Electronic Supplementary Material (ESI) for RSC Advances.

Low-viscosity ether-functionalized pyrazolium ionic liquids based on dicyanamide anion: properties and application as electrolytes for lithium metal batteries

ShuminShen[a] , Shaohua Fang [a,c*] , LongQu[a] , Dong Luo [a] , Li Yang [a,b,c*], Shin-ichiHirano[b]

[a] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

[b]*Hirano Institute for Materials Innovation, Shanghai Jiao Tong University, Shanghai 200240, China*

[c]*Shanghai Electrochemical Energy Devices Research Center, Shanghai 200240, China*

*Corresponding author

Tel: +86 21 54748917; Fax: +86 21 54741297

E-mail: housefang@sjtu.edu.cn (S. Fang); liyangce@sjtu.edu.cn (L. Yang)

1 Synthesis of ether-functionalized pyrazoles

1.1 1-(2-Methoxyethyl) pyrazole (PZ2o1)

Pyrazole (0.15 mol), potassium hydroxide powder (0.3 mol) and TBAB powder (tetrabutylammonium bromide, 0.0075 mol) were sonicated with an ultrasound bath for 15 min in a 250 mL flask. 2-Chloroethyl methyl ether (0.15 mol) was added into the flask with an ice bath and the reactants were stirred at the room temperature for 24 hours. The crude product was washed by diethyl ether. The filtrate was distilled with rotary evaporation at 60 ^{o}C and then distilled under reduced pressure by using a 25 cm vigreux column. The product was collected at 49-50 ^{o}C (boiling point) when the pressure was about 3 Pa. Colorless liquid; (chloroform-d as solvent) ^{1}HNMR: δ (ppm) 7.502-7.498 (d, 1H), 7.453-7.447 (d,1H), 6.231-6.222 (t,1H), 4.294-4.268 (t, 2H), 3.737-3.710 (t, 2H), 3.302 (s, 3H).

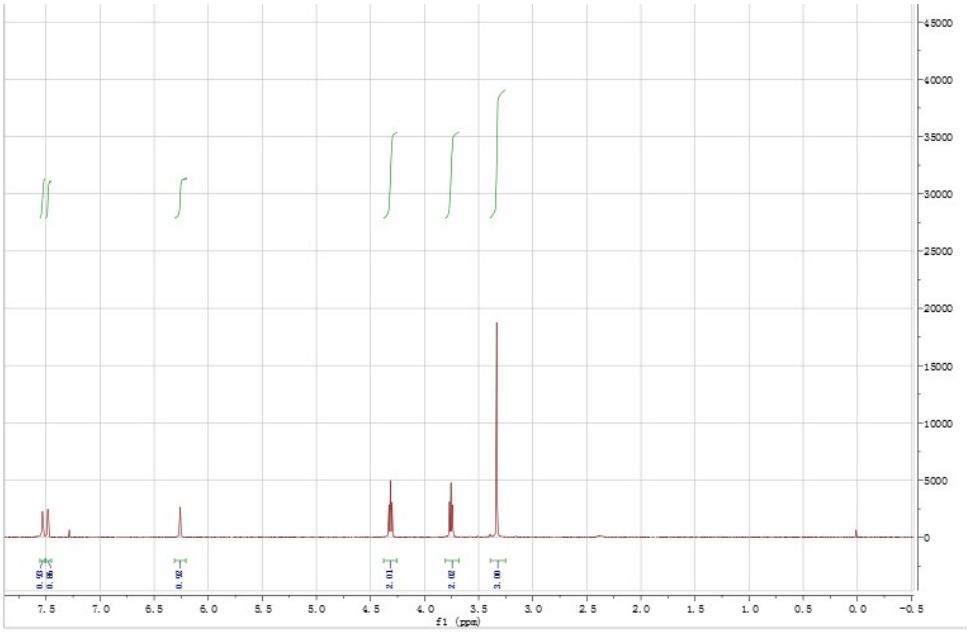

Fig. S1 ^{1}H NMR spectrum of PZ2o1

1.2 1-(2-Ethoxyethyl) pyrazole (PZ2o2)

Pyrazole (0.15 mol), potassium hydroxide powder (0.3 mol) and TBAB powder

(tetrabutylammonium bromide, 0.0075 mol) were sonicated with an ultrasound bath for 15 min in a 250 mL flask. 2-Chloroethyl ethyl ether (0.15 mol) was added into the flask with an ice bath and the reactants were stirred at the room temperature for 24 hours. The following procedures were identical to PZ2o1. At last, the product was collected at 59-60 ^{o}C (boiling point) when the pressure was about 3 Pa. Colorless liquid; (chloroform-d as solvent) ^{1}HNMR: δ (ppm) 7.538-7.514 (d, 1H), 7.511-7.489 (d, 1H), 6.268-6.235 (t, 1H), 4.348-4.281 (t, 2H), 3.819-3.750 (t, 2H), 3.503-3.418 (q, 2H), 1.197-1.134 (t, 3H).

