

## Supplementary Information for:

### A 1,2,3-Triazolate lithium salt with ionic liquid properties at room temperature

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**Materials.** Diisopropylethylamine (DIPEA, 99%), copper(I) iodide triethylphosphite (CuIP(OEt)<sub>3</sub>, 97%), sodium hydroxyde (98%), hydrogen chloride (32 wt% in H<sub>2</sub>O) and lithium carbonate (99.999%) were purchased from Aldrich and used as received. Triethylene glycol monomethyl monopropargyl ether **1**,<sup>1</sup> and azidomethyl pivalate **2**,<sup>2</sup> were synthesized as described earlier.

#### Characterization methods

**NMR spectroscopy** was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for <sup>1</sup>H, 155.5 MHz for <sup>7</sup>Li and 100 MHz for <sup>13</sup>C. Spectra were obtained with a 5-mm QNP probe at 363 K. Chemical shifts ( $\delta$ ) are given in ppm in reference to residual hydrogenated solvents for <sup>1</sup>H NMR, to the signal of the deuterated solvent for <sup>13</sup>C NMR and to an internal standard for <sup>7</sup>Li NMR.

**Differential scanning calorimetry (DSC)** was performed using a DSC Q200 (TA Instrument) calibrated with an indium standard. The sample was prepared using an hermetic pan and the experiment was conducted under a helium purge of 25 mL min<sup>-1</sup> on ca. 5 mg of lithium 1,2,3-triazolate **5**. The sample was first heated to 120 °C at a rate of 10 °C min<sup>-1</sup> and isothermally annealed for 2 min. Then, the temperature was decreased to -80 °C at a rate of 10 °C min<sup>-1</sup> followed by a second heating to 200 °C at a rate of 10 °C min<sup>-1</sup>. The glass transition temperature ( $T_g$ ) was measured at the mid-point of the transition (on the second heating cycle) using the TA Thermal Analysis software.

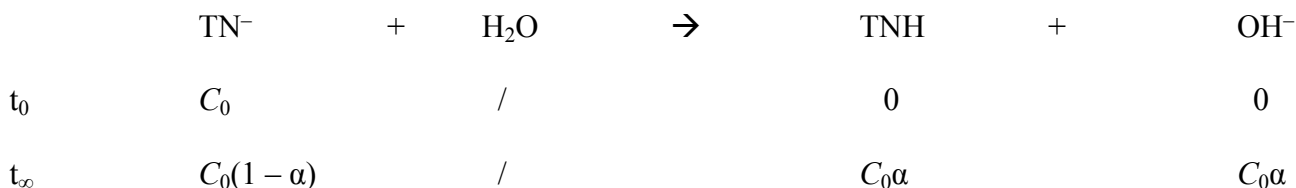
**Thermogravimetric analysis (TGA)** was performed on a TGA Q500 apparatus (TA Instruments). A heating ramp from 20 to 600 °C was applied at 10 °C min<sup>-1</sup> under a helium purge of 60 mL min<sup>-1</sup> to ca. 5 mg of lithium 1,2,3-triazolate **5**.

**Broadband dielectric spectroscopy (BDS).** The bulk ionic conductivity of lithium 1,2,3-triazolate **5** was measured by BDS using a high resolution Alpha-Analyzer (Novocontrol GmbH) assisted by a Quatro temperature controller. The sample was prepared by casting 1 mL of a 100 mg mL<sup>-1</sup> solution of **5** in dichloromethane onto a freshly polished platinum electrode (diameter  $\varnothing = 1''$ ), followed by an overnight annealing treatment at 60 °C under vacuum to eliminate solvent residues and moisture. After annealing, the sample was pressed against another platinum electrode ( $\varnothing = 2''$ ) and the thickness was controlled by employing 100  $\mu\text{m}$  thick Teflon spacers to build-up a measurement cell in a parallel plate configuration with a well-defined separation distance. The complex conductivity function  $\sigma^*(\omega, T) = \sigma'(\omega, T) + i\sigma''(\omega, T)$  was measured several times at 30 °C in the cryostat of the dielectric spectrometer under flow of pure nitrogen, before and during a thermal annealing of 5 hours at 110 °C. Meanwhile, the sample was measured several times under isothermal conditions at temperatures ranging from 110 to -70 °C in steps of 10 °C, using a heating/cooling rate of 2K/min to reach the isothermal plateaus for the dielectric measurements. The dielectric measurements were carried-out by applying frequency sweeps from 10 MHz to 0.1 Hz using a sinusoidal voltage of 0.1 V. The low value of applied voltage excludes any possible non-linear effects that can take place at the interface with the measurement electrodes. The temperature was controlled by heating the sample under a flow of pure nitrogen, which excluded the presence of oxygen and moisture in the measurement chamber. The thermal stability was set to be better than 0.1 K in absolute values with relative variations less than 0.2 K min<sup>-1</sup> for the heating/cooling stabilization process around the setpoint temperature.

