

Puzzle-like molecular assembly of non-flammable solid-state polymer electrolytes for safe and high-voltage lithium metal batteries

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this paper, a crosslinked polymer structure of VEC, F-containing acrylate and phospholipid triolefins was prepared, in which, VEC dissociates Li-salt, F-acrylate passivates Li-metal anode. Different units show different functions and generate a puzzle-like design concept. Although this polymer electrolyte shows improved performance than previously studied PVEC, the detailed non-polymerized VEC content is a critical point and was not convinced enough, based on the proposed ionic conductivity and gel-state. In addition, the simulated solvation structure should fully consider the non-polymerized VEC monomer. This paper could be published after give a clear study on these issues from the residual VEC monomer.

(1) The authors mentioned that "After polymerization, the signals of C=C groups are negligible in the ^{13}C spectrum of IWSWN-SPE (Figure 1b), demonstrating the complete polymerization of the monomers." In this polymer based composite electrolyte, there is no any liquid was added. But the prepared electrolyte shows a state of gel-state. If there is no any liquid, this crosslinked polymer will generate a stiff powder. It has been clearly demonstrated that the VEC show a low polymerization ratio and the residual unpolymerized VEC help to stimulate the ionic conductivity. Whereas, the pure poly(VEC) without VEC monomer only possesses a quite low ionic conductivity. Therefore, according to the gel-state and ionic conductivity, we believe that VEC show a low polymerization degree and the residual VEC contribute the ionic conductivity. Considering the importance of clarify the content of unpolymerized VEC for both the ionic conductivity and simulation of solvation structure, the residual VEC monomer content is suggested to be obtained. The boiling point of VEC is higher than 230 degree, and there is a sharp weight loss of over 60% in the current TGA curves at 220-250. This weight loss can be attributed to the sum of VEC liquid evaporation and some thermal decomposition of polymer. So, to classify the detailed weight ratio, it is suggested to monitor the weight change through a high vacuum evaporation.

(2) Considering the big difference in the dissociation capability of Li-salt and different solvation structure, please provide the chemical structure of IWSWN-SPE unit, which will show clearer difference with the traditionally used PVEC.

(3) Although Fig 3A give a rough ionic conductivity of PVEC and IWSWN-SPE, it is suggested to provide the exact values of the conductivity of PVEC and IWSWN-SPE at room temperature. The roughly 4×10^{-4} S/cm room temperature conductivity also verify there is some liquid VEC residue.

(4) Since there is some residue VEC monomer, which varies from 20% to 40% according from different reports. This amount is not low and should be better considered in the simulation of solvation structure of Li^+ , which should also affect the real molar ratio of polymer to Li^+ . Again, a precise estimation of VEC monomer is necessary to understand the exact solvation structure here. Based on the amount of VEC residue, the simulation of solvation structure should be re-simulated for better understanding the real case.

Reviewer #2

(Remarks to the Author)

The research reports the synthesis of a polymer electrolyte through radical polymerization of three distinct segments (VEC, HFBMA, TAP) with different functionalities. The authors emphasize a "puzzle-like" molecular assembly, suggesting a precise arrangement of these segments within the polymer matrix. However, there is a significant limitation of free radical polymerization, which generally produces random copolymers with high polydispersity and little control over the molecular sequence and topology. This means that achieving precise control over how the molecular segments (VEC, HFBMA, TAP)

are arranged in the polymer chain would be extremely challenging, which contradicts the idea of a "Puzzle-like" assembly. The claim of a "puzzle-like" assembly CANNOT be provided with free radical polymerization. In addition, the authors should discuss the repeatability of the derived material and reproducibility in polymer properties.

The resulting PE presents a high performance including a high lithium transference number, high oxidation voltage, good thermal stability and room-temperature cycling. This suggests that the combination of the three segments can enhance the performance of PEs. However, the work doesn't elucidate the underlying mechanisms well enough to understand the improved performance. This work provided a computational study of the PVEC and IWSWN-SPE. Some details of computational methods are missing. There is also a serious problem related to MD simulation. Therefore, the current manuscript cannot be accepted. The detailed concerns are provided here and need to be addressed.

-Why is the Li transference number very high in this system? Is it correlated to higher Li diffusion and slower anion diffusion compared to the PVEC case? Please provide further evidence such as Li and F diffusivities through NMR.

-Please provide more clear information on the molar ratios of the three segments and the LiTFSI salt.

-Please provide the details regarding the LUMO, HOMO calculations. Also, how was it calculated for IWSWN-SPE? The discussion of Figure 2e is too brief, and the figures are too small to visualize the positions of these orbitals. In particular, the IWSWN-SPE system requires a more detailed analysis of its LUMO and HOMO orbital structures and positions.

- The discussion of fig 2f to illustrate the electrochemical stability is not entirely convincing. First, the colouring map could not tell the difference among different polymer segments very well, it is suggested to add values to quantify these differences. Secondly, the ESP map describes charge distribution in a molecule which could indicate the potential interaction sites for ions, however, it does not directly reflect electrochemical stability, the claim of stability against oxidation and reduction requires more concrete evidence. It would be beneficial to discuss the ESP map in conjunction with the HOMO-LUMO orbitals.

- The MD simulation procedure used in this work is highly questionable and does not sufficiently address the goal of investigating Li transport mechanisms. The simulations appear to suffer from significant methodological flaws, and also without any validation.

Firstly, starting at such an extremely low temperature (10 K) and rapidly heating to the target temperatures (298.15 K or 253.15 K) in 100 ps suggests that the polymer structures did not undergo proper structural relaxation. At 10 K, the polymer chains are likely frozen, and the rapid temperature increase does not allow for sufficient equilibration or relaxation of the system. This can lead to unrepresentative polymer structures that are not well-equilibrated.

Secondly, 5 ns equilibration: For a polymer system at 298 K, a 5 ns equilibration period is far too short. Polymers, particularly those with complex architectures, require significantly longer timescales to achieve equilibrium due to the slower dynamics of chain relaxation and interaction with ions. Therefore, the structural and dynamic properties observed from such short simulations are unreliable.

Although the authors aim to use MD to provide insight into Li transport, however, this discussion was completely missing in the text. MD here is only used to discuss Li-O and Li-N coordination numbers without delving into critical insights, including Li coordination environment in different polymers, TFSI-polymer coordination structures, Li and FSI diffusion, transference number, Li diffusion mechanism, and underlying reasons for high Tli. The slow anion diffusion is believed due to the stronger interaction with polymers, which is also speculated without sound evidence through MD. Overall, MD part failed to meet its goal. It should be recalculated with a proper relaxation process (such as equilibration longer enough at high temperatures first), then provide an analysis of ion dynamics to support this experimental work.

Reviewer #3

(Remarks to the Author)

The authors proposed a "puzzle-like" strategy to design a high-performance SPE with specific functionality at a molecular level. The TAP and HFBMA molecule segments are spliced into the VEC molecule matrix to enhance the attraction towards TFSI- and facilitate the dissociation of LiTFSI. The functionalized SPE achieves a high Li⁺ transference number, a high ionic conductivity, intrinsic high-voltage characteristics, and stable SEI/CEI. Improved electrochemical performances are confirmed in the coin and pouch cells. These results are interesting. However, before the consideration for publication, I still have several concerns.

1. The authors added three monomers for the polymer and realize the three advantages in the synthesized polymer. However, the disadvantages of each monomer still exist in the synthesized polymer, which may damage the electrochemical performances. What is the principle to design 1+1>2 SPE, rather than 1+1<2 SPE?
2. Electrochemical stability of Li-Li cells is much better than that in the full cells. Is it caused that the failure of the full cells is attributed to the cathode? Cathode-cathode symmetric cells are suggested to test.
3. The authors compared the performances in Figure 4h. Are they based on the similar test conditions, such as cathode loading, N/P ratio, electrolyte amount (g/Ah)? These parameters can significantly affect the battery performances.
4. How about the cycling stability of the 349 Wh/kg pouch cell? Why can the designed SPE with these advantages not render good electrochemical performances?
5. The safety tests are suggested to conduct for the cycled batteries, rather than just charged battery for once. Besides, there

are so many battery parameters, such as LFP, NCM622, NCM811, single-layer pouch cell, few-layer pouch cell, 349 Wh/kg pouch cell. Why are the so many different cells employed for different tests? Please explain the reasons.

Reviewer #4

(Remarks to the Author)

The introduced polymer electrolyte demonstrates a wide electrochemical stability window, nonflammability, and benefits for the electrodes, resulting in lithium metal batteries (LMBs) based on this solid electrolyte exhibiting excellent cycling stability and high energy density. However, several critical aspects of this article require further clarification. Given that some studies have employed phosphate fluorides (e.g., TAEP, TFPA) directly and achieved similar performance to your findings, I am concerned with the structural advantages of your approach.

-Choice of Crosslinker and Fluorine Source: Please clarify why TAP was selected as the crosslinker and HFBMA for introducing fluorine into the solid electrolyte, especially since other compounds such as HFMA, HFBA, and PFBA have been utilized in previous studies.

-Necessity of Phosphorus Monomers: While polymer monomers containing fluorine can also exhibit flame-retardant properties, is the introduction of phosphorus monomers truly necessary? Please provide justification.

-Selection of VEC for Polymer Backbone: What motivated the choice of VEC for forming the polymer backbone? Similar studies have used HFBMA to enhance voltage stability in PDOL polymer electrolytes, achieving an electrochemical stability window of 5.1 V.

-Characterization of "Puzzle-like" Structure: Please explain how the polymer can be assembled in a "puzzle-like" form. Can you provide tests or characterization methods to validate this structure?

-GPC Testing for Residual Small Molecules: Since your polymerization method involves normal free radical polymerization and in-situ polymerization, GPC tests may be necessary to determine whether residual small molecules could act as mobile components promoting ion conduction.

-Accuracy of AFM Results: AFM results are generally more accurate when thin polymer films are applied to a hard substrate, given the relatively low modulus of polymers. The in-situ polymerized polymer on the separator is typically thicker and may possess lower mechanical strength than the AFM probe, which raises concerns about the accuracy of the AFM results. This should be further confirmed.

-Weight Loss Platform Temperature: Why is the end temperature of the weight loss platform for IWSWN-SPE significantly lower than that for PVEC? Is this advantageous for the performance of the solid electrolytes?

-Initial Capacity Discrepancy: In Figure 4g, why does the initial capacity of the PVEC full cell appear much lower than that of the IWSWN-SPE full cell, while their initial capacities in Figure 4d do not show such a difference?

-Typographical Error: The term "specific" in Figure S10 is misspelled and should be corrected.

-Need for Pre-Polymerization: Please clarify why the in-situ polymer electrolyte requires pre-polymerization.

-Attribution of Increased LiF Content: How can you confirm that the increased LiF content in the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) is due to the decomposition of your polymer electrolyte?

-Fluorine Content Discussion: The data indicate that the LiF content in the CEI and SEI of IWSWN-SPE is not significantly greater than that in PVEC. This raises questions about the positive role of fluorine-containing polymers in both SEI and CEI, which requires further discussion.

-Exploration of Internal Mechanisms: While this work employs a multi-component approach using various polymer monomers to achieve excellent battery performance, the underlying principles that enable this "1+1>2" performance should be further explored. Specifically, the essential role of the "puzzle-like" structure and the performance correlation under varying fluoride and phosphide ratios need to be addressed.

Reviewer #5

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have revised the paper well according to the comments and can be published now.

Reviewer #2

(Remarks to the Author)

The authors have made revisions in response to all reviewer's comments. The manuscript has been improved. However, I can't support to publish it in Nature Communications.

Why the material achieves a high Li transport is still not clear. The authors attribute the high Li transference number to the enhanced polymer-anion interaction. This concept is not novel. How the Li-polymer interaction facilitates Li diffusion is not known. The High Li transference number can be approved through the NMR measured Li and F diffusivities, but this work does not provide this result. In addition, MD result does not support a high Tli, which is discussed below.

The authors acknowledge that 23% VEC residuals are present in their polymerized electrolyte, which can significantly affect the conductivity results. After vacuum evaporation, the content can be reduced to 2.53%. However, no conductivity testing has been performed on the low VEC content IWSWN-SPE. While the 23% VEC content is lower than the 54% content in PVEC, this does not prove that the high conductivity is due to a special polymer structure rather than the VEC content. Therefore, the claim that high conductivity results from facilitated lithium salt dissociation is not entirely justified. Moreover, if the high conductivity is primarily due to the gel polymer rather than the "puzzle-like" polymer morphology itself, it would diminish the significance of the proposed polymer design. A conductivity of 0.432 mS cm^{-1} for a gel polymer electrolyte is reasonable; generally, gel polymer electrolytes target conductivity in the range of 10^{-2} to $10^{-3} \text{ S cm}^{-1}$ for battery and electrochemical applications.

For the new MD simulations, the force field parameters should be provided to increase transparency.

Figures R7 and R8 show the equilibrated polymer electrolytes, but the structures appear unusual. After NPT equilibration, the structure should fill the entire simulation box, rather than showing significant vacuum space, even after removing periodic boundary conditions. Please clarify.

The molar ratio of (VEC residue: VEC units in a single polymer chain: LiTFSI) should be provided to help understand the lithium coordination environment. I performed a calculation, and the ratios are 6:4:1 for PVEC and 3:6:1 for IWSWN-SPE. When analyzing the Li coordination environment through RDF, which oxygen atoms are used? I suggest using only the carbonyl oxygen for VEC and the polymer, and nitrogen for TFSI as each of these types of atom only have 1 in each unit and can present the number of the unit. Furthermore, to explain Li coordination environment, it is important to compare the number of VEC residues, VEC units in the polymer, and TFSI in the Li coordination shell. Therefore, I recommend including RDFs of Li-O(VEC) in Figure 3, rather than Li-O(TFSI), since you already show Li-N(TFSI).

The MSD of Li in R12 is not linear even after 30 ns, suggesting poor statistical sampling. A low displacement value of only around $8 \text{ \AA}^2$ after 30 ns indicates very localized and slow Li movement. The calculated diffusion coefficient using this type of MSD profile can only provide an approximate value, as the Li diffusion is still subdiffusive. The error bar should be discussed. A diffusion coefficient of $3.32 \times 10^{-13} \text{ m}^2/\text{s}$ is very low, which contradicts the experimentally reported conductivity of $4.32 \times 10^{-4} \text{ S cm}^{-1}$ and a high Li transference number of 0.7. The Li diffusion coefficient is expected to be in the $10^{-12} \text{ m}^2/\text{s}$ range. Additionally, the diffusivity of TFSI in Figure S22 is significantly higher than the Li diffusivity, and the Li transference number from the MD simulations cannot support such a high transference number of 0.7.

Reviewer #3

(Remarks to the Author)

The manuscript can be published.

Reviewer #4

(Remarks to the Author)

My questions have been well addressed in the revised manuscript. I am happy to recommend publication of this work.

Reviewer #5

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

I don't have any other questions now. Support its publication.

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Response to the comments from Reviewer #1

In this paper, a crosslinked polymer structure of VEC, F-containing acrylate and phospholipid triolefins was prepared, in which, VEC dissociates Li-salt, F-acrylate passivates Li-metal anode. Different units show different functions and generate a puzzle-like design concept. Although this polymer electrolyte shows improved performance than previously studied PVEC, the detailed non-polymerized VEC content is a critical point and was not convinced enough, based on the proposed ionic conductivity and gel-state. In addition, the simulated solvation structure should fully consider the non-polymerized VEC monomer. This paper could be published after give a clear study on these issues from the residual VEC monomer.

Reply: We are grateful for your constructive feedback, and we are committed to addressing these issues comprehensively in our revised manuscript. We will provide a detailed study on the residual VEC monomers to enhance the clarity and reliability of our findings.

The non-polymerized VEC content is indeed a critical aspect that requires further elucidation. We have conducted additional experiments and analyses to provide a more comprehensive understanding of the VEC content in the polymer electrolytes. We also revise our simulations to incorporate the influence of residual VEC monomers on the solvation structure.

(1) The authors mentioned that “After polymerization, the signals of C=C groups are negligible in the ^{13}C spectrum of IWSWN-SPE (Figure 1b), demonstrating the complete polymerization of the monomers.” In this polymer based composite electrolyte, there is no any liquid was added. But the prepared electrolyte shows a state of gel-state. If there is no any liquid, this crosslinked polymer will generate a stiff powder. It has been clearly demonstrated that the VEC show a low polymerization ratio and the residual unpolymerized VEC help to stimulate the ionic conductivity. Whereas, the pure poly(VEC) without VEC monomer only possesses a quite low ionic conductivity. Therefore, according to the gel-state and ionic conductivity, we believe that VEC show a low polymerization degree and the residual VEC contribute the ionic conductivity. Considering the importance of clarify the content of unpolymerized VEC for both the ionic conductivity and simulation of solvation structure, the residual VEC monomer content is suggested to be obtained. The boiling point of VEC is higher than 230 degree, and there is a sharp weight loss of over 60% in the current TGA curves at 220-250. This weight loss can be attributed to the sum of VEC liquid evaporation and some thermal decomposition of polymer. So, to classify the detailed weight ratio, it is suggested to monitor the weight change through a high vacuum evaporation.

Reply: We appreciate your insightful comments regarding the residual VEC content in the polymer electrolyte. We have conducted further analyses to address these important points and provide clarity on the composition and state of the polymer electrolyte.

In agreement with your assessment, the in-situ polymerized PVEC indeed retains some residual VEC monomer, as evident in the gel-like appearance observed, as shown in Figure R1. To characterize the residual VEC content in the polymer electrolyte obtained through in-situ polymerization, we conducted ¹H NMR testing, as illustrated in Figure R2. (*Angew. Chem. Int. Ed.* 2023, 62, e202309613)

$$\text{Residual VEC monomers ratio in PVEC} = \frac{1}{1 + (4.25 - 2) \div 3} \times 100\% \approx 57\%$$

By integrating the corresponding peak areas, we calculated that the residual VEC monomer content accounts for 57%, underscoring the substantial influence of VEC monomers on the physicochemical properties of the in-situ polymerized PVEC.

While NMR testing is suitable for assessing the residual VEC content in PVEC, it is not applicable to our synthesized IWSWN-SPE due to the presence of TAP containing three carbon-carbon double bonds that act as crosslinkers. The crosslinked nature of the polymer renders it insoluble in conventional solvents like DMSO or chloroform, precluding the use of standard NMR testing methods to measure the residual VEC content in the IWSWN-SPE. Instead, we employed TGA analysis to determine the residual VEC content, as depicted in Figure R3. The TGA results indicated a residual VEC content of 54% for PVEC and **23% for our IWSWN-SPE**. The weight loss below 200 °C corresponds to VEC liquid evaporation, while weight loss above 200 °C is attributed to polymer and lithium salt decomposition (*Angew. Chem. Int. Ed.* 2023, 62, e202309613). In contrast to the gel-like state of PVEC, the in-situ polymerized IWSWN-SPE exhibits a dry state, as indicated in Figure R4. The presence of bubbles in the polymer without any change in their positions suggests a dry state rather than a gel-like state.

Additionally, we followed your suggestion and employed high vacuum evaporation to monitor weight changes and determine the residual VEC content, with results presented in Table R1. The residual VEC content was calculated to be 3.56% for PVEC and 2.53% for IWSWN-SPE. The discrepancy between these results and previous methods can be attributed to the entrapment of residual monomers within the synthesized polymer, leading to swelling effects that hinder complete evaporation under vacuum conditions, resulting in significant differences in the measured content.

We have incorporated these detailed findings into the manuscript to provide a comprehensive understanding of the residual VEC content and the state of the polymer electrolyte. Thank you for your valuable insights, which contribute to the depth and accuracy of our research findings.

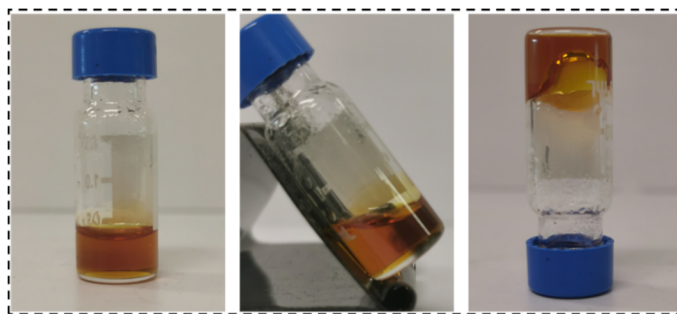


Figure R1. Digital photos of PVEC in different states obtained by in-situ polymerization.

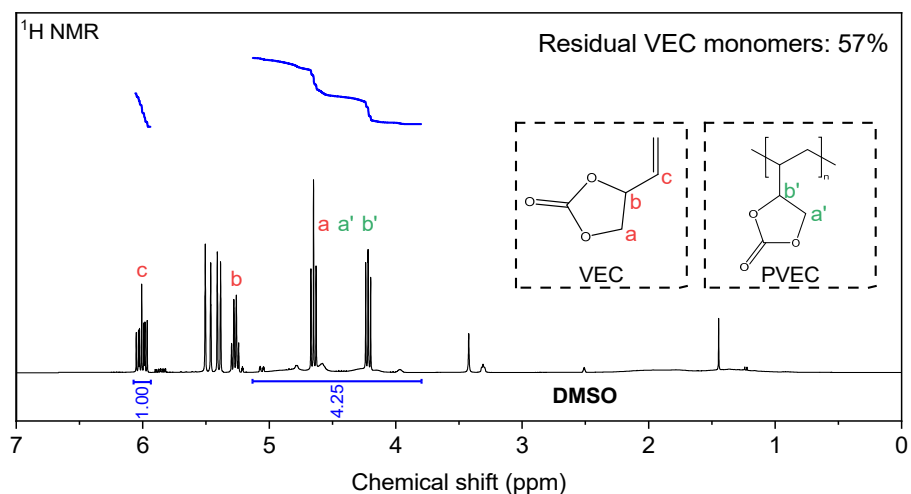


Figure R2. ¹H NMR spectra of PVEC via in-situ polymerization.

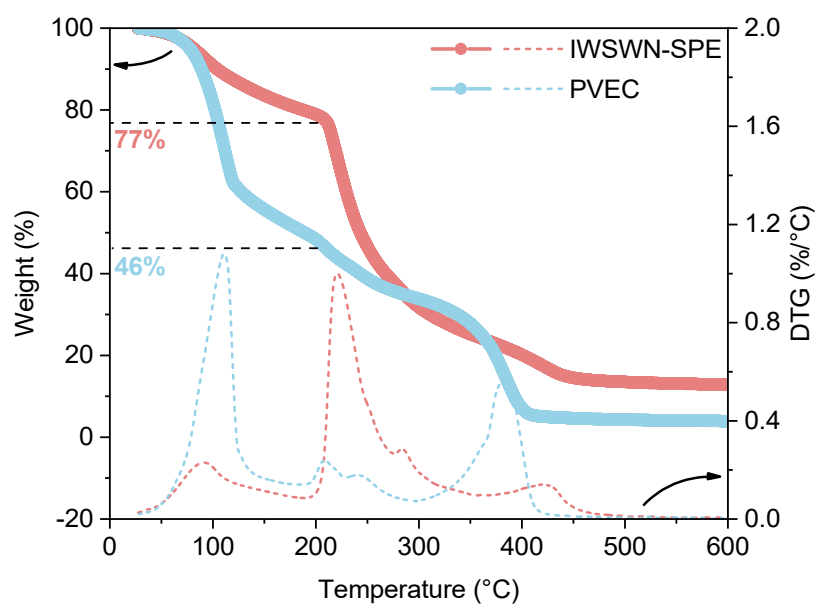


Figure R3. TGA curves of PVEC and IWSWN-SPE.

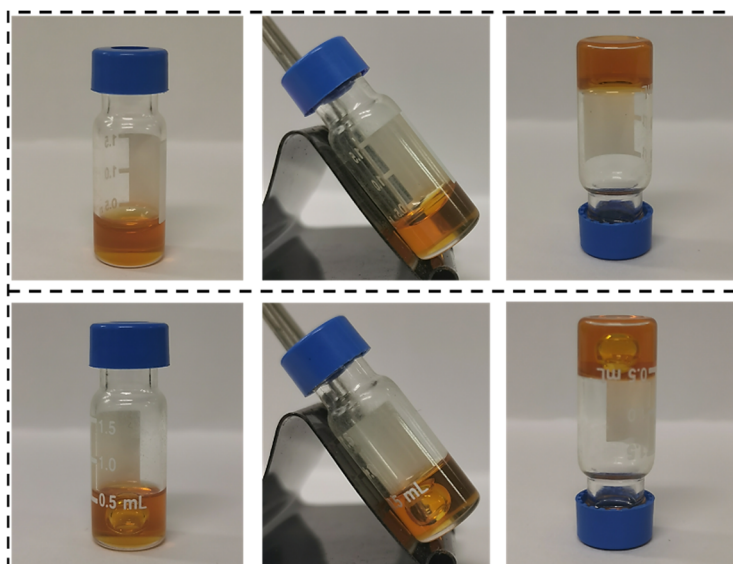


Figure R4. Digital photos of two kinds of IWSWN-SPE (the top row has no bubbles, and the bottom row contains one bubble) in different states obtained by in-situ polymerization.

Table R1. Weight change of PVEC and IWSWN-SPE after high vacuum evaporation.

	Weight before vacuum evaporation / g	Weight after vacuum evaporation / g	VEC monomer ration / %
PVEC	0.505	0.487	3.56
IWSWN-SPE	0.475	0.463	2.53

(2) Considering the big difference in the dissociation capability of Li-salt and different solvation structure, please provide the chemical structure of IWSWN-SPE unit, which will show clearer difference with the traditionally used PVEC.

Reply: We greatly appreciate the reviewer for your valuable comment. Please find below the chemical structure of the IWSWN-SPE unit (Figure R5), which is also supplied in the manuscript.

In contrast to PVEC, our designed IWSWN-SPE incorporates segments containing fluorine and phosphorus. These additions serve to enhance the binding affinity between the polymer and anions, facilitating easier dissociation of lithium salts. This structural modification results in a polymer, IWSWN-SPE, that exhibits distinct interactions with lithium salts compared to traditional PVEC.

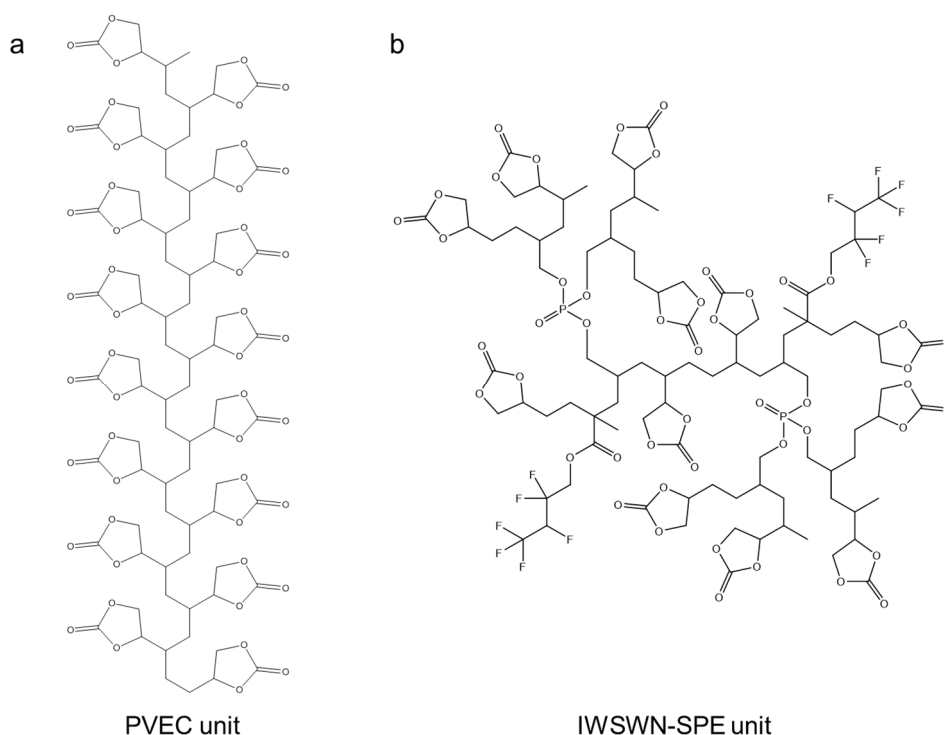


Figure R5. Schematic diagram of the molecular formulas of proposed PVEC (a) and IWSWN-SPE (b) units.

(3) Although Fig 3A give a rough ionic conductivity of PVEC and IWSWN-SPE, it is suggested to provide the exact values of the conductivity of PVEC and IWSWN-SPE at room temperature. The roughly 4×10^{-4} S/cm room temperature conductivity also verify there is some liquid VEC residue.

Reply: We appreciate your suggestion to provide the exact numerical values of the ionic conductivity for PVEC and IWSWN-SPE. We supply the detailed ionic conductivity values at room temperature (Figure R6) and include them in the revised version of the manuscript.

Specifically, the room temperature ionic conductivity of PVEC is 5.97×10^{-4} S cm^{-1} , and the designed IWSWN-SPE exhibits an ionic conductivity of 4.32×10^{-4} S cm^{-1} . The higher ionic conductivity of PVEC can be attributed to its 54% content of unreacted VEC monomers, which is also confirmed by the gel state of the electrolyte.

In contrast, our designed IWSWN-SPE contains only 23% unreacted VEC monomers, yet achieves an ionic conductivity of 4.32×10^{-4} S cm^{-1} at room temperature, partly due to the facilitated dissociation of lithium salts.

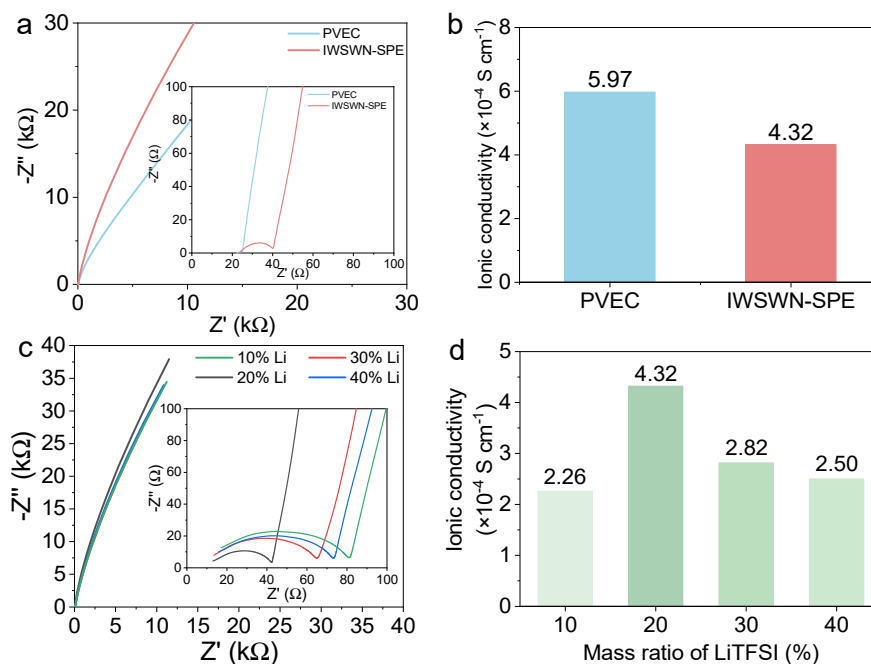


Figure R6. EIS tests (a) and corresponding ionic conductivity (b) of PVEC and IWSWN-SPE. EIS tests (c) and corresponding ionic conductivity (d) of IWSWN-SPE with different weight ratios of LiTFSI.

