Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Structurally Flexible Pyrrolidinium- and Morpholinium-based Ionic Liquid Electrolytes

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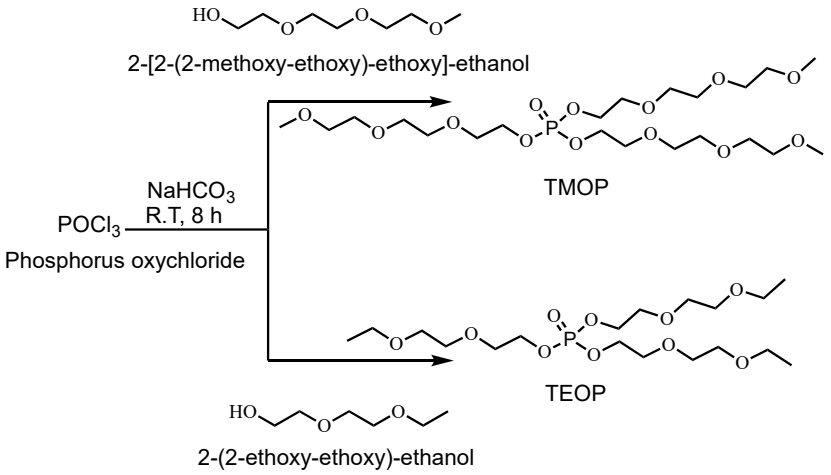
Synthesis of TMOP and TEOP

Phosphorus(V)oxychloride (20.00 g, 0.13 mol) was taken into a round bottom flask and the respective alcohol (0.39 mol) was added slowly and the 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 g, 0.39 mol) and stirred for one hour at room temperature. The reaction mixture was extracted with ethyl acetate and washed with brine at least three times. The organic phase was dried by sodium sulphate and concentrated using a rotary evaporator to obtain the desired product as a clear liquid.



Scheme S1. Synthesis of TMOP and TEOP trialkyl phosphates.

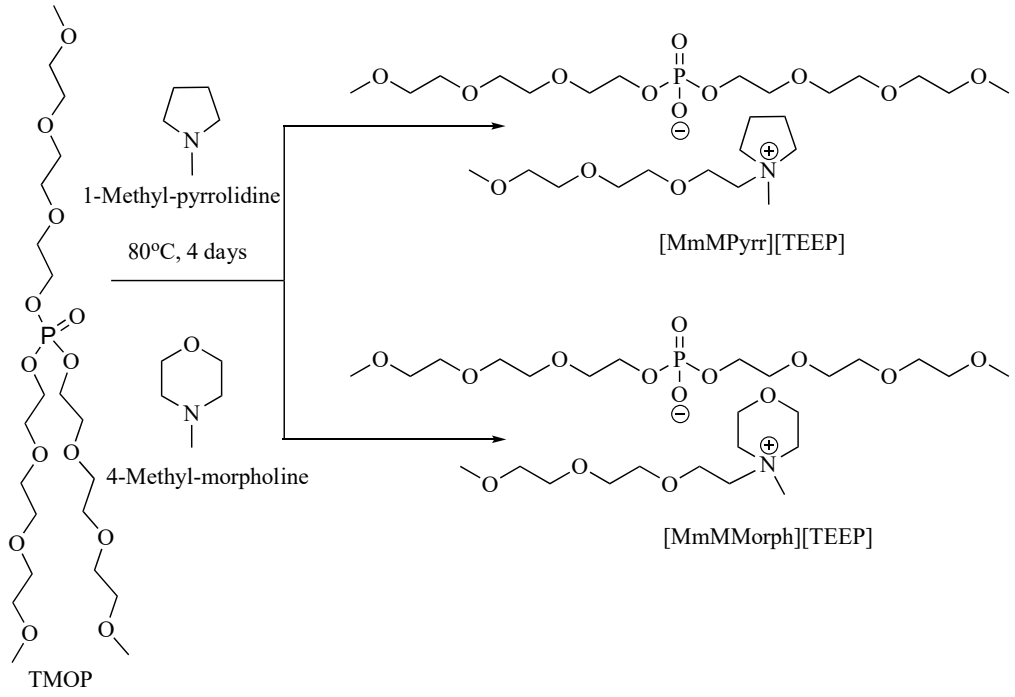
TMOP: Yield: 52.5 g, 90%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.11-4.09 (m, 6H), 3.63-3.61 (m, 6H), 3.57-3.55 (m, 6H), 3.49-3.47 (m, 6H), 3.45-3.40 (m, 6H), 1.12-1.09 (t, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -1.14. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 72.02, 70.66, 70.60, 70.46, 70.14, 66.85, 59.10. 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 [MmMPyrr][TEEP]and [MmMMorph][TEEP]

Trialkyl phosphate (9.32 mmol) and 1-methyl-pyrrolidine (0.97 ml, 9.32 mmol) were added to a Schlenk flask under nitrogen atmosphere. The reaction mixture was heated at 80°C under inert atmosphere for 4 days. After completion, the reaction mixture was washed with hexane three times to get the desired product. The product was dried in a vacuum oven at 80℃ for more than 3 days.



Scheme S2. Synthesis of [MmMPyrr][TEEP] and [MmMMorph][TEEP].

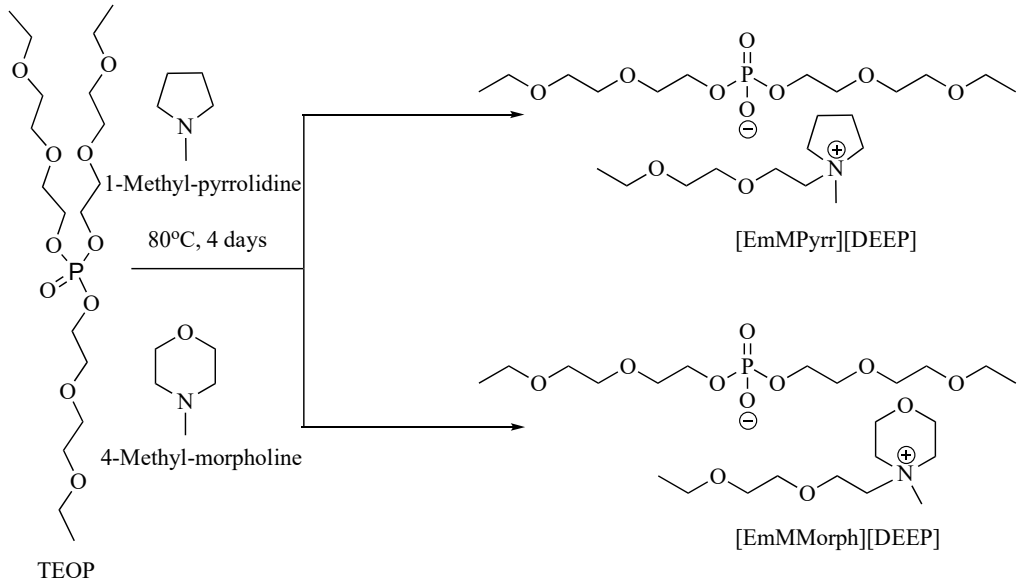
[MmMPyrr][TEEP]: Yield: 5.45 g, 94%. ^1H NMR (400 MHz, CDCl3): δ 3.97-3.82 (m, 6H), 3.80-3.76 (m, 4H), 3.63-3.59 (m, 24H), 3.52-3.50 (m, 6H), 3.36-3.32 (m, 9H), 3.25 (s, 3H), 2.25-2.16 (m, 4H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 0.25. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 70.60, 70.54, 70.47, 70.45, 70.34, 70.26, 65.75, 65.40, 64.25, 64.20, 63.31, 61.69, 59.06, 48.54,

21.58. IR (ATR): 2868.49, 1457.16, 1350.90, 1248.32, 1199.54, 1098.90, 1066.96, 943.09, 850.38, 779.35 cm^{-1}. MS (ESI). $[C_{12}H_{26}NO_3]^+$: Calcd for m/z 232.19. Found m/z 232.19, MS (ESI). $[C_{14}H_{30}O_{10}P]^-$: Calcd for m/z 389.16. Found m/z 389.157.

[MmMMorph][TEEP]: Yield: 5.50 g, 92%. ^1H NMR (400 MHz, CDCl3): δ 4.10-4.09 (m, 2H), 3.98-3.97 (m, 8H), 3.82-3.79 (m, 2H), 3.66-3.49 (m, 32H), 3.47 (s, 3H), 3.37-3.34 (m, 9H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 0.01. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 72.69, 72.08, 72.02, 71.35, 71.27, 70.78, 70.62, 70.54, 70.48, 70.42, 70.24, 70.10, 65.01, 64.40, 64.35, 63.27, 61.74, 61.37, 61.08, 59.05, 48.25. IR (ATR): 2876.88, 1462.36, 1354.30, 1251.07, 1196.77, 1103.76, 1069.35, 953.22, 889.24, 854.30, 784.40 cm^{-1}. MS (ESI). $[C_{12}H_{26}NO_4]^+$: Calcd for m/z 248,19. Found m/z 248,18, MS (ESI). $[C_{14}H_{30}O_{10}P]^-$: Calcd for m/z 389.16. Found m/z 389.158.

Synthesis of [EmMPyrr][DEEP] and [EmMMorph][DEEP]

The same procedure was used as for the synthesis of [MmMPyrr][TEEP]and [MmMMorph][TEEP] ILs.



Scheme S3. Synthesis of [EmMPyrr][DEEP] and [EmMMorph][DEEP].

[EmMPyrr][DEEP]: Yield: 5.4 g, 90%. ^{1}H NMR (400 MHz, CDCl3): δ 3.91-3.41 (m, 34H), 3.20 (s, 3H), 2.17-2.14 (m, 4H), 1.13-1.10 (m, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 0.09. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 72.78, 71.35, 71.27, 70.52, 70.48, 69.94, 69.44, 66.66, 66.56, 65.66, 65.30, 64.21, 64.15, 63.03, 61.49, 48.62, 21.54, 15.24. IR (ATR): 2867.20, 1462.36, 1357.52, 1252.68, 1105.91, 1063.97, 945.16, 777.41 cm^{-1}. MS (ESI). $[C_{11}H_{24}NO_2]^+$: Calcd for m/z 202.18. Found m/z 202.179, MS (ESI). $[C_{12}H_{26}O_8P]^-$: Calcd for m/z 329.14. Found m/z 329.136.

