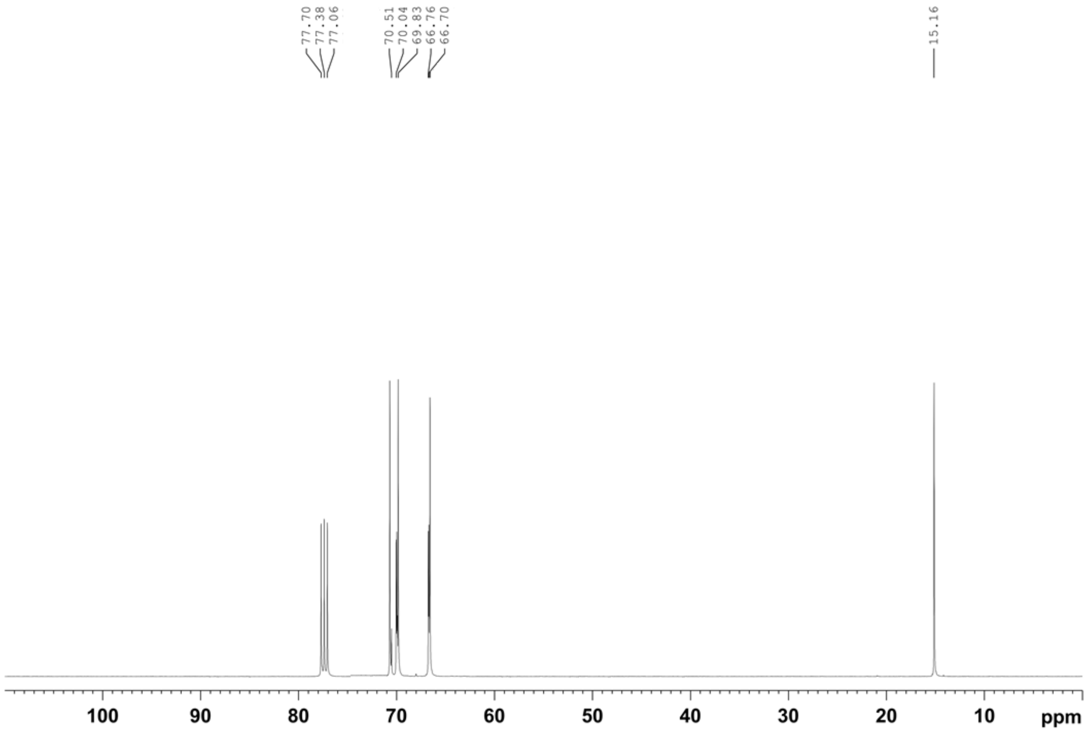

Figure S5. ^{13}C NMR spectrum of TEOP in $CDCl_3$.

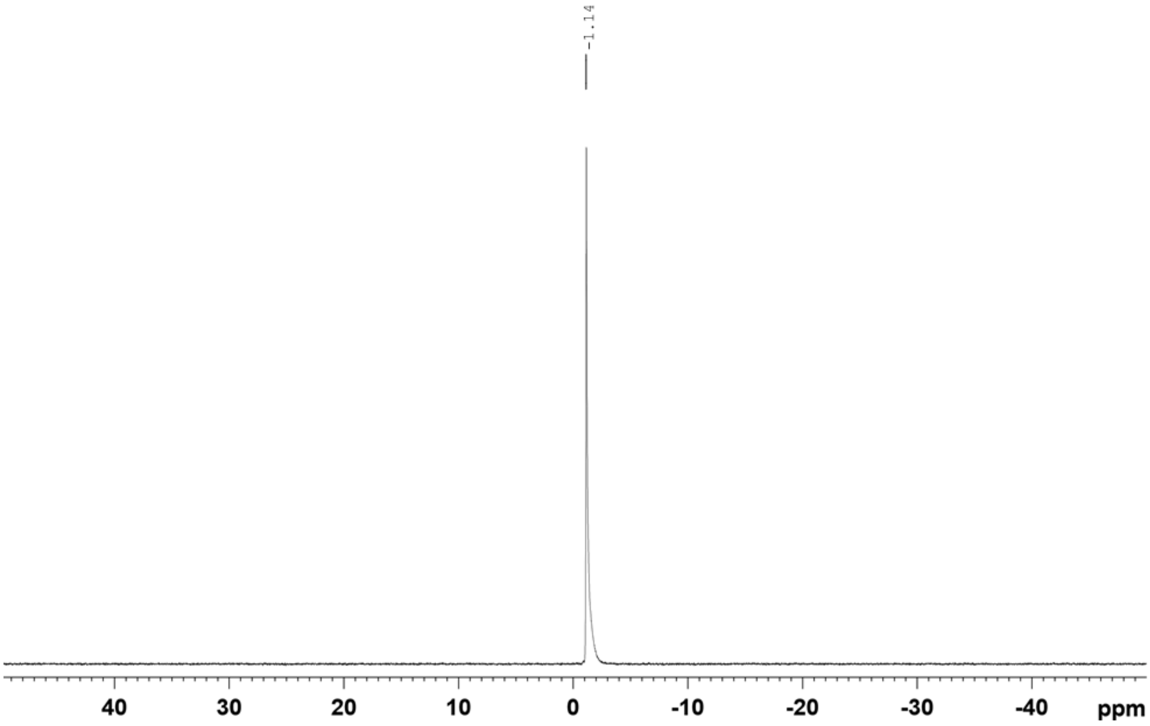

Figure S6. ^{31}P NMR spectrum of TEOP in $CDCl_3$.

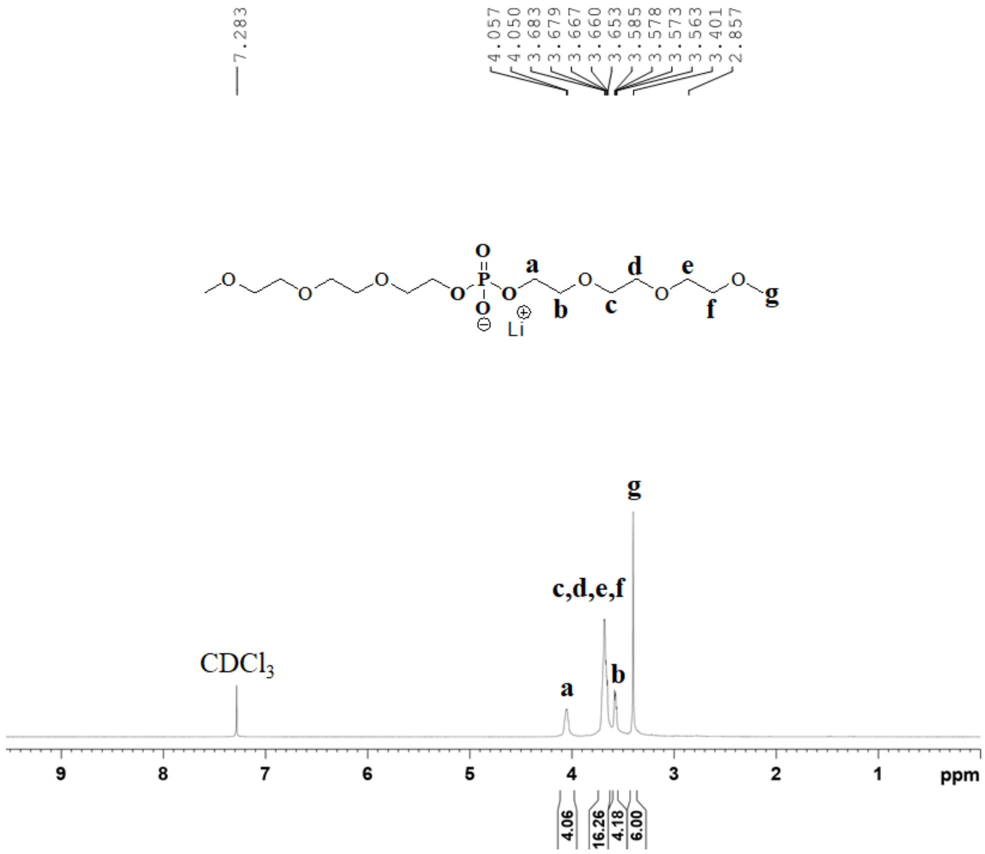

Figure S7. ^{1}H NMR spectrum of LiTEEP in $CDCl_3$.

