Electronic supplementary materials *Mendeleev Commun.*, 2027, **37**, just accepted

Systematic physicochemical profiling of ether-based electrolytes for sodium-ion batteries

Irina V. Kutovaya, Alena I. Komayko, Mikhail D. Agapkin, Arina A. Elagina, Rustem R. Gamirov, Stanislav S. Fedotov and Olga I. Shmatova

Experimental section

Reagents and materials

Tetrahydrofuran (>99.8%, Rushim), 1,2-dimethoxyethane (>99.0%, Chemical Line), 1,2-dimethoxypropane (>99.0%, LeapChem), 1,3-dimethoxypropane (>99.0%, LeapChem), 1,2-diethoxyethane (>99.0%, LeapChem), dimethyl diethyleneglycol (>99.0%, Chemical Line) and dimethyl tetraethyleneglycol (>99.0%, Sigma-Aldrich) were dried by distillation with sodium and diphenylketone. Sodium hydride (60% in mineral oil, Sigma-Aldrich); ethyl iodide (>99.0%, Rushim); 2-methoxyethanol (>99.5%, Himmed); 2-methoxypropan-1-ol (>99.5%, Rushim); sodium metal (>99.9%, Gelon Lib); sodium hexafluorophosphate (99%, Kishida); sodium tetrafluoroborate (99.0%, Sigma-Aldrich).

Synthesis of electrolyte solvents

1D NMR ^{1}H and ^{13}C spectra were registered using a Bruker Fourier 300 (300 MHz/54m) spectrometer. Chemical shifts of the tetramethylsilane (δ = 0 ppm) and $CDCl_3$ (δ = 77 ppm) were used as a reference data for ^{1}H and ^{13}C NMR spectroscopic data.

Synthesis of 1-Methoxy-2-ethoxyethane EME: To a solution of 2-methoxyethan-1-ol (0.660 mol, 52.0 mL) in diglyme (340 mL), under stirring, a 60% suspension of sodium hydride in mineral oil (0.670 mol, 25.9 g) was added portionwise, maintaining the temperature at 0 – 5°C using an ice bath. Upon completion of sodium hydride addition, ethyl iodide (0.670 mol, 57.0 mL) was added dropwise to the cooled suspension. The reaction mixture was then warmed to room temperature, stirred for 2 hours, and subsequently heated at 40°C overnight. After completion of the reaction, the mixture was cooled to room temperature and the resulting precipitate was filtered off. The desired product was distilled from the mother liquor at atmospheric pressure in 69% yield (0.455 mol, 47.4 g), followed by further purification with sodium and benzophenone, and subsequent distillation.

1-Methoxy-2-ethoxyethane: colorless liquid, bp 100–101°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (t, 3H, CH_3, *J 7.0 Hz*), 3.29 (s, 3H, OCH_3), 3.40–3.50 (m, 6H, $3CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 58.8, 66.4, 69.5, 71.8.

Synthesis of 1-Ethoxy-2-methoxypropane EMP: To a solution of 2-methoxypropan-1-ol (0.510 mol, 50.0 mL) in diglyme (350 mL), under stirring, a 60% suspension of sodium hydride in mineral oil (0.775 mol, 31.0 g) was added portionwise, maintaining the temperature at 0–5°C using an ice bath. Upon completion of sodium hydride addition, ethyl iodide (0.769 mol, 61.8 mL) was added dropwise to the cooled suspension. The reaction mixture was then warmed to room temperature, stirred for 2 hours, and subsequently heated at 40°C overnight. After completion of the reaction, the mixture was cooled to room temperature and the resulting precipitate was filtered off. The desired product was distilled from the

mother liquor at atmospheric pressure in 23% yield (0.117 mol, 13.8 g), followed by further purification via reflux with sodium and benzophenone, and subsequent distillation.

1-Ethoxy-2-methoxypropane: colorless liquid, bp 106–108°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05–1.14 (m, 6H, $2CH_3$), 3.21–3.34 (m, 5H, OCH_3 + CH_2), 3.43–3.55 (m, 3H, CH + CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 16.9, 59.0, 64.1, 73.8, 76.5.

Synthesis of 1,2-Diethoxypropane DEP: To a solution of propan-1,2-diol (0.410 mol, 31.7 mL) in diglyme (350 mL), under stirring, a 60% suspension of sodium hydride in mineral oil (1.025 mol, 41.0 g) was added portionwise, maintaining the temperature at 0–5°C using an ice bath. Upon completion of sodium hydride addition, the reaction mixture was stirred overnight at room temperature. Subsequently, ethyl iodide (1.025 mol, 82.4 mL) was added dropwise to the cooled suspension. The reaction mixture was then warmed to room temperature, stirred for 2 hours, and subsequently heated at 40°C overnight. After completion of the reaction, the mixture was cooled to room temperature and the resulting precipitate was filtered off. The desired product was distilled from the mother liquor at atmospheric pressure in 35% yield (0.144 mol, 18.9 g), followed by further drying with sodium and benzophenone, and subsequent distillation.

1,2-Diethoxypropane: colorless liquid, bp 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13–1.21 (m, 9H, $3CH_3$), 3.20–3.63 (m, 7H, $3CH_2$ + CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ 15.1, 15.6, 17.3, 64.3, 66.7, 74.1, 75.5. NMR spectra are shown in Figures S5 and S6.

Materials preparation

Anode materials: Metal foils of Bi and Pb were evaporated atop Al/C foils in a high vacuum ($2 \cdot 10^{-5}$ mbar) evaporation chamber installed inside MBraun nitrogen glovebox. The evaporation technique was provided from thermoresistive source with Tungsten boat. The deposition rate was in the range 12-17 Å/s, thickness was varied to obtain different capacities per area. The areal capacity loading was approximately 1 mAh cm^{-2}. The preparation and characterisation of all-metal Bi and Pb anodes were described previously [S1].

Electrolytes characterization

DOSY NMR: Diffusion-ordered NMR spectroscopy experiments were performed on Fourier-transform Avance III-400 WB NMR spectrometers. Proton (^{1}H) and sodium cation (^{23}Na) diffusion coefficients were measured using an Avance III-400 WB spectrometer equipped with a pulsed magnetic field gradient probe. The maximum amplitude of the magnetic field gradient pulse was 10 T/m. ^{1}H and ^{23}Na NMR spectra were recorded at frequencies of 400.22 MHz and 52 MHz, respectively. The stimulated echo pulse sequence was employed for diffusion coefficient measurements. For DOSY NMR analysis of the electrolytes, two sets of samples were prepared: 1 M $NaPF_6$ in an ether-based solvent, and the pure ether solvent without salt. All samples contained 10 vol.% toluene as a non-solvating internal reference standard, along with an external C_6D_6 standard.

Viscosimetry: Viscosity measurements were conducted at 25°C using an Electro Magnetically Spinning Viscosimeter EMS-1000 by Kyoto Electronics Manufacturing Co. Ltd. Typically, the liquid sample volume was 0.3 cm^3.

Ionic conductivity: For ionic conductivity measurements, a two-electrode pressurized cell with a volume of 2.65 mL was used; it consists of two stainless steel cylinders: one features a central cavity, and the

other has a cylindrical protrusion designed to fit precisely into this cavity. The metal cylinders are electrically insulated by a Teflon spacer, leaving two disc-shaped electrode-electrolyte contact surfaces, each with an area of 1.77 cm^2, separated by a distance of 0.7 cm. A free volume between the two Teflon spacers is provided to accommodate the electrolyte. The cell was cooled linearly over 30 minutes in a climate chamber (PRO KTVH -60/180 - 120). Upon reaching the target temperature, the cell was held isothermally for an additional 30 minutes. Impedance measurements were performed using electrochemical impedance spectroscopy (EIS) at a signal frequency of 100 kHz and an AC voltage amplitude of 5 mV, employing potentiostat/galvanostat Elins R-45X.

Dielectric constant: Measurements were performed using a broadband dielectric spectrometer (NovoControl Technologies GmbH, Germany) at room temperature (T = 20°C) over a frequency range of 0.1 Hz to 100 kHz, in a cell standardized with air and water (electrode radius R = 1 cm, electrode spacing d = 50 μm).

Electrochemical measurements

Galvanostatic tests: Measurements were conducted in coin-type two-electrode CR2032 cells. The cells were assembled in an Ar-filled glovebox (MBraun, $p(O_2)$ = 0.1 ppm, $p(H_2O)$ = 0.1 ppm). The electrolytes were prepared by dissolving $NaPF_6$ in the corresponding solvent to reach 1M concentration. Electrolyte preparation was also carried out in an Ar-filled glovebox. Combination of a borosilicate glass (GF/A Whatman) separator and a polypropylene (Tob New Energy, China) film was used. Cells testing was done using BTS4000-5V50mA Battery Testing System (Neware). The long-term testing was performed via next cycling conditions: 0.1C rate for the first three cycles, 0.5C for the next 20 cycles and 1C rate for the remainder. The operational voltage windows were 0.3–1.0 V for Na||Bi and 0.05–1.0 V for Na||Pb versus Na^+/Na. The 1C rates corresponded to 385 and 485 mA g^{-1} for Bi and Pb, respectively.

Linear-sweep voltammetry: Na||steel cells were assembled in a two-electrode configuration within CR2032 coin cell housings (Xiamen Tob New Energy Technology Co.) using polypropylene separators (25 μm thickness, Xiamen Tob New Energy Technology Co.). All cells were assembled inside an argon-filled glovebox (MBraun, H_2O < 0.1 ppm, O_2 < 0.1 ppm). Electrochemical measurements were performed using a Corrtest CS310X potentiostat/galvanostat using open-circuit voltage at a scan rate of 0.1 $mV \cdot s^-$ up to potential limits of 6 V and 0 V versus Na^+/Na. The investigated electrolyte formulations consisted of 1 M $NaPF_6$ dissolved in the following solvents: 1,3-DMP, THF, DiG, DEE, EME, EMP, 1,2-DMP, and DME.

Overpotential: Symmetric Na||Na cells were assembled in a two-electrode configuration within CR2032 coin cell housings (Xiamen Tob New Energy Technology Co.) using polypropylene separators (25 μm thickness, Xiamen Tob New Energy Technology Co.). All cells were assembled inside an argon-filled glovebox (Mbraun, H_2O < 0.1 ppm, O_2 < 0.1 ppm). Electrochemical measurements were performed using a Corrtest CS310X potentiostat/galvanostat.