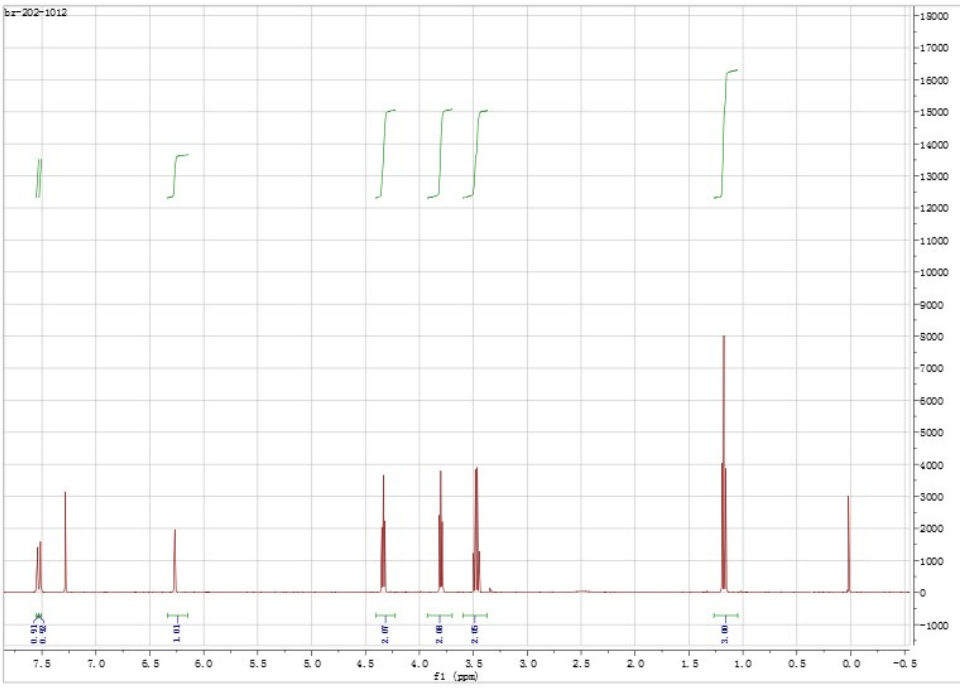

Fig. S2 ^{1}H NMR spectrum of PZ2o2

2 Synthesis procedure of ether-functionalized pyrazolium ILs

2.1 1-(2-Methoxyethyl)-2-methylpyrazolium dicyanamide (PZ2o1-1-DCA)

PZ2o1 (7g, 55.5 mmol), iodomethane (8.7g, 61.1 mmol) and acetonitrile (10 mL) were mixed in a sealed 250 mL flask, and stirred for 2 days at room temperature. After washed with diethyl ether three times, the corresponding iodide was obtained. Silver dicyanamide was precipitated after an aqueous solution of sodium dicyanamide was added to an aqueous solution of silver nitrate. The

precipitation was filtered and then washed with water. The aqueous solution of the iodide was mixed with a slightly excess of freshly prepared silver dicyanamide and stirred at 40 °C for 2 hours. The solid was filtered off and the water was removed by rotary evaporation. The crude product was dissolved in dichloromethane, and the solution stayed in a refrigerator (low than -15 °C) for 24 hours to ensurecomplete elimination of silver salts. After filtration and rotary evaporation, the clean product could be obtained. Finally, the IL was dried under high vacuum at 100 °C for more than 12 hours. Pale yellow liquid; (acetone-d_6 as solvent) ^{1}H NMR: δ (ppm) 8.558-8.478 (d, 2H), 6.957-6.889 (t, 1H), 4.942-4.863 (t, 2H), 4.410-4.350 (s, 3H), 3.953-3.881 (t, 2H), 3.401-3.331 (s, 3H). ^{13}C NMR: δ (ppm) 138.347, 137.754, 119.748, 107.423, 69.534, 58.176, 49.905, 37.063.

