

Supplementary Materials

Supramolecular Thixotropic Ionogel Electrolyte for Sodium Batteries

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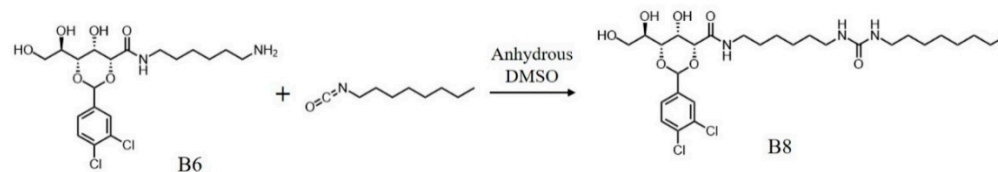


Figure S1. Synthetic route of B8.

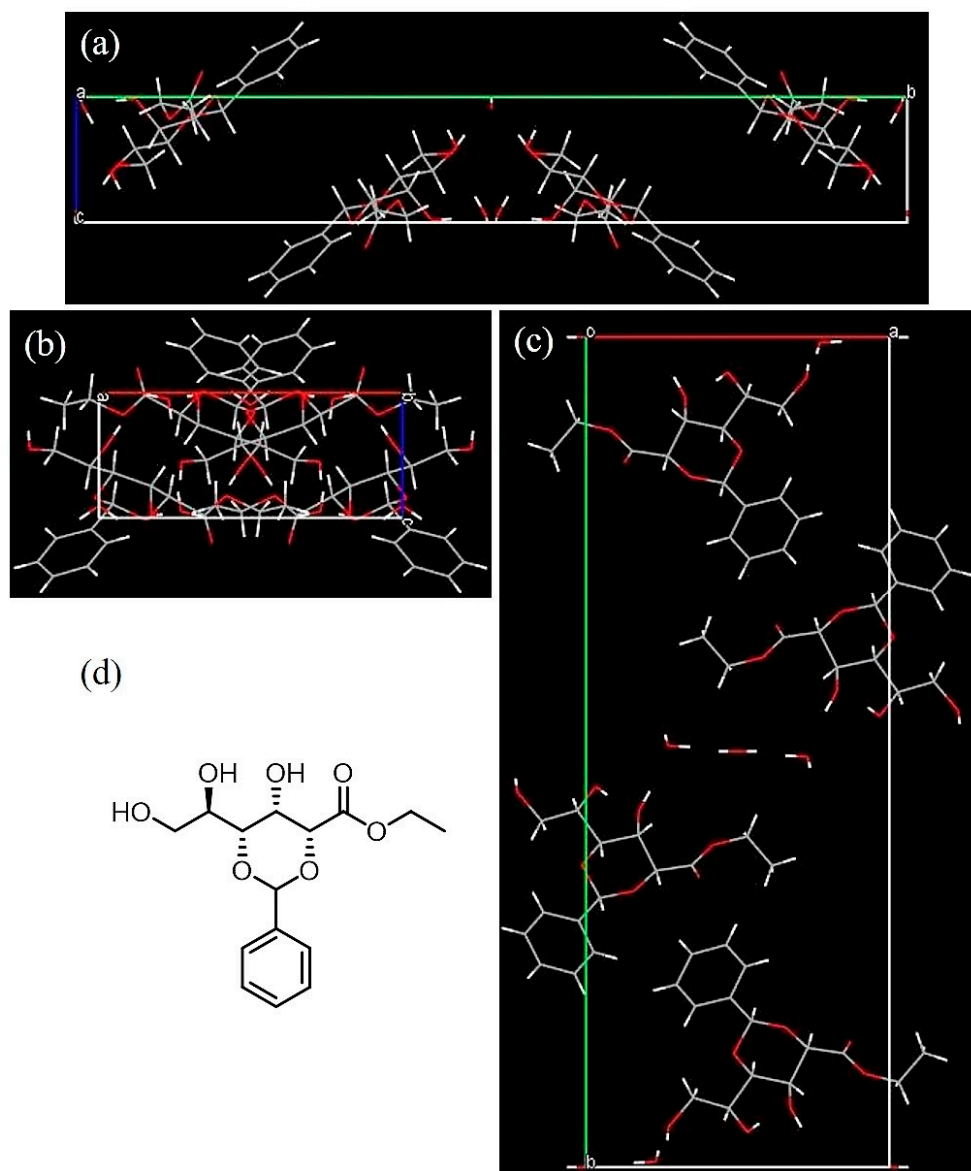


Figure S2. Unit cell of the co-crystal of Z1 and H₂O along the (a) a-axis, (b) b-axis, (c) c-axis. Color code: C = gray; H = white; O = red. (d) The chemical formula of Z1.

Table S1. Crystallographic details of the co-crystal of Z1 and H₂O.

| | |
|--|--|
| CCDC No. | 1960998 |
| Formula | C ₁₅ H ₂₀ O ₇ |
| Formula weight | 692.69 |
| Crystal system | Orthorhombic |
| Space group | P 21 21 2 |
| T, K | 293 |
| λ (Cu Kα), Å | 1.54184 |
| a, Å | 11.3217(3) |
| b, Å | 30.9860(7) |
| c, Å | 4.6792(1) |
| α, ° | 90 |
| β, ° | 90 |
| γ, ° | 90 |
| V, Å³ | 1641.53(7) |
| Z | 2 |
| Dx, g cm⁻³ | 1.401 |
| μ, mm⁻¹ | 0.973 |
| F (000) | 740.0 |
| GOF | 1.068 |
| R1 | 0.0522 |
| wR2 | 0.1484 |

Table S2. Performance parameters of ionogels for Na batteries.

| Year | Electrolyte ingredients | Ionic conductivity | Self-healing | T_{Na+} | Ref. |
|-------------|--|---|---------------------|------------------------|-------------|
