

Branched-type nanocluster-junction fluorofluidic-gels for interface-adaptive thermal conduction and mechanical resistance

Corresponding Author: Professor Ziguang Zhao

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 proposes an interface-adaptive thermal interface fluorofluidic-gel (TIF) featuring a branched-type nanocluster-junction fluoronetwork. Through elegant molecular design, the authors successfully constructed a temperature-responsive hydrogen-bonding nanocluster network utilizing the urethanization reaction between perfluoropolyether precursors and IPDI. This thermal interface material effectively balances high thermal conductivity (5.89 W/mK) and low contact thermal resistance ($0.15 \text{ cm}^2\cdot\text{K}\cdot\text{W}^{-1}$), presenting significant application prospects in fields such as flexible electronics and electronic packaging. However, prior to formal acceptance, several key issues require further clarification or supplementation by the authors.

1. On page 5, line 127, the thermal conductivity of the TIF was stated as 5.89 W/mK. However, in the performance comparison radar chart in Figure 1e, the thermal conductivity value for the TIF appears to exceed 6 W/mK. The authors are requested to double-check and rectify this discrepancy to ensure the accuracy of the reported values.
2. In Figure 2a, the directional arrows indicating the states below and above the glass transition temperature (T_g) appear to be reversed. It is advised to verify this illustration and ensure it correctly aligns with the textual description in the manuscript.
3. To enhance thermal conductivity, the authors incorporated a high loading of up to 60 wt% Al_2O_3 and MgO composite fillers into the TIF matrix. In practical applications, when the TIF transitions into a fluidic state at high temperatures, is there a risk of these high-density inorganic fillers settling or phase-separating under the influence of gravity or continuous vibration? It is recommended to provide cross-sectional SEM and EDS mapping analyses of the samples after long-term high-temperature treatment to demonstrate the long-term dispersion uniformity of the fillers.
4. Regarding Supplementary Figure 13, it is ambiguous whether the image merely shows the morphology of the standalone Al_2O_3 and MgO composite fillers, or their actual distribution morphology within the TIF matrix. Please clarify this by providing a more explicit description in the figure caption to prevent any potential misunderstandings.
5. Figure 4i demonstrates the thermal cycling performance of TIF0.25 in 100 cycles between 25°C and 85°C . For practical electronic packaging applications, 100 cycles are generally insufficient to meet standard reliability requirements. The authors are advised to refer to existing literature or relevant industry standards and significantly increase the number of thermal cycles in their testing protocol.
6. Following up on the previous point, it is recommended to evaluate and provide the thermal conductivity and adhesion strength of TIF0.25 after the extended long-term thermal cycling tests to robustly substantiate its operational stability.

Reviewer #2

(Remarks to the Author)

In this manuscript, a novel adaptive thermal interface fluorofluidic-gel (TIF) was successfully developed, in which a branched

nanocluster-junction fluoronetwork, constructed from HO-PFPE-OH, PFPE-OH₂ and IPDI, is combined with micro–nano hybrid thermally conductive fillers composed of Al₂O₃ microparticles and MgO nanoparticles. The material is designed to simultaneously exploit the thermoreversible dissociation of hydrogen-bonding nanoclusters for interface-adaptive wetting and gap filling, and the synergistic thermal transport pathways formed by the hybrid fillers for efficient heat conduction. The TIF achieves a combination of high thermal conductivity, low contact thermal resistance, reversible adhesion, mechanical impact resistance, electrical insulation, and broad temperature stability, demonstrating promising potential for thermal management of high-heat-flux electronic devices. However, although the work is technically solid and the multifunctional performance is impressive, the overall advance appears to rely more on an elegant integration and optimization of existing adaptive TIM concepts than on a sufficiently broad conceptual breakthrough or universally impactful mechanism. Therefore, I recommend that the manuscript be reconsidered after major revision.

1.Existing studies on adaptive TIMs, phase-change/flow-state TIMs, and dynamic-network TIMs are already quite extensive, and the fundamental distinction between the present work and prior adaptive thermal interface materials therefore needs to be further clarified. The authors are encouraged to more clearly define the unique aspects of this work in terms of network topology, dynamic response mechanism, and application scope, so as to more convincingly highlight its novelty and academic positioning.

2.For the practical application of TIMs, long-term reliability is a critical metric. The manuscript currently demonstrates stability over only 100 thermal cycles. The authors are therefore encouraged to further provide performance data under prolonged high-temperature and high-pressure conditions over a longer timescale (e.g., 1000 h), in order to determine whether the material may suffer from pump-out effects, interfacial contact failure, or chemical degradation.

3.The thermally responsive phase-transition behavior of the material is fundamental to its ability to reduce contact thermal resistance, and this process is closely related to T_g. Although the Supplementary Information provides T_g data for samples with different matrix compositions, the manuscript does not further discuss the potential influence of high filler loading (up to 60 wt%) on T_g, the phase-transition window, or the phase-transition kinetics.

4.The key advantage of TIF lies in its phase-transition capability above T_g; however, at temperatures below T_g, its thermal resistance remains relatively high. For devices that require frequent cold starts or operate for extended periods under low-power conditions, this initially high thermal resistance may become a performance bottleneck. It would therefore be valuable for the authors to discuss how T_g could be tuned through adjustment of the chemical formulation, so that the thermal-response window can be better matched to the specific operating temperature ranges of different application scenarios.

Reviewer #3

(Remarks to the Author)

This is a well-executed study on thermally adaptive thermal interface materials. The authors present a branched nanocluster-junction fluorofluidic-gel and provide a fairly complete set of data on its structure, adhesion, mechanical buffering, and thermal transport behavior. The idea of coupling thermally responsive interfacial infiltration with thermal resistance reduction is interesting, and the device-level cooling results further support the practical relevance of the work. Overall, I find the manuscript is suitable for publication in Nature Communications after minor revision. My specific comments are provided below.

1. The authors propose that dissociation of the hydrogen-bonding nanoclusters at elevated temperature improves interfacial infiltration and thus lowers the thermal resistance. This mechanism is reasonable. However, the corresponding discussion in the main text could be clarified further, with a more direct connection between the structural characterization, the SEM observations, and the thermal resistance results.

2. The comparison with commercial TIMs is important to the manuscript, but the testing conditions are not always described with sufficient clarity. Key parameters such as sample thickness, applied pressure, and temperature should be stated more explicitly so that readers can better assess the basis of the comparison.

3. The selection of TIF0.25 as the optimal formulation could be explained more clearly. Since different formulations appear to show different advantages in different measurements, a brief summary of why TIF0.25 was chosen as the representative sample would help improve the readability of the manuscript.

4. The mechanical resistance results are interesting, but its connection to practical TIM applications could be clarified further. A brief explanation of how these tests relate to the intended application scenario would improve this part of the manuscript.

5. The figure presentation could be improved further. In particular, the captions could highlight the key message of each figure more clearly. In addition, the colors used in many plots are rather light, and the contrast between different curves is sometimes insufficient, making the data difficult to distinguish, for example in Fig. 2d and Fig. 2g. A clearer color scheme throughout the figures would improve readability.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Authors have made a detail reply to the comments from all reviewers, and all questions have been well resolved. The current version can be accepted for publication.

Reviewer #2

(Remarks to the Author)

The revised manuscript can be accepted.

Reviewer #3

(Remarks to the Author)

The authors have addressed all my previous concerns. I recommend its publication.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Responses to Referees' Comments

Reviewer 1:

This manuscript proposes an interface-adaptive thermal interface fluorofluidic-gel (TIF) featuring a branched-type nanocluster-junction fluoronetwork. Through elegant molecular design, the authors successfully constructed a temperature-responsive hydrogen-bonding nanocluster network utilizing the urethanization reaction between perfluoropolyether precursors and IPDI. This thermal interface material effectively balances high thermal conductivity (5.89 W/mK) and low contact thermal resistance ($0.15 \text{ cm}^2 \cdot \text{K} \cdot \text{W}^{-1}$), presenting significant application prospects in fields such as flexible electronics and electronic packaging. However, prior to formal acceptance, several key issues require further clarification or supplementation by the authors.

Response:

We sincerely thank the reviewer for your careful reading and constructive comments. We are delighted to see your appreciation of our work. Also, we greatly appreciate the time and effort devoted to providing such a comprehensive evaluation. These comments have offered invaluable guidance for refining and enhancing the quality of our work. In response, we have carefully addressed each suggestion and implemented the necessary revisions to improve the manuscript.

1. On page 5, line 127, the thermal conductivity of the TIF was stated as 5.89 W/mK. However, in the performance comparison radar chart in Figure 1e, the thermal conductivity value for the TIF appears to exceed 6 W/mK. The authors are requested to double-check and rectify this discrepancy to ensure the accuracy of the reported values.

Response:

We thank the reviewer for this important point. We have re-examined the original measurements and the plotting process and confirmed that the correct thermal conductivity of the TIF is 5.89 W/mK, as stated in the text. The higher value shown in the radar chart resulted from a scaling error during figure preparation. We have now corrected the corresponding data point to exactly 5.89 W/mK, which is consistent with

the numerical result reported in the manuscript. The revised figure is attached below as **Fig. R1**. The original Fig. 1e has been renumbered as **Fig. 1d** in the revised manuscript, and the corresponding modification is highlighted in yellow.

