nature portfolio

Peer Review File

Overcoming polarization-breakdown trade-off via hydrogen bonding-modulated molecular stacking in high-temperature high-energy-density flexible dielectric

Corresponding Author: Professor Zhi-Min Dang

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)
This manuscript reports a hydrogen bonding-modulated molecular stacking strategy for high-temperature polyetherimide (PEI) dielectric polymers. By simultaneously introducing hydrogen bond donors and bulky trifluoromethyl groups into the polymer backbone, the authors regulate intermolecular interactions and molecular packing, leading to enhanced dielectric polarization, breakdown strength and high-temperature energy-storage performance. The manuscript is well organized, the proposed molecular design is interesting, and the obtained dielectric performance is competitive with previously reported intrinsic high-temperature polymer dielectrics. Overall, this work demonstrates good scientific significance and application potential. However, the following issues should be clarified before the manuscript can be considered for publication.

1. The as-prepared PEI dielectric film is expected to remain soluble because no permanent covalent crosslinking is introduced. Since the Introduction highlights the reprocessability of hydrogen-bonded polymers, the authors are encouraged to demonstrate the recyclability of the dielectric films by redissolving the PEI films in an appropriate solvent, recasting new films, and comparing their dielectric and energy-storage performance before and after reprocessing.

2. The optimized dielectric performance is achieved at 75 mol% 6FAP, whereas the corresponding P6FDAM and PBAP systems exhibit optimum performance at full comonomer content. The physical origin of this optimum composition is insufficiently discussed. In particular, the role of the remaining 25 mol% ODA segments in regulating molecular packing, free volume and charge transport should be further clarified.

3. The introduction of hydroxyl groups increases the surface hydrophilicity of the polymer, as confirmed by the contact-angle measurements. In general, enhanced hydrophilicity is expected to increase moisture absorption, which may lead to elevated leakage current, increased conduction loss, and deterioration of dielectric energy-storage performance. However, such adverse effects are not observed in the present work. The authors are encouraged to discuss the underlying reasons and clarify how the proposed molecular design mitigates the potentially negative influence of increased hydrophilicity.

4. According to the Experimental Section, the PI films were thermally imidized at a maximum temperature of 250 °C. Additional evidence confirming complete imidization and solvent removal is desirable. Furthermore, the atmosphere employed during thermal imidization (vacuum, nitrogen or other conditions) should be clearly specified to improve the reproducibility of the experimental procedure.

Minor comments
1. The manufacturer and model of the D-E loop measurement system should be provided in the Experimental Section.
2. The abbreviation “6FDA” in Lines 287 and 290 appears to be a typographical error. It should be corrected to “6FAP”.
3. The discussion could be strengthened by further elaborating on the synergistic roles of hydrogen bonding and steric hindrance in regulating intermolecular packing and high-temperature dielectric performance.

Reviewer #2

(Remarks to the Author)
This work presents a well-designed molecular engineering strategy that incorporates hydrogen-bonding donors (–OH) and acceptors (–CF_3) into a PEI backbone to simultaneously enhance dielectric constant and breakdown strength. The optimized material achieves an impressive energy density , along with excellent cycling stability. Through combined DFT, MD simulations, and comprehensive experimental characterizations, the authors convincingly elucidate the roles of hydrogen-bonding networks and steric hindrance in regulating chain packing, trap levels, and charge transport, offering a valuable approach for high-temperature polymer dielectrics. However, several aspects still require further improvement and revision before the manuscript can be considered for publication in this journal.
1，The authors emphasize the "flexibility" of the dielectric films for roll-to-roll processing. However, the introduction of dense hydrogen bonding networks and bulky –CF_3 groups typically increases stiffness and brittleness. The Young's modulus is reported, but the critical parameter for industrial winding processes—elongation at break or foldability—is missing. Please provide stress-strain curves or bending tests to substantiate the "flexible" claim.
2，n Figures 3h and 4g, the discharged energy density (Ue) of 7.34 J/cm^3 is reported with efficiency >90%. It is unclear whether this Ue value corresponds exactly to the breakdown field (Eb) or a slightly lower field to maintain >90% efficiency. Given that efficiency usually drops sharply near breakdown, the exact field corresponding to this Ue must be clearly stated, and the "maximum Ue at 90% efficiency" should be distinguished from the "maximum Ue at breakdown."
3，There is an apparent discrepancy between the DFT-calculated bandgaps and the experimental UV-vis bandgaps. For PBAP, DFT gives 3.18 eV while the experiment gives 3.30 eV (a ~0.12 eV gap). For P6FAP, DFT gives 3.31 eV and experiment gives 3.31 eV (perfect match). The authors claim the same trend, but the deviation for PBAP suggests that the -OH groups might have different electron correlation effects in the solid state than in the isolated chain model. Please discuss this inconsistency and its implications for the charge-trapping mechanism.
4，The film thickness is consistently maintained at 10–15 μm. The breakdown strength of polymers is highly thickness-dependent (thinner films usually exhibit higher Eb). To demonstrate the scalability and industrial relevance, the authors should discuss how the hydrogen-bonding strategy would perform when the film thickness is scaled down to industrial levels (e.g., 3–5 μm) or scaled up, especially regarding the uniformity of the thermal imidization process.

Reviewer #3

(Remarks to the Author)
This manuscript by Yang et al. investigates overcoming the polarization–breakdown trade-off via hydrogen bonding-modulated molecular stacking in high-temperature, high-energy-density flexible dielectrics. By introducing hydrogen bonding and steric hindrance through molecular design, the authors report enhanced breakdown strength and discharged energy density. The topic is interesting, and the reported performance is promising. However, several aspects of the proposed mechanism and the supporting evidence require further clarification before the conclusions can be fully justified. Therefore, I recommend that the manuscript be considered for publication after the following major issues have been addressed.

1. The introduction of different functional groups may influence the polymerization behavior and consequently the molecular weight of the resulting polymers. Since molecular weight can also affect chain packing and dielectric properties, the authors are encouraged to clarify whether the polymers possess comparable molecular weights and molecular weight distributions (e.g., GPC), or discuss whether this factor could contribute to the observed performance differences.
2. Although the authors identify 75-P6FAP as the optimal composition, the molecular basis for its superior dielectric performance remains unclear. Additional discussion or supporting evidence is needed to explain why this specific composition exhibits the highest breakdown strength and discharged energy density.
3. Although molecular dynamics simulations were performed to evaluate the fractional free volume (FFV), the manuscript does not establish a clear correlation between FFV and the measured leakage current or breakdown strength. Further discussion is needed to explain how the variation in FFV influences charge transport and dielectric performance.
4. The d-spacing values of all copolymer compositions (25–85% 6FAP) are larger than those of both pristine PEI and P6FAP. The authors should clarify the origin of this unexpected structural evolution and explain why the copolymerization leads to a larger interchain spacing than either of the two pristine polymers.
5. 75-P6FAP exhibits the highest Young's modulus among the investigated samples. Further discussion is needed to explain, at the molecular level, why this specific copolymer composition exhibits greater resistance to deformation than the other compositions.
6. The high glass-transition temperature (~250 °C) of 75-P6FAP suggests the potential for operation at even higher temperatures. Evaluating its dielectric performance at temperatures closer to Tg would provide a more comprehensive assessment of its practical high-temperature operating capability.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The revised manuscript is significantly improved and meets the standards for publication in Nature Communications. Before final acceptance, I would like the authors to clarify two minor experimental details regarding the reprocessing film preparation. (1) The recycled film was prepared by spin-coating, whereas the original films were fabricated by casting. Why were different fabrication methods used? (2) Since the recycled film requires no additional imidization, a more appropriate

phrasing should be used in the Methods section instead of "imidization procedure".