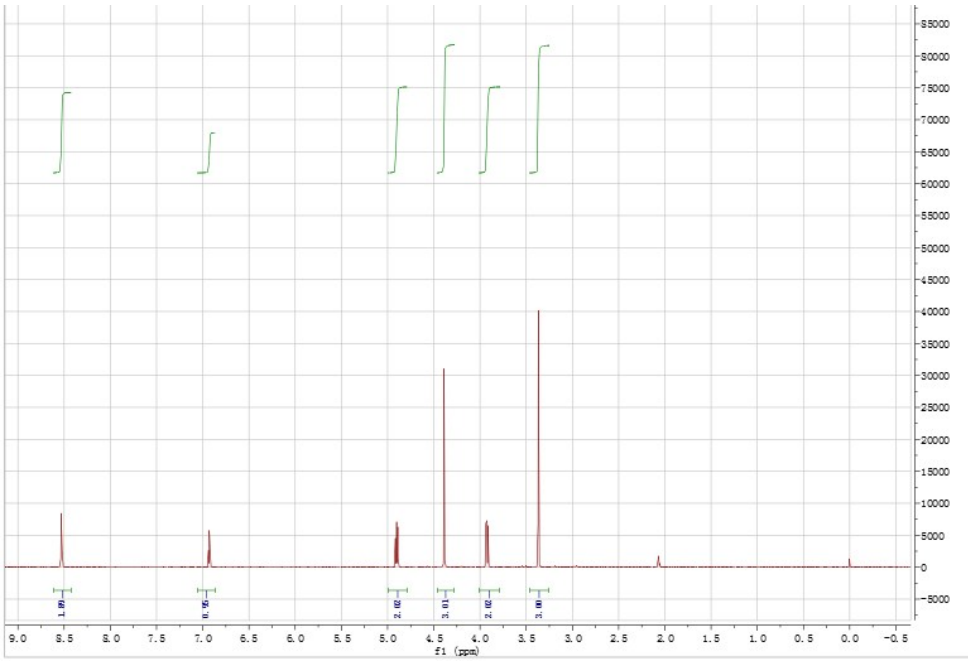

Fig. S3 ^{1}H NMR spectrum of PZ2o1-1-DCA

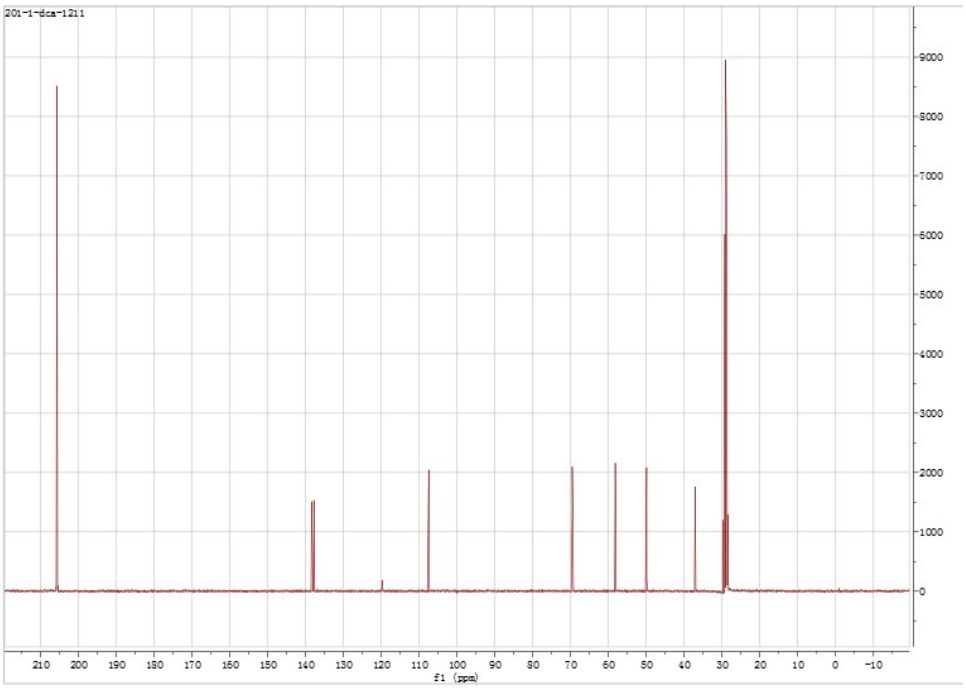

Fig. S4 ^{13}CNMR spectrum of PZ2o1-1-DCA

2.2 1-(2-Methoxyethyl)-2-ethylpyrazolium dicyanamide (PZ2o1-2-DCA)

