### **Supporting Information**

#### Alternatives to Fluorinated Binders: Recyclable Copolyester/carbonate Electrolytes for High-Capacity Solid Composite Cathodes

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#### 1. Experimental Details, Methods and Reagents

Materials. All solvents and reagents were purchased and used as obtained from commercial sources (Sigma Aldrich) unless stated otherwise. The synthesis of 4-tert-butyl-2,6-diformylphenol,  $[H_4L]$ )(ClO<sub>4</sub>)<sub>2</sub> and H<sub>2</sub>L were carried out in air. The synthesis of the catalyst, [LZn<sub>2</sub>(Ph)<sub>2</sub>], monomer purification and subsequent polymerisations and depolymerisations were carried out under inert conditions using standard Schlenk line techniques and a nitrogen-filled glovebox. Vinyl cyclohexene oxide (vCHO) and  $\epsilon$ -caprolactone ( $\epsilon$ -CL) were dried by stirring over CaH<sub>2</sub>, distilled under reduced pressure and stored under nitrogen. 1,4-Benzene dimethanol (BDM) was recrystallised from toluene (three times) and stored under nitrogen. Trimethylene carbonate (TMC) was purchased from TCI, recrystallised (dry Et<sub>2</sub>O) under nitrogen and dried in vacuo before use. Research grade carbon dioxide (BOC, 99.99%) was passed through two drying columns (Micro Torr, Model number: MC1-804FV) prior to polymerisation. Single crystal NMC811 (MSE), Li<sub>6</sub>PS<sub>5</sub>CI (MSE) and carbon nanofiber (Merck) were dried at 110 °C under vacuum (1 ×10<sup>-2</sup> mbar). Tin(II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>) was used as received. Glycerol ethoxylate (GEO,  $M_n \sim 1000 \text{ g mol}^{-1}$ ) for depolymerisation was dried at 120 °C, under high vacuum (1 x10<sup>-2</sup>, mbar), and stored over 3 Å sieves for 2 days prior to use. Zinc(II) 2-ethylhexanoate was purchased from Fluorochem and used as received. The recycling catalyst, Zn(Oct)<sub>2</sub>, was synthesised according to literature reports.1

**Synthesis of H**<sub>2</sub>**L**. The ligand was synthesised according to the published procedure.<sup>2</sup> [H<sub>4</sub>L](ClO<sub>4</sub>) (5.0 g, 6.7 mmol) and MeOH (500 mL) were added to a round-bottom flask to obtain a red/orange solution. The solution was cooled to 0 °C, before the slow addition of NaBH<sub>4</sub> (7.58 g, 200 mmol) to yield a colourless solution. The solution was left stirring at room temperature, for 1 h, before water was added until precipitation was observed (400 mL). The resultant suspension was left standing for 10 h, before being filtered, washed with water and dried under vacuum (at 40 °C) to yield a white solid. The precipitate was crystallised from MeOH to yield white crystals (2.56 g, 4.63 mmol, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ (ppm) = 6.93 (s, 4H, Ar-H), 3.73 (s, 8H, CH<sub>2</sub>), 2.52 (s, 8H, CH<sub>2</sub>), 1.25 (s, 18H, CH<sub>3</sub>), 1.01 (s, 12H, CH<sub>3</sub>).

**Synthesis of**  $[LZn_2(Ph)_2]$  **Catalyst.** The catalyst was synthesised according to the published procedure.<sup>2</sup> Under anaerobic conditions, two separate solutions of [H<sub>2</sub>L] (0.40 g, 0.7 mmol) in THF (5 mL) and ZnPh<sub>2</sub> (0.25 g, 1.2 mmol) in THF (2 mL) were pre-cooled to -40 °C, before being added to a glass vial together to obtain a cloudy solution. The mixture was stirred for 25 h at 25 °C and filtered to obtain a white solid (260 mg, 0.31 mmol, 55%).

**Polymer Electrolyte Preparation.** Under anaerobic conditions, the polymer (500 mg) was dissolved in THF (1.5 mL). To the stirring solution, LiTFSI (100 mg) was added and dissolved. The solution was filtered and cast in a PTFE mold. The solvent was allowed to evaporate, at ambient temperature and pressure, for 48 h before being transferred to a vacuum oven, at 60 °C, to remove all solvent as confirmed by NMR spectroscopy and TGA.

**Exemplar Switch Catalysis of vCHO, CO<sub>2</sub>, TMC, and**  $\epsilon$ **-CL.** To a 100 mL Schlenk flask in a glove box (N<sub>2</sub> atmosphere), TMC (530 mg, 5.2 mmol), 1,4-BDM (11 mg, 0.08 mmol),  $\epsilon$ -CL (2.30 mL, 20.8 mmol), vCHO (12.5 mL, 85.0 mmol), toluene (15 mL), and [LZn<sub>2</sub>Ph<sub>2</sub>] (20 mg, 0.024 mmol) were added.