Reviewer #2

(Remarks to the Author)
I have carefully read the authors' point-by-point response to my previous comments and examined the revised manuscript.I am pleased to state that the authors have addressed all of my concerns in a thorough and thoughtful manner. Their rebuttal letter is clear, well-structured, and provides compelling evidence for each modification.
Given the comprehensive revisions, I am satisfied with the current version. I recommend that the manuscript be accepted for publication in its present form.

Reviewer #3

(Remarks to the Author)
The authors have adequately addressed my concerns and provided reasonable molecular-level explanations for the composition-dependent structural, mechanical, and dielectric properties. The revisions have improved the clarity of the manuscript. I have no further comments.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all my remaining concerns. I have no further questions and recommend the manuscript for publication.

Response Letter to Reviewers

Minhao Yang
PhD, Associate Professor
Department of Electrical Engineering
North China Electric Power University
Beinong road 2, Changping District
Beijing, China, 102206
(86) 10 61771286
minhao.yang@ncepu.edu.cn

Aug 04, 2026

Dear Editor and Reviewers,

Thanks very much for your critical and constructive comments on our manuscript entitled "***Overcoming polarization-breakdown trade-off via hydrogen bonding-modulated molecular stacking in high-temperature high-energy-density flexible dielectric***" *(Manuscript ID: NCOMMS-26-052619)*. These comments are very valuable for us to improve the quality of our manuscript further through this revision. We have carefully addressed your concerns, and the following part is a point-to-point response to your comments and concerns. The revision contents are highlighted in yellow in the **Revised Manuscript** and **Supporting Information**. We sincerely hope that the point-to-point response and revised manuscript have addressed all the concerns raised by reviewers and the revised version is suitable for publication in **Nature Communications**.

Comments from reviewers:

Reviewer #1

Comments:

This manuscript reports a hydrogen bonding-modulated molecular stacking strategy for high-temperature polyetherimide (PEI) dielectric polymers. By simultaneously introducing hydrogen bond donors and bulky trifluoromethyl groups into the polymer backbone, the authors regulate intermolecular interactions and molecular packing, leading to enhanced dielectric polarization, breakdown strength and high-temperature energy-storage performance. The manuscript is well organized, the proposed molecular design is interesting, and the obtained dielectric performance is competitive with previously reported intrinsic high-temperature polymer dielectrics. Overall, this work demonstrates good scientific significance and application potential. However, the following issues should be clarified before the manuscript can be considered for publication.

Our Response: Thank you for your positive comments and valuable suggestions. We have carefully revised the manuscript and supporting information according to your suggestions. Please refer to the replies below.

1. The as-prepared PEI dielectric film is expected to remain soluble because no permanent covalent crosslinking is introduced. Since the Introduction highlights the reprocessability of hydrogen-bonded polymers, the authors are encouraged to demonstrate the recyclability of the dielectric films by redissolving the PEI films in an appropriate solvent, recasting new films, and comparing their dielectric and energy-storage performance before and after reprocessing.

Our Response: Thanks for your valuable suggestion. We have recycled the 75-P6FAP copolymer in NMP solvent and compared its dielectric and energy storage performance before and after reprocessing. As displayed in **Fig. R1**, compared with the original sample (75-P6FAP), the recycled film (R-75-P6FAP) exhibits a slight increase in dielectric constant, which is attributed to the partial destruction of hydrogen bonding network and the generation of free -OH groups. In contrast, the breakdown strength slightly decreases owing to the disruption of hydrogen bonding network. Furthermore, the recycled film achieves a maximum discharged energy density of 6.78 J/cm^3 with an efficiency above 90% at 650 MV/m and 200 °C, retaining 92.37% of the energy density of the original film (**Fig. R2**). The above analysis confirms that the as-prepared PEI dielectric film remains soluble and the recycled sample exhibits excellent capacitive energy storage performance.

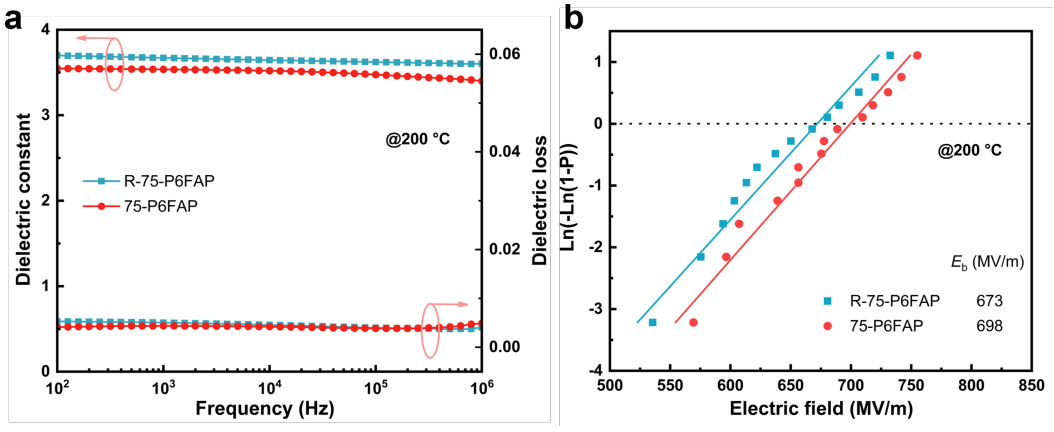

Fig. R1 Comparison of the dielectric properties and breakdown strength of 75-P6FAP copolymer before and after reprocessing.

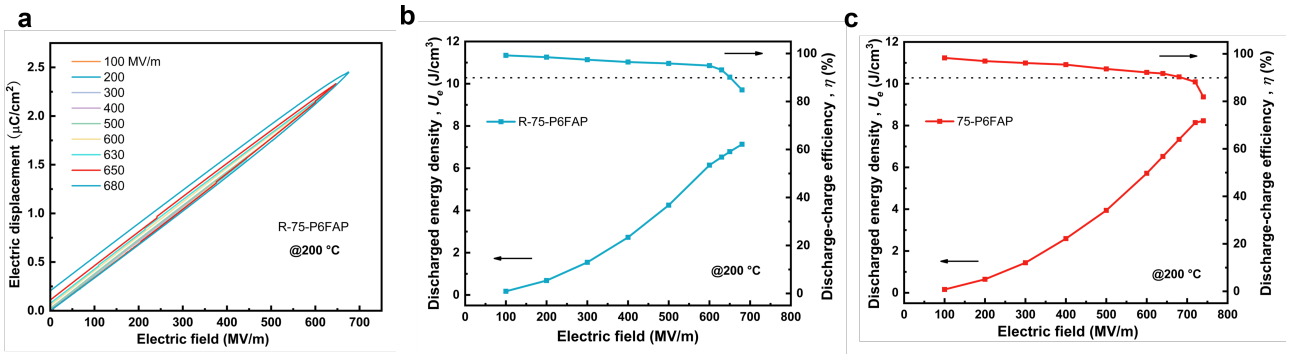

Fig. R2 Comparison of the high-temperature capacitive energy storage performance of 75-P6FAP copolymer before and after reprocessing.