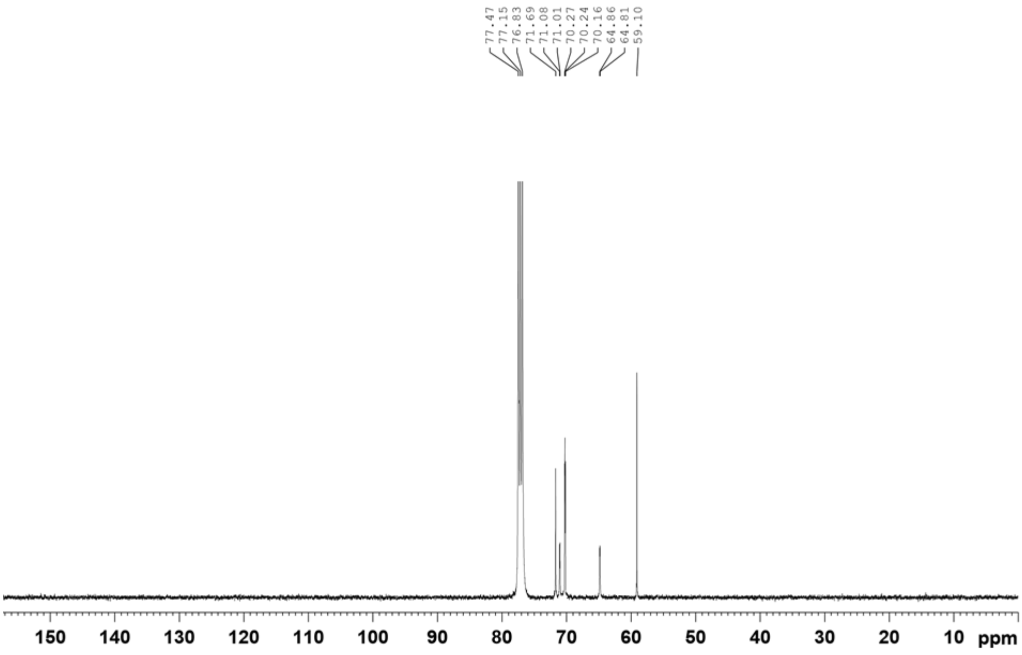

Figure S8. ^{13}C NMR spectrum of LiTEEP in $CDCl_3$.

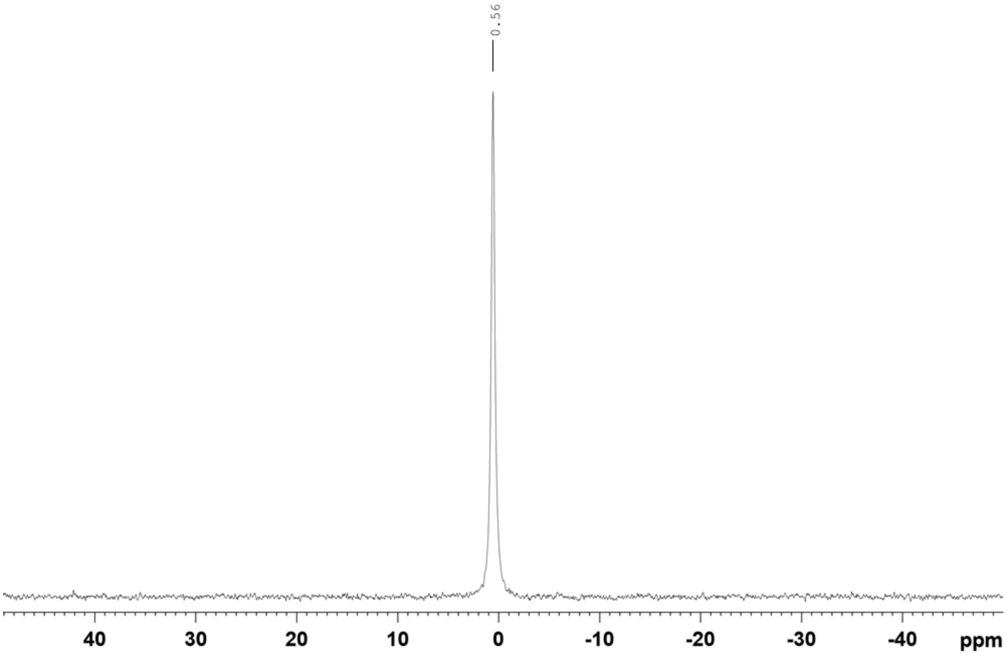

Figure S9. ^{31}P NMR spectrum of LiTEEP in $CDCl_3$.

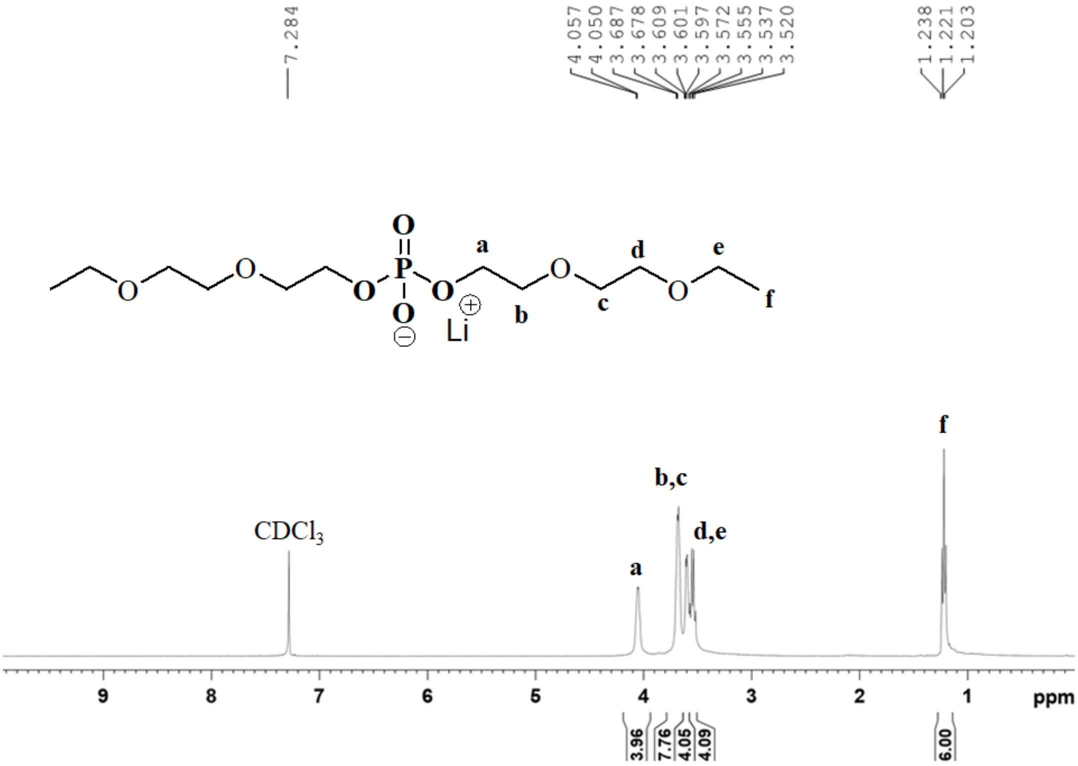

Figure S10. ^{1}H NMR spectrum of LiDEEP in $CDCl_3$.

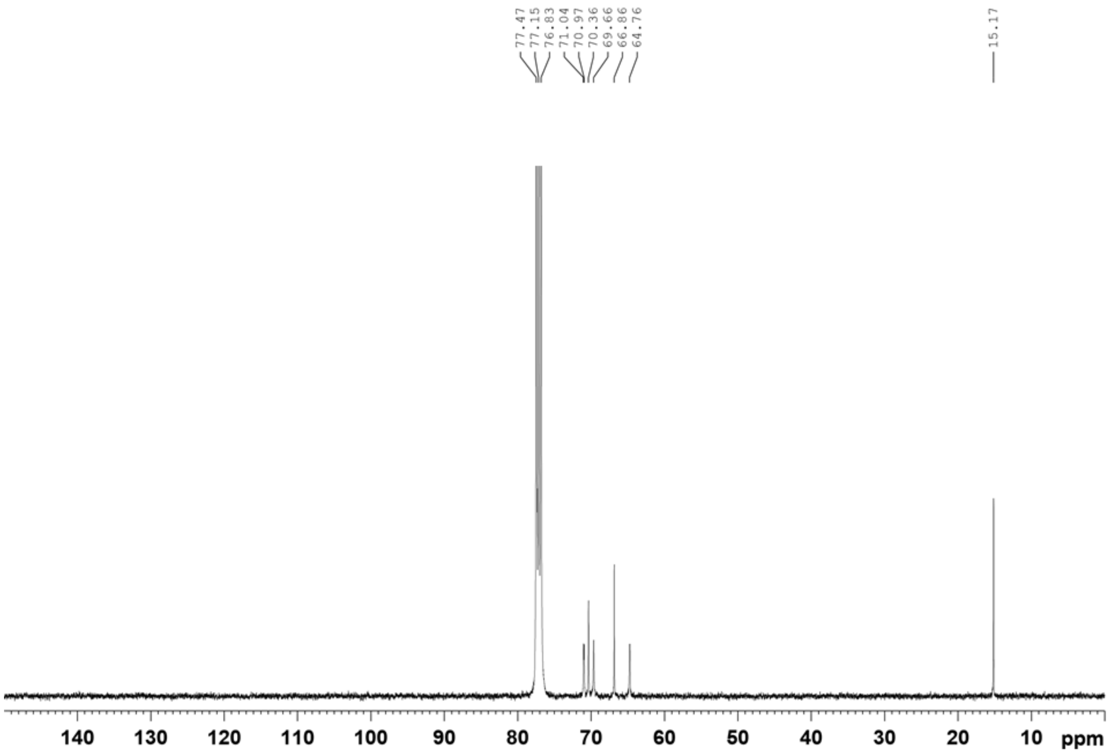

Figure S11. ^{13}C NMR spectrum of LiDEEP in $CDCl_3$.