The flask was transferred to a triple manifold (vacuum/N<sub>2</sub>/CO<sub>2</sub>) Schlenk line and heated to 100 °C with rapid stirring. Once the temperature had reached 100 °C, the conditions were maintained for 1 h. The flask atmosphere was then switched from N<sub>2</sub> to CO<sub>2</sub>, by partial removal of N<sub>2</sub>, under vacuum, and refilling with 1 bar CO<sub>2</sub>. After a further 22 h, the flask was cooled and exposed to air and the catalysis was quenched (benzoic acid in chloroform). The conversion of  $\varepsilon$ -CL was determined by <sup>1</sup>H NMR spectroscopic analysis of the crude reaction mixture (95 % for  $\varepsilon$ -CL, 12% for vCHO, Fig. S3). The reaction mixture was precipitated three times from methanol (3 × 200 mL) to yield a white gummy solid. The material was dried in vacuo and the triblock copolymer is isolated as a colourless solid (3.4 g). See Figure S4 for the assigned <sup>1</sup>H NMR spectrum.

**Nuclear Magnetic Resonance (NMR).** <sup>1</sup>H and <sup>31</sup>P{H} NMR spectra were obtained using a Bruker AVII HD 400 NMR spectrometer. <sup>13</sup>C{H} NMR spectra were obtained using a Bruker AVII 500 NMR spectrometer.

Size Exclusion Chromatography (SEC). Data was obtained using a Shimadzu LC-20AD instrument, equipped with Refractive Index (RI) and UV-Vis detectors and two PSS SDV 5  $\mu$ m linear M columns. HPLC grade THF was used as the eluent, flowing at 1.0 mL/min, at 30 °C. Monodisperse polystyrene standards were used for calibration. Samples were passed through 0.2  $\mu$ m syringe filters prior to analysis.

**Differential Scanning Calorimetry (DSC).** A DSC3+ (Mettler-Toledo Ltd) instrument was used. A sealed, empty crucible was used as a reference and the DSC was calibrated using zinc and indium standards. Samples were cooled, from 25 °C to -80 °C, at a rate of 20 °C min<sup>-1</sup>, under a N<sub>2</sub> flow (80 mL min<sup>-1</sup>), followed by a 5-minute isotherm, at -80 °C. Samples were then heated to 200 °C, at a rate of 20 °C min<sup>-1</sup>; kept at 200°C for a further 5 minutes; followed by a cooling-heating procedure from 200 °C to -80 °C, at 10 °C min<sup>-1</sup>. Glass transition temperatures ( $T_g$ ) are reported as the midpoint of the transition taken from the second cycle.

**Thermal Gravimetric Analysis (TGA).** Data was collected on a TGA5500 System (TA Instruments), equipped with the TRIOS software package. For determination of thermal stability, polymer samples were heated from 30 to 500 °C, at a rate of 5 °C min<sup>-1</sup>, under a N<sub>2</sub> flow (100 mL min<sup>-1</sup>).

**Tensile Testing.** Dumbbell specimens were cut from polymer electrolyte films according to ISO 527-2, specimen type 5B with Zwick ZCP020 cutting press (length= 35 mm, gauge length = 10 mm, width = 2 mm). Monotonic uniaxial extension experiments were carried out on a Shimadzu EZ-LZ Universal. Cyclic tensile tests were conducted to 20% strain at a rate of 10 mm min<sup>-1</sup>. 10 Cycles were measured for each specimen, 3 specimens for each sample.

**180° Peel Tests.** Solid polymer electrolyte (0.4 g) in THF ( 4 ml) was cast onto alumina sheets ( $20 \times 80$  mm), and the solvent was allowed to evaporate at RT. The coated alumina sheets were then dried in a vacuum oven for 72 h before testing. 3M® scotch tape was applied to the polymer electrolyte coated alumina. A corner of the coating was manually de-bonded from the alumina substrate, and a Shimadzu EZ-LZ universal tensile tester was used to peel the coating off at a 180° angle and rate of 305 mm/min. The force required to remove the coating was measured. Peel strength (N mm<sup>-1</sup>) = Peel force/width.

**Rheology.** Oscillatory rheology measurements were conducted on an ARES-G2 instrument (TA Instruments) equipped with 8 mm parallel plates. Frequency sweep analysis was conducted, at 10 °C

intervals, between 30 and 130 °C, with  $\gamma$  = 1%, and a logarithmic frequency ramp between 0.1 Hz and 100 Hz – under these conditions, the polymer was in its linear viscoelastic region. Temperature sweep analyses were conducted between 30 and 120 °C, with  $\gamma$  = 1%, at an oscillation frequency of 1 Hz.

**Electrochemical Impedance Spectroscopy (EIS).** Ionic conductivity was measured by impedance spectroscopy using an MTZ-35 Impedance Analyzer (Biologic), over the frequency range 10 MHz – 0.01 Hz, with the amplitude set to 10 mV. The electrolytes were sandwiched between gold electrodes in a controlled environment sample holder which was then enclosed in an intermediate temperature system. Measurements were taken at 10 °C intervals, between 20 and 70 °C. The samples were equilibrated at each temperature for 20 min before a new recording was made. The resistance was calculated with EC-Labs, using a modified Debye equivalent circuit. Measurements were taken on three occasions and the error was recorded as a standard deviation.

