

Supplementary Information for

Enhancing Ionic Conductivity in Tablet-Bottlebrush Block Copolymer Electrolytes with Well-Aligned Nanostructures via Solvent Vapor Annealing

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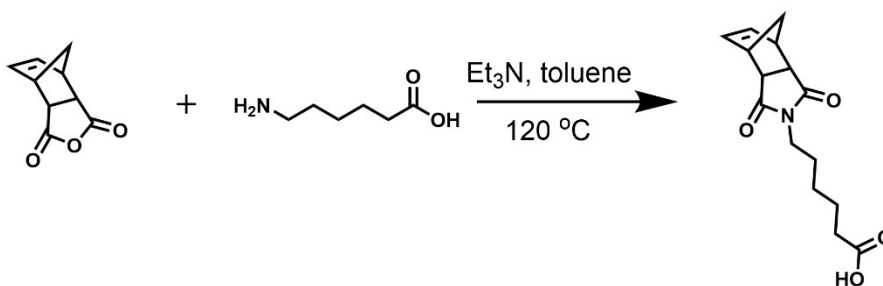
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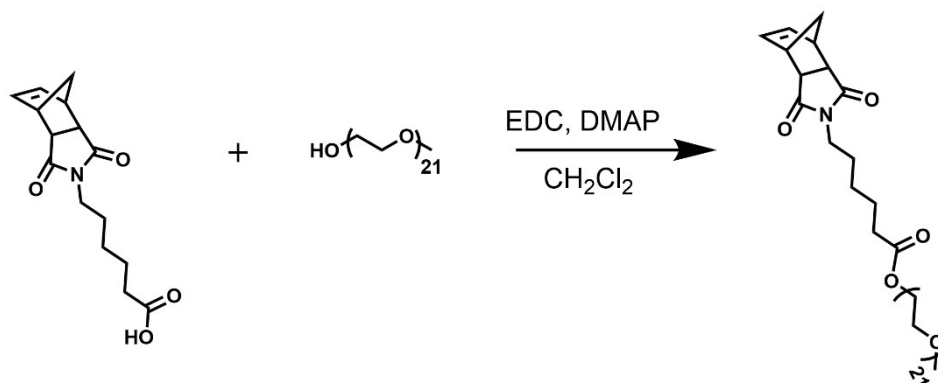
Synthesis

Synthesis of NbCOOH. The synthetic route is shown in Scheme S1. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (1.00 eq, 4.00 g, 24.4 mmol), 6-aminocaproic acid (1.00 eq, 3.20 g, 24.4 mmol), trimethylamine (0.100 eq, 0.340 mL, 2.44 mmol), and 60 mL of toluene were added into a 100 mL flask. After reflux at 120 °C for 12 h, the solution was condensed, and 50 mL CH₂Cl₂ was added. The solution was washed with water and brine for three times and dried with Na₂SO₄. The white solid was collected after removal of the solvent.



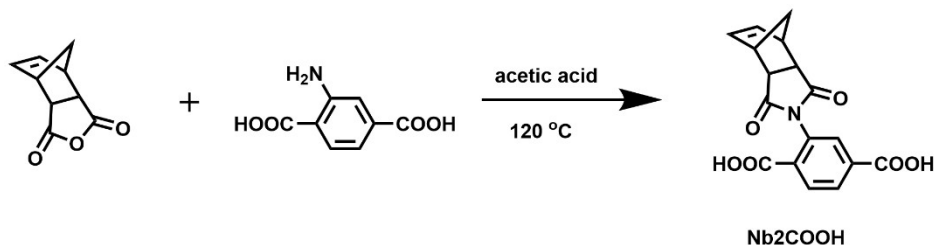
Scheme S1. Synthesis of NbCOOH.