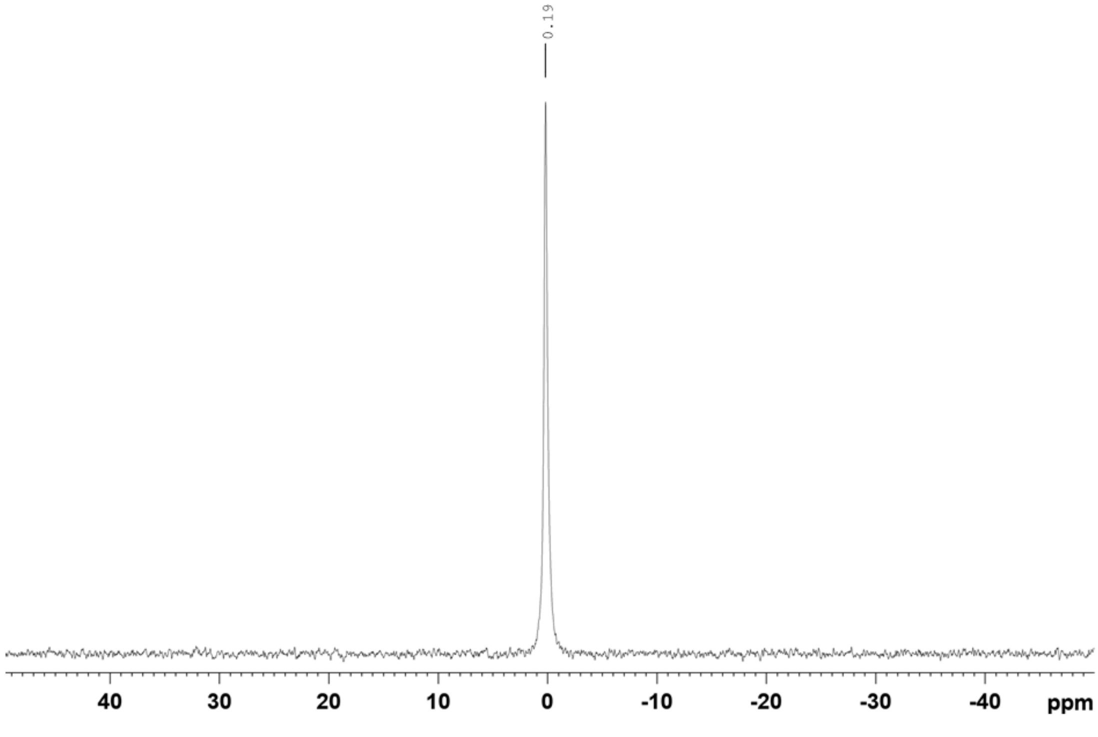

Figure S12. ^{31}P NMR spectrum of LiDEEP in $CDCl_3$.

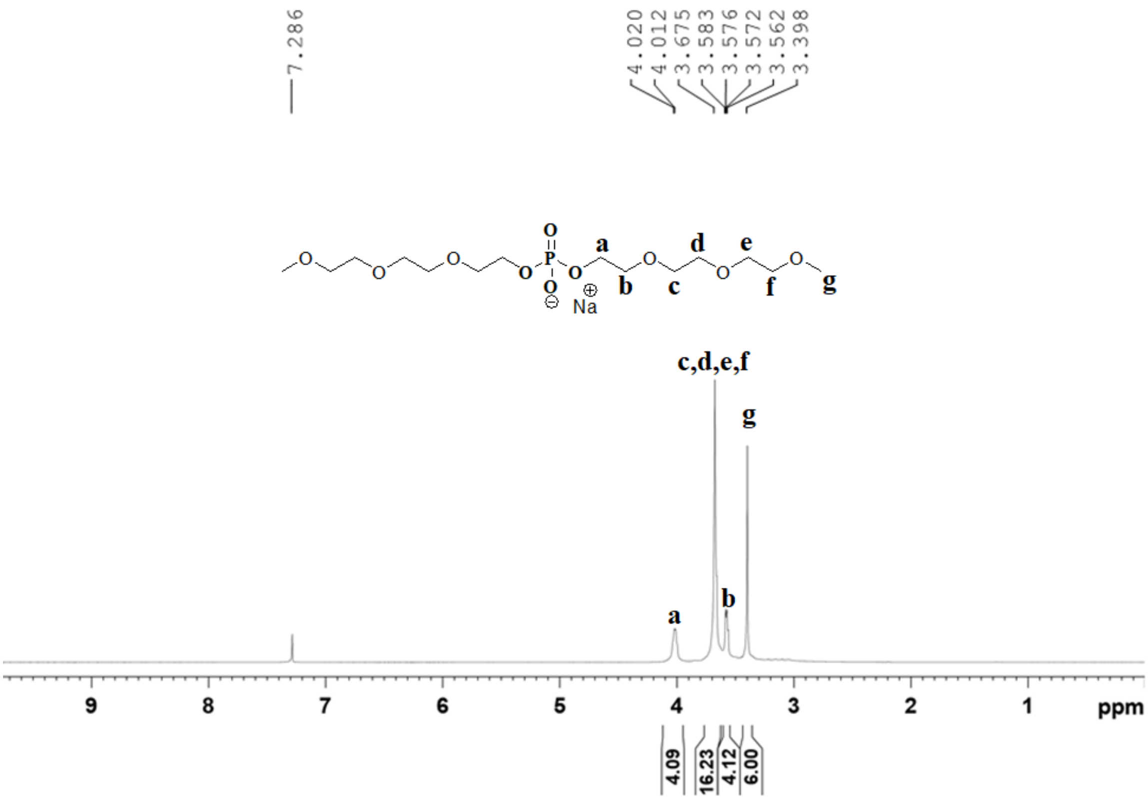

Figure S13. ^{1}H NMR spectrum of NaTEEP in $CDCl_3$.

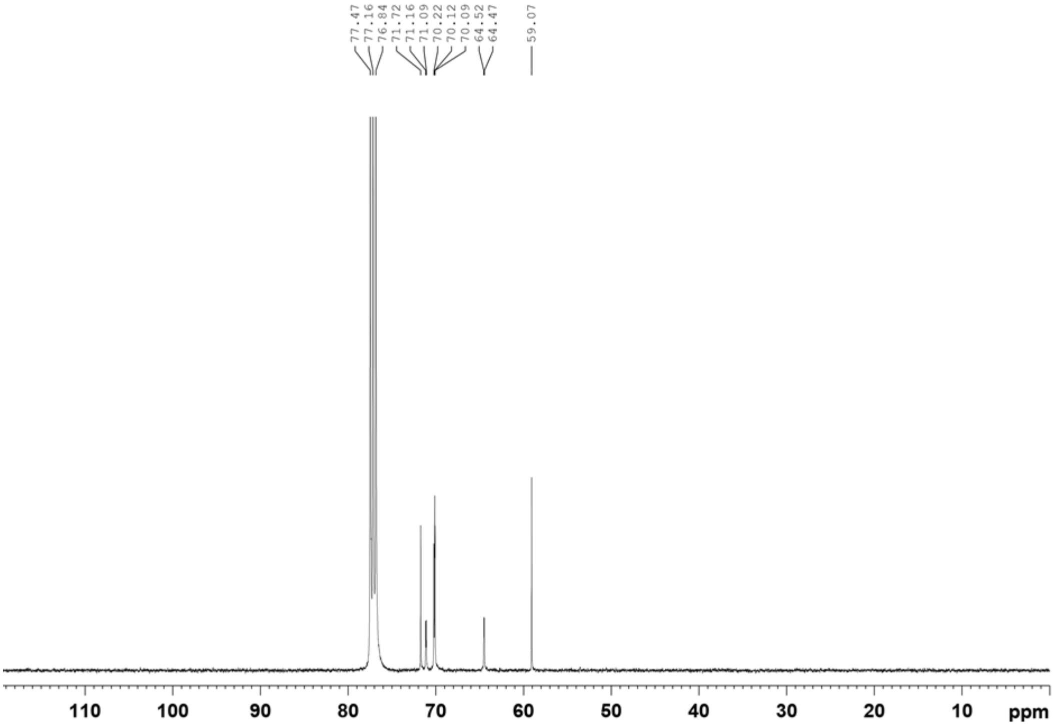

Figure S14. ^{13}C NMR spectrum of NaTEEP in $CDCl_3$.

