Thermal Conductivity of Covalent-Organic Frameworks

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ABSTRACT

Covalent-organic frameworks (COFs) are a highly promising class of materials that can provide an excellent platform for thermal management applications. In this perspective, we first review previous works on the thermal conductivities of COFs. Then we share our insights on achieving high, low, and switchable thermal conductivity of future COFs. To obtain desired thermal conductivity, a comprehensive understanding of their thermal transport mechanisms is necessary but lacking. We discuss current limitations in atomistic simulations, synthesis, and thermal conductivity measurements of COFs and share potential pathways to overcome these challenges. We hope to stimulate collective, interdisciplinary efforts to study the thermal conductivity of COFs and enable their wide thermal applications.

KEYWORDS: Covalent-organic frameworks, thermal conductivity, thermal management

COFs are an emerging class of crystalline porous materials usually consisting of light elements (B, C, N, O, Si) linked *via* strong covalent bonds. Particularly, COFs are fully pre-designable polymers with designated pore apertures, ordered channel structures, and versatile chemical compositions.[1] Their cage-like structures with large surface areas result in COFs being considered candidates for gas capture, storage, and separation systems. Moreover, their modular and periodic architectures make them attractive for diverse fields of catalysis, chemo-sensing, optoelectronics, gas storage and separation, and drug delivery.[2]

The COF synthesis is primarily based on fundamental concepts of dynamic covalent chemistry.[3] Preparation of COFs or COF-containing materials typically relies on the use of Schiff base reactions, self-condensation of boronic acid, or reactions between boronic acid and catechol-based linkers. Recently, a synthetic approach utilizing multi-substituted monomers was successfully applied to prepare two-dimensional COFs. The latter allowed for the integration of organic linkers containing heavy elements, enhancing COF structural diversity. Another powerful and commonly employed synthetic methodology is a COF's post-synthetic modification with desired multifunctional moieties, allowing frameworks' properties to be tailored after the material synthesis.[4] COF crystallinity is highly dependent on the formation of dynamic bonds, which allows for self-correction to occur. However, the presence of highly robust bonds in COF structures is driven by industrial demands, and therefore, the COF synthesis is a compromise between crystallinity and structural framework integrity. The current trends in the COF field integrate studies of COF morphology and its effect on material properties,[5] reconstruction routes for enhancement of framework crystallinity and porosity, and on-surface COF synthesis.[6,7]

Although a considerable amount of research has been carried out to understand a range of physical and chemical properties in COFs, their thermal transport mechanisms have received far less attention. However, COFs can be engineered to possess exceptional thermal functionalities for various applications, as illustrated in Figure 1. One advantage of COFs is the extensive control over pore sizes and shapes facilitated by the diverse combinations of organic building units based on carbon chemistry. Moreover, compared to metal-organic frameworks (MOFs), COFs are generally more thermally and chemically stable due to the stronger covalent bonds holding the framework together and absence of metals prone to reduction, making COFs potentially more suitable for use in harsh environments or high temperatures than MOFs.[8]