PZ2o1 (7g, 55.5 mmol), iodoethane (9.5g, 61.1 mmol) and acetonitrile (10 mL) were mixed in a sealed 250 mL flask, and stirred for 2 days at 60 °C. The following procedures were identical to PZ2o1-1-DCA. Pale yellow liquid; (acetone-d_6 as solvent) ^{1}H NMR: δ (ppm) 8.650-8.598 (d, 1H), 8.586-8.530 (d, 1H), 7.003-6.925 (t, 1H), 4.984-4.875 (t, 2H), 4.845-4.705 (q, 2H), 3.977-3.867 (t, 2H), 4.406-3.314 (s, 3H), 1.724-1.591 (t, 3H). ^{13}C NMR: δ (ppm) 138.070, 136.682, 119.788, 107.691, 69.516, 58.171, 49.967, 45.772, 13.662.

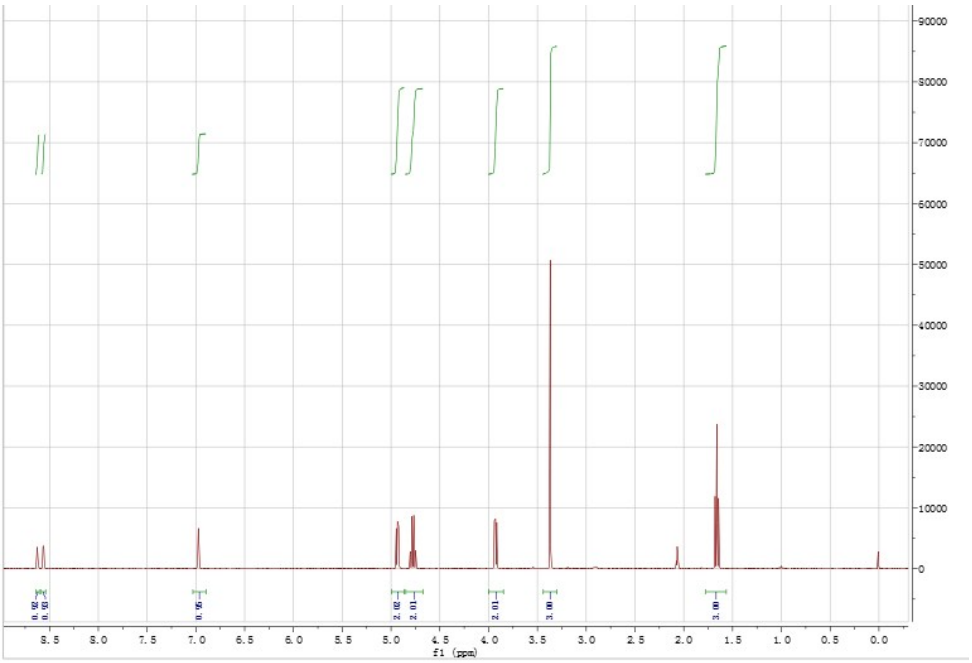

Fig. S5 ^{1}H NMR spectrum of PZ2o1-2-DCA

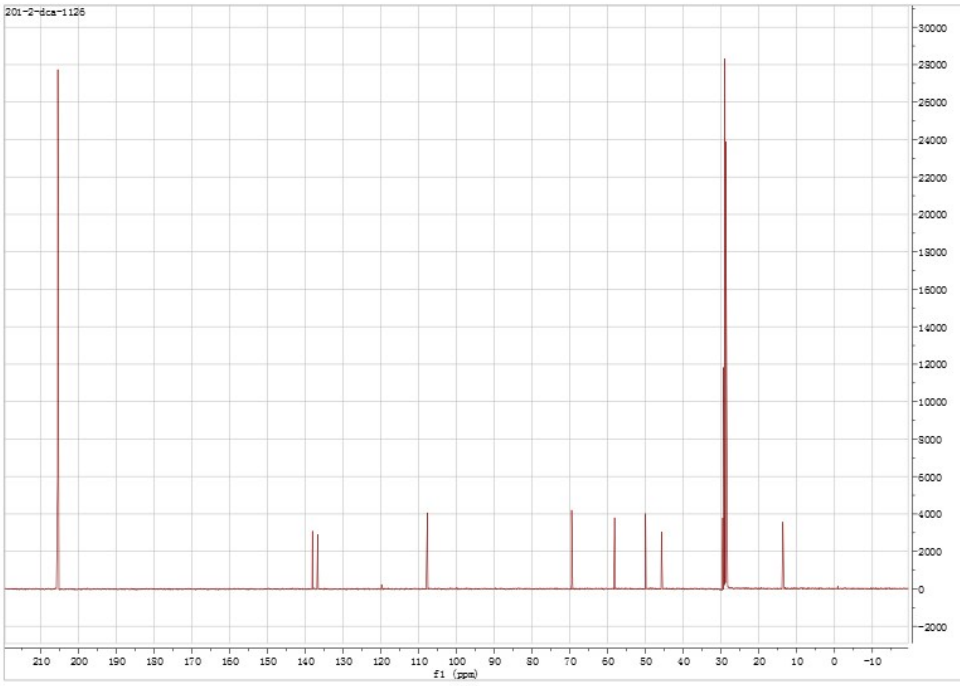

Fig. S6 ^{13}CNMR spectrum of PZ2o1-2-DCA

2.3 1-(2-Ethoxyethyl)-2-methylpyrazolium dicyanamide (PZ2o2-1-DCA)

PZ2o2 (7.8g, 55.5 mmol), iodomethane (8.7g, 61.1 mmol) and acetonitrile (10 mL) were mixed in a sealed 250 mL flask, and stirred for 2 days at room temperature. The following procedures were also identical to PZ2o1-1-DCA. Pale yellow liquid; (acetone-d_6 as solvent) ^{1}H NMR: δ (ppm)

8.578-8.495 (m, 2H), 6.952-6.890 (t, 1H), 4.944-4.819 (t, 2H), 4.444-4.330 (s, 3H), 4.009-3.878 (t, 2H), 3.610-3.443 (q, 2H), 1.179-1.036 (t, 3H). ^{13}C NMR: δ (ppm) 138.321, 137.741, 119.729, 107.413, 67.642, 66.273, 50.076, 37.097, 14.417.