[EmMMorph][DEEP]: Yield: 5.60 g, 91%. ^{1}H NMR (400 MHz, CDCl3): δ 4.14-4.03 (m, 2H), 4.01-3.87 (m, 8H), 3.86-3.84 (m, 2H), 3.83-3.48 (m, 29H), 1.23-1.16 (m, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 0.03. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 72.75, 71.33, 71.26, 70.54, 69.98, 69.35, 66.62, 64.97, 64.41, 64.36, 63.06, 61.31, 61.03, 48.51, 15.29. IR (ATR): 2867.20, 1462.36, 1359.13, 1251.07, 1108.60, 1063.97, 955.91, 884.40, 784.45 cm^{-1}. MS (ESI). $[C_{11}H_{24}NO_3]^+$: Calcd for m/z 218.18. Found m/z 218.176, MS (ESI). $[C_{12}H_{26}O_8P]^-$: Calcd for m/z 329.14. Found m/z 329.14.

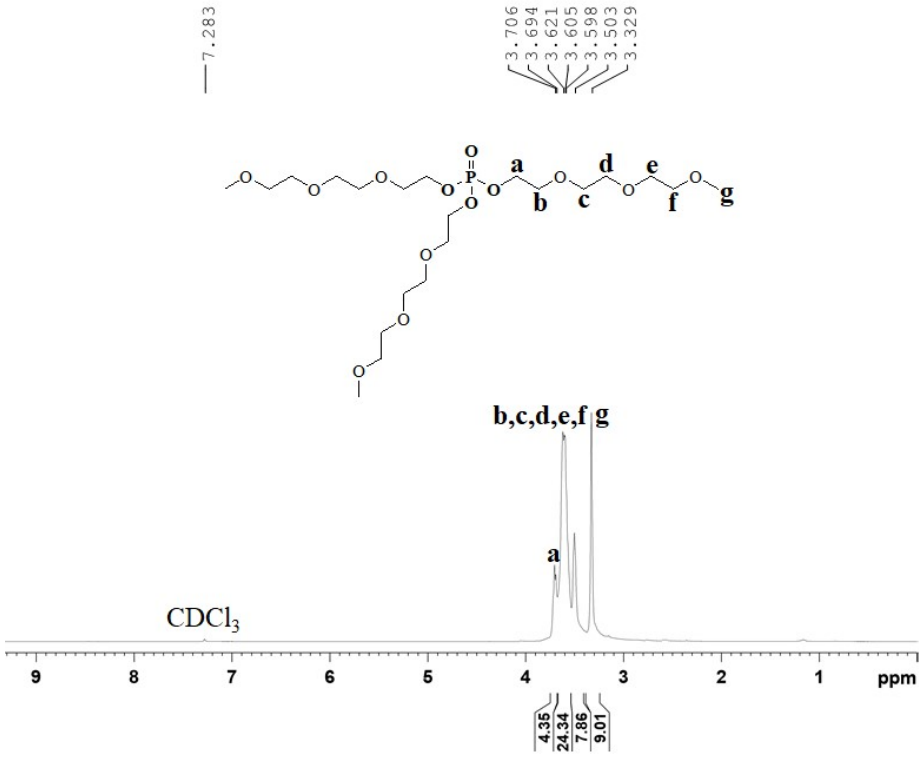


Figure S1: ^{1}H NMR spectrum of TMOP.

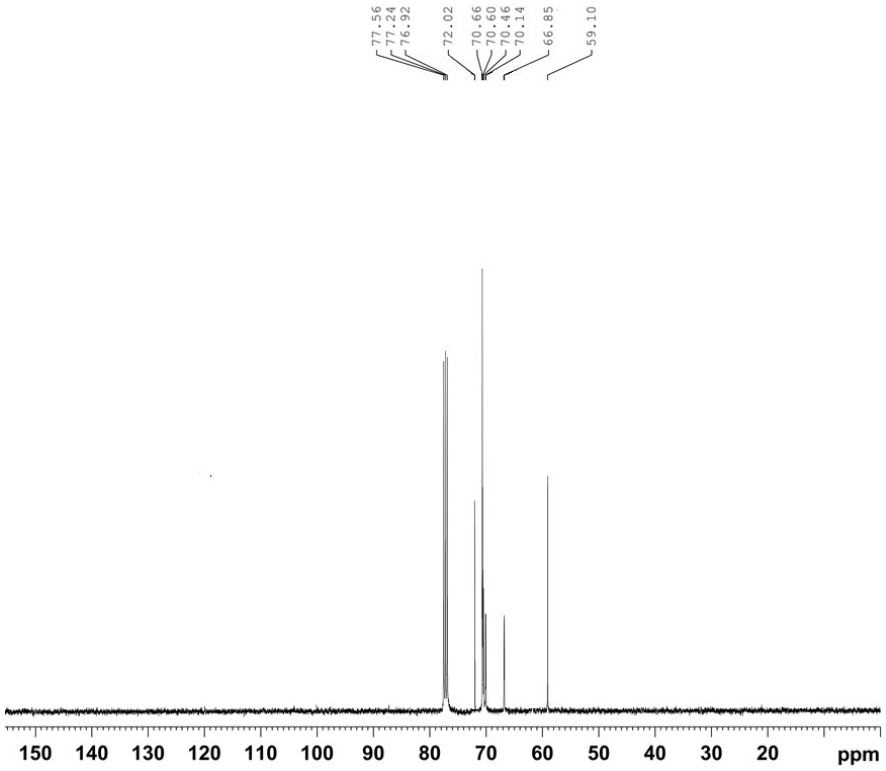


Figure S2: ^{13}C NMR spectrum of TMOP.

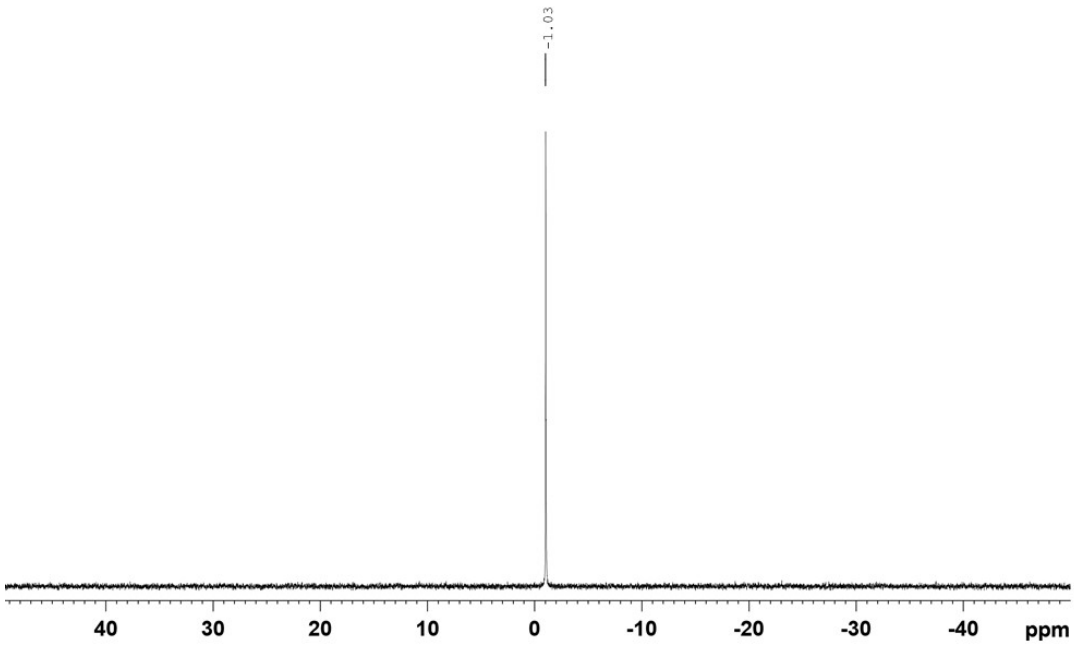


Figure S3: ^{31}P NMR spectrum of TMOP.

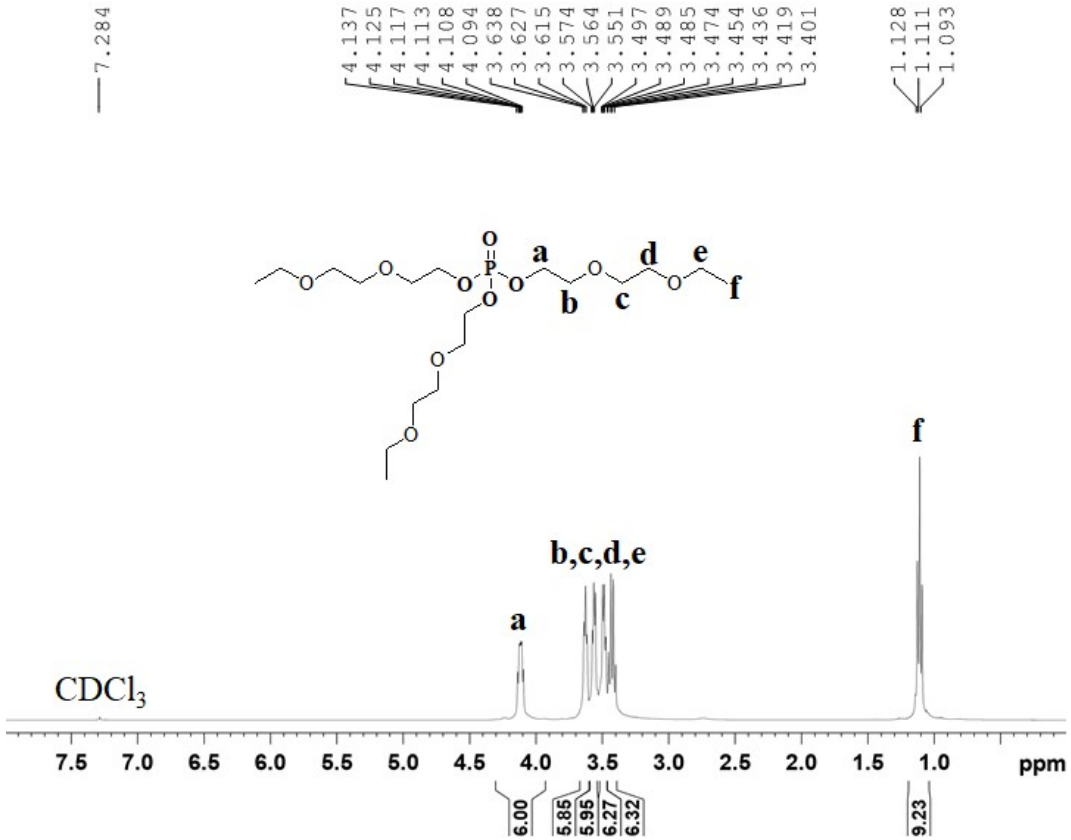


Figure S4: ^{1}H NMR spectrum of TEOP.