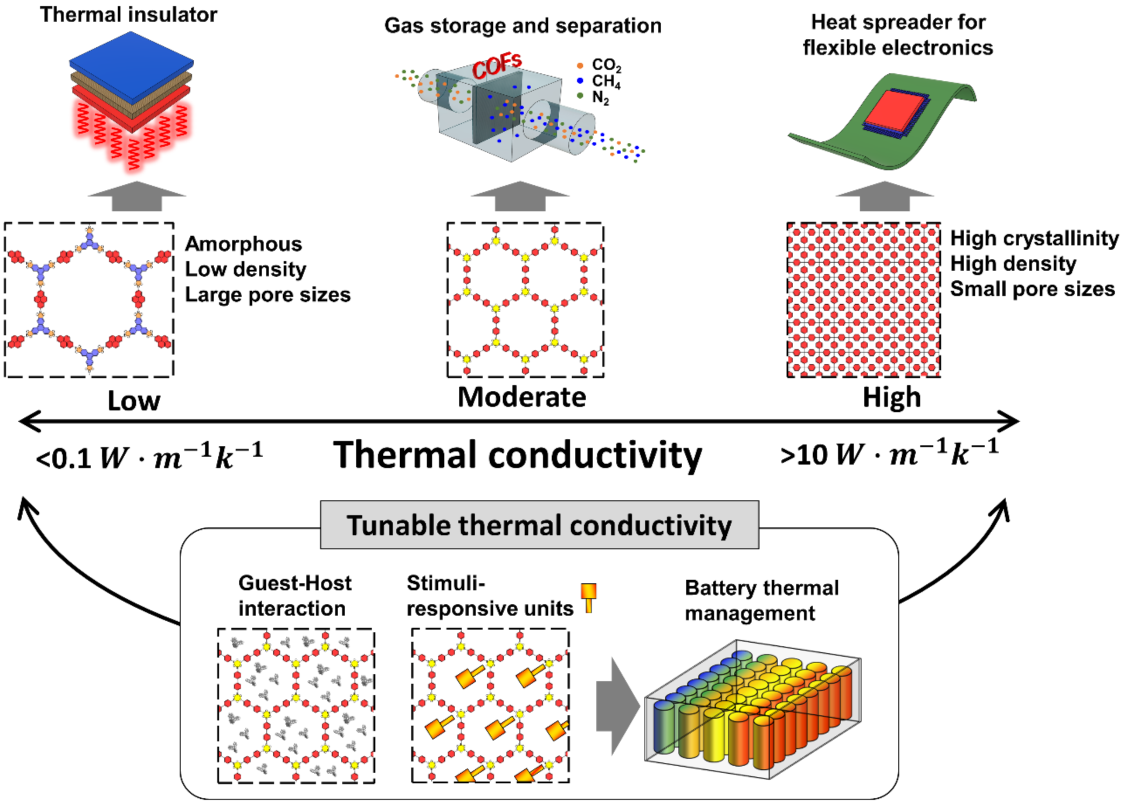

Figure. 1 Schematic of various thermal conductivities of COFs. COFs with low thermal conductivity have low density and large pore sizes, which can be used as thermal insulators. In contrast, COFs with high thermal conductivity possess high crystallinity, high density, and small pore sizes with potential applications as lightweight heat spreaders for electronics including flexible electronics. The thermal conductivity of COFs can be tuned by guest-host interactions or integration with stimuli-responsive units, which can be potentially used for on-demand thermal management applications, such as battery thermal management modules.

The large tunability in the nanostructured architecture of COFs based on hierarchical manipulation of the chemical structure and morphology provides the opportunity not only to obtain low thermal conductivities like other porous materials but also to attain high thermal conductivities that other porous materials are hard to attain, providing solutions for various thermal applications. For instance, a 2D COF layer engineered to obtain high thermal conductivity with ultra-low dielectric permittivity can be utilized for nanoscale integrated circuit components, reducing the parasitic capacitance effect.[9] Furthermore, attaining high thermal conductivities with strong bonds in COFs positions them as ideal candidates for lightweight thermal management applications in flexible electronics and traditional microelectronics.[1,10] In addition, 2D COFs inherently show anisotropic thermal conductivity, which can be employed for heat-spreading applications where higher thermal conductivities are preferred in certain directions. Beyond these applications, recent computational studies have shown that the thermal conductivity of COFs can be tuned by guest-host interactions, such as by filling the nanopores with guest molecules,[11,12] suggesting potential thermal switch applications. Although COFs have shown plenty of opportunities for diverse thermal applications, the underlying thermal transport mechanisms in COFs have not been comprehensively understood.

This perspective first reviews previous studies on the thermal conductivities of various COFs and then suggests potential ways to achieve high, low, and tunable thermal conductivity. Additionally, it presents the current challenges and possible solutions in COF synthesis, atomistic simulations, and thermal conductivity measurements to gain a deeper understanding of COFs' thermal transport properties.

Review of Previous Work

Thermal Conductivity of Pristine COFs

A broad spectrum of thermal conductivity values has been reported for COFs. For amorphous COFs, the experimental study on powdered 3D COFs, such as reticular innovative organic materials (RIOs) and COF-300, exhibited even lower thermal conductivities of less than 0.05 $Wm^{-1}K^{-1}$ at room temperature.[13] On the other hand, crystalline COFs have displayed high thermal conductivities. For instance, boronate ester-linked 2D COF films, namely TP-COF and COF-5, were experimentally measured to possess a thermal conductivity of 0.89 $Wm^{-1}K^{-1}$ and 1.03 $Wm^{-1}K^{-1}$ in the direction of the laminar pores (cross-plane direction), which was attributed to their structural regularity, crystallinity, and relatively strong interlayer interactions.[9] MD simulations showed that a 3D COF-300 derivative with extremely narrow pores (0.63 nm) exhibits an exceptionally high thermal conductivity of > 15 $Wm^{-1}K^{-1}$ in all directions.[14]