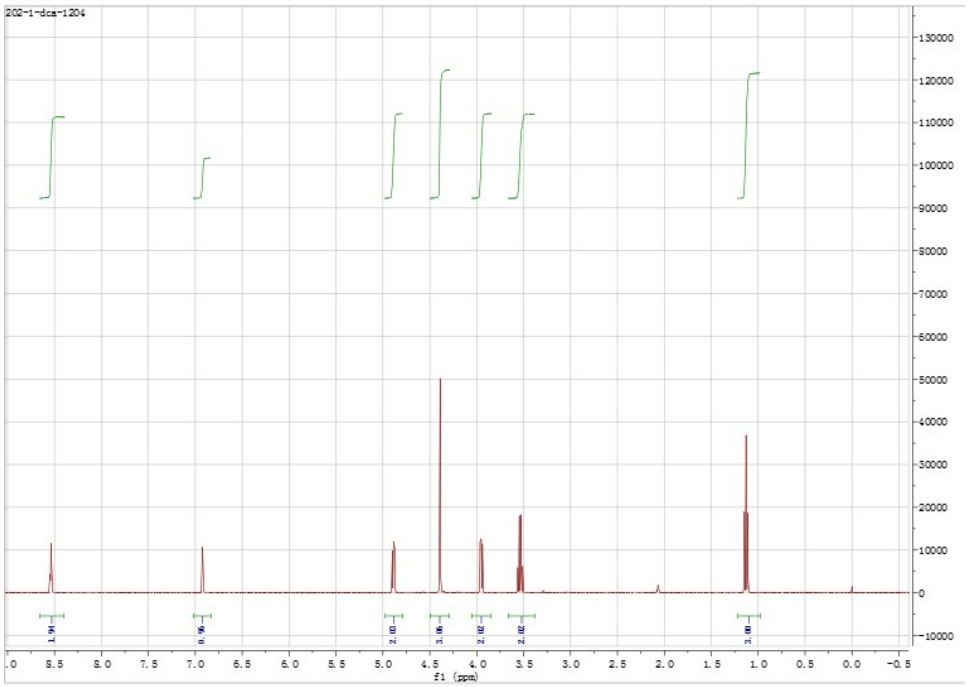

Fig. S7 ^{1}H NMR spectrum of PZ2o2-1-DCA

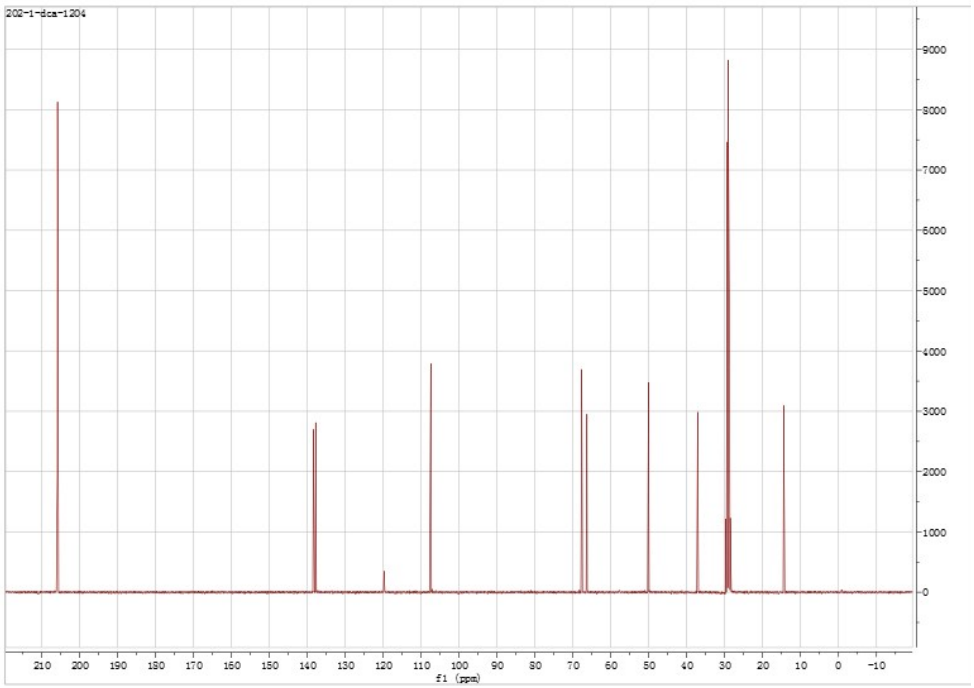

Fig. S8 ^{13}CNMR spectrum of PZ2o2-1-DCA

2.4 1-(2-Ethoxyethyl)-2-ethylpyrazolium dicyanamide (PZ2o2-2-DCA)

PZ2o2 (7.8g, 55.5 mmol), iodoethane (9.5g, 61.1 mmol) and acetonitrile (10 mL) were sealed in a 50 mL autoclave for one day at 80°C. The following procedures were identical to PZ2o1-1-DCA. Pale yellow liquid; (acetone-d_6 as solvent) ^{1}H NMR: δ (ppm) 8.630-8.596 (d, 1H), 8.581-8.545 (d,1H), 7.042-6.855 (t, 1H), 4.967-4.865 (t, 2H), 4.842-4.699 (q, 2H), 4.017-3.869 (t, 2H), 3.614-3.471 (q, 2H), 1.721-1.567 (t, 3H), 1.192-1.039 (t, 3H). ^{13}C NMR: δ (ppm) 138.034, 136.631, 119.762, 107.694, 67.587, 66.276, 50.136, 45.782, 14.390.