Synthesis of NbPEO. The synthetic route is shown in Scheme S2. NbCOOH (1.20 eq, 1.97 g, 7.12 mmol), polyethylene glycol monomethylether ($M_n = 950 \text{ g mol}^{-1}$, 1.00 eq, 3.20 g, 24.4 mmol), and 80 mL of CH₂Cl₂ were added into a 150 mL flask. 1-Ethyl-3-(3-dimethylamino-propyl)carbodiimide hydrochloride (EDC•HCl, 2.40 eq, 2.72 g, 14.2 mmol) and 4-(dimethylamino)pyridine (DMAP, 0.200 eq, 0.145 g, 1.18 mmol) were added into the solution slowly. After stirring at ambient temperature for 36 h, the solution was condensed and washed with 1 M HCl aqueous solution. Then the resulting solution was washed with brine for three times and dried with Na₂SO₄. The mixture was dropped into cold petroleum ether. The white solid collected was dissolved with 5 mL of CH₂Cl₂ and dropped into cold petroleum ether. The white precipitation was NbPEO.



Scheme S2. Synthesis of NbPEO.

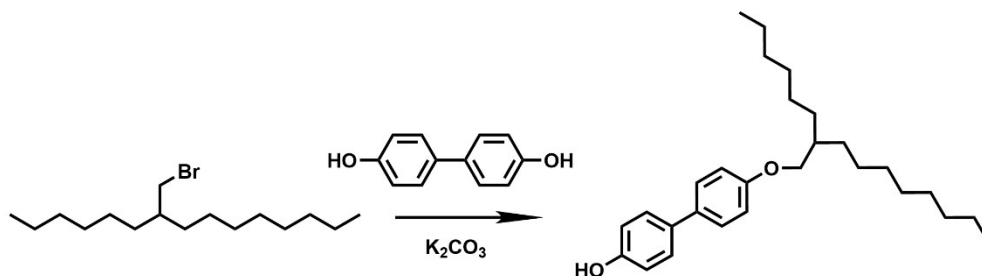
Synthesis of Nb2COOH. The synthetic route is shown in Scheme S3. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (1.00 eq, 3.28 g, 20.0 mmol), 2-aminoterephthalic acid (1.00 eq, 3.62 g, 20.0 mmol), and 40 mL of acetic acid were added into a 100 mL flask. After reflux at 120 °C for 12 h, the solution was poured into 200 mL of an ice/water mixture, and the resulting white solid was collected after filtration. Yield: 84%. ¹H NMR (400 MHz, dimethyl sulfoxide (DMSO), δ , ppm): 13.53 (s, 2H), 7.77–8.11 (m, 3H), 6.37 (s, 2H), 3.19–3.26 (d, 2H), 2.85–2.89 (d, 2H), 1.36–2.02 (m, 2H).



Scheme S3. Synthesis of Nb2COOH.

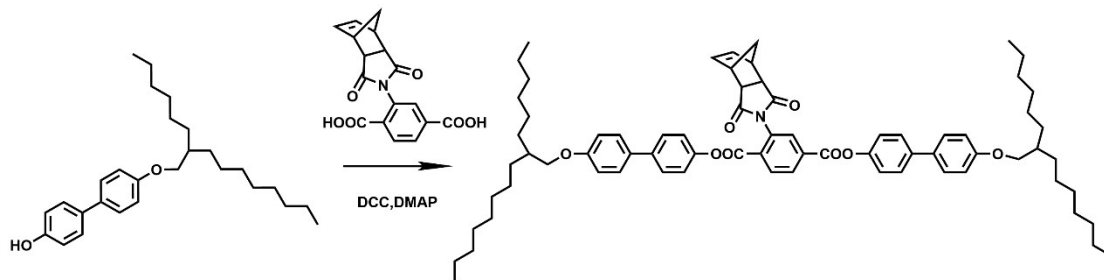
Synthesis of R₁₆BPOH. The synthetic route is shown in Scheme S4. 4,4'-Dihydroxybiphenyl (1.20 eq, 4.08 g, 24.0 mmol), 1-bromo-2-hexyldecane (1.00 eq, 6.10 g, 20.0 mmol), anhydrous K₂CO₃ (1.20 eq, 3.30 g, 24.0 mmol), and 50 mL of DMF were added into a 100 mL flask. The mixture was stirred at 90 °C for 12 h, and the solvent was removed. The residual solid was purified by silica gel column chromatography. Yield: 52%. ¹H NMR (400 MHz, DMSO, δ , ppm): 9.43 (s, 1H), 7.44–7.48 (d, 1H), 7.38–7.42 (d,

1H), 6.92–6.97 (d, 1H), 6.78–6.83 (d, 1H), 3.83–3.87 (d, 2H), 1.69–1.77 (m, 1H), 1.18–1.46 (m, 24H), 0.82–0.88 (t, 6H).