| 2010 | [P(VDF-HFP) + 0.5 M EMITf/NaCF ₃ SO ₃] | 5.74 × 10 ⁻³ S/cm at 27 °C | — | 0.23 | 1 |
| 2015 | [Silica fumed powder + 0.3 M NaNTf ₂ /C ₄ mpyrNTf ₂] | 1.1 × 10 ⁻³ S/cm at rt | — | — | 2 |
| | [PMMA + 0.3 M NaNTf ₂ /C ₄ mpyrNTf ₂] | 7 × 10 ⁻⁴ S/cm at rt | — | — | |
| 2016 | [(PEO + 10 wt.% NaMS) + 60 wt.% BMIM-MS] | 1.05 × 10 ⁻⁴ S/cm at 30 °C | — | 0.46 | 3 |
| 2016 | [NaTFSI(PEO) ₉ + 20 wt.% Pyr ₁₃ TFSI] | 10 ⁻⁴ S/cm at 20 °C | — | | 4 |
| | [(P(VDF-HFP) + 0.5 M NaTf/EMITf) + 5 wt.% Al ₂ O ₃] | 6.3 – 6.8 × 10 ⁻³ S/cm at rt | — | 0.27 | |
| 2016 | [(P(VDF-HFP) + 0.5 M NaTf/EMITf) + 5 wt.% NaAlO ₂] | 5.5 – 6.5 × 10 ⁻³ S/cm at rt | — | 0.42 | 5 |
| 2017 | [(PEO ₂₀ /NaClO ₄) + 5 wt.% SiO ₂ + 70 wt.% Emim FSI] | 1.3 × 10 ⁻³ S/cm at rt | — | 0.61 | 6 |
| 2017 | [PEO/NaClO ₄ + 30 wt.% 1-butyl-3-methylimidazolium thiocyanate] | 5 × 10 ⁻⁴ S/cm at rt | — | — | 7 |
| 2017 | [P(VDF-HFP)/NaN(CF ₃ SO ₂) ₂]/Mono cationic ionic liquids(70:30, w/w) | 2.2 × 10 ⁻⁴ S/cm at rt | — | 0.1 – 0.5 | 8 |
| 2017 | [PVC + Na[FSA]/[C ₂ C ₁ im][FSA]] | 5.6 × 10 ⁻³ S/cm at 45 °C | — | — | 9 |
| 2020 | [SBVI/MPC/TFEMA + 0.5M NaTFSI/BMP TFSI] | 1.6 × 10 ⁻³ S/cm at rt | — | 0.19 | 10 |
| 2020 | [SBA-15/ P(VDF-HFP) + NaTFSI/PY ₁₃ FSI] | 2.48 × 10 ⁻³ S/cm at 30 °C | — | 0.37 | 11 |

