Electronic Supplementary Information (ESI)

Molecular-Level Engineering of Gel Polymer Electrolytes in Sodium-ion Batteries: A Comprehensive Computational Study

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Table S1: Non-bonding force field parameters for Na^+ ions and polymeric anions. Values correspond to the central monomer unit (unit 8 of 16-mer) in the anion chain.

System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
Na	Na	1	2.876	0.52
PSO-BTFM-TFSI	O1	-0.31313004	2.90	0.586
-	O2	-0.60877255	2.96	0.711
-	O3	-0.60171388	2.96	0.711
-	O4	-0.59441649	2.96	0.711
-	O5	-0.60013359	2.96	0.711
-	C1	0.02184412	3.55	0.293
-	C2	-0.01142259	3.55	0.293
-	C3	-0.02469588	3.55	0.293
-	C4	0.01537166	3.55	0.293
-	C5	0.00647872	3.55	0.293
-	C6	-0.02123205	3.55	0.293
-	C7	0.04472542	3.50	0.276
-	C8	0.09075688	3.50	0.276
-	C9	0.47680067	3.50	0.276
-	C10	0.47052954	3.50	0.276
-	C11	0.40646574	3.50	0.276
-	H1	0.04181095	2.50	0.126
-	H2	0.09789164	2.50	0.126
-	H3	0.05540383	2.50	0.126
-	H4	0.11374015	2.42	0.126
-	H5	0.07472178	2.42	0.126
-	F1	-0.18736110	2.90	0.251

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System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
-	F2	-0.15054671	2.90	0.251
-	F3	-0.18397445	2.90	0.251
-	F4	-0.19909256	2.90	0.251
-	F5	-0.17193387	2.90	0.251
-	F6	-0.19981331	2.90	0.251
-	F7	-0.14440919	2.90	0.251
-	F8	-0.18394600	2.90	0.251
-	F9	-0.15285012	2.90	0.251
-	S1	0.97723922	3.55	1.046
-	S2	0.95865222	3.55	1.046
-	N1	-0.49902992	3.25	0.711
PSO-NTFM-TFSI	O1	-0.32909463	2.90	0.586
-	O2	-0.58186558	2.96	0.711
-	O3	-0.66729935	2.96	0.711
-	O4	-0.53900871	2.96	0.711
-	O5	-0.59661465	2.96	0.711
-	O6	-0.35833109	2.96	0.711
-	O7	-0.36324029	2.96	0.711
-	C1	0.02016384	3.55	0.293
-	C2	-0.03238310	3.55	0.293
-	C3	-0.02728663	3.55	0.293
-	C4	0.02188558	3.55	0.293
-	C5	-0.00345624	3.55	0.293
-	C6	-0.07655593	3.55	0.293

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System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
-	C7	0.03715866	3.50	0.276
-	C8	0.09075688	3.50	0.276
-	C9	0.49049901	3.50	0.276
-	C10	0.37572009	3.50	0.276
-	H1	0.05709929	2.50	0.126
-	H2	0.11258544	2.50	0.126
-	H3	0.08342525	2.50	0.126
-	H4	0.12217467	2.42	0.126
-	H5	0.14192149	2.42	0.126
-	F1	-0.20480952	2.90	0.251
-	F2	-0.18413369	2.90	0.251
-	F3	-0.18654695	2.90	0.251
-	F4	-0.16343914	2.90	0.251
-	F5	-0.21847518	2.90	0.251
-	F6	-0.16958916	2.90	0.251
-	S1	1.31378662	3.55	1.046
-	S2	1.19042457	3.55	1.046
-	N1	-0.62710820	3.25	0.711
-	N2	0.56791033	3.25	0.276
PSO-DN-TFSI	O1	-0.31334769	2.90	0.586
-	O2	-0.60861379	2.96	0.711
-	O3	-0.56328219	2.96	0.711
-	O4	-0.56288379	2.96	0.711
-	O5	-0.60772910	2.96	0.711

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System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
-	O6	-0.39168725	2.96	0.711
-	O7	-0.38506302	2.96	0.711
-	O8	-0.36884627	2.96	0.711
-	O9	-0.41864898	2.96	0.711
-	C1	0.00366299	3.55	0.293
-	C2	-0.03414233	3.55	0.293
-	C3	-0.04209595	3.55	0.293
-	C4	0.01027419	3.55	0.293
-	C5	0.00304429	3.55	0.293
-	C6	-0.08179750	3.55	0.293
-	C7	0.05970982	3.50	0.276
-	C8	0.09188300	3.50	0.276
-	C9	0.37342331	3.50	0.276
-	H1	0.02974493	2.50	0.126
-	H2	0.06300213	2.50	0.126
-	H3	0.06649608	2.50	0.126
-	H4	0.09481899	2.42	0.126
-	H5	0.07400834	2.42	0.126
-	F1	-0.22041510	2.90	0.251
-	F2	-0.17346378	2.90	0.251
-	F3	-0.19406334	2.90	0.251
-	S1	1.22228592	3.55	1.046
-	S2	1.14978029	3.55	1.046
-	N1	-0.66838438	3.25	0.711

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System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
-	N2	0.54452335	3.50	0.276
-	N3	0.53487056	3.25	0.276

Table S2: Non-bonding force field parameters for solvents.