Scheme S4. Synthesis of R₁₆BPOH.

Synthesis of Nb5M. The synthetic route is shown in Scheme S5. Nb₂COOH (1.00 *eq*, 1.64 g, 5.00 mmol), R₁₆BPOH (2.00 *eq*, 4.10 g, 10.0 mmol), *N,N'*-dicyclohexylcarbodiimide (2.00 *eq*, 2.06 g, 10.0 mmol), and DMAP (0.200 *eq*, 0.120 g, 1.00 mmol) were added into a dry 100 mL flask. After three pump-purge cycles, 40 mL of CH₂Cl₂ was injected into the flask under a N₂ atmosphere. The insolubilities were removed at ambient temperature after 48 h. The crude product obtained after evaporation of the solvent was purified by silica gel column chromatography. Yield: 76%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.01–8.55 (m, 3H), 7.55–7.66 (m, 4H), 7.45–7.55 (m, 4H), 7.16–7.33 (m, 4H), 6.92–7.03 (m, 4H), 6.30–6.35 (d, 2H), 3.84–3.91 (m, 4H), 3.35–3.46 (s, 2H), 2.89–2.92 (d, 2H), 1.20–1.86 (m, 52H), 0.89 (m, 12H).



Scheme S5. Synthesis of Nb₅M.

Methods

Measurement of Densities of Homopolymer. PNb5M was polymerized through ROMP. The polymer was melt on a hot stage and shrank to form a globule after being cooled to ambient temperature. The globule was dropped into the mixture of ethanol and water. Ethanol or water was injected into the mixture slowly to make the globule suspend in the solution. The density of the solution was determined as that of PNb5M (ρ_{PNb5M}), which is 0.96 g mL^{-1} . The density of PNbPEO (ρ_{PNbPEO}) was determined to be 1.09 g mL^{-1} via the same method.

Process of the Solvent Vapor Annealing (SVA) Technique. The sample was dissolved in 2 mL of THF and stirred at ambient temperature for 24 h. The solution was passed through a filter membrane to remove the undissolved substance. The filtrate was injected into a bottle with a substrate underneath. The bottle was sealed with an aluminum foil with several holes punched to control the evaporation rate. After the slow evaporation of the solvent, the sample would deposit uniformly on the substrate. The process is shown in Figure S1.

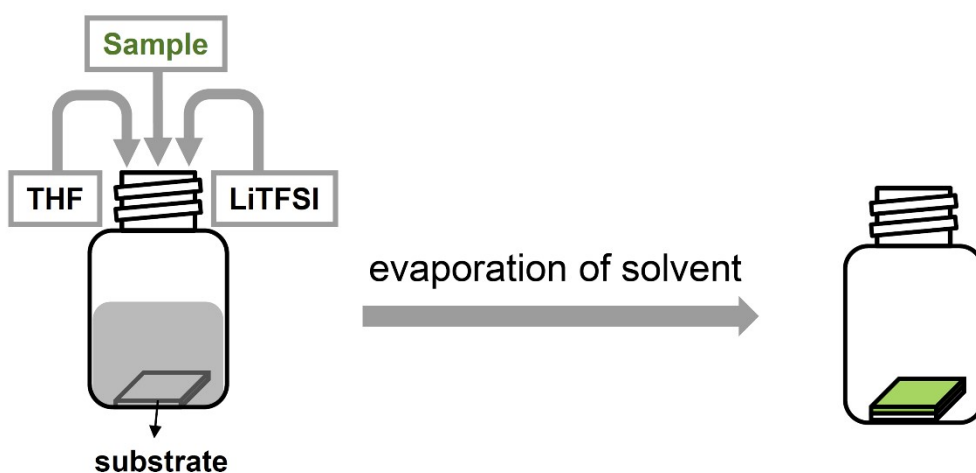


Figure S1. Schematic illustration of the SVA process.