2. The optimized dielectric performance is achieved at 75 mol% 6FAP, whereas the corresponding P6FDAM and PBAP systems exhibit optimum performance at full comonomer content. The physical origin of this optimum composition is insufficiently discussed. In particular, the role of the remaining 25 mol% ODA segments in regulating molecular packing, free volume and charge transport should be further clarified.

Our Response: Thanks for your critical comments. The physical origin of the optimum composition of P6FDAM and PBAP systems has been supplemented in the **Revised manuscript**. As a strong electron-withdrawing group, the -CF_3 groups in P6FDAM reduce the π-electron density of aromatic chains and suppress the formation of intermolecular charge-transfer complexes (CTCs). This effect disrupts continuous π-π stacking, blocks charge tunneling, and enlarges the band gap of polymers. Additionally, the incorporated -CF_3 groups induce abundant deep traps, which effectively capture charge carriers and lower their mobility. Furthermore, the bulky -CF_3 moieties create significant steric hindrance, thereby disturbing ordered molecular chain packing and restricting segmental motion. These synergistic effects greatly inhibit the formation of intermolecular CTCs and improve thermal stability. Consequently, P6FDAM with 100 mol% 6FDAM monomer content exhibits optimal insulation performance among all P6FDAM-based copolymers. As for the BAP monomer, the -OH groups introduce abundant intra- and intermolecular hydrogen bonds between -OH and imide carbonyl groups. The constructed hydrogen bonding contributes to tight intermolecular stacking, thereby reducing structural free volume and improving thermal stability. Coupled with the high dielectric constant ascribed to the high polarizability of -OH moieties, PBAP with 100 mol% BAP monomer content exhibits optimal dielectric and insulation performance among all PBAP-based

copolymers. Please refer to the **Revised manuscript**.

In addition, the effect of residual 25 mol% ODA segments on regulating the molecular packing, free volume, and charge transport of P6FAP copolymers has been discussed in the replies below. As shown in **Fig. R3**, the hydrogen bonding density gradually increases with the 6FAP content. Nevertheless, the *d*-spacing first increases and then decreases with increasing 6FAP content. At a low 6FAP monomer fraction, the steric hindrance effect of bulky -CF_3 groups dominates molecular stacking and charge transport behavior due to the limited hydrogen bonding density. With the gradual increase in 6FAP content, the hydrogen bonding network originating from -OH moieties gradually dominates the microstructural evolution and charge transfer. For the 75-P6FAP copolymer, ether linkages in the ODA units act as flexible sites on the rigid copolymer backbone owing to their low rotational barrier. These linkages can enhance polymer segmental mobility and chain conformational freedom, thereby effectively modulating the *d*-spacing. Meanwhile, ether moieties can also widen the bandgap of copolymer, which suppresses intermolecular charge transfer and reduces polarization loss. Such features mitigate the unfavorable impacts originating from bulky -CF_3 steric hindrance and robust -OH-based hydrogen bonding network, ultimately leading to balanced molecular stacking and optimized high-temperature dielectric energy storage performance.

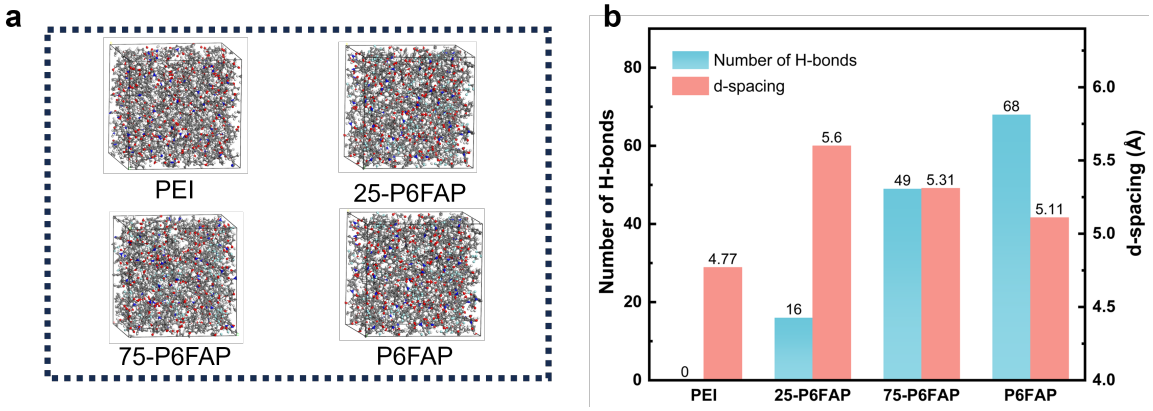

Fig. R3 a MD simulations of P6FAP-based dielectrics. **b** Comparison of the hydrogen bonding density and *d*-spacing of P6FAP copolymers with different contents of 6FAP monomer.

3. The introduction of hydroxyl groups increases the surface hydrophilicity of the polymer, as confirmed by the contact-angle measurements. In general, enhanced hydrophilicity is expected to increase moisture absorption, which may lead to elevated leakage current, increased conduction loss, and deterioration of dielectric energy-storage performance. However, such adverse effects are not

observed in the present work. The authors are encouraged to discuss the underlying reasons and clarify how the proposed molecular design mitigates the potentially negative influence of increased hydrophilicity.

Our Response: Thanks for your valuable comments. The presence of -OH groups inevitably increases the hydrophilicity of the copolymer and may induce moisture absorption, which further increases dielectric loss and degrades insulation performance. Nevertheless, such adverse effects were not observed in this work. Although moisture sensitivity is an unavoidable limitation inherent to the molecular structural design of -OH-containing copolymers, the adverse impacts of water absorption can be effectively eliminated by standardized sample pretreatment and storage protocols. In this contribution, all films were preserved in a vacuum atmosphere before electrical characterization, and additional high-temperature vacuum thermal treatment was performed to completely remove adsorbed water before testing. This rigorous pretreatment effectively eliminates moisture-induced dielectric deterioration during measurement. For industrial metallized film capacitor applications, roll-to-roll metallized films are usually stored under vacuum conditions after metallization. Furthermore, the final capacitors are fully encapsulated with epoxy resin or polyurethane (PU) to block atmospheric moisture penetration. Therefore, the inherent hydrophilic drawback of -OH-containing copolymers can be well inhibited through reasonable process control and encapsulation strategies, ensuring stable dielectric and insulation performance.

4. According to the Experimental Section, the PI films were thermally imidized at a maximum temperature of 250 °C. Additional evidence confirming complete imidization and solvent removal is desirable. Furthermore, the atmosphere employed during thermal imidization (vacuum, nitrogen or other conditions) should be clearly specified to improve the reproducibility of the experimental procedure.