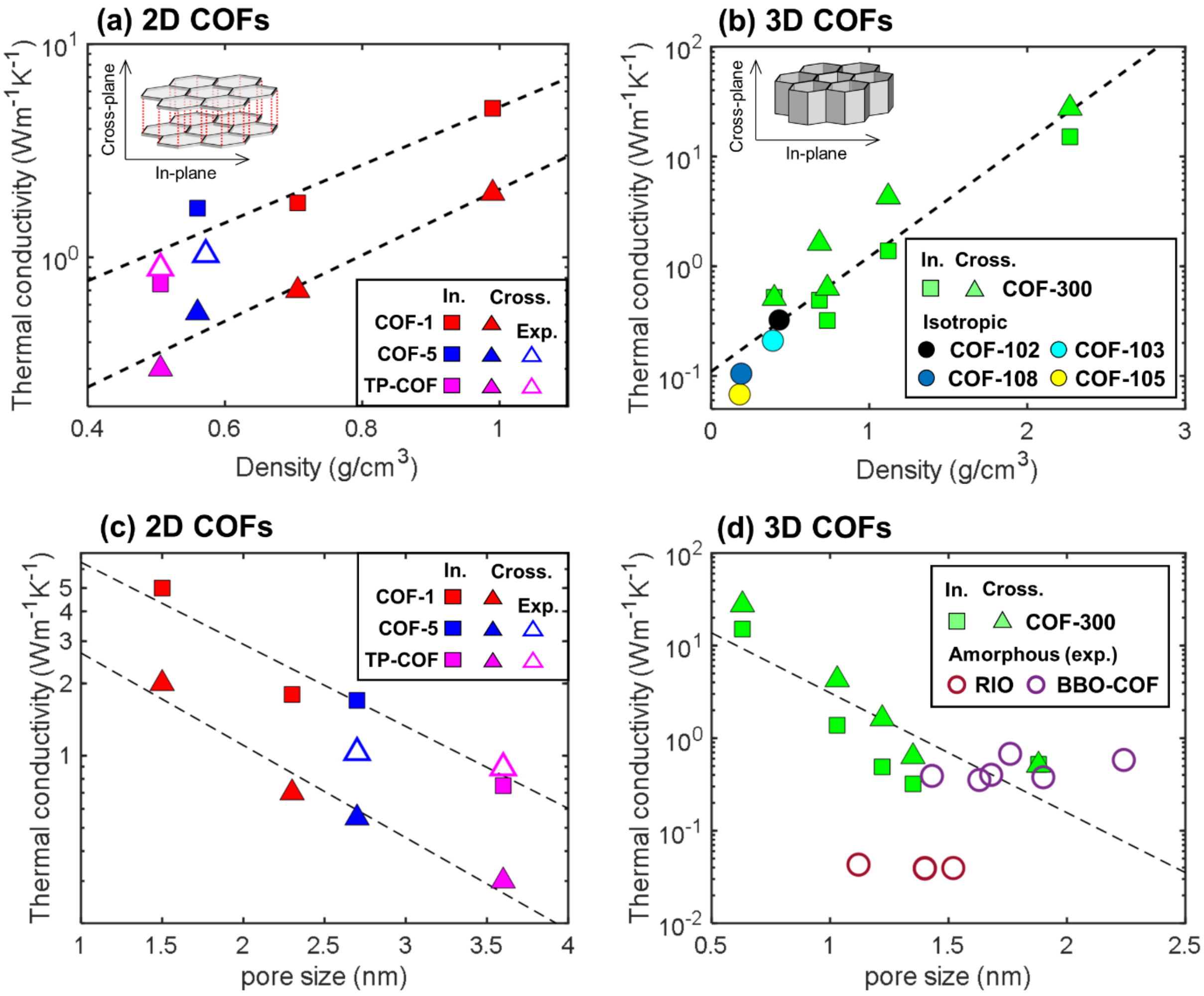

Figure. 2 Thermal conductivities of (a) 2D COFs and (b) 3D COFs as a function of their densities. The rectangular, triangular, and circular shapes indicate the in-plane, cross-plane, and isotropic or amorphous thermal conductivities, respectively. COF-1 (red), COF-5 (blue), and TP-COF (magenta) are plotted in 2D COFs, while COF-300 and its derivatives (green), COF-102 (black), COF-103 (cyan), COF-108 (dark blue), and COF0105 (yellow) are plotted in 3D COFs. Thermal conductivities of (c) 2D COFs and (d) 3D COFs as a function of their pore sizes. All thermal conductivities were from MD simulations except the unfilled triangles for COF-5 (blue) and TP-COF (magenta) in (a) and (c), and unfilled circles for RIO powder (brown) and BBO-COF pellets (purple) in (d), which are experimental thermal conductivity.

Figure 2 summarizes the reported thermal conductivities of pristine 2D and 3D COFs. Figures 2a-b show the thermal conductivities of 2D and 3D COFs with respect to their densities containing pores. Typically, the in-plane direction is defined as perpendicular to the pore axes, whereas the cross-plane direction is defined as parallel to the pore axes, as depicted in the insets of Figures 2a-b. In both 2D and 3D COFs, the clear ascending trend of thermal conductivities with respect to their densities is observed, as expected. Inherently, 2D COFs display large anisotropic thermal conductivities owing to the distinct interactions that strong covalent bonds occur within the 2D layers while relatively weak van der Waals interactions exist between the layers.[9] For 3D COFs, COF powders (black circles in Fig. 2b) show low experimental thermal conductivities due to their amorphous morphology.[15] On the other hand, MD simulations show that crystalline 3D COF-300 derivatives (green markers) exhibit high thermal conductivities.[14] 3D COFs exhibit relatively low anisotropic thermal conductivity compared to 2D COFs because of continuous heat conduction pathways formed by strong covalent bonds in all directions.