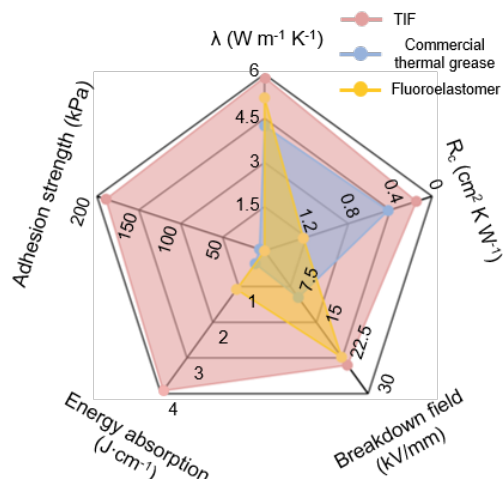


Fig. R1. Functional characteristics of the TIF, the commercial thermal grease and the fluoroelastomer.

2. In Figure 2a, the directional arrows indicating the states below and above the glass transition temperature (T_g) appear to be reversed. It is advised to verify this illustration and ensure it correctly aligns with the textual description in the manuscript.

Response:

We thank the reviewer for pointing out this issue. We have reviewed Fig. 2a and confirmed that the arrow directions in the original figure were inadvertently reversed. We have corrected the figure so that the arrows accurately represent the transition states: the leftward arrow correctly points to the state below T_g , while the rightward arrow correctly points to the state above T_g . This correction is fully consistent with the description in the manuscript. The corrected figure is provided below (**Fig. R2**), and the corresponding revised **Fig. 2a** is highlighted in yellow in the revised manuscript.

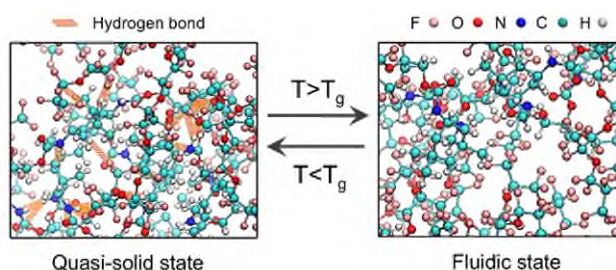


Fig. R2. Molecular dynamics simulation snapshots of the TIF in the quasi-solid state and fluidic state.

3. To enhance thermal conductivity, the authors incorporated a high loading of up to 60 wt% Al₂O₃ and MgO composite fillers into the TIF matrix. In practical applications, when the TIF transitions into a fluidic state at high temperatures, is there a risk of these high-density inorganic fillers settling or phase-separating under the influence of gravity or continuous vibration? It is recommended to provide cross-sectional SEM and EDS mapping analyses of the samples after long-term high-temperature treatment to demonstrate the long-term dispersion uniformity of the fillers.

Response:

We appreciate the reviewer's insightful comment, which helps improve the clarity and rigor of our manuscript. The potential for settling or phase separation of high-density inorganic fillers in a fluid state is indeed a significant issue affecting the practical reliability of high-filler thermal management materials. To address this concern, we conducted a long-term high-temperature treatment on the TIF_{0.25} sample with 60 wt% fillers at 80 °C continuously for 100 h, followed by SEM and EDS mapping analyses from both the surface and cross-sectional views. The SEM and EDS results from the sample surface showed that after 100 hours of heating, the Al₂O₃/MgO particles remained embedded in the TIF matrix, without obvious particle exposure, aggregation, or phase separation (Fig. R3a (the revised Supplementary Fig.16a)). The elemental mapping analyses of Al, Mg, O, and F also showed their uniform distribution on the sample surface. Based on the semi-quantitative EDS analysis, we could find that the relative contents of each element remained almost unchanged before and after heating, indicating that the surface composition of TIF remained stable during long-term heat treatment (Fig. R3b (the revised Supplementary Fig.16b)).

Similarly, the SEM and EDS results from the cross section also confirmed the stability of the internal dispersion of the filler. After 100 hours of heating at 80°C, the inorganic filler remained uniformly distributed in the TIF matrix, and no obvious filler-rich layer, vertical compositional gradient, or layered accumulation near the substrate

was observed (Fig. R4a (the revised Supplementary Fig.17a)). The corresponding Al, Mg, O, and F elements were also uniformly distributed across the entire cross-section, and semi-quantitative analysis showed no significant changes in elemental content before and after heat treatment (Fig. R4b (the revised Supplementary Fig.17b)). These results indicated that the high-loading Al₂O₃/MgO fillers did not undergo significant gravity settling or macroscopic phase separation after long-term high-temperature treatment.

As the reviewers noted, we strongly agree that filler stability is crucial for long-term thermal management applications, especially for highly filled composites, where filler content, filler-matrix interactions, and interparticle interactions significantly influence sedimentation and phase stability. Our supplementary experiments have confirmed the stability of the nanocomposites without sedimentation. In fact, in our material design strategy, the surface of Al₂O₃/MgO particles was chemically modified with fluorosilanes, thereby improving the interfacial wettability and compatibility between the fluorinated matrix and the inorganic filler (as also detailed in the Methods and Supporting Information). As a result, the polarity mismatch between the oxide fillers and the fluorinated matrix is reduced, thus suppressing filler-matrix phase separation and preventing the formation of large filler aggregates. On the other hand, based on volume conversion of the material composition, a 60 wt.% filler content corresponds to a volume fraction of approximately 40-45 vol.%. At such a high particle concentration, the fillers are not isolated particles freely dispersed in a dilute liquid medium. Instead, the Al₂O₃ microparticles and MgO nanoparticles are densely distributed in the matrix and forming a distributed filler framework. Although this structure does not reach ideal close-packing structure, this particle framework provides mutual physical confinement and reduces the free migration space of individual fillers, thereby effectively limiting gravity-driven sedimentation. In addition, the thermal interface materials are typically applied as thin bond layers confined between two rigid substrates. This confined geometry greatly limits the vertical migration distance of the fillers and suppresses the formation of macroscopic concentration gradients or bottom-rich filler layers, further contributing to the long-term dispersion stability of the TIF.

Therefore, the combined SEM/EDS evidence and structural analysis confirmed that the TIF_{0.25} sample did not exhibit significant filler sedimentation or phase separation after long-term high-temperature treatment. This stable filler dispersion ensures the integrity of the thermally conductive network, thereby supporting the long-term reliability and stable thermal conduction performance of the TIF in practical thermal interface applications.

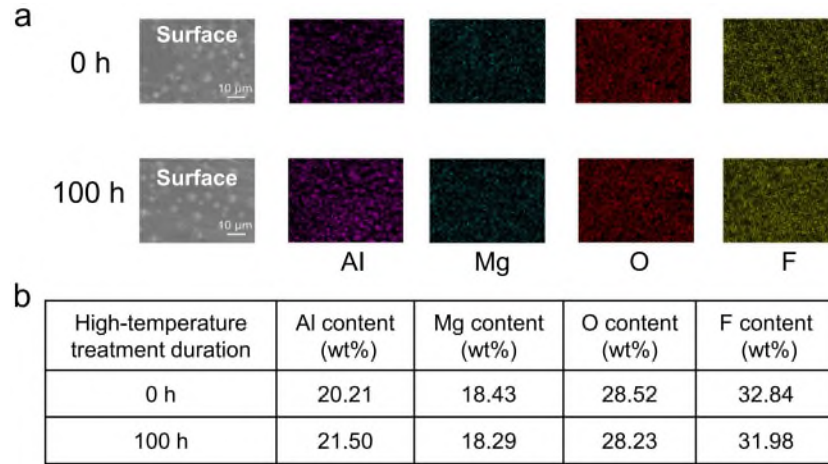


Fig. R3. (a) The SEM image of the surface view of TIF_{0.25} after continuous heat treatment at 80 °C for different durations, and the corresponding EDS element distribution diagrams. **(b)** The mass contents of Al, Mg, O, and F calculated from the EDS elemental distribution map of the surface view of TIF_{0.25} after long-term high-temperature treatment at 80 °C for different durations.

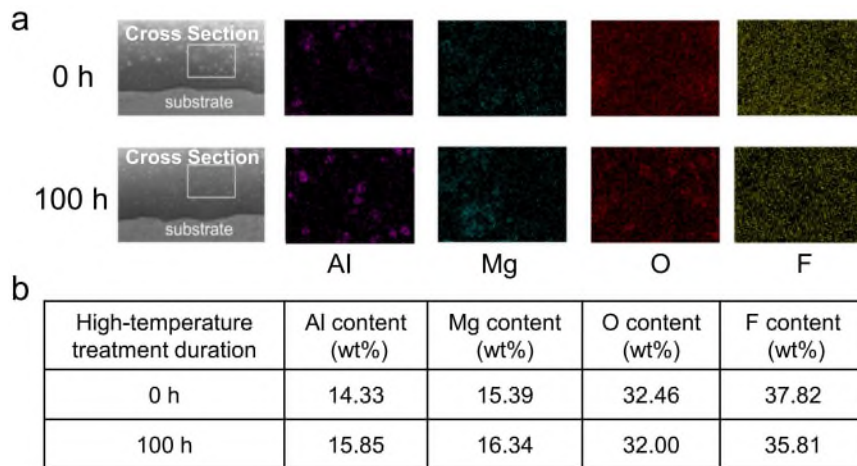


Fig. R4. (a) The SEM image of the cross section of TIF_{0.25} after continuous heat treatment at 80 °C for different durations, and the corresponding EDS element distribution diagrams. **(b)** The mass contents of Al, Mg, O, and F calculated from the EDS elemental distribution map of the cross section of TIF_{0.25} after long-term high-

temperature treatment at 80 °C for different durations.

The relevant explanations and supporting data have been incorporated into the revised manuscript, with the corresponding revisions highlighted in yellow (Page 12). The SEM/EDS characterization results have also been included in the Supporting Information (Supplementary Fig. 16 and 17).