**Small-Angle X-ray Scattering (SAXS).** Performed at beamLine station I-22, located at Diamond Light Source, Harwell, United Kingdom. Samples were mounted between two pieces of Kapton®. A monochromatic X-ray radiation ( $\lambda$  = 0.1 nm) and 2D SAXS detector (Pilatus P3-2M, DECTRIS Ltd.) were used for the experiments. 2D scattering patterns were reduced to 1D using Dawn software developed at the Diamond Light Source.<sup>3</sup>

**Voltammetry.** Linear sweep and cyclic voltammetry were conducted on a VMP2 (Bio-Logic). A 4 mm disc of ABA(50, 0.35) and a 3 mm lithium disc were sandwiched between two stainless steel discs. The cell was stabilised at the open circuit voltage (OCV) for 3 h at 60 °C, before cycling was performed at 0.5 mV s<sup>-1</sup>. All procedures were carried out in an argon-filled glovebox.

**Li-Ion Transference Number.** All pulsed field gradient (PFG) nuclear magnetic resonance (NMR) measurements were completed at 9.45 T ( $u_0(^{19}\text{F}) = 376.58$ , and  $u_0(^{7}\text{Li}) = 155.53$  MHz) on Bruker Avance III HD spectrometer, using a 5 mm single-axis diffusion probe with exchangeable <sup>19</sup>F and <sup>7</sup>Li ceramic heads. A stimulated echo pulse sequence was used, with an effective gradient pulse duration ( $\delta$ ) of between 1-3 ms, and a diffusion time ( $\Delta$ ) of 20-100 ms, with the gradient amplitude varying between 0.1 and 22 T/m. The experimental temperature was stabilised at 333.1 K, and a 5-second recycle delay

was used throughout. All data is fitted to  $f(x) = I_0 \times e^{-\gamma^2 g^2 \delta^2 \frac{(\Delta - \delta)}{3}D}$ , where for <sup>19</sup>F;  $\delta$  = 1-2 ms,  $\Delta$  = 20-50 ms, and  $\gamma$  = 25172 rad/sG, and for <sup>7</sup>Li;  $\delta$  = 1-3 ms,  $\Delta$  = 20-100 ms, and  $\gamma$  = 10397 rad/sG. An R<sup>2</sup> of 0.999, errors of <1% (<1x10<sup>-14</sup> m<sup>2</sup> s<sup>-1</sup>) and normal distributions of the residuals were observed for all experiments.

**TGA-FTIR for Depolymerisation/Chemical Recycling Back to Monomer.** Measurements were collected on a Nicolet iS20 FTIR spectrometer (Thermo Scientific Instruments) coupled to a TGA5500 (TA instruments). The mass flow of the TGA was set to 30 mL min<sup>-1</sup>. The FTIR spectrometer was equipped with a KBr/Ge beamsplitter, fast-recovery deuterated triglycine sulfate KBr detector and solid-state diode laser. Spectra were recorded, between 400 – 4000 cm<sup>-1</sup>, with 10 scans per spectrum, at a resolution of 8 cm<sup>-1</sup>.

**Polymer Electrolyte Processing**. Polymer electrolyte films were processed into a powder using a Retsch CryoMill, cooled with liquid  $N_2$ . Small pieces of electrolyte film (1–3 mm diameter) were added to a 5 mL stainless steel jar, with 2 ball bearings of 7 mm diameter. The following cooling and milling

procedure was conducted: 8 min pre-cooling at 5 Hz; 2 min milling step at 30 Hz; 0.5 min rest at 5 Hz; with 5 mill/rest cycles conducted. Once the procedure was complete, the jar was allowed to warm to ambient temperature yielding a white polymer electrolyte powder.

**Composite Cathode Fabrication and Cell Assembly.** Single crystal NMC811,  $Li_6PS_5CI$ , polymer electrolyte, and carbon nanofiber (CNF, Merck) were mixed in a 70:23:5:2 wt% ratio by pestle and mortar. The resulting powder was pressed at 250 MPa with a layer of pure  $Li_6PS_5CI$  and a composite of  $Li_4Ti_5O_{12}$  (LTO),  $Li_6PS_5CI$ , and CNF in a glovebox filled with argon. The cells were assembled in a custom-designed module with a PEEK mould and two stainless steel plungers.

**Polymer Bromination for Visualisation in the Cathode Composite.** P(vCHC-*b*-CL-*r*-TMC-*b*-vCHC) (1 equiv. vinyl groups, 0.1 M) was dissolved in CHCl<sub>3</sub> (3 mL) and a bromine solution in CHCl<sub>3</sub> (1equiv., 0.1 M) was added, dropwise at 0 °C with stirring. The solution was warmed to ambient temperature and stirred for 1 h, before precipitation with methanol yielded the brominated polymer as a colourless solid. The polymer was characterised by <sup>1</sup>H NMR spectroscopy (Figure S21).