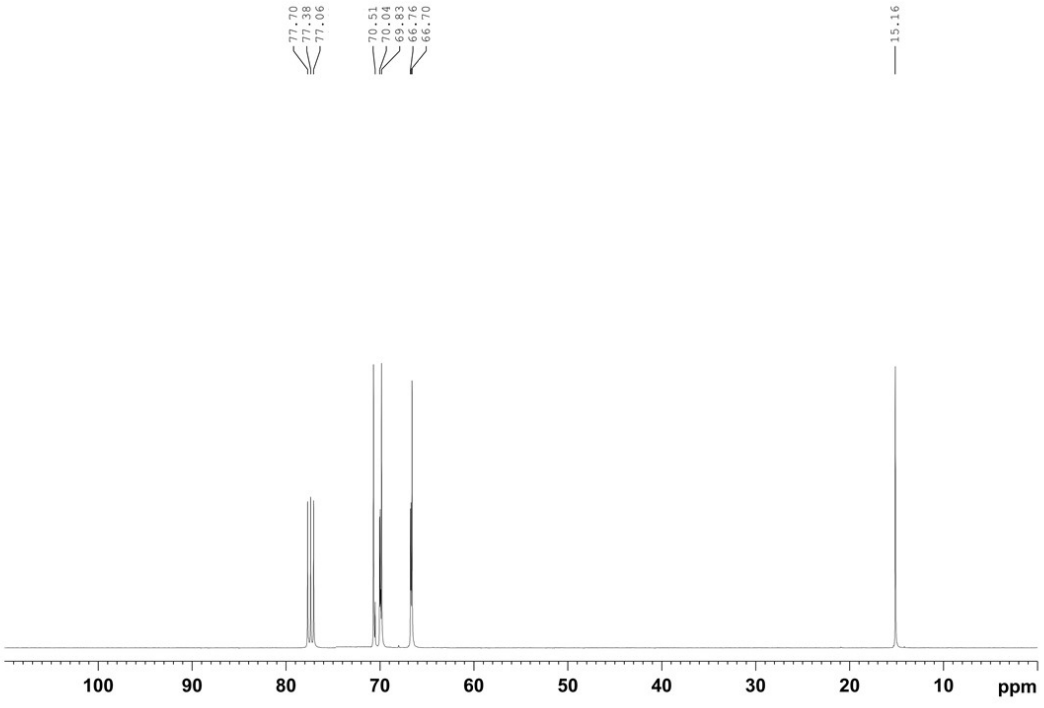


Figure S5: ^{13}C NMR spectrum of TEOP.

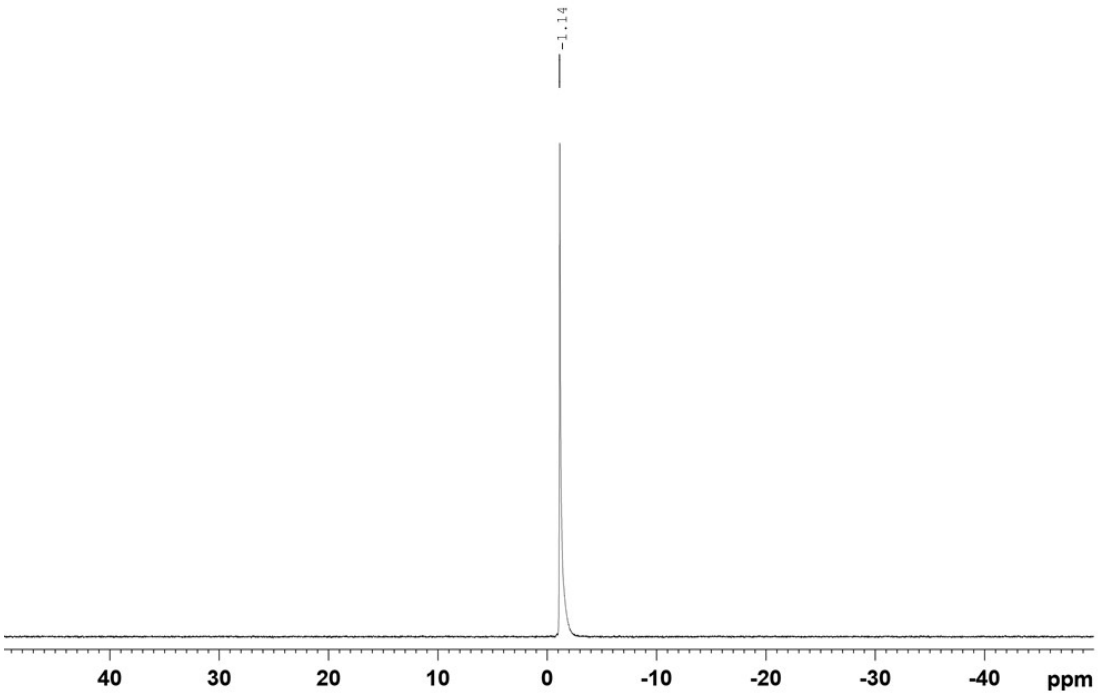


Figure S6: ^{31}P NMR spectrum of TEOP.

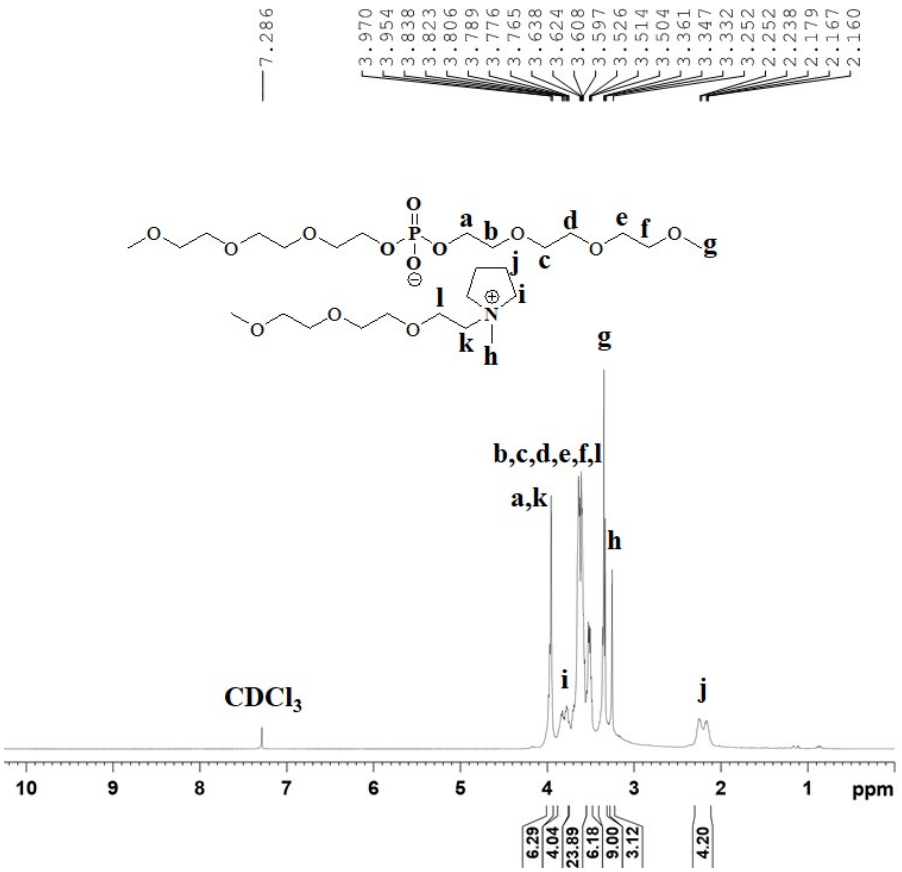


Figure S7: ^{1}H NMR spectrum of [MmMPyrr][TEEP].

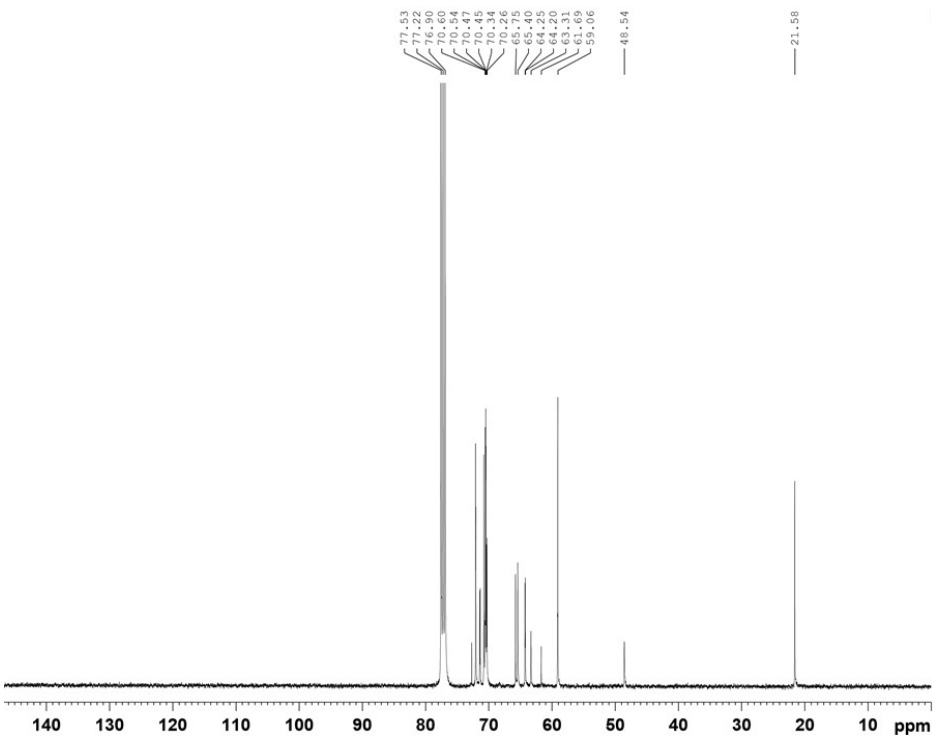


Figure S8: ^{13}C NMR spectrum of [MmMPyrr][TEEP].