| | | | | | |
|------|---|----------------------------------|-----|--------|-----------|
| 2021 | [m-PDMS/MTMS/HCOOH + 0.5M NaFSI/ C ₄ mpyrTFSI] | 1×10^{-3} S/cm at rt | — | — | 12 |
| 2021 | [P(VDF-HFP)/TiO ₂ + 0.5 M NaCF ₃ SO ₃ /BMImCF ₃ SO ₃] | 4×10^{-4} S/cm at rt | — | 0.27 | 13 |
| 2022 | [D-gluconic acetal-based gelator + 0.3 M NaTFSI /BMPTFSI] | 1.43×10^{-3} S/cm at rt | Yes | 0.1835 | This work |

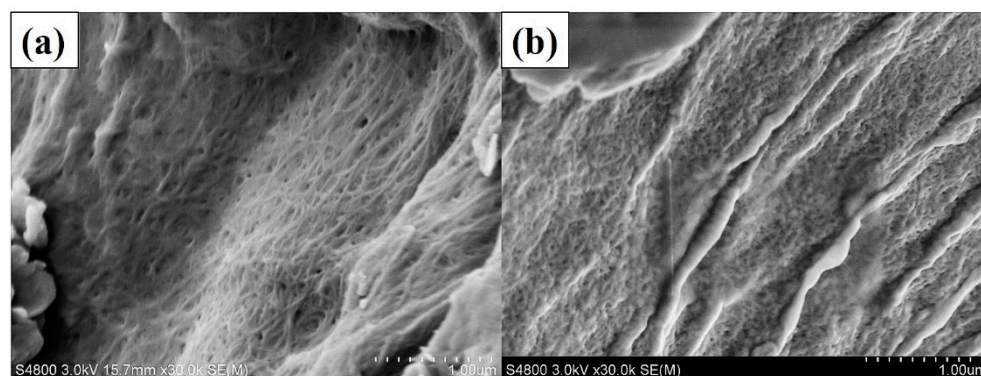


Figure S3. SEM images of the xerogels of (a) B8-BMPTFSI and (b) B8-BMPTFSI-NaTFSI ionogels.

The difference in morphology between SEM and POM images may be related to the preparation of xerogel; during solvent exchange and freeze-drying, the microscopic morphology of the gel is easily damaged, and the gelator originally dispersed in the solvent will also crystallize, resulting in the change of the original morphology.

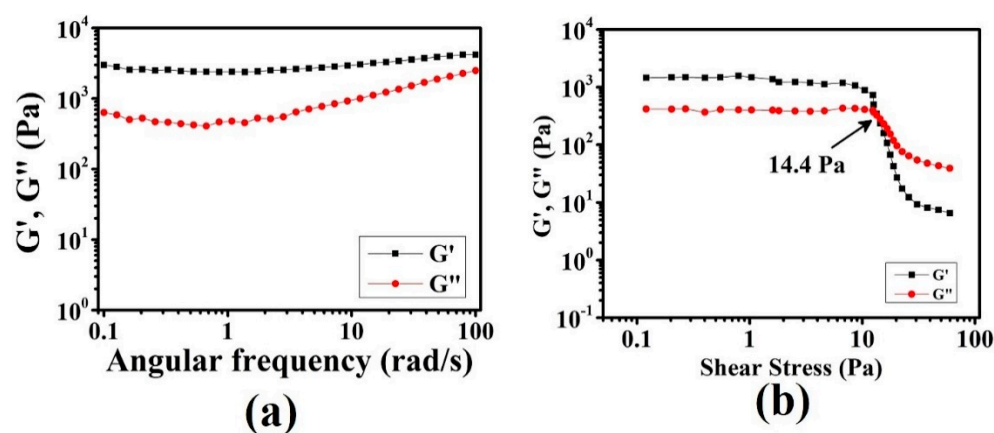


Figure S4. (a) Dynamic frequency sweep measurements and (b) Dynamic stress sweep measurements for B8-BMPTFSI-NaTFSI gel (4% B8, w/v; 0.3M NaTFSI).