Preparation of Samples for TEM Observation. The BCPE was embedded into epoxy resin. The resin was cut into slices with an ultramicrotome. Some slices fixed on copper grids were stained with OsO₄ vapor for a whole night.

Preparation of Samples for AFM Observation. The BCPE was dissolved in THF to afford a solution of 10 mg mL⁻¹. The solution was dipped onto a piece of clean silicon wafer and spin-coated with a speed of 3000 rpm, with the BCPE forming a thin film on the silicon wafer.

Calculation of the Volume Fraction of PEO (f_{PEO}). The value of f_{PEO} was calculated on the basis of the ¹H NMR results. If the integral of the peak at 3.38 ppm in the ¹H NMR spectrum representing the hydrogen atoms of methoxy groups –OCH₃ in PEO segment is a , and the integral of the peak at 0.87 ppm in the ¹H NMR spectrum representing the hydrogen atoms of methyl groups –CH₃ in the MJLCP segment is b , f_{PEO} could be calculated from the following equation. In the equation, $M_w(NbPEO)$ and $M_w(Nb5M)$ represent the molecular weight of NbPEO and Nb5M, respectively.

$$f_{PEO} = \frac{\frac{a}{3} \times M_w(NbPEO)}{\rho_{PNbPEO}} \div \left(\frac{\frac{a}{3} \times M_w(PEOMA)}{\rho_{PNbPEO}} + \frac{\frac{b}{12} \times M_w(Nb5M)}{\rho_{PNb5M}} \right)$$

Results

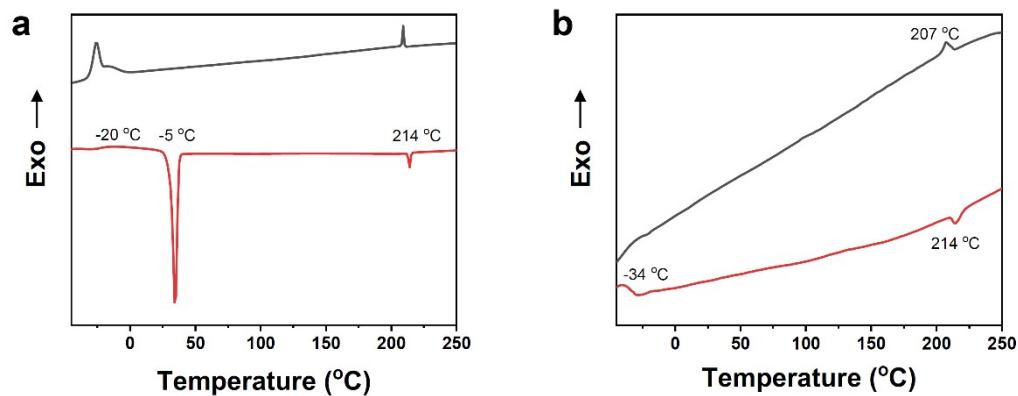


Figure S2. DSC thermograms of $T_{16}B_{10}$ (a) and the corresponding BCPE (b).