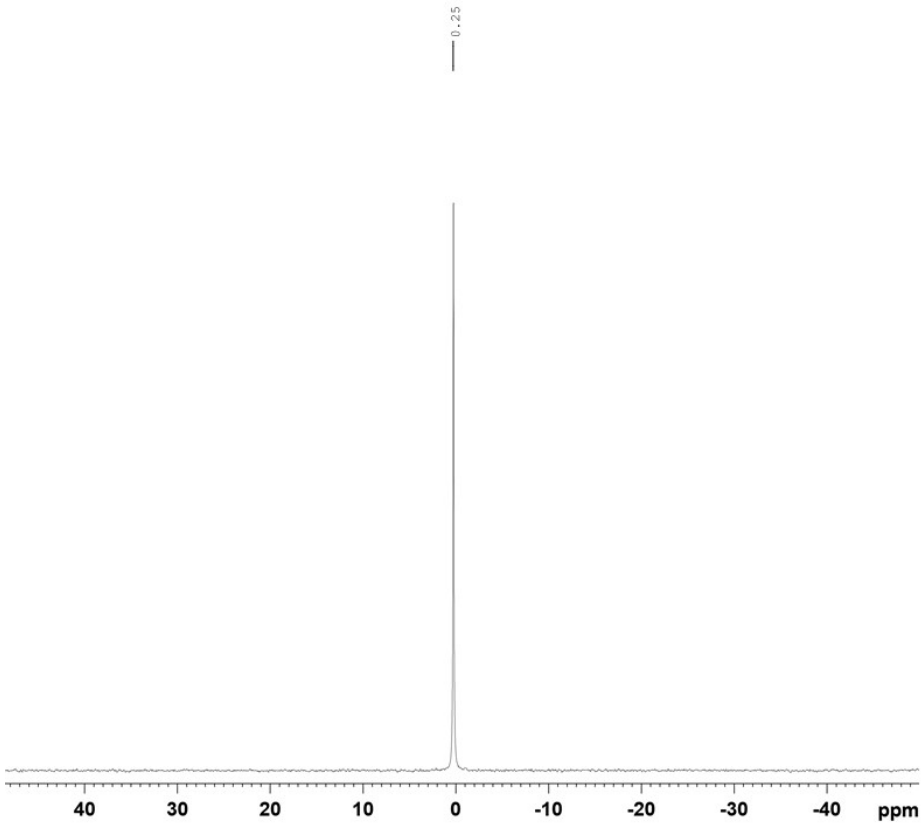


Figure S9: ^{31}P NMR spectrum of [MmMPyrr][TEEP].

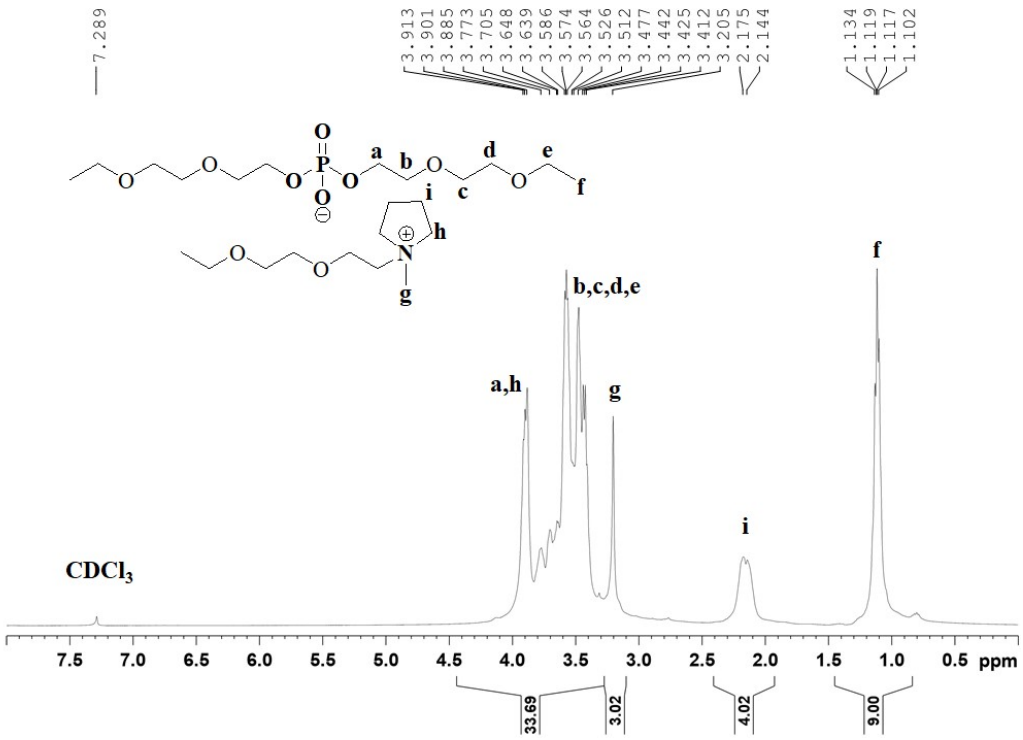


Figure S10: ^{1}H NMR spectrum of [EmMPyrr][DEEP].

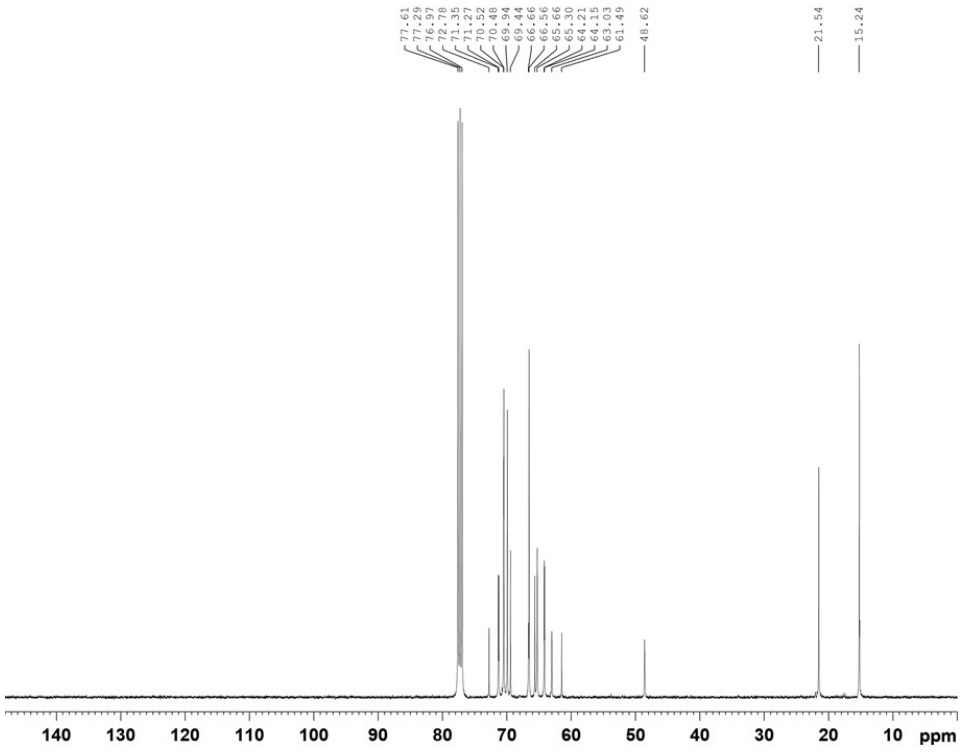


Figure S11: ^{13}C NMR spectrum of [EmMPyrr][DEEP].

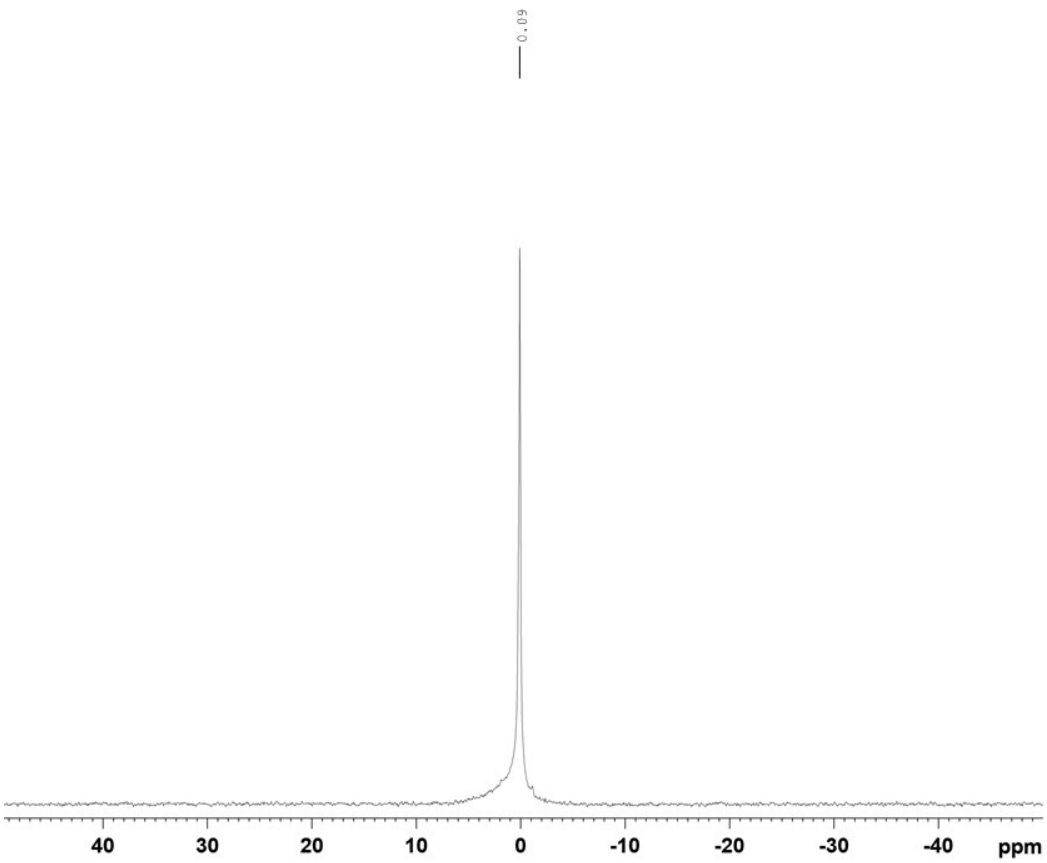


Figure S12: ^{31}P NMR spectrum of [EmMPyrr][DEEP].