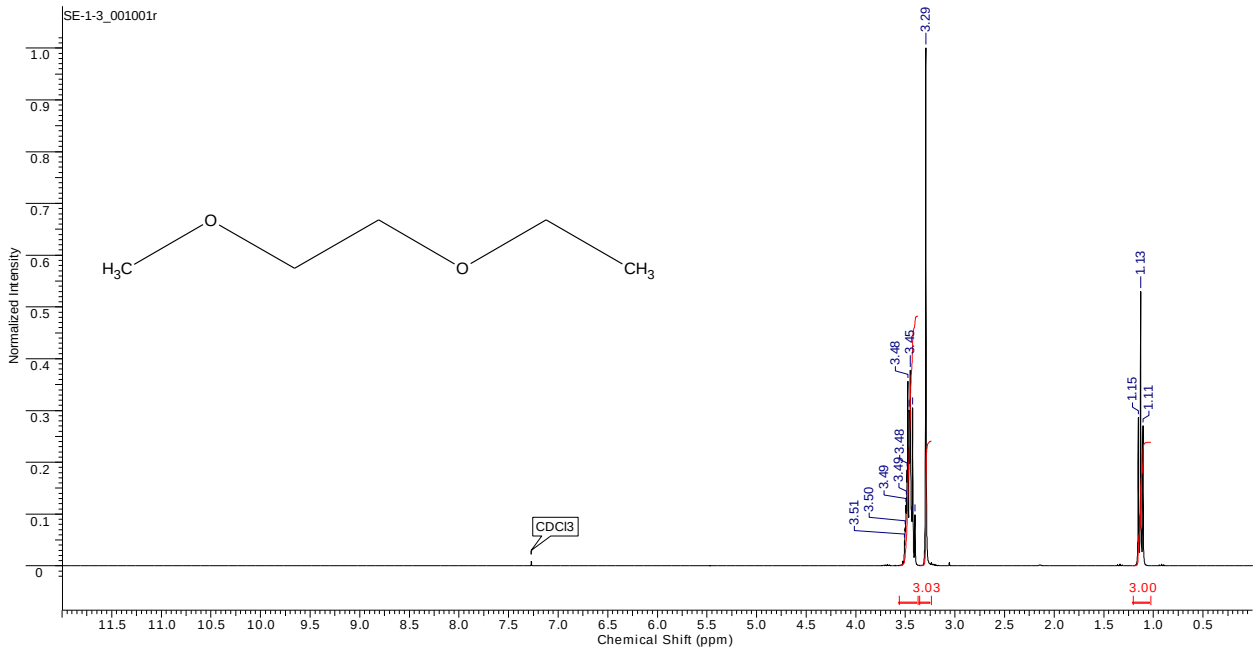


Figure S1. ^{1}H NMR spectra of EME.

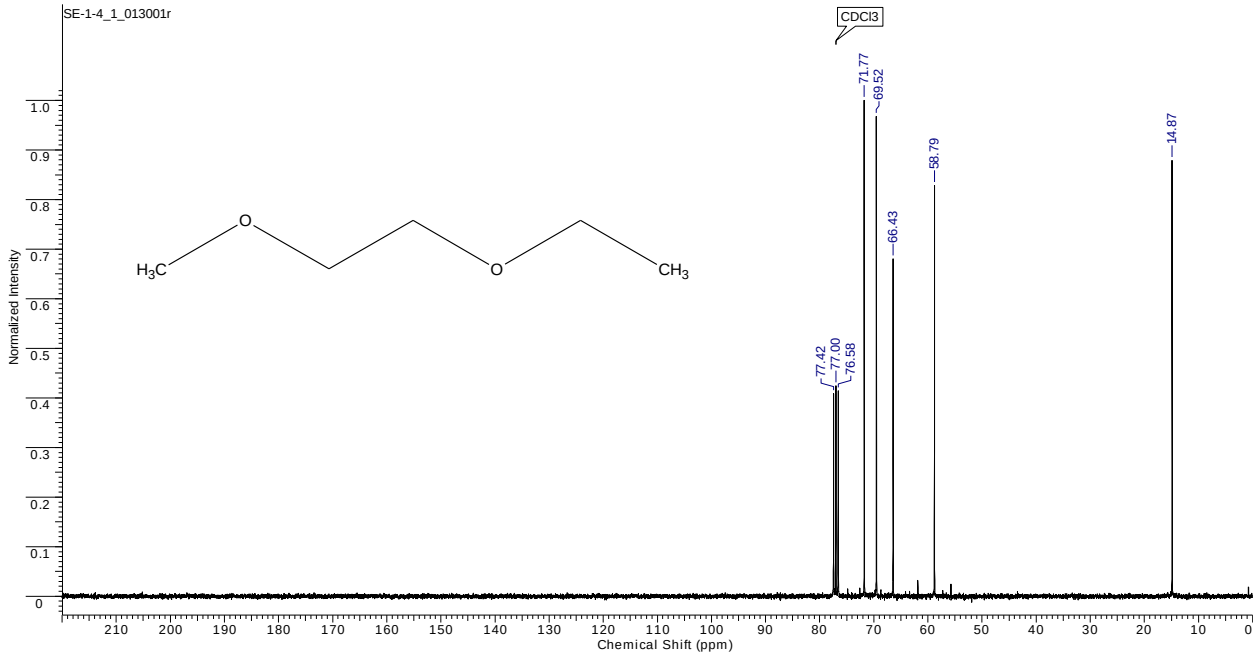


Figure S2. ^{13}C NMR spectra of EME.

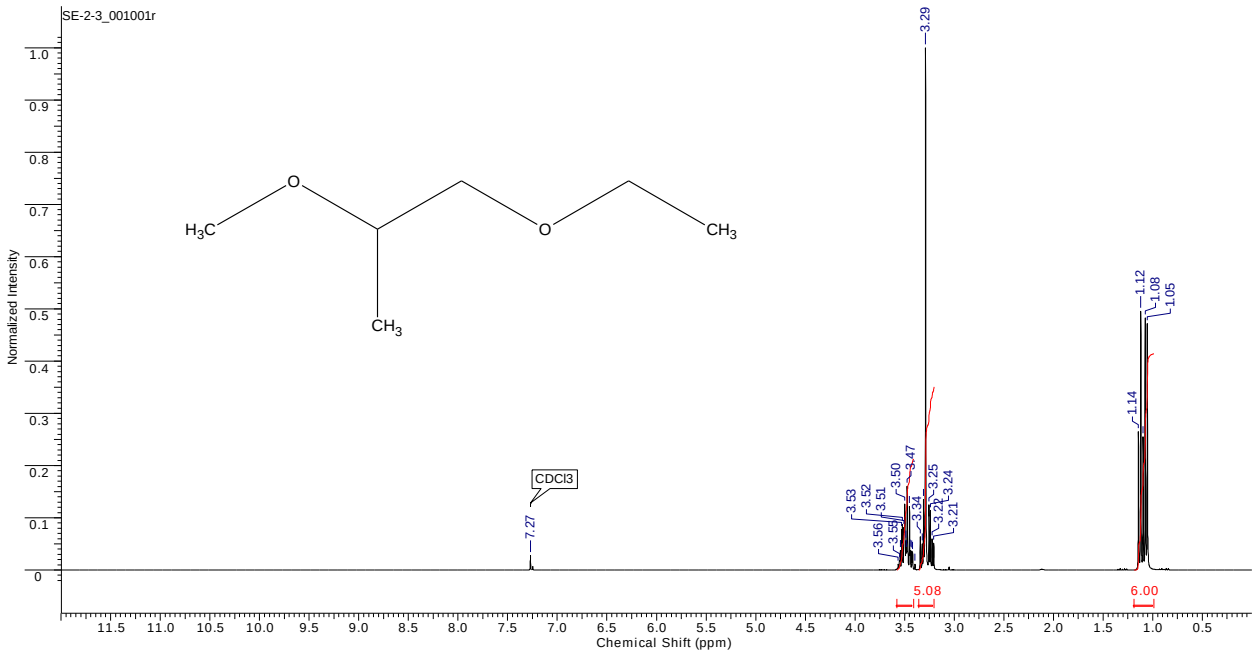


Figure S3. ^{1}H NMR spectra of EMP.

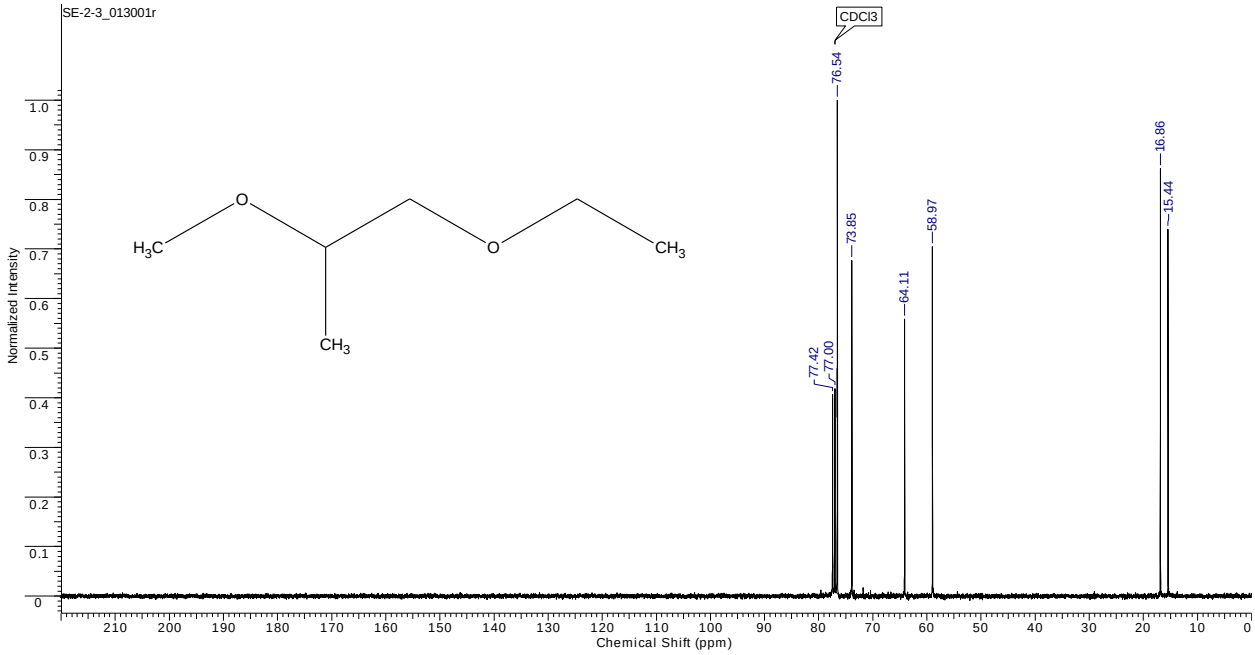


Figure S4. ^{13}C NMR spectra of EMP.