System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
EC	C1	0.936426	3.55	0.293
-	C2	0.072601	3.50	0.276
-	C3	0.072601	3.50	0.276
-	O1	-0.417203	2.9	0.586
-	O2	-0.418726	2.9	0.586
-	O3	-0.570418	2.96	0.879
-	H1	0.080107	2.50	0.1255
-	H2	0.082774	2.50	0.1255
-	H3	0.079583	2.50	0.1255
-	H4	0.079518	2.50	0.1255
DEC	C1	1.074028	3.55	0.293
-	C2	0.295294	3.50	0.276
-	C3	-0.247363	3.50	0.276
-	C4	0.518603	3.50	0.276
-	C5	-0.413127	3.50	0.276
-	O1	-0.636816	2.96	0.879
-	O2	-0.584704	2.90	0.586
-	O3	-0.531175	2.90	0.586
-	H1	0.022487	2.50	0.126

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System	Atom	q (e)	σ (Å)	ϵ (kJ/mol)
-	H2	0.017116	2.50	0.126
-	H3	0.091038	2.50	0.126
-	H4	0.058928	2.50	0.126
-	H5	0.075641	2.50	0.126
-	H6	-0.031665	2.50	0.126
-	H7	-0.039818	2.50	0.126
-	H8	0.079798	2.50	0.126
-	H9	0.126944	2.50	0.126
-	H10	0.124791	2.50	0.126
DMSO	S1	0.340718	3.56	1.653
-	C1	-0.491451	3.50	0.2761
-	C2	-0.424945	3.50	0.2761
-	O1	-0.489692	2.96	0.7113
-	H1	0.195637	2.5	1255
-	H2	0.199746	2.50	0.1255
-	H3	0.164515	2.50	0.1255
-	H4	0.142740	2.50	0.1255
-	H5	0.179334	2.50	0.1255
-	H6	0.183398	2.50	0.1255

Table S3: Comparison of calculated (this work) and experimental density (ρ) and viscosity (η) values for selected solvents at specified temperatures. [a]Value extracted from graphical data in the cited reference.

Solvent	ρ_{cal} (g cm^{-3})	ρ_{exp} (g cm^{-3})	η_{cal} (cP)	η_{exp} (cP)
EC	1.310 @298.15 K	1.321[1] @298.15 K	1.261 @343.15 K	0.930[a, 2] @343.15 K
DEC	0.991 @298.15 K	0.975[3] @298.15 K	0.625 @343.15 K	0.445[4] @343.15 K
DMSO	1.113 @298.15 K	1.096[5] @298.15 K	2.465 @298.15 K	1.99[6] @298.15 K