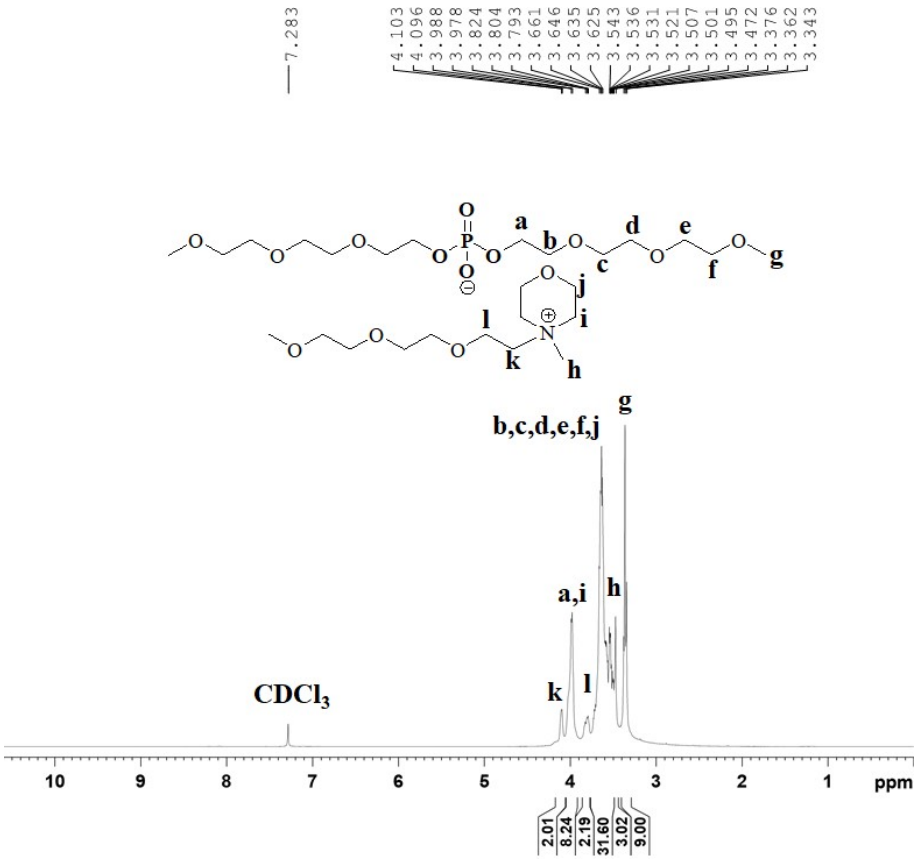


Figure S13: ^{1}H NMR spectrum of [MmMMorph][TEEP].

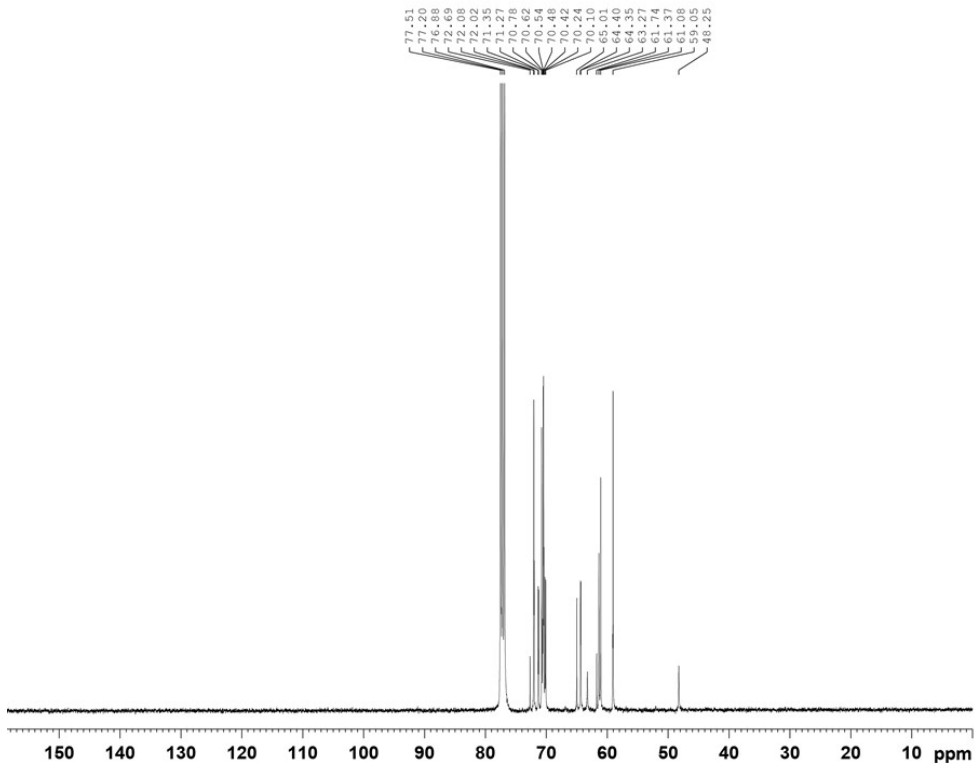


Figure S14: ^{13}C NMR spectrum of [MmMMorph][TEEP].

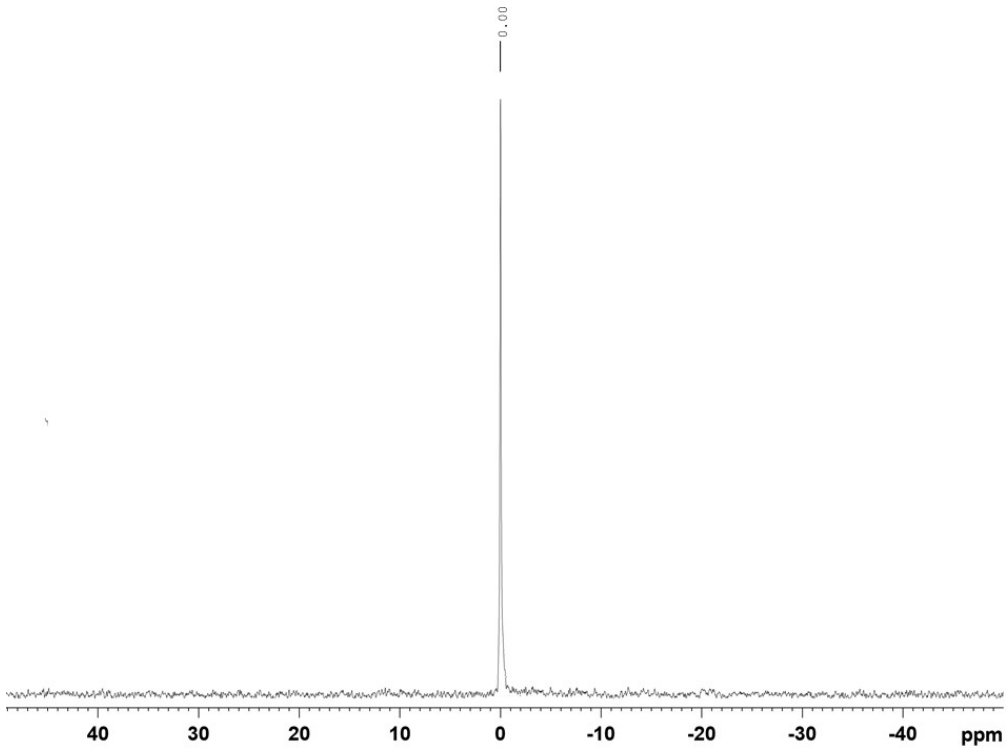


Figure S15: ^{31}P NMR spectrum of [MmMMorph][TEEP].

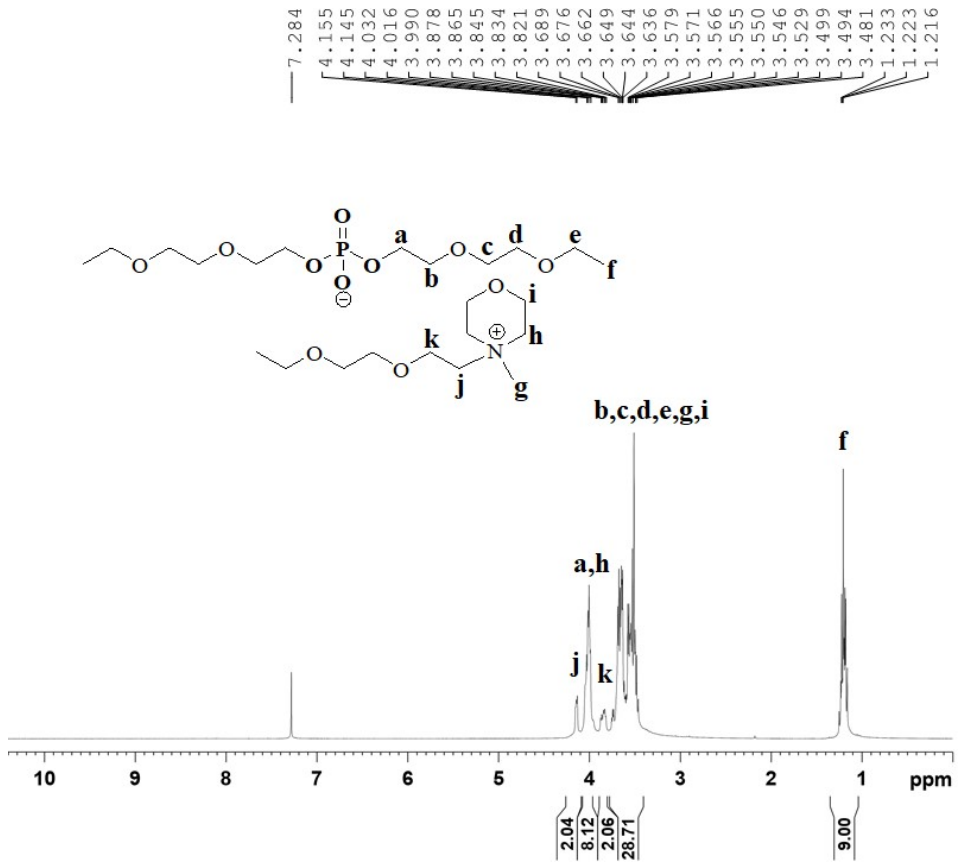


Figure S16: ^{1}H NMR spectrum of [EmMMorph][DEEP].

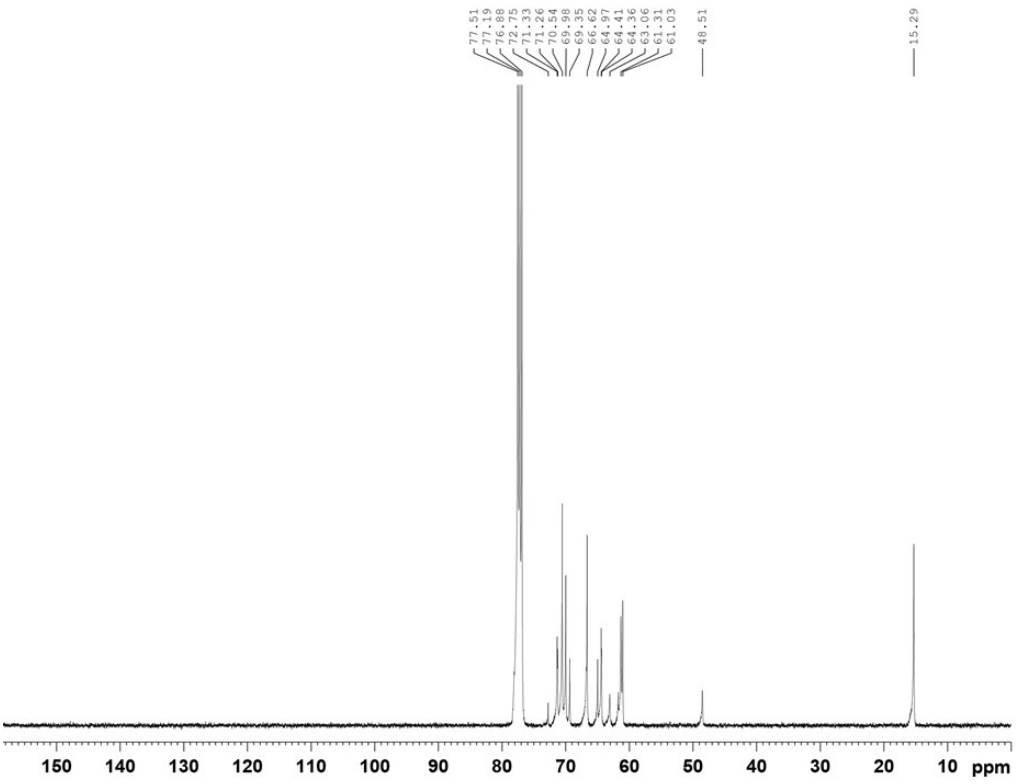


Figure S17: ^{13}C NMR spectrum of [EmMMorph][DEEP].