Our Response: Thank you for your valuable suggestion. Complete imidization and solvent removal are verified by the FT-IR spectra and TGA curve. We have systematically monitored the imidization process by analyzing the evolution of amide and imide characteristic peaks in the FT-IR curves. As shown in **Fig. R4**, the amide peak gradually diminishes, while the imide peak emerges as the temperature rises from 80 °C to 250 °C. More importantly, there is no obvious weight loss below 250 °C, demonstrating that residual solvent has been thoroughly removed. The thermal imidization

in this work was carried out under an air atmosphere, and this condition has been specified in the Experimental section. Please refer to the **Revised Manuscript**.

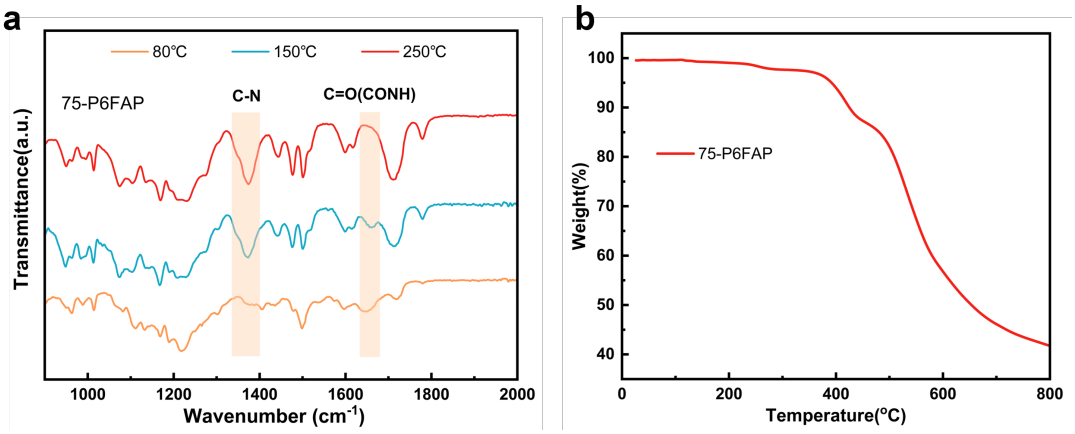

Fig. R4 a FT-IR curves of 75-P6FAP copolymer with different thermal treatment temperatures. **b** TGA curve of 75-P6FAP copolymer.

5. The manufacturer and model of the *D-E* loop measurement system should be provided in the Experimental Section.

Our Response: Thanks for your valuable suggestion. The manufacturer and model of the *D-E* loop measurement system have been indicated in the **Revised Manuscript**. Please refer to the **Revised Manuscript**.

6. The abbreviation “6FDA” in Lines 287 and 290 appears to be a typographical error. It should be corrected to “6FAP”.

Our Response: Thanks for your valuable suggestion. We have corrected this abbreviation. Please refer to the **Revised Manuscript**.

7. The discussion could be strengthened by further elaborating on the synergistic roles of hydrogen bonding and steric hindrance in regulating intermolecular packing and high-temperature dielectric performance.

Our Response: Thanks for your valuable suggestion. We have strengthened the discussion regarding the synergistic effects of hydrogen bonding and steric hindrance. The bulky -CF_3 groups reduce the π-electron density of aromatic chains and suppress the formation of intermolecular charge-transfer complexes (CTCs). This effect disrupts continuous π-π stacking, blocks charge tunneling, and

enlarges the band gap of polymers. Additionally, the incorporated -CF_3 groups introduce abundant deep traps, which effectively capture charge carriers and lower their mobility. Furthermore, the bulky -CF_3 moieties create significant steric hindrance, thereby disturbing ordered molecular chain packing and restricting segmental motion. On the contrary, the -OH groups induce the formation of abundant intra- and intermolecular hydrogen bonds between -OH and imide carbonyl groups. The constructed hydrogen bonding contributes to tight intermolecular stacking, thereby reducing structural free volume and improving thermal stability. Additionally, -OH groups can also increase the dielectric constant due to their high polarizability. These synergistic effects significantly boost the dielectric constant, suppress leakage current, and improve thermal stability, thereby enhancing the insulating properties and high-temperature capacitive energy storage performance. Please refer to the **Revised Manuscript**.

Reviewer #2

Comments:

This work presents a well-designed molecular engineering strategy that incorporates hydrogen-bonding donors (-OH) and acceptors (-CF_3) into a PEI backbone to simultaneously enhance dielectric constant and breakdown strength. The optimized material achieves an impressive energy density, along with excellent cycling stability. Through combined DFT, MD simulations, and comprehensive experimental characterizations, the authors convincingly elucidate the roles of hydrogen-bonding networks and steric hindrance in regulating chain packing, trap levels, and charge transport, offering a valuable approach for high-temperature polymer dielectrics. However, several aspects still require further improvement and revision before the manuscript can be considered for publication in this journal.

Our Response: Thank you for your positive comments and valuable suggestions. We have carefully revised the manuscript and supporting information according to your suggestions. Please refer to the replies below.

1. The authors emphasize the “flexibility” of the dielectric films for roll-to-roll processing. However, the introduction of dense hydrogen bonding networks and bulky -CF_3 groups typically increases stiffness and brittleness. The Young’s modulus is reported, but the critical parameter for industrial winding processes-elongation at break or foldability-is missing. Please provide stress-strain curves or bending tests to substantiate the “flexible” claim.

Our Response: Thanks for your valuable comments. We have supplemented the stress-strain curves of various polymers. As presented in **Fig. R5**, the 75-P6FAP copolymer delivers the highest Young’s modulus and the lowest elongation at break, which is attributed to its dense hydrogen bonding network and steric hindrance of -CF_3 groups. Nevertheless, the 75-P6FAP copolymer film still maintains outstanding flexibility even after repeated bending cycles. These results support our statement that the obtained copolymer films are flexible and potentially compatible with roll-to-roll manufacturing.

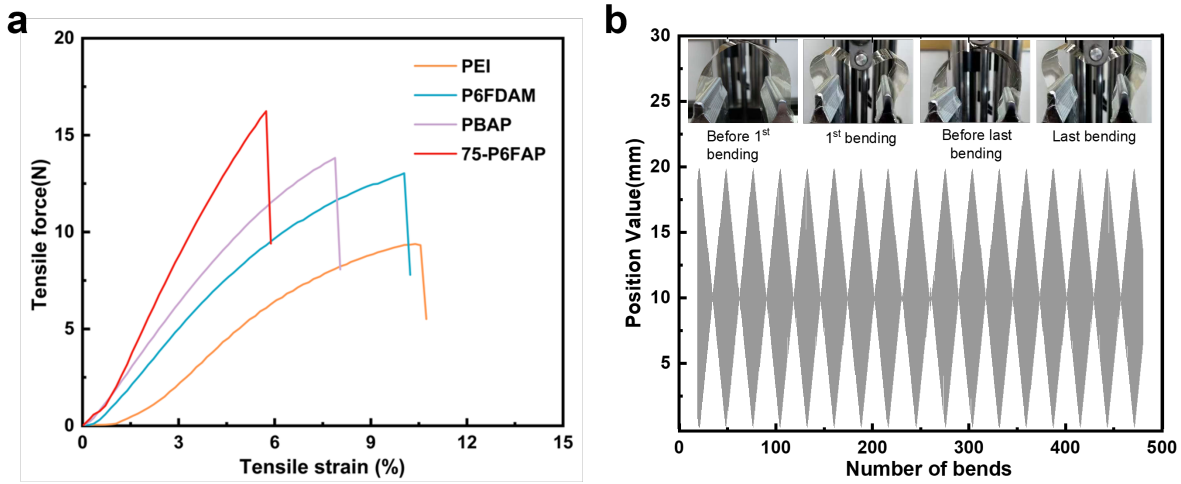

Fig. R5 a Stress-strain curves of various polymers. **b** Bending cycles of 75-P6FAP copolymer.