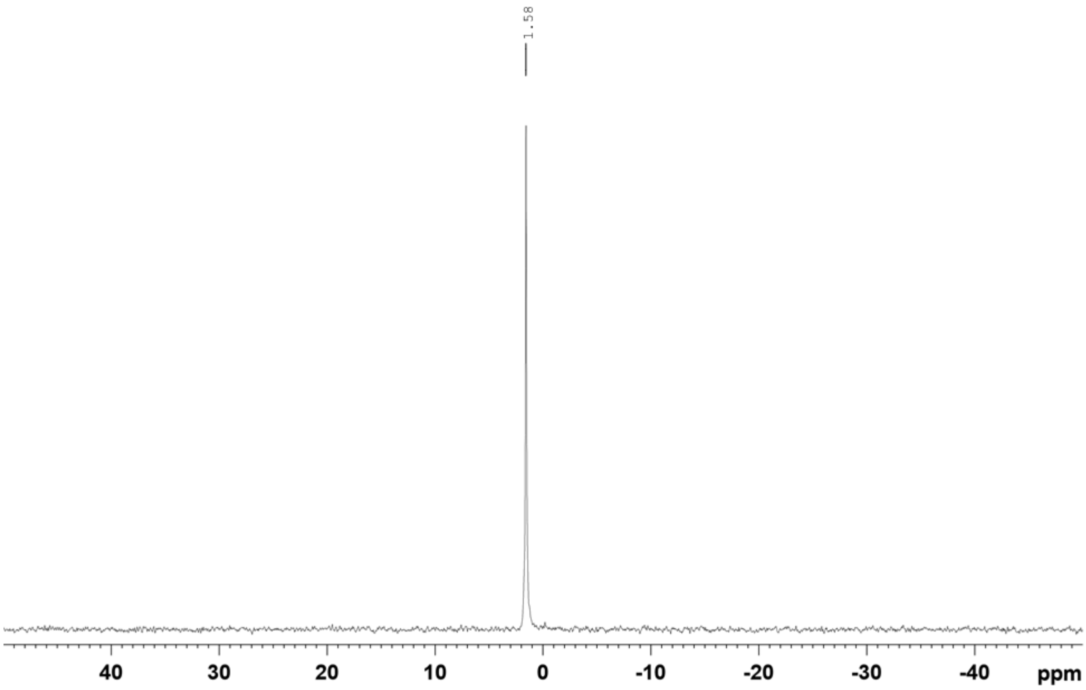

Figure S15. ^{31}P NMR spectrum of NaTEEP in $CDCl_3$.

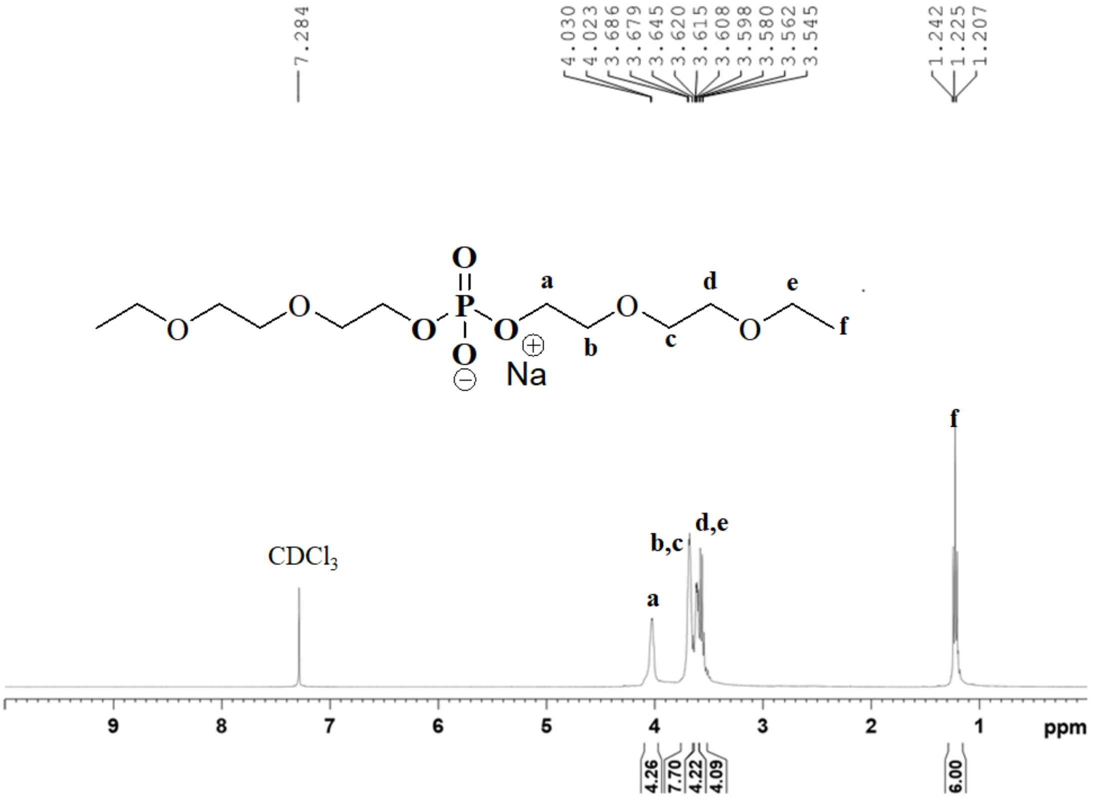

Figure S16. ^{1}H NMR spectrum of NaDEEP in $CDCl_3$.

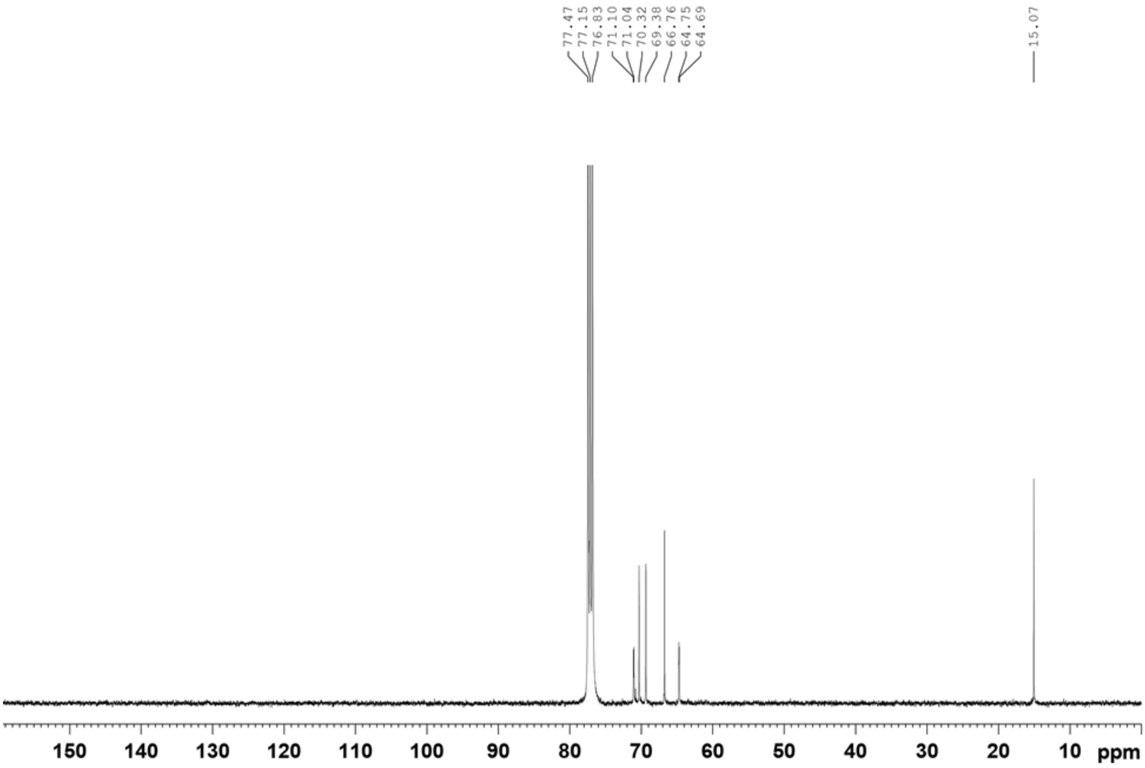

Figure S17. ^{13}C NMR spectrum of NaDEEP in $CDCl_3$.

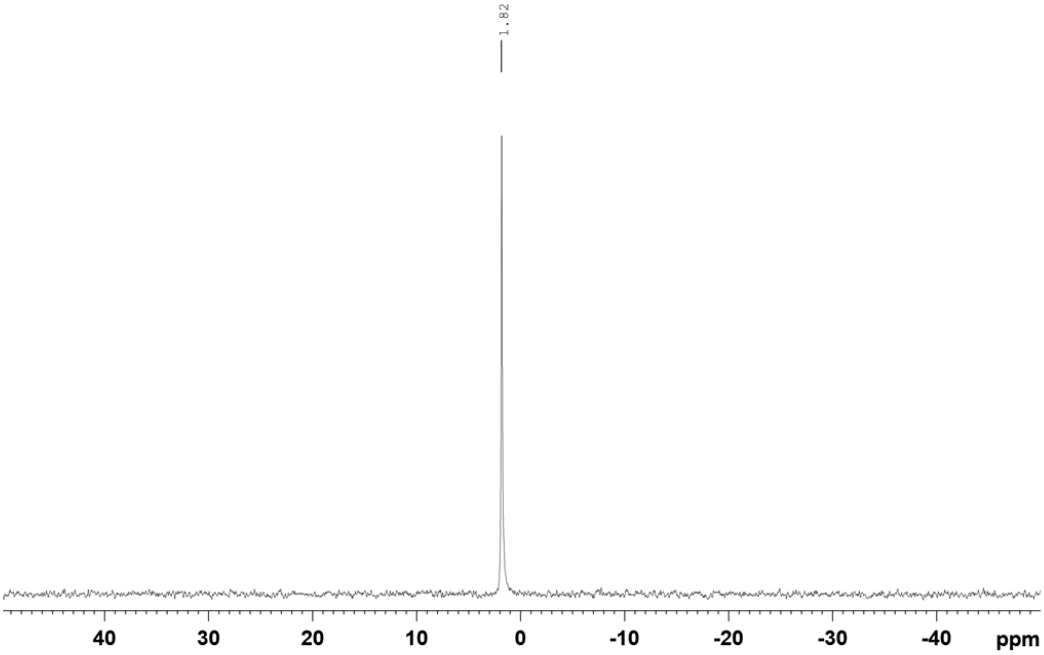

Figure S18. ^{31}P NMR spectrum of NaDEEP in $CDCl_3$.