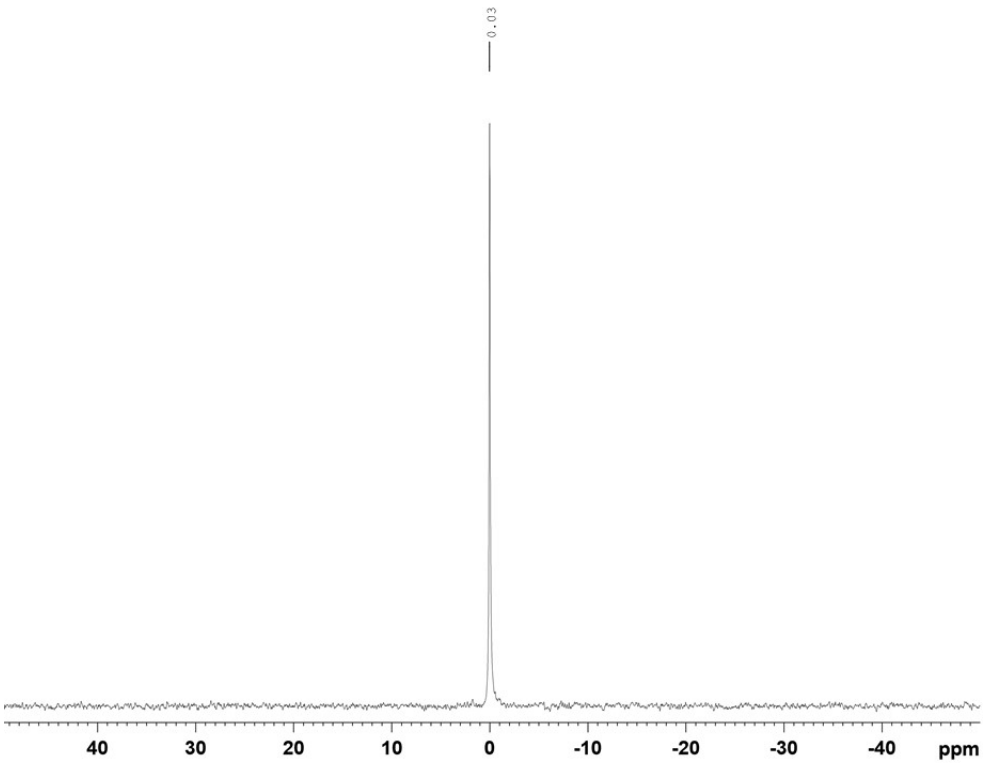


Figure S18: ^{31}P NMR spectrum of [EmMMorph][DEEP].

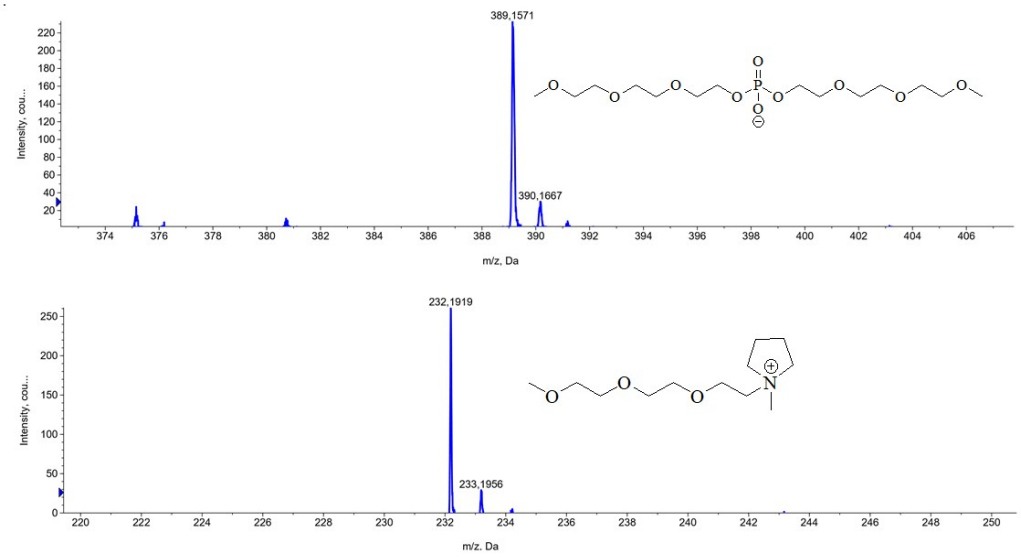


Figure S19. ESI-MS of [MmMPyrr][TEEP].

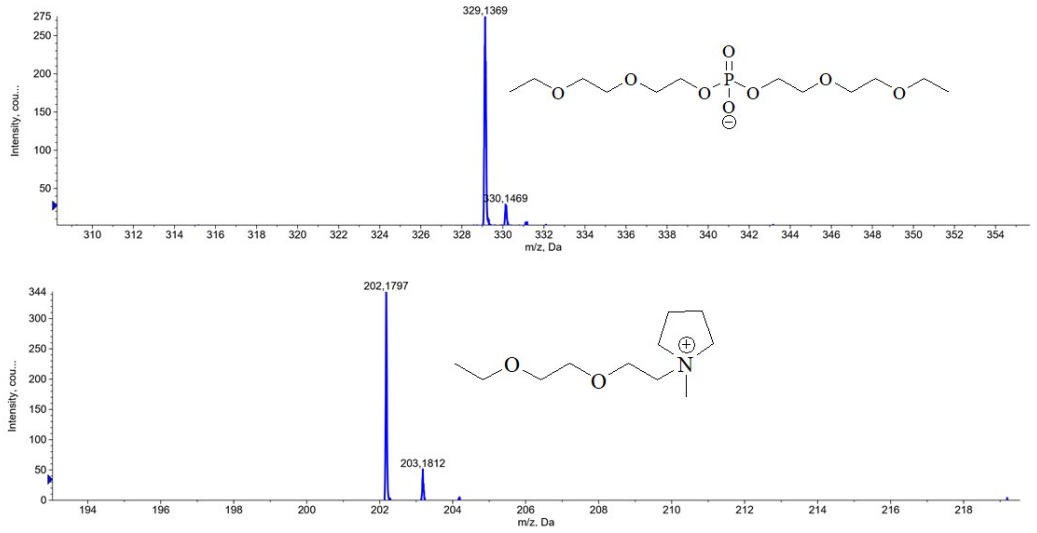


Figure S20. ESI-MS of [EmMPyrr][DEEP].

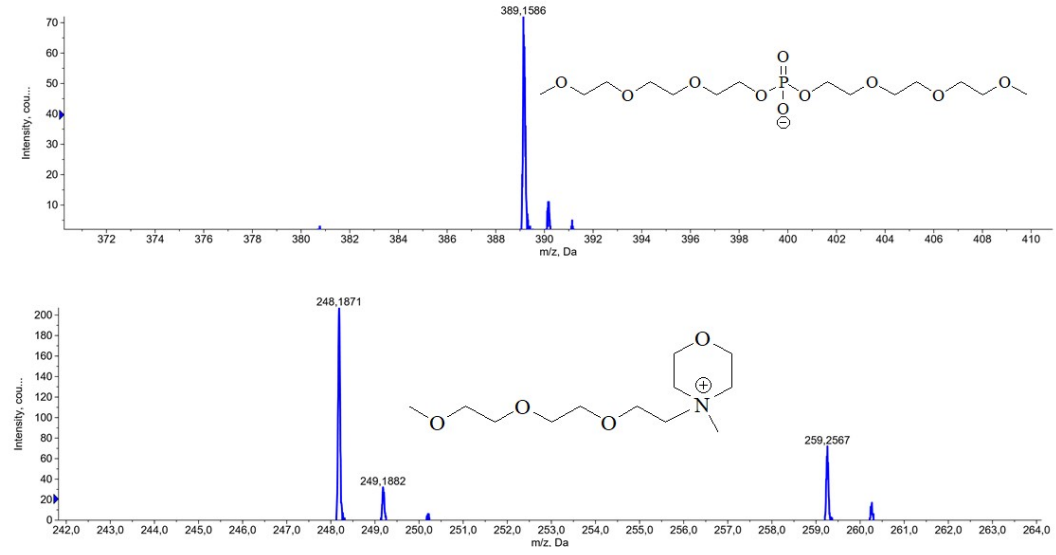


Figure S21. ESI-MS of [MmMMorph][TEEP].

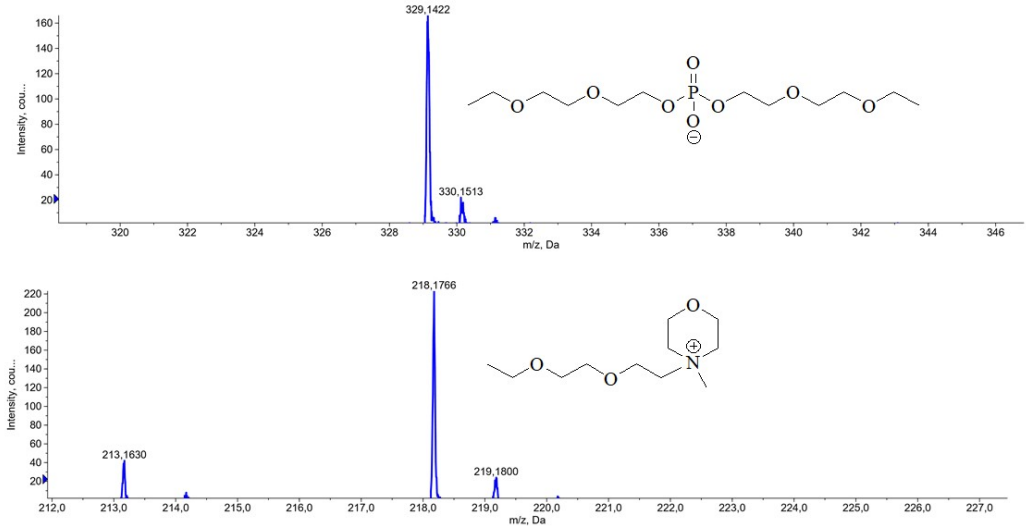


Figure S22. ESI-MS of [EmMMorph][DEEP].