**Electrochemical impedance spectroscopy (EIS).** The conductivity of a 1 M solution of lithium 1,2,3-triazolate **5** in a 1:1 vol./vol. mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was measured by EIS using a VMP300 (Biologic). The solution was prepared in an argon filled glove box (Jacomex, O<sub>2</sub>, H<sub>2</sub>O < 0.5ppm) and a home-made tightened conductimetric cell assembled using a conductivity micro-electrode (Hack Lange). After assembly the cell was placed in a climatic chamber (Vötsch 4002) outside of the glovebox to perform the electrochemical characterizations. For the AC impedance spectroscopy, an excitation signal between 10 and 40 mV in a frequency range between 10<sup>7</sup> and 1 Hz, was used to determine the electrolyte ionic conductivity,  $\sigma$ . The temperature program consists of a heating scan from 25 to 60 °C in 5 °C steps. A stabilization time of 1 h was used at each step. The electrolyte resistance,  $R_{\text{el}}$ , was extracted from the impedance spectra fitted by means of an equivalent electrical circuit simply composed of the  $R_{\text{el}}$  in parallel with the electrolyte pseudo-capacitance, CPE<sub>el</sub> (Constant Phase Element).  $R_{\text{el}}$  corresponds to the low frequency extrapolation of the semi-circle on the real axis. The conductivity is calculated by dividing the conductivity cell constant by the electrolyte resistance  $R_{\text{el}}$ . The cell constant was calibrated before and after each experiment using a reference solution of KCl.

**Acid/base titration, pK<sub>a</sub> and dissociation ratio.** Before pH titrations, the pH meter MeterLab PHM210 was calibrated according to the instructions supplied by the manufacturer. 0.01 M Aqueous solutions of 1,2,3-triazolate **5** were titrated using a 0.1 M aqueous solution of hydrochloric acid. During the titrations, the titrant was added in increments of 0.1 mL and the pH values were recorded. The titration was repeated three times. pK<sub>a</sub> was taken as the pH of the titration solution at  $V_{\text{eq}}/2$ . The protonation ratio ( $\alpha$ ) was calculated as follows assuming that the activity is equal to the concentration:

Considering the following reaction



with TN<sup>-</sup> the 1,2,3-triazolate anion, TNH the protonated 1,2,3-triazole **4**, C<sub>0</sub> the concentration of **5** at time t<sub>0</sub>, and α the protonation ratio.

α was calculated by resolving the quadratic equation in α resulting from the ICE table, using the acidity constant and the equation below:

$$\alpha = (1 + (1 + 4(K_a \cdot C / K_w)^{0.5}) / (2(K_a / K_w \cdot C)))$$

with K<sub>a</sub> = 2.5 × 10<sup>-9</sup>, K<sub>w</sub> = 1.0 × 10<sup>-14</sup> the ionic product of water and C = 1 M.

For a 1 M aqueous solution of **5** the dissociation ratio α = 2 × 10<sup>-3</sup>.

**Ionic conductivity in water.** Ionic conductivity of 1 M aqueous solutions of 1,2,3-triazolate **5** were measured using a high resolution Alpha – Analyzer (Novocontrol GmbH). In a typical procedure, solutions (200 μL) were introduced between two brass electrodes (Ø = 2 cm) using 300 μm thick teflon spacers. Isothermal frequency sweeps were then performed from 10 MHz to 0.1 Hz by applying a sinusoidal voltage of 0.1 V at room temperature. The conductivity was derived from the plateau-value observed in the spectral dependence of the conductivity function (σ' = ωε''ε<sub>0</sub>, where ω is the frequency, ε<sub>0</sub> the vacuum permittivity and ε'' the dielectric loss).

**Cyclic voltamperometry (CV).** A 1 M solution of lithium 1,2,3-triazolate **5** in a 1:1 (vol./vol.) mixture EC and DMC was soaked into a Celgard separator and sandwiched between a lithium foil and a working electrode before being assembled in a two electrode coin cell in an argon filled glove box. For the analysis of the oxidation stability a stainless steel electrode was used as working electrode, whereas for the reduction stability a copper electrode was used. The lithium foil served both as reference and counter electrode. After assembly, the coin cells are placed in an oven (Memmert IP30) at 25 °C. The cyclic voltammetry were made thanks to a potentiostat/galvanostat VMP300 from Biologic at a scan rate of 1 mV s<sup>-1</sup> in the range 3 to 4.2 V vs Li<sup>+</sup>/Li in oxidation and 2 to -0.3 V vs Li<sup>+</sup>/Li in reduction.

## Synthesis procedures

### Synthesis of 1,2,3-triazole **3**.

CuIP(OEt)<sub>3</sub> (0.27 g, 0.74 mmol) and DIPEA (1.92 g, 14.9 mmol) were added to a solution of triethylene glycol monomethyl monopropargyl ether **1** (3.00 g, 14.9 mmol) and azidomethyl pivalate **2** (2.91 g, 18.6 mmol) in tetrahydrofuran (30 mL). The mixture was stirred under argon for 24 h at 60 °C before being evaporated to dryness under reduced pressure. The crude product was purified by column chromatography using ethyl acetate as eluent to yield, after evaporation under reduced pressure, **3** as a colorless oil (4.10 g, 76.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.78 (s, CH=CN, 1H), 6.18 (s, NCH<sub>2</sub>OC(O)C(CH<sub>3</sub>)<sub>3</sub>, 2H), 4.65 (s, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 2H), 3.68-3.56 (m, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 10H), 3.52-3.47 (m, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 2H), 3.32 (s, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, 3H), 1.14 (s, NCH<sub>2</sub>OC(O)C(CH<sub>3</sub>)<sub>3</sub>, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 177.54 (NCH<sub>2</sub>OC(O)C(CH<sub>3</sub>)<sub>3</sub>), 145.62 (CH=CN), 123.92 (CH=CN), 71.76 (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 70.43, 70.36, 69.53 (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>, NCH<sub>2</sub>OC(O)C(CH<sub>3</sub>)<sub>3</sub>), 64.34 (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 58.87 (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>), 38.62 (NCH<sub>2</sub>OC(O)C(CH<sub>3</sub>)<sub>3</sub>), 26.67 (NCH<sub>2</sub>OC(O)C(CH<sub>3</sub>)<sub>3</sub>). HRMS: (ESI, m/z): [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>29</sub>N<sub>3</sub>NaO<sub>6</sub>, 382.1949; found, 382.1937.