(4) Since there is some residue VEC monomer, which varies from 20% to 40% according from different reports. This amount is not low and should be better considered in the simulation of solvation structure of Li^+ , which should also affect the real molar ratio of polymer to Li^+ . Again, a precise estimation of VEC monomer is necessary to understand the exact solvation structure here. Based on the amount of VEC residue, the simulation of solvation structure should be re-simulated for better understanding the real case.

Reply: We sincerely thank the reviewer for pointing out the importance of considering the residual VEC monomer in the simulation of the solvation structure of Li^+ . We have carefully revised our simulation methodology to account for the residual VEC monomer content.

Specifically, based on the experimentally determined residual VEC monomer content, we incorporated the corresponding number of VEC monomer molecules into our MD simulations. The molecular ratios in the revised simulations are as follows:

- 1) For the PVEC system, the molar ratio of VEC monomer to PVEC unit to LiTFSI is set to $n(\text{VEC}): n(\text{PVEC unit}): n(\text{LiTFSI}) = 24:1:4$.
- 2) For the IWSWN-SPE system, the molar ratio is set to $n(\text{VEC}): n(\text{IWSWN-SPE unit}): n(\text{LiTFSI}) = 6:1:2$.

The molecular structures of the two proposed polymer units used in the simulations are shown in Figure R5. To ensure the revised simulations accurately reflect the real case, we repeated the MD simulations with the updated system compositions. Here are the updated discussions:

The molecules at the energy equilibrium state and the snapshots that evolve from MD simulations of PVEC and IWSWN-SPE are shown in Figures R7 and R8. In both systems, Li^+ and TFSI^- are surrounded by polymer chains and VEC monomers.

(a) Li^+ Coordination Environment and Diffusion:

The radial distribution function (RDF) and coordination number (CN) analyses are performed to investigate the coordination environment of Li^+ in both PVEC and IWSWN-SPE systems (Figures R9 and R10). The specific value of the coordination number is depicted in Figure R11. Li^+ coordination with oxygen atoms of polymer chains is more pronounced in the IWSWN-SPE system (Li-O: 2.73) than in PVEC (Li-O: 1.49), suggesting that Li^+ is more likely coordinated with the polymer backbone in IWSWN-SPE.

The mean square displacement (MSD) curves of Li^+ are calculated to evaluate their diffusion coefficients (Figure R12). The Li^+ diffusion coefficient in PVEC is found to be slightly higher than in IWSWN-SPE. This can be attributed to the presence of unpolymerized VEC monomers in PVEC, which enhance Li^+ coordination and mobility. RDF analysis further revealed that VEC monomers play a significant role in Li^+ transport in PVEC, as evidenced by the higher CN of Li^+ with O atoms from VEC (2.22 in PVEC system vs. 0.88 in IWSWN-SPE system, Figure R13).

Moreover, from the MD simulation snapshots, we observed distinct coordination environments for Li^+ in the two systems. In the PVEC system, Li^+ primarily coordinates with the C=O groups on the VEC monomer and the PVEC main chain (Figure R14). In contrast, in the IWSWN-SPE system, Li^+ not only coordinates with the C=O groups on the IWSWN-SPE main chain and the VEC monomer but also interacts with the P=O groups on the TAP fragment of the IWSWN-SPE backbone (Figure R15). This introduces a more diverse coordination environment for Li^+ in the IWSWN-SPE system, offering multiple pathways for Li^+ transport.

(b) TFSI^- Coordination Environment and Interaction:

The diffusion coefficients of TFSI^- are also analyzed (Figure R16). In the IWSWN-SPE system, the TFSI^- diffusion coefficient is lower ($2.33 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) compared to PVEC ($5.37 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$). This reduced mobility is attributed to stronger interactions between TFSI^- and the polymer chain in IWSWN-SPE, as confirmed by the following:

Structural snapshots from the simulations (Figures R17 and R18) further confirm this observation. In the PVEC system, the distances between the N atom of TFSI^- and the oxygen atoms of the nearest polymer chain are 4.64 Å and 5.22 Å. In contrast, in the IWSWN-SPE system, these distances are reduced to 3.22 Å and 3.57 Å, indicating stronger interactions.

While the Li^+ diffusion rate in the IWSWN-SPE system is comparable to that in the PVEC system, the diffusion rate of TFSI^- is significantly reduced in IWSWN-SPE due to its strong interactions with the polymer backbone. This reduced TFSI^- mobility is a critical factor contributing to the higher t_{Li^+} observed in the IWSWN-SPE system compared to the PVEC system. These analyses provide a comprehensive understanding of the Li^+ transport mechanisms and the underlying reasons for the observed higher t_{Li^+} in the IWSWN-SPE system.

These updates have been incorporated into the revised manuscript, where the methodology and results are described in detail. We believe these improvements provide a more accurate representation of the solvation environment and enhance the robustness of our conclusions.

Once again, we greatly appreciate the reviewer's insightful suggestions.

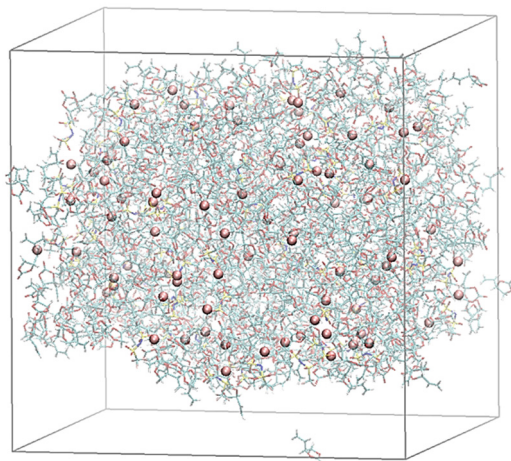


Figure R7. 3D snapshot of PVEC system after equilibration process.

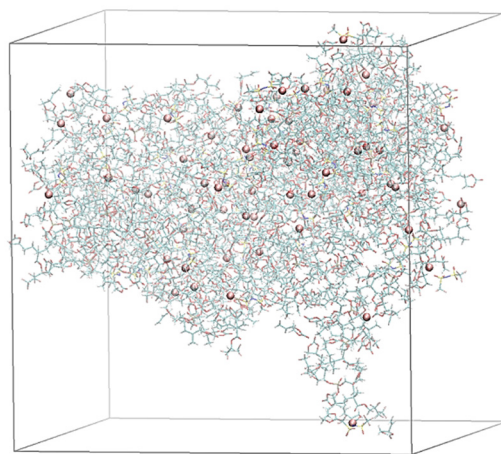


Figure R8. 3D snapshot of the IWSWN-SPE system after the equilibration process.

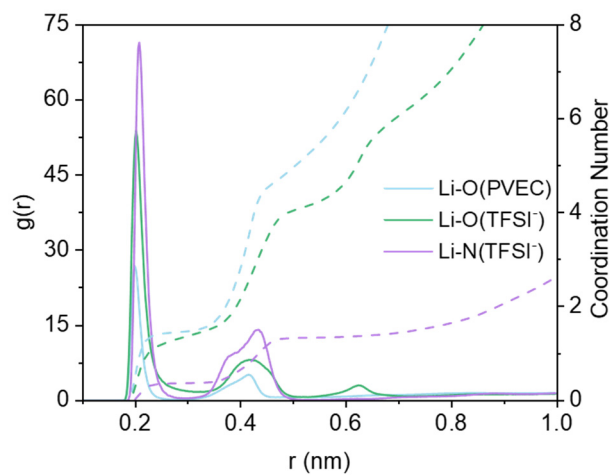


Figure R9. Curves of RDF and CN of the PVEC system.

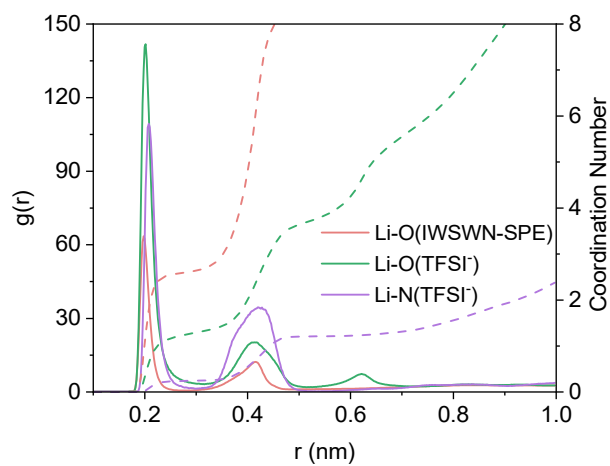


Figure R10. Curves of RDF and CN of the IWSWN-SPE system.

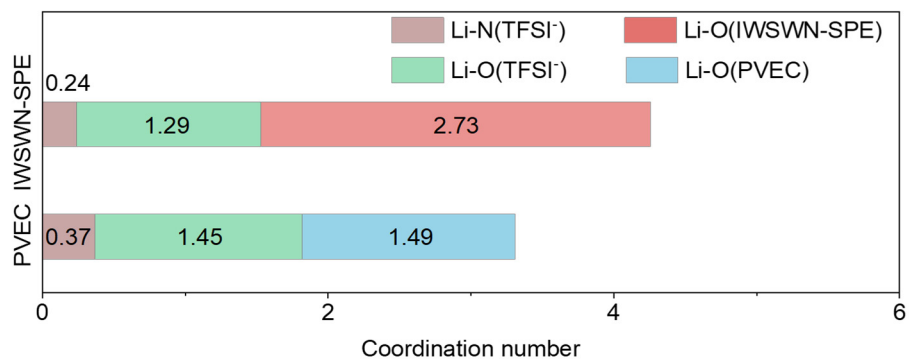


Figure R11. The comparison results of the CN in PVEC and IWSWN-SPE systems.

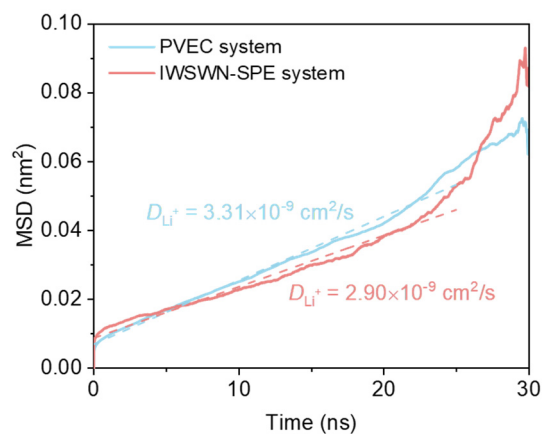


Figure R12. MSD curves of Li^+ in the PVEC and IWSWN-SPE systems.

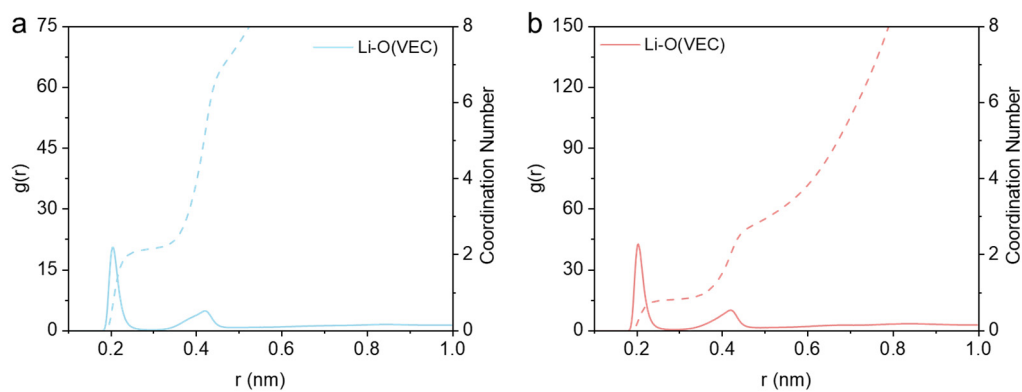


Figure R13. Curves of RDF and CN of Li-O_{VEC} in the PVEC (a) and IWSWN-SPE (b) systems.

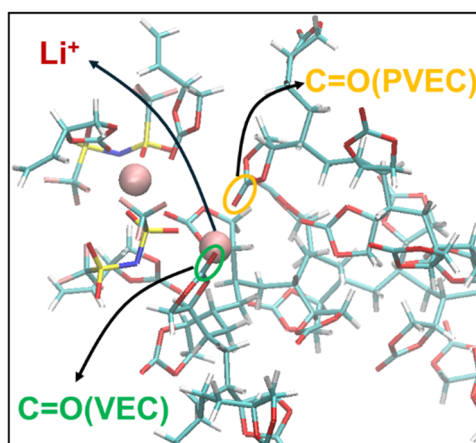


Figure R14. The coordinated environment of Li^+ in the PVEC system.

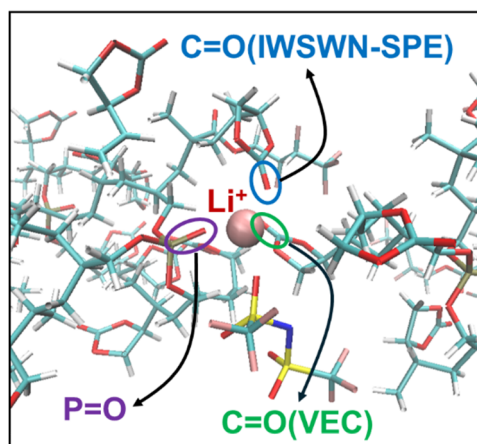


Figure R15. The coordinated environment of Li^+ in the IWSWN-SPE system.

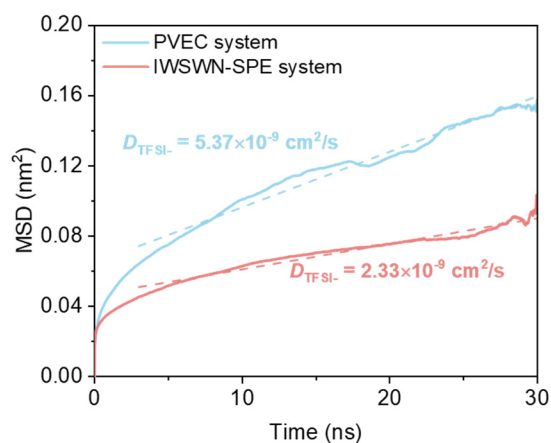


Figure R16. MSD curves of TFSI^- in the PVEC and IWSWN-SPE systems.

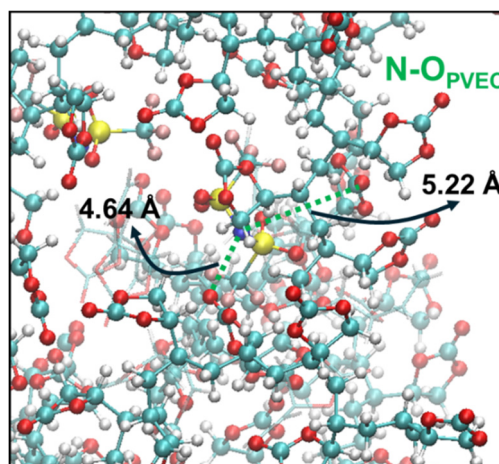


Figure R17. Distance measurement graph between the N atom of TFSI^- and the O atoms of the nearest polymer chain in the PVEC system.

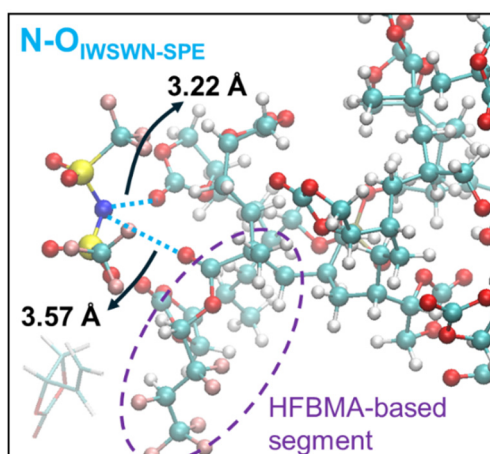


Figure R18. Distance measurement graph between the N atom of TFSl⁻ and the O atoms of the nearest polymer chain in the IWSWN-SPE system.

Response to the comments from Reviewer #2

The research reports the synthesis of a polymer electrolyte through radical polymerization of three distinct segments (VEC, HFBMA, TAP) with different functionalities. The authors emphasize a "puzzle-like" molecular assembly, suggesting a precise arrangement of these segments within the polymer matrix. However, there is a significant limitation of free radical polymerization, which generally produces random copolymers with high polydispersity and little control over the molecular sequence and topology. This means that achieving precise control over how the molecular segments (VEC, HFBMA, TAP) are arranged in the polymer chain would be extremely challenging, which contradicts the idea of a "Puzzle-like" assembly. The claim of a "puzzle-like" assembly CANNOT be provided with free radical polymerization. In addition, the authors should discuss the repeatability of the derived material and reproducibility in polymer properties.

Reply: Thank you for your thoughtful insights regarding the challenges of achieving a "puzzle-like" molecular assembly through free radical polymerization and the importance of discussing the repeatability and reproducibility of the derived material. We appreciate the opportunity to address these critical points.

We are sorry for our unclear explanations. Regarding the concept of "puzzle-like" assembly, we use the analogy of assembling puzzles by **interlocking puzzle pieces** to illustrate how we design and synthesize the solid-state polymer electrolyte at the molecular level. Just as one can use various colored puzzles of similar shapes in daily life, **these puzzles can be arranged randomly or arranged according to preference by the interlocking of the puzzle pieces.**

Radical alkene polymerization can be aptly compared to a "puzzle-like" assembly process due to several key similarities:

1) Randomness and controllability in assembly: In a jigsaw puzzle, while each piece has a fixed shape, the final structure depends on how individual pieces are arranged. Similarly, in radical polymerization, various monomers undergo random radical-initiated reactions to form polymer chains. Although the types and ratios of monomers can be predetermined, their specific sequence within the polymer backbone is generally random, resembling the local structural uncertainty observed in a puzzle.

2) Compatibility and matching of monomers: For puzzle pieces to fit together, they must have compatible shapes. Likewise, in radical polymerization, monomers must possess polymerizable double bonds and similar reactivity for successful copolymerization, **akin to puzzle pieces that interlock correctly based on their shape and pattern.**

3) Structural diversity at the local level: A completed puzzle consists of various local arrangements, each exhibiting a unique pattern. Similarly, in radical copolymerization, monomers can be arranged in different sequences, leading to alternating, random, or block copolymer structures. This localized diversity further supports the analogy between polymerization and puzzle assembly.

4) Macroscopic uniformity: Despite local variations in puzzle piece placement, the overall image could appear uniform from a distance. Likewise, in statistical copolymers, monomers may be randomly distributed on a molecular level, but the bulk properties of the polymer remain homogeneous. This

macroscopic uniformity highlights another parallel between radical polymerization and puzzle construction.

The analogy helps illustrate how polymer formation involves both local sequence variability and macroscopic uniformity, ultimately leading to materials with tunable properties and functions.

Similarly, we employ this analogy to showcase how we utilize three monomers in free radical polymerization to synthesize the solid-state polymer electrolyte. **In our work, we are not attempting to precisely control the self-assembly of the monomers through free radical polymerization. The monomers can polymerize with themselves or with other different monomers.**

However, by **uniformly** mixing different monomers **at the molecular level** in the precursor solution, we can form a homogeneous SPE through free radical polymerization like assembling a puzzle, as illustrated in Figure R1 (Here, we use the interlocking between the puzzle pieces in a "puzzle" as a metaphor for how different polymer monomers interact and connect with each other through free radical polymerization). From a macroscopic perspective, the distribution of the three colored puzzles, representing the three monomers, appears uniform throughout the entire structure. However, upon closer examination, their arrangement is random, encompassing various possible combinations, as indicated by the dashed circles.

In terms of experimental repeatability, we conducted parallel synthesis and testing of three sets of experiments, as illustrated in Figures R2, R3, and R4. Through tests such as EIS, LSV, and SEM analyses, we observed consistent results in terms of ionic conductivity, electrochemical stability window, and elemental distribution of the synthesized SPE across all experiments, indicating the reproducibility of our methodology.

In conclusion, our "puzzle-like" molecular assembly analogy shows the random yet uniform nature of the synthesized polymer electrolyte by "interlocking" monomer molecules. Furthermore, the demonstrated repeatability and consistency in experimental results affirm the reliability and reproducibility of our approach.

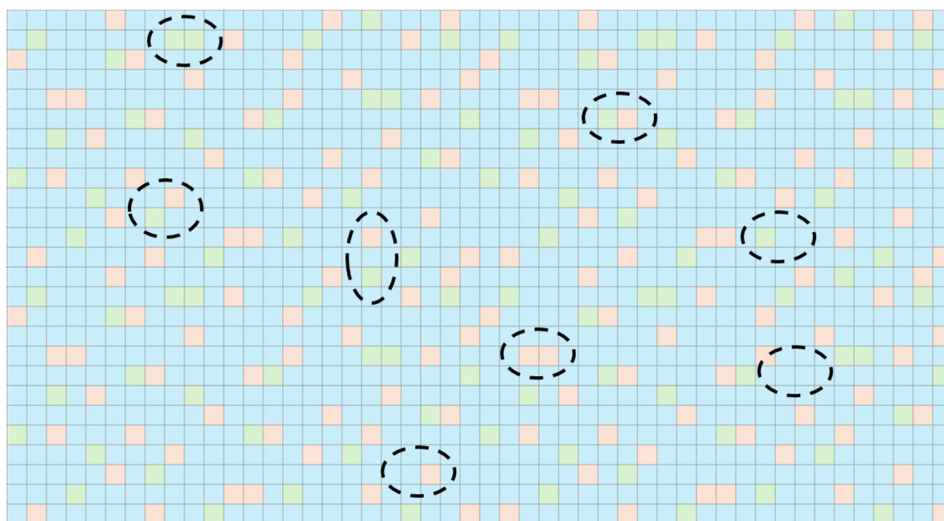


Figure R1. Schematic diagram of the product via "puzzle-like" assembly method (blue: VEC; orange: TAP; green: HFBMA).

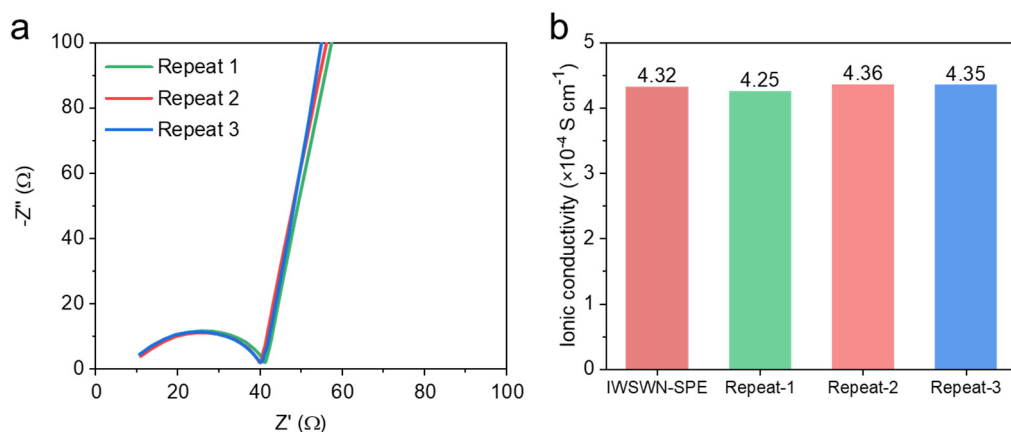


Figure R2. EIS tests (a) and ionic conductivity results (b) of three repeated experiments.

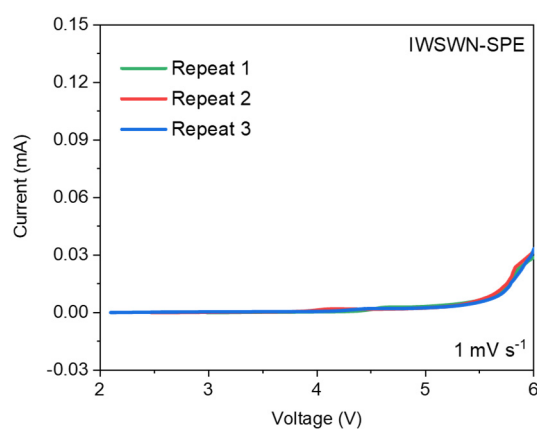


Figure R3. LSV curves of three repeated experiments.

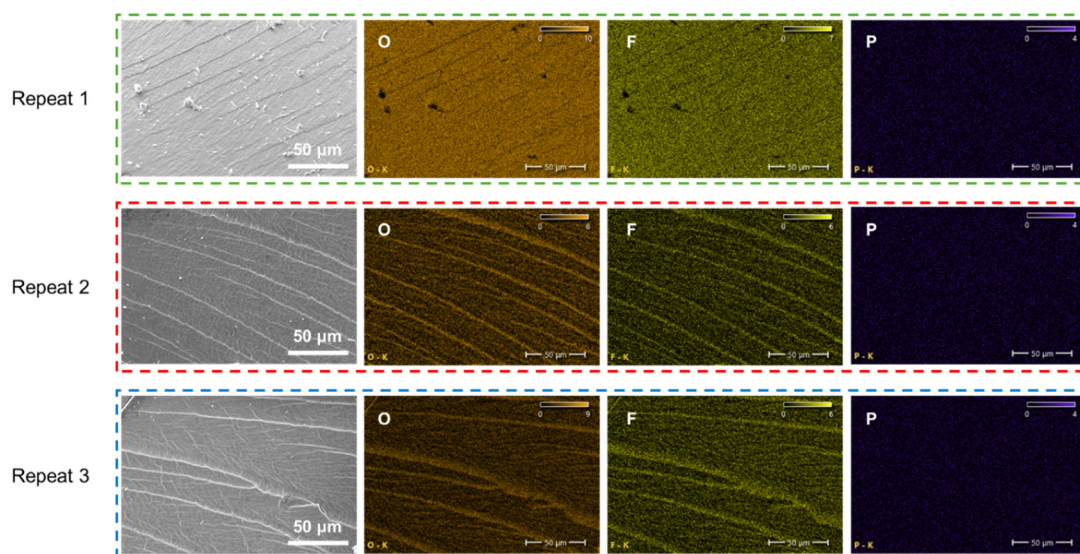


Figure R4. SEM and corresponding mapping results of three repeated experiments.

The resulting PE presents a high performance including a high lithium transference number, high oxidation voltage, good thermal stability and room-temperature cycling. This suggests that the combination of the three segments can enhance the performance of PEs. However, the work doesn't elucidate the underlying mechanisms well enough to understand the improved performance. This work provided a computational study of the PVEC and IWSWN-SPE. Some details of computational methods are missing. There is also a serious problem related to MD simulation. Therefore, the current manuscript cannot be accepted. The detailed concerns are provided here and need to be addressed.

Reply: Thank you for raising the questions and sharing your valuable feedback. We appreciate the opportunity to address the specific concerns highlighted in your review. In the following responses, we have provided detailed explanations and data to address the issues raised one by one.

Q1. Why is the Li transference number very high in this system? Is it correlated to higher Li diffusion and slower anion diffusion compared to the PVEC case? Please provide further evidence such as Li and F diffusivities through NMR.

Reply: Thanks for your query regarding the high Li transference number observed in our system. We appreciate the opportunity to provide detailed explanations.

The TGA test results (Figure R5) indicate that the residual monomer VEC content in the in-situ polymerized PVEC is 54%, whereas in the IWSWN-SPE, it is reduced to 23%. The high VEC monomer content in PVEC facilitates the transport of TFSI⁻ anions, resulting in a lower Li-ion transference number. In contrast, in the designed IWSWN-SPE, although a small amount of residual VEC participates in ion transport, the polymer chains play a more dominant role.

Binding energy calculations reveal that the IWSWN-SPE exhibits a binding energy of -2.11 eV with TFSI⁻ anions, which is higher than that of PVEC with TFSI⁻ anions (-1.51 eV), indicating stronger interactions between the modified IWSWN-SPE and TFSI⁻ anions. This enhanced interaction effectively restricts the TFSI⁻ migration, leading to an increased Li transference number. Furthermore, some related literature also supports the notion that polymer modifications can enhance interactions with anions, thereby improving Li⁺ transference numbers (*Nat. Commun.* 13, 4181 (2022); *Nat. Commun.* 14, 2301 (2023)).

In response to the suggestion, we conducted NMR characterization of Li and F, with results presented in Figure R6. However, due to the gel-like nature of the in-situ polymerized PVEC and its high residual VEC content (54%), solid-state NMR testing was not feasible. Liquid-state NMR testing was also unsuitable, as solvent-ion interactions could alter the intrinsic state of Li⁺ in PVEC.

For F NMR spectroscopy testing, the introduction of HFBMA segments in the IWSWN-SPE, which contain -CF₃ groups analogous to those in TFSI⁻ anions, resulted in overlapping peaks in the spectra (Figure R6a). This overlap hindered the specific characterization of TFSI⁻ anions, making diffusion characterization impractical.

Furthermore, compared with pure LiTFSI, the ⁷Li resonance of IWSWN-SPE shifts to a higher frequency (from -0.60 ppm to -0.45 ppm, Figure R6b), corresponding to the increased mobility of Li⁺.

In conclusion, our findings suggest that modifying the polymer to enhance interactions with anions can effectively improve the Li transference number. This observation is consistent with the measured enhancements in Li transference numbers, further supporting the proposed design strategy.

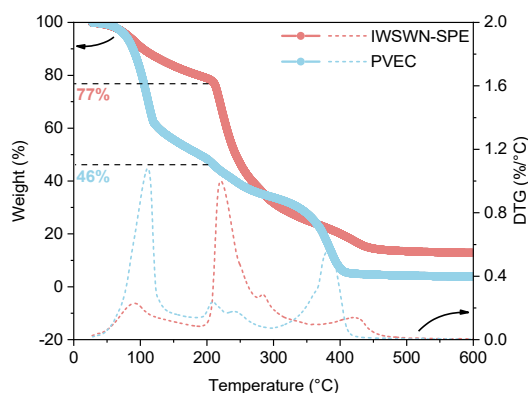


Figure R5. TGA curves of PVEC and IWSWN-SPE.