2. n Figures 3h and 4g, the discharged energy density (U_e) of 7.34 J/cm^3 is reported with efficiency >90%. It is unclear whether this U_e value corresponds exactly to the breakdown field (E_b) or a slightly lower field to maintain >90% efficiency. Given that efficiency usually drops sharply near breakdown, the exact field corresponding to this U_e must be clearly stated, and the "maximum U_e at 90% efficiency" should be distinguished from the "maximum U_e at breakdown."

Our Response: Thanks for your critical comments. We have revised the relevant descriptions and defined the electric field of U_e at 90% efficiency. Please refer to the **Revised Manuscript**.

3. There is an apparent discrepancy between the DFT-calculated bandgaps and the experimental UV-vis bandgaps. For PBAP, DFT gives 3.18 eV while the experiment gives 3.30 eV (a ~0.12 eV gap). For P6FAP, DFT gives 3.31 eV and experiment gives 3.31 eV (perfect match). The authors claim the same trend, but the deviation for PBAP suggests that the -OH groups might have different electron correlation effects in the solid state than in the isolated chain model. Please discuss this inconsistency and its implications for the charge-trapping mechanism.

Our Response: Thanks for your valuable comments. The DFT-calculated bandgaps of pristine PEI, P6FDAM, PBAP, and P6FAP are 3.79 eV, 3.94 eV, 3.18 eV, and 3.55 eV, respectively. The experimentally determined UV-vis bandgaps of the above polymers are 3.37 eV, 3.41 eV, 3.30 eV, and 3.31 eV, respectively. Although there exists an obvious discrepancy in the absolute bandgap values, the bandgap trends obtained from these two approaches are consistent.

4. The film thickness is consistently maintained at 10-15 μm. The breakdown strength of polymers is highly thickness-dependent (thinner films usually exhibit higher E_b). To demonstrate the scalability and industrial relevance, the authors should discuss how the hydrogen-bonding strategy would perform when the film thickness is scaled down to industrial levels (e.g., 3-5 μm) or scaled up, especially regarding the uniformity of the thermal imidization process.

Our Response: Thanks for your valuable suggestion. We have prepared additional samples with different thicknesses and systematically compared their insulation performance and structural evolution as a function of film thickness. As illustrated in **Fig. R6a**, the thinner film indeed exhibits higher breakdown strength relative to the thicker counterpart. Uniform thermal imidization is achieved for both thin and thick samples, as confirmed by the disappearance of the amide characteristic peak at 1680 cm^{-1} (**Fig. R6b**). We further performed variable-temperature infrared spectroscopy (VT-IR) to investigate the hydrogen bonding network in thin and thick films. As displayed in **Fig. R6c-d**, the characteristic absorption band assigned to -OH groups of both samples undergoes a blue shift when the temperature increases from 40 °C to 400 °C. Meanwhile, the peak intensity corresponding to free -OH species rises with temperature. Higher temperatures induce a strong thermal motion of macromolecular chains, which significantly weakens and breaks hydrogen bonding interactions. The dissociation of hydrogen bonding releases free -OH groups, thereby enhancing the stretching vibration signal of free -OH. The above results verify that the thermal treatment procedure adopted in this work enables uniform imidization, and the construction of hydrogen bonding network can be achieved even for thicker films.

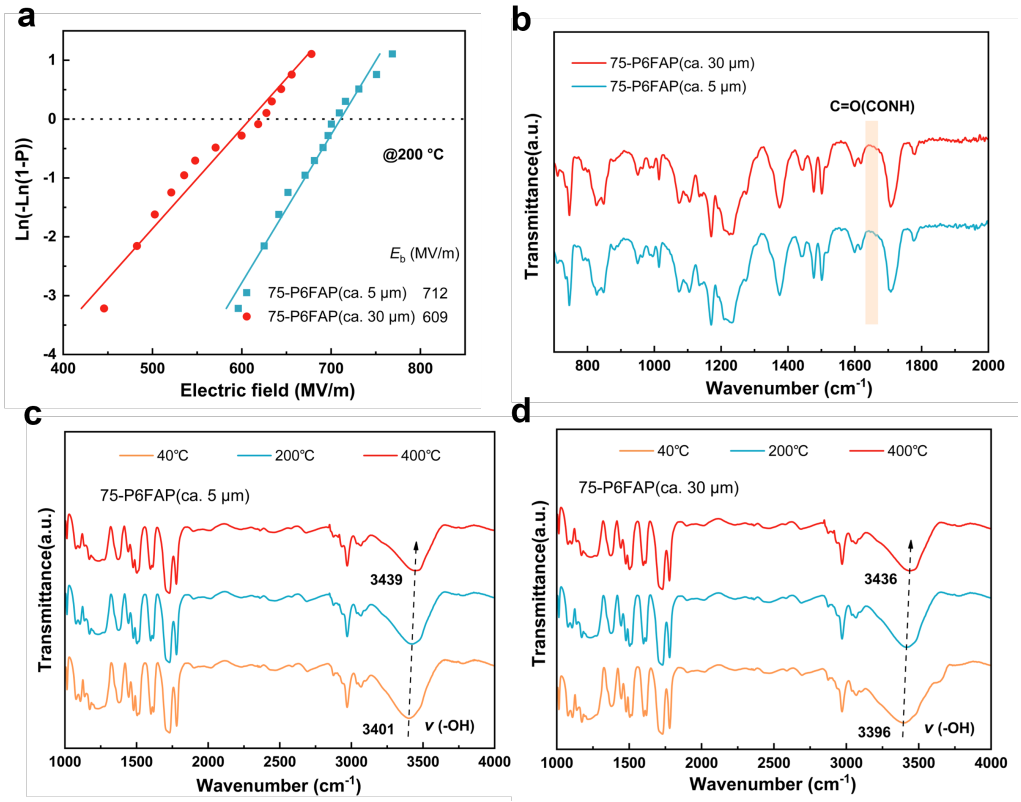

Fig. R6 a Weibull distribution of breakdown strength and **b** FT-IR spectra of 75-P6FAP copolymer films with different thicknesses. VT-IR spectra of the 75-P6FAP copolymer films with **c** small thickness and **d** large thickness.

Reviewer #3

Comments:

This manuscript by Yang et al. investigates overcoming the polarization-breakdown trade-off via hydrogen bonding-modulated molecular stacking in high-temperature, high-energy-density flexible dielectrics. By introducing hydrogen bonding and steric hindrance through molecular design, the authors report enhanced breakdown strength and discharged energy density. The topic is interesting, and the reported performance is promising. However, several aspects of the proposed mechanism and the supporting evidence require further clarification before the conclusions can be fully justified. Therefore, I recommend that the manuscript be considered for publication after the following major issues have been addressed.