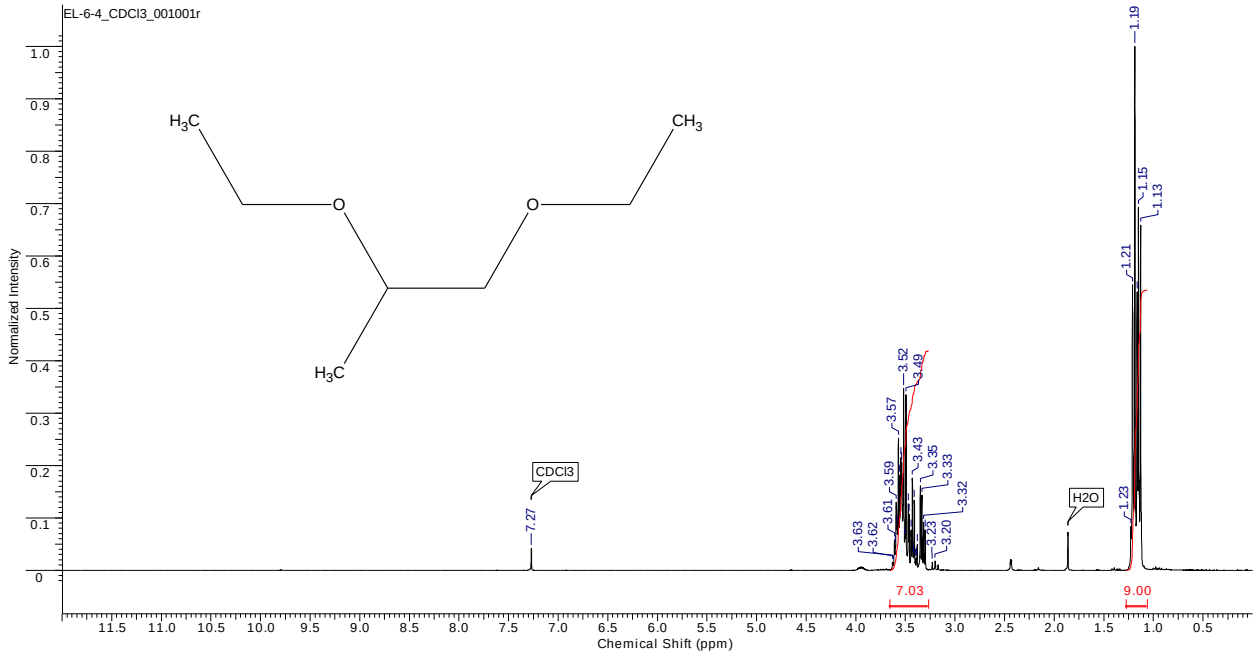


Figure S5. ^{1}H NMR spectra of DEP.

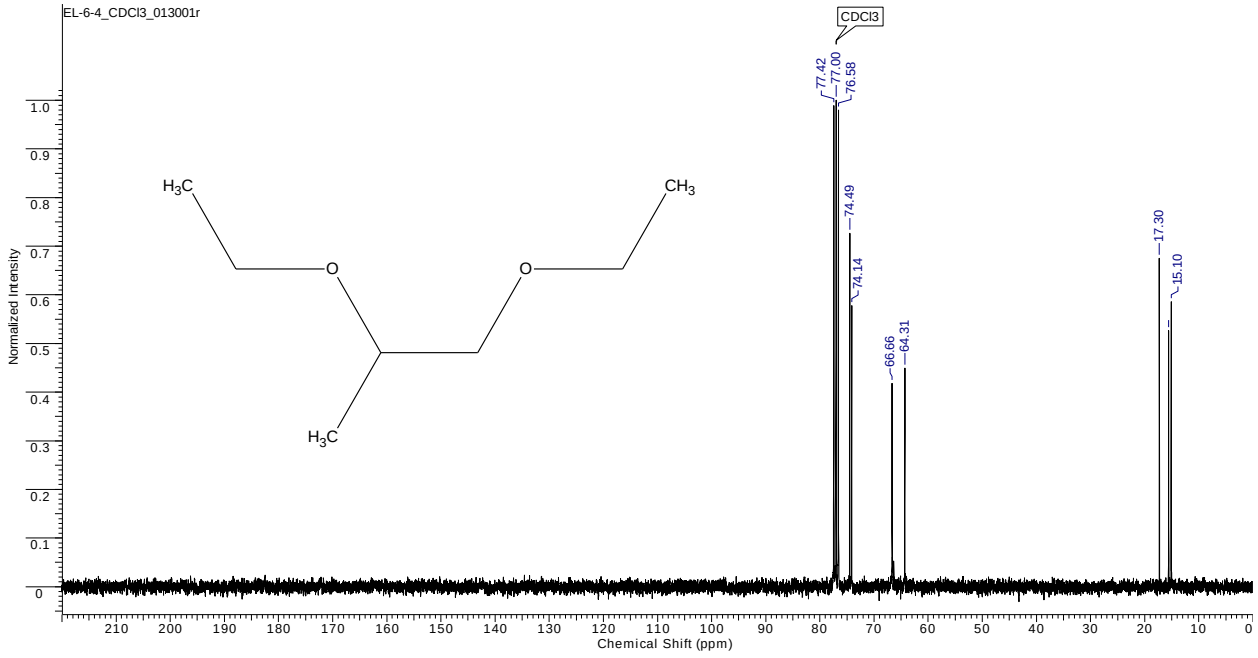
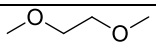
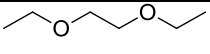
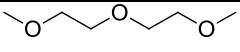


Figure S6. ^{13}C NMR spectra of DEP.

Table S1 – Physical properties of used ether solvents.

Abbreviation	***Structure***	***T_{bp}, °C***	***Viscosity, cP***	***Density, g/cm^3***	***Dielectric constant at 25°C***
DME		85	0.46	0.868	7.2
DEE		122	0.65	0.839	5.0
DiG		163	1.10	0.937	7.3

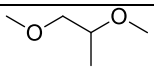
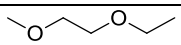
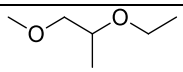
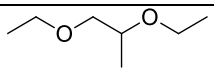
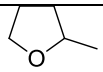
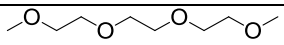
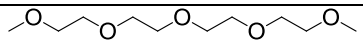
1,2-DMP		92	0.57	0.855	5.8
1,3-DMP		102	0.59	0.841	5.1
EME		101	0.60	0.846	5.9
EMP		108	0.55	0.840	6.8
DEP		132	1.01	0.830	3.9
THF		66	0.36	0.887	7.6
MeTHF		78	0.46	0.854	7.0
TriG		216	2.18	0.986	7.5
TeG		275	3.74	1.010	7.7
DOL		76	0.59	1.060	7.1
DON		101	1.18	1.03	2.2

Table S2 – Diffusion coefficients measured by DOSY NMR, coordination coefficient and Na^+ coordination number.

Sample	***$D_{ether}\times10^{-9}$, m^2/s***	***$D_{Na+}\times10^{-9}$, m^2/s***	***$D_{toluene}\times10^{-9}$, m^2/s***	***Coordination coefficient α_{ether}***	***Coordination number Na_{ether}***
1 M $NaPF_6$ DiG	0.482	0.251	0.656	0.28	**1.90**
DiG	1.100	-	1.260	-	-
1 M $NaPF_6$ DME	1.255	0.545	1.395	0.26	**2.39**
DME	2.710	-	2.520	-	-
1 M $NaPF_6$ DEE	1.175	0.150	0.843	0.23	**1.64**
DEE	0.181	-	2.025	-	-
1 M $NaPF_6$ 1,2-DMP	2.330	0.390	2.490	0.24	**1.88**
1,2-DMP	0.953	-	1.210	-	-
1 M $NaPF_6$ 1,3-DMP	1.040	0.375	1.285	0.20	**1.65**

1,3-DMP	2.080	-	2.210	-	-
1 M $NaPF_6$ EME	0.932	0.386	1.210	0.278	**2.23**
EME	2.190	-	2.320	-	-
1 M $NaPF_6$ EMP	0.801	0.263	1.235	0.334	**2.29**
EMP	1.960	-	2.260	-	-
1 M $NaPF_6$ THF	1.750	0.443	1.225	0.332	**3.04**
THF	2.625	-	2.315	-	-

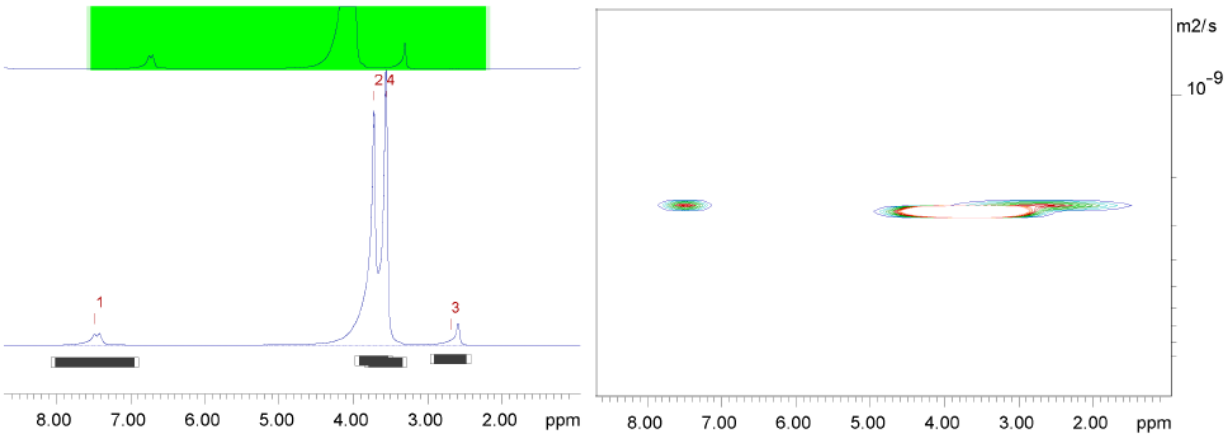


Figure S7. DOSY NMR ^1H (sample DiG with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