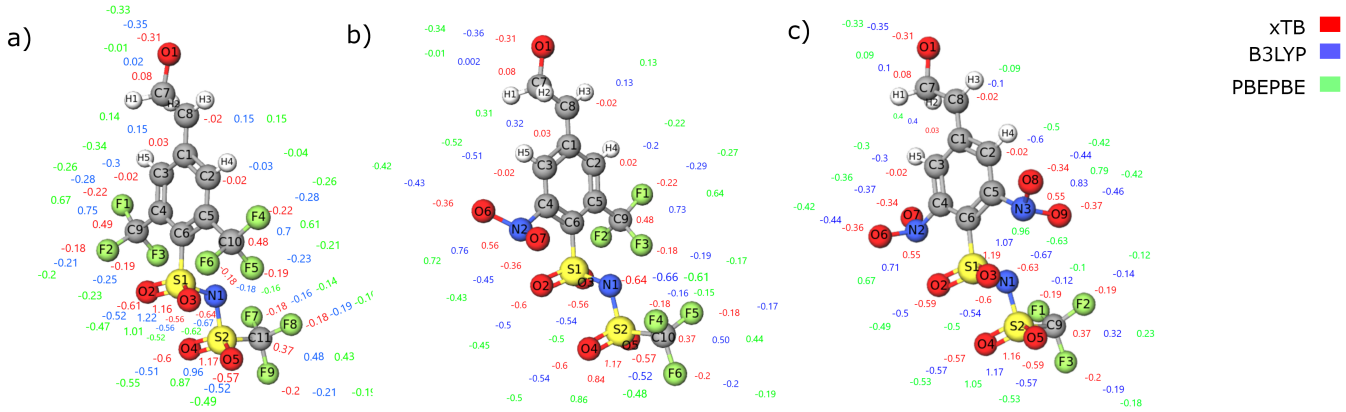

Figure S1: Molecular structures of polymer–anion systems along with the partial atomic ESP charges calculated using xTB (red), B3LYP (blue), and PBEPBE (green): (a) PSO-BTFM-TFSI, (b) PSO-NTFM-TFSI, (c) PSO-DN-TFSI.

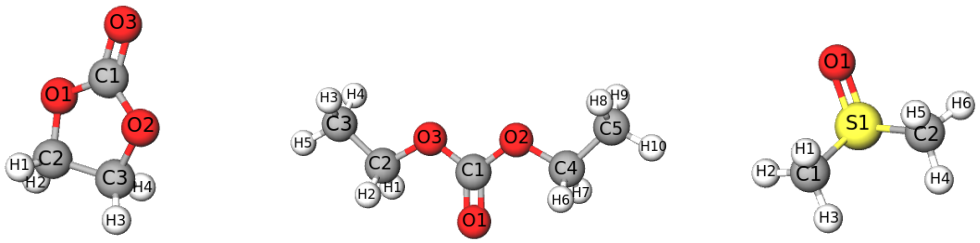

Figure S2: Guidelines for using Supporting Information tables of solvents.

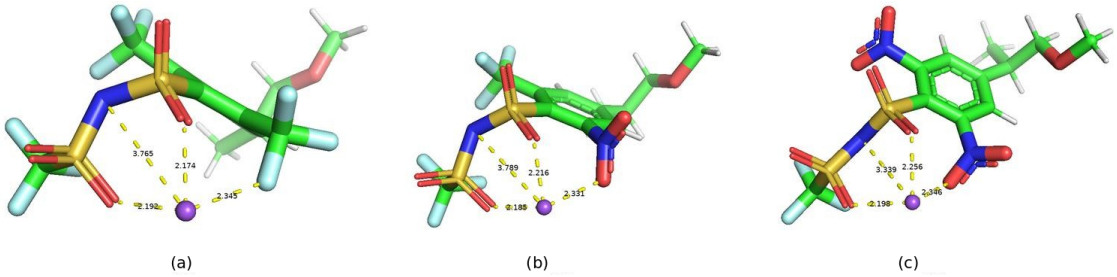

Figure S3: Distances between Na^+ and coordinating atoms (nitrogen, oxygen, fluorine) in three anion systems: (a) PSO-BTFM-TFSI, (b) PSO-NTFM-TFSI, and (c) PSO-DN-TFSI. Color scheme: Na^+ (purple), nitrogen (dark blue), oxygen (red), fluorine (light blue).

Table S4: Calculated HOMO, LUMO energies and HOMO-LUMO gap for the monomer, dimer, and trimer units of the investigated polymers. All calculations were performed using the 6-31+G(d,p) basis set to maintain a feasible computational cost for the oligomer series. All values are in electronvolts (eV).

Polymer	Fragment	HOMO	LUMO	Gap / ECW
PSO-BTFM-TFSI	Monomer	-7.925	-2.756	5.169
-	Dimer	-8.189	-3.144	5.045
-	Trimer	-8.144	-3.182	4.962
PSO-NTFM-TFSI	Monomer	-7.913	-3.470	4.443
-	Dimer	-8.325	-3.941	4.383
-	Trimer	-8.297	-4.081	4.216
PSO-DN-TFSI	Monomer	-8.067	-3.706	4.361
-	Dimer	-8.370	-3.997	4.373
-	Trimer	-8.265	-4.280	3.985

Table S5: Calculated Na^+ binding energies for the monomer, dimer, and trimer units of the investigated polymers. All calculations were performed using the 6-31+G(d,p) basis set to maintain a feasible computational cost for the oligomer series. All values are in electronvolts (eV).