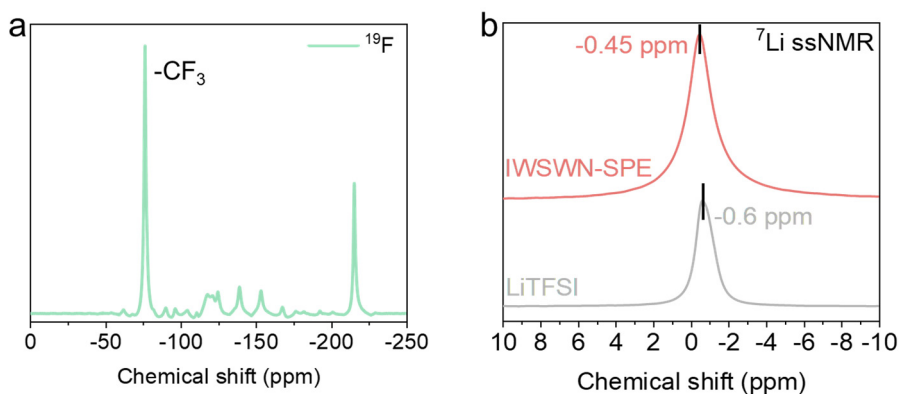


Figure R6. a) ^{19}F ssNMR spectra of the IWSWN-SPE. b) ^7Li ssNMR spectra comparison of IWSWN-SPE and LiTFSI

Q2. Please provide more clear information on the molar ratios of the three segments and the LiTFSI salt.

Reply: We greatly appreciate the reviewer for your valuable comment.

The control of varying fluoride and phosphide ratios follows specific principles. Increasing fluoride content enhances the antioxidant capacity of the polymer electrolyte while potentially reducing ionic conductivity. The LSV and EIS results (Figures R7 and R8) demonstrate that increasing fluoride-based HFBMA molar ratio from 5% to 10% (compared to VEC) significantly boosts antioxidant capacity (low oxidation current), with a slight decrease in ionic conductivity from 0.495 to 0.437 mS cm^{-1} . However, further increasing fluoride-based HFBMA molar ratio to 15% (compared to VEC) shows a less pronounced enhancement in antioxidant capacity but a more significant decrease in conductivity to 0.296 mS cm^{-1} , a 32.3% reduction. Thus, the fluoride-based HFBMA molar ratio in the polymer electrolyte is optimized at 10% (compared to VEC) to achieve a balance between ion transport and antioxidant capacity. In experiments optimizing the fluorine-based HFBMA content, the molar ratio of phosphide-based TAP is 15% (compared to VEC) and the weight ratio of LiTFSI to the total monomer is 20 $\text{wt}\%$.

Then, to evaluate the phosphide-based TAP content, combustion tests were conducted. As shown in Figure R9, a phosphide-based TAP molar ratio of 10% (compared to VEC) still allows the polymer electrolyte to burn while increasing the molar ratio to 15% (compared to VEC) imparts flame-retardant properties. Hence, a phosphide-based TAP molar ratio of 15% (compared to VEC) is deemed appropriate for achieving fire resistance. In experiments optimizing the phosphide-based TAP content, the molar ratio of fluorine-based HFBMA is 10% (compared to VEC) and the weight ratio of LiTFSI to the total monomer is 20 wt%.

Regarding the ratio of Li salt, we adjusted the weight ratio of LiTFSI to the total monomers and screened it based on ionic conductivity, as shown in Figure R10. In experiments optimizing the LiTFSI content, the molar ratio of fluorine-based HFBMA and phosphide-based TAP content is 10% and 15% (compared to VEC), respectively.

When the weight ratio of LiTFSI is 20 wt%, the ionic conductivity of IWSWN-SPE attains its maximum value of $4.32 \times 10^{-4} \text{ S cm}^{-1}$. Therefore, the optimal weight ratio of LiTFSI is chosen to be 20 wt%.

In conclusion, the final molar ratio of VEC to HFBMA to TAP to LiTFSI is calculated to be 1: 0.1: 0.15: 0.12.

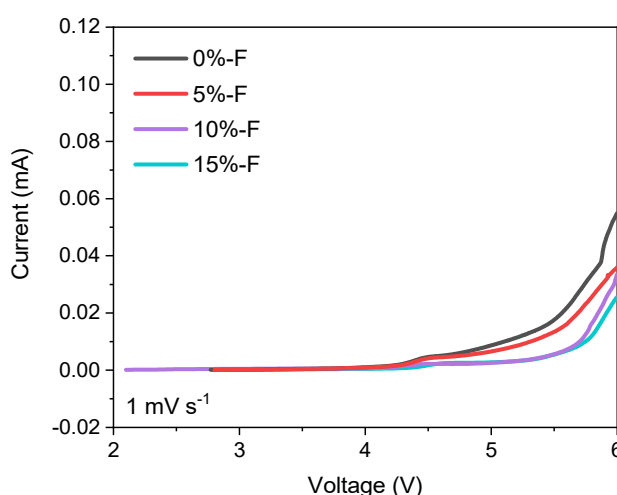


Figure R7. LSV test results for the SPE with different molar ratios of HFBMA (compared to VEC).

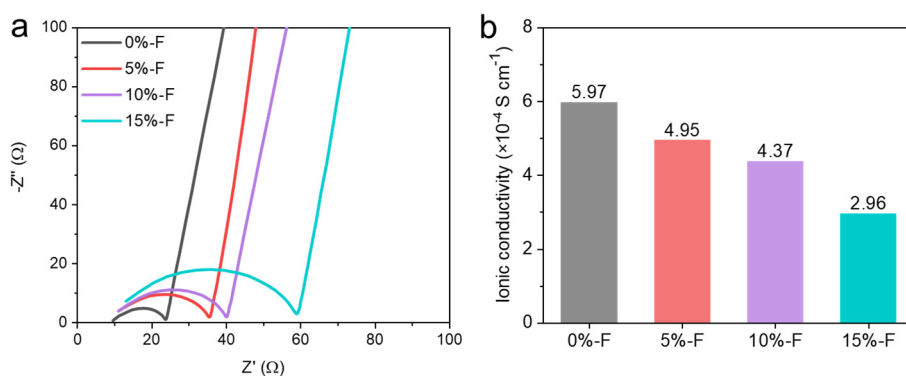


Figure R8. EIS results (a) and corresponding ionic conductivity (b) of the SPE with different molar ratios of HFBMA (compared to VEC).

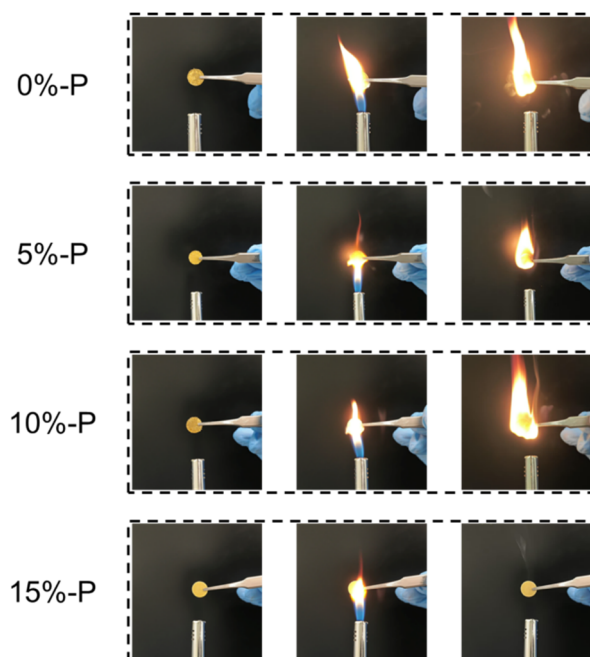


Figure R9. Burning tests of the SPE with different molar ratios of TAP (compared to VEC).

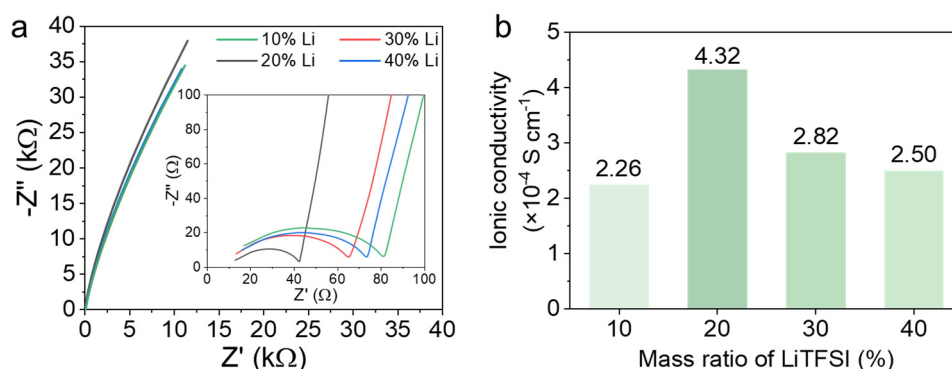


Figure R10. EIS tests (a) and corresponding ionic conductivity (b) of IWSWN-SPE with different weight ratios of LiTFSI.

Q3. Please provide the details regarding the LUMO, HOMO calculations. Also, how was it calculated for IWSWN-SPE? The discussion of Figure 2e is too brief, and the figures are too small to visualize the positions of these orbitals. In particular, the IWSWN-SPE system requires a more detailed analysis of its LUMO and HOMO orbital structures and positions.

Reply: We sincerely appreciate the reviewer's valuable suggestions regarding the analysis and visualization of the HOMO and LUMO orbitals in the IWSWN-SPE system. We have incorporated additional details on the computational methodology and expanded our discussion of the results.

Details of HOMO and LUMO calculations:

The HOMO and LUMO energies were computed using density functional theory (DFT) as implemented in the Gaussian 09 software package. The calculations employed the B3LYP functional and the 6-311G

(d, p) basis set, which has been widely used for electronic structure analysis in polymer electrolytes. Based on the optimized molecular structures, the HOMO and LUMO characteristics were further analyzed using the natural bond orbital (NBO) theory to gain deeper insights into the electronic distributions.

For the IWSWN-SPE system, given that it is a polymer with a repeating unit structure, we conducted the calculations on the representative repeating unit, as shown in Figure R11. This approach is well-established in the literature for studying polymeric materials, as it provides a reasonable approximation of the electronic properties while maintaining computational feasibility [*Nat. Commun.* 13, 4181 (2022); *Nat. Commun.* 14, 482 (2023); *Nat. Commun.* 15, 9150 (2024); *Nat. Commun.* 15, 2500 (2024)].

Expanded discussion of HOMO and LUMO results:

As depicted in Figure R12, the IWSWN-SPE exhibits the lowest HOMO energy level of -8.04 eV, indicating strong oxidative stability. This aligns well with our design strategy, as the SPE is intended to be compatible with high-voltage cathodes. The HOMO orbital distribution primarily resides on the HFBMA-based and TAP-based moieties, suggesting that these segments play a key role in oxidation reactions. The oxidation of these fragments is expected to contribute to the formation of fluorine- and phosphorus-containing cathode electrolyte interphase (CEI), which is consistent with our design rationale.

Furthermore, the IWSWN-SPE demonstrates a relatively high LUMO energy level of -0.45 eV, which represents a significant improvement in reductive stability compared to VEC (-0.83 eV). A comparative analysis of the LUMO values among the three monomeric components indicates that HFBMA has the lowest LUMO energy (-1.80 eV), suggesting its preferential reduction at the Li metal anode. This reduction is expected to lead to the formation of an SEI layer rich in fluorine-containing species, which is a crucial aspect of our design strategy. For IWSWN-SPE, the LUMO orbital distribution, as illustrated in Figure R12, is predominantly localized on the HFBMA-based fragment, further supporting our hypothesis that this segment undergoes preferential reduction to yield an SEI with a high fluorine content.

Based on the reviewer's feedback, we have updated the manuscript to provide a more detailed description of the computational methodology used for HOMO and LUMO calculations, enhance figure clarity, and expand the discussion.

Once again, we sincerely appreciate the reviewer's constructive suggestions, which have helped us refine our analysis and presentation.

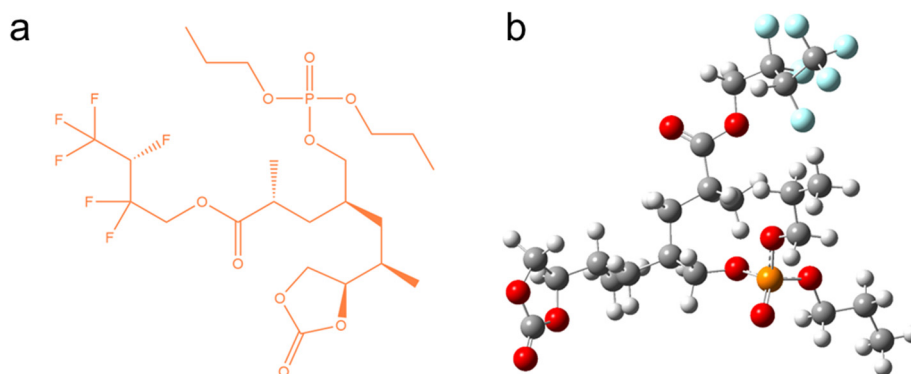


Figure R11. Schematic diagrams of the structure of the IWSWN-SPE unit for HOMO/LUMO calculations. a) Structural formula. b) Ball-and-stick models.

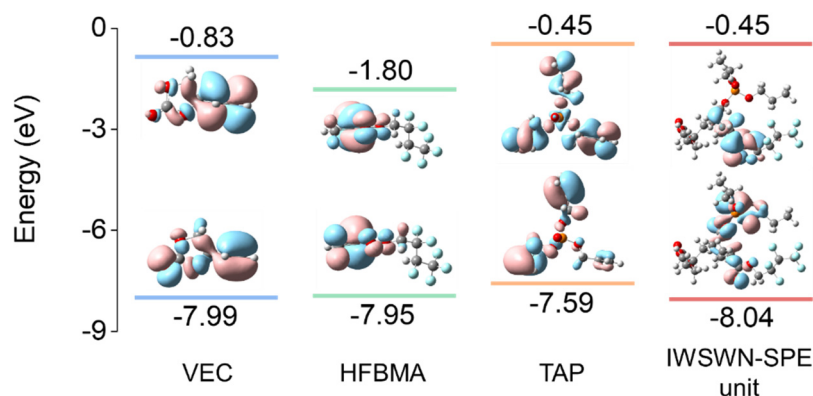


Figure R12. Calculated HOMO/LUMO energy levels of VEC, HFBMA, TAP, and IWSWN-SPE unit.

Q4. The discussion of fig 2f to illustrate the electrochemical stability is not entirely convincing. First, the colouring map could not tell the difference among different polymer segments very well, it is suggested to add values to quantify these differences. Secondly, the ESP map describes charge distribution in a molecule which could indicate the potential interaction sites for ions, however, it does not directly reflect electrochemical stability, the claim of stability against oxidation and reduction requires more concrete evidence. It would be beneficial to discuss the ESP map in conjunction with the HOMO-LUMO orbitals.

Reply: We greatly appreciate the reviewer for your valuable comment. We have taken some steps to improve the clarity and robustness of our analysis.

To enhance the differentiation between three monomers and the IWSWN-SPE unit, we have reprocessed the ESP map with a unified numerical scale and added explicit numerical values to the scale bar, as shown in Figure R13. This modification allows for a more precise comparison of the electrostatic potential distributions within different segments of the IWSWN-SPE system.

For the IWSWN-SPE, the negative electrostatic potential regions (electron-donor sites) are primarily localized on the $\text{O}=\text{C}$ in the VEC-based segment and the $\text{O}=\text{P}$ in the TAP-based segment. These regions

are known to preferentially interact with Li^+ , facilitating Li^+ coordination and transport within the polymer matrix [*Nat. Energy* 5, 526–533 (2020); *Energy Environ. Sci.*, 2024, 17, 8457-8481; *Angew. Chem. Int. Ed.* 2024, 63, e202315608].

Conversely, the positive electrostatic potential regions are mainly concentrated on the $\text{H}_{\text{CF-H}}$ in the HFBMA-based segment. These positively charged H atoms are more likely to interact with TFSI^- , providing potential anion-binding sites. Furthermore, regions with higher positive electrostatic potential are more susceptible to reduction reactions. In the IWSWN-SPE system, the HFBMA-based segment, which exhibits a positive ESP, is expected to undergo preferential reduction at the lithium metal interface, leading to the formation of a fluorine-rich SEI. This is in strong agreement with our computed LUMO results (Figure R12), which indicate that the HFBMA-based fragment is more prone to reduction, further validating our design principles.

We acknowledge the reviewer's concern that ESP maps primarily describe charge distribution and potential ion interaction sites, rather than directly reflecting electrochemical stability. We have revised our discussion to explicitly correlate the ESP map with the HOMO-LUMO analysis. The LUMO distribution is predominantly localized on the HFBMA segment, which also corresponds to the regions with high positive ESP. This alignment reinforces our hypothesis that HFBMA undergoes preferential reduction, leading to SEI formation with high fluorine content.

Based on the reviewer's suggestions, we have revised the ESP map to include a numerical scale for better differentiation, clarified the role of ESP in identifying ion interaction sites, and expanded the discussion to explicitly connect the ESP map with the molecular orbital results.

We sincerely appreciate the reviewer's thoughtful suggestions, which have significantly improved the clarity of our discussion. We have updated the manuscript accordingly.

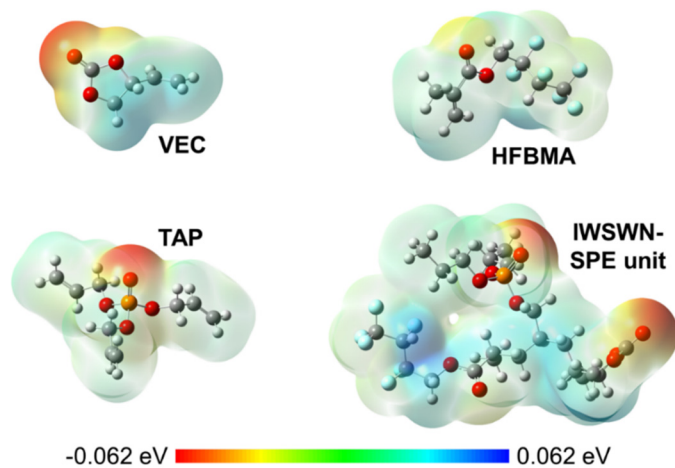


Figure R13. Simulations on electron cloud density distribution of VEC, HFBMA, TAP, and IWSWN-SPE unit.

Q5. The MD simulation procedure used in this work is highly questionable and does not sufficiently address the goal of investigating Li transport mechanisms. The simulations appear to suffer from significant methodological flaws, and also without any validation.

Firstly, starting at such an extremely low temperature (10 K) and rapidly heating to the target temperatures (298.15 K or 253.15 K) in 100 ps suggests that the polymer structures did not undergo proper structural relaxation. At 10 K, the polymer chains are likely frozen, and the rapid temperature increase does not allow for sufficient equilibration or relaxation of the system. This can lead to unrepresentative polymer structures that are not well-equilibrated.

Secondly, 5 ns equilibration: For a polymer system at 298 K, a 5 ns equilibration period is far too short. Polymers, particularly those with complex architectures, require significantly longer timescales to achieve equilibrium due to the slower dynamics of chain relaxation and interaction with ions. Therefore, the structural and dynamic properties observed from such short simulations are unreliable.

Although the authors aim to use MD to provide insight into Li transport, however, this discussion was completely missing in the text. MD here is only used to discuss Li-O and Li-N coordination numbers without delving into critical insights, including Li coordination environment in different polymers, TFSI-polymer coordination structures, Li and TFSI diffusion, transference number, Li diffusion mechanism, and underlying reasons for high Tli. The slow anion diffusion is believed due to the stronger interaction with polymers, which is also speculated without sound evidence through MD. Overall, MD part failed to meet its goal. It should be recalculated with a proper relaxation process (such as equilibration longer enough at high temperatures first), then provide an analysis of ion dynamics to support this experimental work.

Reply: We sincerely thank the reviewer for the insightful comments and constructive feedback regarding the MD simulation procedure. We have carefully addressed each concern raised and made corresponding revisions to our manuscript to clarify and enhance the MD simulation methodology and its results. Below, we provide detailed responses to the reviewer's specific points:

1. Concern regarding the process before equilibration:

The reviewer pointed out that initiating the simulation at an extremely low temperature (10 K) and rapidly heating to the target temperature (298.15 K) in 100 ps might result in frozen polymer structures with inadequate relaxation. We acknowledge this concern and have revised our MD simulation protocol accordingly. To ensure proper structural relaxation and eliminate any artifacts introduced by the initial conditions, we adopted a high-temperature **annealing process** in our updated simulations. Specifically:

The system was first heated to 373.15 K and the temperature was then gradually reduced to the room temperature (298.15 K) over 10 ns. This annealing process allows the polymer chains to overcome the potential energy barriers and ensures that the system achieves a well-relaxed state before further equilibration and sampling.

2. Concern regarding the equilibration time:

The reviewer noted that a 5 ns equilibration period is insufficient for polymer systems, particularly those with complex architectures, due to the slow dynamics of chain relaxation and ion interactions. In response, we significantly extended the equilibration time to ensure the system reaches equilibrium. Specifically:

After the annealing process, the system was equilibrated for **80 ns** at 298.15 K. We monitored key thermodynamic and structural parameters, including cubic box length, system volume, density, and temperature, as a function of simulation time to confirm equilibration. These parameters showed no significant fluctuations after 80 ns, indicating that the system had reached equilibrium (Figure R14). To ensure the robustness of our results, we performed a separate 30 ns production run for data sampling after equilibration. The stability of the system during this production run was further validated by monitoring the same parameters (Figure R15).

3. Details discussions of MD results:

The reviewer commented that our initial manuscript lacked a detailed discussion of the Li-ion transport mechanisms and related insights derived from MD simulations. We recognize the importance of this aspect and have substantially expanded our analysis to address this concern. Key findings from the MD simulations are summarized below:

The molecules at the energy equilibrium state and the snapshots that evolve from MD simulations of PVEC and IWSWN-SPE are shown in Figures R16 and R17. In both systems, Li^+ and TFSI^- are surrounded by the polymer chain and VEC monomer.

(a) Li^+ Coordination Environment and Diffusion:

The radial distribution function (RDF) and coordination number (CN) analyses are performed to investigate the coordination environment of Li^+ in both PVEC and IWSWN-SPE systems (Figures R18 and R19). The specific value of the coordination number is depicted in Figure R20. Li^+ coordination with oxygen atoms of the polymer chain is more pronounced in the IWSWN-SPE system (Li-O: 2.73) than in PVEC (Li-O: 1.49), suggesting that Li^+ is more likely coordinated with the polymer backbone in IWSWN-SPE.

The mean square displacement (MSD) curves of Li^+ are calculated to evaluate their diffusion coefficients (Figure R21). The Li^+ diffusion coefficient in PVEC is found to be slightly higher than in IWSWN-SPE. This can be attributed to the presence of unpolymerized VEC monomers in PVEC, which enhance Li^+ coordination and mobility. RDF analysis further revealed that VEC monomers play a significant role in Li^+ transport in PVEC, as evidenced by the higher CN of Li^+ with O atoms from VEC (2.22 in PVEC system vs. 0.88 in IWSWN-SPE system, Figure R22).

Moreover, from the MD simulation snapshots, we observed distinct coordination environments for Li^+ in the two systems. In the PVEC system, Li^+ primarily coordinates with the C=O groups on the PVEC main chain and the VEC monomer (Figure R23). In contrast, in the IWSWN-SPE system, Li^+ not only coordinates with the C=O groups on the IWSWN-SPE main chain and the VEC monomer but also interacts with the P=O groups on the TAP fragment of the IWSWN-SPE backbone (Figure R24). This introduces a more diverse coordination environment for Li^+ in the IWSWN-SPE system, offering multiple pathways for Li^+ transport.

(b) TFSI^- Coordination Environment and Interaction:

The diffusion coefficients of TFSI^- are also analyzed (Figure R25). In the IWSWN-SPE system, the TFSI^- diffusion coefficient is lower ($2.33 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) compared to PVEC ($5.37 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$). This

reduced mobility is attributed to stronger interactions between TFSI⁻ and the polymer chain in IWSWN-SPE, as confirmed by the following:

Structural snapshots from the simulations (Figures R26 and R27) further confirm this observation. In the PVEC system, the distances between the N atom of TFSI⁻ and the oxygen atoms of the nearest polymer chain are 4.64 Å and 5.22 Å. In contrast, in the IWSWN-SPE system, these distances are reduced to 3.22 Å and 3.57 Å, indicating stronger interactions.

Additionally, binding energy (BE) of TFSI⁻ with PVEC/IWSWN-SPE (Figure 3n) calculations further support this observation. The BE of PVEC-TFSI⁻ is -1.51 eV, which is more positive than the BE of IWSWN-SPE-TFSI⁻ (-2.11 eV), indicating that TFSI⁻ has a higher attractive interaction with the IWSWN-SPE than the PVEC. Moreover, the introduction of TAP and HFBMA fragments makes it easier for the IWSWN-SPE to bind with TFSI⁻ anions (Figure S17).

While the Li⁺ diffusion rate in the IWSWN-SPE system is comparable to that in the PVEC system, the diffusion rate of TFSI⁻ is significantly reduced in IWSWN-SPE due to its strong interactions with the polymer backbone. This reduced TFSI⁻ mobility is a critical factor contributing to the higher t_{Li^+} observed in the IWSWN-SPE system compared to the PVEC system. These analyses provide a comprehensive understanding of the Li⁺ transport mechanisms and the underlying reasons for the observed higher t_{Li^+} in the IWSWN-SPE system.

The reviewer suggested that some of our conclusions regarding Li⁺ and TFSI⁻ interactions were speculative. We have addressed this by incorporating additional quantitative evidence from MD simulations, including 1) RDF and CN analyses for Li⁺ and TFSI⁻ coordination environments. 2) MSD-based diffusion coefficients for Li⁺ and TFSI⁻. 3) Binding energy calculations to quantify the interactions between TFSI⁻ and the polymer matrices. 4) Structural snapshots illustrating specific interaction patterns in both systems. These results provide a solid foundation for the conclusions drawn in our study.

We deeply appreciate the reviewer's comments, which have helped us significantly improve the rigor and clarity of our MD analysis. We have revised the manuscript accordingly and believe the updated results and discussions now provide a more comprehensive and robust understanding of the Li⁺ transport mechanisms in PVEC and IWSWN-SPE systems.

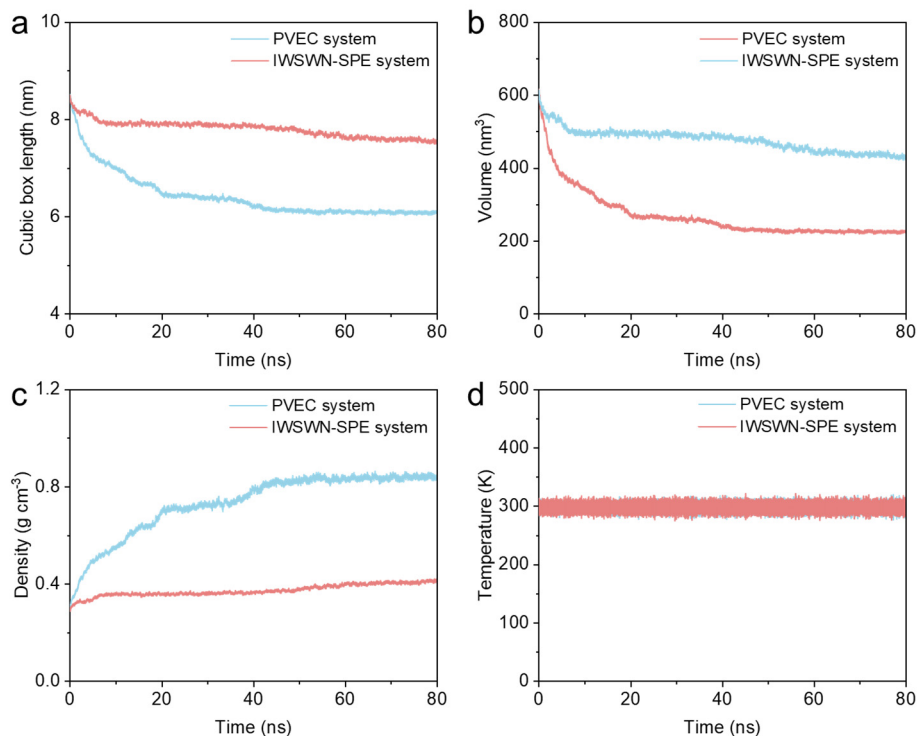


Figure R14. Graph showing the variation of parameters during the 80 ns equilibration process of MD calculations (a, cubic box length; b, volume; c, density; d, temperature).

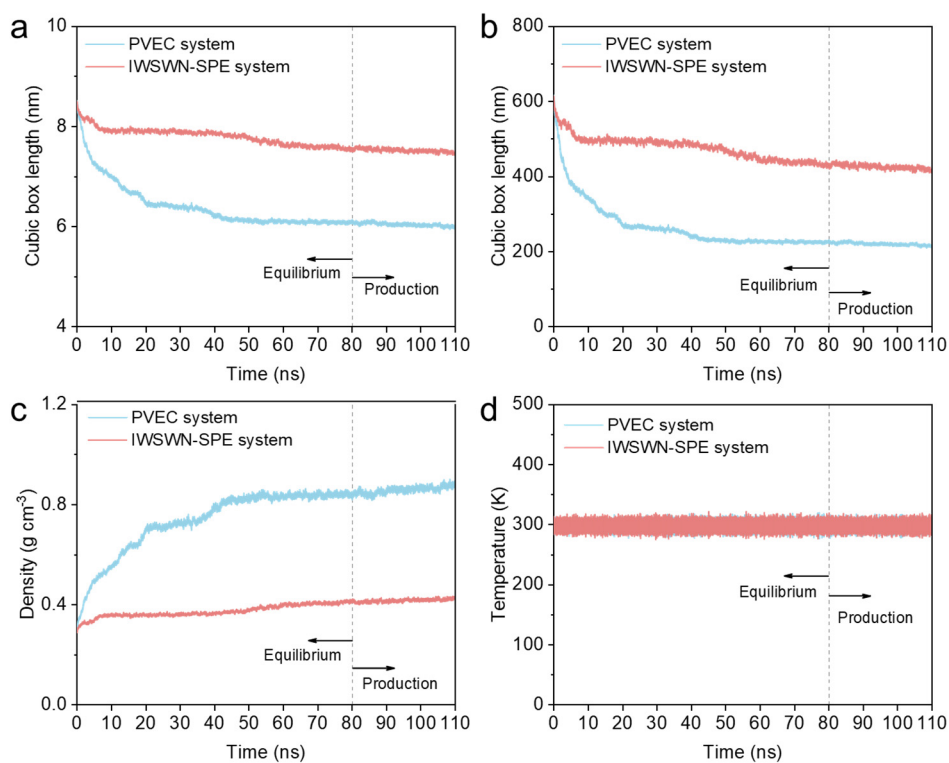


Figure R15. Graph showing the variation of parameters during the 80 ns equilibration process and 30 ns production of MD calculations (a, cubic box length; b, volume; c, density; d, temperature).