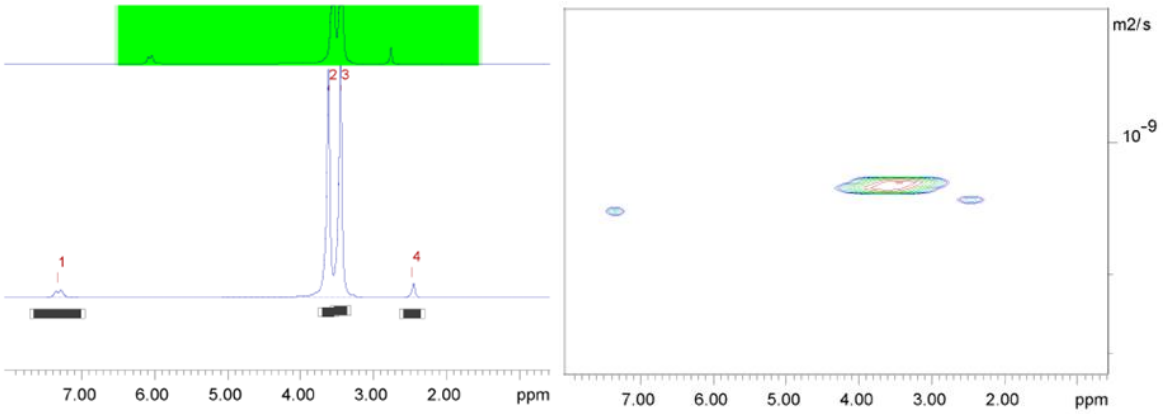


Figure S8. DOSY NMR ^1H (sample DOSY 1M $NaPF_6$ DiG with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

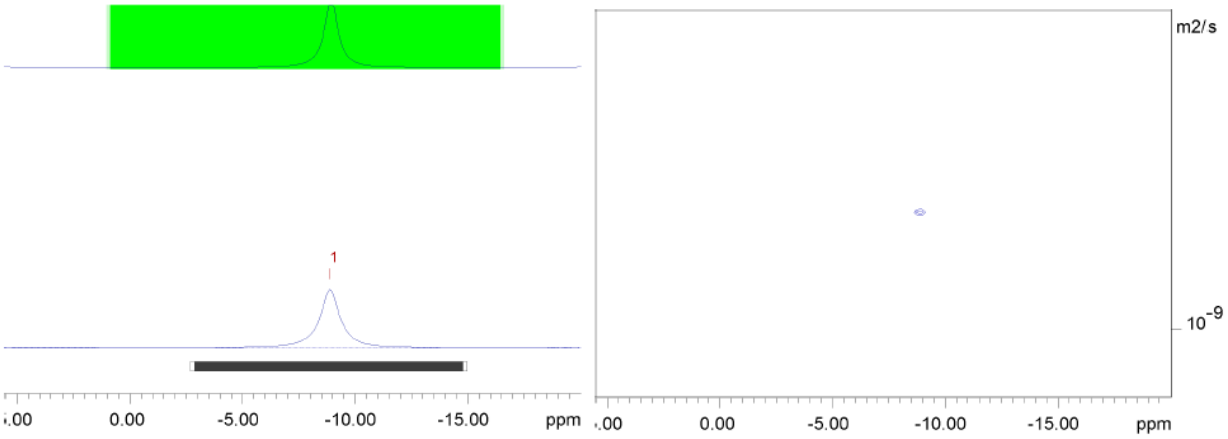


Figure S9. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ DiG with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

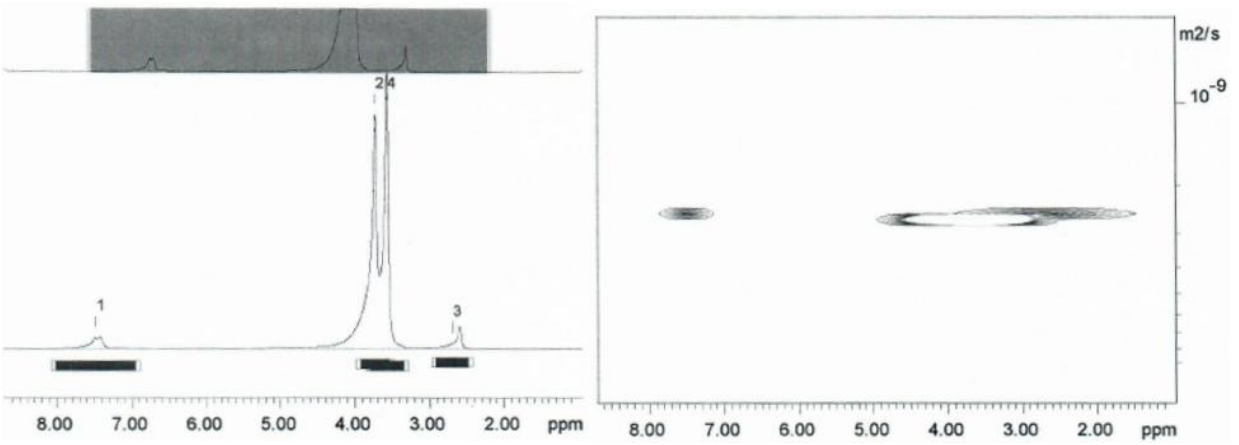


Figure S10. DOSY NMR ^{1}H (sample DME with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

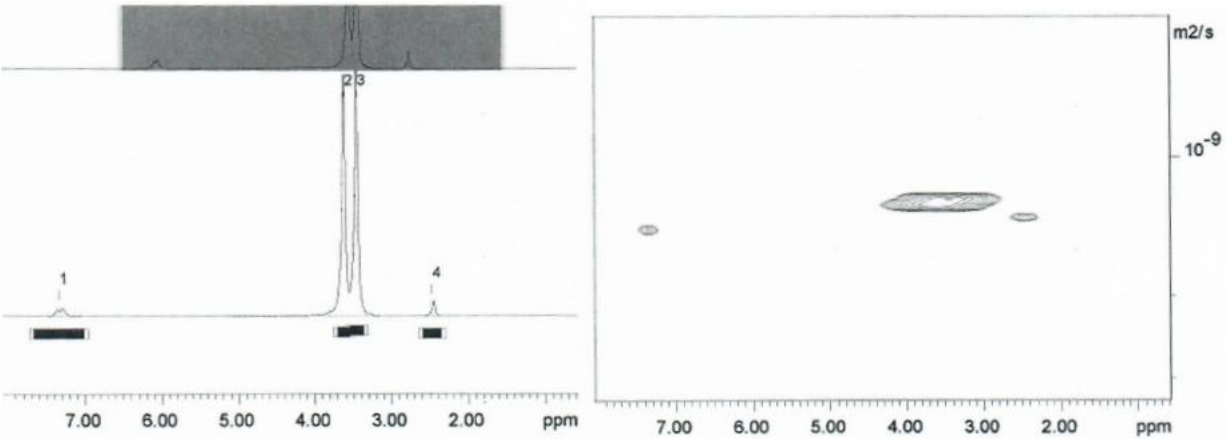


Figure S11. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ DME with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

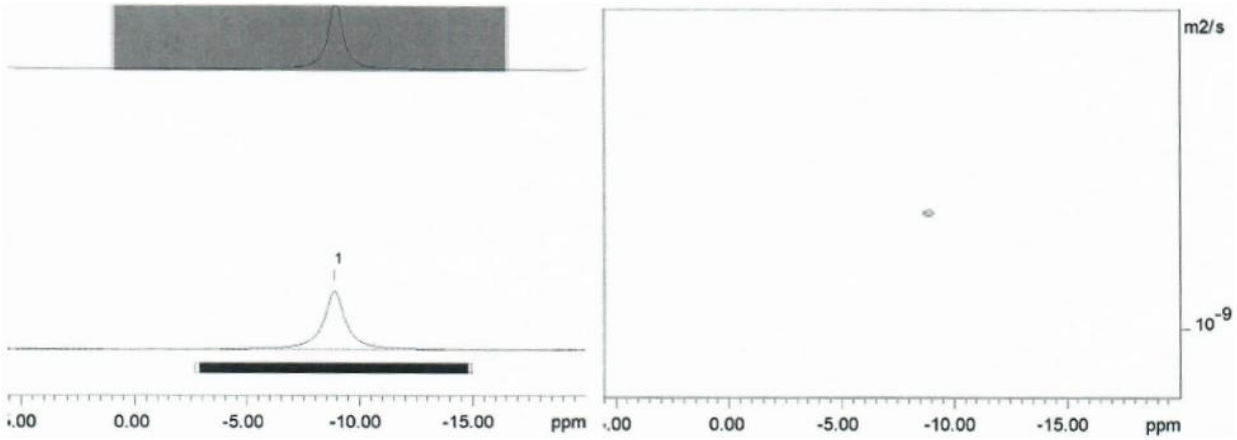


Figure S12. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ DME with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

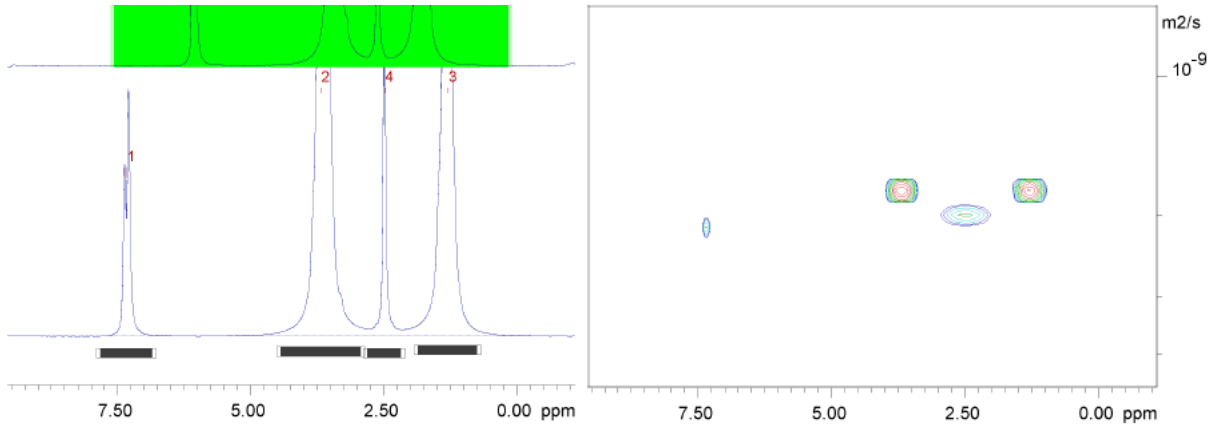


Figure S13. DOSY NMR ^{1}H (sample DEE with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