“To further assess the long-term dispersion stability, TIF_{0.25} containing 60 wt% nanocomposite fillers was heated at 80 °C for 100 h. The SEM/EDS analysis of the surface and cross-section revealed no obvious filler sedimentation, agglomeration, or compositional gradient after thermal treatment (Supplementary Fig. 16 and 17). This stability may be attributed to the fluorosilanes modification, which improves the interfacial wettability and compatibility between the fillers and the fluorinated matrix, thereby reducing the polarity mismatch and suppressing phase separation. Although the fillers did not form an ideal close-packing structure, their high-volume fraction enables the formation of a densely distributed framework that provides interparticle physical confinement and restricts particle migration. Moreover, the constrained thin bond-line geometry in practical applications of thermal interface materials also limits the vertical migration distance of the filler and suppresses the formation of macroscopic concentration gradients or bottom filler-rich layers, further improving long-term dispersion stability.”

4. Regarding Supplementary Figure 13, it is ambiguous whether the image merely shows the morphology of the standalone Al₂O₃ and MgO composite fillers, or their actual distribution morphology within the TIF matrix. Please clarify this by providing a more explicit description in the figure caption to prevent any potential misunderstandings.

Response:

We sincerely thank the reviewer for pointing out this important issue. We confirm that Supplementary Fig. 13 shows the morphology of the Al₂O₃ and MgO micro-nano hybrid fillers before their incorporation into the TIF matrix, rather than their distribution within the matrix. Following the revision of the Supporting Information, this figure has

been renumbered as the new **Supplementary Fig. 14**. To avoid any potential misunderstanding, we have revised the figure caption as follows: “**The SEM images of the Al₂O₃ microparticles and MgO nanoparticles before incorporation into the TIF matrix.**” The corresponding revision is highlighted in yellow in the Supporting Information.

5. Figure 4i demonstrates the thermal cycling performance of TIF0.25 in 100 cycles between 25°C and 85°C. For practical electronic packaging applications, 100 cycles are generally insufficient to meet standard reliability requirements. The authors are advised to refer to existing literature or relevant industry standards and significantly increase the number of thermal cycles in their testing protocol.

Response:

We thank the reviewer for this constructive suggestion, which is important for strengthening the reliability of our work. We agree that 100 thermal cycles test was insufficient to fully evaluate the long-term reliability of TIF_{0.25} for practical electronic packaging applications. Following the reviewer’s suggestion and guided by the general temperature-cycling reliability framework described in relevant literature (**Refs. R1-R3**) and JEDEC JESD22-A104 which is a commonly referenced standard for temperature cycling of electronic devices, we significantly extended the test from 100 to 1000 thermal cycles between 20 °C and 85 °C, with a cycle duration of 1 hour (**Fig. R5 (the revised 4i)**). We should note that this laboratory-scale test was designed to evaluate the prolonged thermal-cycling stability of the material rather than to serve as a formal JEDEC qualification test. The surface temperature of TIF_{0.25} was continuously monitored within the cycling test. As shown in **Fig. R5**, the TIF_{0.25} maintained a highly stable temperature response performance throughout the 1000-cycle test, with negligible variation in the recorded interface temperature profiles. The fluctuation in the steady-state interface temperature was within a narrow variation range of approximately ± 2 °C over the entire cycling test. These results demonstrate the excellent long-term thermal reliability of the TIF under the tested cyclic thermal loading.

The excellent cycling stability may be attributed to the robust structural design of

the TIF system. As mentioned in the manuscript, the Al_2O_3 microparticles and MgO nanoparticles form a micro-nano hybrid filler framework, in which the Al_2O_3 microparticles serve as the main thermal conductive skeleton, while the MgO nanoparticles bridge adjacent microparticles and help to maintain continuous thermal transport pathways. This interconnected filler structure helps preserve the integrity of the thermal conductive network during repeated thermal cycling. The fluorosilanes modification improves the interfacial compatibility between the inorganic fillers and the fluorinated matrix, suppressing filler aggregation and phase separation, and interfacial degradation during repeated heating and cooling. Meanwhile, the incorporating of the fluoronetwork, featuring thermoreversible association-dissociation of hydrogen-bonding nanoclusters, enables $\text{TIF}_{0.25}$ to accommodate repeated temperature changes while maintain dynamic interfacial compliance and stable thermal conduction capabilities. In addition, the chemical inertness of the fluorinated chains provides excellent thermal stability of the material, which prevents thermal degradation during prolonged cycling.

The extended thermal cycling data have been incorporated into the revised Fig. 4i and Supplementary Fig. 19 (Fig. R5), and the corresponding description has been added to the manuscript. These results demonstrate that the thermally reversible fluoronetwork endows the composite with robust thermal interface capabilities, accommodating cyclic expansion and contraction while preserving filler dispersion and interfacial integrity. We hope these additional results adequately address the reviewer's concern and further strengthen the reliability demonstration of our TIF material.

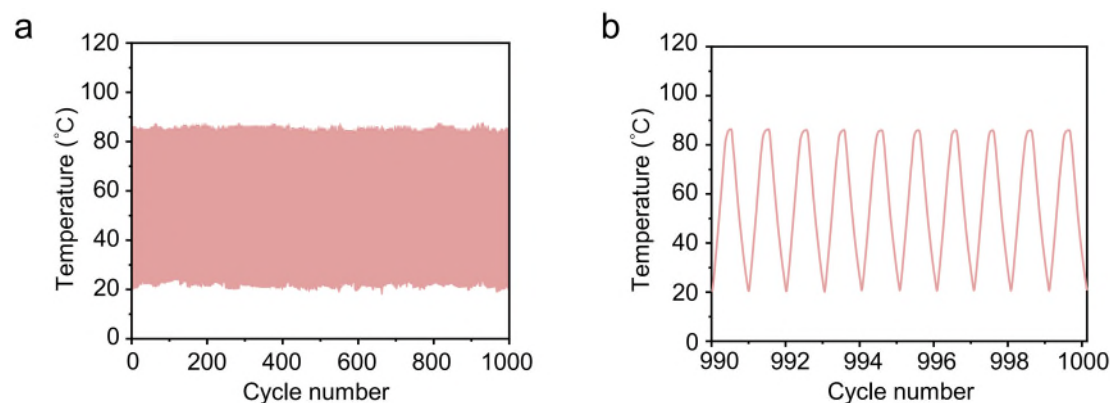


Fig. R5. (a) Temperature variation of $\text{TIF}_{0.25}$ during 1000 heating cycles (1 h per

cycle). **(b)** Temperature variation of TIF_{0.25} from the 990 to the 1000 heating cycles.

References

R1 Zhang X, Sun K, Liu H, et al. Flexible insulating phase change composite film with improved thermal conductivity for wearable thermal management[J]. Nano Energy, 2024, 121(000): 10.

R2 Jing L, Cheng R, Garg R, et al. 3D graphene-nanowire “sandwich” thermal interface with ultralow resistance and stiffness[J]. ACS Nano, 2023, 17(3): 2602-2610.

R3 Hartquist C M, Li B, Zhang J H, et al. Reversible two-way tuning of thermal conductivity in an end-linked star-shaped thermoset[J]. Nature Communications, 2024, 15(1): 5590.

The relevant contents and figures have been added to the revised manuscript and supporting Information, which is highlighted in yellow (Page 14).

“The long-term thermal-cycling stability of TIF_{0.25} was subsequently evaluated over 1000 cycles between 20 and 85 °C under 50 psi, corresponding to a total duration of 1000 h. As shown in Fig. 4i and Supplementary Fig. 19, the cyclic temperatures remained stable throughout the test, without apparent progressive drift in the temperature range. The enlarged curves of cycles 990-1000 further showed a highly repeatable temperature response, indicating no obvious deterioration in thermal management performance under the tested conditions.”

6. Following up on the previous point, it is recommended to evaluate and provide the thermal conductivity and adhesion strength of TIF_{0.25} after the extended long-term thermal cycling tests to robustly substantiate its operational stability.

Response:

We thank the reviewer for this valuable suggestion. We agree that evaluating only the thermal response during cycling is not sufficient to fully demonstrate the operational stability of TIF_{0.25}. To further substantiate the long-term operational stability of our material, we measured the thermal conductivity and adhesion strength of TIF_{0.25} after the extended 1000 thermal cycles between 20 °C and 85 °C. As shown in Fig. R6 (the revised Supplementary Fig.20), the thermal conductivity of TIF_{0.25} remained at 5.86

$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ after the 1000 cycle test, representing an essentially stable value compared to the initial value of $5.89 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Meanwhile, the post-cycling adhesion strength was approximately 188 kPa, retaining over 99% of its pristine value of 189.3 kPa (Fig. R7(the revised Supplementary Fig.21)). And the adhesion energy also remained high at approximately $211 \text{ J}\cdot\text{m}^{-2}$, comparable to its initial value of $220.3 \text{ J}\cdot\text{m}^{-2}$. These results indicate that TIF_{0.25} largely retained its thermal conductivity and interfacial adhesion performance after long-term cyclic thermal loading.

The stable thermal conductivity can be attributed to the robust $\text{Al}_2\text{O}_3/\text{MgO}$ micro-nano filler framework. In this structure, the Al_2O_3 microparticles serve as the main thermal conductive skeleton and the MgO nanoparticles bridge adjacent microparticles, helping to maintain continuous conductive pathways. The high filler loading and improved filler-matrix compatibility enabled by fluorosilanes modification further suppress filler aggregation and phase separation, thereby preserving the integrity of the thermally conductive network during repeated heating and cooling. The maintained adhesion strength mainly stems from two synergistic factors. First, the fluorinated network with low surface energy enables efficient interfacial wetting and conformal contact during the thermally induced fluidic state, thereby increasing the real contact area and reducing interfacial defects. Second, the reassociation of hydrogen-bonding nanoclusters upon cooling restores the quasi-solid network and locks the optimized interfacial configuration. These reversible hydrogen-bonding junctions also dissipate interfacial stress during repeated thermal cycling, suppressing debonding and air-gap reformation. Therefore, the retained adhesion after thermal cycling results from the synergistic effects of thermo-responsive interfacial adaptation enabled by the fluoronetwork and reversible structural recovery mediated by hydrogen-bonding nanoclusters.