Fragment	PSO-BTFM-TFSI	PSO-NTFM-TFSI	PSO-DN-TFSI
Monomer	-4.373	-4.413	-4.408
Dimer	-4.088	-4.097	-4.178
Trimer	-3.972	-4.012	-4.047

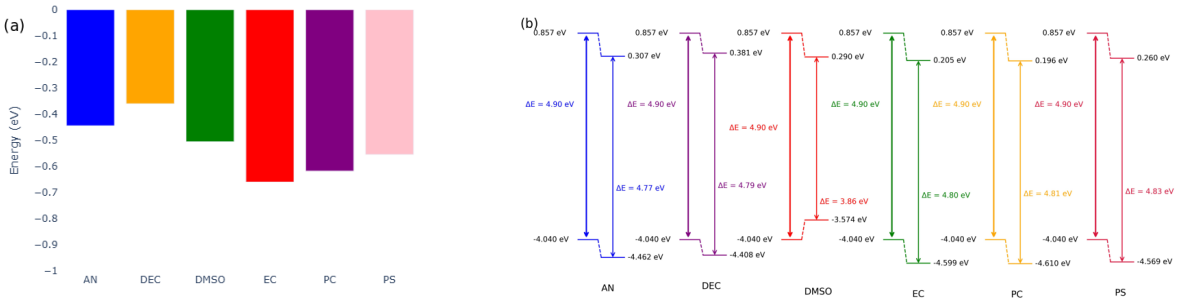

Figure S4: Binding energy between PSO-BTFM-TFSI and solvent. (b) Influence of solvents on PSO-BTFM-TFSI energy levels.

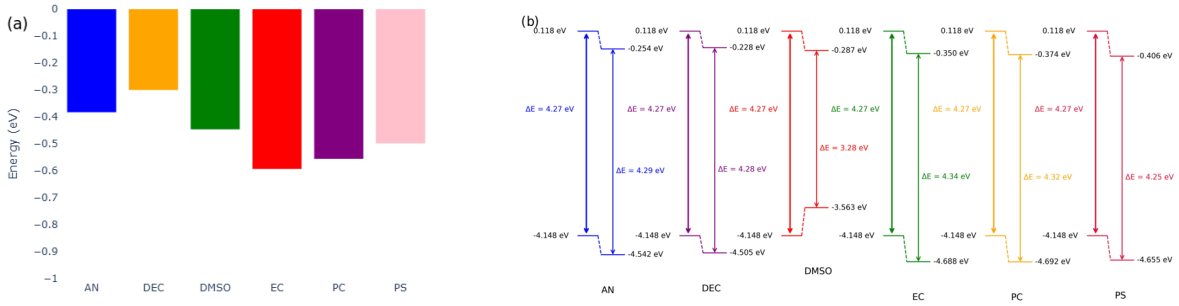

Figure S5: (a) Binding energy between PSO-NTFM-TFSI and solvent. (b) Influence of solvents on PSO-NTFM-TFSI energy levels.

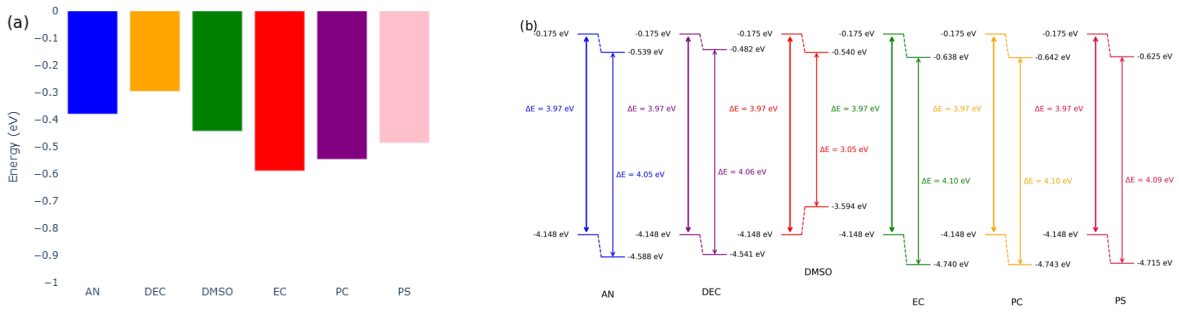

Figure S6: (a) Binding energy between PSO-DN-TFSI and solvent. (b) Influence of solvents on PSO-DN-TFSI energy levels.

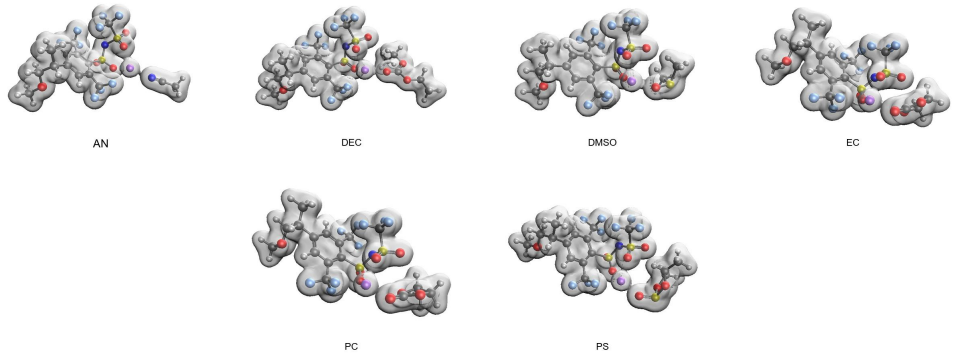

Figure S7: Solvation structures of Na^+ in PSO-BTFM-TFSI-based electrolytes across different solvents.