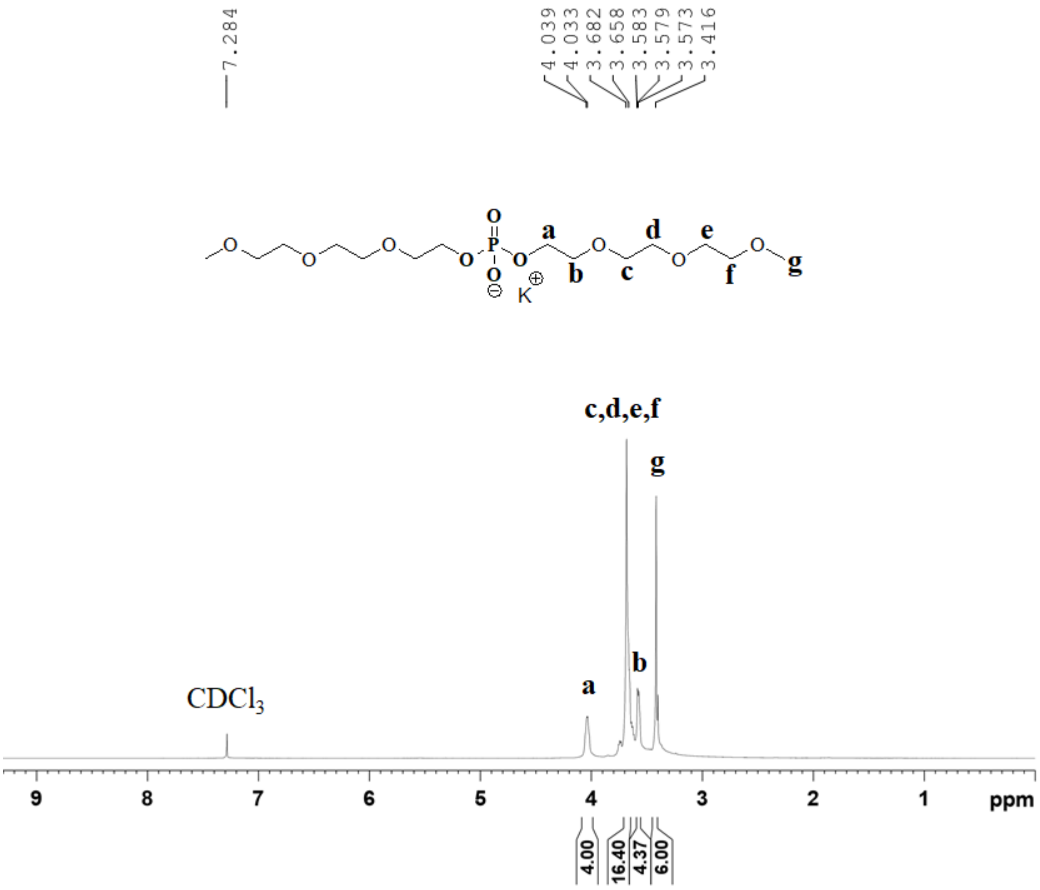

Figure S19. ^{1}H NMR spectrum of KTEEP in CDCl$_3$.

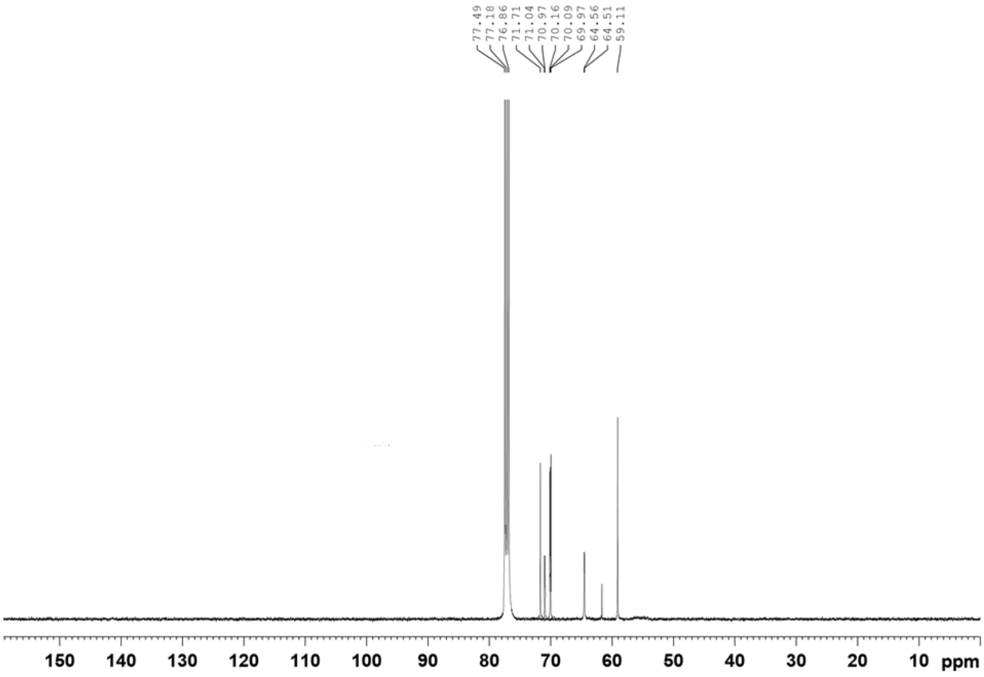

Figure S20. ^{13}C NMR spectrum of KTEEP in CDCl$_3$.

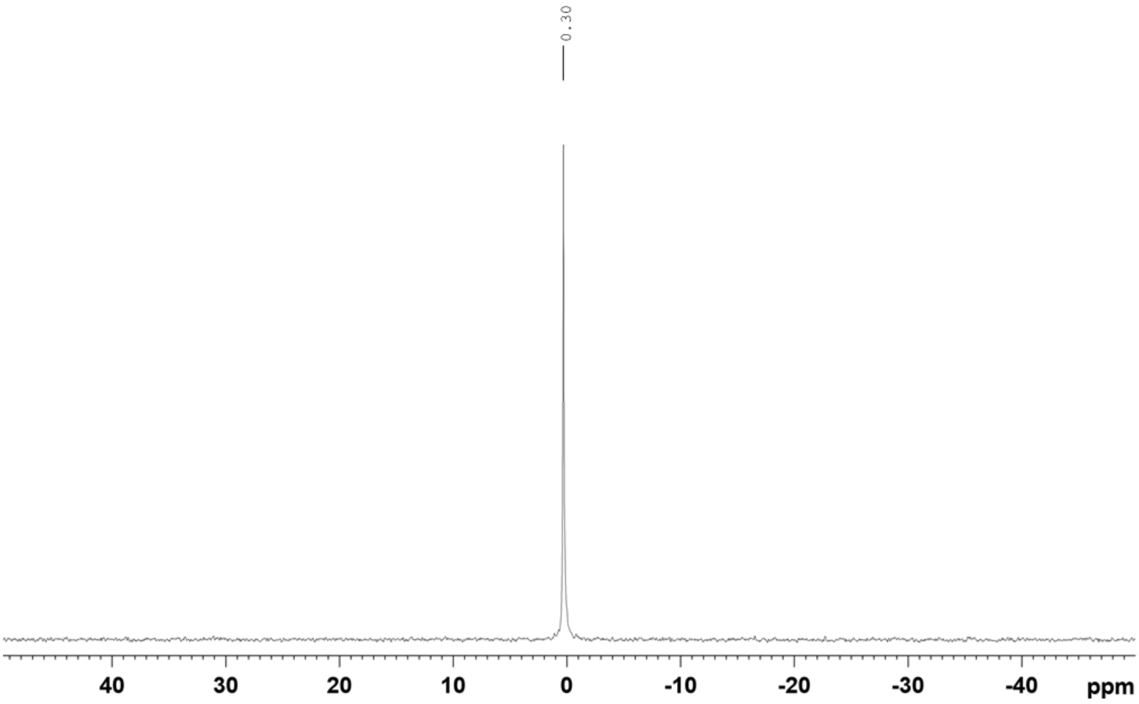

Figure S21. ^{31}P NMR spectrum of KTEEP in $CDCl_3$.