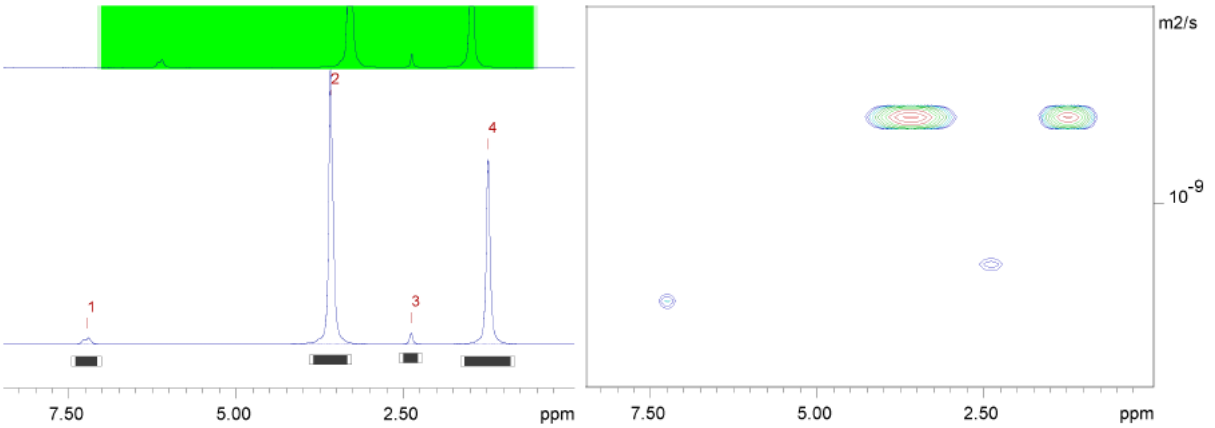


Figure S14. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ DEE with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

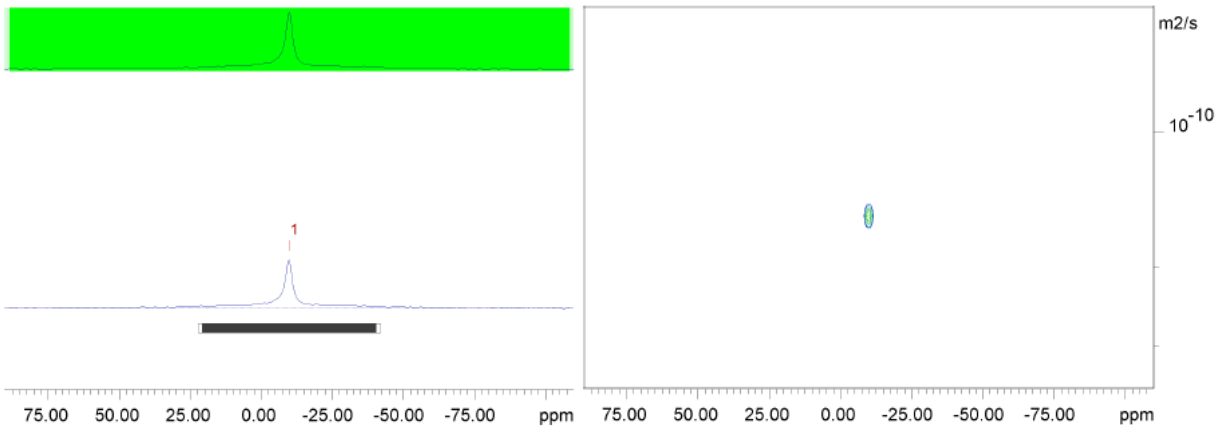


Figure S15. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ DEE with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

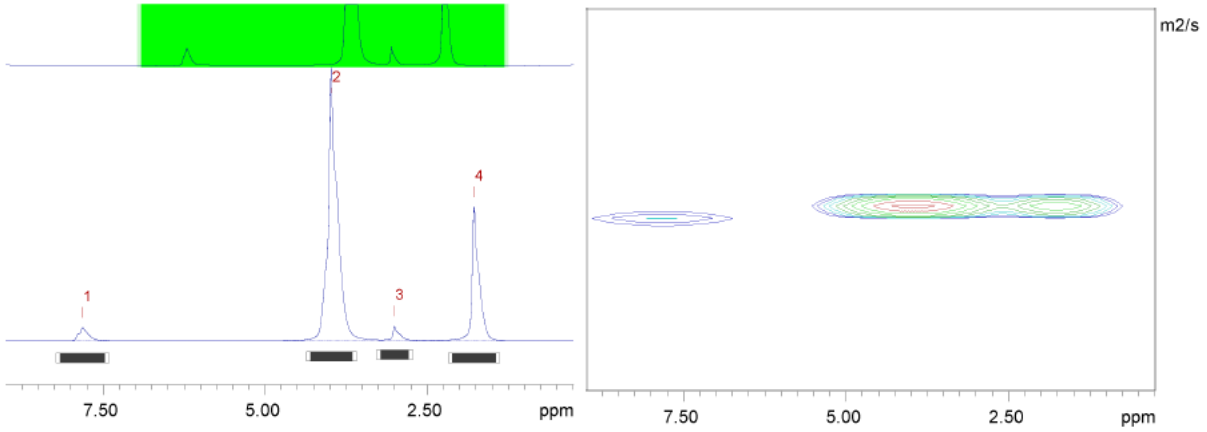


Figure S16. DOSY NMR ^{1}H (sample 1,2-DMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

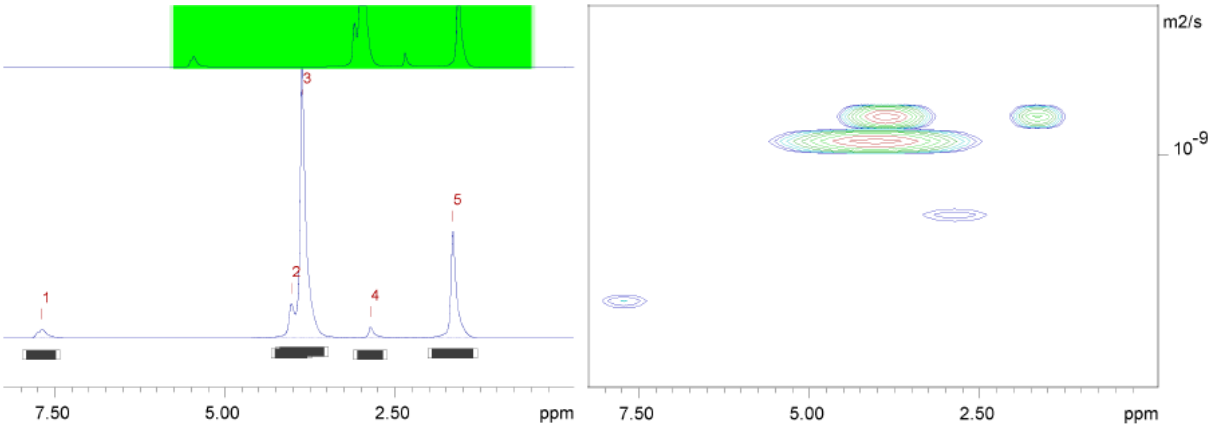


Figure S17. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ 1,2-DMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

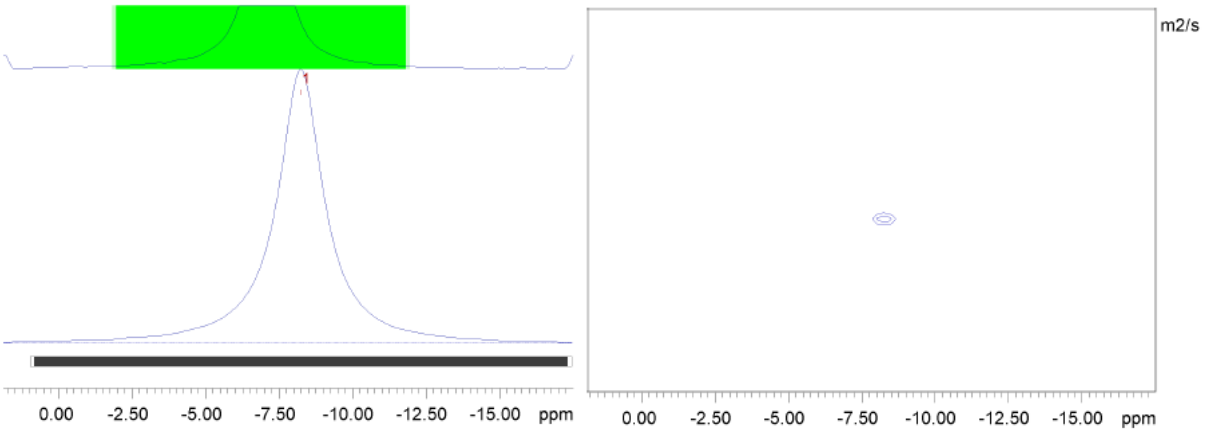


Figure S18. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ 1,2-DMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

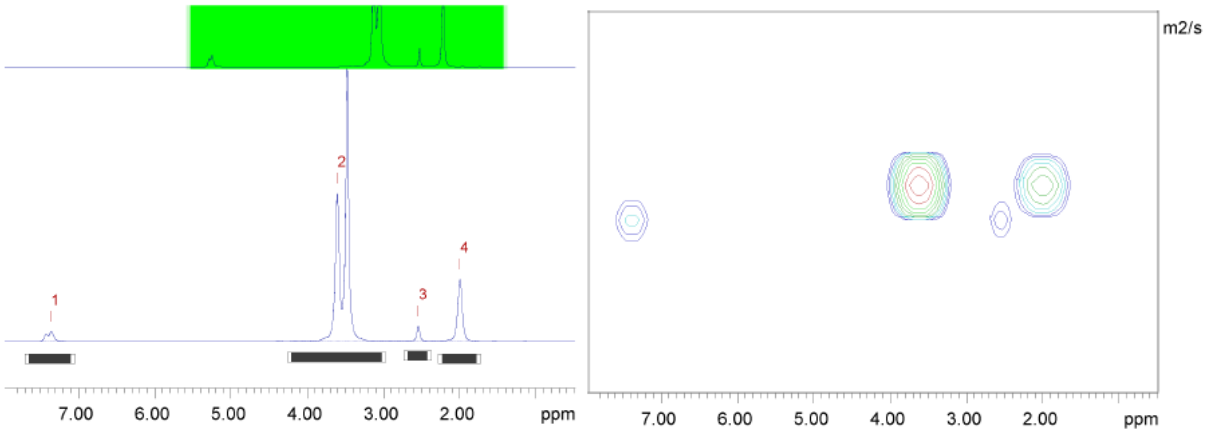


Figure S19. DOSY NMR ^{1}H (sample 1,3-DMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