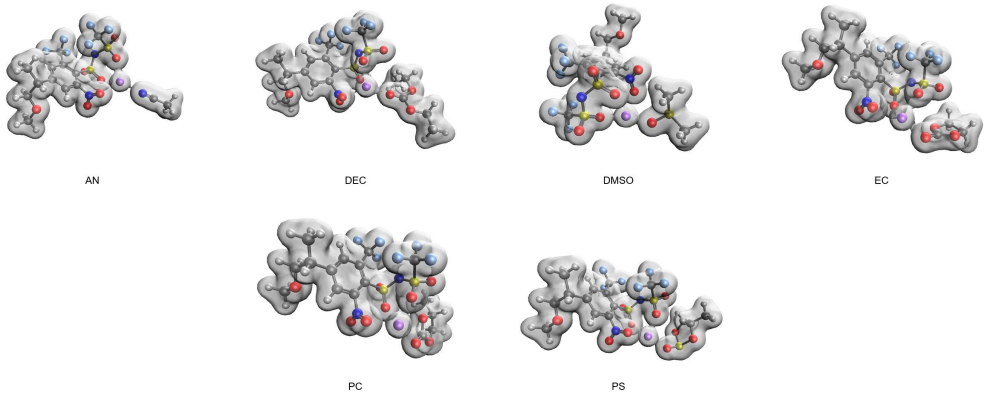

Figure S8: Solvation structures of Na^+ in PSO-NTFM-TFSI-based electrolytes across different solvents.

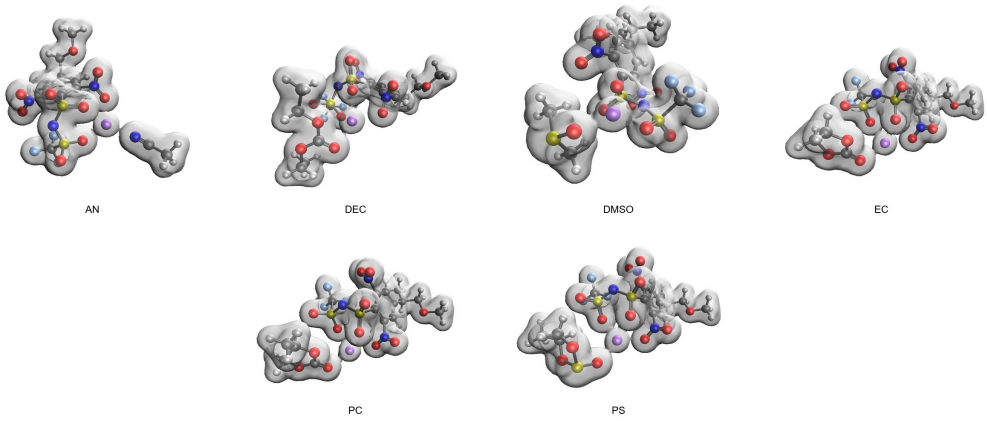

Figure S9: Solvation structures of Na^+ in PSO-DN-TFSI-based electrolytes across different solvents.