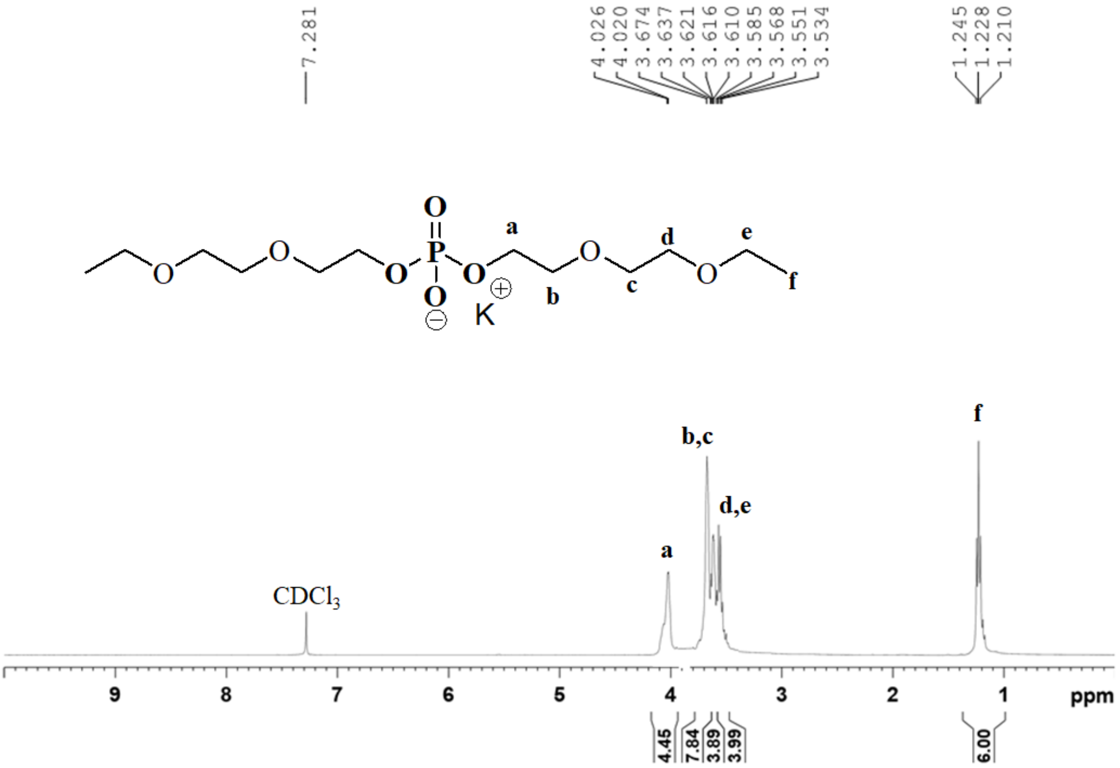

Figure S22. ^{1}H NMR spectrum of KDEEP in $CDCl_3$.

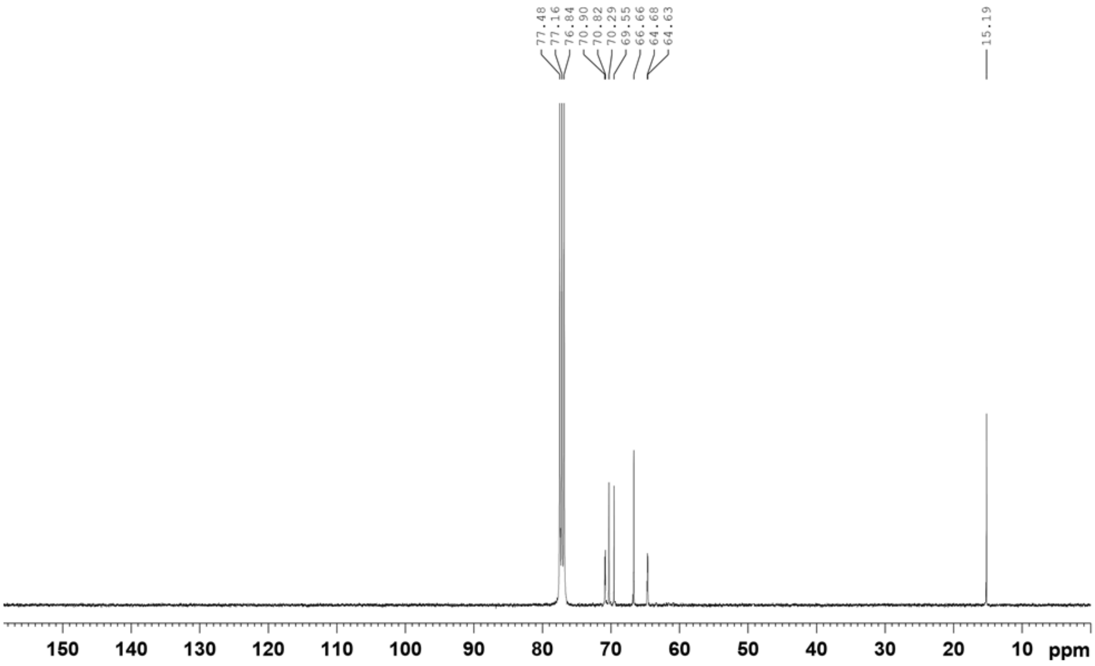

Figure S23. ^{13}C NMR spectrum of KDEEP in $CDCl_3$.

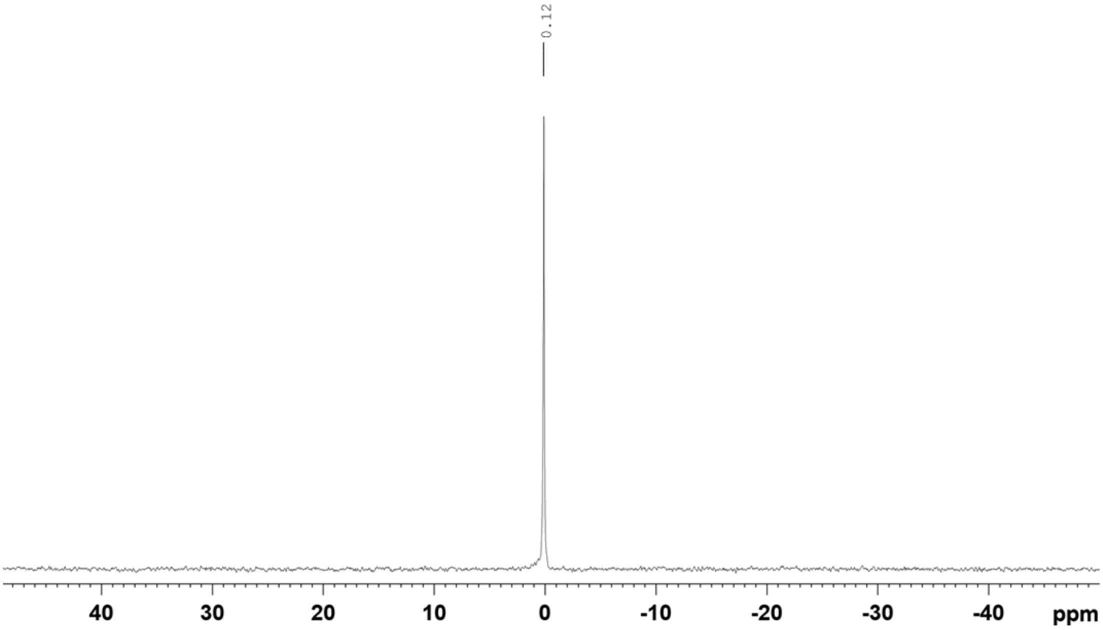

Figure S24. ^{31}P NMR spectrum of KDEEP in $CDCl_3$.

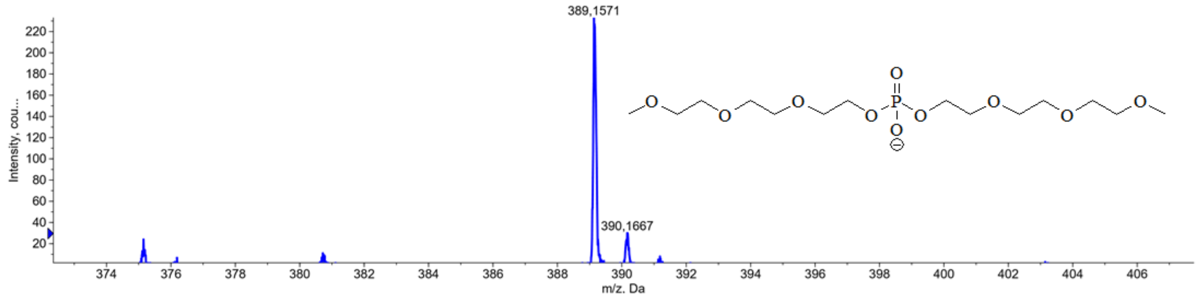

Figure S25. ESI-MS of LiTEEP.