Our Response: Thanks for your positive comments on our manuscript. We have made a careful revision to our manuscript and supporting information. Please refer to the replies below.

1. The introduction of different functional groups may influence the polymerization behavior and consequently the molecular weight of the resulting polymers. Since molecular weight can also affect chain packing and dielectric properties, the authors are encouraged to clarify whether the polymers possess comparable molecular weights and molecular weight distributions (e.g., GPC), or discuss whether this factor could contribute to the observed performance differences.

Our Response: Thanks for your useful suggestions. Accordingly, gel permeation chromatography (GPC) measurements were carried out to analyze the molecular weight characteristics of various polymers. As shown in **Table. R1**, pristine PEI possesses the highest molecular weight, while P6FAP shows the lowest value among all samples. Indeed, molecular weight plays a vital role in regulating the molecular chain stacking and dielectric properties of polymers. Polymers with low molecular weight have shorter molecular chains and higher conformational freedom. Nevertheless, abundant chain-end defects hinder the formation of long-range ordered stacking, resulting in loose chain packing. Moreover, excessively low molecular weight leads to insufficient mechanical and insulating strength due to inadequate chain entanglement. Therefore, constructing stable interchain interactions is critical to optimizing chain packing structure and improving both mechanical robustness and electrical insulation performance for the low-molecular-weight polymers. With increasing molecular

weight, the reduction of chain-end defects favors compact chain packing. Although high molecular weight is beneficial to improving the mechanical strength and insulation properties, excessive molecular weight causes severe chain entanglement, which impedes chain segment rearrangement and suppresses further densification of molecular stacking. In our work, owing to the synergistic effects of steric hindrance and electronic induction from -CF_3 and -OH groups, the 6FAP monomer exhibits the weakest electron-donating ability and chemical reactivity. This further reduces its degree of polymerization and molecular weight, thereby endowing the P6FAP polymer with the lowest molecular weight among all samples. By copolymerizing with a certain proportion of ODA monomers, the molecular weight of 75-P6FAP is effectively increased. Although P6FAP-based polymers possess a relatively low molecular weight, their mechanical strength, thermal stability, and dielectric performance are significantly improved. This further demonstrates that the constructed hydrogen bonding network effectively facilitates molecular stacking, compensating for the deficiencies caused by low molecular weight and promoting dielectric performance enhancement.

Table. R1 GPC results for various polymers

Samples	M_n (×10^4 g/mol)	M_w (×10^4 g/mol)	PDI
PEI	20.15	80.11	3.97
P6FDAM	16.05	42.82	2.66
PBAP	13.40	38.16	2.84
P6FAP	5.10	16.00	3.13
75-P6FAP	5.11	17.63	3.45

2. Although the authors identify 75-P6FAP as the optimal composition, the molecular basis for its superior dielectric performance remains unclear. Additional discussion or supporting evidence is needed to explain why this specific composition exhibits the highest breakdown strength and discharged energy density.

Our Response: Thanks for your constructive comments. The superior insulation performance of 75-P6FAP originates from the synergistic effect of hydrogen bonding network and steric hindrance. At a low 6FAP content, the bulky -CF_3 groups dominate molecular stacking and charge transport behavior owing to the limited hydrogen bonding density. The bulky -CF_3 groups reduce the π-electron density of aromatic chains and suppress the formation of intermolecular charge-transfer complexes (CTCs). This effect disrupts continuous π-π stacking, blocks charge tunneling, and enlarges the band gap of polymers. Additionally, the incorporated -CF_3 groups introduce abundant deep traps, which

effectively capture charge carriers and lower their mobility. Furthermore, the bulky -CF_3 moieties create significant steric hindrance, thereby disturbing ordered molecular chain packing and restricting segmental motion. Consequently, the breakdown strength shows a gradual upward trend as the loading of 6FAP monomer increases. With further increasing 6FAP fraction, the density of -OH groups rises significantly. The -OH moieties become predominant in regulating microstructural evolution and charge transport by forming a robust intermolecular hydrogen bonding network. The -OH groups induce the formation of abundant intra- and intermolecular hydrogen bonds between -OH and imide carbonyl groups. The constructed hydrogen bonding contributes to tight intermolecular stacking, thereby enhancing the breakdown strength and thermal stability. However, a dense hydrogen bonding network can also aggravate intermolecular charge transfer, thereby lowering the breakdown strength with further increasing the 6FAP content. Meanwhile, -OH groups can also increase the dielectric constant due to their high polarizability. Additionally, the ether linkages in ODA units act as flexible sites on the rigid copolymer backbone owing to their low rotational barrier. These linkages can enhance polymer segmental mobility and chain conformational freedom, thereby effectively modulating the *d*-spacing. Meanwhile, ether moieties can also widen the bandgap of copolymer, which suppresses intermolecular charge transfer and reduces polarization loss. Such features mitigate the unfavorable impacts originating from bulky -CF_3 steric hindrance and robust -OH-based hydrogen bonding network, ultimately leading to the balanced molecular stacking and optimized high-temperature dielectric energy storage performance. These synergistic effects significantly boost the dielectric constant, suppress leakage current, and improve thermal stability, thereby enhancing the high-temperature capacitive energy storage performance. We have supplemented the above mechanism analysis in the **Revised Manuscript**.

3. Although molecular dynamics simulations were performed to evaluate the fractional free volume (FFV), the manuscript does not establish a clear correlation between FFV and the measured leakage current or breakdown strength. Further discussion is needed to explain how the variation in FFV influences charge transport and dielectric performance.

Our Response: Thanks for your critical suggestions. Loose intermolecular stacking in polymers typically induces the generation of structural voids, thereby contributing to a higher FFV. For aromatic polyimides, insufficient FFV causes tight chain packing, restricts chain segmental motion

yet intensifies dipole aggregation and local electric field concentration. A moderately loose intermolecular stacking can break intermolecular donor-acceptor (D-A) interactions. Accordingly, the elevated FFV originating from this structural feature effectively hinders interchain charge transfer, suppressing charge transport and improving breakdown strength. Nevertheless, excessive disorder in molecular packing creates abundant structural voids and yields an overly high FFV. These voids can serve as transport pathways for charge migration and trigger local electric field concentration, which increases leakage current and deteriorates breakdown strength. A reduction in *d*-spacing reflects tighter molecular packing and a decreased FFV. On this basis, we systematically correlate the molecular stacking behavior with the dielectric and insulation performances of the copolymers. As shown in **Fig. R7**, the hydrogen bonding density gradually increases with the 6FAP content. Nevertheless, the *d*-spacing first increases and then decreases with increasing 6FAP content. At a low 6FAP monomer fraction, the steric hindrance effect of bulky -CF_3 groups dominates molecular stacking and charge transport behavior due to the limited hydrogen bonding density. The bulky -CF_3 groups disrupt continuous π-π stacking, blocks charge tunneling, and enlarges the band gap of polymers. Additionally, the incorporated -CF_3 groups introduce abundant deep traps, which effectively capture charge carriers and lower their mobility. Furthermore, the bulky -CF_3 moieties create significant steric hindrance, thereby disturbing ordered molecular chain packing and restricting segmental motion. Consequently, the breakdown strength shows a gradual upward trend as the loading of 6FAP monomer increases. With further increasing 6FAP fraction, the density of -OH groups rises significantly. The -OH moieties become predominant in regulating microstructural evolution and charge transport by forming a robust intermolecular hydrogen bonding network. The -OH groups induce the formation of abundant intra- and intermolecular hydrogen bonds between -OH and imide carbonyl groups. The constructed hydrogen bonding contributes to tight intermolecular stacking, thereby enhancing the breakdown strength and thermal stability. However, a dense hydrogen bonding network can also aggravate intermolecular charge transfer, thereby lowering the breakdown strength with further increasing 6FAP content.