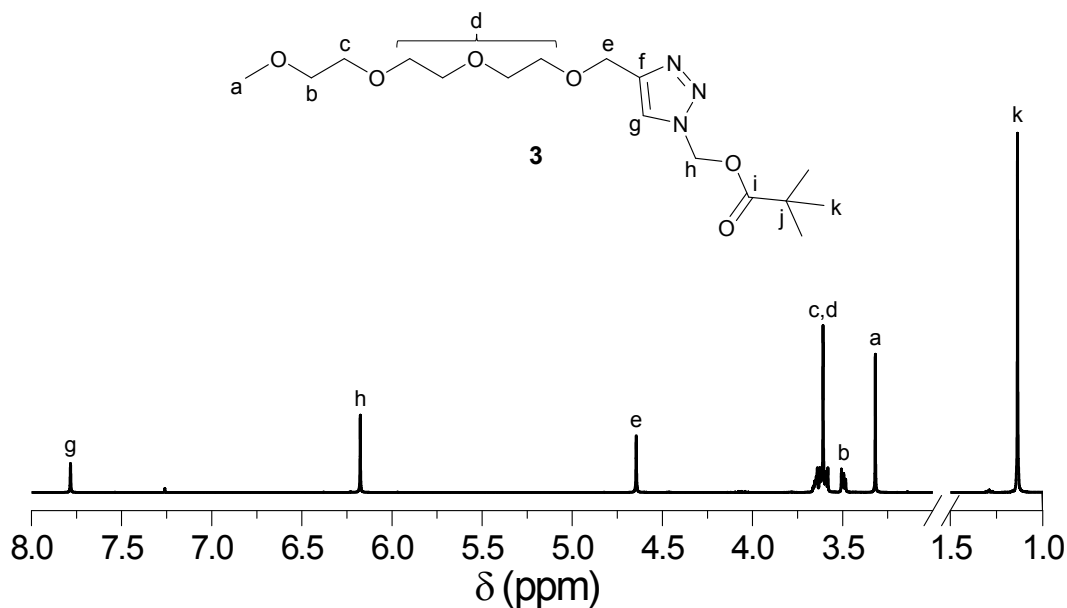
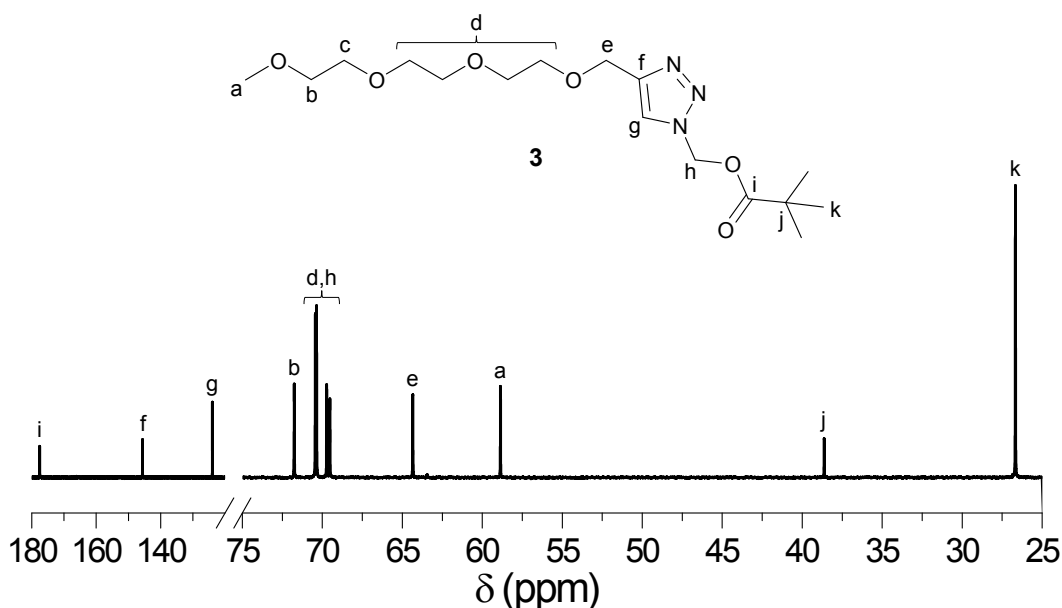