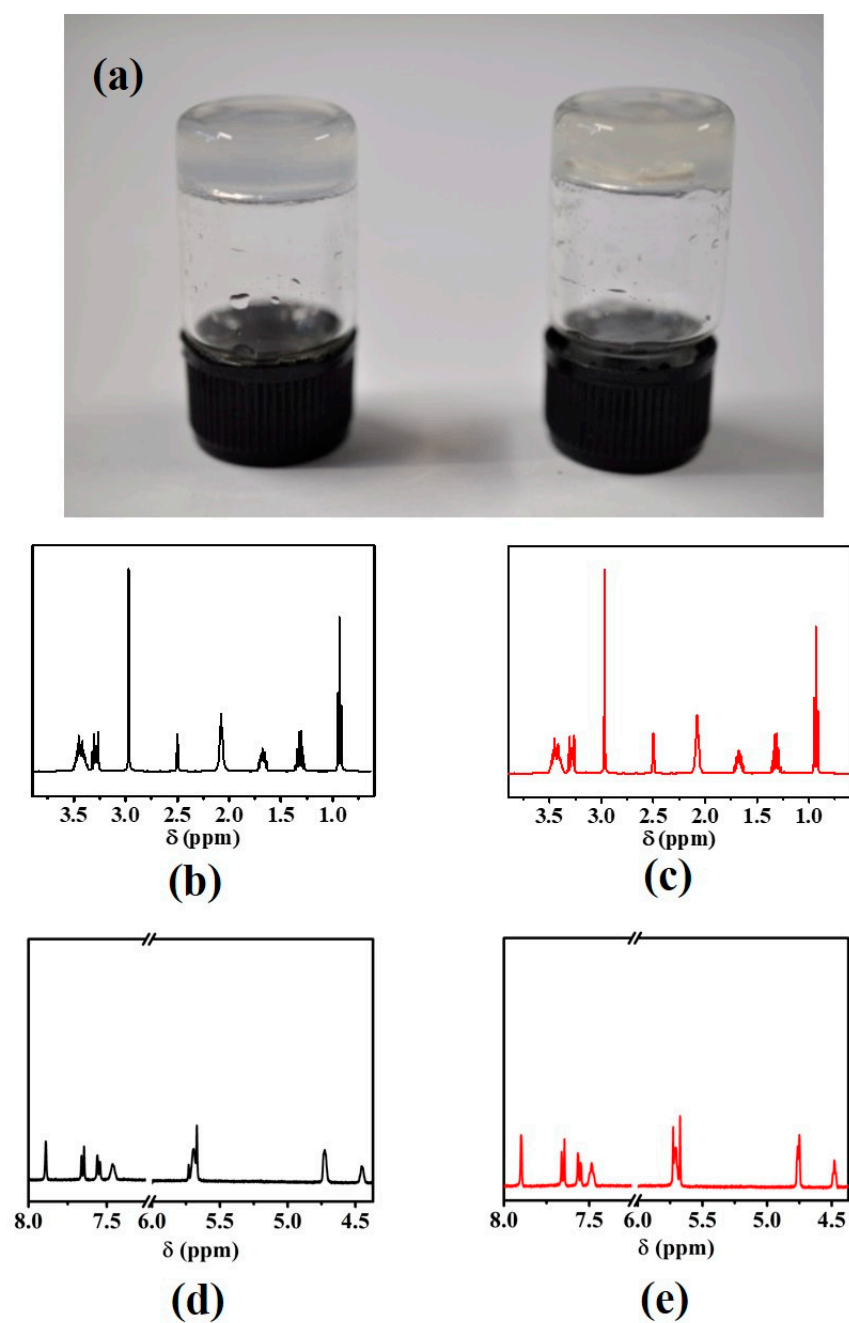


Figure S5. (a) B8-BMPTFSI-NaTFSI ionogel (4% B8, w/v, 0.3 M NaTFSI) (left), B8-BMPTFSI-NaTFSI ionogel (4% B8, w/v, 0.3 M NaTFSI) kept in inert environment at 50 °C for 30 days with Na (right); (b) ^1H -NMR data of BMPTFSI of newly prepared ionogel; (c) ^1H -NMR data of BMPTFSI of ionogel