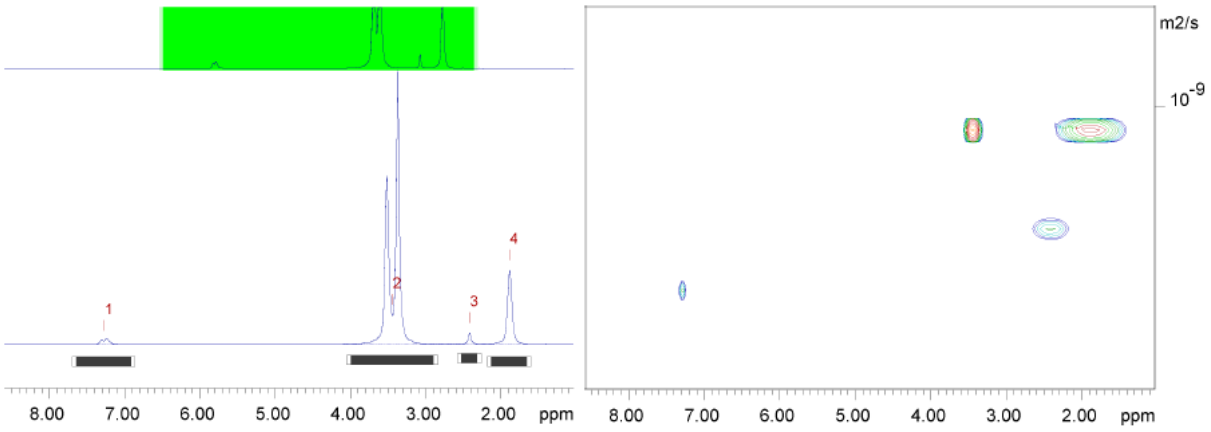


Figure S20. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ 1,3-DMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

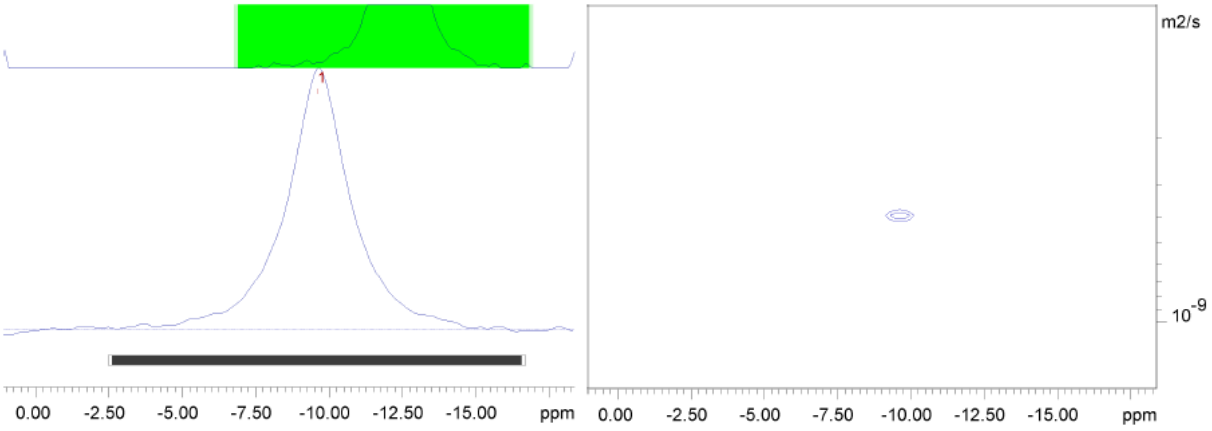


Figure S21. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ 1,3-DMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

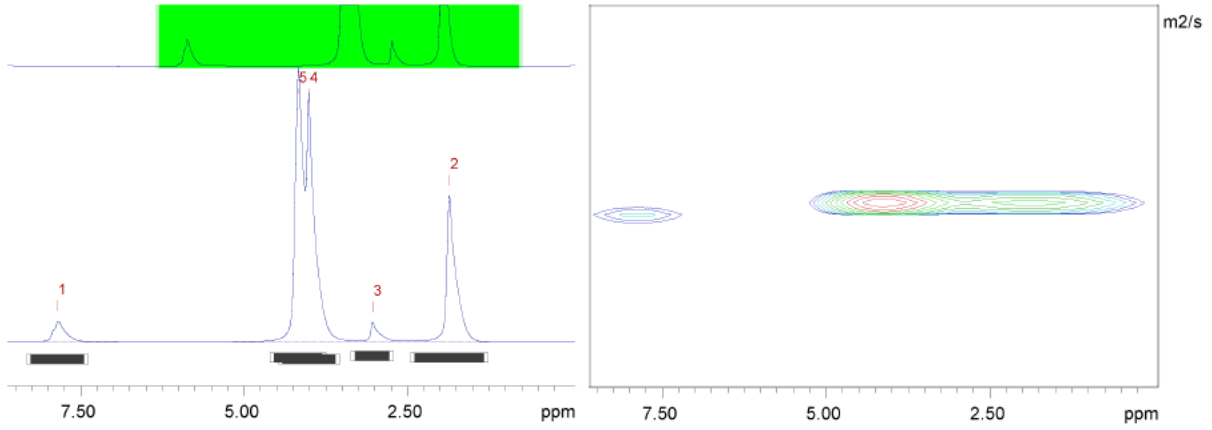


Figure S22. DOSY NMR ^{1}H (sample EME with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

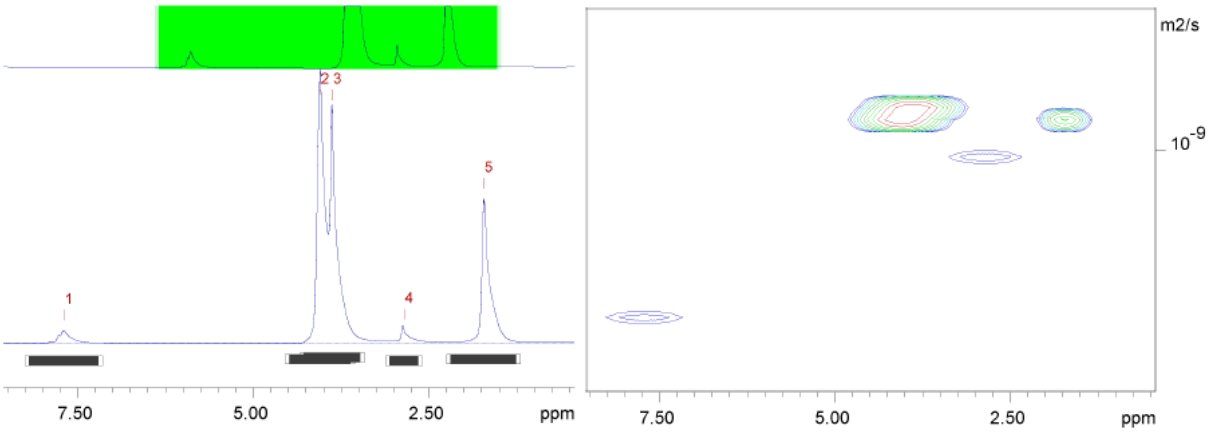


Figure S23. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ EME with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

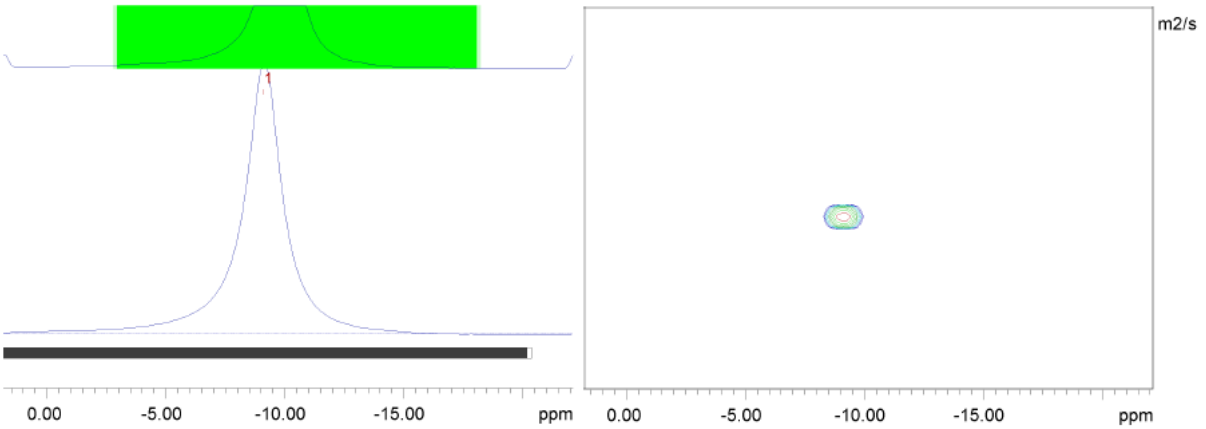


Figure S24. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ EME with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