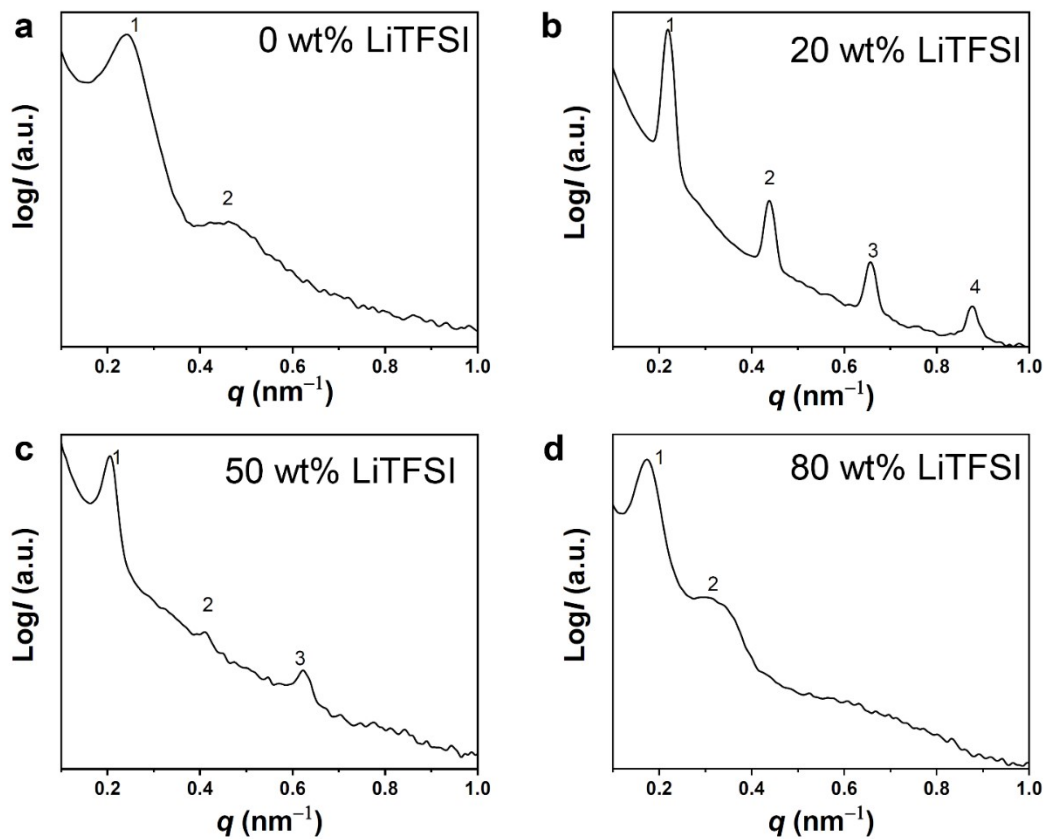


Figure S3. SAXS profiles of $T_{17}B_9$ /LiTFSI samples with different contents of LiTFSI: (a) 0 wt%; (b)

20 wt%; (c) 50 wt%; (d) 80 wt %.

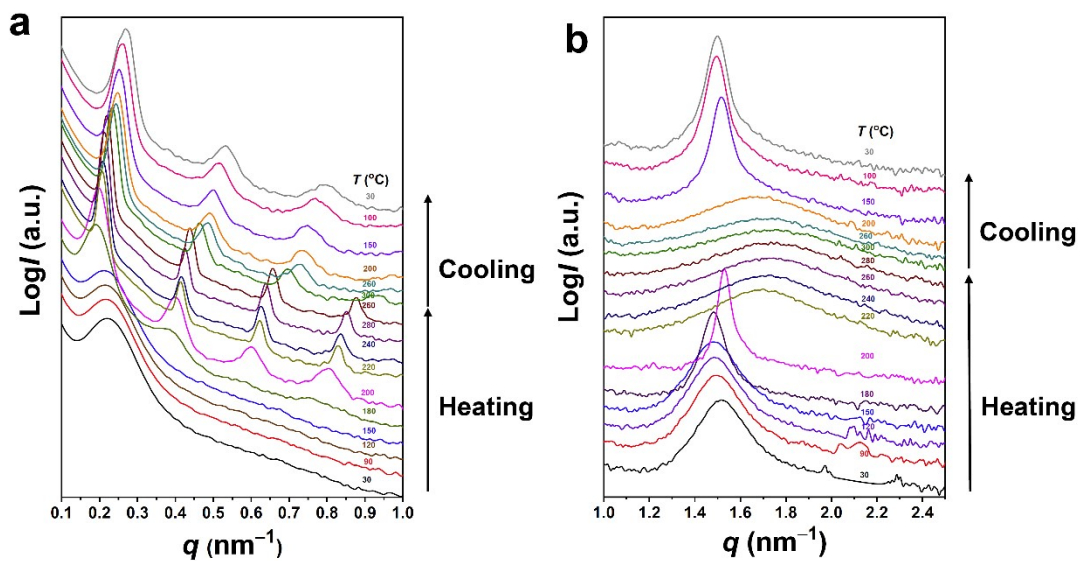


Figure S4. SAXS profiles of the BCPE composed of T₁₆B₁₀ with 20 wt% of LiTFSI in the q range of 0.1–1.0 nm⁻¹ (a) and 1.0–2.5 nm⁻¹ (b) at different temperature. .