**Polymer Chemical Recycling to Monomer by TGA**. In the glovebox, stock solutions of P(vCHC-b-CL-r-TMC-b-vCHC) (1.00 M, 124 mg P(vCHC-b-CL-r-TMC-b-vCHC) in 1.00 mL of THF),  $Zn(Oct)_2$  (1.00 x 10 <sup>-2</sup> M,10.6 mg of  $Zn(Oct)_2$  in 3.00 mL of THF) and GEO (0.03 M, 33.3 mg of GEO in 1.00 mL of THF) were prepared. The P(vCHC-b-CL-r-TMC-b-vCHC) solution (100 µL, 0.1 mmol, 1000.0 equiv.) was added to a vial containing  $Zn(Oct)_2$  (10.0 µL, 1.00 x 10 <sup>-4</sup> mmol, 1.0 equiv.) and GEO (20.0 µL, 6.67 x 10 <sup>-4</sup> mmol, 6.7 equiv.). The  $Zn(Oct)_2/GEO/P(vCHC-b-CL-r-TMC-b-vCHC)$  solution was thoroughly mixed before being dropcast (*c.a.* 3 drops) onto Platinum TGA crucibles. The solvent was allowed to evaporate before the crucible was loaded into the TGA for monitored depolymerisation. The following TGA method template was used for the reaction: N<sub>2</sub> flow of 25.0 mL min<sup>-1</sup>; heat from room temperature to 200 °C; isotherm for 300 minutes; heat at 20 °C min<sup>-1</sup> to 600 °C; heat to 30 °C. The catalyst loading, GEO loading, reaction temperature and length of the isotherm were varied as required. To account for residual solvent loss from the polymer films, which will also be detected as a mass loss in TGA, data from the first 1.5 minutes were excluded and wt.% losses were measured after this point. For reactions where GEO was present, the residual mass of the GEO was accounted for as follows:

- 1) The mass at 1.5 minutes is the initial polymer, GEO and catalyst mass.
- 2) Subtract the theoretical %mass of GEO in the run:
- Take the mass in step 2) as the initial mass for calculation of the change in mass% of the sample.

**Bulk Depolymerisation of P(vCHC-***b***-CL**-*r***-TMC**-*b***-vCHC) to Isolated Monomer Mixture.** In the glovebox,  $Zn(Oct)_2$  (927 µL of a 0.01 M stock solution in THF, 9.26 x 10<sup>-3</sup> mmol, 1.00 equiv.) and GEO (10.5 mg, 0.0105 mmol, 1.13 equiv.) were added to a flask containing P(vCHC-*b*-CL-*r*-TMC-*b*-vCHC) (1.15 g, 9.26 mmol, 1000 equiv.). The mixture was dissolved in the minimum amount of THF (*ca* 7 mL) and the solvent was completely removed *in vacuuo*. The flask was attached to a water-cooled, short-path distillation apparatus and heated to 200 °C, under 1 mbar pressure. The product was collected in a flask cooled over dry ice. After 11 h, the collection flask was disconnected to yield a clear oil (1.03 g, 90% yield). Analysis by <sup>1</sup>H NMR spectroscopy confirmed it contained vCHO, CL and TMC in approximately the same ratio as in the polymer (depolymerisation mixture = VCHO/VCHCC: TMC: ε-

CL molar ratio = 1.27: 1.00: 4.43 *vs* polymer VCHO/VCHCC: TMC:  $\epsilon$ -CL molar ratio = 1.23: 1.00: 4.00). Note that pure polymer was used for this study; there was an insufficient quantity of polymer in the cell for depolymerisation monitoring.

#### 2. Catalyst Structure and Initiation



**Scheme S1.** The structure of the catalyst used in polymerisations, [LZn<sub>2</sub>Ph<sub>2</sub>] and its initiation with BDM. Alcohol reacts with the catalyst in situ to form the alkoxide initiator essential for ROP and ROCOP. Initiation occurs analogously with the monofunctional initiator Me-BnOH: BDM is used to make triblock (ABA) polymers; Me-BnOH is used to make diblock (AB) polymers.

3. Ring-Opening Polymerisation and Copolymerisation Mechanisms



**Scheme S2.** Switchable catalysis mechanisms where the epoxide/CO<sub>2</sub> ring-opening copolymerisation (ROCOP) and the CL/TMC ring-opening polymerisation (ROP) cycles are accessed by the di-zinc catalyst. By using a diol or alcohol initiator, either ABA (triblock) or AB (diblock) polymers are produced.