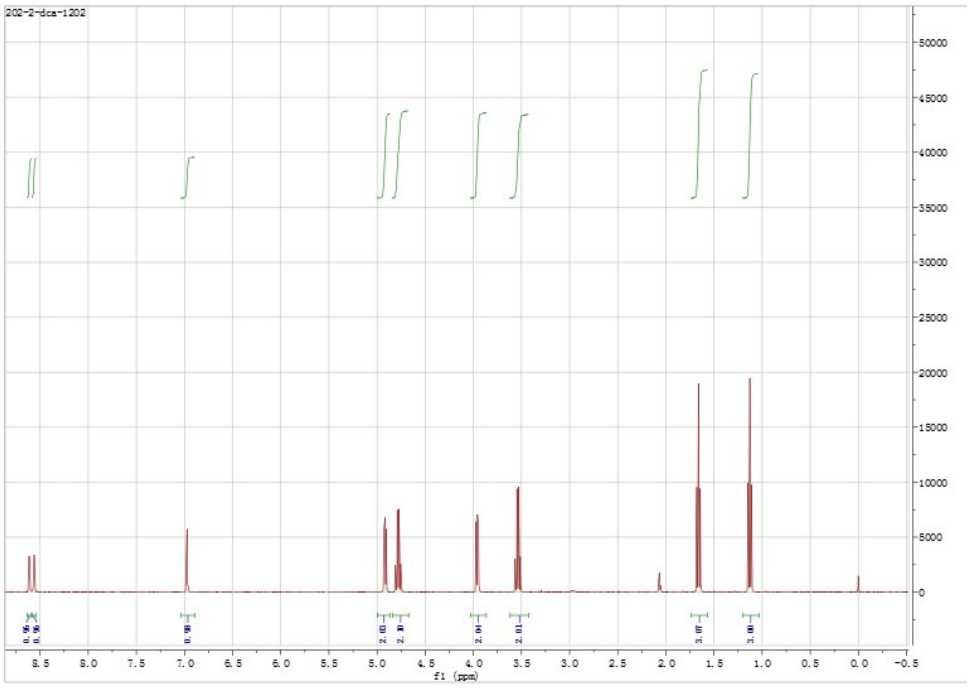

Fig. S9 ^{1}H NMR spectrum of PZ2o2-2-DCA

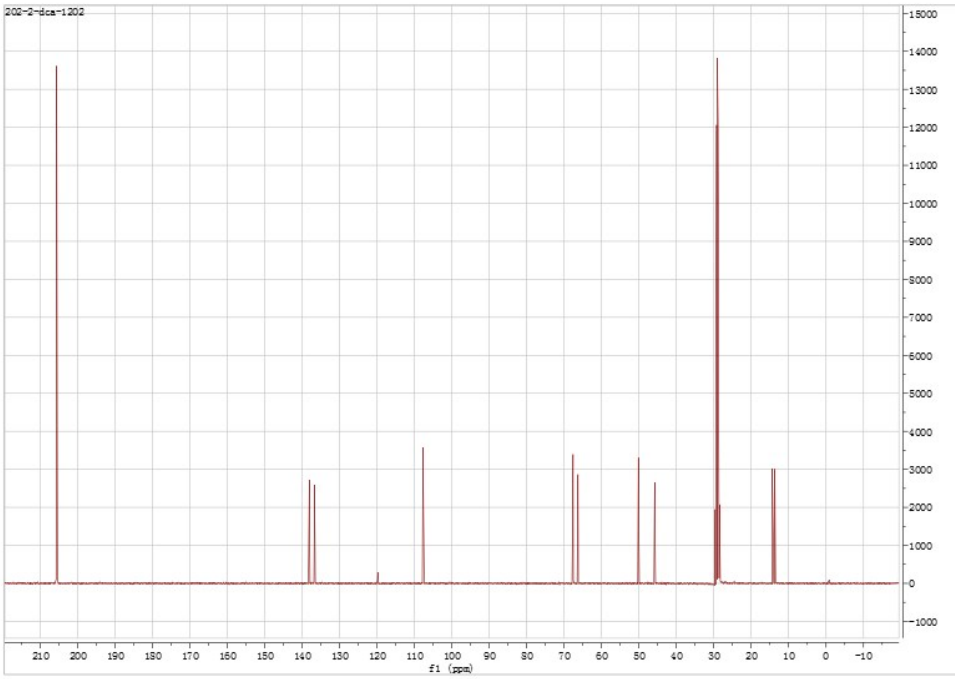

Fig. S10 ^{13}CNMR spectrum of PZ2o2-2-DCA

2.5 1-(2-Ethoxyethyl)-2-ethylpyrazolium bis(trifluoromethanesulfonyl)imide (PZ2o2-2-TFSI)

The corresponding iodide was obtained according to PZ2o2-2-DCA. The iodide and the same molar amount of LiTFSI were dissolved in deionized water, and then stirred for 24 hours at room temperature. The crude IL was mixed with dichloromethane and washed with deionized water for three times until no residual halide anions could be detected by $AgNO_3$ solution. The solvent was removed by rotary evaporation. The IL was dried under high vacuum at 105^{o}C for 24 hours. Colorless liquid; (chloroform-d as solvent) ^{1}H NMR: δ (ppm) 8.207-8.156 (d, 1H), 8.149-8.098 (d, 1H), 6.778-6.718 (t, 1H), 4.678-4.615 (t, 2H), 4.609-4.516 (q, 2H), 3.849-3.778 (t, 2H), 3.548-3.434 (q, 2H), 1.650-1.570 (t, 3H), 1.185-1.100 (t, 3H); ^{13}C NMR: δ (ppm) 137.656, 135.964, 124.515-114.991, 108.064, 67.643, 66.924, 50.383, 45.970, 14.754, 13.871.