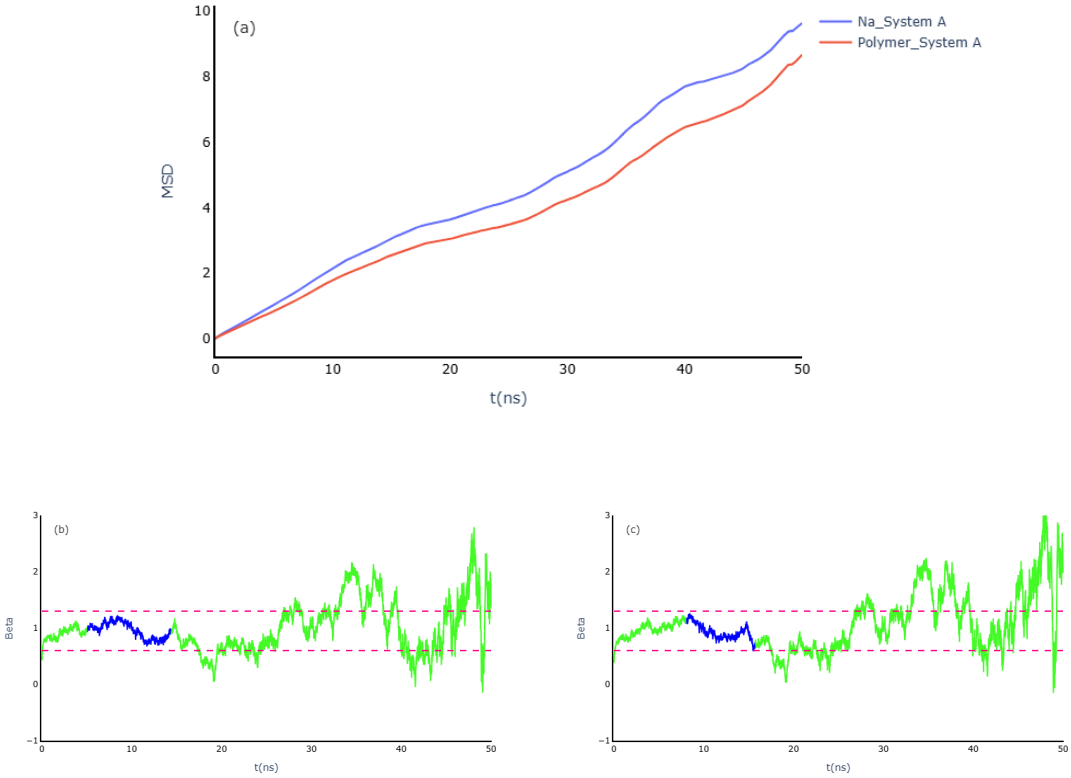

Figure S10: Dynamical properties of Na/PSO-BTFM-TFSI in DEC electrolyte: (a) Mean squared displacement (MSD) of Na^+ ions and anionic polymer; (b,c) Time-dependent β value for (b) Na^+ and (c) polymer. Blue-shaded regions indicate diffusive regimes ($\beta \approx 1$).

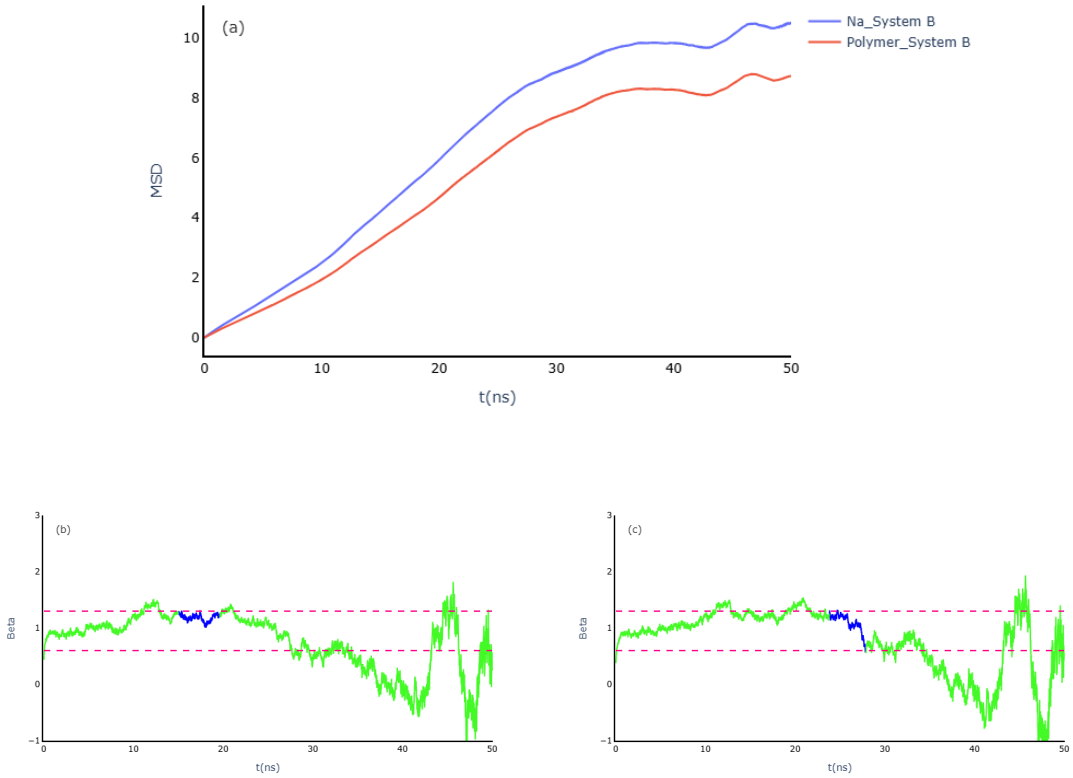

Figure S11: Dynamical properties of Na/PSO-NTFM-TFSI in DEC electrolyte: (a) Mean squared displacement (MSD) of Na^+ ions and anionic polymer; (b,c) Time-dependent β value for (b) Na^+ and (c) polymer. Blue-shaded regions indicate diffusive regimes ($\beta \approx 1$).