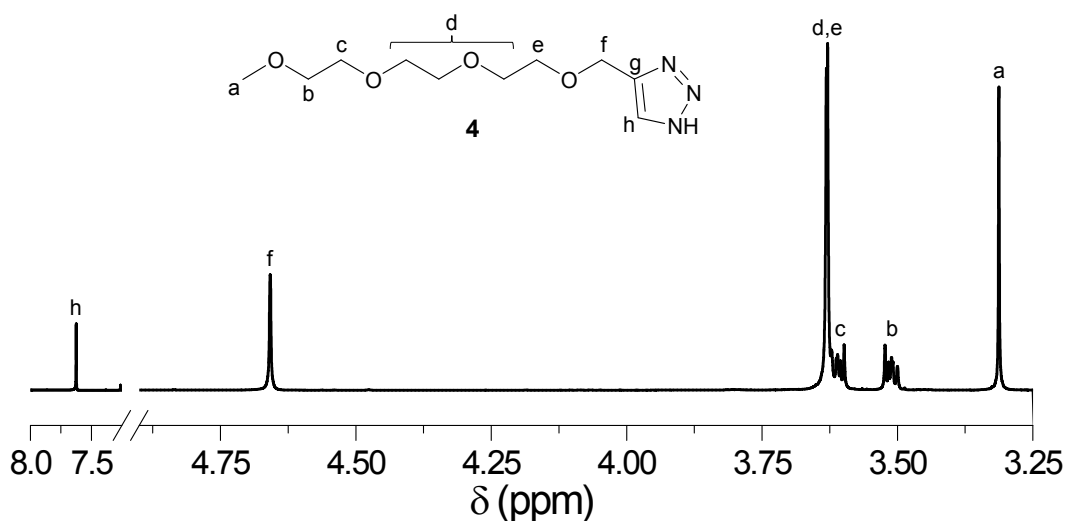
Figure S1. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of 1,2,3-triazole **3**.



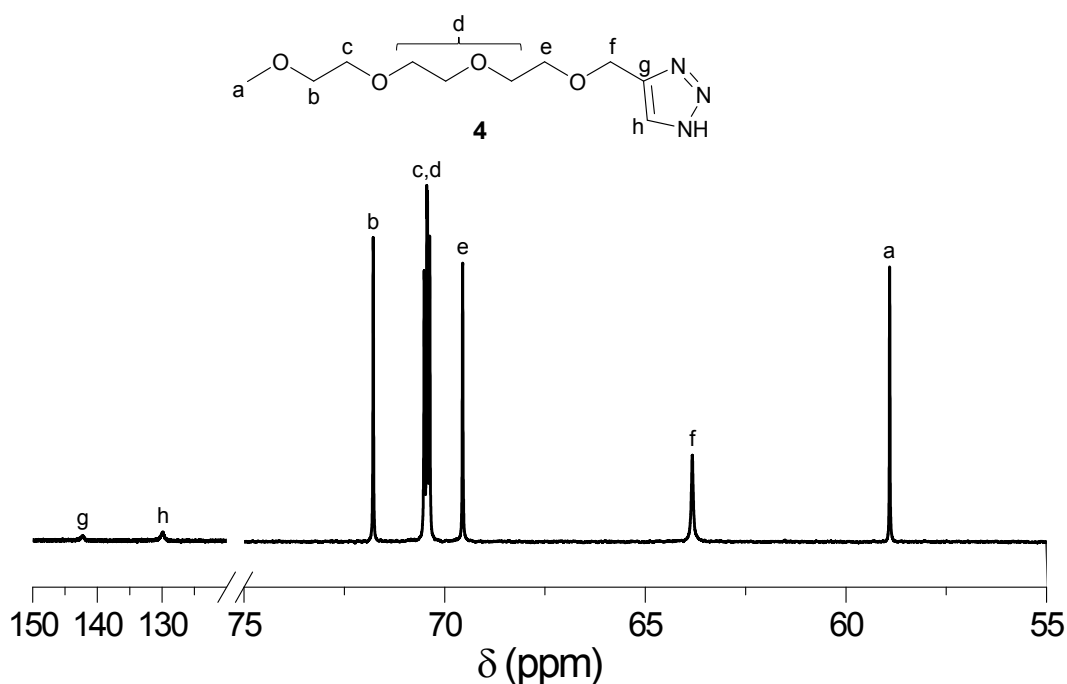
**Figure S2.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of 1,2,3-triazole **3**.

#### Synthesis of 1H-1,2,3-triazole **4**.

$\text{NaOH}_{\text{aq}}$  (1 M, 43.9 mL, 43.9 mmol) was added to a solution of **3** (6.30 g, 17.5 mmol) in methanol (80 mL). The reaction was stirred at 60 °C for 18 h or until the total disappearance of the intermediate derivative having a  $\text{CH}_2\text{OH}$  substituent at the *N*-1 position of the 1,2,3-triazole ring (the disappearance of the  $\text{CH}_2$  singlet signal at 5.77 ppm in  $\text{CDCl}_3$  could be monitored by  $^1\text{H}$  NMR).  $\text{HCl}_{\text{aq}}$  (1 M, 43.9 mL, 43.9 mmol) was then added and the solution was evaporated to dryness under vacuum. The remaining solid was washed several times with dichloromethane to extract the crude product as a slightly colored oil after solvent evaporation. The crude product was then purified by column chromatography using ethyl acetate to yield, after evaporation of the solvent under reduced pressure, **4** as a colorless oil (3.38 g, 78.7%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 15.29-11.34 (bs,  $\text{NH}$ , 1H), 7.63 (s,  $\text{CH}=\text{CN}$ , 1H), 4.66 (s,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ , 2H), 3.82-3.56 (m,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ , 10H), 3.56-3.44 (m,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ , 2H), 3.31 (s,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ , 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 142.11 ( $\text{CH}=\text{CN}$ ), 129.73 ( $\text{CH}=\text{CN}$ ), 71.64 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 70.37, 70.30, 70.23 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 69.41 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 63.69 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 58.77 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ). HRMS: (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{10}\text{H}_{20}\text{N}_3\text{O}_4$ , 246.1448; found, 246.1444.