Therefore, the simultaneous retention of thermal conductivity and adhesion strength after 1000 thermal cycles demonstrates that TIF_{0.25} can preserve both continuous internal conductive pathways and stable interfacial adhesion under long-term cyclic thermal loading. These results provide direct evidence for the long-term operational stability of TIF_{0.25} as a practical thermal interface material.

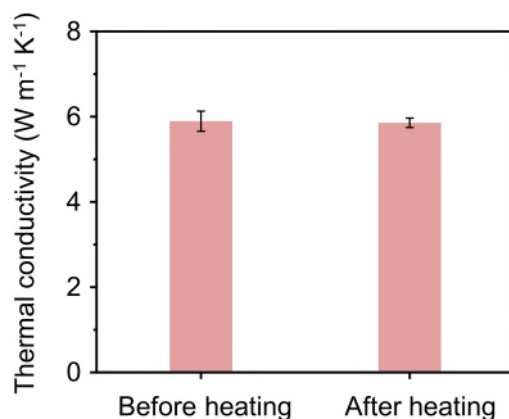


Fig. R6. Thermal conductivity of the TIF_{0.25} before and after 1000 heating cycles.

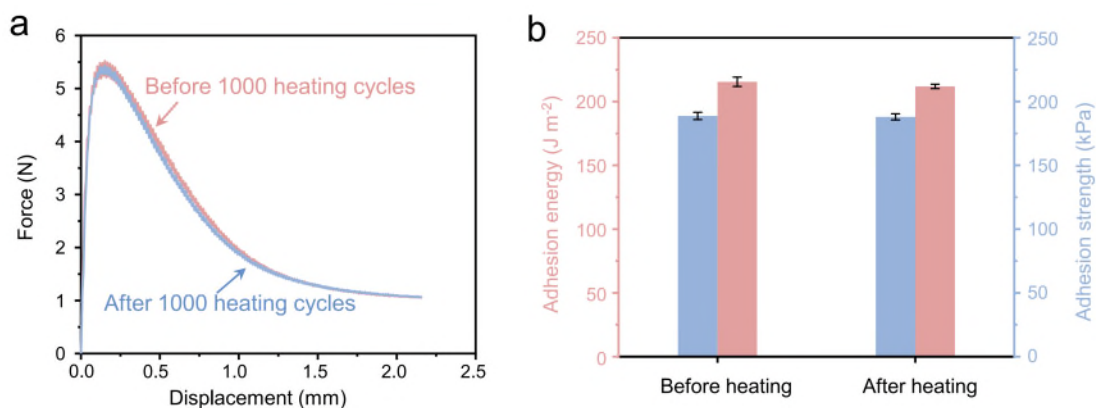


Fig. R7. (a) Force-displacement curves, **(b)** adhesion strength and adhesion energy of the TIF_{0.25} before and after 1000 heating cycles.

The post-cycling thermal conductivity and adhesion results have been added as **Supplementary Fig. 20 and 21**, respectively, and the corresponding discussion has been incorporated into the revised manuscript (**Page 14**), which is highlighted in yellow as below.

“Meanwhile, following the long-term thermal cycling, the thermal conductivity remained nearly unchanged at $5.86 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ compared with the initial value of $5.89 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (Supplementary Fig. 20). The adhesion strength also remained at approximately 188 kPa, retaining more than 99% of its initial value of 189.3 kPa, while the adhesion energy remained high at approximately $211 \text{ J} \cdot \text{m}^{-2}$, comparable to its initial value of $220.3 \text{ J} \cdot \text{m}^{-2}$ (Supplementary Fig. 21).” And “These evidences directly demonstrated the long-term operational stability of TIF_{0.25} as a practical thermally conductive interface material.”

In conclusion, we are grateful to the reviewer for the careful assessment and constructive recommendations. The revised manuscript and Supporting Information have been comprehensively updated to correct the identified inconsistencies and strengthen the experimental validation of the long-term reliability of TIF_{0.25}. The newly added SEM/EDS characterization, extended 1000-cycle thermal reliability test, and post-cycling thermal conductivity and adhesion measurements collectively demonstrate the stability of the filler distribution, thermal conductive pathways, and interfacial bonding under prolonged thermal loading. We believe that these revisions have substantially strengthened the mechanistic understanding, experimental completeness, and practical significance of this work, and we hope that they fully address the reviewer's concerns.

Reviewer 2:

In this manuscript, a novel adaptive thermal interface fluorofluidic-gel (TIF) was successfully developed, in which a branched nanocluster-junction fluoronetwork, constructed from HO-PFPE-OH, PFPE-OH₂ and IPDI, is combined with micro–nano hybrid thermally conductive fillers composed of Al₂O₃ microparticles and MgO nanoparticles. The material is designed to simultaneously exploit the thermoreversible dissociation of hydrogen-bonding nanoclusters for interface-adaptive wetting and gap filling, and the synergistic thermal transport pathways formed by the hybrid fillers for efficient heat conduction. The TIF achieves a combination of high thermal conductivity, low contact thermal resistance, reversible adhesion, mechanical impact resistance, electrical insulation, and broad temperature stability, demonstrating promising potential for thermal management of high-heat-flux electronic devices. However, although the work is technically solid and the multifunctional performance is impressive, the overall advance appears to rely more on an elegant integration and optimization of existing adaptive TIM concepts than on a sufficiently broad conceptual breakthrough or universally impactful mechanism. Therefore, I recommend that the manuscript be reconsidered after major revision.

Response:

We sincerely appreciate the reviewer's valuable and constructive comments. Regarding the concerns raised, we have performed targeted supplements and revisions in the revised manuscript. We particularly value the reviewer's focus on the principles of composition, structure-property relationships, and design concepts.

1.Existing studies on adaptive TIMs, phase-change/flow-state TIMs, and dynamic-network TIMs are already quite extensive, and the fundamental distinction between the present work and prior adaptive thermal interface materials therefore needs to be further clarified. The authors are encouraged to more clearly define the unique aspects of this work in terms of network topology, dynamic response mechanism, and application scope, so as to more convincingly highlight its novelty and academic positioning.

Response:

We sincerely appreciate the reviewer's insightful suggestion regarding the distinction between this work and existing adaptive thermal interface materials (TIMs). We fully agree that a clearer delineation of our system from reported paradigms is essential. In the revised manuscript, we have comprehensively reorganized the discussion to explicitly highlight our unique advantages in terms of network topology, dynamic response mechanisms, and multi-scenario applications.

Existing adaptive TIMs generally achieve conformal interfacial contact through phase transition, persistent fluidity, or dynamic network rearrangement. Phase-change TIMs typically achieve interfacial adaptation via the melting-crystallization or solid-liquid transitions of their phase-change polymer networks or fillers. However, this phase transition inherently compromises their macro-mechanical stability, rendering the materials highly susceptible to edge leakage, internal void formation, and interfacial delamination during long-term operation under variable thermal loads. Similarly, while flow-state TIMs, such as thermal greases, effectively minimize interfacial thermal resistance by eliminating micro voids through liquid-mediated wetting, their long-term reliability is frequently plagued by oil bleeding and dry-out phenomena. Consequently, dynamic-network TIMs have emerged as a promising paradigm to mitigate interfacial thermal resistance through reversible bonding. Nevertheless, for these existing TIM systems, the integration of multi-scenario functionalities at the thermal interface—such as interfacial impact resistance, tailored dielectric/electrostatic performance, and robust yet reversible adhesion—remains a critical yet largely unaddressed imperative.

To address these multi-faceted requirements, our thermal interface fluorofluidic-gel (TIF) featuring a unique branched-type nanocluster-junction network serves as an exceptional adaptive TIM, coupling outstanding long-term stability and reversible adhesion with robust impact damping and tailored antistatic/dielectric performance. Crucially, the design strategy of the present work is distinct from conventional phase-change or dynamic-network TIMs. Our TIF is engineered from a hierarchically branched nanocluster-junction fluoronetwork integrated with micro–nano hybrid fillers.

Within this tailored topology, the hydrogen-bonding nanoclusters serve as reversible physical junctions that impart dynamic viscoelasticity; their reversible dissociation and re-association provide a highly efficient energy-dissipation pathway, thereby endowing the TIF with exceptional interfacial impact resistance. Meanwhile, the perfluoropolyether (PFPE)-based backbones sustain the structural and thermal integrity of the network. Together with the insulating oxide fillers, they deliver a low dielectric constant and high breakdown voltage, ensuring excellent insulation to prevent electrostatic buildup. Concurrently, the branched fluorochains provide low-surface-energy segments that drastically enhance interfacial wetting and filler-matrix compatibility. Ultimately, this hierarchical architecture seamlessly integrates dynamic physical crosslinking, chain entanglement, interfacial wet-out, filler stabilization, mechanical shock absorption, and electrostatic regulation within a single fluorinated network.