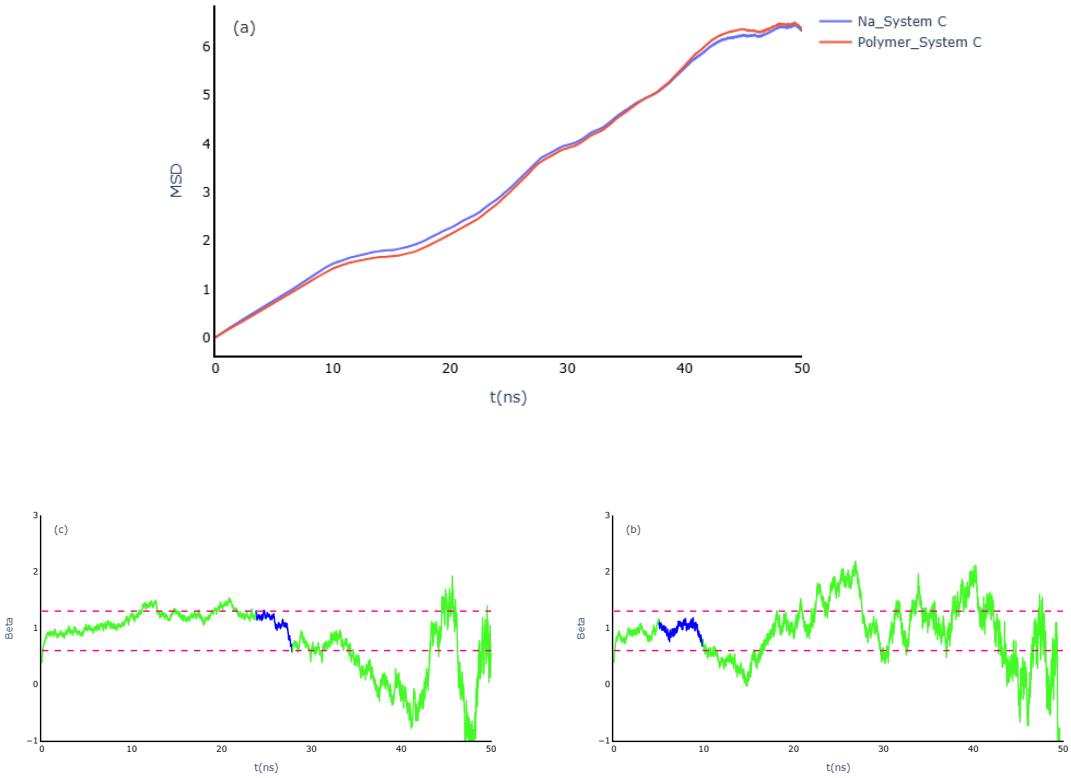

Figure S12: Dynamical properties of Na/PSO-DN-TFSI in DEC electrolyte: (a) Mean squared displacement (MSD) of Na^+ ions and anionic polymer; (b,c) Time-dependent β value for (b) Na^+ and (c) polymer. Blue-shaded regions indicate diffusive regimes ($\beta \approx 1$).

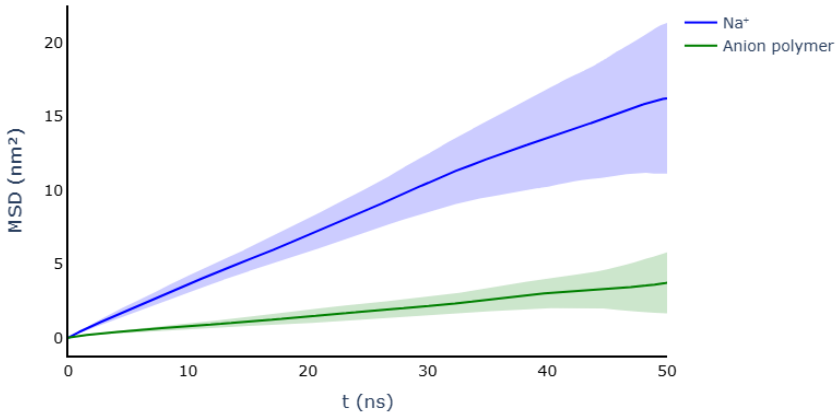

Figure S13: Mean Square Displacement (MSD) of the optimized system, averaged over six independent repetitions. The shaded regions represent the variance across these repetitions.