kept in inert environment at 50 °C for 30 days with Na; (d) ^1H -NMR data of active groups of B8 in newly prepared ionogel; (e) ^1H -NMR data of active groups of B8 in ionogel kept in inert environment at 50 °C for 30 days with Na.

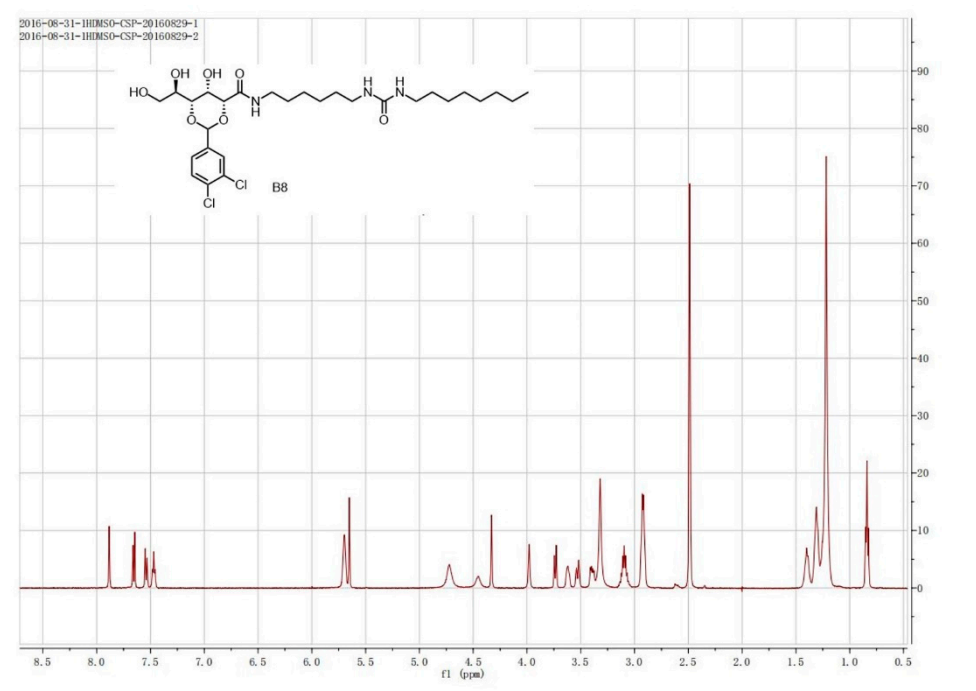


Figure S6. ¹H NMR (400MHz) Spectra of B8 in DMSO-d₆.

