Supplementary information

Optimizing transport and redox properties of PVDF-based electrolytes through structural design of residual solvents

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Supplementary Notes

Note S1: Classical molecular dynamics simulations protocols

To investigate the solvation structures and transport properties of electrolytes, allatom classical molecular dynamics (MD) simulations were performed by GROMACS package.¹ The bonded and non-bonded parameters were obtained from the Optimized Potentials for Liquid Simulations All Atom (OPLS-AA) force field^{2, 3}, while those for Li⁺ and FSI⁻ are taken from Jensen et al.⁴ and Lopes et al.⁵, respectively. The partial atomic charges were fitted using the RESP2 method⁶ for solvents and polymer and the unit charge of Li⁺ (+1) and FSI⁻ (-1) were scaled to 0.6 to account for the overestimation of ion-ion interaction in nonpolarizable force fields.⁷ Long–range electrostatic interactions in reciprocal space were handled by the particle-mesh Ewald (PME) summation method⁸ with a grid spacing of 0.15 nm. A cutoff distance of 1.4 nm was used for electrostatic and 12–6 Lennard–Jones interactions. The molecules were initially packed randomly in a cubic box using PACKMOL (Fig. S1).⁹

All simulation box consists of 115 lithium salts, 115 solvent molecules, and 10 PVDF polymer chains with a degree of polymerization of 50, which was determined by density convergence test (Fig. S2). The initial configurations were first energetically minimized by steepest descent energy minimization scheme and then equilibrated for 1 ns in the isothermal–isobaric ensemble (NPT) using the V-rescale thermostat¹⁰ and Berendsen barostat¹¹ to maintain a pressure of 1 bar and a temperature of 373 K. Annealing processes were conducted to avoid local configuration confinement. All systems were heated from 373 K to 723 K for 7 ns, then annealed from 723K to 373 K in 7 ns, and subsequently maintained at 373 K for 5 ns. Finally, production runs of 200 ns were

conducted in the canonical ensemble (NVT) at 373 K for analysis. The simulation time was long enough to sample adequately the Fickian (diffusive) regime of all systems. At least three independent duplicate runs were performed for each electrolyte in order to estimate the statistical uncertainties.

Note S2: Calculation of transport properties

The self-diffusion coefficients for cations and anions were extracted from the MD simulation by analyzing the mean square displacement (MSD, $(\delta r)^2$) over time.¹² The slope of the linear regime in the MSD was determined for each 5 ns simulation segment and the self-diffusion coefficients can be obtained via the following relationship:

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} < (\delta \mathbf{r})^2 > \tag{1}$$

where δr is the displacement of particle *i* during time t over a possible starting time t₀ within the studied trajectory, and <> denotes the ensemble average.

The ionic conductivity is related to the electrical current autocorrelation function via Green–Kubo relation. And as with the self-diffusivity, the ionic conductivity can also be computed using the following formally equivalent Einstein expression¹³:

$$\sigma = \frac{F^2}{6k_B T V} \lim_{t \to \infty} \frac{d}{dt} \left\langle \sum_i z_i [r_i^{\alpha}(t) - r_i^{\alpha}(0)] \cdot \sum_j z_j \Big[r_j^{\beta}(t) - r_j^{\beta}(0) \Big] \right\rangle$$
(2)

where, *F* is Faraday's constant, z_i is the charge valence of species *i*, *V* is the volume, k_BT is the thermal energy, and r_i^{α} is the position of particle α relative to the center-ofmass position of the entire system. The simulations performed here all reached the linear regime. Results from representative simulations are shown in Fig. S6, S7 to illustrate the linear behavior observed in the calculations of both self-diffusion coefficients and ionic conductivities. The residence times of Li⁺-X pairs (Li⁺-solvent and Li⁺-anion) were calculated by computing the lifetime correlation function:

$$\xi_{ij}(t) = \langle H_{ij}(t) . H_{ij}(0) \rangle$$
(3)

where $H_{ij}(t)$ is 1 if i and j are neighbors at time t and zero otherwise. From the autocorrelation function $\xi_{ij}(t)$, a biexponential fit allows for inspection of the residence time τ_{ij}^{res} defined via the following relationship (Fig. S8):

$$\xi_{ij}(t) = aexp\left(\frac{-t}{\tau_{ij}^{res}}\right)^{\beta} + (1-a)\exp\left(\frac{-t}{\tau_{ij}^{short}}\right)$$
(4)

Where a, τ_{ij}^{res} , τ_{ij}^{short} , and β are fitting parameters. The second term corresponds to a shorter timescale, describing sub-diffusive processes, while the first term is relevant to the time scale of the diffusion processes.¹⁴

Furthermore, the mode of diffusion can be determined by comparing the characteristic diffusional length scale L_{ij}^c and the solvation shell length scale L_{ij}^s defined via the following equations:

$$L_{ij}^c = \sqrt{6D_i \tau_{ij}^{res}} \tag{5}$$

Where D_i is the self-diffusion coefficient of *i*, and τ_{ij}^{res} is the residence time between *i* and *j*. And L_{ij}^s is the size of solvation shells, which is obtained by adding the minimum after the first peak of the relevant radial distribution function g(r) and the radius of gyration of Ligands (Table S1, S2).¹⁵

Nernst-Einstein lithium-ion transference numbers t_{+}^{NE} were calculated based on the self-diffusion coefficients of cations and anions. It is defined by the following equation¹³:

$$t_{+}^{NE} = \frac{D_{+}}{D_{+} + D_{-}} \tag{6}$$

 t_{+}^{NE} qualitatively reflect the proportion of lithium-ion transport in the overall ionic transport. A higher value indicates a greater contribution of lithium ions to the total ionic conductivity (Fig. S13).