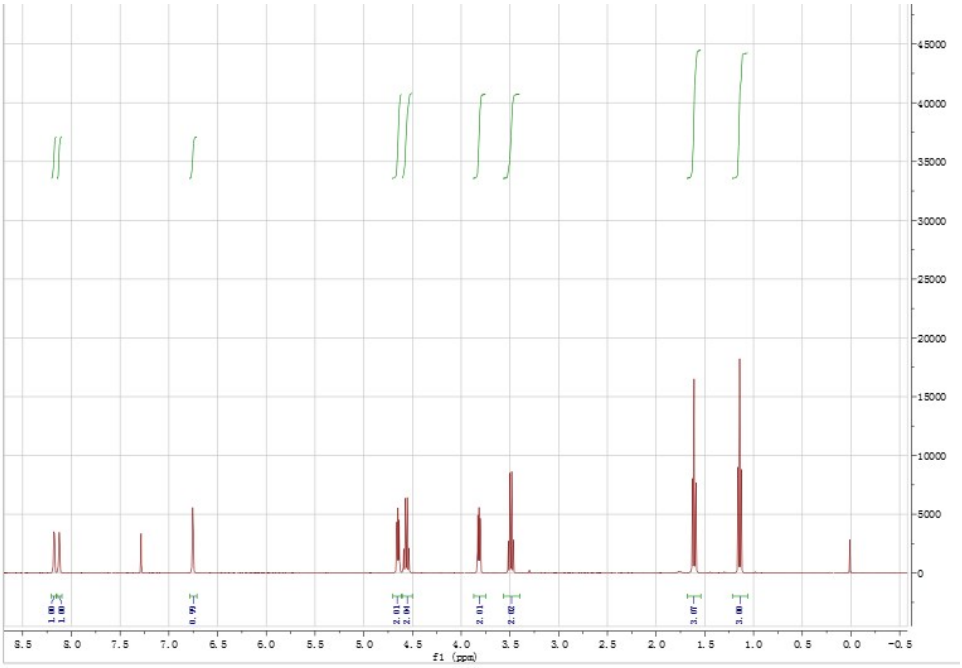

Fig. S11 ^{1}H NMR spectrum of PZ2o2-2-TFSI

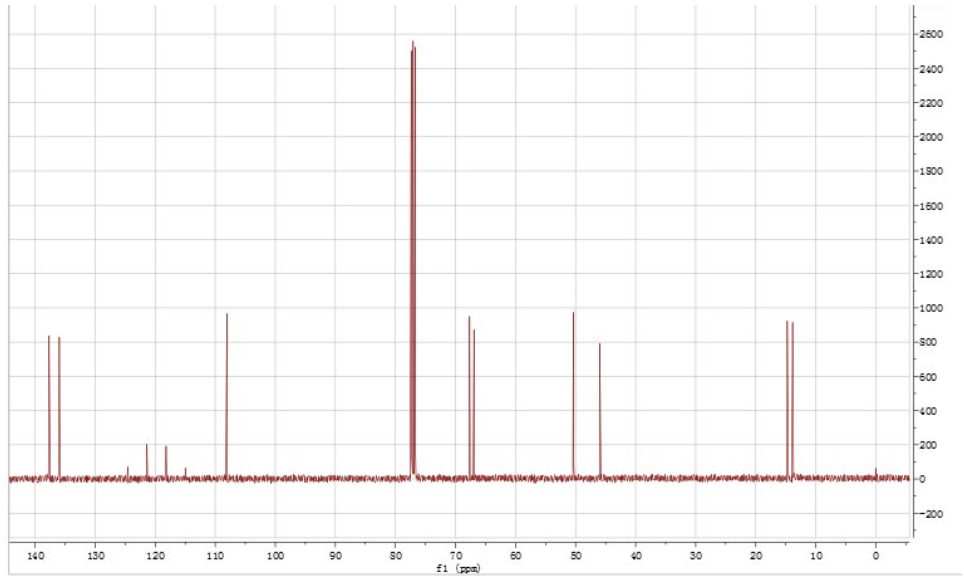

Fig. S12 ^{13}CNMR spectrum of PZ2o2-2-TFSI

Table S1 Conductivities of PZ2o1-1-DCA and PZ2o1-2-DCA electrolytes at different temperatures

T / °C	Conductivity / mS cm^{-1}	
	PZ2o1-1-DCA electrolyte	PZ2o1-2-DCA electrolyte
25	5.01	5.81
20	4.35	5.29
10	2.89	3.91
0	1.59	2.47
-10	0.76	1.22
-20	0.22	0.37