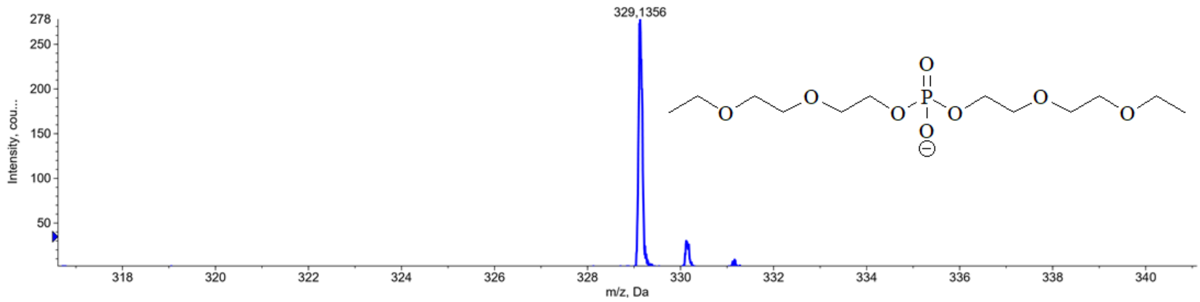

Figure S26. ESI-MS of LiDEEP.

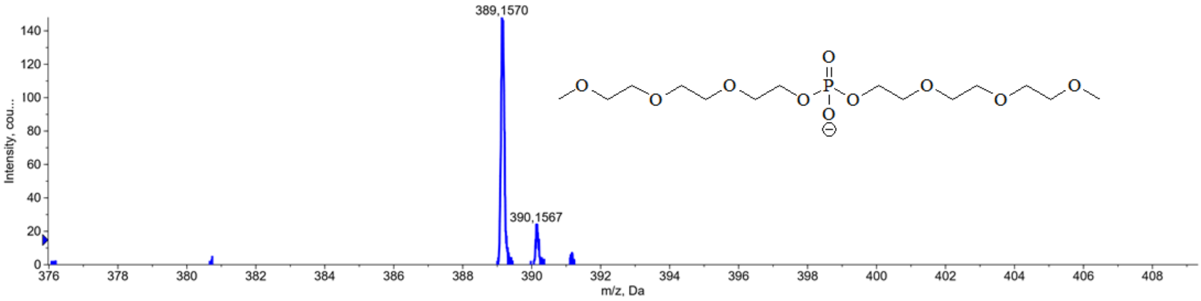

Figure S27. ESI-MS of NaTEEP.

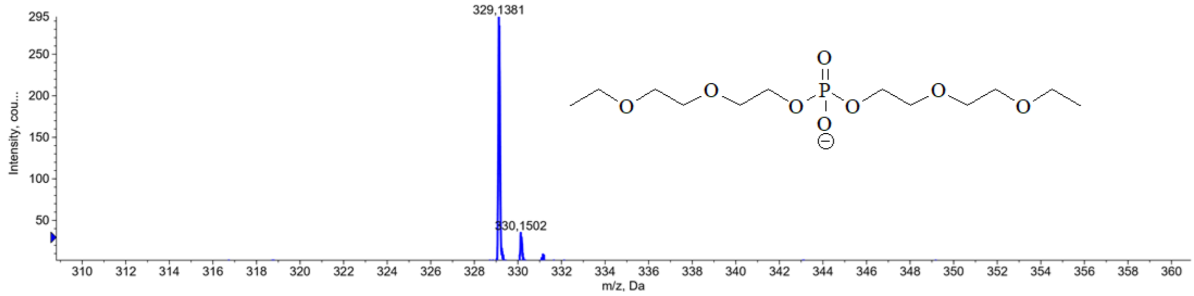

Figure S28. ESI-MS of NaDEEP.

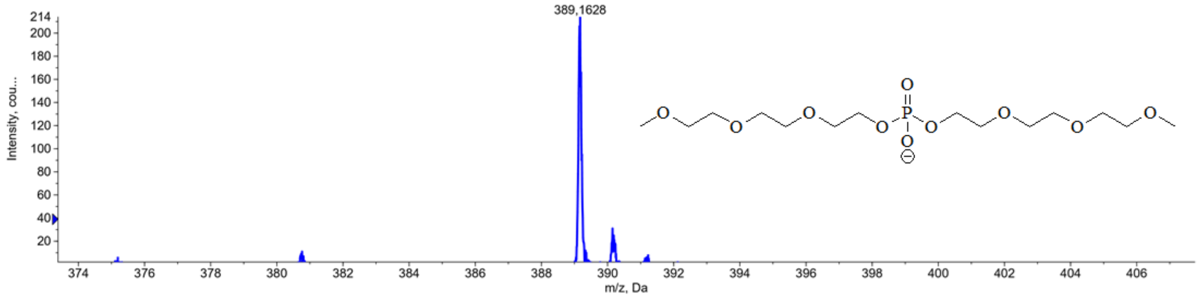

Figure S29. ESI-MS of KTEEP.

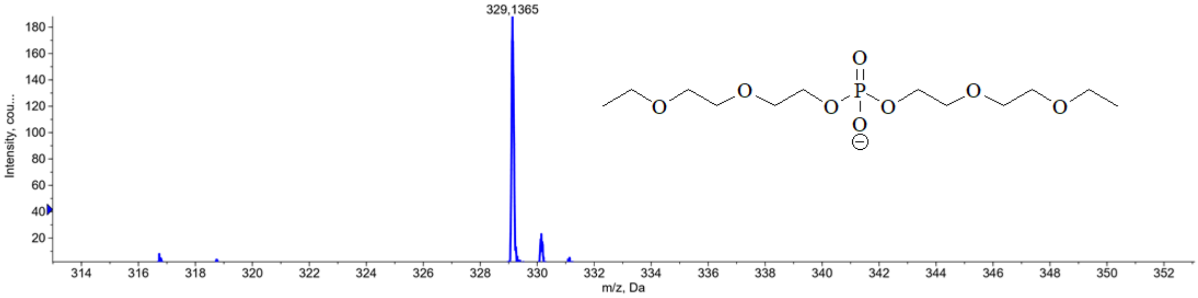

Figure S30. ESI-MS of KDEEP.

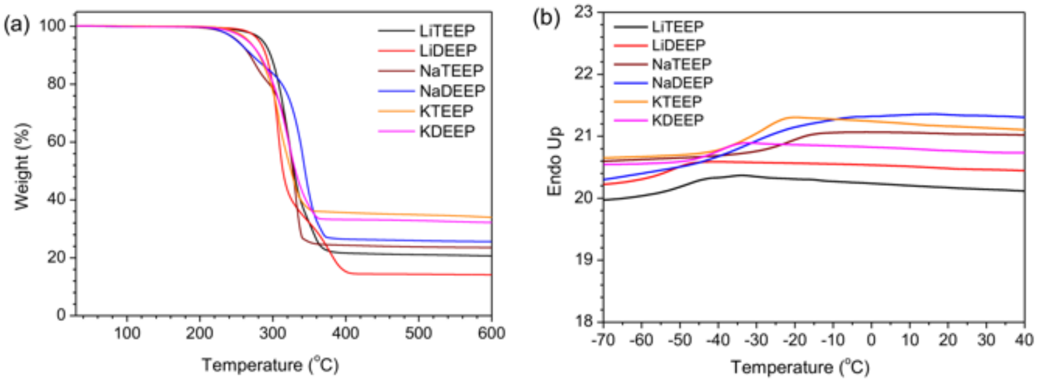

Figure S31. (a) Dynamic TGA thermograms and (b) DSC traces of our six salts.

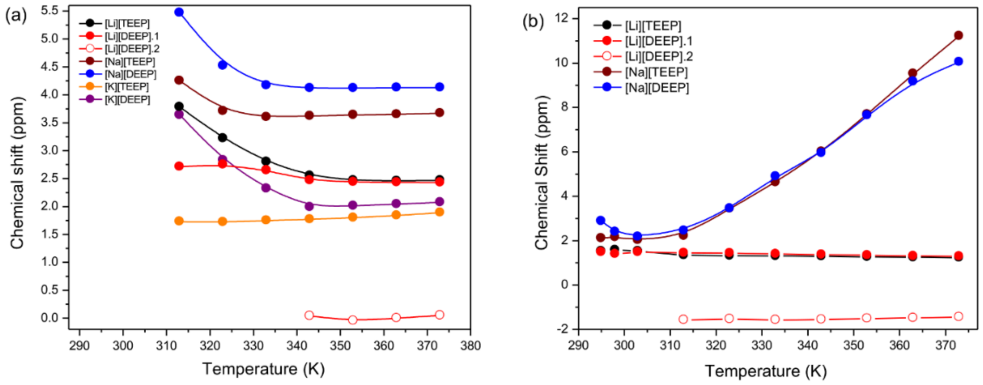

Figure S32. Chemical shift of (a) ^{31}P NMR and (b) ^{7}Li and ^{23}Na NMR spectra of the alkali metal salts as a function of temperature.