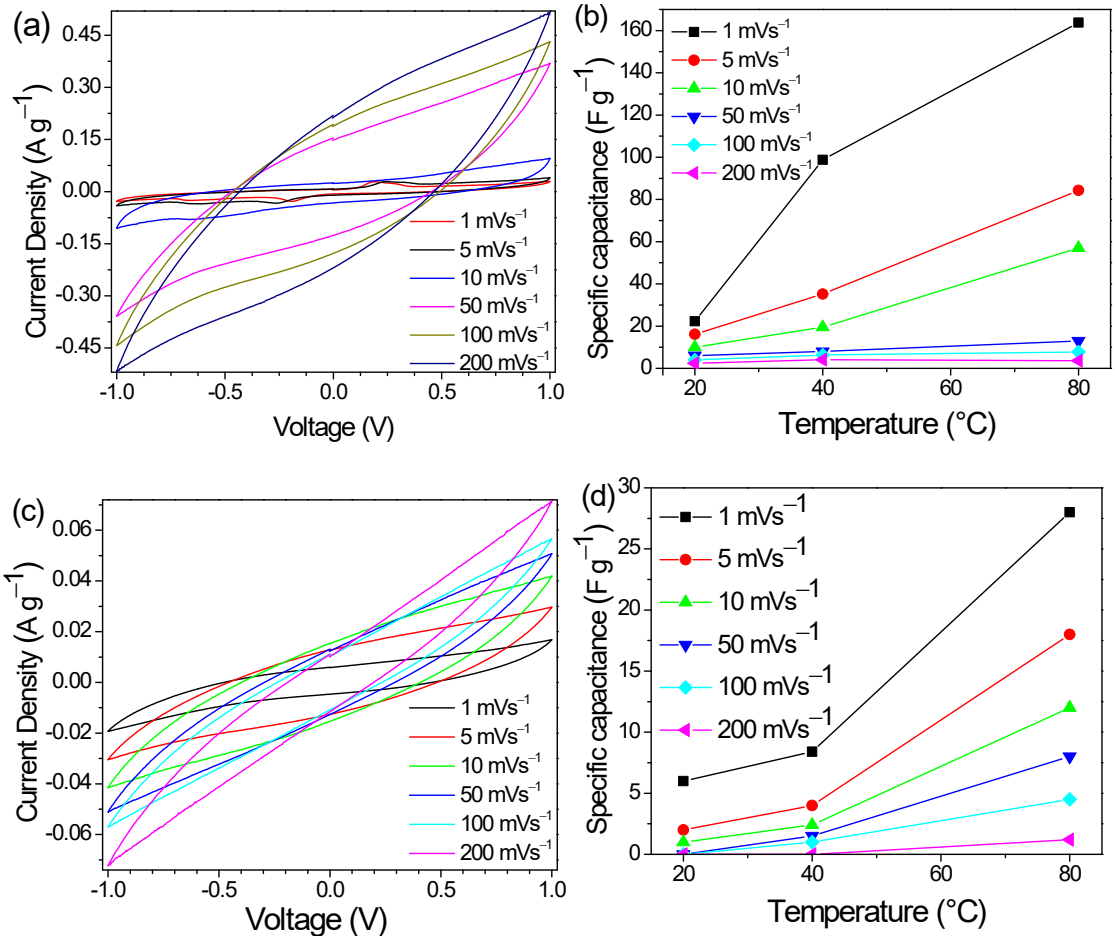


Figure S23. CVs using different scan rates at 80 °C (a and c) and specific capacitance as a function of temperature (b and d) for SCs made with [EmMPyrr][DEEP] and [EmMMorph][DEEP] electrolytes, respectively.

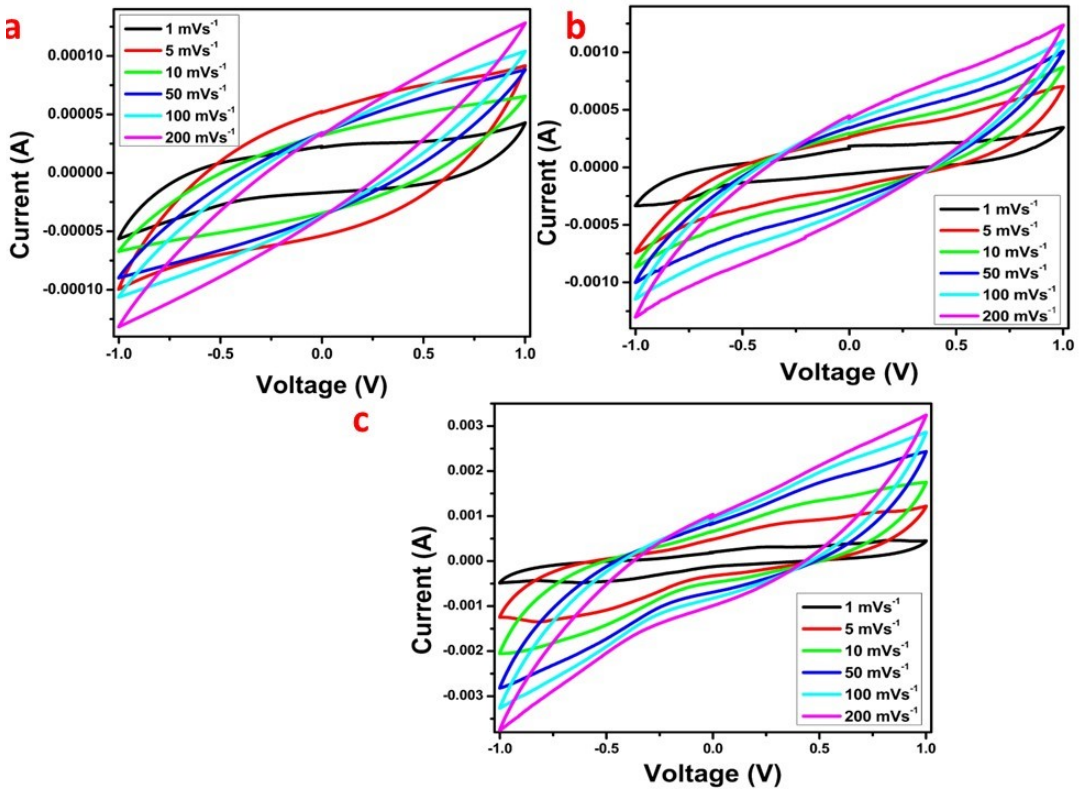


Figure S24. CVs of [EmMPyrr][DEEP] at different scan rates at: (a) -20 °C, (b) 40 °C and (c) 80 °C.

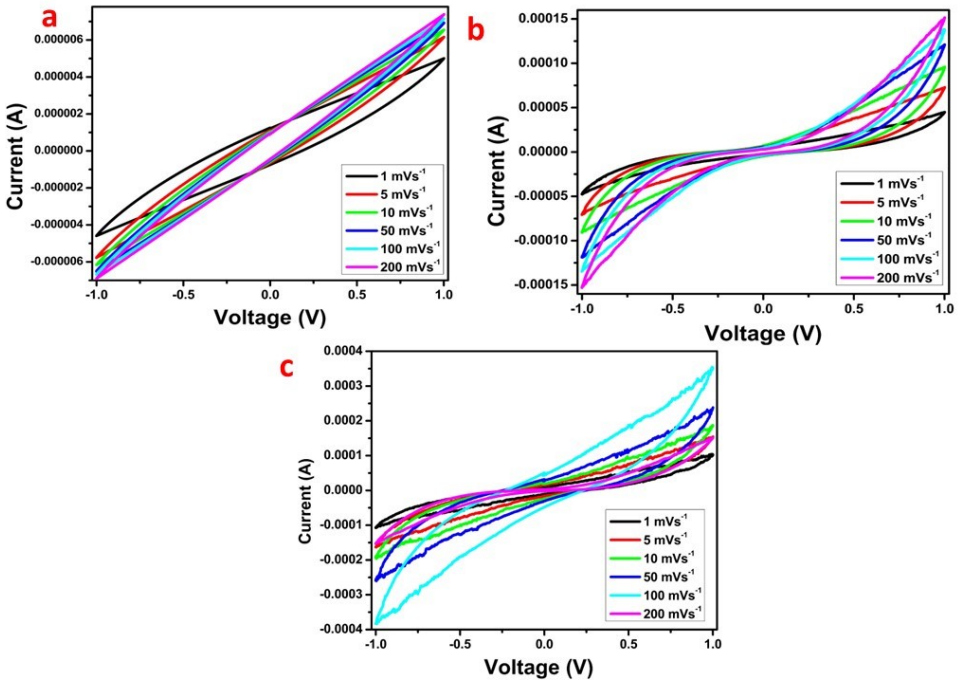


Figure S25. CVs of [EmMMorph][DEEP] at different scan rates at: (a) -20 °C, (b) 40 °C and (c) 80 °C.

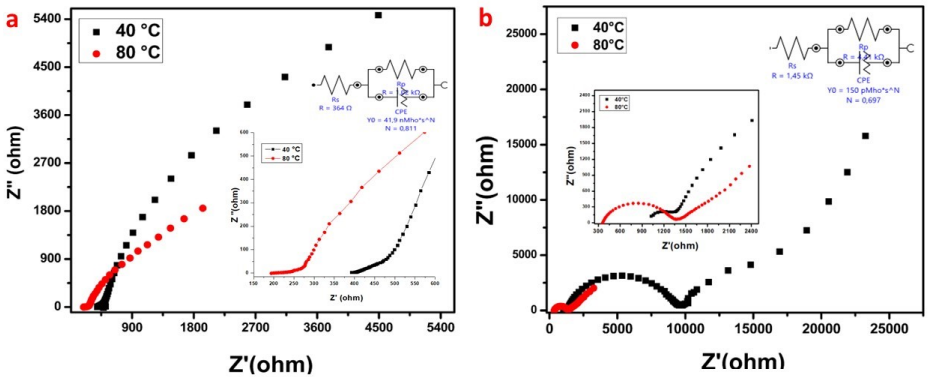


Figure S26. EIS plots at 40 °C and 80 °C, (a) [EmMPyrr][DEEP], (b) [EmMMorph][DEEP].