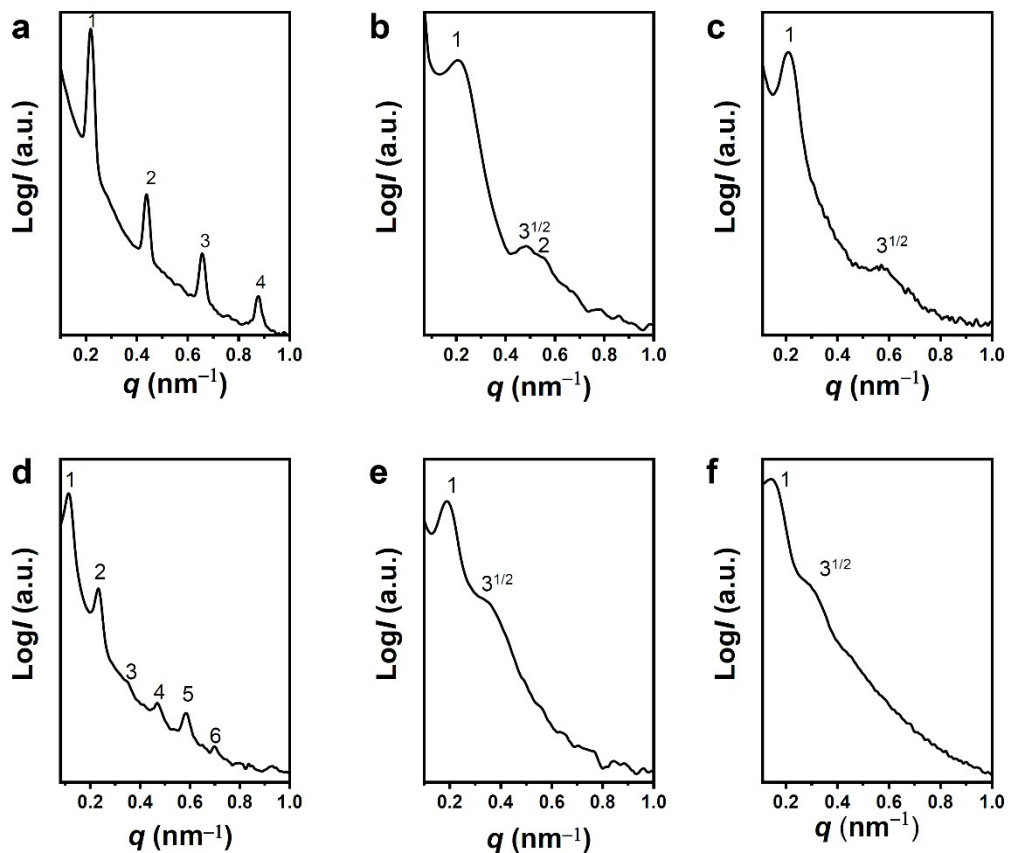


Figure S5. SAXS profiles of the $T_{16}B_{10}/LiTFSI$ (a), $T_{10}B_{15}/LiTFSI$ (b), $T_9B_{20}/LiTFSI$ (c), $T_{58}B_{13}/LiTFSI$ (d), $T_{46}B_3/LiTFSI$ (e), and $T_{59}B_6/LiTFSI$ (f) BCPEs. The content of LiTFSI in all samples is 20 wt%.