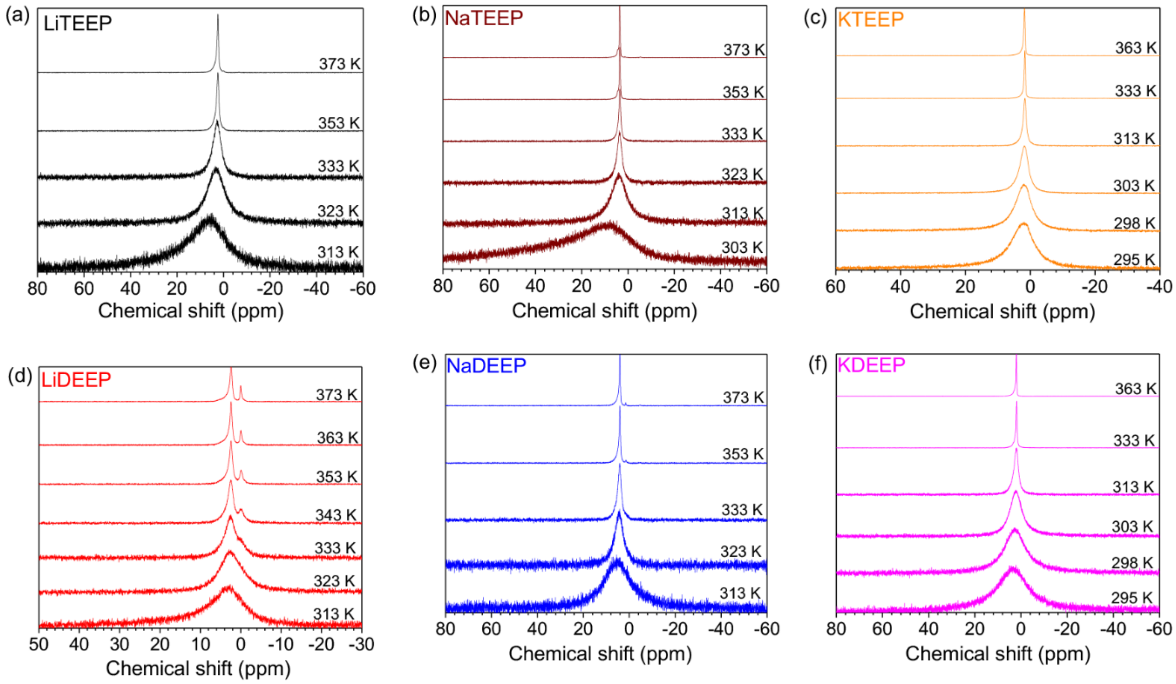

Figure S33. Temperature dependent ^{31}P NMR spectra of the neat alkali metal salts.

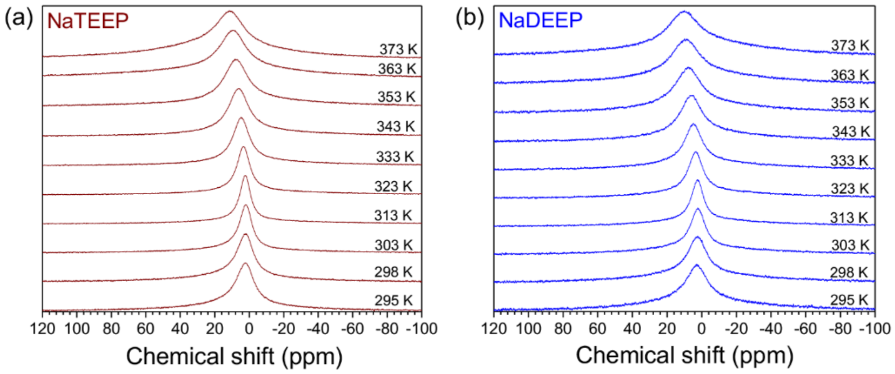

Figure S34. Temperature dependent ^{23}Na NMR spectra of (a) NaTEEP and (b) NaDEEP.

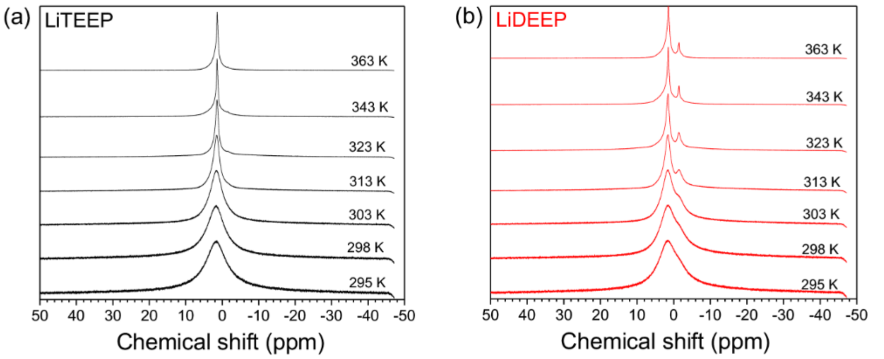

Figure S35. Temperature dependent ^{7}Li NMR spectra of (a) LiTEEP and (b) LiDEEP.

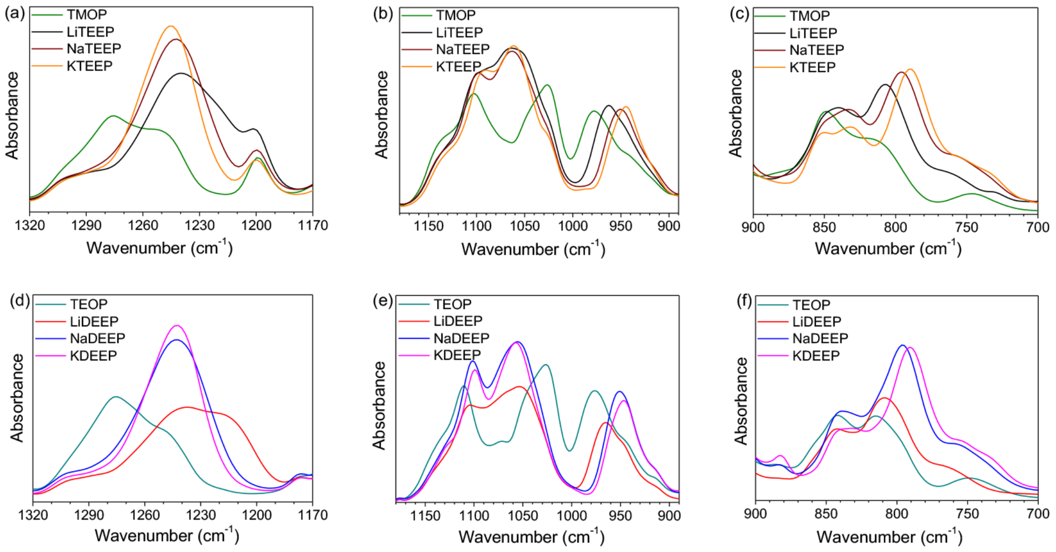

Figure S36. ATR-FTIR spectra of TMOP and Li/Na/K-TEEP (top) and TEOP and Li/Na/K-DEEP (bottom), in selected frequency ranges.

Table S1. Water content of the alkali metal dalts

Alkali metal salts	Water content (ppm)
LiTEEP	74 ± 5
LiDEEP	99 ± 5
NaTEEP	95 ± 5
NaDEEP	83 ± 5
KTEEP	88 ± 5
KDEEP	98 ± 5

Table S2. VFT equation parameters and apparent energies of activation for ionic conductivity for the alkali metal salts.

Salt	σ_0 m^2/s	B K	T_0 K	E_σ kJ/mol
LiTEEP	0.132	-1137 ± 3	164	9.5
LiDEEP	0.864	-1724 ± 3	149	14.3
NaTEEP	0.129	-1361 ± 2	137	11.3
NaDEEP	0.192	-180 ± 2	159	11.5
KTEEP	0.770	-1351 ± 2	171	11.2
KDEEP	1.643	-1647 ± 5	159	13.7

Table S3. Anodic limits on Pt and GC WEs, respectively, at 20°C using a scan rate of 1 mV/sec and 0.10 mA cm^{-2} cut-off current density.

Electrolyte	Pt WE	GC WE
	(E_A *vs.* Li/Li$^+$)	(E_A *vs.* Li/Li$^+$)
LiTEEP	4.23	4.94
LiDEEP	5.42	5.77
	(E_A *vs.* Na/Na$^+$)	(E_A *vs.* Na/Na$^+$)
NaTEEP	4.42	6.20
NaDEEP	5.59	5.75
	(E_A *vs.* K/K$^+$)	(E_A *vs.* K/K$^+$)
KTEEP	4.74	6.25
KDEEP	5.51	6.36

Table S4. VFT equation parameters and apparent energies of activation from ^{1}H NMR diffusion data.

System	$D_0 \times 10^{-9}$ m^2/s	B K	T_0 K	E_D kJ/mol
LiTEEP	7.28	1564	185	13.0
LiDEEP	9.62	1539	190	12.7
NaTEEP	0.748	676	224	5.6
NaDEEP	1.00	621	257	5.2
KTEEP	9.37	1001	217	8.3
KDEEP	11.7	1345	191	11.2

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