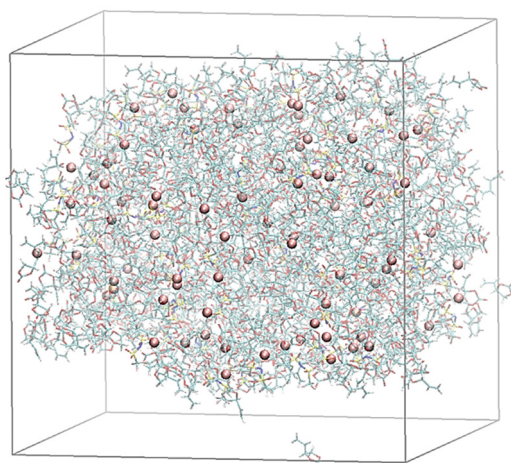


Figure R16. 3D snapshot of the PVEC system after the equilibration process.

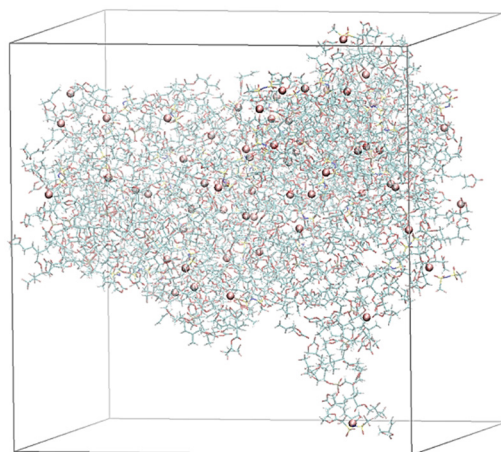


Figure R17. 3D snapshot of the IWSWN-SPE system after the equilibration process.

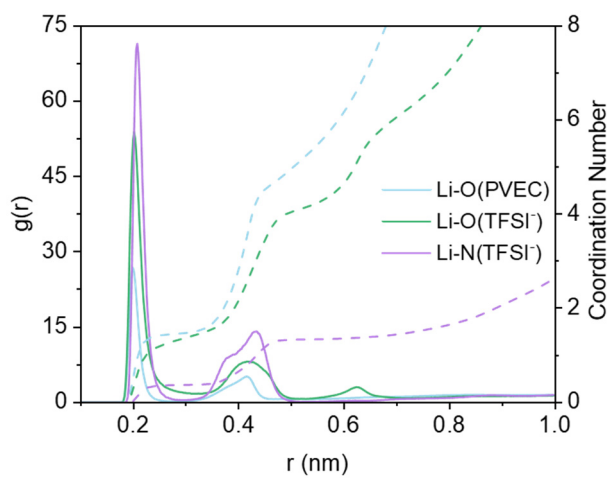


Figure R18. Curves of RDF and CN of the PVEC system.

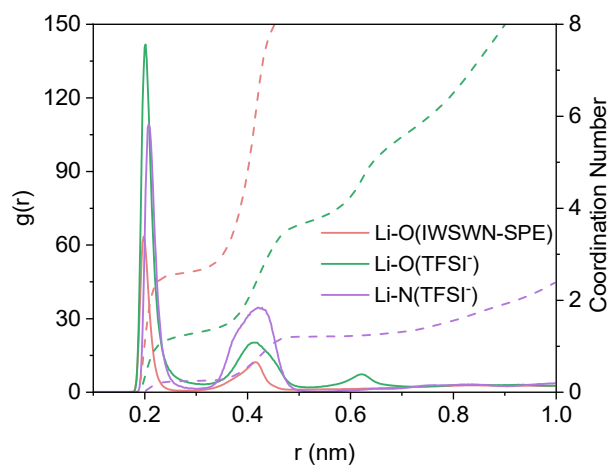


Figure R19. Curves of RDF and CN of the IWSWN-SPE system.

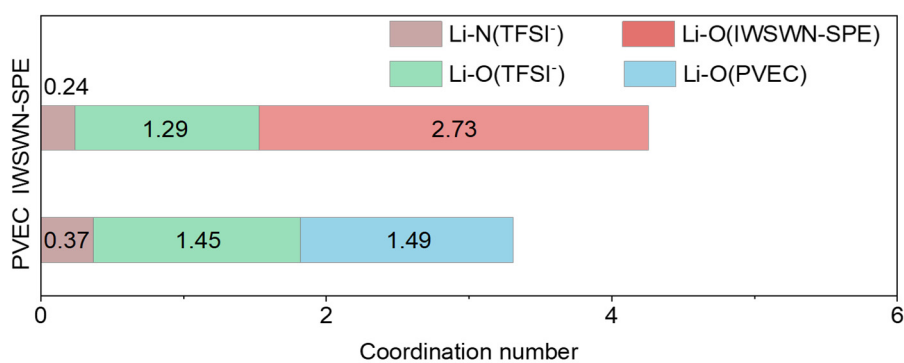


Figure R20. The comparison results of the CN in PVEC and IWSWN-SPE systems.

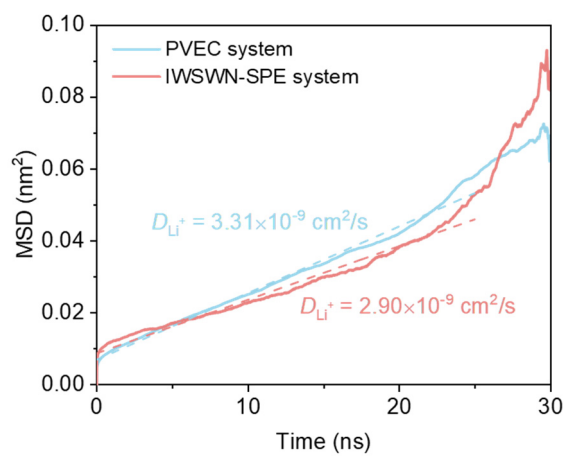


Figure R21. MSD curves of Li^+ in the PVEC and IWSWN-SPE systems.

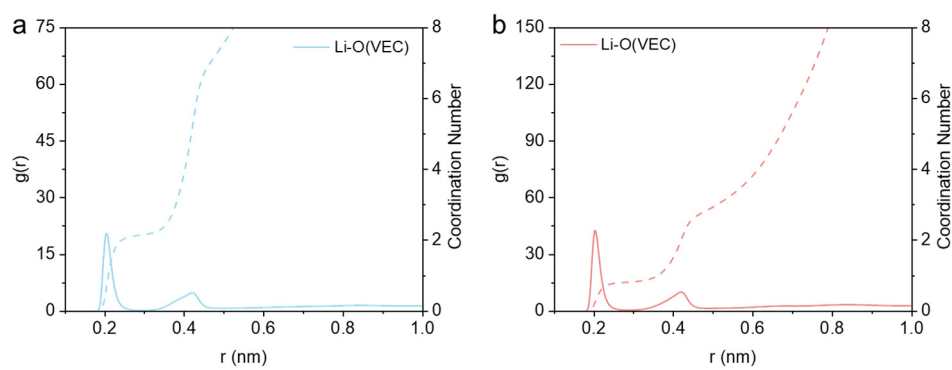


Figure R22. Curves of RDF and CN of Li-O_{VEC} in the PVEC (a) and IWSWN-SPE (b) systems.

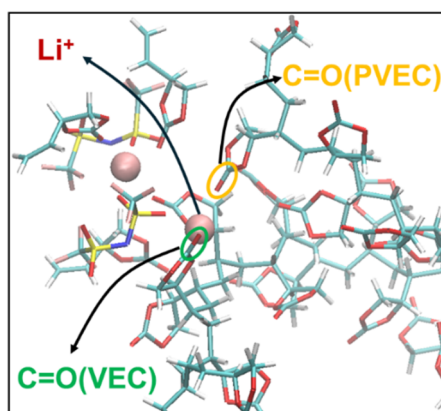


Figure R23. The coordinated environment of Li^+ in the PVEC system.

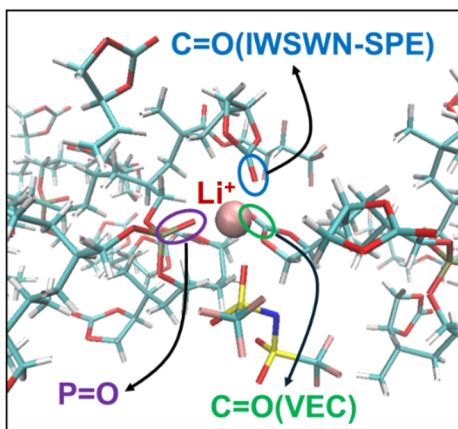


Figure R24. The coordinated environment of Li^+ in the IWSWN-SPE system.

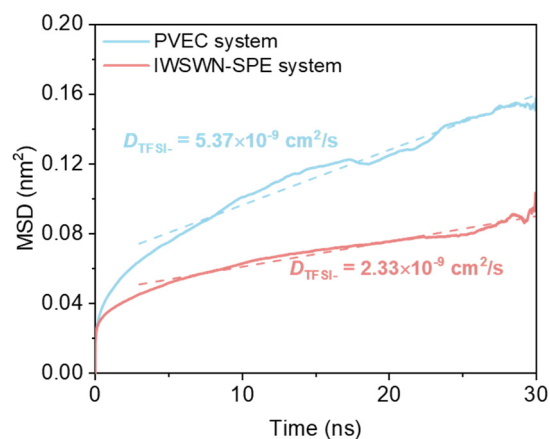


Figure R25. MSD curves of TFSI⁻ in the PVEC and IWSWN-SPE systems.

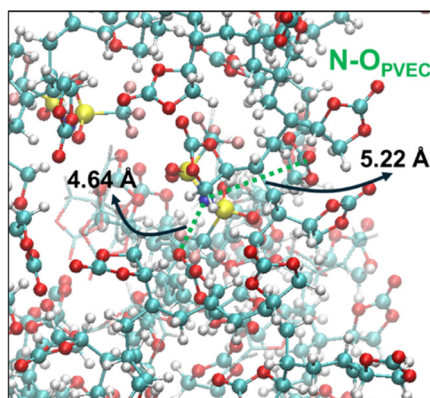


Figure R26. Distance measurement graph between the N atom of TFSI⁻ and the O atoms of the nearest polymer chain in the PVEC system.

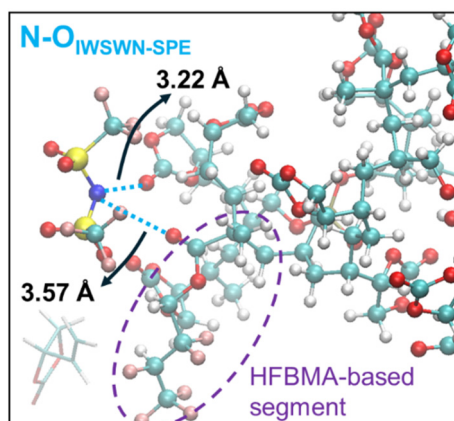


Figure R27. Distance measurement graph between the N atom of TFSI⁻ and the O atoms of the nearest polymer chain in the IWSWN-SPE system.

Response to the comments from Reviewer #3

The authors proposed a “puzzle-like” strategy to design a high-performance SPE with specific functionality at a molecular level. The TAP and HFBMA molecule segments are spliced into the VEC molecule matrix to enhance the attraction towards TFSI⁻ and facilitate the dissociation of LiTFSI. The functionalized SPE achieves a high Li⁺ transference number, a high ionic conductivity, intrinsic high-voltage characteristics, and stable SEI/CEI. Improved electrochemical performances are confirmed in the coin and pouch cells. These results are interesting. However, before the consideration for publication, I still have several concerns.

Reply: We greatly appreciate the reviewer’s comments. We have carefully answered the questions one by one and revised the manuscript according to these valuable suggestions.

Q1. The authors added three monomers for the polymer and realize the three advantages in the synthesized polymer. However, the disadvantages of each monomer still exist in the synthesized polymer, which may damage the electrochemical performances. What is the principle to design 1+1>2 SPE, rather than 1+1<2 SPE?

Reply: We greatly appreciate the reviewer for your valuable comment.

In our research, the design principle of a 1+1>2 SPE is based on the strategic selection and combination of monomers with complementary properties. By carefully considering the interactions and compatibility between the monomers, we aim to mitigate the potential disadvantages that individual monomers may introduce. This approach is intended to synergistically enhance the overall performance of the SPE by leveraging the strengths of each monomer while minimizing or compensating for their respective limitations within the polymer electrolyte.

In designing a 1+1>2 SPE, we meticulously consider the distinct roles and characteristics of each monomer. Following the concept of the barrel effect, we understand that enhancing the weakest link can lead to a substantial overall improvement in performance. VEC was selected as the primary monomer due to its high-voltage compatibility and strong interactions with Li⁺, which facilitate high ionic conductivity. However, its drawbacks—such as flammability and incompatibility with lithium metal anodes—necessitate the introduction of complementary monomers. To enhance lithium metal compatibility, we incorporated HFBMA, a fluorine-rich monomer, while TAP, a phosphorus-containing monomer, was introduced to impart flame retardancy.

Importantly, the disadvantages of individual monomers are effectively mitigated through the strengths of others. For instance, while HFBMA is flammable and TAP exhibits limited compatibility with lithium metal anodes, their combination with VEC results in an optimized SPE with high ionic conductivity, good nonflammability, enhanced voltage stability, and improved lithium metal compatibility. This design strategy ensures that the advantages of each monomer complement one another, leading to a synergistic enhancement that exceeds the sum of its parts.

Q2. Electrochemical stability of Li-Li cells is much better than that in the full cells. Is it caused that the failure of the full cells is attributed to the cathode? Cathode-cathode symmetric cells are suggested to test.

Reply: We greatly appreciate the reviewer for your valuable comment. We have conducted additional analyses to address these points and provide a more comprehensive understanding of the implications.

Li|Li symmetric cells are conventionally employed to evaluate the effective plating and stripping behavior of Li metal anodes [*Nat. Energy*, 5, 561–568 (2020); *Chem. Soc. Rev.*, 2020, 49, 3040–3071]. These cells utilize thick Li foil, whose theoretical capacity far exceeds the plating/stripping areal capacity, ensuring a stable Li reservoir. This setup provides valuable insights into the reversibility and interfacial stability of Li deposition and dissolution during cycling.

In Li|Li symmetric cells, the excess Li source replenishes itself during plating and stripping cycles, enabling prolonged cycling stability. However, despite their ability to sustain extended cycling, the continuous rise in overpotential suggests increasing interfacial impedance over time. This trend reflects the progressive accumulation of detrimental components, which ultimately degrades overall cycling performance.

The cycling process becomes more intricate for Li|NCM cells when matching the ternary NCM cathodes and the Li metal anode. The chemical systems between Li|Li cells and Li|NCM cells are significantly different. Indeed, the interfaces at the cathode and anode sides differ significantly (*Nat. Rev. Chem.* 8, 30–44 (2024); *Nat. Energy*. 9, 1463–1473 (2024)). Since the factors affecting the cycle life of these two systems are different, they usually cannot be directly compared, making it difficult to obtain useful information from such a comparison.

The cycling stability of Li|NCM cells is influenced by many factors, such as the cathode material itself, the cathode/electrolyte interface, the Li metal anode, and the anode/electrolyte interface. For instance, as cycling progresses, impedance increases at both the cathode electrolyte interphase (CEI) and the solid electrolyte interphase (SEI), leading to a corresponding rise in overpotential. This increase in resistance restricts ion transport, ultimately resulting in capacity fade within a constant charge-discharge voltage window. [*Science*, 351,1253292(2016); *Nat. Energy*, 4, 180–186 (2019); *Adv. Energy Mater.* 2022, 12, 2100748]

Moreover, **these factors are often coupled**. For example, in a Li|NCM cell, the crossover effects caused by the dissolution of cathode metal elements can also impact the deposition and stripping behavior of Li metal, leading to differences from the Li deposition and stripping behavior observed in a Li|Li symmetric cell [*ACS. Energy Lett.* 2018, 3, 12, 2921–2930; *Sci. Bull.*, 68 (2023) 813–825]. **Therefore, we cannot simply attribute Li|NCM cell failure to cathode failure**, nor can we directly compare the cycling stability of a Li|NCM full cell with that of a Li|Li symmetric cell.

For our designed IWSWN-SPE, the Li|NCM cell using the PVEC control electrolyte retained only 53.8% of its capacity after 130 cycles, whereas the cell with IWSWN-SPE maintained 73.5% capacity after 300 cycles. This significant improvement highlights the effectiveness of IWSWN-SPE in enhancing the stability of both the Li anode and NCM cathode (Figure R1).

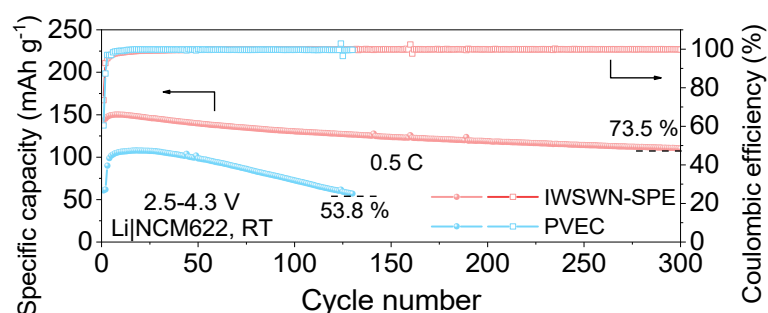


Figure R1. Cycle performances of the Li | PVEC | NCM622 and Li | IWSWN-SPE | NCM622 cells at 0.5 C at RT.

Thank you very much for suggesting the testing of cathode-cathode symmetric cells. However, pristine NCM cathode materials are typically **fully lithiated**. When assembling and testing a cathode-cathode symmetric cell, Li ions undergo deposition and stripping on the surface of one of the cathodes, which is fundamentally different from the insertion and extraction mechanism of Li ions in the bulk phase of NCM materials. Furthermore, the storage mechanisms of Li ions in these two cathodes are completely **different** (one involves insertion and extraction, while the other follows a deposition and stripping mechanism). Therefore, cathode-cathode symmetric cells are typically not used to evaluate the stability of the cathode. Instead, we generally assess the cathode stability through the phase, morphology, and elemental changes of the NCM cathode material, as well as the electrochemical performance of the NCM cathode in a half-cell configuration [*Nat. Energy* 9, 1463–1473 (2024); *Joule* 3, 1662–1676]. These experimental tests have also been conducted in our work (Figure 6).

We sincerely appreciate the reviewer for his/her valuable comments, which significantly help improve the quality of our work.

Q3. The authors compared the performances in Figure 4h. Are they based on the similar test conditions, such as cathode loading, N/P ratio, electrolyte amount (g/Ah)? These parameters can significantly affect the battery performances.

Reply: We greatly appreciate the reviewer for your valuable comment.

Thanks for the question regarding the comparison of performances in Figure 4h and the important influence of test conditions such as cathode loading, N/P ratio, and electrolyte amount on battery performance.

We have compiled the detailed parameters in Table R1 as requested, which demonstrate that the test conditions are largely consistent across the experiments. The cathode loading levels are intentionally kept relatively low to clearly highlight the performance differences of cathodes without interference from other engineering factors (e.g., electrolyte wettability).

Additionally, thick Li metal foils are uniformly used as anodes, with theoretical areal capacities significantly exceeding those of the cathodes, resulting in notably high N/P ratios in all cases (excluding

the effects related to the Li anode). Furthermore, the electrolyte quantities used are not constrained and are intentionally provided in excess, ensuring that electrolyte consumption does not affect the results.

We appreciate your attention to these critical details, and we have supplied them in the manuscript.

Table R1. Comparison details of cycling performance for different solid-state Li metal batteries based on polymer electrolytes.

Reference No.	Charging voltage (V)	Cycle numbers	Cathode loading (mg cm ⁻²)	N/P ratio	electrolyte amount
7	4.3	100	2.5	Compared with the cathodes, the capacity of the used lithium metal anodes is far in excess.	Sufficient electrolyte quantity
23	4.3	200	5		
24	3.7	60	9.4		
27	4.3	200	2		
28	4.3	100	2		
30	4.3	200	2		
31	4.2	400	2		
32	4.3	150	3		
35	4.2	300	1.9		
39	3.8	420	1.6		
40	4.2	300	1.6		
43	4.3	100	2		
45	4.3	150	5		
46	4.4	100	2		
47	4.3	150	1.5		
Our work	4.3	300	3		

Q4. How about the cycling stability of the 349 Wh/kg pouch cell? Why can the designed SPE with these advantages not render good electrochemical performances.

Reply: We greatly appreciate the reviewer for your valuable comment.

The solid-state pouch cell demonstrates a high energy density of 349 Wh kg⁻¹, with its voltage profile shown in Figure R2. After 25 cycles, the capacity retention reaches 80.3% even at room temperature. Although the cycling performance is lower than that of coin cells, achieving an Ah-level solid-state pouch cell with an energy density approaching **350 Wh kg⁻¹** is relatively rare in the literature on solid-state polymer-based electrolytes, particularly **without the introduction of additional liquid electrolytes** (as shown in Table R2).

Furthermore, achieving excellent cycling performance in high-energy-density Ah-level solid-state Li metal pouch cells requires optimization from **both scientific and engineering perspectives**, considering a multitude of factors that make the process significantly more complex than for coin cells. These factors include stacking architecture, assembly processes, electrolyte-electrode interfacial contact, in-situ polymerization conditions, pouch sealing pressure, battery activation techniques, and more (Nat. Commun. 15, 5860 (2024); Electrochem. Energy Rev. 6, 22 (2023)).

Only through a comprehensive investigation of these critical steps and processes can outstanding long-term cycling performance be realized for the Ah-level solid-state Li metal pouch cells. Notably, many of these challenges are primarily engineering-related and require precise process optimization to ensure stability and reliability in practical applications.

Our current research focuses on molecular design to develop high-performance solid-state polymer electrolytes, without specifically optimizing the engineering aspects. This approach allows us to primarily investigate the intrinsic electrochemical properties of the designed SPE while demonstrating its potential for high-energy-density applications. In future studies, we will further explore the feasibility of large-scale applications by optimizing key aspects, including composition refinement of solid-state polymer electrolytes, interface engineering to improve electrode-electrolyte compatibility, optimization of cathode and anode materials, and enhancement of battery assembly processes to ensure scalable fabrication. By systematically addressing these factors, we aim to further improve the electrochemical performance and long-term stability of Ah-level solid-state Li metal pouch cells based on our designed SPE.

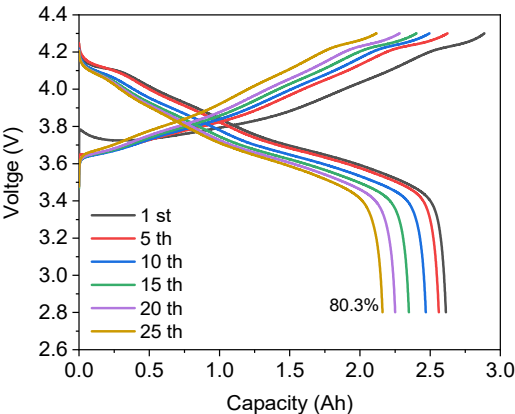


Figure R2. Voltage profiles of the Li|NCM811 pouch cell operated from 2.8 to 4.3 V at room temperature (rate: 0.1 C).

Table R2. Details comparisons of different related SPE-based Li metal pouch cells.

Literature	Cathode loading (mg cm ⁻²)	Capacity (mAh)	Energy density (Wh kg ⁻¹)	Cycle number
Nat. Commun. 14, 482 (2023)	2.5	\	<250	10
Nat. Commun. 14, 6296 (2023)	8	15	<250	20
Nat. Commun. 15, 6781 (2024)	7.15	/	<250	<10
This work	49	2600	349	25

Q5. The safety tests are suggested to conduct for the cycled batteries, rather than just charged battery for once. Besides, there are so many battery parameters, such as LFP, NCM622, NCM811, single-layer pouch cell, few-layer pouch cell, 349 Wh/kg pouch cell. Why are the so many different cells employed for different tests? Please explain the reasons.

Reply: We greatly appreciate the reviewer for your valuable comment.

According to the suggestions, a 1-Ah-based pouch cell was cycled for 10 cycles (Figure R3), followed by a series of safety tests. Even after being cut open, the pouch cell continued to power an LED without any signs of liquid leakage, smoke, sparks, or explosions (Figure R4), demonstrating its inherent stability. To further assess its safety performance, a nail puncture test was conducted. As depicted in Figure R5, the pouch cell successfully passed the nail puncture test, exhibiting no signs of smog, fire, or combustion. After penetration, the surface temperature increased by only 3.8°C, without the occurrence of thermal runaway. These results strongly indicate that the batteries assembled with our IWSWN-SPE exhibit exceptional safety, making them promising candidates for reliable and secure energy storage applications.

Thank you for your inquiry regarding the utilization of various cathodes in our testing procedures. We appreciate the opportunity to elucidate the rationale behind employing different cathodes for our experiments.

LFP-based batteries: LFP batteries are utilized for high-temperature safety testing to evaluate the thermal stability of cells assembled with our IWSWN-SPE electrolyte. Commercially, LFP-based batteries are well known for their superior safety characteristics. However, under 100°C conditions, conventional LFP batteries with commercial carbonate electrolytes typically experience gas generation, leading to cell swelling and the inability to charge and discharge normally. In contrast, LFP cells assembled with our IWSWN-SPE demonstrated stable cycling performance even at 100°C, highlighting the enhanced thermal stability and superior safety characteristics of our designed solid-state polymer electrolyte.

NCM622 coin cells: NCM622 coin cells serve as the primary platform for evaluating the performance of our batteries. As a high-voltage, high-capacity ternary cathode material, NCM622 is widely recognized in Li-based battery research. Its well-established electrochemical properties make it an ideal choice for conducting comprehensive cross-comparisons and benchmarking analyses, ensuring a thorough assessment of our solid-state polymer electrolyte's performance.

Single-layer pouch cell: Single-layer pouch cells, comprising a single layer of NCM622 cathode and Li metal anode, are employed for evaluating thermal safety under controlled heating conditions. The single-layer configuration ensures consistent thermal behavior, allowing for accurate temperature change assessment while minimizing variations in internal heat dissipation. Additionally, from a safety standpoint, utilizing a single-layer design mitigates the risk of thermal runaway, which is more likely to occur in multi-layer configurations during heating experiments. This approach provides a reliable and controlled strategy for evaluating the thermal stability of the solid-state polymer electrolyte in high-temperature conditions.

NCM811-based 1-Ah pouch cell: NCM811-based 1-Ah pouch cells are designated for puncture testing to rigorously evaluate the safety performance of our IWSWN-SPE-assembled batteries. Achieving a higher capacity (~1 Ah) is crucial for enhancing the effectiveness of puncture tests, as it provides more

substantial and reliable results compared to smaller-capacity cells. Given its high theoretical capacity and inherently higher safety risks, NCM811 serves as an ideal cathode material for validating the robustness of our solid-state polymer electrolyte under extreme mechanical abuse conditions.

NCM811-based 349 Wh kg⁻¹ pouch cell: Assembled with NCM811 to achieve higher energy density, the 349 Wh kg⁻¹ pouch cell tests the electrolyte's capability to realize high energy density targets, a critical aspect for future commercial viability. NCM811's higher theoretical specific capacity makes it particularly well-suited for achieving the goal of high-energy-density pouch cells, further emphasizing its potential for advancing energy storage technologies.

More importantly, the diverse selection of cathode materials for assembly underscores the broad adaptability of our designed IWSWN-SPE, demonstrating its versatile applicability and potential for widespread utility.

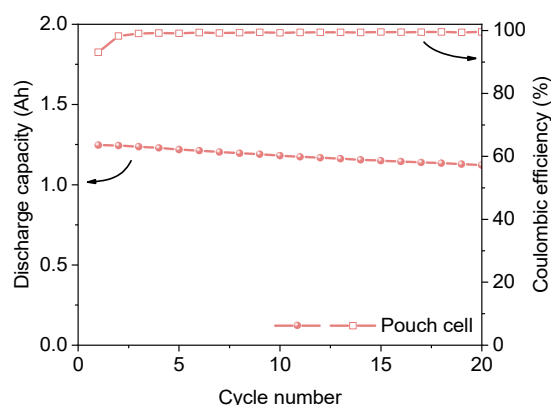


Figure R3. Cycling performance of the 1-Ah Li|NCM811 pouch cell.

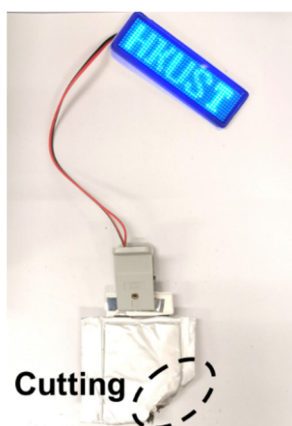


Figure R4. Digital images of LED lighting tests for the cycled Li|NCM811 pouch cell after cutting.

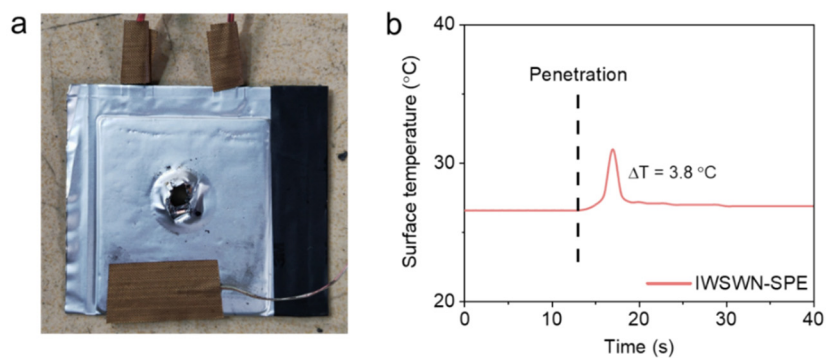


Figure R5. The nail penetration (SOC: 100%) (a) and the corresponding surface temperature variations (b) of cycled 1-Ah Li|NCM811 pouch cell.