**Figure S3.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of 1H-1,2,3-triazole **4**.

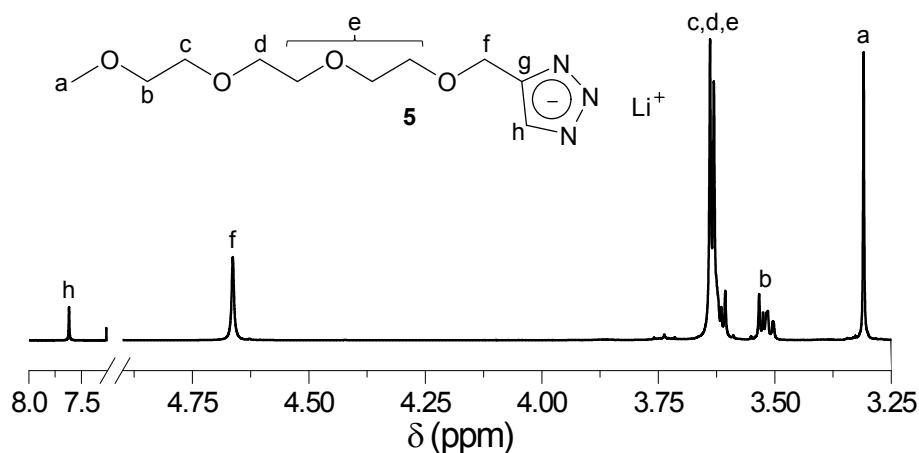


**Figure S4.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of 1H-1,2,3-triazole **4**.

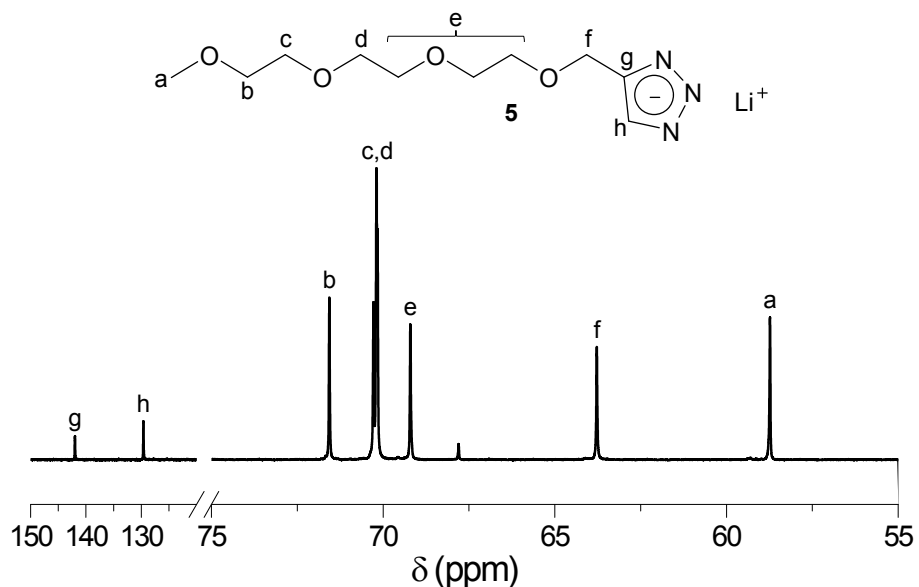
### Synthesis of lithium 1,2,3-triazolate **5**.

Lithium hydride (50 mg, 6.29 mmol) was added to a solution of **4** (1.54 g, 6.29 mmol) in anhydrous tetrahydrofuran (10 mL). The reaction was stirred at 25 °C for 2 h. The solution was filtered through 0.45  $\mu\text{m}$  PTFE filters and was evaporated to dryness under vacuum. The crude product was dissolved in acetone, maintained at  $-40$  °C overnight, centrifuged and the liquid phase was evaporated to dryness under reduced pressure. This procedure was repeated using chloroform and dichloromethane. The final solution was passed through a short plug of calcium chloride to yield, after evaporation of the solvent under reduced pressure, **5** as a colorless oil (1.56 g, 99.0%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.40 (s,  $\text{CH}=\text{CN}$ , 1H), 4.48 (s,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ , 2H), 3.70-3.32 (m,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ , 12H), 3.17 (s,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ,

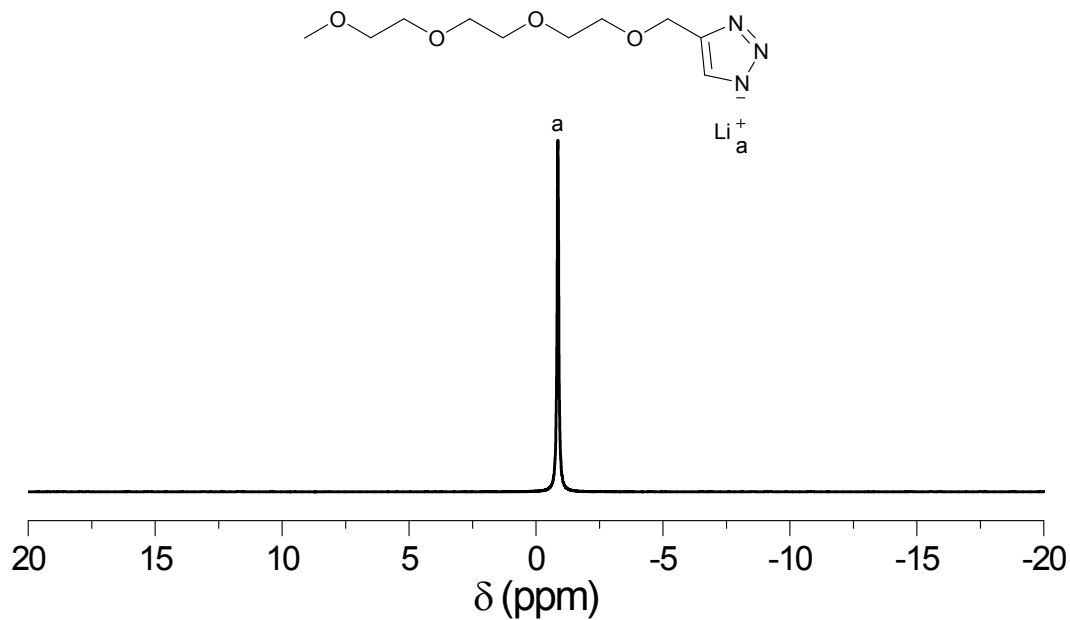
3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 140.98 (CH=CN), 130.60 (CH=CN), 71.38 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 70.13, 70.03, 69.97, 69.79 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 67.72 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 64.31 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 58.68 ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ).  $^7\text{Li}$  NMR (155.5 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm):  $-0.863$  ( $\text{Li}^+$ ). HRMS: (ESI,  $m/z$ ):  $[\text{M}]^-$  calcd for  $\text{C}_{10}\text{H}_{18}\text{N}_3\text{O}_4$ , 244.1303; found, 244.1307.