P(vCHC-b-ε-CL-r-TMC-b-vCHC)

**Scheme S3.** Polymerisation with the bifunctional initiator, BDM, to produce the ABA polymers (Series II and III). The initiator was BDM, to access polymers with an ABA block structure.  $[LZn_2Ph_2] = 0.8 \text{ mM}, [vCHO] = 2.8 \text{ M}, [TMC + \varepsilon-CL]_0 = 0.9 \text{ M}.$  Exemplar ratio:  $[LZn_2Ph_2]/[BDM]/[TMC]/[\varepsilon-CL]/[vCHO] = 1/4/200/800/3500$ , where [BDM], [ $\varepsilon$ -CL], and [TMC +  $\varepsilon$ -CL]\_0 are adjusted to achieve the desired composition and  $M_n$ . i) ROP at 100 °C for 1 h, under an N<sub>2</sub> atmosphere in a 15 mL toluene solution. iii) ROCOP at 100 °C for 16–44 h, under a CO<sub>2</sub> atmosphere.



PvCHC-b-P(ε-CL-r-TMC)

**Scheme S4.** Polymerisation with the monofunctional initiator, Me-BnOH, to produce the AB polymers (Series I). The Me-BnOH ensures the formation of the polymers AB structure.  $[LZn_2Ph_2] = 0.8 \text{ mM}, [VCHO] = 2.8 \text{ M}, [TMC + \varepsilon-CL]_0 = 0.9 \text{ M}.$  Exemplar ratio:  $[LZn_2Ph_2]/[Me-BnOH]/[TMC]/[\varepsilon-CL]/[vCHO] = 1/4/200/800/3500$ , where [Me-BnOH], [ $\varepsilon$ -CL], and [TMC +  $\varepsilon$ -CL]\_0 are adjusted to achieve the desired composition and  $M_n$ . i) ROP at 100 °C for 1 h, under an N<sub>2</sub> atmosphere in a 15 mL toluene solution. ii) ROCOP at 100 °C for 16–44 h, under a CO<sub>2</sub> atmosphere.

Entry <sup>a</sup>	Calculated polymer composition, DP <sub>n,A</sub> – DP <sub>n,B</sub> (–DP <sub>n,A</sub> ) <sub>calc.</sub> <sup>b</sup>	Experimental polymer composition, DP <sub>n,A</sub> – DP <sub>n,B</sub> (–DP <sub>n,A</sub> ) <sub>NMR</sub> <sup>c</sup>	Initiator <sup>d</sup> (mmol)	ε-CL ° (mmol)	TMC ° (mmol)
AB(26, 0.45)	82–129	77–139	0.154	17.6	4.4
AB(32, 0.51)	128–141	95–152	0.125	15.7	3.9
AB(45, 0.47)	142–214	126–215	0.089	17	4.2
AB(69, 0.58)	274–298	238–260	0.058	15.4	3.8
ABA(35, 0.52)	55–111–55	52–144–52	0.114	12	3
ABA(44, 0.53)	88–187–88	71–194–71	0.091	15.1	3.8
ABA(50, 0.47)	95–213–95	71–250–71	0.08	15.1	3.8
ABA(66, 0.52)	124–221–124	101–266–101	0.061	12	3
ABA(51, 0.26)	43–342–43	42–352–42	0.078	23.7	5.9
ABA(47, 0.30)	49–296–49	42-315-42	0.085	22.4	5.6
ABA(50, 0.35)	63–293–63	54-306-54	0.08	20.8	5.2
ABA(50, 0.62)	100–204–100	95–176–95	0.067	12.2	3

Table S1. Reaction conditions for synthesis of ABA/AB- poly(vCHC-b-CL-r-TMC-b-vCHC).

<sup>a</sup> Polymers labelled as ABA/AB ( $M_n$ ,  $w_{PC}$ ) where  $M_n$  = overall molar mass in kg mol<sup>-1</sup> and  $w_{PC}$  = weight fraction of PC; <sup>b</sup> Degree of polymerisation, DP<sub>n</sub> of the PvCHC (A) block(s) and P( $\varepsilon$ -CL*r*-TMC) block (B), equivalent to labels *n* and *m* in Scheme S1, respectively. Calculated compositions (DP<sub>n</sub>) were determined by the monomer to initiator ratios and conversions; <sup>c</sup> Experimental compositions (DP<sub>n</sub>) were calculated using the <sup>1</sup>H NMR spectra of the purified polymer, by integration of the initiator resonances (7.34 ppm for 1,4-BDM, 7.17 ppm for Me-BnOH) against those of PvCHC (5.76 ppm) and P( $\varepsilon$ -CL-*r*-TMC) (2.00, 1.38 ppm); <sup>d</sup> Quantity of initiator, either BDM (ABA) or Me-BnOH (AB); <sup>e</sup> Quantity of  $\varepsilon$ -CL and TMC in the reaction mixture. For all entries, there were 0.24 mmol [LZn<sub>2</sub>Ph<sub>2</sub>] and 84 mmol vCHO.

#### 4. NMR Characterisation



**Figure S1.** Crude <sup>1</sup>H NMR spectra of the polymerisation process, identifying the signals used to calculate monomer conversions (labelled). Top: Product after 1 hour of stirring, at 100 °C, under N<sub>2</sub>. Bottom: Product after a further 44 h of stirring at 100 °C, under CO<sub>2</sub> (1 bar).