Response to the comments from Reviewer #4

The introduced polymer electrolyte demonstrates a wide electrochemical stability window, nonflammability, and benefits for the electrodes, resulting in lithium metal batteries (LMBs) based on this solid electrolyte exhibiting excellent cycling stability and high energy density. However, several critical aspects of this article require further clarification. Given that some studies have employed phosphate fluorides (e.g., TAEP, TFPA) directly and achieved similar performance to your findings, I am concerned with the structural advantages of your approach.

Reply: We greatly appreciate the reviewer's comments. We aim to provide further clarification on the distinctiveness of our methodology and its inherent benefits.

In highlighting the structural advantages of our approach, we emphasize the modification of polymer chains in a manner akin to assembling building puzzles, resulting in a solid polymer electrolyte (SPE) intrinsically endowed with nonflammability, high voltage tolerance, and compatibility with Li metal anode. Unlike other studies that directly use phosphorus and fluorine-containing organic liquids or incorporate phosphorus and fluorine-containing organic liquids into SPE, where these liquids interact with Li salts to achieve similar outcomes, our approach focuses on directly modifying the polymer chains themselves. While the additional organic liquids in other studies serve functional roles, they do not directly modify the polymer structure directly. This fundamental distinction underscores the uniqueness of our design methodology, which targets the intrinsic properties of the polymer chains themselves.

Furthermore, incorporating additional liquids poses risks such as leakage in practical applications, **which is one of the reasons we have opted not to include extra liquid components in our approach.** By modifying the polymer chains directly, we aim to mitigate potential risks associated with liquid additives, ensuring the stability and reliability of the SPE in commercial applications.

In summary, our approach emphasizes the structural modification of polymer chains to achieve desired properties, distinguishing it from studies that incorporate phosphate fluorides directly. By focusing on enhancing the polymer structure itself, we aim to maximize the inherent advantages of our polymer electrolyte design for advanced Li metal batteries.

Q1. Choice of Crosslinker and Fluorine Source: Please clarify why TAP was selected as the crosslinker and HFBMA for introducing fluorine into the solid electrolyte, especially since other compounds such as HFMA, HFBA, and PFBA have been utilized in previous studies.

Reply: We thank the reviewer for the comment. Thanks for your inquiry concerning the selection of TAP as the crosslinker and HFBMA for introducing fluorine into the solid electrolyte. We aim to provide a detailed clarification on the rationale behind our compound selection.

1. Selection of TAP:

TAP, with its unique three-dimensional molecular structure, is selected as a phosphorus-containing monomer to impart flame-retardant properties to the solid polymer electrolyte (SPE), forming the foundation of our design for a non-flammable SPE. Featuring three carbon-carbon double bonds, TAP acts as a versatile crosslinker, facilitating the formation of a uniform, interconnected network structure

within the solid-state polymer electrolyte matrix. This network enhances the mechanical integrity and stability of the SPE, while also contributing to its flame resistance and overall performance.

2. Comparison with other fluorine-containing monomers: The structures of various fluorine-containing monomers are depicted in Figure R1.

1) HFMA is essentially the same compound, differing only in nomenclature.

2) In contrast to HFBA, HFBMA features a methyl group at the α position instead of hydrogen. This methyl substitution helps stabilize the radical intermediates formed during polymerization, potentially enhancing the stability of the process and facilitating polymerization with other monomers. Therefore, HFBMA is chosen over HFBA.

3) PFBA contains a $-\text{CF}_2\text{CF}_3$ fluorine moiety. In contrast, HFBMA includes $-\text{CF}-$, $-\text{CF}_2-$, and $-\text{CF}_3$ groups, offering a higher and more diverse range of fluorine sources. This abundance and diversity in fluorine types potentially enhance the formation of varied fluorine-containing species at the interface, which could improve interface stability [*Chem. Rev.* 2024, 124, 6, 3494–3589; *Joule* 3, 2647–2661; *Nat. Commun.* 15, 9356 (2024)].

By selecting HFBMA to introduce fluorine into the SPE, we aimed to leverage its structural advantages—such as the diverse fluorine groups—to enhance stability and performance in the polymer electrolyte design.

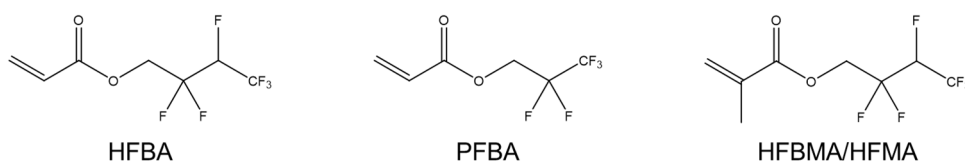


Figure R1. Molecular structure of different fluorine-containing monomers.

Q2. Necessity of Phosphorus Monomers: While polymer monomers containing fluorine can also exhibit flame-retardant properties, is the introduction of phosphorus monomers truly necessary? Please provide justification.

Reply: We thank the reviewer for the comment. Thank you for your inquiry regarding the necessity of incorporating phosphorus monomers alongside fluorine-containing monomers in achieving flame-retardant properties. We appreciate the opportunity to justify the inclusion of phosphorus monomers in our polymer electrolyte design.

1. Flame retardancy of halogen elements:

While halogen elements are known for their flame-retardant properties, **the practical application of fluorine-based flame retardants is limited due to the exceptionally strong C-F bonds**, which are ineffective in capturing free radicals for flame inhibition. Moreover, a higher proportion of fluorine content is required to achieve significant flame-retardant effects, making it challenging to rely solely on

a small ratio of fluorine-containing monomers for flame retardancy. (*Fire Safety Journal* 41 (2006) 46–56; *Energy Environ. Mater.* 2023, 6, e12297)

2. Role of phosphorus monomers:

Phosphorus monomers, such as TAP, play a crucial role in enhancing flame retardancy due to their ability to effectively inhibit combustion processes and promote char formation, creating a protective layer that hinders further propagation of flames. **In contrast, fluorine-containing monomers like HFBMA, HFBA, or PFBA used in previous studies are inherently flammable and are classified with GHS02 hazardous codes (flammable).** These classifications highlight their potential fire hazards and underscore the limitation of relying solely on fluorine-containing monomers for flame retardancy.

3. Experimental validation:

Through combustion experiments, as depicted in Figure R2, we conducted tests on a polymer modified solely with HFBMA, without the inclusion of TAP. The results revealed the flammable nature of the polymer without phosphorus monomer incorporation, validating the necessity of phosphorus monomers for achieving flame retardancy.

By incorporating phosphorus monomers alongside fluorine-containing monomers in our solid-state polymer electrolyte design, we aim to synergistically harness the flame-retardant properties of both elements, achieving enhanced safety and stability in Li metal batteries.

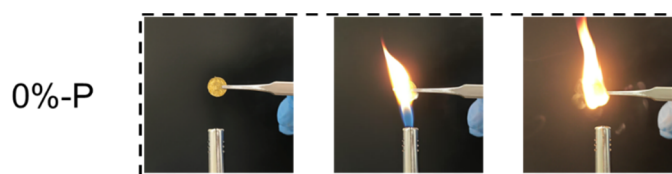


Figure R2. Burning test of the polymer without TAP modification.

Q3. Selection of VEC for Polymer Backbone: What motivated the choice of VEC for forming the polymer backbone? Similar studies have used HFBMA to enhance voltage stability in PDOL polymer electrolytes, achieving an electrochemical stability window of 5.1 V.

Reply: We greatly appreciate the reviewer for your valuable comment. Thank you for your inquiry regarding the rationale behind selecting VEC for forming the polymer backbone in our study.

The inherent oxidation voltage of PDOL (polyether) is insufficient to exceed 5.0 V, making it challenging to pair with high-voltage NCM cathodes for long-term cycling applications (*Nat. Energy* 4, 365–373 (2019)). While various strategies—such as additives, lithium salt modifications, or composite fillers—can enhance the overall electrolyte’s oxidation resistance through synergistic effects, they do not fundamentally improve the intrinsic oxidation stability of PDOL itself. There is still a risk of electrolyte breakdown. This limitation highlights the need for alternative polymer electrolyte designs with inherently higher oxidative stability to enable compatibility with high-voltage cathodes (*Adv. Mater.* 2020, 32, 1905629; *Adv. Energy Mater.* 2022, 12, 2201762; *Chem. Mater.* 2019, 31, 8466–8472).

PDOL is usually synthesized through ring-opening polymerization [*Nat. Energy* 4, 365–373 (2019)]. Incorporating fluorine-containing compounds in PDOL can improve the oxidation resistance of

composite electrolytes to a certain extent. However, this approach does not fundamentally alter the low intrinsic antioxidant properties of PDOL itself. Furthermore, the resulting linear polymer chains lack the necessary crosslinked structure, leading to insufficient mechanical strength, which is crucial for maintaining the structural integrity of the electrolyte in solid-state batteries (*Adv. Energy Mater.* 2024, 14, 2402671; *Nat. Commun.* 14, 2301 (2023)].

Furthermore, literature (*Angew. Chem. Int. Ed.* 2023, 62, e202309613) suggests that free radical polymerization methods are more suitable for solid-state battery research, prompting us to pursue a modification approach using VEC-based double bond free radical polymerization to develop a flame-retardant, high-voltage-tolerant, and lithium metal-compatible polymer electrolyte.

VEC, as a starting point for double bond free radical polymerization, enables the development of an SPE with enhanced properties. Unlike PDOL, which predominantly consists of polyether with poor oxidation resistance, VEC-based PVEC offers superior high-voltage stability due to its polycarbonate backbone. This structural advantage enhances PVEC's electrochemical stability, making it more suitable for applications requiring high-voltage tolerance. Relevant literature supports the benefits of PVEC in improving the oxidative stability of solid-state polymer electrolytes (*Nat. Commun.* 14, 2301 (2023); *Nano Energy* 96 (2022) 107105).

In summary, the unique properties and synthesis approach of SPE derived from VEC monomers align with our research objectives of developing a flame-retardant, high-voltage-tolerant solid-state polymer electrolyte that is compatible with Li metal electrodes. This design strategy leverages the intrinsic stability of the polycarbonate backbone, ensuring enhanced electrochemical performance, safety, and long-term cycling stability in advanced solid-state Li metal batteries.

Q4. Characterization of “Puzzle-like” Structure: Please explain how the polymer can be assembled in a “puzzle-like” form. Can you provide tests or characterization methods to validate this structure?

Reply: We thank the reviewer for your valuable comment. We appreciate the opportunity to elaborate on this aspect of our research methodology.

“Puzzle-like” assembly analogy:

Regarding the concept of "puzzle-like" assembly, we use the analogy of assembling puzzles by interlocking puzzle pieces to illustrate how we design and synthesize the solid-state polymer electrolyte at the molecular level. Just as one can use various colored puzzles of similar shapes in daily life, these puzzles can be arranged randomly or arranged according to preference by the interlocking of the puzzle pieces.

Similarly, we employ this analogy to showcase how we utilize three monomers in free radical polymerization to synthesize the solid-state polymer electrolyte. The monomers can polymerize with themselves or with different monomers. However, by uniformly mixing different monomers at the molecular level in the precursor solution, we can form a homogeneous SPE through free radical polymerization like assembling a puzzle, as illustrated in Figure R3 (Here, we use the interlocking between the puzzle pieces in a "puzzle" as a metaphor for how different polymer monomers interact and

connect with each other through free radical polymerization). From a macroscopic perspective, the distribution of the three colored puzzles, representing the three monomers, appears uniform throughout the entire structure. However, upon closer examination, their arrangement is random, encompassing various possible combinations, as indicated by the dashed circles.

Characterization and validation methods:

Our "puzzle-like" molecular assembly analogy shows the random yet uniform nature of the synthesized polymer electrolyte by "interlocking" monomer molecules.

Based on the characterization results from FTIR, there is no apparent presence of C=C double bonds in the synthesized IWSWN-SPE (powder obtained after grinding and vacuum drying, Figure R4). Additionally, according to the GPC test results (which will be explained in detail in the next question, Figure R6 and Table R1), long-chain polymers have been successfully synthesized. These findings collectively indicate the formation of long-chain polymers from monomer polymerization.

To validate the uniform distribution and assembly of the polymer, we conducted SEM and EDS mapping tests on three sets of target polymers synthesized in parallel (Figure R5). The results reveal the even distribution of oxygen (O), fluorine (F), and phosphorus (P) elements, indicating the homogeneous dispersion of different monomer segments, aligning with our intended design objectives.

We sincerely appreciate the reviewer for his/her valuable comments, which significantly help improve the quality of our work. We hope that this explanation clarifies how the "puzzle-like" assembly analogy relates to the synthesis of the SPE and the methods used to validate the structure.

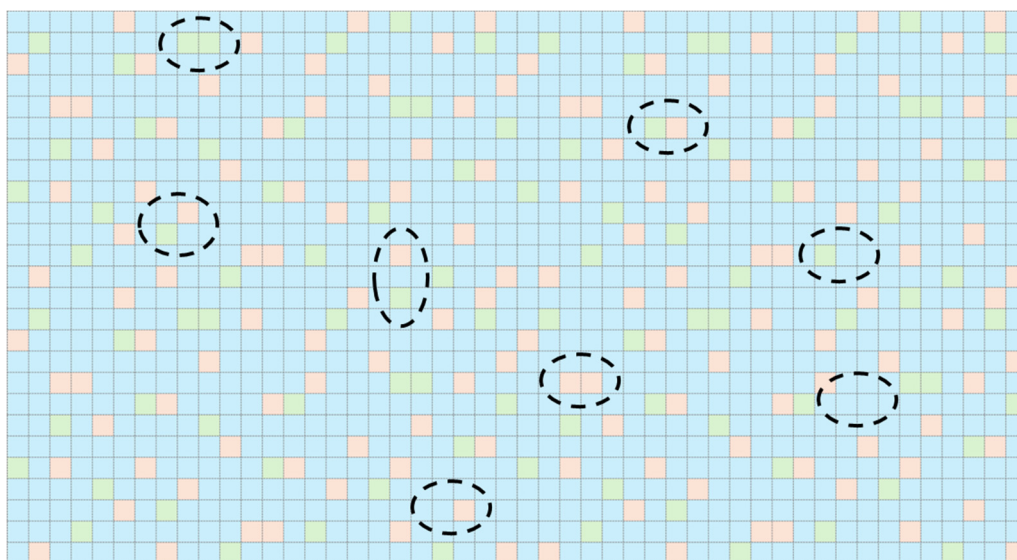


Figure R3. Schematic diagram of the product via "puzzle-like" assembly method (blue: VEC; orange: TAP; green: HFBMA).

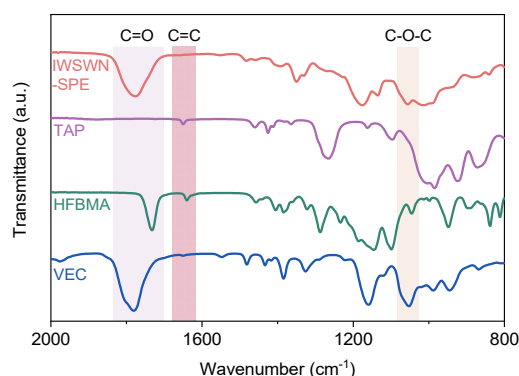


Figure R4. FTIR spectra of the VEC, HFBMA, TAP, and IWSWN-SPE.

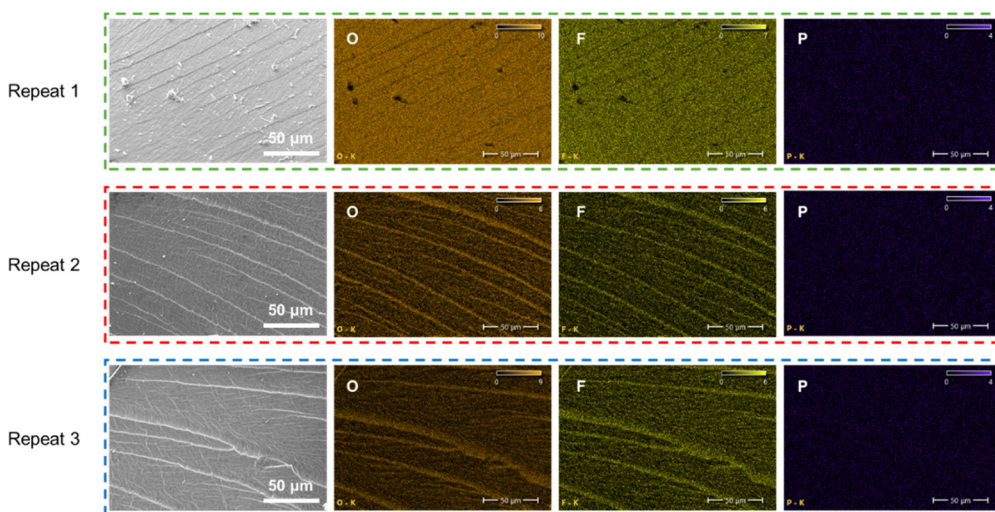


Figure R5. SEM and corresponding mapping results of three repeated experiments

Q5. GPC Testing for Residual Small Molecules: Since your polymerization method involves normal free radical polymerization and in-situ polymerization, GPC tests may be necessary to determine whether residual small molecules could act as mobile components promoting ion conduction.

Reply: We appreciate your suggestion regarding the utilization of Gel Permeation Chromatography (GPC) testing in our polymerization process.

GPC is commonly used to determine the molecular weight and molecular weight distribution of polymer materials, as it is an analytical technique designed for high molecular weight polymers. Since low molecular weight compounds typically do not possess sufficient molecular weight to yield significant signals in gel permeation chromatography, GPC is generally not suitable for the analysis of small molecules [Constr. Build. Mater. 278 (2021) 122386].

We conducted GPC testing on PVEC using DMSO as the eluent, with the results depicted in Figure R6 and Table R1. The molecular weight distribution of the synthesized PVEC ranges between 2000 and 800000 and the number average molecular weight (M_n) was determined to be 55097 g mol⁻¹. However, GPC testing was found to be unsuitable for our synthesized IWSWN-SPE due to the incorporation of TAP as a crosslinker. The presence of a crosslinking agent in the polymerization process rendered the

resulting polymer insoluble in organic solvents. Even after an extended **3-month** dissolution attempt in DMSO, the polymer remained undissolved, thereby precluding the application of GPC testing for molecular weight determination.

To address concerns regarding residual small molecules of IWSWN-SPE, we employed TGA testing, as illustrated in Figure R7. The results reveal that the residual VEC content is 54% in the PVEC control sample, whereas it is significantly reduced to 23% in the IWSWN-SPE.

Detailed discussions and explanations regarding this observation have been incorporated into the revised manuscript, elucidating the implications of residual small molecules on the polymer electrolyte properties.

We are grateful for the reviewer's valuable suggestion, which has enhanced the credibility and thoroughness of our research findings.

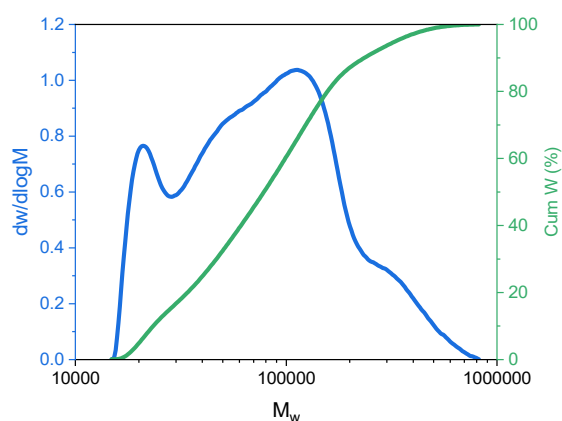


Figure R6. GPC result of the PVEC.

Table R1. Statistical average results of GPC test.

M_p	M_n	M_w	M_z	M_v	PD
113834	55097	109042	205170	98206	1.97909

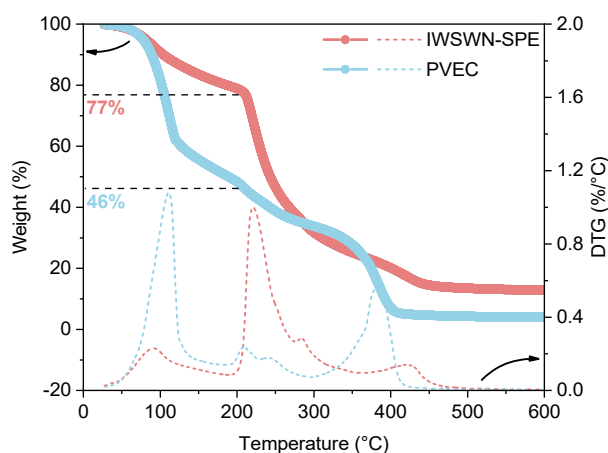


Figure R7. TGA curves of PVEC and IWSWN-SPE.

Q6. Accuracy of AFM Results: AFM results are generally more accurate when thin polymer films are applied to a hard substrate, given the relatively low modulus of polymers. The in-situ polymerized polymer on the separator is typically thicker and may possess lower mechanical strength than the AFM probe, which raises concerns about the accuracy of the AFM results. This should be further confirmed.

Reply: We appreciate your valuable comments and would like to provide further clarification on this matter.

In our study, we acknowledge the challenge posed by the relatively low modulus of polymers in AFM characterization. To ensure the accuracy of our AFM results, we took specific measures by in-situ polymerizing the polymer on a stainless steel substrate. Upon completion of the reaction, the polymer adhered tightly to the surface of the stainless steel sheet, as illustrated in Figure R8. This method of sample preparation aligns with the suggested approach of applying thin polymer films to hard substrates for enhanced accuracy in AFM characterizations.

We are grateful for your insightful question and recommendation. We will incorporate a detailed explanation of this sample preparation process in the manuscript to address the concerns regarding the accuracy of AFM results.

Thank you once again for your valuable input, which will contribute to the robustness and clarity of our research findings.

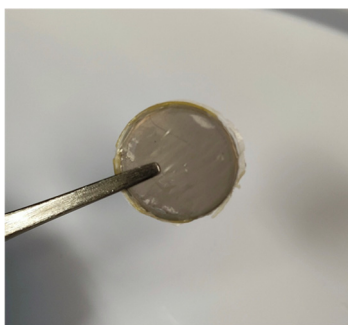


Figure R8. Digital photo of the prepared IWSWN-SPE membrane for AFM testing.

Q7. Weight Loss Platform Temperature: Why is the end temperature of the weight loss platform for IWSWN-SPE significantly lower than that for PVEC? Is this advantageous for the performance of the solid electrolytes?

Reply: Thank you for your inquiry regarding the discrepancies in weight loss platform temperatures between IWSWN-SPE and PVEC observed during TGA testing. We appreciate the opportunity to provide further clarification based on our updated TGA results.

TGA serves as a crucial tool for determining the decomposition temperature of polymers, assessing thermal stability, and evaluating liquid content. The updated TGA results, as depicted in Figure R9, shed light on the thermal behavior of the polymers under investigation. The weight loss around 100 °C is attributed to the volatilization of residual VEC monomers encapsulated within the polymer. Subsequent weight loss between 200-300 °C signifies polymer decomposition, while decomposition around 400 °C indicates the breakdown of the polymer-LiTFSI complex (*Angew. Chem. Int. Ed.* 2023, 62, e202309613).

We observe that during the decomposition temperatures, the peaks in the DTG curve of IWSWN-SPE consistently lag behind those of PVEC, indicating that the decomposition temperatures of IWSWN-SPE are higher than those of PVEC. This demonstrates that IWSWN-SPE exhibits higher thermal stability than PVEC.

The differences in weight loss platform temperatures compared with previous results can be attributed to sample preparation methods. Previous testing involved grinding the samples into powder and handling them within a glovebox environment, leading to significant volatilization of residual VEC monomers, particularly impacting the PVEC samples. Despite the seemingly higher weight loss end temperature for PVEC, primarily due to the excessive volatilization of VEC, the thermal decomposition temperatures of the polymers still reflect the superior thermal stability of IWSWN-SPE.

We sincerely appreciate the valuable insights provided by the reviewer. We are grateful for the reviewer's feedback, which contributes to the refinement and accuracy of our research findings.

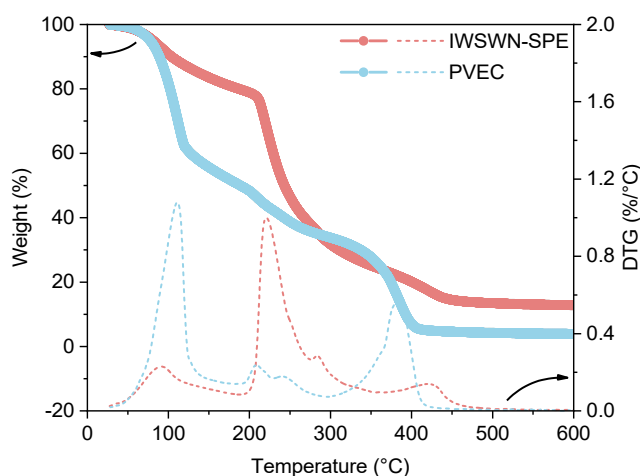


Figure R9. TGA curves of PVEC and IWSWN-SPE.

Q8. Initial Capacity Discrepancy: In Figure 4g, why does the initial capacity of the PVEC full cell appear much lower than that of the IWSWN-SPE full cell, while their initial capacities in Figure 4d do not show such a difference?

Reply: Thanks for your question regarding the disparities in the initial capacities of the PVEC and IWSWN-SPE full cells as depicted in Figure 4g and Figure 4d, respectively. We appreciate the opportunity to provide further clarification for this discrepancy.

Analysis of Figure 4d reveals that at a small rate (**0.1 C**), the capacity of the two cell systems is not much different, but at a **0.5 C** rate, the discharge capacity of the Li | PVEC | NCM622 cell is 69.5% of that of the IWSWN-SPE's cell. Moreover, at a **1 C** rate, the Li | PVEC | NCM622 cell exhibits a discharge capacity of only 44.5% compared to the IWSWN-SPE's cell, indicating a significant performance gap in rate capability between the two cell systems.

The cycling shown in Figure 4g is initiated directly at a **0.5 C** rate without prior low-rate (**0.1 C**) activation, underscoring the poor rate performance of the Li | PVEC | NCM622 cell. The notable

disparity in initial capacities further underscores the inferior rate capability of the PVEC's cell compared to the IWSWN-SPE's cell.

It is essential to note that the rate performance tests depicted in Figure 4d commenced from a low 0.1 C rate, allowing for the effective utilization of the cathode's capacity. The comparison between these two sets of data reinforces the significant enhancement in rate performance achieved by the batteries assembled with our IWSWN-SPE.

We sincerely appreciate the reviewer's valuable insights, and we have incorporated a detailed discussion of these findings in the revised manuscript.

Q9. Typographical Error: The term "specific" in Figure S10 is misspelled and should be corrected.

Reply: Thank you for bringing to our attention the typographical error in Figure S10, where the term "specific" is misspelled.

We appreciate your keen observation, and we have promptly corrected this error in the revised version of the manuscript to ensure accuracy and clarity (Figure R10).

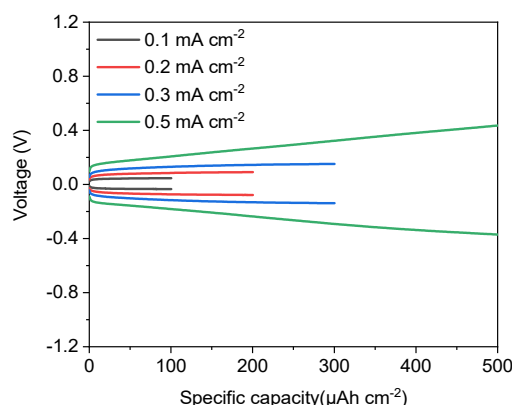


Figure R10. The charge/discharge voltage profiles of Li | IWSWN-SPE | Li cell at different current densities.

Q10. Need for Pre-Polymerization: Please clarify why the in-situ polymer electrolyte requires pre-polymerization.

Reply: Thank you for raising the query regarding the necessity of pre-polymerization in the in-situ polymer electrolyte synthesis process.

Pre-polymerization is essential for several reasons:

Firstly, the use of AIBN as an initiator in the reaction generates nitrogen gas. Conducting this reaction after the battery assembly may lead to the formation of gas pockets within the polymer or at the polymer-electrodes interface. Such gas pockets could compromise the Li^+ conduction of the SPE or disrupt the contact between the SPE and the electrodes, particularly pronounced in high-capacity batteries.

Secondly, pre-polymerization enhances homogeneity. The stirring involved in the pre-polymerization process promotes a more uniform reaction. This process can result in the formation of pre-polymers or intermediate products that enhance the distribution of polymer chains and functional groups within the SPE, ensuring a more homogeneous final product.

Moreover, the diffusion of radicals in solution is constrained by the movement range of monomer molecules, leading to a cage effect. Pre-polymerization allows for control over reaction temperature, time, and stirring speed, mitigating the impact of the cage effect. This control enables radicals to diffuse over a larger area, reducing the confinement effect and enhancing the efficiency of the reaction [*J. Appl. Polym.*, 12, 1863–1867 (2009)].

Thanks for your valuable feedback, which contributes to the refinement of our research explanation.

Q11. Attribution of Increased LiF Content: How can you confirm that the increased LiF content in the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) is due to the decomposition of your polymer electrolyte?

Reply: Thank you for raising the question regarding the source of the increased LiF content in the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI). We greatly appreciate the reviewer for your valuable comment.

In our designed IWSWN-SPE, the fluorine content originates from both the polymer chains and the LiTFSI salt. Therefore, the primary sources of LiF in the SEI and CEI are these two components. In contrast, for PVEC, the fluorine source is solely the LiTFSI salt. Our emphasis lies in the molecular design of our polymer, which diversifies the fluorine sources, potentially leading to increased LiF generation, as supported by some references (*Nat. Commun.* 14, 2301 (2023); *Nat. Rev. Mater.* 9, 119–133 (2024)).

Furthermore, we underscore that our tailored molecular design in the IWSWN-SPE facilitates easier dissociation of the lithium salt, resulting in a higher abundance of free TFSI⁻ anions. This increased availability of TFSI⁻ anions enhances the potential of generating more LiF at both the SEI and CEI.

Therefore, the elevated LiF content not only stems from the IWSWN-SPE itself but can also be attributed to the enhanced dissociation of TFSI⁻ anions.

We sincerely appreciate the reviewer's valuable comments, and we have updated some relevant descriptions in the revised manuscript.

Q12. Fluorine Content Discussion: The data indicate that the LiF content in the CEI and SEI of IWSWN-SPE is not significantly greater than that in PVEC. This raises questions about the positive role of fluorine-containing polymers in both SEI and CEI, which requires further discussion.

Reply: We greatly appreciate the reviewer for your valuable comment. We would like to conduct the LiF content comparison with a detailed analysis based on our experimental data.