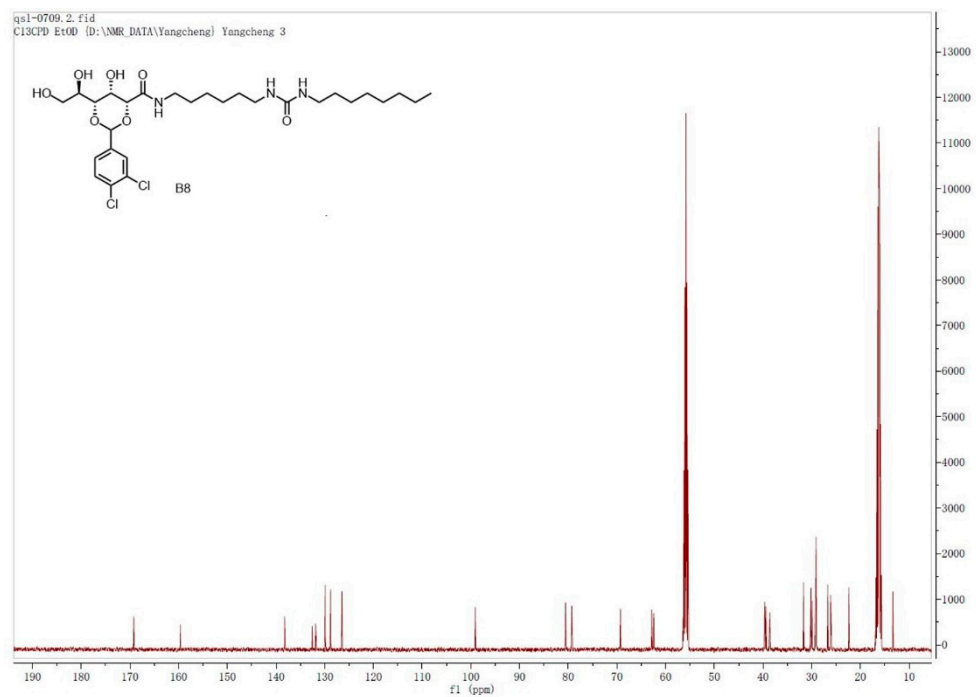


Figure S7. ¹³C NMR (100MHz) Spectra of B8 in C₂D₆O.

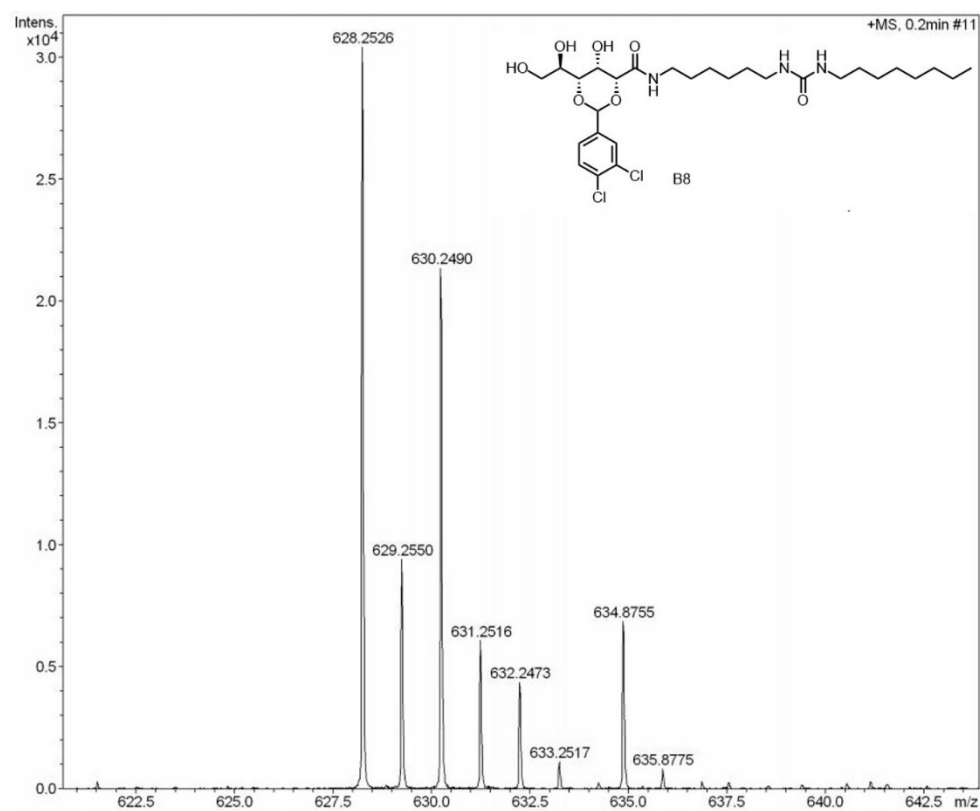


Figure S8. HRMS Spectra of B8 in DMF.

Supporting CIF S1, 2: Single-crystal XRD data of Z1 and the self-assembly mode of B8.