Note S3: Hydrogen bond analysis

Hydrogen bond analysis was performed using MDAnalysis package¹⁶. Based on the criteria of N-O distance ≤ 3.2 Å and N-H-O angle $\geq 105^{\circ}$,¹⁷ a substantial number of hydrogen bonds were identified in the SPEs containing FMA, ACA, and TFA. For example, in the SPE with FMA, an average of approximately 35.6 hydrogen bonds were observed per trajectory frame. Representative hydrogen-bonding configurations are shown in Fig. S14.

Note S4: Density functional theory calculations

All density functional theory (DFT) calculations were performed using Gaussian 16 package¹⁸. The geometry optimization was performed using B3LYP-D3(BJ)/def2-TZVP^{19, 20} level of theory with implicit solvent model IEF-PCM(UFF, ε =12)²¹ (ε =12 is the dielectric constant of PVDF)²².

Note S5: Calculation of donor number

The concept of donor number (DN) was originally introduced by Gutmann to characterize the Lewis basicity of a solvent and reflect its ability to donate electrons to electron acceptors²³. A higher DN value generally indicates a stronger interaction between the electron acceptors and solvents. In this work, the values of DN were calculated at the same level in gas phase, which can be fitted by the following equation:

$$DN = \frac{1}{8} \frac{(I_{SbCl_5} + A_{SbCl_5} - (I_s + A_s))^2}{(I_{SbCl_5} - A_{SbCl_5} + I_s - A_s)}$$
(7)

Where I_{SbCl_5} , I_s , A_{SbCl_5} , and A_s are the values of vertical ionization energy of SbCl₅, solvent and electron affinity of SbCl₅, solvent, respectively. These values are derived from the frontier molecular orbital energies, where the ionization energy $I = -E_{HOMO}$ and the electron affinity $A = -E_{LUMO}$.²⁴

Note S6: Classification of solvents

The electrostatic potential (ESP) represents the potential generated in the space surrounding a molecule by its nuclei and electrons and reflects an uneven distribution of charge, which was calculated using Multiwfn package²⁵ in this work. The parameter ESP_{min} refers to the most negative surface potentials of molecule. Based on their DN values and ESP_{min}, the solvents can be broadly classified into three groups²⁶. Antisolvents usually show a high ESP_{min} ≥ -1.0 eV and a low DN value ≤ 3.0 kcal mol⁻¹, indicating very weak interactions with cations. In contrast, strongly solvating solvents generally possess a high DN value ≥ 11.0 kcal mol⁻¹ and a low ESP_{min} ≤ -2.0 eV, suggesting strong coordination ability. Weakly solvating solvents fall between these two groups, exhibiting intermediate values of ESP_{min} and DN value.

Note S7: Calculation of redox properties

The electrochemical window (ECW) refers to the voltage range within which the electrolyte remains stable without undergoing oxidation or reduction reactions²⁷. It serves as a key indicator of the thermodynamic stability of the electrolyte. The ECW can be obtained through theoretical calculations, often referred to as the calculated ECW.

In previous studies, the electrochemical stability of electrolytes has commonly been assessed by calculating the energy levels of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), based on their correlation with redox potentials²⁸. In general, Typically, a lower LUMO energy indicates stronger electron-accepting ability and thus a higher reduction potential, while a higher HOMO energy implies a stronger electron-donating ability and a lower oxidation potential.

Although HOMO–LUMO energy level calculations are convenient and can provide a qualitative estimate of electrochemical stability, it is not appropriate to directly equate the energy gap between HOMO and LUMO with the ECW. This is because the HOMO and LUMO levels primarily describe the electronic structure of isolated molecules and may not accurately represent the actual species involved in redox reactions. Moreover, interactions with other species, such as lithium salts or other solvents, can substantially affect the redox behavior of the electrolyte, leading to deviations from these predictions²⁹.