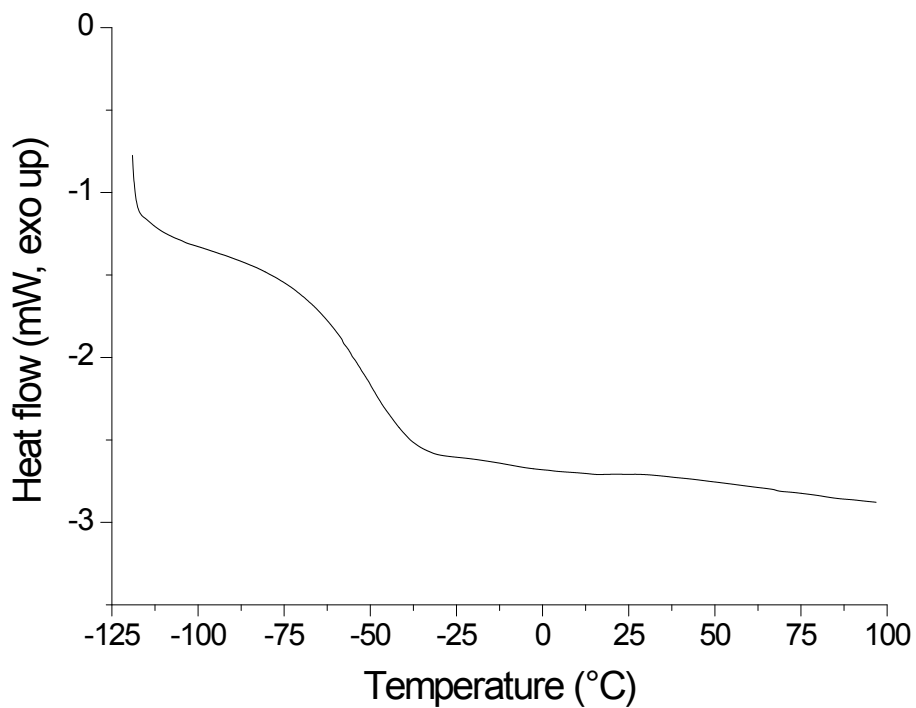
**Figure S5.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of lithium 1,2,3-triazole **5**.