Table S6: Transport properties of EC-DEC-DMSO electrolytes as function of composition: Molar fractions of EC, DEC, and DMSO with corresponding ionic conductivity (σ) and cation transference number (t_+) at 343.15 K.

System	EC	DEC	DMSO	σ (mS cm^{-1})	t_+
1	0	0	1	4.9439	0.2460
2	0	0.2	0.8	2.8362	0.2087
3	0	0.4	0.6	4.5240	0.1807
4	0	0.6	0.4	6.3929	0.0879
5	0	0.8	0.2	3.2738	0.0651
6	0	1	0	5.9331	0.0843
7	0.2	0	0.8	3.2995	0.4081
8	0.2	0.2	0.6	4.9228	0.1391
9	0.2	0.4	0.4	2.8941	0.5121
10	0.2	0.6	0.2	4.8799	0.1228
11	0.2	0.8	0	3.4817	0.1893
12	0.4	0	0.6	3.7809	0.4847
13	0.4	0.2	0.4	4.2089	0.2267
14	0.4	0.4	0.2	4.9090	0.2625
15	0.4	0.6	0	4.1858	0.0690
16	0.6	0.2	0.2	2.5852	0.5400
17	0.6	0.2	0.2	5.3033	0.1529
18	0.6	0.4	0	1.1098	0.5784
19	0.8	0	0.2	3.1946	0.2683
20	0.8	0.2	0	6.6370	0.1076
21	1	0	0	2.9915	0.2549
22	0.714	0.143	0.143	3.0127	0.2919

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System	EC	DEC	DMSO	σ (mS cm^{-1})	t_+
23	0.571	0.286	0.143	2.9992	0.1532
24	0.571	0.143	0.286	1.8626	0.4378
25	0.429	0.429	0.143	4.9995	0.1161
26	0.429	0.286	0.286	4.3202	0.2227
27	0.429	0.143	0.429	1.9958	0.5685
28	0.286	0.571	0.143	3.2353	0.0683
29	0.286	0.429	0.286	2.2802	0.2377
30	0.286	0.286	0.429	5.6516	0.1150
31	0.286	0.143	0.571	3.2370	0.3335
32	0.143	0.714	0.143	1.7090	0.3519
33	0.143	0.571	0.286	5.5518	0.0618
34	0.143	0.429	0.429	3.1865	0.4236
35	0.143	0.286	0.571	3.6929	0.1324
36	0.143	0.143	0.714	7.4544	0.1075
37	0.078	0.167	0.755	6.5069	0.1216
38	0.402	0.094	0.504	7.3334	0.1050
39	0.33	0.024	0.646	2.6086	0.5551
40	0.542	0.389	0.069	1.8279	0.2645
41	0.101	0.34	0.558	3.6938	0.1355
42	0.1437	0.21	0.65	0.6111	0.7465
43	0.2033	0.0251	0.7714	1.4335	0.6685
44	0.2	0.1	0.7	3.0242	0.5854
45	0.2	0.7	0.1	2.1120	0.0913
46	0.7	0.2	0.1	2.9367	0.1708

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System	EC	DEC	DMSO	σ (mS cm^{-1})	t_+
47	0.7	0.1	0.2	2.2409	0.2803
48	0.1	0.7	0.2	5.0846	0.0715
49	0.1	0.2	0.7	6.9215	0.1079
50	0.333	0.333	0.333	3.6977	0.2233
51	0.25	0.15	0.6	6.6185	0.1562
52	0.25	0.1	0.65	2.5813	0.5084
53	0.65	0.1	0.25	5.0833	0.1403
54	0.3	0.1	0.6	6.7065	0.2341
55	0.2	0.05	0.75	4.4974	0.3528
56	0.15	0	0.85	6.3226	0.2401
57	0.6666	0	0.3333	2.6322	0.3318
58	0.19	0.01	0.8	3.0415	0.4476
59	0.17	0.03	0.8	2.7128	0.5222
60	0.13	0.07	0.8	2.8114	0.5084

Table S7: Transport properties of the electrolyte system (EC:0.15 DEC:0.05 DMSO:0.80) across six independent repetitions at 343.15 K.

Repetition	σ (mS cm^{-1})	t_+	η (cP)
1	2.712	0.728	9.71
2	2.695	0.601	11.49
3	2.466	0.742	8.66
4	3.078	0.645	8.95
5	2.278	0.855	7.12
6	2.865	0.703	7.59

References

(1) ChemicalBook, Ethylene carbonate - Chemical properties. https://www.chemicalbook.com/ChemicalProductProperty_EN_CB3488966.htm.

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