A more rigorous and accurate approach for evaluating the oxidation and reduction potentials of electrolytes is to calculate the Gibbs free energy changes of specific redox reactions. These voltages represent the potentials at which reduction and oxidation processes occur, respectively. The relevant equations are as follows³⁰:

$$E_{red} = -\frac{G_{reduced} - G_{inital} + \Delta G_{solv}^{0}(reduced) - \Delta G_{solv}^{0}(inital)}{F} - 1.4V \quad (8)$$

$$E_{ox} = -\frac{G_{inital} - G_{oxidized} + \Delta G_{solv}^{0}(inital) - \Delta G_{solv}^{0}(oxidized)}{F} - 1.4V$$
(9)

The adiabatic reduction potentials E_{red} and oxidation potentials E_{ox} for the solvents and related complexes (including solvent-solvent, solvent-anion, and solvent-

cation complexes) were calculated at B3LYP- D3(BJ)/6-311+g(d,p) level of theory (Fig. S10, S11) in this work. Here, $G_{reduced}$, $G_{oxidized}$, and G_{inital} are the free energies of the reduced, oxidized and initial complexes in gas-phase at 298.15 K, respectively. ΔG_{solv}^{0} are the corresponding free energies of solvation, and F is the Faraday constant. A standard-state correction was considered to account for work to bring 1 mol of gas from 1 atm (22.47 L/mol) to 1 M (1 mol/L), which resulted in the addition of a correction constant RT ln(24.47/1).³¹ Geometries were allowed to relax after the electron transfer, and subtraction of 1.4 V accounts for the conversion from the absolute electrochemical scale to the commonly used Li/Li⁺ potential scale.

The calculated ECW is defined as the potential range between the minimum oxidation potential and the maximum reduction potential among various complexes, primarily reflecting the thermodynamic driving forces behind electrolyte decomposition. Although experimental results often show that electrolytes exhibit higher electrochemical stability and a wider ECW than predicted, this discrepancy arises because the experimentally observed ECW is influenced not only by thermodynamic factors but also by kinetic parameters and the formation of passivating interfacial layers^{29, 32}. Nonetheless, the calculated ECW can provide a valuable theoretical framework and reference point for assessing the experimental ECW, thereby helping to guide material screening and reduce experimental costs.

Supplementary Figures



Fig. S1 The MD simulation box of the SPEs with (a) DMF (b) DMAC (c) FDMA (d) FMA (e) ACA (f) TFA (g) BTF (h) BTA (i) TFBTA.



Fig. S2 Calculated density of polymers with different polymerization degrees.



Fig. S3 Calculated radial distribution functions g(r) and the corresponding integrals N(r)

of SPEs with (a) DMF (b) DMAC (c) FDMA (d) FMA (e) ACA (f) TFA (g) BTF (h) BTA (i) TFBTA.



Fig. S4 Statistical chart of the solvation structures 1 Li⁺ - x anions - y solvents from MD simulations of SPEs with (a) DMF (b) DMAC (c) FDMA (d) FMA (e) ACA (f) TFA (g) BTF (h) BTA (i) TFBTA.



Fig. S5 Populations of SSIP, CIP, and AGG species in SPEs with (a) DMAC (b) FDMA

(c) FDMA (d) FMA (e) ACA (f) BTA.



Fig. S6 Representative MSDs of Li⁺ and FSI⁻ in SPEs with (a) DMF (b) DMAC (c) FDMA (d) FMA (e) ACA (f) TFA (g) BTF (h) BTA (i) TFBTA.



Fig. S7 Representative collective MSDs of SPEs with (a) DMF (b) DMAC (c) FDMA

(d) FMA (e) ACA (f) TFA (g) BTF (h) BTA (i) TFBTA.



Fig. S8 Examples fit for the autocorrelation function of the residence times of SPEs with (a) DMF (b) DMAC (c) FDMA (d) FMA (e) ACA (f) TFA (g) BTF (h) BTA (i) TFBTA.



Fig. S9 Evolution of Li^+ solvation environment in SPE with TFBTA. And the representative Li^+ solvation structures corresponding to different times, as indicated by the dashed vertical lines (t = 100 ps, 250 ps, 750 ps, 900ps), are presented.



Fig. S10 Calculated reduction potential of the single solvents and Li⁺-solvent complexes.



Fig. S11 Calculated oxidation potential of the single solvents, solvent-solvent complexes, and anion-solvent complexes.



Fig. S12 Calculated lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy values of solvent molecules.



Fig. S13 Calculated Nernst–Einstein lithium-ion transference number of different SPEs.



Fig. S14 The snapshots depicting the hydrogen bond in SPE with FMA.

Supplementary Tables

Electrolytes	L° of Li ⁺ -solvent pairs (Å)	L ^c of Li ⁺ -anion pairs (Å)
DMF	5.077	1.063
DMAC	5.809	1.188
FDMA	5.166	1.542
FMA	3.840	1.132
ACA	4.248	1.018
TFA	4.239	1.489
BTF	3.557	1.679
BTA	5.351	1.847
TFBTA	0.753	1.956

Table S1. The calculated L^c of Li^+ -solvent and Li^+ -anion pairs in different electrolytes.

Pairs	L ^s (Å)
Li ⁺ -DMF	6.624
Li ⁺ -DMAC	6.900
Li ⁺ -FDMA	7.418
Li ⁺ -FMA	5.552
Li ⁺ -ACA	6.012
Li ⁺ -TFA	6.638
Li ⁺ -BTF	7.540
Li ⁺ -BTA	7.708
Li ⁺ -TFBTA	8.600
Li ⁺ -FSI ⁻	7.274

Table S2. The calculated L^s of Li^+ -solvent and Li^+ -anion pairs.

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