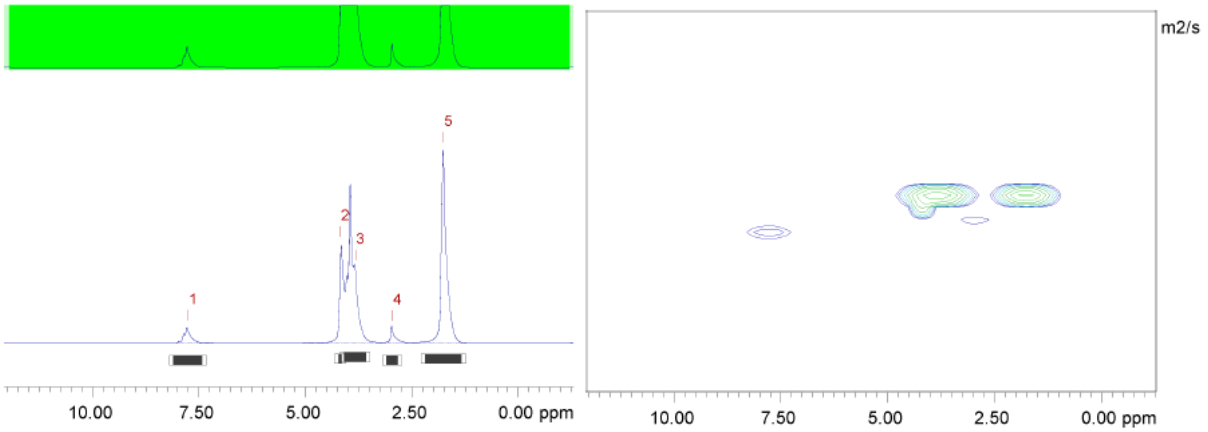


Figure S25. DOSY NMR ^{1}H (sample EMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

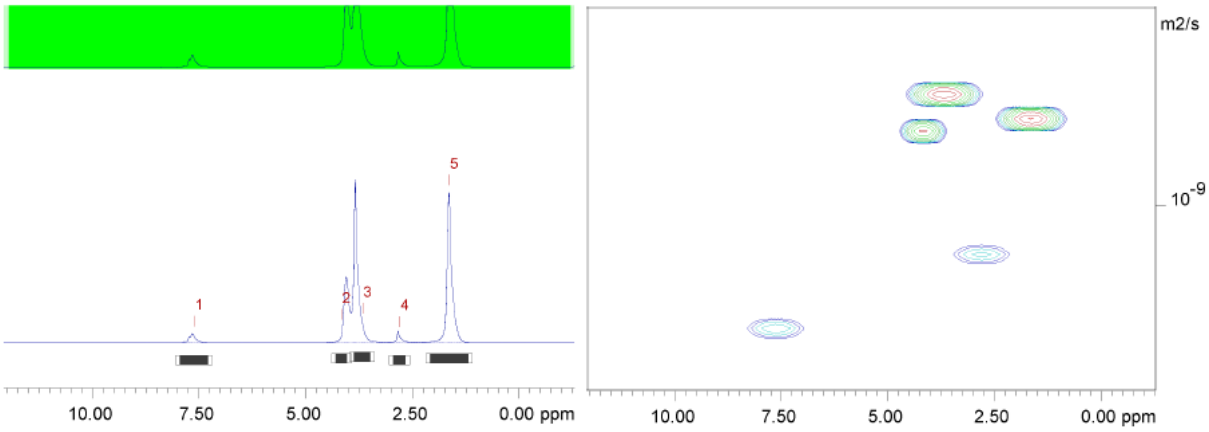


Figure S26. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ EMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

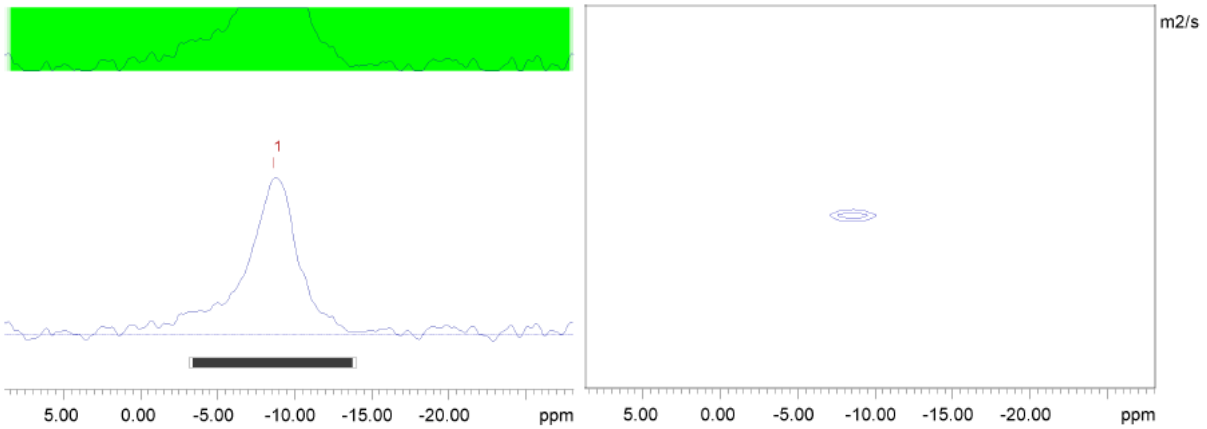


Figure S27. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ EMP with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

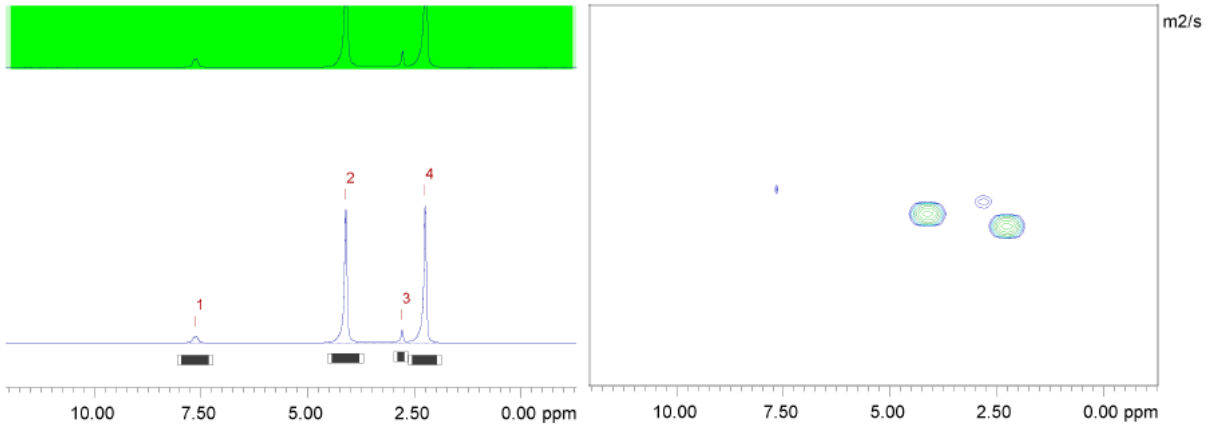


Figure S28. DOSY NMR ^{1}H (sample THF with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

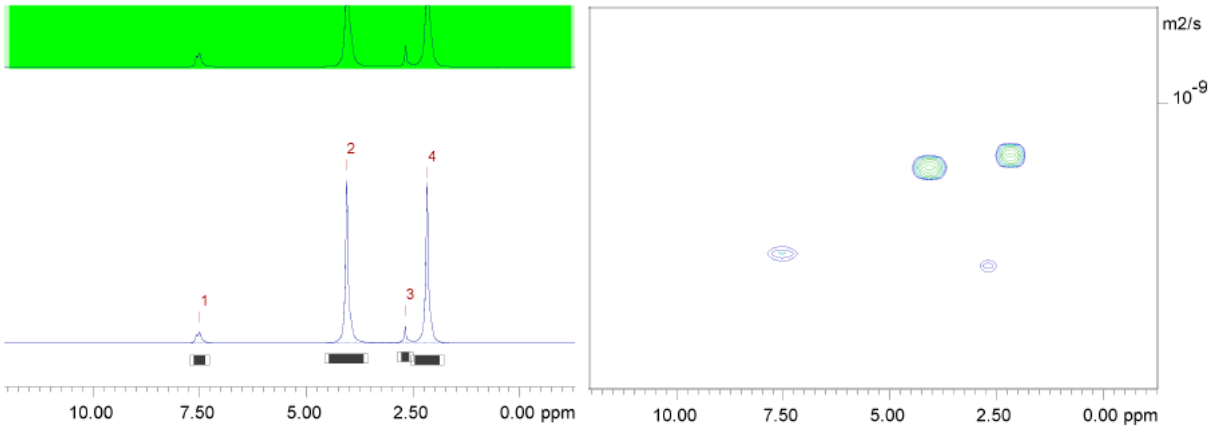


Figure S29. DOSY NMR ^{1}H (sample DOSY 1M $NaPF_6$ THF with internal standard $C_6H_5CH_3$ and external standard C_6D_6).

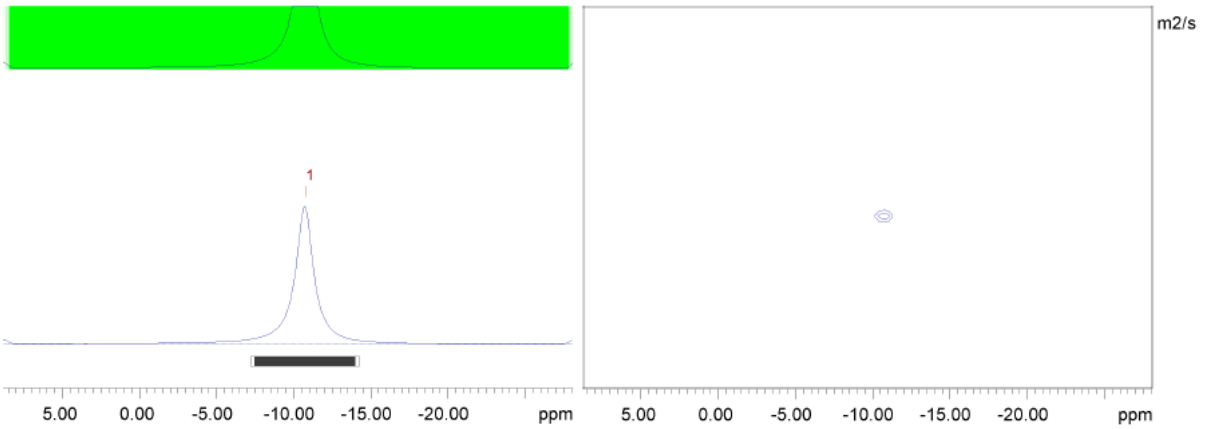


Figure S30. DOSY NMR ^{23}Na (sample DOSY 1M $NaPF_6$ THF with internal standard $C_6H_5CH_3$ and external standard C_6D_6)

Table S3 – Ionic conductivities of electrolytes 1M $NaPF_6$ in ether at various temperatures (mS/cm).