**Figure S6.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of lithium 1,2,3-triazole **5**.

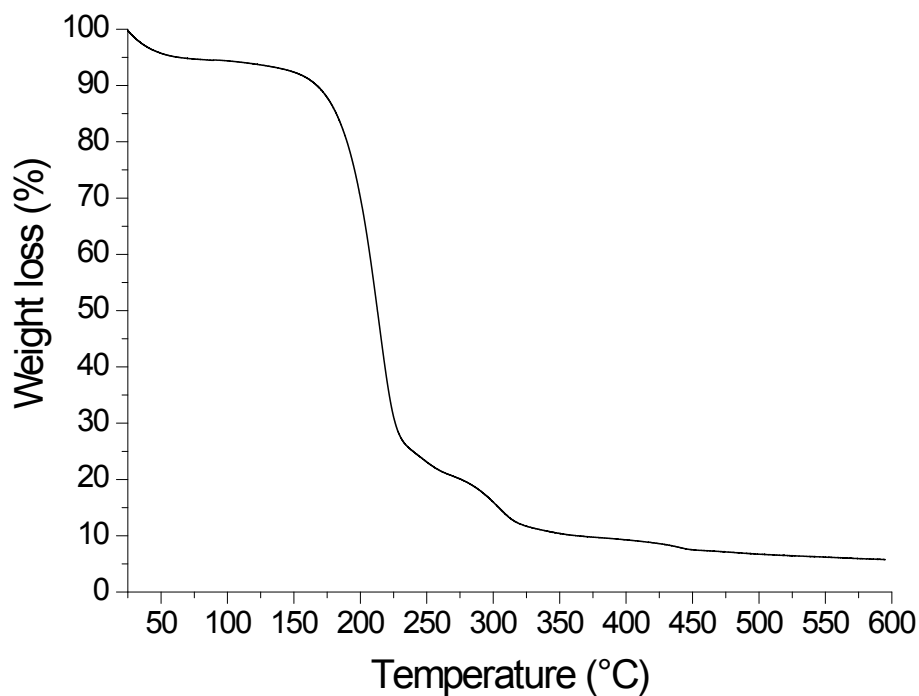


**Figure S7.**  $^7\text{Li}$  NMR ( $\text{CDCl}_3$ , 155.5 MHz) of lithium 1,2,3-triazolate **5**.

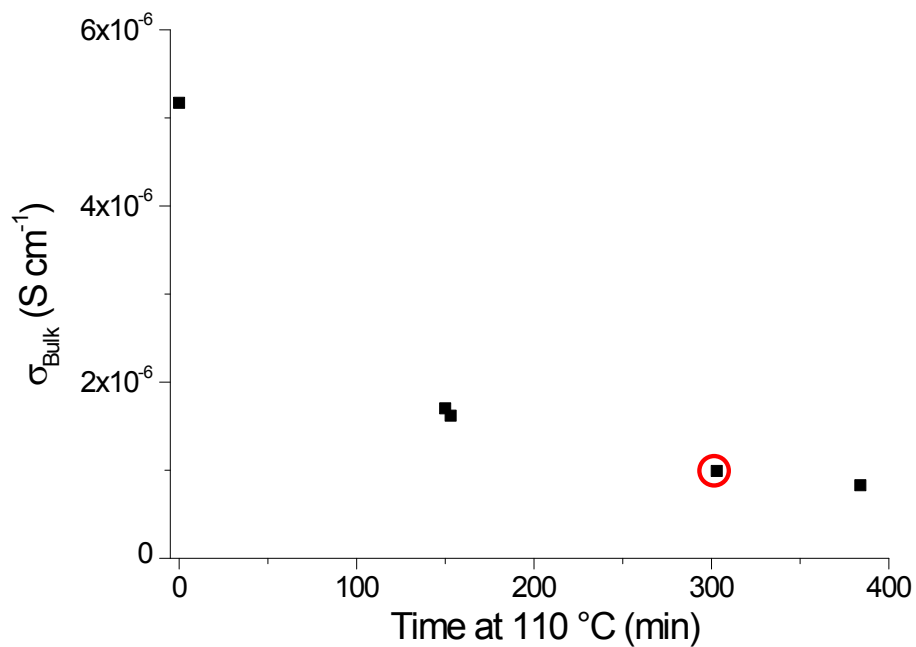


**Figure S8.** DSC trace of lithium 1,2,3-triazolate **5**.

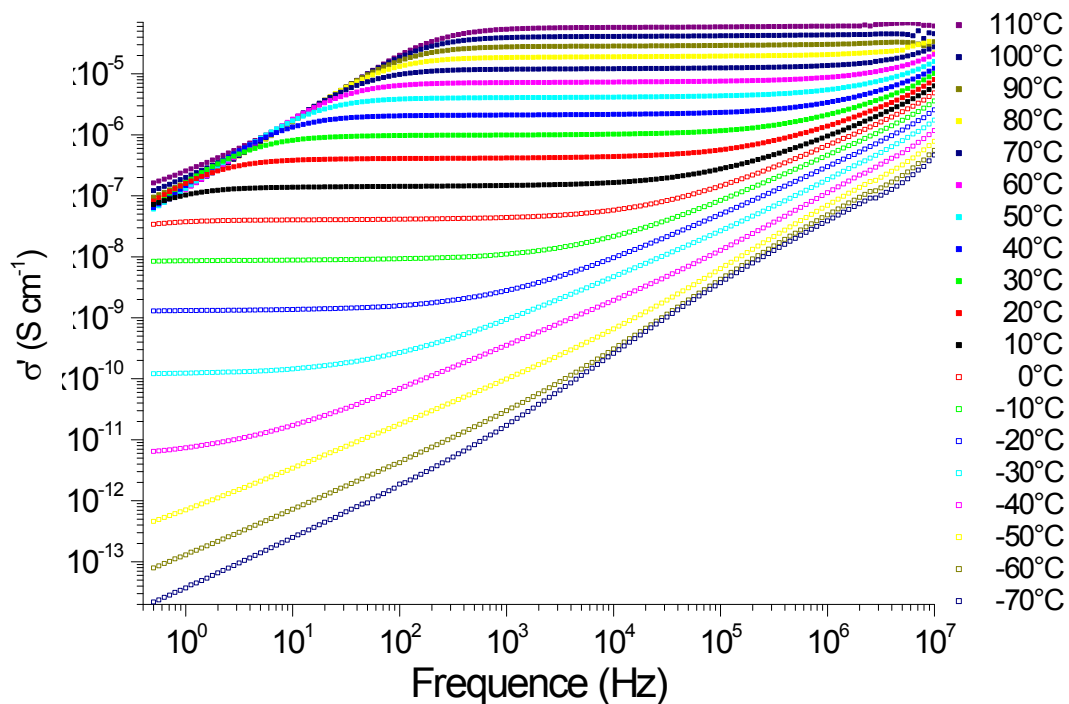




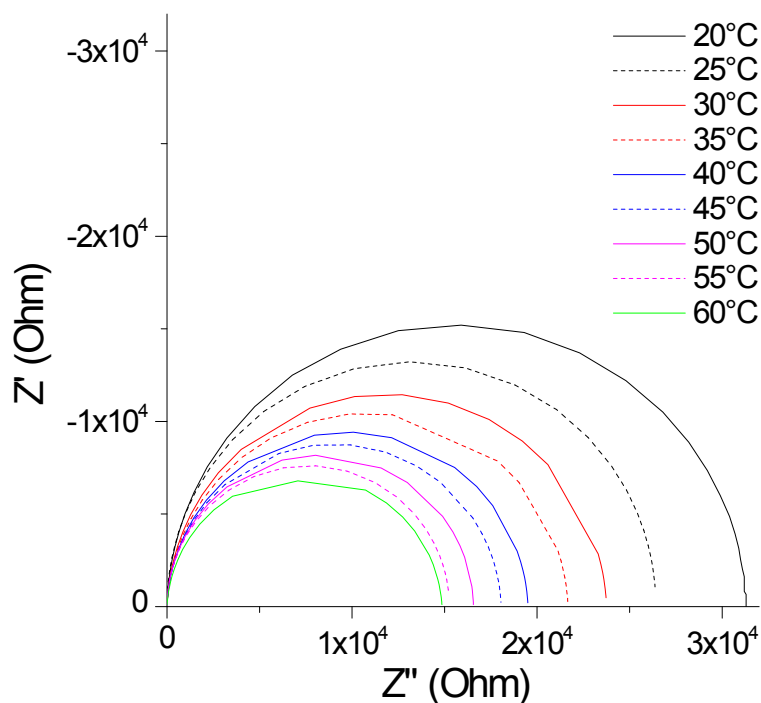
**Figure S9.** TGA trace of lithium 1,2,3-triazolate **5**.



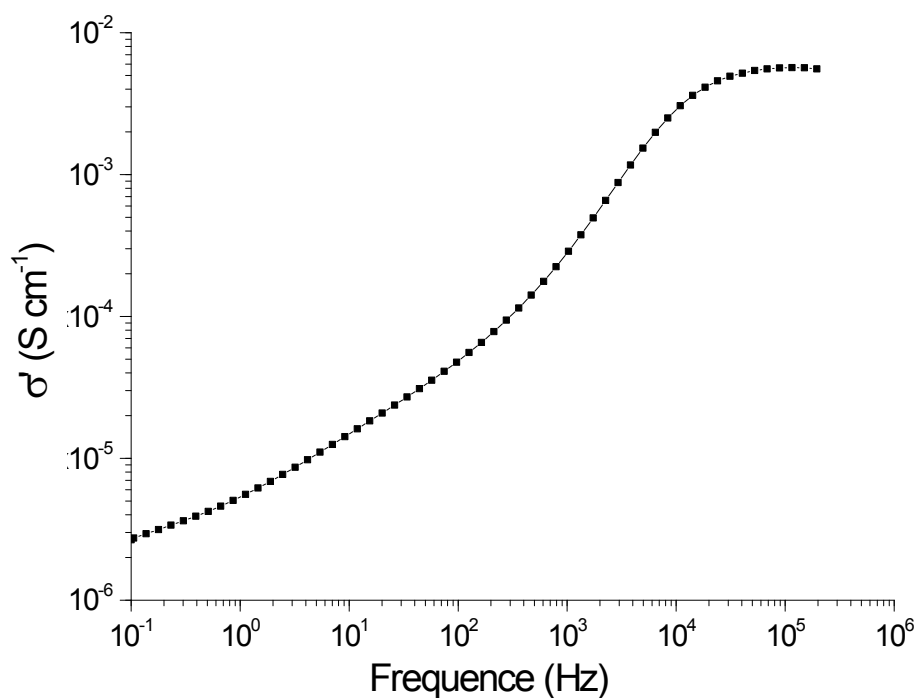
**Figure S10.** Ionic conductivity ( $\sigma_{\text{Bulk}}$ ) at 30 °C measured by BDS in bulk and under anhydrous conditions versus annealing time at 110 °C under nitrogen within the spectrometer for lithium 1,2,3-triazolate **5**. Data point circled in red corresponds to experimental results given in Table 1, Figure 2 and Figure S8.



**Figure S11.** Conductivity  $\sigma'$  as a function of frequency at temperatures ranging from 110 to  $-70$  °C for lithium 1,2,3-triazolate **5**. Measurements were performed after annealing the sample for ca. 5h at 110 °C which correspond to the data circled in red in Figure S7.