Following the reviewer's important suggestion, we added a schematic comparison in **Fig. R8 (revised Supplementary Fig. S1)** to discuss how network topology governs the interfacial thermal transport. Conventional crosslinked or bottlebrush topology architectures feature static, irreversible networks that restrict conformal infiltration into rough interfaces, leaving performance-limiting air gaps and causing high thermal contact resistance. In stark contrast, our branched fluoronetwork undergoes a thermally controlled, reversible quasi-solid-to-fluidic transition via the cooperative dissociation and re-association of hydrogen-bonding nanoclusters. Distinct from uncrosslinked free liquid flow or simple crystal melting, this dynamic transition allows the gel to fluidize at elevated temperatures to fully reduce residual air gaps, while instantly reconstructing the quasi-solid framework upon cooling. Supported by the percolating filler pathways, this topological transition guarantees ultra-low contact thermal resistance without sacrificing macro-structural stability during continuous thermal cycling.

In summary, this study positions the TIF as a multi-scenario functional adaptive thermal interface material, separating it conceptually from single-function phase-change, flow-state, or conventional dynamic-network TIMs. These clarifications, along with the newly added schematic comparison in the **revised Supplementary Fig.1**, have

been thoroughly integrated into the revised manuscript to better highlight the novelty and academic positioning of this work.

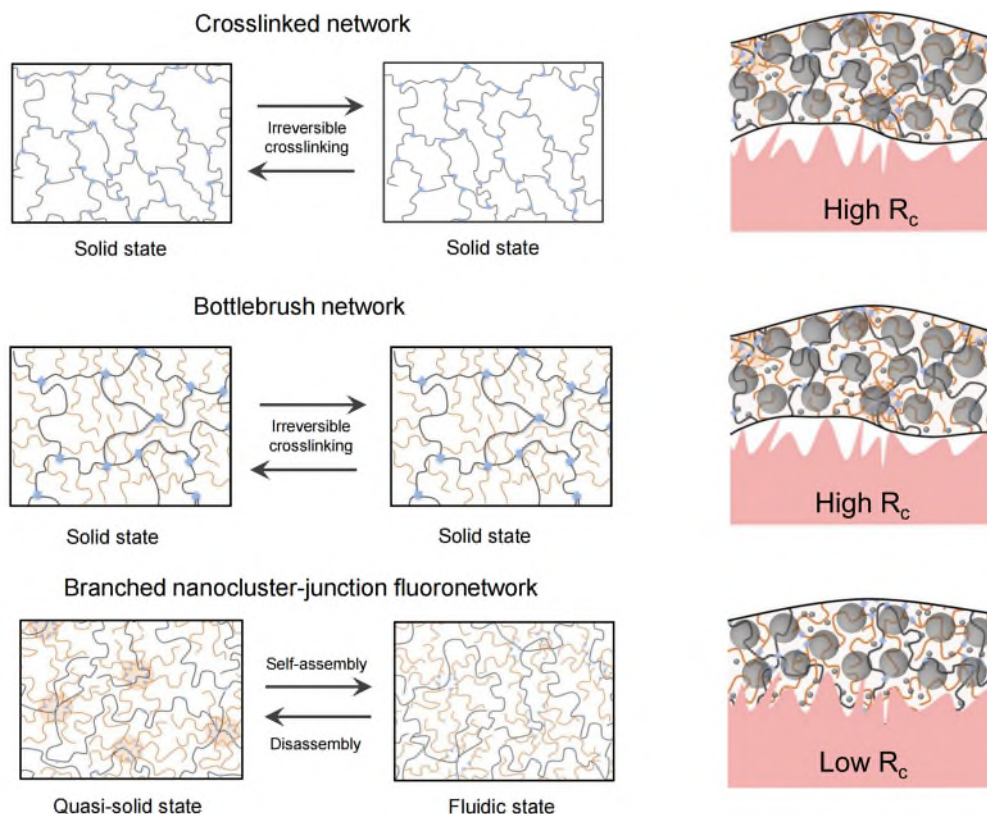


Fig. R8. Schematic illustration of diverse polymeric network designs and their corresponding thermal conduction performances.

To address this point, we have added a dedicated discussion and schematic illustration in the revised manuscript (Page 4 and 5) and supporting information (Supplementary Fig. 1), clarifying the distinctions between our TIF and existing adaptive TIMs in terms of network topology, dynamic response mechanism, and application scope, with the corresponding revisions highlighted in yellow as below.

“As shown in Fig. 1c and Supplementary Fig. 1, the conventional covalently crosslinked network and bottlebrush network can serve as the representative topology structure for the solid TIMs. Although the conductive fillers can provide high bulk thermal conductivity, the crosslinked network topology limits conformal contact with rough interfaces, resulting in residual air gaps and high contact thermal resistance. In contrast, the TIF in our work contains the hydrogen-bond interactions of the nanoclusters within this fluoronetwork that serve as dynamic physical junctions and

exhibit thermally reversible association-dissociation, which endow the TIF with temperature response and interfacial adaptability.” And “Compared with existing dynamic TIMs, the TIF integrates excellent interface adaptive thermal conductivity, interfacial adhesion and high mechanical resistance within a single material system, in which we expect it to become the candidate material for thermal management in high-power electronic devices, especially on confined interfaces subjected to repeated thermal cycling and mechanical disturbances.”

2.For the practical application of TIMs, long-term reliability is a critical metric. The manuscript currently demonstrates stability over only 100 thermal cycles. The authors are therefore encouraged to further provide performance data under prolonged high-temperature and high-pressure conditions over a longer timescale (e.g., 1000 h), in order to determine whether the material may suffer from pump-out effects, interfacial contact failure, or chemical degradation.

Response:

We sincerely thank the reviewer for this valuable suggestion. We fully agree that long-term reliability under sustained high-temperature and mechanical loading conditions is a critical requirement for practical thermal interface materials. To address this concern, we have extended the reliability test to 1000 thermal cycles between 20 and 85 °C under a constant pressure of 50 psi. Each cycle lasted 1 h, corresponding to a total testing duration of 1000 h, thereby enabling evaluation of the prolonged thermomechanical stability of TIF_{0.25}. As shown in **Fig. R9a and 9b**, TIF_{0.25} maintained a stable temperature response throughout the 1000 cycle test. The measured upper and lower temperatures showed no progressive drift, and the enlarged profiles of cycles 990–1000 exhibited highly repeatable heating and cooling responses. These results indicate no obvious deterioration in the thermal-management performance under the tested conditions. In addition, the thermal conductivity of TIF_{0.25} was maintained at 5.86 W·m⁻¹·K⁻¹ after the long-term test, compared with its initial value of 5.89 W·m⁻¹·K⁻¹ (**Fig. R9c (the revised Supplementary Fig.20)**). This retention supports the stability of the thermally conductive pathways during repeated thermal changes.

Furthermore, TGA analyses were conducted after the long-term thermal cycling test to evaluate possible thermal degradation and material loss (Fig. R9d (the revised Supplementary Fig.22)). The results confirmed that the thermal stability of TIF_{0.25} did not significantly deteriorate after the 1000 h test, with no obvious decrease in decomposition temperature or increase in weight loss observed. These results indicate that no substantial thermal degradation or volatilization or drying-out occurred during prolonged high-temperature and high-pressure operation. In addition, the structural morphology of TIF_{0.25} remained essentially unchanged and its elemental composition remained stable, further confirming its structural integrity under prolonged thermomechanical loading (Supplementary Fig. 16 and 17).

The excellent long-term reliability of TIF_{0.25} can be attributed to the synergistic structural design of the material. The fluorosilanes modified Al₂O₃/MgO micro-nano filler framework provides stable and continuous thermal conduction pathways while suppressing filler migration and phase separation under pressure. Meanwhile, the dynamic hydrogen-bonding fluoronetwork retains viscoelastic characteristics, enabling stress relaxation and interfacial recovery during repeated heating-cooling cycles. In addition, the chemical inert fluorinated chains contribute to thermal stability and help prevent chemical degradation during long-term operation.

Therefore, the combined evidence from 1000 h thermal cycling under constant pressure, retained thermal conductivity and TGA analyses demonstrates that TIF_{0.25} does not suffer from obvious pump-out, interfacial contact failure, or thermal degradation under prolonged thermomechanical loading. These results further substantiate the long-term operational reliability of TIF_{0.25} for practical thermal interface applications.