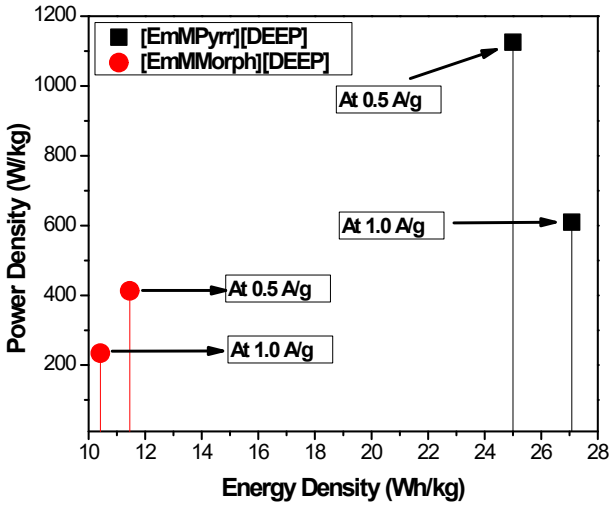


Figure S27. Ragone plot of the supercapacitors with [EmMPyrr][DEEP] and [EmMMorph][DEEP] ILs as electrolytes – all based on mass of electrodes and electrolytes.

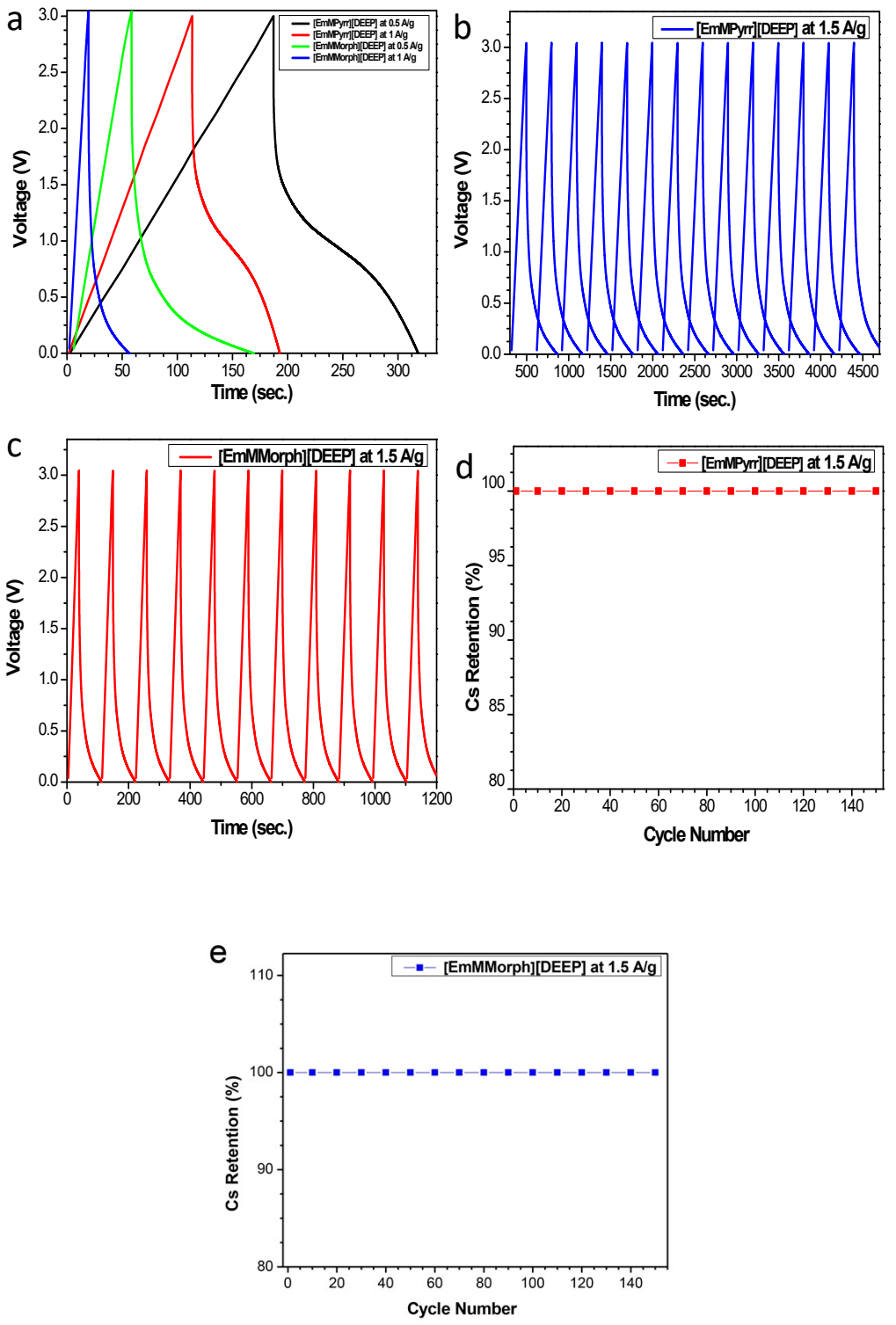


Figure S28. (a) GCD plots for [EmMPyrr][DEEP] and [EmMMorph] [DEEP], (b) and (c) cyclic stability up to 150 cycles at 1.5 A g^{-1} for [EmMPyrr][DEEP] and [EmMMorph] [DEEP], (d) capacity retention of [EmMPyrr][DEEP] and [EmMMorph] [DEEP] as function of cycling.

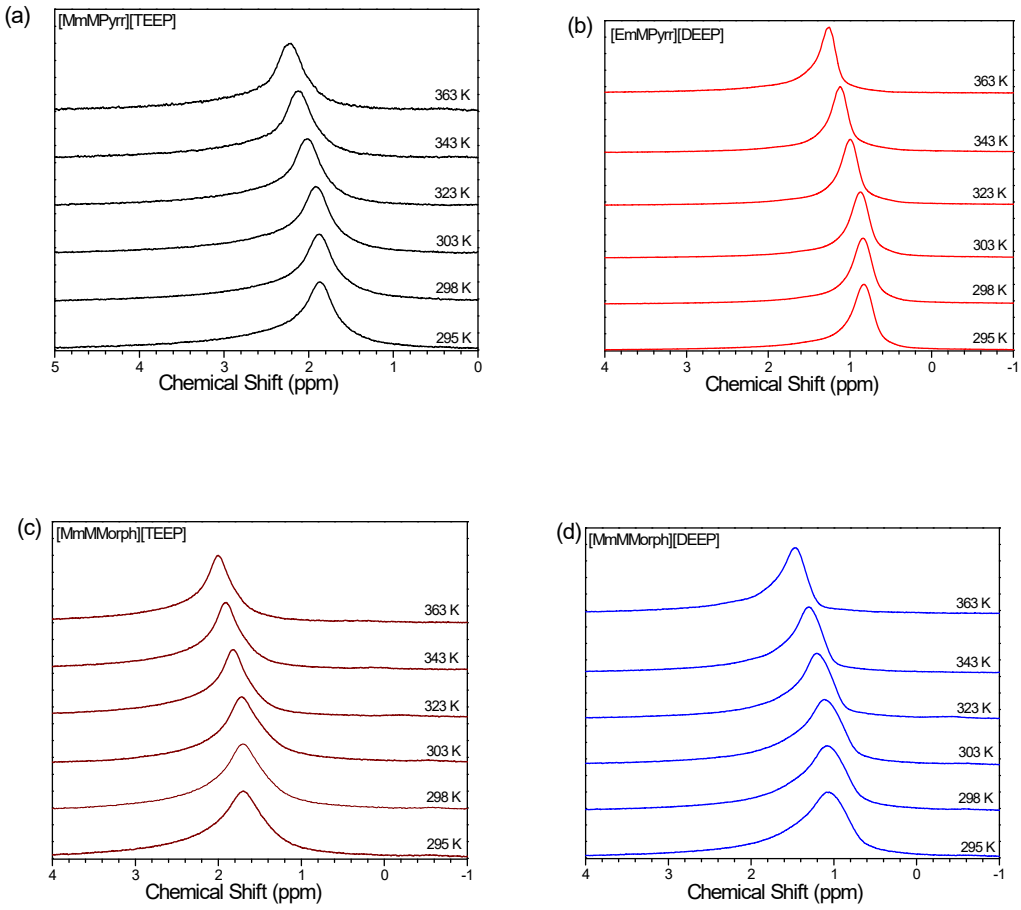


Figure S29. Temperature dependent ^{31}P NMR spectra of the ILs.

Table S1. VFT equation parameters and apparent activation energies of ionic conductivity for the neat ILs.

Ionic liquid	σ_0, m^2/s	B, K	T_0, K	E_σ, kJ/(mol)
[MmMPyrr][TEEP]	0.440	1191	149	9.9
[EmMPyrr][DEEP]	0.775	1435	133	11.9
[MmMMorph][TEEP]	0.459	1438	147	12.0
[EmMMorph][DEEP]	0.777	1586	145	13.2

Table S2. VFT equation parameters and apparent activation energy of diffusivity for the neat ILs.

Ionic liquid	Ion	$D_0 \times 10^{-9}$ m^2/s	B,K	T_0, K	E_D, kJ/(mol)
[MmMPyrr][TEEP]	anion	9.3	746	199	6.2
	cation	7.0	655	206	5.4
[EmMPyrr][DEEP]	anion	17.5	944	188	7.8
	cation	18.9	928	192	7.7
[MmMMorph][TEEP]	anion and cation	7.9	827	206	6.9
[EmMMorph][DEEP]		7.14	770	208	6.4
	anion	8.0	794	207	6.6
	cation				

Table S3. Anodic and cathodic limits, and electrochemical stability windows (ESWs) using a Pt WE and a scan rate of 1 mV/s at 20 °C. The limits are determined by using a 0.1 mA cm^{-2} cut-off current density.

Ionic liquid	Electrochemical stability		
	E_C (V *vs.* Fc/Fc^+)	E_A (V *vs.* Fc/Fc^+)	ESW
[MmMPyrr][TEEP]	−1.53	2.94	4.47
[EmMPyrr][DEEP]	−1.50	3.09	4.59
[MmMMorph][TEEP]	−1.75	3.32	5.07
[EmMMorph][DEEP]	−1.54	2.99	4.53

Table S4. Energy and Power density at 90 °C.

Energy density (E_D) and power density (P_D)	At 0.5 A g^{-1}	At 1 A g^{-1}
[EmMPyrr][DEEP]	27 Wh kg^{-1}	24 Wh kg^{-1}
	610 W kg^{-1}	1100 W kg^{-1}
[EmMMorph][DEEP]	11 Wh kg^{-1}	10 Wh kg^{-1}
	410 W kg^{-1}	230 W kg^{-1}