**Figure S12.** Impedance spectra in Nyquist coordinates obtained at temperatures ranging from 25 °C to 60 °C of a 1 M solution of 1,2,3-triazolate **5** in a 1:1 (vol/vol) mixture of EC and DMC.



**Figure S13.** Conductivity  $\sigma'$  as a function of frequency at 25 °C for a 1 M aqueous solution of lithium 1,2,3-triazolate **5**.

**Table S1.** Solubility of lithium 1,2,3-triazolate **5**.

H <sub>2</sub> O <sup>[a]</sup>	Heptane	MeOH	EtOAc	Acetone	Et <sub>2</sub> O	THF	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CH <sub>3</sub> CN	EC	DMC	PhCH <sub>3</sub>	DMF	DMSO
++	-	++	-	++	-	++	++	++	++	++	++	-	++	++

[a]: “++” indicates solubility at 10 mg mL<sup>-1</sup> while “-” indicates no detectable solubility at 1 mg mL<sup>-1</sup>.

## References

- 1) Y. Feng, J. Li, L. Jiang, Z. Gao, W. Huang, F. Jiang, N. Luo, S. Han, R. Zeng and D. Yang, *Eur. J. Chem.*, 2011, **2011**, 562.
- 2) J. C. Loren, A. Krasinski, V. V. Fokin and K. B. Sharpless, *Synlett.*, 2005, **18**, 2847.