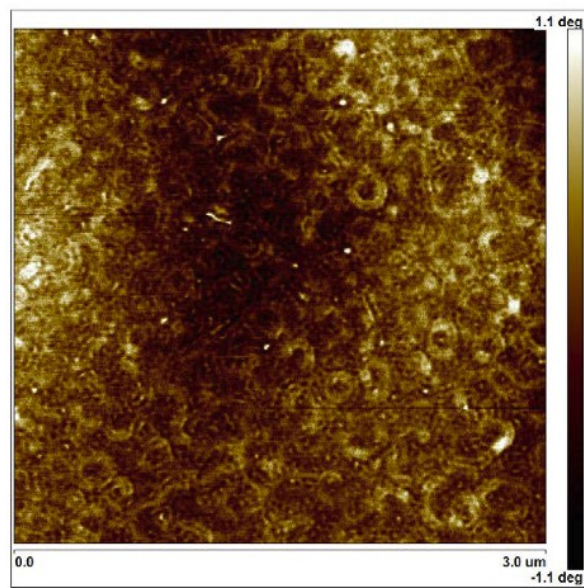


Figure S6. AFM phase image of $T_{44}B_{26}$ /LiTFSI on silicon substrate.

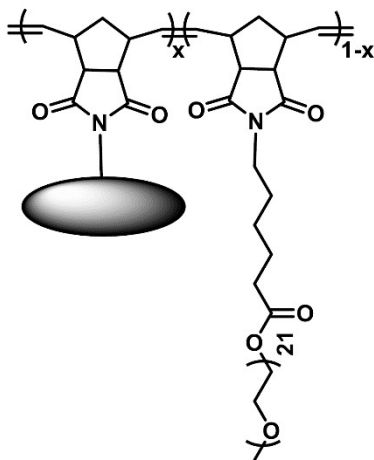


Figure S7. Chemical structure of T-*r*-B.

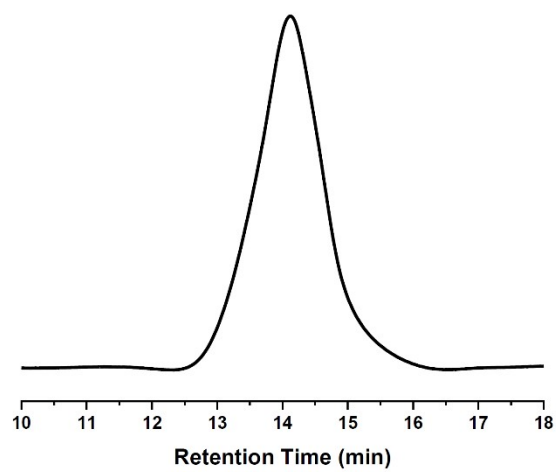


Figure S8. GPC curve of T-*r*-B.

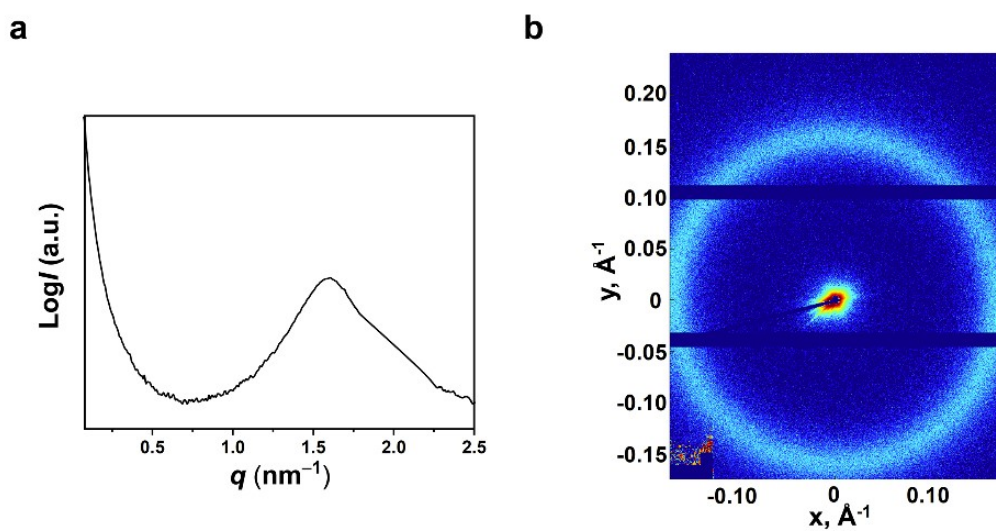


Figure S9. SAXS profile (a) and 2D SAXS pattern (b) of T-*r*-B.