In the XPS analysis of the SEI (Figure R11), at an etching time of 20 s, the LiF content of SEI derived from the IWSWN-SPE is 15.3%, while from the PVEC, it is 9.2%. This represents a 66.3% increase in LiF content in the SEI of the IWSWN-SPE compared to PVEC. Similarly, at an etching time of 100 s, the LiF content of SEI from the IWSWN-SPE cell is 14.4%, compared to 7.1% in the PVEC cell, indicating a 102.8% increase in LiF content in the SEI of the IWSWN-SPE.

Regarding the CEI XPS results (Figure R12), at etching times of 50 s, 100 s, and 200 s, the LiF content of CEI derived from the PVEC is 7.8%, 7.9%, and 7.8%, respectively. In contrast, for the CEI from IWSWN-SPE, the LiF content is 20.6%, 22.5%, and 22.1%, respectively, representing 2.64, 2.85, and 2.83 times the LiF content from PVEC.

These findings demonstrate a significantly higher LiF content both in the SEI and CEI from the IWSWN-SPE compared to PVEC. In conclusion, our data support the necessity of fluorine-containing polymer modification for enhancing the formation of SEI and CEI with increased LiF content.

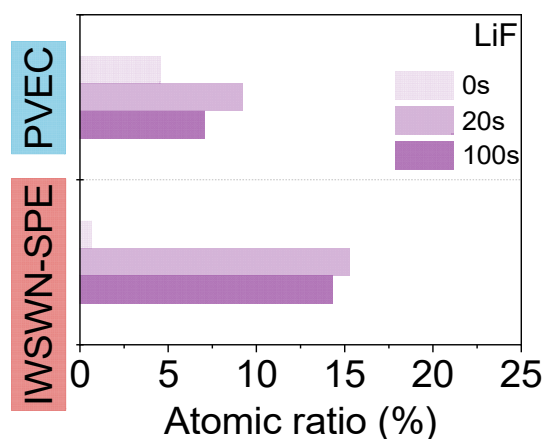


Figure R11. LiF contents derived from XPS results of the cycled LMAs with PVEC and IWSWN-SPE

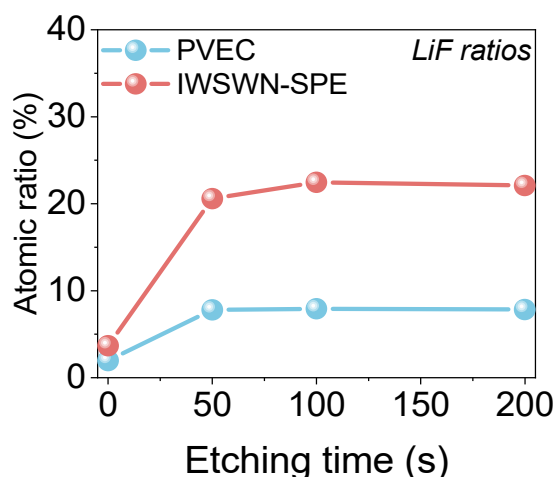


Figure R12. LiF content distribution derived from XPS results of the cycled NCM622 cathodes in the PVEC and IWSWN-SPE.

Q13. Exploration of Internal Mechanisms: While this work employs a multi-component approach using various polymer monomers to achieve excellent battery performance, the underlying principles that enable this "1+1>2" performance should be further explored. Specifically, the essential role of the "puzzle-like" structure and the performance correlation under varying fluoride and phosphide ratios need to be addressed.

Reply: We appreciate your insightful query regarding the fundamental principles behind the enhanced performance achieved through our multi-component approach in designing the polymer electrolyte. We aim to delve deeper into the essential role of the "puzzle-like" structure and the performance correlation under varying fluoride and phosphide ratios, building upon the principles guiding our research.

In our study, the design principle of a 1+1>2 SPE is based on the strategic selection and combination of monomers with complementary properties. By carefully considering the interactions and compatibility between the monomers, we aim to mitigate the potential disadvantages that individual monomers may introduce. This approach is intended to synergistically enhance the overall performance of the SPE by leveraging the strengths of each monomer while minimizing or compensating for their respective limitations within the polymer electrolyte.

In designing a 1+1>2 SPE, we meticulously consider the distinct roles and characteristics of each monomer. Following the concept of the barrel effect, we understand that enhancing the weakest link can lead to a substantial overall improvement in performance. VEC was selected as the primary monomer due to its high-voltage compatibility and strong interactions with Li^+ , which facilitate high ionic conductivity. However, its drawbacks—such as flammability and incompatibility with lithium metal anodes—necessitate the introduction of complementary monomers. To enhance lithium metal compatibility, we incorporated HFBMA, a fluorine-rich monomer, while TAP, a phosphorus-containing monomer, was introduced to impart flame retardancy.

Importantly, the disadvantages of individual monomers are effectively mitigated through the strengths of others. For instance, while HFBMA is flammable and TAP exhibits limited compatibility with lithium metal anodes, their combination with VEC results in an optimized SPE with high ionic conductivity, good nonflammability, enhanced voltage stability, and improved lithium metal compatibility. This design strategy ensures that the advantages of each monomer complement one another, leading to a synergistic enhancement that exceeds the sum of its parts.

Regarding the concept of "puzzle-like" assembly, we use the analogy of assembling puzzles to illustrate how we design and synthesize the solid-state polymer electrolyte at the molecular level. Just as one can use various colored puzzles of similar shapes in daily life, these puzzles can be arranged randomly or arranged according to preference by the interlocking of the puzzle pieces.

Similarly, we employ this analogy to showcase how we utilize three monomers in free radical polymerization to synthesize the solid-state polymer electrolyte. The monomers can polymerize with themselves or with different monomers. By uniformly mixing different monomers at the molecular level in the precursor solution, monomers are polymerized in double bond free radical polymerization, leading to random yet uniform chain growth and resulting in the formation of interconnected long-chain polymers, like assembling a puzzle (Here, we use the interlocking between the puzzle pieces in a "puzzle" as a metaphor for how different polymer monomers interact and connect with each other

through free radical polymerization). The obtained solid-state polymer electrolyte with homogeneously distributed functional monomer segments contributes to fast and even Li^+ ion transport and favorable properties (e.g., good flame retardancy, high voltage resistance, high ionic conductivity, and good interface).

The control of varying fluoride and phosphide ratios follows specific principles. Increasing fluoride content enhances the antioxidant capacity of the polymer electrolyte while potentially reducing ionic conductivity. The LSV and EIS results (Figures R13 and R14) demonstrate that increasing fluoride-based HFBMA molar ratio from 5% to 10% (compared to VEC) significantly boosts antioxidant capacity, with a slight decrease in ionic conductivity from 0.495 to 0.437 mS cm^{-1} . However, further increasing fluoride-based HFBMA molar ratio to 15% (compared to VEC) shows a less pronounced enhancement in antioxidant capacity but a more significant decrease in conductivity to 0.296 mS cm^{-1} , a 32.3% reduction. Thus, the fluoride-based HFBMA molar ratio is optimized at 10% (compared to VEC). In experiments optimizing the fluorine-based HFBMA content, the molar ratio of phosphide-based TAP is 15% (compared to VEC) and the weight ratio of LiTFSI to the total monomer is 20 *wt%*.

Then, to evaluate the phosphide-based TAP content, combustion test experiments were conducted. Results from Figure R15 indicate that a phosphide-based TAP molar ratio of 10% (compared to VEC) still allows the polymer electrolyte to burn while increasing the molar ratio to 15% exhibits flame-retardant properties. Hence, a phosphide-based TAP molar ratio of 15% (compared to VEC) is deemed appropriate for achieving fire resistance. In experiments optimizing the phosphide-based TAP content, the molar ratio of fluorine-based HFBMA is 10% (compared to VEC) and the weight ratio of LiTFSI to the total monomer is 20 *wt%*.

Therefore, the molar ratio of VEC to HFBMA to TAP is 1: 0.1: 0.15.

In conclusion, our selection process aims to synthesize a high-voltage-resistant and flame-retardant SPE through a “puzzle-like” molecular assembly. By combining monomers to jointly address their drawbacks, we aim to counteract the weakest link in the chain, mitigating the "barrel effect" and achieving the desired performance synergistically.

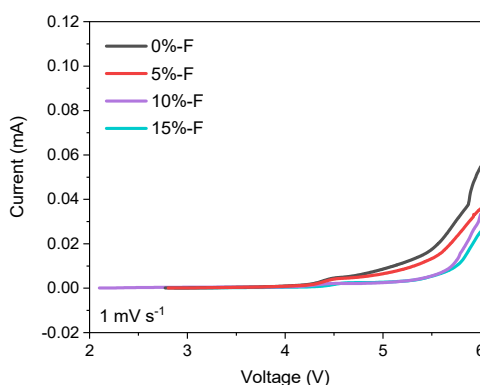


Figure R13. LSV test results for the SPE with different molar ratios of HFBMA (compared to VEC).

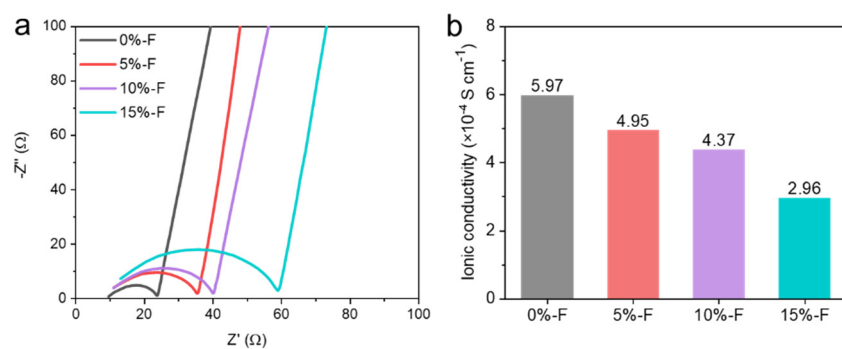


Figure R14. EIS results (a) and corresponding ionic conductivity (b) of the SPE with different molar ratios of HFBMA (compared to VEC).

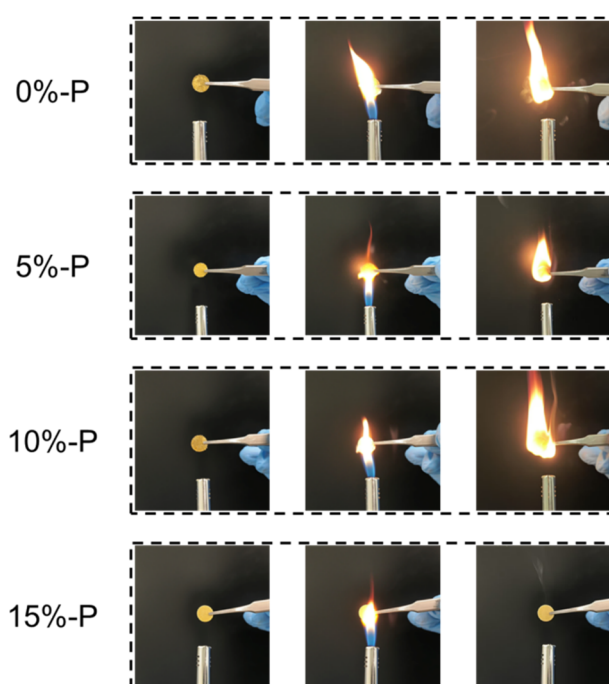


Figure R15. Burning tests of the SPE with different molar ratios of TAP (compared to VEC).

Response to the comments from Reviewer #5

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reply: We greatly appreciate the reviewer's comments. We have carefully reviewed and revised the entire manuscript, aiming to express the intended points as directly as possible, while avoiding redundancy and ambiguous expressions.

Comments from reviewers: Blue

Author response: Black

Response to the comments from Reviewer #1

The authors have revised the paper well according to the comments and can be published now.

Reply: We sincerely thank the reviewer for their valuable and insightful comments, which have contributed meaningfully to improving the quality of our work.

Response to the comments from Reviewer #3

The manuscript can be published.

Reply: We sincerely thank the reviewer for their valuable and insightful comments, which have contributed meaningfully to improving the quality of our work.

Response to the comments from Reviewer #4

My questions have been well addressed in the revised manuscript. I am happy to recommend publication of this work.

Reply: We sincerely thank the reviewer for their valuable and insightful comments, which have contributed meaningfully to improving the quality of our work.

Response to the comments from Reviewer #5

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Reply: We sincerely thank the reviewer for their valuable and insightful comments, which have contributed meaningfully to improving the quality of our work.

Response to the comments from Reviewer #2

The authors have made revisions in response to all reviewer's comments. The manuscript has been improved. However, I can't support to publish it in Nature Communications.

Reply: We sincerely thank the reviewer for their valuable and insightful comments. Below, we address each point raised in the reviewer's feedback, providing detailed clarifications, updated analyses, and revisions to the manuscript.

Why the material achieves a high Li transport is still not clear. The authors attribute the high Li transference number to the enhanced polymer-anion interaction. This concept is not novel. How the Li-polymer interaction facilitates Li diffusion is not known. The High Li transference number can be approved through the NMR measured Li and F diffusivities, but this work does not provide this result. In addition, MD result does not support a high Tli, which is discussed below.

Reply: We thank the reviewer for his/her comment regarding the Li^+ transport mechanism and how Li^+ -polymer interaction facilitates Li^+ diffusion.

Our hypothesis, supported by both the original discussion and new computational evidence, is that the strategic incorporation of HFBMA segments into the IWSWN-SPE is key to enhancing Li^+ transport by modulating the Li^+ -polymer interactions.

To provide a more explicit understanding, we have performed additional binding energy (BE) calculations: i) Monomer- Li^+ interaction (Figure R1): We calculated the BE between Li^+ and the individual monomer units. The binding energy for VEC with Li^+ was found to be -2.09 eV, while for HFBMA with Li^+ , it was -1.89 eV. This result indicates that the HFBMA monomer intrinsically exhibits a weaker binding affinity for Li^+ compared to VEC.

ii) Polymer- Li^+ interaction (Figure R2): More importantly, we assessed the BE of Li^+ with the polymer systems. The binding energy between PVEC and Li^+ was calculated to be -3.75 eV. In contrast, our IWSWN-SPE showed a weaker BE of -3.40 eV. This reduced binding strength is crucial for Li^+ transport. A weaker interaction implies that the Li^+ is less tightly bound to the polymer chains, facilitating a more labile solvation environment [*J. Am. Chem. Soc.* 2024, 146, 40, 27668 – 27678; *Nat. Commun.* 16, 3517 (2025)]. Consequently, the energy barrier for Li^+ to dissociate from one coordination site and hop to an adjacent one is lowered. This aligns with the principle that overly strong cation-dipole interactions can hinder ion mobility. For IWSWN-SPE, we effectively reduce these interactions, providing a moderate environment for Li^+ . This, in turn, promotes easier desolvation and re-solvation processes, which are fundamental steps in the ion migration mechanism through the polymer matrix, thereby enhancing Li^+ diffusion.

Therefore, the improved Li^+ transport in IWSWN-SPE is achieved because the modified structure via 'puzzle-like' molecular assemblies systematically weaken the Li^+ -polymer interactions. This

creates a more favorable energetic landscape for Li^+ migration. We will incorporate these new values of BE and this detailed explanation into the revised manuscript to explicitly clarify the mechanism by which the modified polymer structure facilitates Li^+ diffusion.

We thank the reviewer for pointing out that the role of enhanced polymer-anion interactions in elevating the Li transference number (t_{Li^+}) is well-established in the field of polymer electrolytes. Our primary innovative contribution, however, does not lie in proposing a new fundamental mechanism for t_{Li^+} enhancement. **Instead, our novelty stems from the rational design and synthesis of a solid-state polymer electrolyte via “puzzle - like ” co - assembly of three functional monomers** (VEC, HFBMA, and TAP) to realize a high-voltage-stable, LMA-stable, and flame-retardant goal, ultimately aiming to improve overall battery cycle life and significantly enhance safety performance compared to PVEC-based electrolytes.

The observed increase in the t_{Li^+} is a highly beneficial outcome of this specific molecular design. To understand this phenomenon within our system, we performed binding energy (BE) calculations. These calculations revealed that our synthesized IWSWN-SPE exhibits a stronger BE with the TFSI⁻ anion (-2.11 eV) compared to PVEC (-1.51 eV). This stronger interaction between the SPE and the anion effectively restricts anion mobility, thereby leading to the observed higher t_{Li^+} . [*J. Am. Chem. Soc.* 2024, 146, 40, 27668–27678; *Nat. Commun.* 16, 3517 (2025); *Adv. Funct. Mater.* 2023, 33, 2209828]

We are not claiming to introduce a novel fundamental mechanism for achieving a high t_{Li^+} . Rather, we are presenting a novel polymer architecture, designed with multiple functionalities in mind (flame retardancy, high-voltage stability, LMA compatibility), which, as a consequence of its unique composition and structure, also exhibits an enhanced t_{Li^+} . We utilize the established understanding of polymer-anion interactions to explain this observed improvement.

For the NMR characterizations, in our previous response, the solid-state NMR was conducted for ^7Li and ^{19}F of our IWSWN-SPE. However, the gel-like PVEC control samples are not amenable to solid-state, as they cannot be compressed into a dense powder suitable for such measurements. On the other hand, liquid-state NMR is also not fully applicable to either the gel-like PVEC or the solid-like IWSWN-SPE due to the nature of these materials. **Nevertheless**, to provide a comparative perspective on Li^+ and TFSI⁻ diffusion coefficients as suggested, we employed a coaxial NMR tube setup: the precursor solution was injected into the outer tube and subjected to mild heating to initiate in-situ polymerization, enabling liquid-state NMR measurements. **It is important to note that this approach introduces certain discrepancies from the actual state of our electrolyte, due to mild polymerization. Therefore, the diffusion coefficients obtained in this manner should be interpreted as qualitative indicators of the relative differences in Li^+ and TFSI⁻ mobility, rather than exact reflections of their behavior in the actual formed polymer-based electrolytes.**

The varied coordination between Li^+ and TFSI⁻ in our IWSWN-SPE is further confirmed by ^7Li and ^{19}F NMR spectroscopy (Figure R3a, b). The ^7Li NMR spectrum of IWSWN-SPE exhibits a noticeable downfield shift compared with that of PVEC, indicating a lower degree of electron

shielding around Li^+ and, consequently, a more complete dissociation of LiTFSI, which promotes Li^+ mobility within the polymer matrix [*J. Am. Chem. Soc.* 2024, 146, 40, 27668–27678; *Nat. Commun.* 16, 3517 (2025)]. Moreover, the full width at half-maximum (FWHM) of the ^7Li resonance in IWSWN-SPE is broader than in PVEC (Figure R4a), indicating that Li^+ resides in a less ordered solvation environment. This broadening arises from our IWSWN-SPE's intentionally diversified monomer composition, which creates multiple coordination sites that give rise to a variety of Li^+ binding environments (*J. Am. Chem. Soc.* 2024, 146, 40, 27668 – 27678). Complementary ^{19}F NMR analysis reveals an upfield shift of the TFSI $^-$ fluorine resonance in IWSWN-SPE relative to PVEC (Figure R3b), pointing to an increased electron density around the TFSI $^-$ as a result of stronger coordination by IWSWN. The ^{19}F peak also displays a larger FWHM in IWSWN-SPE versus PVEC (Figure R4b), underscoring a variety of local chemical environments for TFSI $^-$, for example, the interactions with both Li^+ and the polymer backbones. These findings confirm that our IWSWN-SPE enhances LiTFSI salt dissociation and diversifies ion solvation in the electrolytes. In other words, compared to PVEC, our designed IWSWN-SPE enables Li^+ to move more freely while promoting stronger interactions with TFSI $^-$, thereby offering the potential to enhance the Li^+ transference number.

Diffusion coefficients of Li^+ and TFSI $^-$ are determined from ^7Li and ^{19}F pulsed-field-gradient NMR spectra using Stejskal-Tanner analysis (Figures R5 and R6) [*J. Am. Chem. Soc.* 2024, 146, 40, 27668 – 27678; *Nat. Commun.* 16, 3517 (2025)]. The Li^+ self-diffusion coefficient in IWSWN-SPE ($6.51 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) is substantially higher than in PVEC ($1.08 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), further confirming that our designed IWSWN-SPE promotes enhanced Li^+ transport. Conversely, the diffusion coefficient of TFSI $^-$ in IWSWN-SPE ($3.35 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) is markedly lower than in PVEC ($8.87 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), indicating that stronger polymer-anion interactions effectively suppress anion mobility and thereby increase the Li^+ transference number. The self-diffusion coefficients obtained from pulsed-field-gradient NMR were used to calculate the Li^+ transference number (t_{Li^+}) according to the following relation [*Nat. Commun.* 16, 3517 (2025)]:

$$t_{\text{Li}^+} = \frac{c_{\text{Li}^+} \cdot D_{\text{Li}^+}}{c_{\text{Li}^+} \cdot D_{\text{Li}^+} + c_{\text{TFSI}^-} \cdot D_{\text{TFSI}^-}}$$

As shown in Figure R7, the t_{Li^+} value for IWSWN-SPE is 0.66, substantially higher than the 0.11 measured for PVEC. This pronounced increase in t_{Li^+} provides further evidence that our SPE design effectively promotes high t_{Li^+} .

It should be noted that the diffusion coefficients tested here (on the order of $10^{-7} \text{ cm}^2 \text{ s}^{-1}$) are unusually large for solid-state polymer-based electrolytes. This is attributable to the NMR sample preparation, in which the prepolymer solution (not the real polymer electrolytes) is loaded into the NMR tube and polymerized in situ by gentle heating. The resulting viscous yet flowable sample satisfies the requirements for pulsed-field-gradient NMR, leading to higher apparent diffusion coefficients.

As highlighted by the reviewer, the inclusion of these NMR tests nonetheless provides independent support for our conclusions regarding the high Li^+ transference number in

IWSWN-SPE.

We thank the reviewer for pointing out the discrepancy between the MD simulation results and the experimentally observed. In response to this concern, we have re-evaluated our MD simulations to ensure consistency with experimental conditions and a more accurate reflection of ion transport behavior in our systems and we will provide detailed discussion and clarification on this specific point in our subsequent response below.

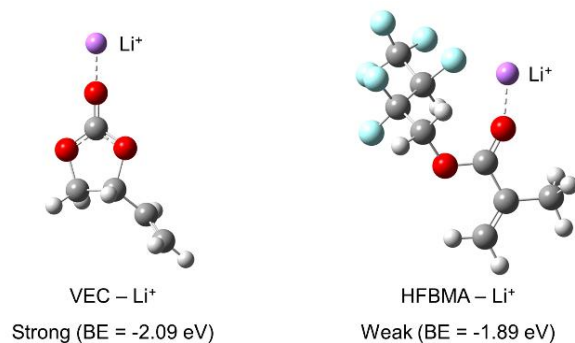


Figure R1. Binding energies between Li⁺ and different monomers (VEC and HFBMA).

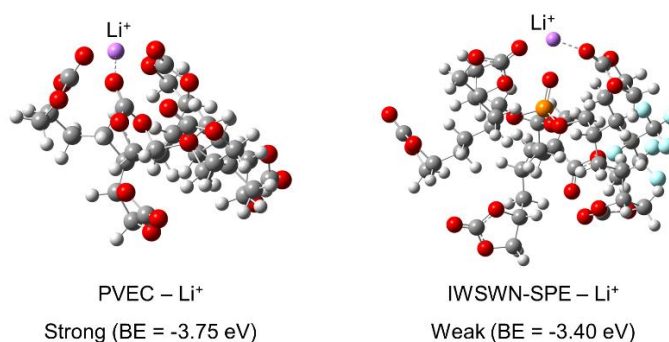


Figure R2. Binding energies between Li⁺ and two polymers (PVEC and IWSWN-SPE).

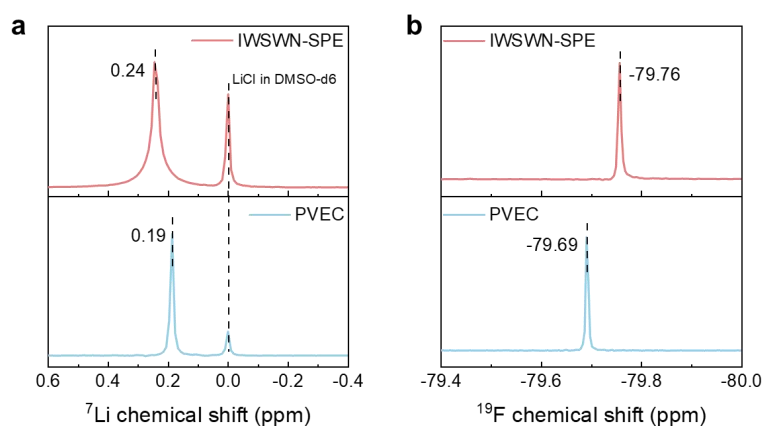


Figure R3. ⁷Li NMR (a) and ¹⁹F NMR (b) spectra of the PVEC and IWSWN-SPE to examine the chemical environment of Li⁺ and anions.

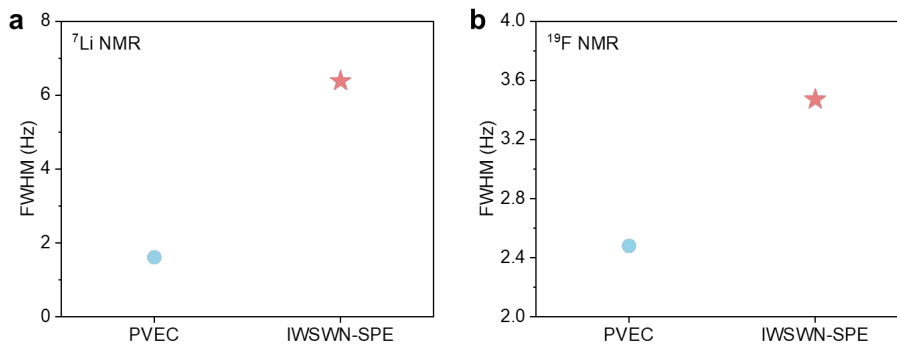


Figure R4. Full-width at half-maximum (FWHM) of ${}^7\text{Li}$ and ${}^{19}\text{F}$ NMR spectra to reveal the local coordination environment of the Li^+ and TFSI $^-$. The summary plot of FWHM obtained from ${}^7\text{Li}$ NMR (a) and ${}^{19}\text{F}$ NMR spectra (b).

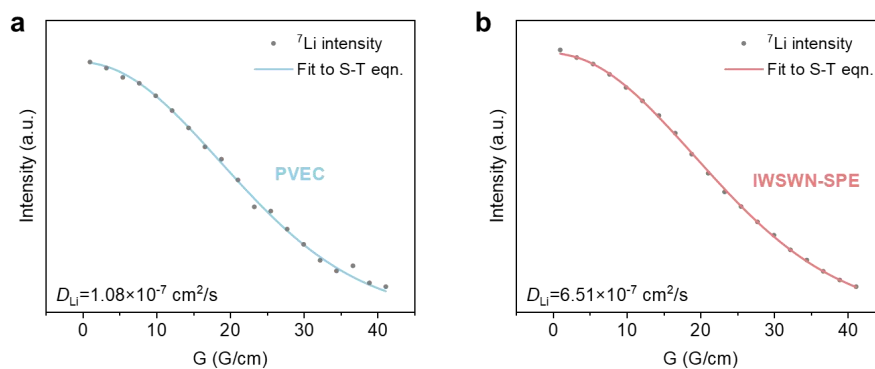


Figure R5. Intensity of ${}^7\text{Li}$ NMR and fitted attenuation curves to calculate the diffusion coefficient of Li^+ in the PVEC (a) and IWSWN-SPE (b). The integrated intensity (I/I_0) of the ${}^7\text{Li}$ resonances corresponding to Li^+ is plotted as a function of the gradient strength (G).

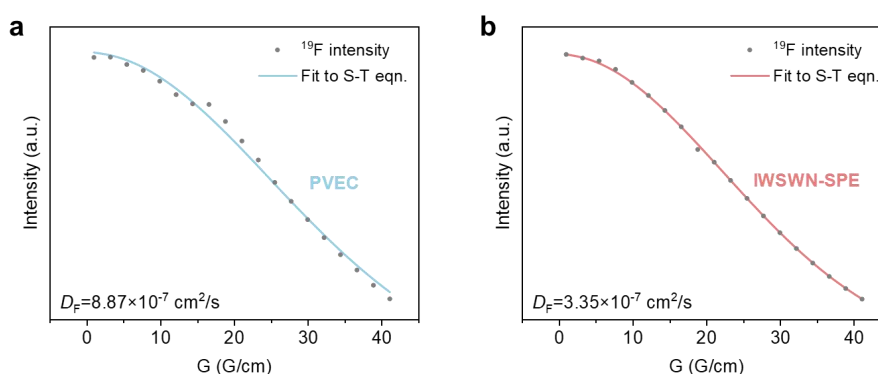


Figure R6. Intensity of ${}^{19}\text{F}$ NMR and fitted attenuation curves to calculate the diffusion coefficient of TFSI $^-$ in the PVEC (a) and IWSWN-SPE (b). The integrated intensity (I/I_0) of the ${}^{19}\text{F}$ resonances corresponding to TFSI $^-$ is plotted as a function of the gradient strength (G).

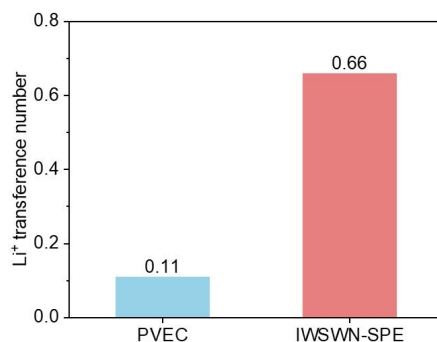


Figure R7. Calculated Li⁺ transference number using the results of diffusion coefficients from NMR results.

The authors acknowledge that 23% VEC residuals are present in their polymerized electrolyte, which can significantly affect the conductivity results. After vacuum evaporation, the content can be reduced to 2.53%. However, no conductivity testing has been performed on the low VEC content IWSWN-SPE. While the 23% VEC content is lower than the 54% content in PVEC, this does not prove that the high conductivity is due to a special polymer structure rather than the VEC content. Therefore, the claim that high conductivity results from facilitated lithium salt dissociation is not entirely justified.

Reply: We thank the reviewer for raising this point regarding the influence of residual VEC on ionic conductivity.

We would like to clarify a misunderstanding: the “2.53%” value obtained after vacuum drying refers to the fraction of VEC monomer that volatilizes during that process, **NOT** to the final VEC content in the IWSWN-SPE. This result demonstrates that the VEC content determined *via* vacuum drying is substantially lower than the value obtained by TGA and is therefore unreliable.

This clarification addressed another reviewer’s inquiry regarding the VEC monomer quantification and does not bear on any conclusions presented in the manuscript.