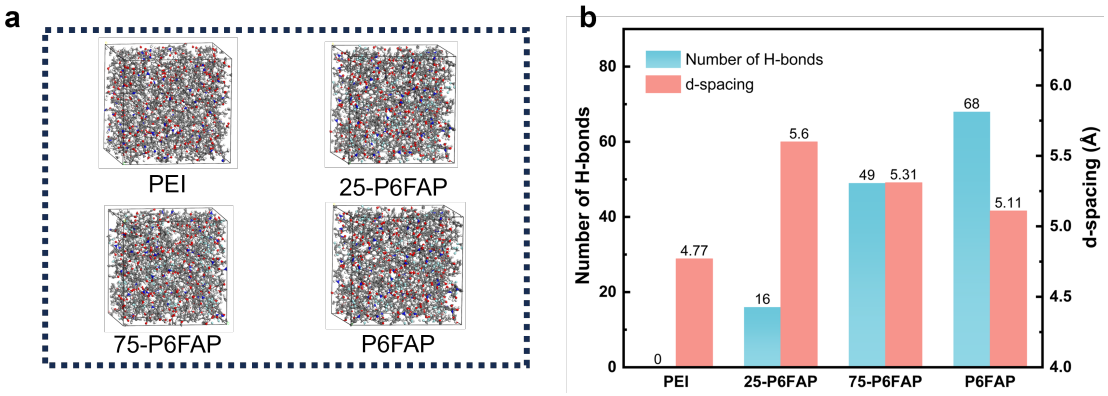

Fig. R7 a MD simulations of P6FAP-based dielectrics. **b** Comparison of the hydrogen bonding density and *d*-spacing of P6FAP copolymers with different contents of 6FAP monomer.

4. The *d*-spacing values of all copolymer compositions (25-85% 6FAP) are larger than those of both pristine PEI and P6FAP. The authors should clarify the origin of this unexpected structural evolution and explain why the copolymerization leads to a larger interchain spacing than either of the two pristine polymers.

Our Response: Thanks for your kind comments. The larger *d*-spacing observed in all 6FAP-containing copolymers, compared with both pristine PEI and pure P6FAP homopolymers, arises from the structural perturbation induced by the random copolymerization process, bulky -CF_3 moieties and flexible ether linkages. In neat homopolymers, the molecular chains possess uniform and regular backbone structures, allowing ordered molecular stacking and tight chain packing. In contrast, the random incorporation of comonomers of 6FAP or ODA units along the backbone breaks the intrinsic structural regularity of the polymer chains. The bulky -CF_3 from 6FAP units introduce strong steric hindrance, while ether linkages from ODA units enhance polymer segmental mobility and chain conformational freedom. The above synergistic effects expand the interchain distance, and consequently increase the *d*-spacing for all copolymer compositions (25-85% 6FAP).

5. 75-P6FAP exhibits the highest Young's modulus among the investigated samples. Further discussion is needed to explain, at the molecular level, why this specific copolymer composition exhibits greater resistance to deformation than the other compositions.

Our Response: Thanks for your valuable suggestion. The excellent Young's modulus and deformation resistance of 75-P6FAP are attributed to the optimal balance between the strong intermolecular hydrogen bonding network and moderate molecular chain spacing. On the one hand,

the appropriate content of -OH groups is helpful to form dense and uniform intermolecular hydrogen bonding network. These reversible hydrogen bonding can act as physical crosslinked points that restrict chain segment motion, effectively improving molecular rigidity and resisting interchain slippage. On the other hand, the incorporation of a suitable amount of bulky -CF_3 and ether linkages weakens the chain stacking and reduces internal structural stress. At lower 6FAP contents, insufficient hydrogen bonding leads to weak physical crosslinking and low structural rigidity. In contrast, an excessive number of -OH groups causes overly tight molecular packing and severe structural inhomogeneity, which introduces residual stress and brittle characteristics, accordingly leading to a reduction in mechanical stiffness. Therefore, the 75-P6FAP copolymer achieves the highest Young's modulus among these samples.

6. The high glass-transition temperature (~250 °C) of 75-P6FAP suggests the potential for operation at even higher temperatures. Evaluating its dielectric performance at temperatures closer to T_g would provide a more comprehensive assessment of its practical high-temperature operating capability.

Our Response: Thanks for your valuable comment. Given that the glass transition temperature of 75-P6FAP reaches 247.3 °C, we have systematically characterized the dielectric spectra, breakdown strength and capacitive energy storage performance at 240 °C. As shown in **Fig. R8**, the dielectric constant increases slightly as temperature rises from 200 °C to 240 °C, which is attributed to the enhanced local motion of polar moieties. However, the breakdown strength decreases markedly at elevated temperatures due to accelerated charge transport. Consequently, the discharged energy density maintained at an efficiency above 90% declines from 7.34 J/cm^3 to 3.17 J/cm^3 when the temperature increases from 200 °C to 240 °C (**Fig. R9**).

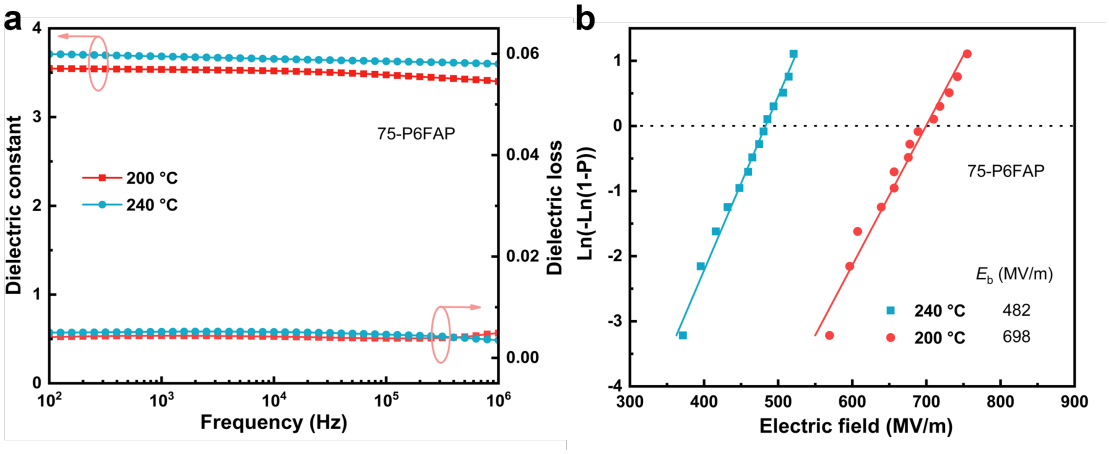

Fig. R8 Comparison of the dielectric properties and breakdown strength of 75-P6FAP copolymer at 200 °C and 240 °C.