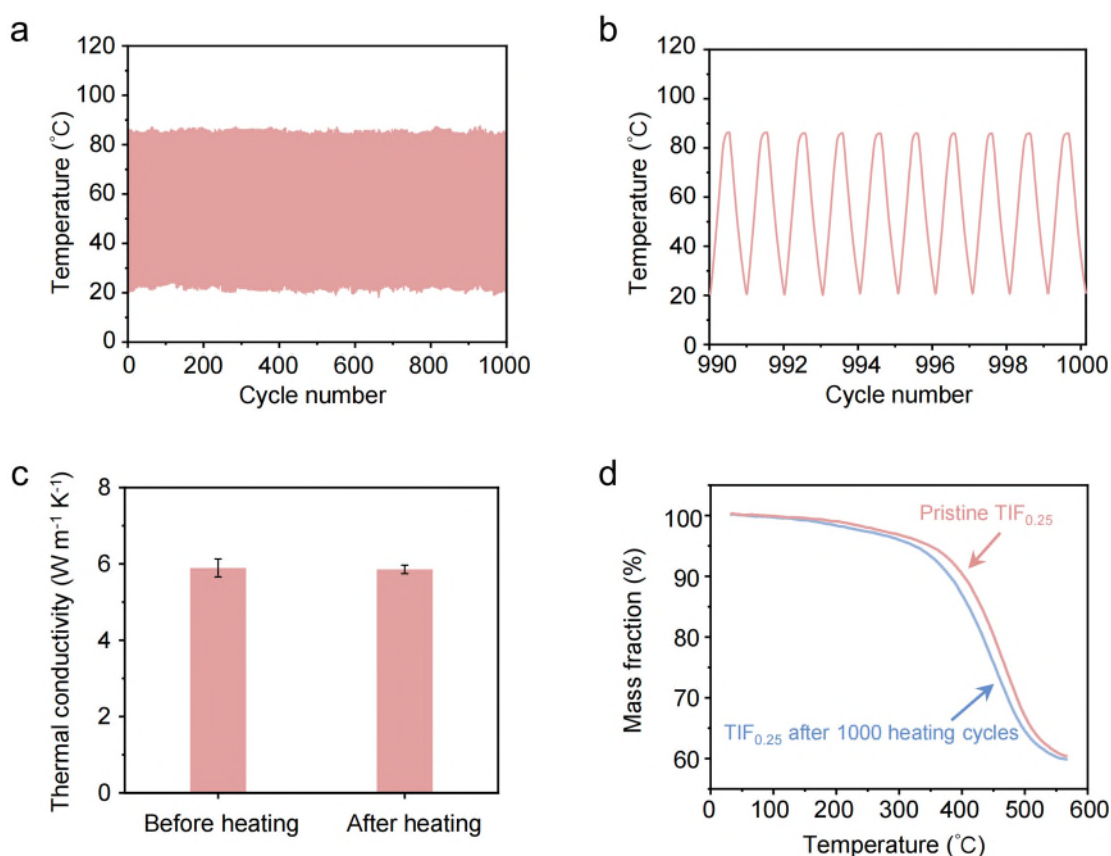


Fig. R9. (a) Temperature variation of TIF_{0.25} during 1000 heating cycles (1 h per cycle). (b) Temperature variation of TIF_{0.25} from the 990th to the 1000th heating cycles. (c) Thermal conductivity of the TIF_{0.25} before and after 1000 heating cycles. (d) The TGA analyses of pristine TIF_{0.25} and TIF_{0.25} after 1000 heating cycles.

Accordingly, we have added the 1000 h thermal cycling test under constant pressure, post-cycling thermal conductivity, and TGA results in the revised manuscript (the revised Fig. 4i, Supplementary Fig. 19, Fig. 20 and Fig. 22). The corresponding revisions are highlighted in yellow (Page 13).

“The long-term thermal-cycling stability of TIF_{0.25} was subsequently evaluated over 1000 cycles between 20 and 85 °C under 50 psi, corresponding to a total duration of 1000 h. As shown in Fig. 4i and Supplementary Fig. 19, the cyclic temperatures remained stable throughout the cycling test, without apparent progressive drift in the temperature range. The enlarged curves of cycles 990-1000 further showed a highly repeatable temperature response, indicating no obvious deterioration in thermal management performance under the tested conditions. Meanwhile, following the long-term thermal cycling, the thermal conductivity remained nearly unchanged at 5.86

$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ compared with the initial value of $5.89 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (Supplementary Fig. 20).” AND “The TGA results confirmed that the thermal stability of $\text{TIF}_{0.25}$ did not significantly deteriorate after the 1000 h test, with no obvious decrease in decomposition temperature or increase in weight loss observed (Supplementary Fig. 22). These evidences directly demonstrated the long-term operational stability of $\text{TIF}_{0.25}$ as a practical thermally conductive interface material.”

3.The thermally responsive phase-transition behavior of the material is fundamental to its ability to reduce contact thermal resistance, and this process is closely related to T_g . Although the Supplementary Information provides T_g data for samples with different matrix compositions, the manuscript does not further discuss the potential influence of high filler loading (up to 60 wt%) on T_g , the phase-transition window, or the phase-transition kinetics.

Response:

We thank the reviewer for raising this important point. To evaluate the influence of high filler loading on the thermally responsive phase-transition behavior, we performed differential scanning calorimetry (DSC) measurements on the unfilled $\text{TIF}_{0.25}$ matrix and $\text{TIF}_{0.25}$ containing 30 and 60 wt% $\text{Al}_2\text{O}_3/\text{MgO}$ nanocomposites (Fig. R10 (the revised Supplementary Fig.7b)).

As shown in the DSC curves, the T_g of $\text{TIF}_{0.25}$ containing 60 wt% nanocomposite is approximately 34.5°C , which is very close to that of the unfilled $\text{TIF}_{0.25}$ matrix ($\sim 35^\circ\text{C}$). No obvious shift in the glass transition region was observed with increasing filler loading. These results indicate that the thermally responsive transition is predominantly governed by the branched fluorinated network and the reversible association–dissociation of hydrogen-bonding nanoclusters, rather than by the inorganic fillers. The negligible influence of filler loading on T_g can be attributed to several factors. First, the $\text{Al}_2\text{O}_3/\text{MgO}$ fillers are physically dispersed within the fluorinated matrix and do not alter the chemical composition, hydrogen-bonding junction density, or covalent connectivity of the fluorinated network. Second, the micro-nano filler structure was insufficient to confine the fluorinated network within

uniformly nanoscale domains comparable to the characteristic scale of segmental rearrangement. Consequently, any restriction of chain mobility does not significantly alter the bulk-averaged segmental dynamics. Third, the fluorosilanes modified filler surfaces improve filler-matrix compatibility and limits filler aggregation, while avoiding excessively strong interfacial interactions that immobilize the surrounding segments motion. Consequently, the intrinsic segmental mobility of the fluorinated network is largely preserved even at a filler loading of 60 wt% and the hydrogen-bonding nanoclusters can still undergo thermally triggered dissociation without significant disruption by the filler framework.

The DSC results confirmed that high filler loading does not significantly affect T_g or the apparent thermal-response window of TIF_{0.25}, and the fundamental quasi-solid-to-fluidic transition behavior is well maintained.

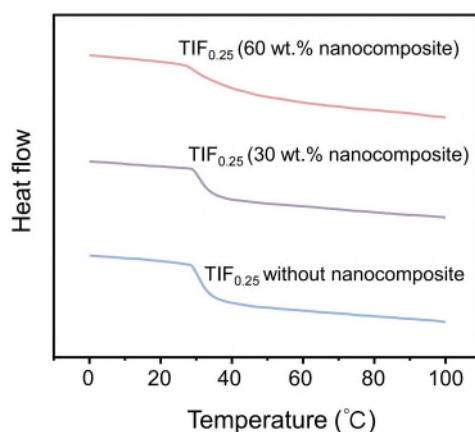


Fig. R10. DSC curves of TIFs with varied nanocomposite loadings.

We have revised the corresponding data and discussion in the Supplementary Information (Supplementary Fig. 7b) and manuscript (Page 7) to clarify the influence of filler loading on T_g and the thermally responsive transition behavior. The corresponding revisions was highlighted in yellow as below.

“Meanwhile, at a high nanocomposite loading of 60 wt%, the TIF_{0.25} maintained a nearly unchanged T_g of approximately 34.5 °C, compared with 35 °C for the unfilled matrix (Supplementary Fig. 7b). This negligible change can be attributed to the preserved fluoronetwork chemistry and connectivity, the limited effect of the relatively large fillers on bulk segmental mobility, and the enhanced filler-matrix compatibility

enabled by fluorosilanes modification. To ensure a consistent thermal history and interfacial state, the samples were first preheated to 80 °C and then cooled to 20 °C before measurement.”

4.The key advantage of TIF lies in its phase-transition capability above T_g ; however, at temperatures below T_g , its thermal resistance remains relatively high. For devices that require frequent cold starts or operate for extended periods under low-power conditions, this initially high thermal resistance may become a performance bottleneck. It would therefore be valuable for the authors to discuss how T_g could be tuned through adjustment of the chemical formulation, so that the thermal-response window can be better matched to the specific operating temperature ranges of different application scenarios.

Response:

We thank the reviewer for this pertinent practical consideration. We agree that the relatively high contact thermal resistance below T_g may be a concern for devices requiring frequent cold starts or long-term low-power operation. In response to the reviewer’s concern, we would like to discuss this issue from two aspects: thermal pre-activation of the interface and chemical tuning of T_g .

The thermal pre-activation of the interface provides a practical strategy for addressing the operation scenarios featuring with the cold-start or low-power state. Specifically, although TIF exhibits a relatively high initial contact thermal resistance below T_g , it can be thermally pre-activated during device assembly, burn-in, or initial operation. Upon the first heating above T_g , the hydrogen-bonding nanoclusters dissociate, allowing the fluorinated network to enter a fluidic state and conformally infiltrate microscopic interfacial gaps. After cooling below T_g , the nanoclusters re-associate and the TIF returns to a quasi-solid network. Importantly, the conformal interfacial contact formed during the fluidic state can be substantially retained due to the intrinsic adhesion of the fluorinated network and the geometric confinement at the thermal interface, thereby suppressing the re-formation of interfacial gaps. As a result, the contact thermal resistance after thermal activation does not fully revert to its initial

pre-activation value. Therefore, for practical devices, TIF may be pre-activated before service or during the first operating cycle, which can alleviate the cold-start limitation in subsequent operation.

The T_g of the TIF materials can be systematically tuned through rational chemical design of the fluorinated polymer network. As demonstrated in the manuscript, adjusting the molar ratio of the fluorinated soft segments and network-forming components enables T_g modulation from approximately 13.5 °C to 52.2 °C, while maintaining the structural integrity of the material. This compositional variation changes the relative fractions of flexible fluorinated backbones, branched pendant fluorochains, and urethane-rich hydrogen-bonding nanoclusters. Increasing the content of flexible and branched PFPE segments enhances segmental mobility and lowers the thermal activation temperature, whereas increasing the fraction of network-connecting segments and hydrogen-bonding junctions strengthens structural constraints and shifts the response window to higher temperatures. Therefore, for applications requiring frequent cold starts or near-ambient activation, lower- T_g TIFs can be designed by increasing the flexible PFPE content, optimizing the soft-segment length and branching degree, and reducing the effective hydrogen-bonding junction density. Conversely, higher- T_g formulations can be used for devices operating at elevated temperatures.