Our designed IWSWN-SPE contains 23% VEC, substantially lower than the 54% VEC in the PVEC. To avoid the effect of VEC content on conductivity, we subjected PVEC to vacuum-heating and determined, from the mass loss, that its VEC content could be reduced to ~25%. Ionic conductivity measurements on the (25%-VEC) PVEC yielded $2.12 \times 10^{-4} \text{ S cm}^{-1}$, which is lower than the conductivity of $4.35 \times 10^{-4} \text{ S cm}^{-1}$ observed for the 23%-VEC IWSWN-SPE (Figure R8). Thus, at comparable VEC levels, our IWSWN network outperforms PVEC, demonstrating that the enhanced ionic conductivity arises from the polymer’s unique architecture—which promotes more LiTFSI salt dissociation and facilitates Li⁺ transport—rather than from VEC content alone.

Finally, we note that all of our polymer-based electrolytes (both IWSWN-SPE and PVEC) are formed by in-situ thermal polymerization of the monomer directly within the cell. A PVEC sample

prepared by post-polymerization vacuum drying to reduce VEC cannot be processed in this way and would therefore not provide a consistent basis for comparison under our experimental protocol. We have retained the 54%-VEC PVEC control in the main manuscript to ensure that both systems are prepared via identical in-situ polymerization conditions.

We appreciate the reviewer's suggestions.

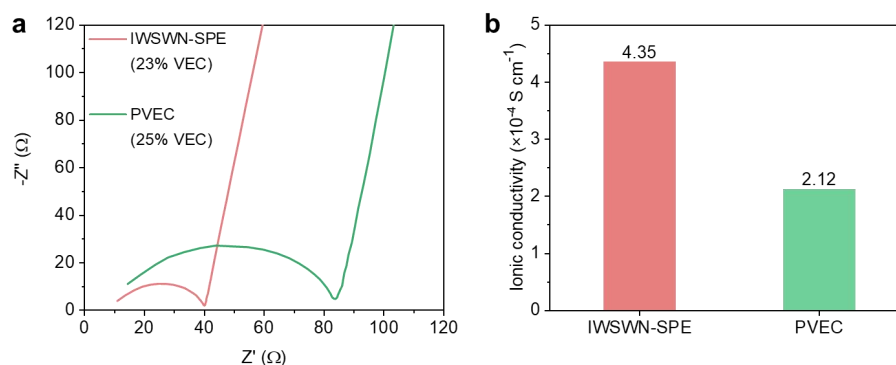


Figure R8. EIS curves and calculated ionic conductivity results of IWSWN-SPE and PVEC with similar weight ratios of VEC.

Moreover, if the high conductivity is primarily due to the gel polymer rather than the "puzzle-like" polymer morphology itself, it would diminish the significance of the proposed polymer design. A conductivity of 0.432 mS cm^{-1} for a gel polymer electrolyte is reasonable; generally, gel polymer electrolytes target conductivity in the range of 10^{-2} to $10^{-3} \text{ S cm}^{-1}$ for battery and electrochemical applications.

Reply: We thank the reviewer for emphasizing the importance of de-convoluting monomer content and polymer architecture in determining ionic conductivity. We respectfully submit the following clarifications and additional data:

1. Monomer content vs. polymer structure. While a high VEC fraction can indeed contribute to segmental mobility, it cannot alone account for the dramatic ionic conductivity enhancement we observe in IWSWN-SPE. When both electrolytes contain the close content VEC, as discussed above (IWSWN-SPE: 23%; vacuum-dried PVEC: 25%), the ionic conductivity of IWSWN-SPE is $4.35 \times 10^{-4} \text{ S cm}^{-1}$, versus only $2.12 \times 10^{-4} \text{ S cm}^{-1}$ for PVEC—i.e. PVEC achieves merely 48.7 % of the conductivity of our IWSWN-SPE (as mentioned above). **This clear divergence demonstrates that the “puzzle-like” molecular assembly of IWSWN-SPE meaningfully promotes LiTFSI dissociation and Li^+ mobility beyond what can be attributed to monomer content alone.**

2. Scope of our design objectives. We fully agree that gel polymers doped with external liquid electrolytes can reach conductivity on the order of 10^{-2} - $10^{-3} \text{ S cm}^{-1}$ [*Nat. Commun.* 14, 482 (2023); *Nat. Commun.* 15, 2500 (2024); *Nat. Commun.* 15, 10015 (2024); *Nat. Commun.* 15, 5375 (2024)], but such systems operate under fundamentally different principles, which contain external solvents

to solvate ions. In contrast, our IWSWN-SPE is synthesized by in-situ polymerization of neat monomer solution, **without** any added liquid plasticizer or filler. Under these **solvent-free conditions**, conductivities among the 10^{-4} - 10^{-6} S cm⁻¹ range are both expected and well supported by the references (as shown in Table R1). Our primary goal is not to chase the highest possible conductivity via external liquid addition but to demonstrate that a rationally designed, **solvent-free** polymer network can (i) achieve competitive conductivities for solid-state lithium metal batteries, (ii) suppress anion transport to raise Li⁺ transference number, and (iii) simultaneously deliver robust Li-metal compatibility, high-voltage stability, and flame retardancy.

Table R1. Related references of SPEs.

Reference	Ionic conductivity (mS cm ⁻¹)
<i>Nat. Energy</i> , 9, 386–400 (2024)	0.3
<i>Nat. Commun.</i> 15, 2500 (2024)	0.204
<i>J. Am. Chem. Soc.</i> 2024, 146, 27668–27678	0.66
<i>Angew. Chem. Int. Ed.</i> 2023, 62, e202309613	0.2
<i>Angew. Chem. Int. Ed.</i> 2023, 62, e202213606	0.068
<i>Nat. Commun.</i> 14, 4617 (2023)	0.109
<i>Nat. Commun.</i> 13, 4181 (2022)	0.01
<i>Angew. Chem. Int. Ed.</i> 2022, 61, e202209169	0.05
This work	0.43

3. Significance of ‘puzzle-like’ architecture. The IWSWN-SPE both enhances LiTFSI dissociation and constrains TFSI⁻ mobility. This ‘puzzle-like’ construction underpins the nearly two-fold conductivity boost over PVEC at equal VEC content, validating our design strategy as a powerful route toward high ionic conductivity solid-state polymer-based electrolytes. More importantly, the ‘puzzle-like’ assembly yields a polymer-based electrolyte that is intrinsically non-flammable, high-voltage tolerant, and lithium-metal stable, providing unique advantages and critical significance for solid-state lithium metal battery applications.

We trust that these points demonstrate that the exceptional conductivity of IWSWN-SPE arises from its purposely engineered polymer network, and not merely from VEC content. We appreciate the reviewer's insight, which has sharpened our discussion of structure-property relationships, and have incorporated these clarifications into the revised manuscript.

For the new MD simulations, the force field parameters should be provided to increase transparency.

Reply: We thank the reviewer for the suggestion. We have now provided a comprehensive

description of the force field parameters used, as follows:

The molecular dynamics (MD) simulations in this study were conducted using the GROMACS simulation package (version 2024.2) with an OPLS-AA force field. The parameters and atomic charges of Li^+ as reported by Soetens et al were used, while the force field parameters of TFSI⁻, VEC, PVEC, and SPE were obtained from LigParGen. For TFSI⁻ anion, the Restricted Electrostatic Potential (RESP) atomic charges were used, while 1.2*CM5 atomic charges were employed in organic molecules. All atomic charges were obtained with the Multiwfn 3.8 program based on the DFT calculations at B3LYP/6-311G(d,p) level in Gaussian 09 software. All simulations used an MD timestep of 2 fs. Particle Mesh Ewald (PME) algorithm was used to compute the short-range electrostatics in 2.0 nm, while the cut-off for van der Waals interactions was set as 2.0 nm. The Temperature and pressure were controlled through V-rescale coupling and C-rescale barostat, respectively. In a typical simulation, the systems were initially equilibrated in the NPT ensemble at 398.15 K and 1.01325 bar for 5 ns, after the energy minimization step, in order to allow the polymer molecules to fully relax. Then the systems were annealed from 398.15 K to 298.15 K with a cooling rate of 10 K/ps. Subsequently, simulation in the NPT ensemble at 298.15 K was carried out for 50 ns to ensure that the system is fully equilibrated. Finally, the production runs of three parallel sampling processes in the NPT ensemble at 298.15 K for 30 ns were performed at the end.

The detailed topology parameters were defined explicitly, including atoms, bonds, angles, and dihedrals, ensuring an accurate representation of molecular interactions and structural properties (as shown in Tables R2-R5 at the end of this Response). The key parameters are as follows:

i) Atoms: Each atom type was specified with defined partial charges consistent with OPLS-AA conventions. Key atom types included: Carbon atoms: partial charges ranging typically from -0.35 to +0.83. Oxygen atoms: partial charges typically range from approximately -0.38 to -0.61. Phosphorus atoms: carrying relatively higher positive charges around +0.93.

ii) Bonds and Constraints: Bonds involving hydrogen atoms were constrained using the LINCS (Linear Constraint Solver) algorithm.

iii) Non-covalent interactions: Non-covalent interactions were described through the standard Lennard-Jones potentials (for van der Waals interactions) and Coulombic potentials (for electrostatic interactions), adhering to OPLS-AA parameterization.

iv) Electrostatic Interactions: Long-range electrostatic interactions were calculated using the Particle Mesh Ewald (PME) method, ensuring accurate and efficient treatment of electrostatic interactions.

These customized force field parameters effectively captured the essential physicochemical characteristics necessary for the accurate simulation of the polymer electrolyte systems designed in this study. We have also updated the Methods section in the revised manuscript to reflect this clarification and have cited the relevant sources where applicable. We hope this improved level of

detail addresses the reviewer's concern and enhances the transparency of our MD simulation results.

Figures R7 and R8 show the equilibrated polymer electrolytes, but the structures appear unusual. After NPT equilibration, the structure should fill the entire simulation box, rather than showing significant vacuum space, even after removing periodic boundary conditions. Please clarify.

Reply: Thank you for the reviewer's valuable feedback and insightful suggestions regarding the structures. In response to the reviewer's comments on the simulation setup, we carefully revisited our simulation parameters and made refined adjustments to the force field parameters to further enhance the accuracy of our model (as illustrated in the last question). After these adjustments, we re-ran the simulations and obtained the updated equilibrated snapshot shown in Figure R9.

The new simulation outcomes demonstrate that the polymer chains uniformly fill the simulation box, and no significant voids are visible once periodic boundary conditions are removed. We believe these refined results provide stronger support for our research conclusions and offer a more comprehensive characterization of the systems.

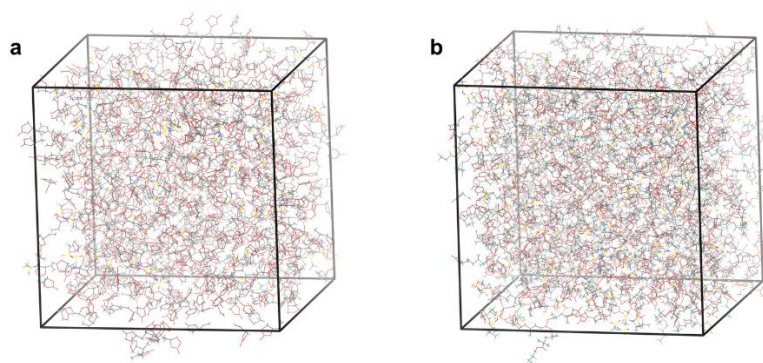


Figure R9. 3D snapshot of polymer structure within the simulation model for PVEC (a) and IWSWN-SPE (b) systems.

The molar ratio of (VEC residue: VEC units in a single polymer chain: LiTFSI) should be provided to help understand the lithium coordination environment. I performed a calculation, and the ratios are 6:4:1 for PVEC and 3:6:1 for IWSWN-SPE. When analyzing the Li coordination environment through RDF, which oxygen atoms are used? I suggest using only the carbonyl oxygen for VEC and the polymer, and nitrogen for TFSI as each of these types of atom only have 1 in each unit and can present the number of the unit. Furthermore, to explain Li coordination environment, it is important to compare the number of VEC residues, VEC units in the polymer, and TFSI in the Li coordination shell. Therefore, I recommend including RDFs of Li-O(VEC) in Figure 3, rather than Li-O(TFSI), since you already show Li-N(TFSI).

Reply: We thank the reviewer for the suggestions regarding details for RDF analysis. In response,

we have made the following revisions and additions:

1. Molar ratios of VEC residues, VEC units in a single polymer chain, and LiTFSI.

To address the reviewer's request for clarity on the composition of our systems, we provided the molar ratios as follows:

In the PVEC system, the molar ratio of (VEC residue : VEC unit in a single polymer chain : LiTFSI) is 12 : 8 : 1.5. In the IWSWN-SPE system, this ratio is 5 : 5 : 1.5.

2. Choice of atom types for RDF integration.

In accordance with the reviewer's suggestion, we calculated the Li coordination numbers by considering only the atoms that primarily contribute to coordination. For VEC, we count only the carbonyl oxygen ($O_{C=O}$) when computing Li-O coordination numbers. For the IWSWN-SPE, we evaluated the coordination between Li^+ ions and the oxygen atoms from $C=O$ and $P=O$ groups ($O_{C/P=O}$). For the PVEC, carbonyl oxygen ($O_{C=O}$) atoms were used for the coordination number calculation. For TFSI⁻, we have chosen to count Li-O(TFSI⁻) rather than Li-N(TFSI⁻), because our analysis showed that Li-O interactions dominate (>90% of Li-anion coordination), whereas Li-N contacts are negligible.

3. Updated RDF and coordination-number results.

We have re-calculated the radial distribution functions (RDFs) and corresponding coordination numbers (CNs) for Li^+ with respect to: Carbonyl oxygen ($O_{C=O}$) of VEC monomer ($Li-O_{C=O}$), $O_{C=O}$ of PVEC backbones ($Li-O_{C=O}$), Oxygen atoms from carbonyl groups and phosphoester groups ($O_{C/P=O}$), and Oxygen of TFSI⁻ ($Li-O$).

The new RDF curves are shown in Figures R10 and R11, and the integrated coordination numbers are summarized in Figure R12. The key findings are below:

i) $Li-O_{C=O}$ (VEC monomer) coordination:

In the PVEC system, $CN(Li-O_{C=O_VEC}) = 2.73$. For the IWSWN-SPE system, $CN(Li-O_{C=O_VEC}) = 2.53$. This indicates that, in the PVEC system, a slightly larger fraction of Li^+ remains coordinated to monomeric VEC residues, reflecting the higher VEC-to-polymer ratio (12 : 8 vs. 5 : 5 in IWSWN-SPE).

ii) $Li-O$ (polymers) coordination:

For the PVEC system, $CN(Li-O_{C=O_PVEC}) = 0.95$. For the IWSWN-SPE system, $CN(Li-O_{C/P=O_IWSWN-SPE}) = 1.28$. The elevated $Li-O_{polymer}$ coordination in IWSWN-SPE demonstrates that, despite the lower monomer content, Li^+ prefers to bind more frequently to coordinated oxygen units on the 'puzzle-like' polymer backbone.

iii) $Li-O$ (TFSI⁻) coordination:

For the PVEC system, $CN(Li-O_{TFSI^-}) = 0.41$. For the IWSWN-SPE system, $CN(Li-O_{TFSI^-}) = 0.21$. A lower $Li-O_{TFSI^-}$ coordination in IWSWN-SPE indicates weaker Li^+ -TFSI⁻ association compared to PVEC.

4. Revision of Figure 3 in the revised manuscript.

Per the reviewer's recommendation, we have revised Figure 3 of the manuscript to include the RDF of $\text{Li-O}_{\text{C=O_VEC}}$. This adjustment reveals the coordination of Li^+ with the VEC monomer and ensures consistency with the reviewer's suggestion to focus on the most representative interactions. The updated figure better elucidates the role of VEC and the polymer in the Li^+ coordination environment. The revised manuscript now describes these updated CN values and highlights that Li^+ coordinates more with the polymer backbone and reduces Li^+ -anion pairing in IWSWN-SPE compared to PVEC.

We trust these additions address the reviewer's concerns by providing a clear, quantitative picture of Li^+ coordination in both systems. The revised figures and accompanying discussion demonstrate that, the 'puzzle-like' assembly IWSWN-SPE drives Li^+ to coordinate preferentially with the polymer backbone while weakening Li^+ -TFSI⁻ interactions, which further substantiates our claims regarding enhanced salt dissociation and high Li^+ transportation.

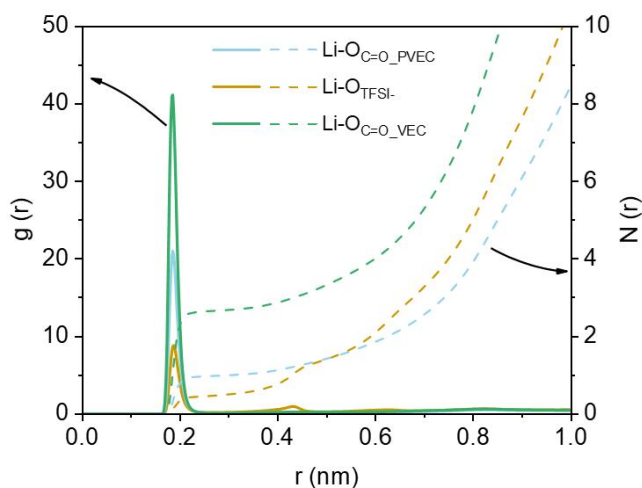


Figure R10. RDF and CN of the PVEC system.

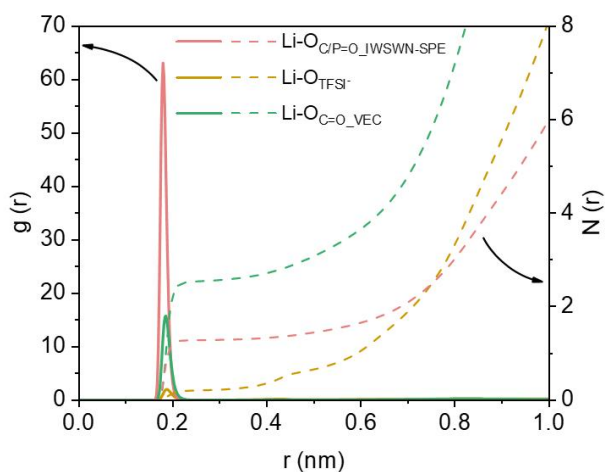


Figure R11. RDF and CN of the IWSWN-SPE system.

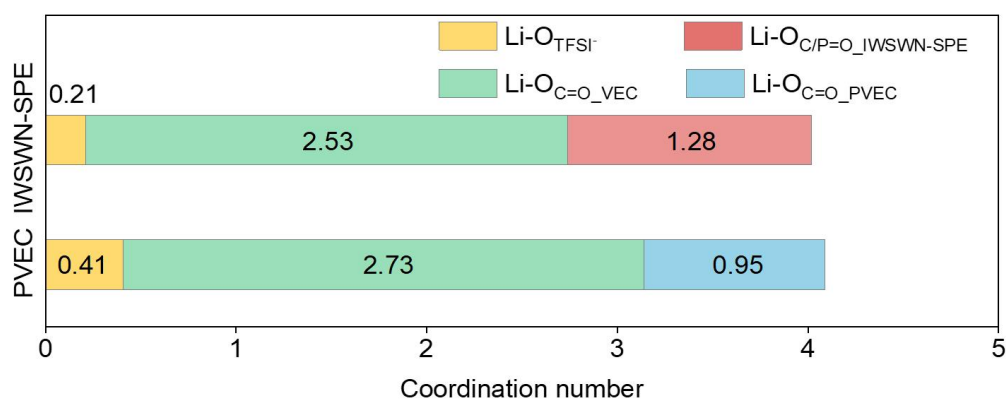


Figure R12. The comparison results of the CN in PVEC and IWSWN-SPE systems.

The MSD of Li in R12 is not linear even after 30 ns, suggesting poor statistical sampling. A low displacement value of only around 8 Å² after 30 ns indicates very localized and slow Li movement. The calculated diffusion coefficient using this type of MSD profile can only provide an approximate value, as the Li diffusion is still subdiffusive. The error bar should be discussed. A diffusion coefficient of 3.32×10^{-13} m²/s is very low, which contradicts the experimentally reported conductivity of 4.32×10^{-4} S cm⁻¹ and a high Li transference number of 0.7. The Li diffusion coefficient is expected to be in the 10⁻¹² m²/s range. Additionally, the diffusivity of TFSI⁻ in Figure S22 is significantly higher than the Li diffusivity, and the Li transference number from the MD simulations cannot support such a high transference number of 0.7.

Reply: We sincerely thank the reviewer for the detailed and insightful comments. The careful attention to the mean squared displacement (MSD) analysis, diffusion coefficients, and lithium transference number has guided us to refine our molecular dynamics (MD) simulations and strengthen our conclusions.

1. Improved sampling and equilibration

To ensure reliable statistics, each system (PVEC and IWSWN-SPE) was subjected to three independent NPT production runs, each lasting 30 ns. The resulting MSD curves (Figure R13) now display linear behavior over the entire time window, indicating that Li⁺ and TFSI⁻ diffusion have reached the normal diffusive regime. Also, we calculated the standard deviation of the diffusion coefficients across the three runs and concluded error bars to quantify statistical uncertainty.

2. Recomputed self-diffusion coefficients

Upon reviewing the related research [*J. Am. Chem. Soc.* 2025, 147, 17, 14554-14563; *Energy Environ. Sci.*, 2024, 17, 8874-8884; *Angew. Chem. Int. Ed.* 2021, 60, 11919-11927; *Energy Storage Mater.* 74 (2025) 103941], we note that Li⁺ diffusion coefficients in polymer electrolytes on the order of 10⁻¹³ m² s⁻¹ (10⁻⁹ cm² s⁻¹) are commonly reported and considered reasonable. The range is

also reasonable for MD simulations because differences in force fields, system size, polymer architecture, and sampling details can easily produce variations around this range.

Following the reviewer's suggestion, we recomputed and updated the results according to the revised simulations. From the three replicas, we extracted Li^+ and TFSI^- self-diffusion coefficients (averaged over replicas with standard deviations, as shown in Figure R14) of two systems as follows:

$$\text{PVEC: } D_{\text{Li}^+} = (3.73 \pm 0.47) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}; D_{\text{TFSI}^-} = (8.64 \pm 1.07) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$$

$$\text{IWSWN-SPE: } D_{\text{Li}^+} = (3.51 \pm 0.34) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}; D_{\text{TFSI}^-} = (3.24 \pm 0.32) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$$

3. Relative differences of TFSI^- diffusion coefficients

More importantly, the updated results clearly show that the TFSI^- diffusion coefficient in the PVEC system ($8.64 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) is 2.67 times higher than in the IWSWN-SPE system ($3.24 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$), while Li^+ diffusion coefficients in the two systems (3.73×10^{-8} vs. $3.51 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) remain similar. **This relative suppression of anion mobility in IWSWN-SPE is fully consistent with the experimentally observed high Li^+ transference number and confirms that our 'puzzle-like' polymer architecture can restrict TFSI^- motion.**

We concur with the reviewer that directly inserting MD-derived self-diffusion coefficients into the ideal Nernst-Einstein equation is problematic. As noted in a study (*Phys. Rev. Lett.* 122, 136001, 2019), this approach often underestimates t_{Li^+} by neglecting ion clustering effects (such as negatively charged Li^+ - TFSI^- complexes) whose net movement opposes that of free Li^+ ions, reducing the effective cationic current. Accounting for such effects requires post-processing optimizations beyond the scope of this work, though it presents an intriguing direction for future research.

We have updated the figures and the corresponding discussion in the revised manuscript to reflect these new data. We trust these revisions address the reviewer's concerns and strengthen the agreement between simulation and experiment.

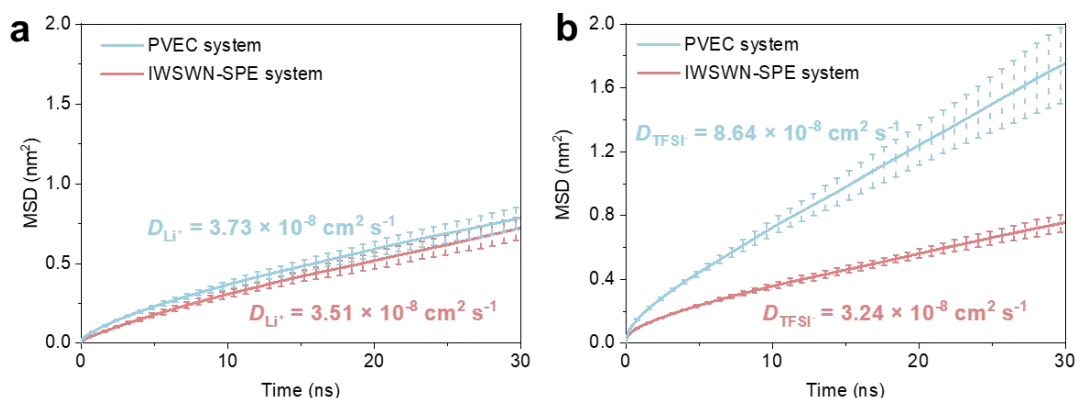


Figure R13. The mean and variance of MSD curves of Li^+ (a) and TFSI^- (b) in the PVEC and IWSWN-SPE systems.

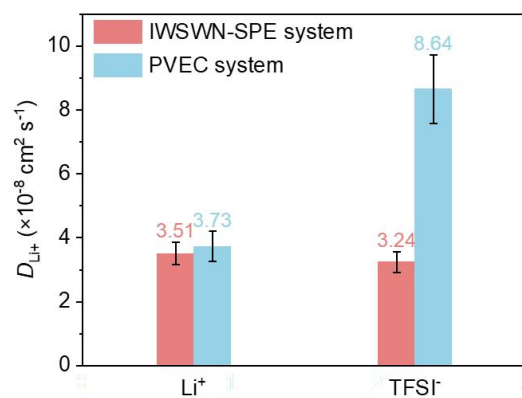


Figure R14. The mean and variance values of diffusion coefficients of Li^+ and TFSI^- in the PVEC and IWSWN-SPE systems.

Table R2. Atom Force Field Parameters of IWSWN-SPE.