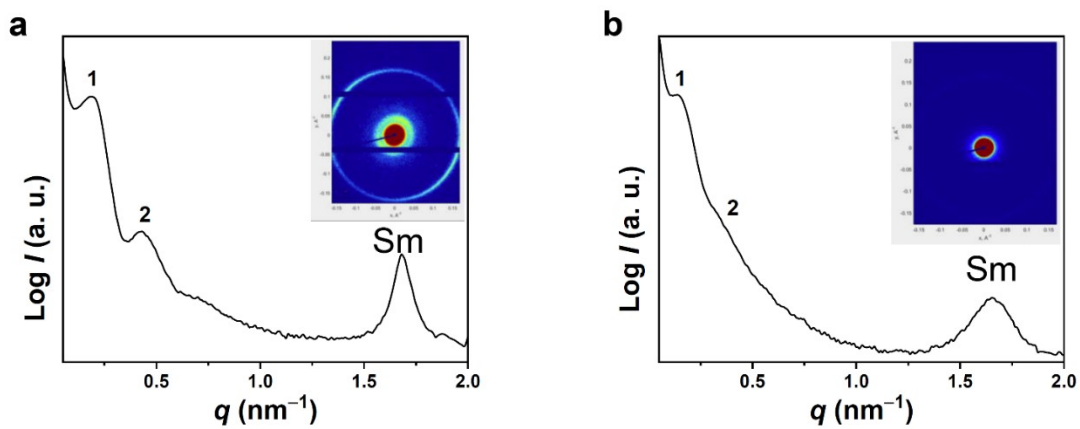


Figure S10. SAXS profiles and 2D SAXS patterns of $\text{T}_{44}\text{B}_{26}/\text{LiTFSI}$ after (a) and before (b) alignment.

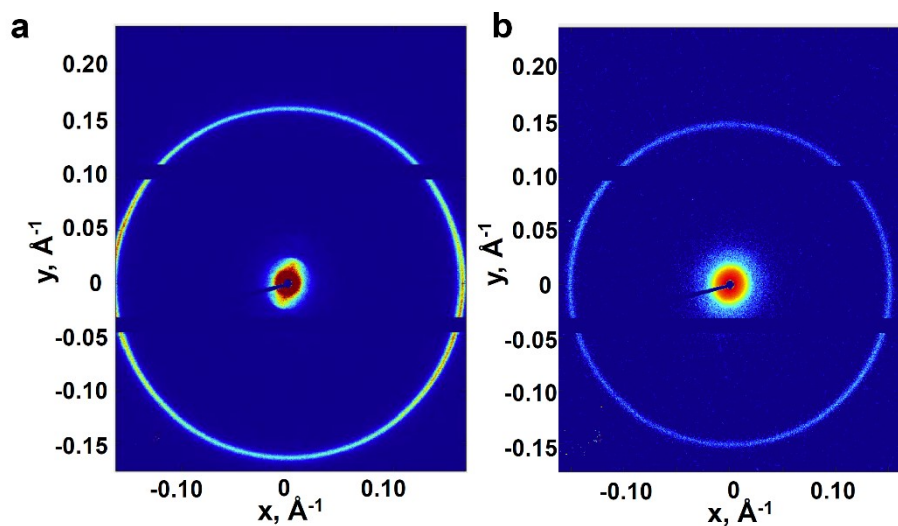


Figure S11. 2D SAXS patterns of the BCPE composed of $\text{T}_{44}\text{B}_{26}$ with 20 wt% of LiTFSI after the SVA process with different solvents: (a) CHCl_3 ; (b) DMF.

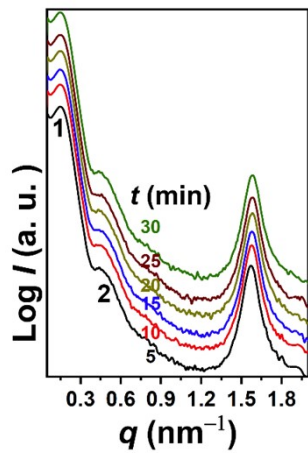


Figure S12. SAXS profiles of T₄₄B₂₆/LiTFSI during heating at 200 °C.