T, °C	*DiG*	*DME*	*1,2-DMP*	*1,3-DMP*	*DEE*	*EME*	*EMP*	*THF*
25	8.6	16.7	6.0	2.6	2.5	6.1	1.6	8.3
20	7.4	15.4	5.8	2.3	2.3	5.7	1.5	6.4
10	6.0	14.4	5.2	1.8	1.8	5.1	1.1	6.2
0	4.8	2.2	4.8	1.6	1.6	4.5	1.0	5.8
-10	3.8	1.1	4.3	1.3	1.3	3.8	0.6	5.3
-20	1.5	0.8	3.8	1.3	1.2	1.6	0.5	4.7
-30	0.6	0.9	3.0	0.8	1.0	1.0	0.6	4.1
-40	0.4	0.6	2.1	0.5	0.8	0.5	0.5	3.2

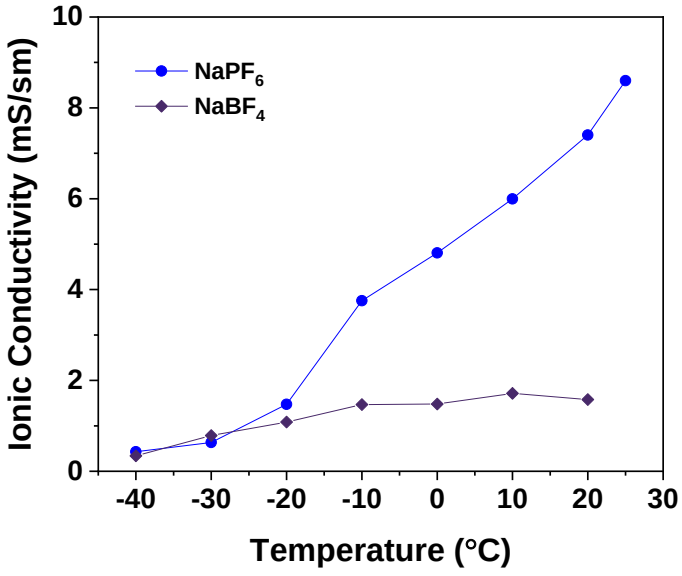


Figure S31. Ionic conductivities of 1M $NaBF_4$ in DiG and 1M $NaPF_6$ in DiG at different temperatures.

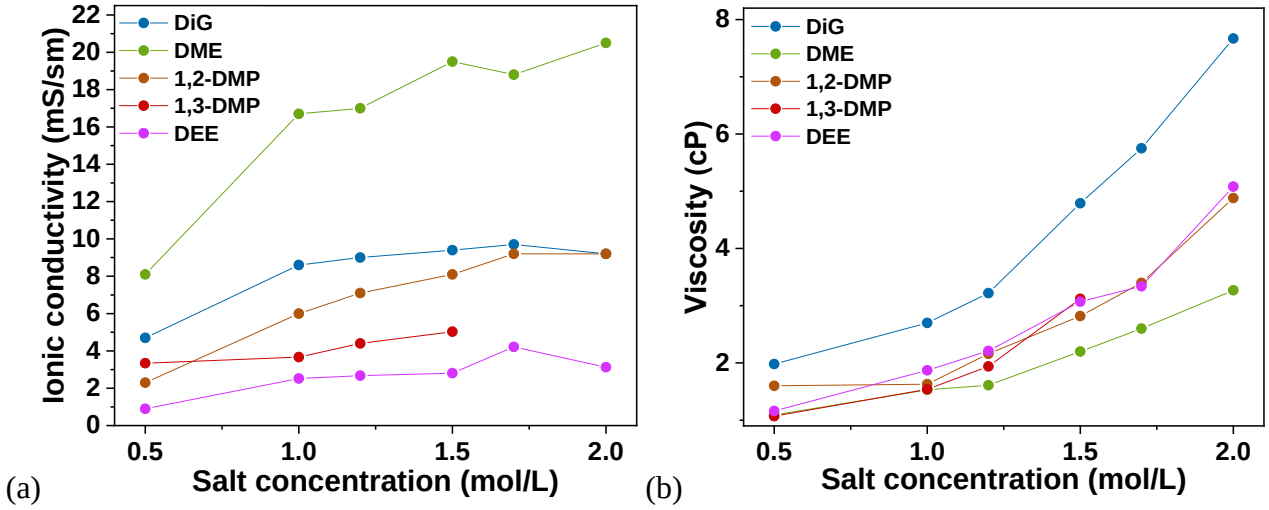


Figure S32. Ionic conductivities (a) and viscosities (b) of ether-based electrolytes at various $NaPF_6$ concentrations. [1]

Table S4 - Viscosities (cP) and ionic conductivities (mS cm^{-1}) of electrolytes with $NaPF_6$ concentrations 0.5 - 2 M in DME, DiG, 1,2-DMP, 1,3-DMP and DEE.

DME						
Concentration, M	0.5	1.0	1.2	1.5	1.7	2.0
Viscosity, cP	1.09	1.53	1.61	2.20	2.60	3.27
Ionic conductivity, mS cm^{-1}	8.1	16.7	17.0	19.5	18.8	20.5
DiG						
Concentration, M	0.5	1.0	1.2	1.5	1.7	2.0
Viscosity, cP	1.98	2.70	3.22	4.79	5.75	7.67
Ionic conductivity, mS cm^{-1}	4.7	8.6	9.0	9.4	9.7	9.2
1,3-DMP						
Concentration, M	0.5	1.0	1.2	1.5	-	-
Viscosity, cP	1.07	1.54	1.94	3.12	-	-
Ionic conductivity, mS cm^{-1}	3.3	3.7	4.4	5.0	-	-
1,2-DMP						
Concentration, M	0.5	1.0	1.2	1.5	1.7	2.0
Viscosity, cP	1.60	1.63	2.16	2.82	3.40	4.88
Ionic conductivity, mS cm^{-1}	2.3	6.0	7.1	8.1	9.2	9.2

[1] In 1,3-DMP, solubility limited maximum concentration to ~1.5 M.

DEE						
Concentration, M	0.5	1.0	1.2	1.5	1.7	2.0
Viscosity, cP	1.16	1.87	2.21	3.07	3.34	5.08
Ionic conductivity, mS cm^{-1}	0.9	2.5	2.7	2.8	4.2	3.1

Table S5 – Overpotential in symmetric Na||Na cells with electrolytes 1 M $NaPF_6$ in ether at current densities 0.5, 1, 1.5 and 2 mA/cm^2.

Current density, mA cm^{-2}	***Overpotential, mV***							
	DME	***THF***	***1,2-DMP***	***1,3-DMP***	***EME***	***DiG***	***EMP***	***DEE***
0.5	2.0	2.5	5.4	8.7	4.5	5.2	12.6	14.1
1.0	2.9	3.6	5.9	9.2	7.4	8.8	18.8	21.3
1.5	3.8	4.7	6.7	9.7	9.7	12.4	23.5	27.7
2.0	4.8	5.7	8.1	10.7	11.8	15.8	28.9	30.1

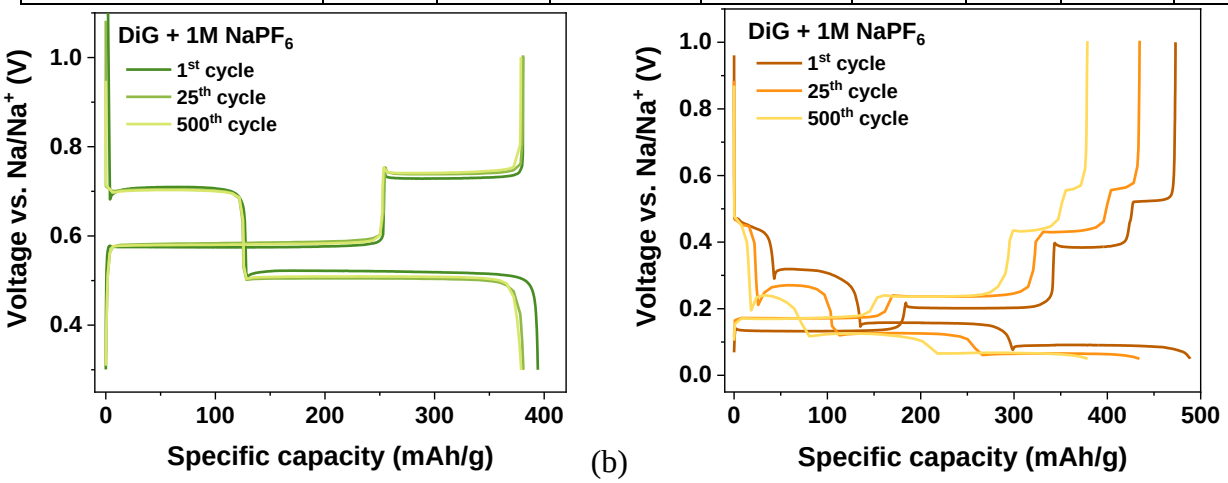


Figure S33. Charge/discharge curves of Na||Bi (a) and Na||Pb (b) cells with 1M $NaPF_6$ in DiG electrolyte at cycles 1, 25, and 500.

Table S6 – Electrochemical parameters (discharge capacity retention over 500 cycles and average Coulombic Efficiency) of Na||Bi and Na||Pb cells with electrolytes 1 M $NaPF_6$ in different ethers. All experiments reproduced in at least two coin-cells.

Na||Bi								
Ether	***DiG***	***DME***	***1,2-DMP***	***1,3-DMP***	***DEE***	***EME***	***EMP***	***THF***
Capacity retention, %	99.4	94.9	97.1	94.3	94.0	94.8	80.0	97.4
Coulombic efficiency, %	99.95	99.96	99.94	99.91	99.92	99.86	99.87	99.81
Na||Pb								
Ether	***DiG***	***DME***	***1,2-DMP***	***1,3-DMP***	***DEE***	***EME***	***EMP***	
Capacity retention, %	88.3	91.4	92.0	77.7	78.3	68.3	53.7	
Coulombic efficiency, %	99.95	99.97	99.93	99.90	99.90	99.91	99.90	

Supplementary references

S1. M. D. Agapkin, N. D. Luchinin, S. N. Marshenya, M. V. Zakharkin, E. V. Antipov and S. S. Fedotov, Dokl. Chem., 2026, 528, 146–157; https://doi.org/10.7868/S3034511126030139.