Figure S2. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of ABA(47, 0.30).



Figure S3. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) spectrum of ABA(47, 0.30).



**Figure S4.** <sup>13</sup>C{H} NMR spectrum of the  $\varepsilon$ -CL carbonyl regions of poly(vCHC-*b*- $\varepsilon$ -CL-*r*-TMC-*b*-vCHC), sample ABA(50, 0.35), with the triads labelled; C refers to the repeating  $\varepsilon$ -CL units and T refers to TMC units, with the centre unit in each triad giving rise to the observed signal.



**Figure S5.** <sup>13</sup>C{H} NMR spectrum of the TMC carbonyl regions of poly(vCHC-*b*- $\epsilon$ -CL-*r*-TMC-*b*-vCHC), sample ABA(50, 0.35), with the triads labelled; C refers to the repeating  $\epsilon$ -CL units and T refers to TMC units, with the centre unit in each triad giving rise to the observed signal.

### 5. Polymer Chain End Group Analysis



**Figure S6** Exemplar <sup>31</sup>P{<sup>1</sup>H} NMR spectra (CDCl<sub>3</sub>) after reaction of the polymer hydroxyl end groups with 2-chloro-4,4,5,5-tetramethyldioxaphospholone. Top: poly(vCHC-*b*- $\epsilon$ -CL-*r*-TMC-*b*-vCHC), ABA(47, 0.30) displaying poly(vCHC)-OH end groups. Bottom: poly( $\epsilon$ -CL-*r*-TMC), displaying poly( $\epsilon$ -CL)-OH and poly(TMC)-OH end groups.

# 6. DOSY NMR Spectra



**Figure S7.** Exemplar DOSY NMR spectrum of ABA(47, 0.30), showing a single diffusion coefficient.

7. Size Exclusion Chromatography (SEC)



**Figure S8.** SEC trace of ABA(44, 0.53), measured in THF eluent with an RI detector vs. narrow PS standards.

### 8. Optimisation of Polymer Electrolyte Lithium Salt Content



**Figure S9.** Effect of LiTFSI concentration on the thermal properties and Li-ion conductivity of ABA(51, 0.26). (a) DSC data, with the lower  $T_g$  labelled; (b) Li-ion conductivity as a function of temperature.

### 9. Thermal Gravimetric Analysis (TGA)

Polymer <sup>a</sup>	<i>T</i> <sub>d, 5%</sub> (°C) <sup><i>b</i></sup>	% mass lost <sup>c</sup>
AB(26, 0.45)	210	86.6
AB(32, 0.51)	226	87.8
AB(45, 0.47)	228	97.3
AB(69, 0.58)	231	97.9
ABA(35, 0.52)	204	89.1
ABA(44, 0.53)	235	96.1
ABA(50, 0.47)	242	95.6
ABA(66, 0.52)	231	97.8
ABA(51, 0.26)	233	97.5
ABA(47, 0.30)	240	96.9
ABA(50, 0.35)	241	96.2
ABA(50, 0.62)	230	96.0

**Table S2:** Thermal degradation data for the ABA and AB polymer electrolytes.

Polymers labelled as ABA/AB( $M_n$ ,  $w_{PC}$ ) where  $M_n$  = overall molar mass in kg mol<sup>-1</sup> and  $w_{PC}$  = weight fraction of PC; <sup>*b*</sup> Thermal degradation temperature of the polymer with 17 wt.% LiTFSI, determined by TGA. Recorded as the temperature at 5% mass loss. ° Between 100 and 500 °C.



Figure S10. TGA data for ABA(50, 0.35)/17wt.% LiTFSI.

#### 10. Electrochemical Impedance Spectroscopy (EIS)

Entry <sup>a</sup>	σ <sub>70 °C</sub> (S cm⁻¹) <sup>b</sup>	σ <sub>30 °C</sub> (S cm⁻¹) <sup>c</sup>	<i>E</i> <sub>a</sub> (kJ mol <sup>-1</sup> ) <sup>d</sup>	InA <sup>e</sup>
AB(26, 0.45)	2.0 × 10 <sup>-5</sup>	1.5 × 10 <sup>-6</sup>	15.4	4.0
AB(32, 0.51)	1.9 × 10 <sup>-5</sup>	8.4 x 10 <sup>-7</sup>	23.6	12.5
AB(45, 0.47)	9.0 × 10 <sup>-6</sup>	2.0 × 10 <sup>-7</sup>	9.1	3.8
AB(69, 0.58)	7.0 × 10 <sup>-7</sup>	2.1 × 10 <sup>-8</sup>	8.8	0.9
ABA(35, 0.52)	1.6 × 10 <sup>-5</sup> *	6.6 × 10 <sup>-7</sup>	15.3	5.6
ABA(44, 0.53)	1.2 × 10 <sup>-5</sup>	9.8 × 10 <sup>-7</sup>	8.7	2.9
ABA(50, 0.47)	2.8 × 10 <sup>-5</sup>	2.6 × 10 <sup>-6</sup>	13.0	0.0
ABA(66, 0.52)	5.6 × 10 <sup>-5</sup> *	5.5 × 10 <sup>-6</sup>	12.8	6.3
ABA(51, 0.26)	4.4× 10⁻⁵	1.2 × 10 <sup>-6</sup>	16.0	7.3
ABA(47, 0.30)	2.6 × 10 <sup>-5</sup>	4.3 × 10 <sup>-6</sup>	11.2	2.5
ABA(50, 0.35)	2.2 × 10 <sup>-4</sup> *	5.9 × 10 <sup>-6</sup>	17.0	8.3
ABA(50, 0.47)	2.8 × 10 <sup>-5</sup>	2.6 × 10 <sup>-6</sup>	13.0	0.0
ABA(50, 0.62)	3.7 × 10 <sup>-6</sup>	1.8 × 10 <sup>-7</sup>	14.6	1.7