We have incorporated this discussion into the revised manuscript highlighted in yellow (Page 11), together with the revised Supplementary Fig.7, to clarify how the thermal-response window of TIF can be matched to different operating temperature ranges.

“These results demonstrate that T_g determines the thermal response window of TIF, therefore it can be tailored through compositional regulation to match different device operating temperatures. For applications involving frequent cold starts or long-term low-power operation, the interface may also be thermally pre-activated during device assembly or the initial operating cycle to improve conformal interfacial contact and reduce the initial contact thermal resistance.”

In conclusion, we sincerely thank the reviewer for the insightful and constructive comments. Following these suggestions, we have clarified the distinctive network topology and dynamic response mechanism of TIF, strengthened the long-term reliability evaluation through extended thermomechanical testing, and added further discussion on filler-dependent phase-transition behavior, cold-start performance, and T_g tunability. We hope that the revised manuscript adequately addresses the reviewer's concerns.

Reviewer 3:

This is a well-executed study on thermally adaptive thermal interface materials. The authors present a branched nanocluster-junction fluorofluidic-gel and provide a fairly complete set of data on its structure, adhesion, mechanical buffering, and thermal transport behavior. The idea of coupling thermally responsive interfacial infiltration with thermal resistance reduction is interesting, and the device-level cooling results further support the practical relevance of the work. Overall, I find the manuscript is suitable for publication in Nature Communications after minor revision. My specific comments are provided below.

Response:

We sincerely appreciate the reviewer's positive evaluation and insightful comments on our work. We have carefully addressed each comment and suggestion in the revised manuscript, with detailed revisions described below.

1. The authors propose that dissociation of the hydrogen-bonding nanoclusters at elevated temperature improves interfacial infiltration and thus lowers the thermal resistance. This mechanism is reasonable. However, the corresponding discussion in the main text could be clarified further, with a more direct connection between the structural characterization, the SEM observations, and the thermal resistance results.

Response:

We sincerely thank the reviewer for this valuable suggestion. We agree that the relationship among the structural characterization, interfacial morphology, and thermal resistance reduction should be described more explicitly in the main text.

To address this concern, we have revised the main text to provide a more direct and logically connected description of the structure-property relationship. In the branched fluoronetwork, the hydrogen-bonding nanoclusters serve as thermoreversible physical junctions. The temperature-dependent molecular dynamics simulations and structural characterization show that increasing temperature weakens the hydrogen-bonding interactions and promotes the disassembly of the nanocluster junctions. Below T_g , the associated nanoclusters maintain the TIF in a quasi-solid state, which limits

interfacial infiltration and leaves microscopic air gaps at the rough thermal interface. Upon heating above T_g , the hydrogen-bonding nanoclusters dissociate, increasing the mobility of the fluorinated chains and enabling the fluorinated network to transition into a fluidic state. This transition allows the TIF to conformally infiltrate surface asperities and to fill interfacial gaps. The corresponding SEM observations directly support this thermally induced interfacial evolution (Fig. R11 and the revised Fig. 4b). At low temperature, obvious interfacial gaps can be observed between the TIF_{0.25} and the substrate, indicating incomplete interfacial contact. After thermal activation at 80°C, these gaps are substantially reduced, and TIF_{0.25} forms intimate and conformal contact with the substrate.

This morphological evolution provides a direct physical explanation for the measured reduction in thermal resistance. The elimination of low-thermal-conductivity air gaps and the increase in real interfacial contact area reduce the resistance to heat transfer across the interface. Consistent with the SEM observations, the effective thermal resistance of TIF_{0.25} decreases sharply when the temperature exceeds T_g , confirming that nanocluster dissociation-induced interfacial infiltration is responsible for the enhanced interfacial thermal transport. Upon subsequent cooling, the hydrogen-bonding nanoclusters re-associate and restore the quasi-solid network, helping to stabilize the conformal interface and suppress the re-formation of interfacial voids.

Therefore, the revised manuscript now establishes a direct correlation between molecular-level nanocluster dissociation, mesoscale interfacial morphology evolution observed by SEM, and the macroscopic reduction in thermal resistance. We believe that this clarification makes the proposed mechanism and the structure-property relationship of the TIF system more transparent and convincing.

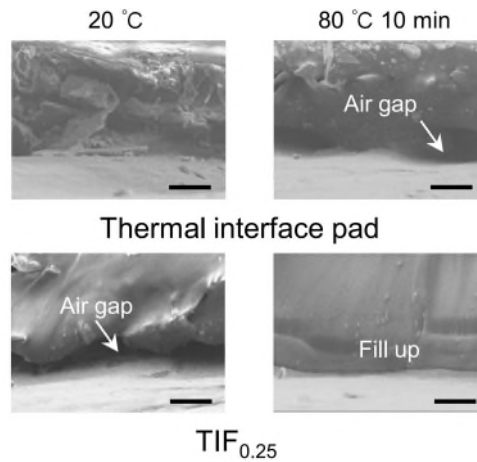


Fig. R11. SEM images of thermal interfaces with thermal interface grease and with TIF_{0.25}. Scale bar, 20 μm .

The corresponding discussion has been incorporated into the revised manuscript (Page 11), with the relevant revisions highlighted in yellow.

“At 20 °C, the visible interfacial air gap existed at the thermal interface of the commercial TIMs, which significantly raised the interfacial thermal resistance and blocked the outward conduction of internal heat within the thermal interface. Upon heating to 80 °C, the commercial TIMs underwent marginal creep and deformation and partially reduced the interfacial gaps. In contrast, the thermally induced dissociation of the hydrogen-bonding nanoclusters drove TIF_{0.25} from a quasi-solid state to a fluidic state, enabling conformal infiltration into the surface asperities and intimate contact with the substrate without visible gaps. The resulting removal of entrapped air substantially eliminates the contact thermal resistance arising from the air gap. This phenomenon was also verified in Fig. 4c, where the effective thermal resistance (R_{eff}) was quantified.”

2. The comparison with commercial TIMs is important to the manuscript, but the testing conditions are not always described with sufficient clarity. Key parameters such as sample thickness, applied pressure, and temperature should be stated more explicitly so that readers can better assess the basis of the comparison.

Response:

We sincerely appreciate the reviewer’s insightful comments. In the revised manuscript, we have explicitly added the key experimental parameters, including

sample thickness, applied pressure, and testing temperature, in both the Experimental Section and the corresponding figure captions. All comparative measurements between the TIF and commercial TIMs were performed under identical testing conditions to ensure a direct and reliable comparison.

Specifically, for the effective thermal resistance test, comparisons between TIF_{0.25} and the commercial TIMs were conducted under an applied pressure of 50 psi, with a sample thickness of 100 μm and a testing temperature range of 20-85 °C at 5 °C intervals. In the practical thermal performance tests of different TIFs and the commercial TIMs, the heating temperature was controlled within 20-85 °C. All samples were heated starting from 20 °C, kept at a thickness of 100 μm , and measured under 50 psi pressure.

These testing conditions have now been explicitly stated in the **revised Supporting Information**, which was highlighted in yellow. We believe that these revisions improve the transparency, reproducibility, and reliability of the performance comparison, and provide a more rigorous basis for evaluating the performance advantage of the proposed TIF system over commercial thermal interface materials.

“For the effective thermal resistance test, comparisons between TIF_{0.25} and the commercial TIM, both with a thickness of 100 μm , were conducted under an applied pressure of 50 psi, and a testing temperature range of 20-85 °C at 5 °C intervals. In the practical thermal performance tests of different TIFs and the commercial TIM, the heating temperature was controlled within 20-85 °C. All samples were heated starting from 20 °C, kept at a thickness of 100 μm , and measured under 50 psi pressure. For thermal stability evaluation, the sample with a thickness of 100 μm underwent 1000 heating cycles over a total duration of 1000 h, with temperature cycled between 20-85 °C.”

3. The selection of TIF0.25 as the optimal formulation could be explained more clearly. Since different formulations appear to show different advantages in different measurements, a brief summary of why TIF0.25 was chosen as the representative sample would help improve the readability of the manuscript.

Response:

We thank the reviewer for these valuable comments and constructive suggestions. Given that different TIF formulations exhibit respective superiorities in multiple characterization tests, we have supplemented a comprehensive comparison and justification for choosing TIF_{0.25} as the representative sample to enhance the readability of this manuscript.

In this work, TIF_{0.25} was selected as the representative sample because it exhibits the most balanced overall performance among the investigated formulations, rather than the maximum value in any single parameter. Among the TIF samples, TIF₀ exhibits strong hydrogen-bonding nanoclusters and favorable adhesion and damping behavior. However, its T_g is lower than room temperature, leading to excessive fluidity under ambient conditions. The TIF₀ cannot maintain a stable shape or provide sufficient dimensional stability during handling, assembly, or protective applications. Meanwhile, formulations with higher HO-PFPE-OH content, such as TIF₁, possess better room-temperature shape stability, but their weaker thermally responsive interfacial infiltration leads to less efficient reduction of contact thermal resistance.