Index	Atom Name	Charge Group	Charge (e)	Mass (amu)
1	C1	1	-0.096151	12.01
2	C2	2	0.428767	12.01
3	O1	3	-0.399056	16
4	P1	4	0.930077	30.97
5	O2	5	-0.394316	16
6	C3	6	0.400507	12.01
7	C4	7	-0.094517	12.01
8	O3	8	-0.605286	16
9	O4	9	-0.396915	16
10	C5	10	0.234027	12.01
11	C6	11	-0.095382	12.01
12	C7	12	-0.099136	12.01
13	C8	13	-0.096484	12.01
14	C9	14	-0.091194	12.01
15	C10	15	-0.099136	12.01
16	C11	16	0.034627	12.01
17	C12	17	0.304567	12.01
18	C13	18	0.348451	12.01
19	O5	19	-0.454294	16
20	C14	20	0.809402	12.01
21	O6	21	-0.478462	16
22	O7	22	-0.503975	16
23	C15	23	0.092736	12.01
24	C16	24	0.05608	12.01
25	O8	25	-0.404458	16
26	C17	26	0.826353	12.01
27	O9	27	-0.388544	16
28	O10	28	-0.493894	16
29	C18	29	0.034627	12.01
30	C19	30	-0.356898	12.01
31	C20	31	-0.096484	12.01
32	C21	32	-0.091194	12.01
33	C22	33	0.092736	12.01
34	C23	34	0.05608	12.01
35	O11	35	-0.404458	16
36	C24	36	0.826353	12.01
37	O12	37	-0.388544	16
38	O13	38	-0.493894	16
39	C25	39	0.348451	12.01
40	C26	40	0.304567	12.01

41	O14	41	-0.478462	16
42	C27	42	0.809402	12.01
43	O15	43	-0.454294	16
44	O16	44	-0.503975	16
45	C28	45	-0.089759	12.01
46	C29	46	-0.087258	12.01
47	C30	47	-0.097136	12.01
48	C31	48	0.239238	12.01
49	C32	49	-0.096484	12.01
50	C33	50	-0.091194	12.01
51	C34	51	0.159929	12.01
52	C35	52	0.193553	12.01
53	O17	53	-0.423964	16
54	C36	54	0.849285	12.01
55	O18	55	-0.427833	16
56	O19	56	-0.509598	16
57	C37	57	-0.296869	12.01
58	C38	58	0.726458	12.01
59	O20	59	-0.361273	16
60	C39	60	-0.123556	12.01
61	C40	61	0.524601	12.01
62	C41	62	-0.064934	12.01
63	C42	63	0.607999	12.01
64	O21	64	-0.546532	16
65	F1	65	-0.234015	19
66	F2	66	-0.207272	19
67	F3	67	-0.186016	19
68	F4	68	-0.190608	19
69	F5	69	-0.172892	19
70	F6	70	-0.200676	19
71	C43	71	0.304567	12.01
72	C44	72	0.348451	12.01
73	O22	73	-0.454294	16
74	C45	74	0.809402	12.01
75	O23	75	-0.478462	16
76	O24	76	-0.503975	16
77	C46	77	-0.356898	12.01
78	C47	78	-0.099136	12.01
79	C48	79	-0.096151	12.01
80	C49	80	0.428767	12.01
81	O25	81	-0.399056	16
82	P2	82	0.930077	30.97
83	O26	83	-0.394316	16

84	C50	84	0.400507	12.01
85	C51	85	-0.094517	12.01
86	O27	86	-0.605286	16
87	O28	87	-0.396915	16
88	C52	88	0.234027	12.01
89	C53	89	-0.095382	12.01
90	C54	90	-0.099136	12.01
91	C55	91	-0.096484	12.01
92	C56	92	-0.091194	12.01
93	C57	93	-0.099136	12.01
94	C58	94	0.034627	12.01
95	C59	95	0.304567	12.01
96	C60	96	0.348451	12.01
97	O29	97	-0.454294	16
98	C61	98	0.809402	12.01
99	O30	99	-0.478462	16
100	O31	100	-0.503975	16
101	C62	101	0.092736	12.01
102	C63	102	0.05608	12.01
103	O32	103	-0.404458	16
104	C64	104	0.826353	12.01
105	O33	105	-0.388544	16
106	O34	106	-0.493894	16
107	C65	107	0.034627	12.01
108	C66	108	-0.356898	12.01
109	C67	109	-0.096484	12.01
110	C68	110	-0.091194	12.01
111	C69	111	0.092736	12.01
112	C70	112	0.05608	12.01
113	O35	113	-0.404458	16
114	C71	114	0.826353	12.01
115	O36	115	-0.388544	16
116	O37	116	-0.493894	16
117	C72	117	0.348451	12.01
118	C73	118	0.304567	12.01
119	O38	119	-0.478462	16
120	C74	120	0.809402	12.01
121	O39	121	-0.454294	16
122	O40	122	-0.503975	16
123	C75	123	-0.089759	12.01
124	C76	124	-0.087258	12.01
125	C77	125	-0.097136	12.01
126	C78	126	0.239238	12.01

127	C79	127	-0.096484	12.01
128	C80	128	-0.091194	12.01
129	C81	129	0.159929	12.01
130	C82	130	0.193553	12.01
131	O41	131	-0.423964	16
132	C83	132	0.849285	12.01
133	O42	133	-0.427833	16
134	O43	134	-0.509598	16
135	C84	135	-0.296869	12.01
136	C85	136	0.726458	12.01
137	O44	137	-0.361273	16
138	C86	138	-0.123556	12.01
139	C87	139	0.524601	12.01
140	C88	140	-0.064934	12.01
141	C89	141	0.607999	12.01
142	O45	142	-0.546532	16
143	F7	143	-0.234015	19
144	F8	144	-0.207272	19
145	F9	145	-0.186016	19
146	F10	146	-0.190608	19
147	F11	147	-0.172892	19
148	F12	148	-0.200676	19
149	C90	149	0.304567	12.01
150	C91	150	0.348451	12.01
151	O46	151	-0.454294	16
152	C92	152	0.809402	12.01
153	O47	153	-0.478462	16
154	O48	154	-0.503977	16
155	C93	155	-0.356898	12.01
156	C94	156	-0.099136	12.01
157	H1	157	0.031557	1.008
158	H2	158	0.035516	1.008
159	H3	159	0.030257	1.008
160	H4	160	0.07721	1.008
161	H5	161	-0.010937	1.008
162	H6	162	0.108091	1.008
163	H7	163	0.07721	1.008
164	H8	164	0.106091	1.008
165	H9	165	-0.010937	1.008
166	H10	166	0.089654	1.008
167	H11	167	0.060945	1.008
168	H12	168	0.131791	1.008
169	H13	169	-0.010937	1.008

170	H14	170	0.031557	1.008
171	H15	171	0.035516	1.008
172	H16	172	0.030257	1.008
173	H17	173	0.07721	1.008
174	H18	174	-0.010937	1.008
175	H19	175	0.108091	1.008
176	H20	176	0.07721	1.008
177	H21	177	0.106091	1.008
178	H22	178	-0.010937	1.008
179	H23	179	0.089654	1.008
180	H24	180	0.060945	1.008
181	H25	181	0.131791	1.008
182	H26	182	-0.010937	1.008
183	H27	183	-0.013648	1.008
184	H28	184	-0.013648	1.008
185	H29	185	-0.026535	1.008
186	H30	186	-0.026535	1.008
187	H31	187	0.033308	1.008
188	H32	188	0.033308	1.008
189	H33	189	0.046972	1.008
190	H34	190	0.046972	1.008
191	H35	191	0.045141	1.008
192	H36	192	0.045141	1.008
193	H37	193	0.058934	1.008
194	H38	194	0.058934	1.008
195	H39	195	0.046972	1.008
196	H40	196	0.046972	1.008
197	H41	197	-0.017612	1.008
198	H42	198	-0.017612	1.008
199	H43	199	0.085915	1.008
200	H44	200	0.085915	1.008
201	H45	201	0.07721	1.008
202	H46	202	0.07721	1.008
203	H47	203	0.07721	1.008
204	H48	204	0.045141	1.008
205	H49	205	0.045141	1.008
206	H50	206	0.058934	1.008
207	H51	207	0.058934	1.008
208	H52	208	0.085915	1.008
209	H53	209	0.085915	1.008
210	H54	210	-0.017612	1.008
211	H55	211	-0.017612	1.008
212	H56	212	0.045551	1.008

213	H57	213	0.045551	1.008
214	H58	214	0.017383	1.008
215	H59	215	0.017383	1.008
216	H60	216	0.045141	1.008
217	H61	217	0.045141	1.008
218	H62	218	0.058934	1.008
219	H63	219	0.058934	1.008
220	H64	220	0.046972	1.008
221	H65	221	0.046972	1.008
222	H66	222	0.086608	1.008
223	H67	223	0.086608	1.008
224	H68	224	0.086608	1.008
225	H69	225	0.134909	1.008
226	H70	226	0.134909	1.008
227	H71	227	-0.017612	1.008
228	H72	228	-0.017612	1.008
229	H73	229	0.07721	1.008
230	H74	230	0.07721	1.008
231	H75	231	0.07721	1.008
232	H76	232	0.046972	1.008
233	H77	233	0.046972	1.008
234	H78	234	-0.013648	1.008
235	H79	235	-0.013648	1.008
236	H80	236	-0.026535	1.008
237	H81	237	-0.026535	1.008
238	H82	238	0.033308	1.008
239	H83	239	0.033308	1.008
240	H84	240	0.046972	1.008
241	H85	241	0.046972	1.008
242	H86	242	0.045141	1.008
243	H87	243	0.045141	1.008
244	H88	244	0.058934	1.008
245	H89	245	0.058934	1.008
246	H90	246	0.046972	1.008
247	H91	247	0.046972	1.008
248	H92	248	-0.017612	1.008
249	H93	249	-0.017612	1.008
250	H94	250	0.085915	1.008
251	H95	251	0.085915	1.008
252	H96	252	0.07721	1.008
253	H97	253	0.07721	1.008
254	H98	254	0.07721	1.008
255	H99	255	0.045141	1.008

256	H100	256	0.045141	1.008
257	H101	257	0.058934	1.008
258	H102	258	0.058934	1.008
259	H103	259	0.085915	1.008
260	H104	260	0.085915	1.008
261	H105	261	-0.017612	1.008
262	H106	262	-0.017612	1.008
263	H107	263	0.045551	1.008
264	H108	264	0.045551	1.008
265	H109	265	0.017383	1.008
266	H110	266	0.017383	1.008
267	H111	267	0.045141	1.008
268	H112	268	0.045141	1.008
269	H113	269	0.058934	1.008
270	H114	270	0.058934	1.008
271	H115	271	0.046972	1.008
272	H116	272	0.046972	1.008
273	H117	273	0.086608	1.008
274	H118	274	0.086608	1.008
275	H119	275	0.086608	1.008
276	H120	276	0.134909	1.008
277	H121	277	0.134909	1.008
278	H122	278	-0.017612	1.008
279	H123	279	-0.017612	1.008
280	H124	280	0.07721	1.008
281	H125	281	0.07721	1.008
282	H126	282	0.07721	1.008
283	H127	283	0.046972	1.008
284	H128	284	0.046972	1.008

Table R3. Bond Force Field Parameters of IWSWN-SPE.

Atom <i>i</i>	Atom <i>j</i>	Length (nm)	Force Constant (kJ/mol/nm ²)
1	2	0.15354	191540
1	13	0.15354	191540
1	15	0.15354	191540
1	157	0.10962	288910
2	3	0.14273	236200
2	183	0.10969	288040
2	184	0.10969	288040
3	4	0.16182	324340
4	5	0.16182	324340
4	8	0.14885	479510
4	9	0.16182	324340

5	6	0.14273	236200
6	7	0.15354	191540
6	185	0.10969	288040
6	186	0.10969	288040
7	45	0.15354	191540
7	47	0.15354	191540
7	158	0.10962	288910
9	10	0.14273	236200
10	11	0.15354	191540
10	187	0.10969	288040
10	188	0.10969	288040
11	12	0.15354	191540
11	31	0.15354	191540
11	159	0.10962	288910
12	29	0.15354	191540
12	189	0.10962	288910
12	190	0.10962	288910
13	14	0.15354	191540
13	191	0.10962	288910
13	192	0.10962	288910
14	17	0.15372	190490
14	193	0.10962	288910
14	194	0.10962	288910
15	16	0.15354	191540
15	195	0.10962	288910
15	196	0.10962	288910
16	24	0.15372	190490
16	77	0.15354	191540
16	160	0.10962	288910
17	18	0.15483	184180
17	21	0.14346	230630
17	161	0.10972	287680
18	19	0.14346	230630
18	197	0.10972	287680
18	198	0.10972	287680
19	20	0.13621	293980
20	21	0.13621	293980
20	22	0.1219	494210
23	24	0.15483	184180
23	27	0.14346	230630
23	199	0.10972	287680
23	200	0.10972	287680
24	25	0.14346	230630

24	162	0.10972	287680
25	26	0.13621	293980
26	27	0.13621	293980
26	28	0.1219	494210
29	30	0.15354	191540
29	34	0.15372	190490
29	163	0.10962	288910
30	201	0.10962	288910
30	202	0.10962	288910
30	203	0.10962	288910
31	32	0.15354	191540
31	204	0.10962	288910
31	205	0.10962	288910
32	40	0.15372	190490
32	206	0.10962	288910
32	207	0.10962	288910
33	34	0.15483	184180
33	37	0.14346	230630
33	208	0.10972	287680
33	209	0.10972	287680
34	35	0.14346	230630
34	164	0.10972	287680
35	36	0.13621	293980
36	37	0.13621	293980
36	38	0.1219	494210
39	40	0.15483	184180
39	43	0.14346	230630
39	210	0.10972	287680
39	211	0.10972	287680
40	41	0.14346	230630
40	165	0.10972	287680
41	42	0.13621	293980
42	43	0.13621	293980
42	44	0.1219	494210
45	46	0.15354	191540
45	212	0.10962	288910
45	213	0.10962	288910
46	52	0.15372	190490
46	78	0.15354	191540
46	166	0.10962	288910
47	48	0.15354	191540
47	214	0.10962	288910
47	215	0.10962	288910

48	49	0.15354	191540
48	57	0.15354	191540
48	58	0.1527	196520
49	50	0.15354	191540
49	216	0.10962	288910
49	217	0.10962	288910
50	71	0.15372	190490
50	218	0.10962	288910
50	219	0.10962	288910
51	52	0.15483	184180
51	55	0.14346	230630
51	220	0.10972	287680
51	221	0.10972	287680
52	53	0.14346	230630
52	167	0.10972	287680
53	54	0.13621	293980
54	55	0.13621	293980
54	56	0.1219	494210
57	222	0.10962	288910
57	223	0.10962	288910
57	224	0.10962	288910
58	59	0.13621	293980
58	64	0.1219	494210
59	60	0.14273	236200
60	61	0.15354	191540
60	225	0.10969	288040
60	226	0.10969	288040
61	62	0.15354	191540
61	65	0.13512	279730
61	66	0.13512	279730
62	63	0.15354	191540
62	67	0.13512	279730
62	168	0.10969	288040
63	68	0.13512	279730
63	69	0.13512	279730
63	70	0.13512	279730
71	72	0.15483	184180
71	75	0.14346	230630
71	169	0.10972	287680
72	73	0.14346	230630
72	227	0.10972	287680
72	228	0.10972	287680
73	74	0.13621	293980

74	75	0.13621	293980
74	76	0.1219	494210
77	229	0.10962	288910
77	230	0.10962	288910
77	231	0.10962	288910
78	156	0.15354	191540
78	232	0.10962	288910
78	233	0.10962	288910
79	80	0.15354	191540
79	91	0.15354	191540
79	93	0.15354	191540
79	170	0.10962	288910
80	81	0.14273	236200
80	234	0.10969	288040
80	235	0.10969	288040
81	82	0.16182	324340
82	83	0.16182	324340
82	86	0.14885	479510
82	87	0.16182	324340
83	84	0.14273	236200
84	85	0.15354	191540
84	236	0.10969	288040
84	237	0.10969	288040
85	123	0.15354	191540
85	125	0.15354	191540
85	171	0.10962	288910
87	88	0.14273	236200
88	89	0.15354	191540
88	238	0.10969	288040
88	239	0.10969	288040
89	90	0.15354	191540
89	109	0.15354	191540
89	172	0.10962	288910
90	107	0.15354	191540
90	240	0.10962	288910
90	241	0.10962	288910
91	92	0.15354	191540
91	242	0.10962	288910
91	243	0.10962	288910
92	95	0.15372	190490
92	244	0.10962	288910
92	245	0.10962	288910
93	94	0.15354	191540

93	246	0.10962	288910
93	247	0.10962	288910
94	102	0.15372	190490
94	155	0.15354	191540
94	173	0.10962	288910
95	96	0.15483	184180
95	99	0.14346	230630
95	174	0.10972	287680
96	97	0.14346	230630
96	248	0.10972	287680
96	249	0.10972	287680
97	98	0.13621	293980
98	99	0.13621	293980
98	100	0.1219	494210
101	102	0.15483	184180
101	105	0.14346	230630
101	250	0.10972	287680
101	251	0.10972	287680
102	103	0.14346	230630
102	175	0.10972	287680
103	104	0.13621	293980
104	105	0.13621	293980
104	106	0.1219	494210
107	108	0.15354	191540
107	112	0.15372	190490
107	176	0.10962	288910
108	252	0.10962	288910
108	253	0.10962	288910
108	254	0.10962	288910
109	110	0.15354	191540
109	255	0.10962	288910
109	256	0.10962	288910
110	118	0.15372	190490
110	257	0.10962	288910
110	258	0.10962	288910
111	112	0.15483	184180
111	115	0.14346	230630
111	259	0.10972	287680
111	260	0.10972	287680
112	113	0.14346	230630
112	177	0.10972	287680
113	114	0.13621	293980
114	115	0.13621	293980

114	116	0.1219	494210
117	118	0.15483	184180
117	121	0.14346	230630
117	261	0.10972	287680
117	262	0.10972	287680
118	119	0.14346	230630
118	178	0.10972	287680
119	120	0.13621	293980
120	121	0.13621	293980
120	122	0.1219	494210
123	124	0.15354	191540
123	263	0.10962	288910
123	264	0.10962	288910
124	130	0.15372	190490
124	156	0.15354	191540
124	179	0.10962	288910
125	126	0.15354	191540
125	265	0.10962	288910
125	266	0.10962	288910
126	127	0.15354	191540
126	135	0.15354	191540
126	136	0.1527	196520
127	128	0.15354	191540
127	267	0.10962	288910
127	268	0.10962	288910
128	149	0.15372	190490
128	269	0.10962	288910
128	270	0.10962	288910
129	130	0.15483	184180
129	133	0.14346	230630
129	271	0.10972	287680
129	272	0.10972	287680
130	131	0.14346	230630
130	180	0.10972	287680
131	132	0.13621	293980
132	133	0.13621	293980
132	134	0.1219	494210
135	273	0.10962	288910
135	274	0.10962	288910
135	275	0.10962	288910
136	137	0.13621	293980
136	142	0.1219	494210
137	138	0.14273	236200

138	139	0.15354	191540
138	276	0.10969	288040
138	277	0.10969	288040
139	140	0.15354	191540
139	143	0.13512	279730
139	144	0.13512	279730
140	141	0.15354	191540
140	145	0.13512	279730
140	181	0.10969	288040
141	146	0.13512	279730
141	147	0.13512	279730
141	148	0.13512	279730
149	150	0.15483	184180
149	153	0.14346	230630
149	182	0.10972	287680
150	151	0.14346	230630
150	278	0.10972	287680
150	279	0.10972	287680
151	152	0.13621	293980
152	153	0.13621	293980
152	154	0.1219	494210
155	280	0.10962	288910
155	281	0.10962	288910
155	282	0.10962	288910
156	283	0.10962	288910
156	284	0.10962	288910

Table R4. Angle Force Field Parameters of IWSWN-SPE.

Atom <i>i</i>	Atom <i>j</i>	Atom <i>k</i>	Angle (deg)
1	2	3	107.62
1	2	183	109.59
1	2	184	109.59
1	13	14	112.63
1	13	191	109.68
1	13	192	109.68
1	15	16	112.63
1	15	195	109.68
1	15	196	109.68
2	1	13	112.63
2	1	15	112.63
2	1	157	109.68
2	3	4	119.7
3	2	183	110.34

3	2	184	110.34
3	4	5	101.72
3	4	8	115.44
3	4	9	101.72
4	5	6	119.7
4	9	10	119.7
5	4	8	115.44
5	4	9	101.72
5	6	7	107.62
5	6	185	110.34
5	6	186	110.34
6	7	45	112.63
6	7	47	112.63
6	7	158	109.68
7	6	185	109.59
7	6	186	109.59
7	45	46	112.63
7	45	212	109.68
7	45	213	109.68
7	47	48	112.63
7	47	214	109.68
7	47	215	109.68
8	4	9	115.44
9	10	11	107.62
9	10	187	110.34
9	10	188	110.34
10	11	12	112.63
10	11	31	112.63
10	11	159	109.68
11	10	187	109.59
11	10	188	109.59
11	12	29	112.63
11	12	189	109.68
11	12	190	109.68
11	31	32	112.63
11	31	204	109.68
11	31	205	109.68
12	11	31	112.63
12	11	159	109.68
12	29	30	112.63
12	29	34	113.7
12	29	163	109.68
13	1	15	112.63

13	1	157	109.68
13	14	17	113.7
13	14	193	109.68
13	14	194	109.68
14	13	191	109.68
14	13	192	109.68
14	17	18	113.6
14	17	21	108.97
14	17	161	109.24
15	1	157	109.68
15	16	24	113.7
15	16	77	112.63
15	16	160	109.68
16	15	195	109.68
16	15	196	109.68
16	24	23	113.6
16	24	25	108.97
16	24	162	109.24
16	77	229	109.68
16	77	230	109.68
16	77	231	109.68
17	14	193	110.53
17	14	194	110.53
17	18	19	106.14
17	18	197	111.17
17	18	198	111.17
17	21	20	110.93
18	17	21	106.14
18	17	161	111.17
18	19	20	110.93
19	18	197	108.46
19	18	198	108.46
19	20	21	111.29
19	20	22	123.2
21	17	161	108.46
21	20	22	123.2
23	24	25	106.14
23	24	162	111.17
23	27	26	110.93
24	16	77	113.7
24	16	160	110.53
24	23	27	106.14
24	23	199	111.17

24	23	200	111.17
24	25	26	110.93
25	24	162	108.46
25	26	27	111.29
25	26	28	123.2
27	23	199	108.46
27	23	200	108.46
27	26	28	123.2
29	12	189	109.68
29	12	190	109.68
29	30	201	109.68
29	30	202	109.68
29	30	203	109.68
29	34	33	113.6
29	34	35	108.97
29	34	164	109.24
30	29	34	113.7
30	29	163	109.68
31	11	159	109.68
31	32	40	113.7
31	32	206	109.68
31	32	207	109.68
32	31	204	109.68
32	31	205	109.68
32	40	39	113.6
32	40	41	108.97
32	40	165	109.24
33	34	35	106.14
33	34	164	111.17
33	37	36	110.93
34	29	163	110.53
34	33	37	106.14
34	33	208	111.17
34	33	209	111.17
34	35	36	110.93
35	34	164	108.46
35	36	37	111.29
35	36	38	123.2
37	33	208	108.46
37	33	209	108.46
37	36	38	123.2
39	40	41	106.14
39	40	165	111.17

39	43	42	110.93
40	32	206	110.53
40	32	207	110.53
40	39	43	106.14
40	39	210	111.17
40	39	211	111.17
40	41	42	110.93
41	40	165	108.46
41	42	43	111.29
41	42	44	123.2
43	39	210	108.46
43	39	211	108.46
43	42	44	123.2
45	7	47	112.63
45	7	158	109.68
45	46	52	113.7
45	46	78	112.63
45	46	166	109.68
46	45	212	109.68
46	45	213	109.68
46	52	51	113.6
46	52	53	108.97
46	52	167	109.24
46	78	156	112.63
46	78	232	109.68
46	78	233	109.68
47	7	158	109.68
47	48	49	112.63
47	48	57	112.63
47	48	58	111.43
48	47	214	109.68
48	47	215	109.68
48	49	50	112.63
48	49	216	109.68
48	49	217	109.68
48	57	222	109.68
48	57	223	109.68
48	57	224	109.68
48	58	59	110.8
48	58	64	122.9
49	48	57	112.63
49	48	58	111.43
49	50	71	113.7

49	50	218	109.68
49	50	219	109.68
50	49	216	109.68
50	49	217	109.68
50	71	72	113.6
50	71	75	108.97
50	71	169	109.24
51	52	53	106.14
51	52	167	111.17
51	55	54	110.93
52	46	78	113.7
52	46	166	110.53
52	51	55	106.14
52	51	220	111.17
52	51	221	111.17
52	53	54	110.93
53	52	167	108.46
53	54	55	111.29
53	54	56	123.2
55	51	220	108.46
55	51	221	108.46
55	54	56	123.2
57	48	58	111.43
58	59	60	115.82
59	58	64	123.2
59	60	61	107.62
59	60	225	110.34
59	60	226	110.34
60	61	62	112.63
60	61	65	109.48
60	61	66	109.48
61	60	225	109.59
61	60	226	109.59
61	62	63	112.63
61	62	67	109.48
61	62	168	109.59
62	61	65	109.48
62	61	66	109.48
62	63	68	109.48
62	63	69	109.48
62	63	70	109.48
63	62	67	109.48
63	62	168	109.59

65	61	66	107.37
67	62	168	108.28
68	63	69	107.37
68	63	70	107.37
69	63	70	107.37
71	50	218	110.53
71	50	219	110.53
71	72	73	106.14
71	72	227	111.17
71	72	228	111.17
71	75	74	110.93
72	71	75	106.14
72	71	169	111.17
72	73	74	110.93
73	72	227	108.46
73	72	228	108.46
73	74	75	111.29
73	74	76	123.2
75	71	169	108.46
75	74	76	123.2
77	16	160	109.68
78	46	166	109.68
78	156	124	112.63
78	156	283	109.68
78	156	284	109.68
79	80	81	107.62
79	80	234	109.59
79	80	235	109.59
79	91	92	112.63
79	91	242	109.68
79	91	243	109.68
79	93	94	112.63
79	93	246	109.68
79	93	247	109.68
80	79	91	112.63
80	79	93	112.63
80	79	170	109.68
80	81	82	119.7
81	80	234	110.34
81	80	235	110.34
81	82	83	101.72
81	82	86	115.44
81	82	87	101.72

82	83	84	119.7
82	87	88	119.7
83	82	86	115.44
83	82	87	101.72
83	84	85	107.62
83	84	236	110.34
83	84	237	110.34
84	85	123	112.63
84	85	125	112.63
84	85	171	109.68
85	84	236	109.59
85	84	237	109.59
85	123	124	112.63
85	123	263	109.68
85	123	264	109.68
85	125	126	112.63
85	125	265	109.68
85	125	266	109.68
86	82	87	115.44
87	88	89	107.62
87	88	238	110.34
87	88	239	110.34
88	89	90	112.63
88	89	109	112.63
88	89	172	109.68
89	88	238	109.59
89	88	239	109.59
89	90	107	112.63
89	90	240	109.68
89	90	241	109.68
89	109	110	112.63
89	109	255	109.68
89	109	256	109.68
90	89	109	112.63
90	89	172	109.68
90	107	108	112.63
90	107	112	113.7
90	107	176	109.68
91	79	93	112.63
91	79	170	109.68
91	92	95	113.7
91	92	244	109.68
91	92	245	109.68

92	91	242	109.68
92	91	243	109.68
92	95	96	113.6
92	95	99	108.97
92	95	174	109.24
93	79	170	109.68
93	94	102	113.7
93	94	155	112.63
93	94	173	109.68
94	93	246	109.68
94	93	247	109.68
94	102	101	113.6
94	102	103	108.97
94	102	175	109.24
94	155	280	109.68
94	155	281	109.68
94	155	282	109.68
95	92	244	110.53
95	92	245	110.53
95	96	97	106.14
95	96	248	111.17
95	96	249	111.17
95	99	98	110.93
96	95	99	106.14
96	95	174	111.17
96	97	98	110.93
97	96	248	108.46
97	96	249	108.46
97	98	99	111.29
97	98	100	123.2
99	95	174	108.46
99	98	100	123.2
101	102	103	106.14
101	102	175	111.17
101	105	104	110.93
102	94	155	113.7
102	94	173	110.53
102	101	105	106.14
102	101	250	111.17
102	101	251	111.17
102	103	104	110.93
103	102	175	108.46
103	104	105	111.29

103	104	106	123.2
105	101	250	108.46
105	101	251	108.46
105	104	106	123.2
107	90	240	109.68
107	90	241	109.68
107	108	252	109.68
107	108	253	109.68
107	108	254	109.68
107	112	111	113.6
107	112	113	108.97
107	112	177	109.24
108	107	112	113.7
108	107	176	109.68
109	89	172	109.68
109	110	118	113.7
109	110	257	109.68
109	110	258	109.68
110	109	255	109.68
110	109	256	109.68
110	118	117	113.6
110	118	119	108.97
110	118	178	109.24
111	112	113	106.14
111	112	177	111.17
111	115	114	110.93
112	107	176	110.53
112	111	115	106.14
112	111	259	111.17
112	111	260	111.17
112	113	114	110.93
113	112	177	108.46
113	114	115	111.29
113	114	116	123.2
115	111	259	108.46
115	111	260	108.46
115	114	116	123.2
117	118	119	106.14
117	118	178	111.17
117	121	120	110.93
118	110	257	110.53
118	110	258	110.53
118	117	121	106.14

118	117	261	111.17
118	117	262	111.17
118	119	120	110.93
119	118	178	108.46
119	120	121	111.29
119	120	122	123.2
121	117	261	108.46
121	117	262	108.46
121	120	122	123.2
123	85	125	112.63
123	85	171	109.68
123	124	130	113.7
123	124	156	112.63
123	124	179	109.68
124	123	263	109.68
124	123	264	109.68
124	130	129	113.6
124	130	131	108.97
124	130	180	109.24
124	156	283	109.68
124	156	284	109.68
125	85	171	109.68
125	126	127	112.63
125	126	135	112.63
125	126	136	111.43
126	125	265	109.68
126	125	266	109.68
126	127	128	112.63
126	127	267	109.68
126	127	268	109.68
126	135	273	109.68
126	135	274	109.68
126	135	275	109.68
126	136	137	110.8
126	136	142	122.9
127	126	135	112.63
127	126	136	111.43
127	128	149	113.7
127	128	269	109.68
127	128	270	109.68
128	127	267	109.68
128	127	268	109.68
128	149	150	113.6

128	149	153	108.97
128	149	182	109.24
129	130	131	106.14
129	130	180	111.17
129	133	132	110.93
130	124	156	113.7
130	124	179	110.53
130	129	133	106.14
130	129	271	111.17
130	129	272	111.17
130	131	132	110.93
131	130	180	108.46
131	132	133	111.29
131	132	134	123.2
133	129	271	108.46
133	129	272	108.46
133	132	134	123.2
135	126	136	111.43
136	137	138	115.82
137	136	142	123.2
137	138	139	107.62
137	138	276	110.34
137	138	277	110.34
138	139	140	112.63
138	139	143	109.48
138	139	144	109.48
139	138	276	109.59
139	138	277	109.59
139	140	141	112.63
139	140	145	109.48
139	140	181	109.59
140	139	143	109.48
140	139	144	109.48
140	141	146	109.48
140	141	147	109.48
140	141	148	109.48
141	140	145	109.48
141	140	181	109.59
143	139	144	107.37
145	140	181	108.28
146	141	147	107.37
146	141	148	107.37
147	141	148	107.37

149	128	269	110.53
149	128	270	110.53
149	150	151	106.14
149	150	278	111.17
149	150	279	111.17
149	153	152	110.93
150	149	153	106.14
150	149	182	111.17
150	151	152	110.93
151	150	278	108.46
151	150	279	108.46
151	152	153	111.29
151	152	154	123.2
153	149	182	108.46
153	152	154	123.2
155	94	173	109.68
156	78	232	109.68
156	78	233	109.68
156	124	179	109.68
183	2	184	108.55
185	6	186	108.55
187	10	188	108.55
189	12	190	107.73
191	13	192	107.73
193	14	194	107.73
195	15	196	107.73
197	18	198	108.13
199	23	200	108.13
201	30	202	107.73
201	30	203	107.73
202	30	203	107.73
204	31	205	107.73
206	32	207	107.73
208	33	209	108.13
210	39	211	108.13
212	45	213	107.73
214	47	215	107.73
216	49	217	107.73
218	50	219	107.73
220	51	221	108.13
222	57	223	107.73
222	57	224	107.73
223	57	224	107.73

225	60	226	108.55
227	72	228	108.13
229	77	230	107.73
229	77	231	107.73
230	77	231	107.73
232	78	233	107.73
234	80	235	108.55
236	84	237	108.55
238	88	239	108.55
240	90	241	107.73
242	91	243	107.73
244	92	245	107.73
246	93	247	107.73
248	96	249	108.13
250	101	251	108.13
252	108	253	107.73
252	108	254	107.73
253	108	254	107.73
255	109	256	107.73
257	110	258	107.73
259	111	260	108.13
261	117	262	108.13
263	123	264	107.73
265	125	266	107.73
267	127	268	107.73
269	128	270	107.73
271	129	272	108.13
273	135	274	107.73
273	135	275	107.73
274	135	275	107.73
276	138	277	108.55
278	150	279	108.13
280	155	281	107.73
280	155	282	107.73
281	155	282	107.73
283	156	284	107.73

Table R5. Dihedral Force Field Parameters of IWSWN-SPE.

Atom <i>i</i>	Atom <i>j</i>	Atom <i>k</i>	Atom <i>l</i>	Phase/Constant
1	2	3	4	0
1	2	3	4	180
1	13	14	17	0
1	13	14	193	0

1	13	14	194	0
1	15	16	24	0
1	15	16	77	0
1	15	16	160	0
2	1	13	14	0
2	1	13	191	0
2	1	13	192	0
2	1	15	16	0
2	1	15	195	0
2	1	15	196	0
2	3	4	5	0
2	3	4	8	0
2	3	4	8	0
2	3	4	9	0
3	4	5	6	0
3	4	9	10	0
4	3	2	183	0
4	3	2	184	0
4	5	6	7	0
4	5	6	7	180
4	5	6	185	0
4	5	6	186	0
4	9	10	11	0
4	9	10	11	180
4	9	10	187	0
4	9	10	188	0
5	4	9	10	0
5	6	7	45	0
5	6	7	47	0
5	6	7	158	0
5	6	7	158	0
6	5	4	8	0
6	5	4	8	0
6	5	4	9	0
6	7	45	46	0
6	7	45	212	0
6	7	45	213	0
6	7	47	48	0
6	7	47	214	0
6	7	47	215	0
7	45	46	52	0
7	45	46	78	0
7	45	46	166	0

7	47	48	49	0
7	47	48	57	0
7	47	48	58	0
7	47	48	58	0
7	47	48	58	180
8	4	9	10	0
8	4	9	10	0
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267	127	128	270	0
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