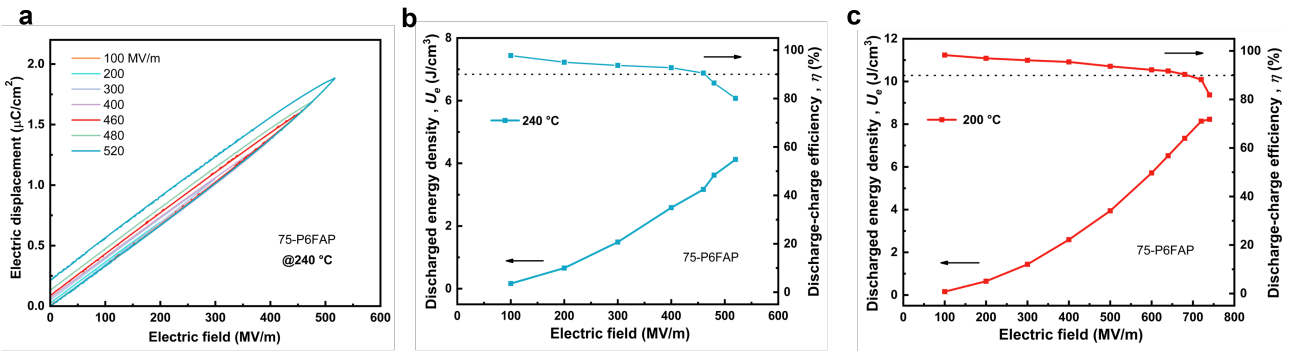

Fig. R9 Comparison of the high-temperature capacitive energy storage performance of 75-P6FAP copolymer at 200 °C and 240 °C.

We feel these changes fully address the Reviewers' comments. Again, we thank the referees for their appreciation of this work. Thank you for your consideration and help with this manuscript. Please feel free to contact me if any additional information is needed for your decision.

Sincerely yours,

Prof. Minhao Yang & Prof. Bobo Tian & Prof. Jun Liu & Prof. Zhi-Min Dang

North China Electric Power University

East China Normal University

Beijing University of Chemical Technology

Tsinghua University

Response Letter to Reviewers

Minhao Yang
PhD, Associate Professor
Department of Electrical Engineering
North China Electric Power University
Beinong road 2, Changping District
Beijing, China, 102206
(86) 10 61771286
minhao.yang@ncepu.edu.cn

Aug 12, 2026

Dear Editor and Reviewers,

Thanks very much for your critical and constructive comments on our revised manuscript entitled "***Overcoming polarization-breakdown trade-off via hydrogen bonding-modulated molecular stacking in high-temperature high-energy-density flexible dielectric***" *(Manuscript ID: NCOMMS-26-052619A)*. These comments are very valuable for us to improve the quality of our manuscript further through this revision. We have carefully addressed your concerns, and the following part is a point-to-point response to your comments and concerns. The revision contents are highlighted in yellow in the **Revised Manuscript** and **Supporting Information**. We sincerely hope that the point-to-point response and revised manuscript have addressed all the concerns raised by reviewers and the revised version is suitable for publication in **Nature Communications**.

Comments from reviewers:

Reviewer #1

Comments:

The revised manuscript is significantly improved and meets the standards for publication in Nature Communications. Before final acceptance, I would like the authors to clarify two minor experimental details regarding the reprocessing film preparation. (1) The recycled film was prepared by spin-coating, whereas the original films were fabricated by casting. Why were different fabrication methods used? (2) Since the recycled film requires no additional imidization, a more appropriate phrasing should be used in the Methods section instead of "imidization procedure".

Our Response: Thank you for your valuable suggestions. We have carefully revised the manuscript and supporting information according to your suggestions. Indeed, the recycled film was fabricated by spin-coating. Our supply of the pristine film was limited, and solution casting for film fabrication

requires a considerable volume of polymer solution with a proper concentration. Accordingly, we fabricated the recycled film by dissolving a small quantity of original film in solvent and then performing spin-coating. Notably, spin-coating was conducted at a low rotational speed of 300 rpm to avoid the orientation of polymer chains. The description regarding thermal treatment conditions of the recycled film has been corrected in the **Revised Manuscript**. Please refer to the **Revised Manuscript**.

Reviewer #2

Comments:

I have carefully read the authors' point-by-point response to my previous comments and examined the revised manuscript.I am pleased to state that the authors have addressed all of my concerns in a thorough and thoughtful manner. Their rebuttal letter is clear, well-structured, and provides compelling evidence for each modification.

Given the comprehensive revisions, I am satisfied with the current version. I recommend that the manuscript be accepted for publication in its present form.

Our Response: Thanks again for your valuable comments, which have significantly improved the quality of our manuscript.

Reviewer #3

Comments:

The authors have adequately addressed my concerns and provided reasonable molecular-level explanations for the composition-dependent structural, mechanical, and dielectric properties. The revisions have improved the clarity of the manuscript. I have no further comments.

Our Response: Thanks again for your valuable comments, which have significantly improved the quality of our manuscript.

We feel these changes fully address the Reviewers' comments. Again, we thank the referees for their appreciation of this work. Thank you for your consideration and help with this manuscript. Please feel free to contact me if any additional information is needed for your decision.

Sincerely yours,

Prof. Minhao Yang & Prof. Bobo Tian & Prof. Jun Liu & Prof. Zhi-Min Dang

North China Electric Power University

East China Normal University

Beijing University of Chemical Technology

Tsinghua University

Response Letter to Reviewers

Minhao Yang
PhD, Associate Professor
Department of Electrical Engineering
North China Electric Power University
Beinong road 2, Changping District
Beijing, China, 102206
(86) 10 61771286
minhao.yang@ncepu.edu.cn

Aug 21, 2026

Dear Editor and Reviewers,

Thanks very much for your critical and constructive comments on our revised manuscript entitled "***Overcoming polarization-breakdown trade-off via hydrogen bonding-modulated molecular stacking in high-temperature high-energy-density flexible dielectric***" *(Manuscript ID: NCOMMS-26-052619B)*. These comments are very valuable for us to improve the quality of our manuscript further through this revision. We have carefully addressed your concerns, and the following part is a point-to-point response to your comments and concerns. The revision contents are highlighted in yellow in the **Revised Manuscript** and **Supporting Information**. We sincerely hope that the point-to-point response and revised manuscript have addressed all the concerns raised by reviewers and the revised version is suitable for publication in **Nature Communications**.

Comments from reviewers:

Reviewer #1

Comments:

The authors have addressed all my remaining concerns. I have no further questions and recommend the manuscript for publication.

Our Response: Thanks again for your valuable comments, which have significantly improved the quality of our manuscript.

We feel these changes fully address the Reviewers' comments. Again, we thank the referees for their appreciation of this work. Thank you for your consideration and help with this manuscript. Please feel free to contact me if any additional information is needed for your decision.

Sincerely yours,

Prof. Minhao Yang & Prof. Bobo Tian & Prof. Jun Liu & Prof. Zhi-Min Dang

North China Electric Power University

East China Normal University

Beijing University of Chemical Technology

Tsinghua University