**Table S3:** Summary of polymer electrolyte ionic conductivity data and parameters determined by VTF plots.

<sup>a</sup> Polymers labelled as ABA/AB( $M_n$ ,  $w_{PC}$ ) where  $M_n$  = overall molar mass in kg mol<sup>-1</sup> and  $w_{PC}$  = weight fraction of PC; <sup>b</sup> lonic conductivity at 70 °C, except for \*, measured at 60 °C. Measured using impedance spectroscopy, values have a 9% error. The ionic conductivity was calculated from the resistance that was obtained by fitting the acquired data to a modified Debye circuit; <sup>c</sup> Li-ion conductivity at 30 °C, values have an 11% error; <sup>d</sup> Activation energy of Li-ion transfer, obtained from the VFT fit; <sup>e</sup> Relative free charge carrier concentration of the polymer electrolyte, obtained from the VFT fit.



**Figure S11.** Representative Nyquist curves, where points are the collected data, lines represent the fits to the data (Inset: equivalent circuit; model used for determine R, then used to estimate  $\sigma$  where t = electrolyte thickness, A = electrolyte area).



Figure S12. Li-ion conductivity as a function of temperature for (a) Series I, AB ( $M_n$ , 0.5), (b)



Series II, ABA(M<sub>n</sub>, 0.5), and (c) Series III, ABA(50, w<sub>PC</sub>), all with 17 wt.% LiTFSI.

Figure S13. VTF fit for ABA(50, 0.35)/17wt% LiTFSI.



11. Small-angle X-Ray Scattering (SAXS) Data

**Figure S14**. SAXS data for (a) Series **II** ABA( $M_n$ , 0.50) and (b) Series **III** ABA(50,  $w_{PC}$ ) of polymer electrolytes. ABA(47, 0.30) and ABA(50, 0.35) are assigned to hexagonally packed spheres morphology. Principal scattering peak, q<sup>\*</sup>, and the expected Bragg maxima/allowed higher order SAXS reflections for microphase separated cylinders arranged on a hexagonal lattice: q<sup>\*</sup>,  $\sqrt{3}q^*$ ,  $\sqrt{4}q^*$ ,  $\sqrt{7}q^*$ ,  $\sqrt{9}q^*$ , etc are labelled.

# 12. <sup>7</sup>Li and <sup>19</sup>F NMR Spectroscopy



**Figure S15.** NMR spectra of ABA(50, 0.35), P(CL-*r*-TMC), and P(vCHC) electrolytes. (a) <sup>7</sup>Li NMR spectra. (b) <sup>19</sup>F NMR spectra.



**Figure S16.** Diffusion coefficients of ABA(50, 0.35) electrolyte by (a) <sup>7</sup>Li and (b) <sup>19</sup>F pulsed field gradient NMR spectroscopy. The colours are analogous to the deconvoluted resonances in Fig. S15 and given in Table S4.

**Table S4:** Calculated diffusion coefficients and transference numbers from pulsed-field gradient NMR for the ABA(50, 0.35) electrolyte.

Nucleus	Chemical Shift (ppm)	Assignment	<i>D</i> (m <sup>2</sup> s <sup>-1</sup> ) <sup>a</sup>	<b>t</b> <sub>Li+</sub> <sup>b</sup>
<sup>7</sup> Li	0.85	P(CL- <i>r</i> -TMC)	5.7 × 10 <sup>-13</sup>	0.44
<sup>7</sup> Li	2.73	PvCHC	4.6 × 10 <sup>-13</sup>	0.52
<sup>19</sup> F	-78.8	P(CL- <i>r</i> -TMC)	7.4 × 10 <sup>-13</sup>	0.44
<sup>19</sup> F	-77.0	PvCHC	4.2 × 10 <sup>-13</sup>	0.52
			$2 2 2 \delta^2 (\Delta - \delta)$	

<sup>a</sup> Diffusion coefficient data, determined from the fit  $f(x) = I_0 \times e^{-\gamma g \cdot \delta}$ , where for <sup>19</sup>F;  $\delta$  = 1-2 ms,  $\Delta$  = 20-50 ms, and  $\gamma$  = 25172 rad/sG, and for <sup>7</sup>Li;  $\delta$  = 1-3 ms,  $\Delta$  = 20-100 ms,

and  $\gamma = 10397 \text{ rad/sG}$ ; <sup>b</sup> Li-ion transference number, where  $t_{Li}^{+} = \frac{D_{Li}^{+}}{D_{Li}^{+}} / (D_{Li}^{+} + D_{F}^{-})$ .