As the HO-PFPE-OH content gradually increases, TIF_{0.25}, TIF_{0.5}, and TIF_{0.75} exhibit a certain performance balance among these conflicting requirements. However, TIF_{0.5} and TIF_{0.75} have lower adhesion and which is detrimental to thermal interface materials. And the TIF_{0.5} has higher interfacial thermal resistance. Therefore, through the comparison, TIF_{0.25} provides the best balance among these competing requirements. It maintains a quasi-solid state at room temperature, ensuring dimensional stability and interfacial positioning, while still undergoing a clear thermally triggered quasi-solid-to-fluidic transition above the response temperature. This enables effective interfacial infiltration and reduction in interfacial thermal resistance, while preserving high adhesion strength, mechanical resistance, effective mechanical damping, and stable thermal conductive performance. Therefore, TIF_{0.25} is the most appropriate representative formulation for demonstrating the hydrogen-bonding nanocluster-mediated phase-transition behavior and interfacial thermal regulation mechanism.

Accordingly, we have added a brief clarification in the revised manuscript (Page

10 and 13) to explicitly state the rationale for selecting TIF_{0.25} as the representative formulation. The corresponding revisions was highlighted in yellow as below.

“These results demonstrated that TIF_{0.25} possesses the thermal stability and electrical insulation required for practical thermal interface applications. Beyond these intrinsic properties, we also comprehensively compared the dimensional stability, adhesion, and mechanical resistance of different TIFs. It was observed that TIF₀ is too fluid to maintain sufficient dimensional stability at room temperature, while TIF_{0.75} and TIF₁ exhibit lower adhesion due to the excessively high HO-PFPE-OH content and weakened hydrogen-bonding nanocluster interactions. In comparison, TIF_{0.5} showed insufficient interfacial mechanical resistance due to its intermediate nanocluster structure provided less effective energy dissipation under impact loading. By regulating the fluoronetwork topology and hydrogen-bonding nanocluster structure within the material system, TIF_{0.25} achieved the best overall balance among thermo-responsive behavior, adhesion performance, and mechanical resistance, was therefore selected as the representative formulation for subsequent studies.” And “Among the different TIFs evaluated, TIF_{0.25} exhibited superior heat-dissipation performance with low interfacial thermal resistance, confirming its efficient thermal interface transport capability (Supplementary Fig. 18). Together with its balanced dimensional stability, thermo-responsive interfacial adaptability, adhesion performance, and mechanical resistance, TIF_{0.25} was identified as the most suitable representative fluorofluidic-gels for the practical applications.”

4. The mechanical resistance results are interesting, but its connection to practical TIM applications could be clarified further. A brief explanation of how these tests relate to the intended application scenario would improve this part of the manuscript.

Response:

We sincerely appreciate the reviewer’s insightful comment. We agree that the relevance of the mechanical resistance tests to practical TIM applications should be further clarified.

In practical electronic packaging, TIMs are usually confined between rigid

components such as chips, substrates, and heat sinks. During assembly and operation, they experience compressive clamping pressure, thermal expansion-contraction stresses, pressure fluctuations, and occasional mechanical perturbations. Under these service conditions, sufficient mechanical resistance is essential for maintaining dimensional stability, stable bond-line thickness, and intimate interfacial contact. Otherwise, excessive deformation, material extrusion, interfacial debonding, or air-gap reformation may occur, leading to increased contact thermal resistance and degraded long-term heat dissipation performance.

Therefore, the mechanical resistance tests in this work provides insight into the ability of TIFs to preserve interfacial structural stability under practical compressive and dynamic loading conditions. This property is particularly important for the present TIF system because it undergoes a thermally induced quasi-solid-to-fluidic transition above T_g . Although this transition facilitates interfacial wetting and void elimination, the fluorinated network and interconnected $\text{Al}_2\text{O}_3/\text{MgO}$ filler framework provide structural reinforcement, thereby suppressing uncontrolled extrusion and maintaining interfacial integrity under pressure. In addition, the viscoelastic nature of TIF helps buffer mechanical perturbations and reduce interfacial stress concentration, which is beneficial for inhibiting debonding and air-gap formation. Thus, the mechanical resistance of TIF is closely associated with interfacial contact stability, pump-out resistance, and long-term interfacial thermal transport reliability.

Accordingly, we have revised this part of the manuscript (Page 10) to clarify how the mechanical resistance tests are connected to practical TIM service scenarios and to emphasize the relationship among mechanical stability, interfacial contact, and thermal transport reliability. The corresponding revisions was highlighted in yellow as below.

“Owing to this capability, TIFs sandwiched between rigid components such as chip substrates and heat sinks in practical electronic packaging systems can withstand long-term and complex mechanical loads, including thermal cycling stress, equipment vibration and shock, assembly pressure fluctuations, and drop impacts. This provides critical mechanical reliability for their long-term stable application in harsh operating environments, such as high-power chips, communication modules, and automotive

electronics.”

5. The figure presentation could be improved further. In particular, the captions could highlight the key message of each figure more clearly. In addition, the colors used in many plots are rather light, and the contrast between different curves is sometimes insufficient, making the data difficult to distinguish, for example in Fig. 2d and Fig. 2g. A clearer color scheme throughout the figures would improve readability.

Response:

We sincerely thank the reviewer for these constructive suggestions to improve the clarity and impact of our figures. We agree that clear figure presentation and improved caption clarity are important for enhancing the readability and accessibility of the manuscript.

In the revised manuscript, we have carefully revised the figure captions throughout the paper. The captions have been modified not only to describe the displayed data, but also to highlight the key message and central conclusion of each figure more clearly. This allows readers to better understand the relationship between the experimental observations, material structure, and functional performance. In addition, we have systematically improved the visual presentation of the figures. The color scheme throughout the manuscript has been comprehensively adjusted. We adopted darker and more distinguishable hues, increased line thickness, and introduced varied line styles (dashed and dotted lines) where necessary to achieve optimal visual contrast. The revised versions of Fig. 2d and Fig. 2g are presented below as **Fig. R12 (the revised Fig. 2d and Fig. 2g)**.

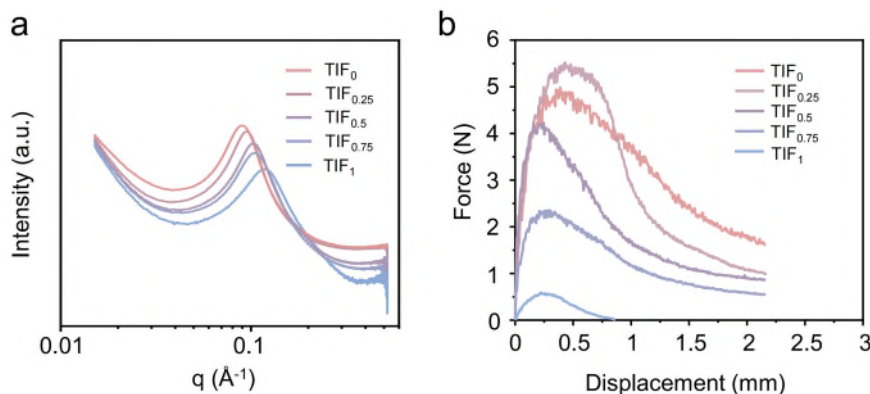


Fig. R12. (a) SAXS data for different TIFs and **(b)** Force-displacement curves of different TIFs.

Furthermore, we have carefully checked the remaining figures and applied a consistent high-contrast visual style across the manuscript to ensure overall readability and graphical consistency. We believe that these revisions improve the clarity, interpretability, and presentation quality of the figures, and better support the communication of the key scientific findings in the manuscript. In addition, the figure captions were revised to more clearly convey the key scientific message of each figure. All the corresponding caption revisions are highlighted in yellow in the revised manuscript as below.

Figure 2

d and e, SAXS data of different TIFs with varied perfluoropolyether precursor compositions, together with the distance and diameter of the hydrogen-bonding nanoclusters derived from SAXS analysis.

f, SAXS data and corresponding two-dimensional scattering patterns of TIF_{0.25} at 25°C and 80°C.

g and h, Force-displacement curves of different TIFs with varied perfluoropolyether precursor compositions, together with the corresponding adhesion energy and adhesion strength derived from the curves.

j and k, The adhesion strength and the photographs of the TIF_{0.25} with different substrates including glass, PTFE, wood, Al, stainless steel, and silicone rubber.

l, The adhesion strength and the photographs of the TIF_{0.25} from 25°C to -80°C, exhibiting the effective interfacial adhesion over a wide temperature range.

Figure 3

a and b, Demonstration of the impact-stiffening behavior and substrate protection capabilities of the TIF_{0.25} by heavy strike, showing the rapid shape recovery of the sample and effective protection of the underlying glass substrate.

c and d, Frequency-sweep rheological curves of different TIF formulations from 0.1 to 100 Hz, together with the corresponding loss factor as a function of frequency.

e and f, Time-dependent attenuation waves of impact force for stainless steel, silicone

rubber, polyurethane (PU), and TIF_{0.25} under identical drop-impact conditions, together with the corresponding impact energy absorption of the silicone rubber, PU and TIF_{0.25}.

Figure 4

b, Cross-sectional SEM images of thermal interfaces formed by commercial thermal interface grease and TIF_{0.25} after treatment at different temperatures. Scale bar, 20 μm .

g and h, Temperature evolution of different TIMs as a function of heating time at an applied power of 150 W, together with the corresponding infrared thermal images of the heat sink using TIF_{0.25} and interface thermal grease.

i, Temperature variations of the TIF_{0.25} during 1000 thermal cycles between 20 and 85 °C under a constant pressure of 50 psi.

Again, we sincerely thank the reviewer for the positive assessment and constructive suggestions. In response, we have clarified the structure-morphology and thermal transport relationship, specified the comparative testing conditions, explained the selection of TIF_{0.25}, strengthened the practical relevance of mechanical resistance, and improved the figure presentation. We believe these revisions have significantly enhanced the clarity, rigor, and readability of the manuscript and satisfactorily address the reviewer's concerns.