**Figure S17.** Electrochemical impedance plots of a Ni|PE|Li<sub>6</sub>PS<sub>5</sub>Cl|PE|Ni cell, at 60 °C, with one measurement per hour and where PE is ABA(50, 0.35)/LiTFSI.

# 13. Cyclic Tensile Data



**Figure S18**: Elastic behaviour of the ABA(50, 0.35) polymer electrolyte film, with 17 wt.% LiTFSI. Cyclic tensile testing (20% strain, 10 mm min<sup>-1</sup> extension rate). Alternate cycles, horizontally shifted, show for clarity.



**Figure S19:** Elastic behaviour of PTFE film. Cyclic tensile testing (20% strain, 10 mm min<sup>-1</sup> extension rate). Alternate cycles, horizontally shifted, show for clarity.



**Figure S20:** Force vs displacement for the ABA(50, 0.35) electrolyte, recorded by 180° peel tests on alumina, 20 mm width.

#### 14. Rheology Master Curve





### 15. SEM and XPX Analyses of Composite Cathode





**Figure S22**. SEM and XPS images of the composite cathode NMC:CNF:  $Li_6PS_5CI:PE$ , 70:23:5:2 wt.%. The polymer sample ABA(50, 0.35) was brominated to enhance its visualisation (see below).

# 16. Polymer Bromination



vinyl group of ABA(50, 0.35).

# 16. Additional Cell Cycling Data



**Figure S24.** Charge-discharge profiles for the LTO|  $Li_6PS_5CI$  |NMC-PE cell where PE is ABA(50,0.35)/LiFSI, at cycle numbers 1, 50, 100, 150, and 200.



**Figure S25.** Potential vs. capacity at cycle 1 for the LTO| Li<sub>6</sub>PS<sub>5</sub>Cl |NMC-PE cell, where PE is either ABA(50,0.35)/LiFSI, ABA(50,0.35)/LiTFSI, or PTFE.



**Figure S26.** Capacity retention and coulombic efficiency vs. cycle number of an  $LTO|Li_6PS_5CI|NMC-PE$  solid-state cell, where PE = ABA(50,0.35)/LiFSI, at *T* = 60 °C, 1 MPa stack pressure, 1 mA cm<sup>-2</sup>.



**Figure S27.** Potential vs. capacity at cycle 1, 5 and 10 for the LTO|  $Li_6PS_5CI$  |NMC-PE cell, where PE is ABA(50,0.35)/LiFSI, cycled at 30 °C.

# 17. Chemical Recycling Data



**Figure S28.** Distillation setup used in isolation of VCHO, VCHCC, ε-CL and TMC from the depolymerisation of P(vCHC-*b*-CL-*r*-TMC-*b*-vCHC).From right to left: reaction flask containing polymer, catalyst and GEO, fractionating column and condenser and collection flask.



**Scheme S5.** <sup>1</sup>H NMR spectrum of the monomers isolated from the depolymeri**s**ation of P(vCHC-*b*-CL-*r*-TMC-*b*-vCHC) catalysed by Zn(Oct)<sub>2</sub>/GEO ([Zn(Oct)<sub>2</sub>]<sub>0</sub>: [GEO]<sub>0</sub>: [P(vCHC-*b*-CL-*r*-TMC-*b*-vCHC)]<sub>0</sub> = 1: 1.13: 1000) at 200 °C.

Table S5. Yield Calcu	lations for the Depolyn	nerisation of P(vCHC-l	b-CL- <i>r</i> -TMC- <i>b</i> -vCHC)
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	Component		
	VCHO +VCHCC	ТМС	ε-CL
mmoles of component in 1.15 g of P(vCHC- <i>b</i> -CL- <i>r</i> -TMC- <i>b</i> -vCHC)	1.85	1.50	6.01
(85, 0.27)			
mmoles of component isolated by distillation <sup>a</sup>	1.66	1.31	5.81
% yield of component <sup>a</sup>	90% <sup>b</sup>	87%	97%

<sup>*a*</sup> Determined by <sup>1</sup>H NMR integration of distillate component (VCHO + VCHCC ( $\delta$  = 5.90 – 5.63 ppm (m), TMC ( $\delta$  = 4.45 ppm (t, *J* = 5.7 Hz, 1H),  $\epsilon$ -Cl ( $\delta$  = 2.69 – 2.61 ppm (m)) against internal standard of mesitylene ( $\delta$  = 6.81 ppm (s)). <sup>*b*</sup> The cyclic carbonate and epoxide formed in a 1:1 molar ratio.

#### 18. References

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