[14] Figures 2c-d display the pore size dependency of the thermal conductivities in 2D and 3D COFs. The thermal conductivities of 2D and 3D COFs decrease as the pore size increases, resulting from the proportionality between the number of lattice vibrational modes (phonons) and the number of chain crossings per unit area. However, RIO and BBO-COF in Figure 2d are not following this trend[13,16] probably because RIOs are prepared in powder form, and BBO-COFs are made as pellets by compressing COF powder. This amorphous form of COFs strongly scatters the heat carriers and, thus, less sensitive to the pore size. Note that a direct comparison of the experimental results with MD simulations warrants caution at this stage, given the different conditions such as sample morphology, crystallinity, or defects and the lack of accurate interatomic potentials. For instance, the experimental values of COF-5 (blue) and TP-COF (magenta), indicated by unfilled triangles in Figures 2a and c, demonstrate higher cross-plane thermal conductivities compared to the MD results. This discrepancy could be attributed to the insufficiencies of the interatomic potentials used in the MD simulation.[9] A detailed discussion of the current challenges encountered in MD simulations is presented later.

Thermal conductivity of infiltrated COFs.

Introducing guest molecules into COFs can modify their thermal conductivities, and the effects on thermal conductivity are case-dependent. Figure 3 compares the thermal conductivities of pristine and guest-infiltrated 2D COFs *via* MD simulations. Notably, the dependence of the thermal conductivities on the infiltration of guests is non-monotonic. There are competing effects of enhancing scattering, increasing density, and adding extra heat conduction paths, which of these effects dominates depending on the pore sizes. For COFs with small pores, such as COF-1, the addition of guest molecules mainly enhances solid-gas scattering and results in decreased thermal conductivities in both in-plane and cross-plane directions.[17] For COFs with large pores, such as COF-1-2R, COF-5, and TP-COF, the additional heat conduction channels enabled by guest molecules play a more dominant role and lead to increased cross-plane thermal conductivities, while the resulting scattering effects reduce or maintain a similar in-plane thermal conductivities compared to the unfilled COFs.[12] Note that the small in-plane thermal conductivity differences between 2.25 to 4.5 molecules/nm^3 for COF-5 and TP-COF are within the simulation errors.[12,17] Interestingly, additional phenyl rings to COF-5, as shown in Figure 3, introduce additional in-plane scattering while disturbing the gas flow in the cross-plane direction.[12]

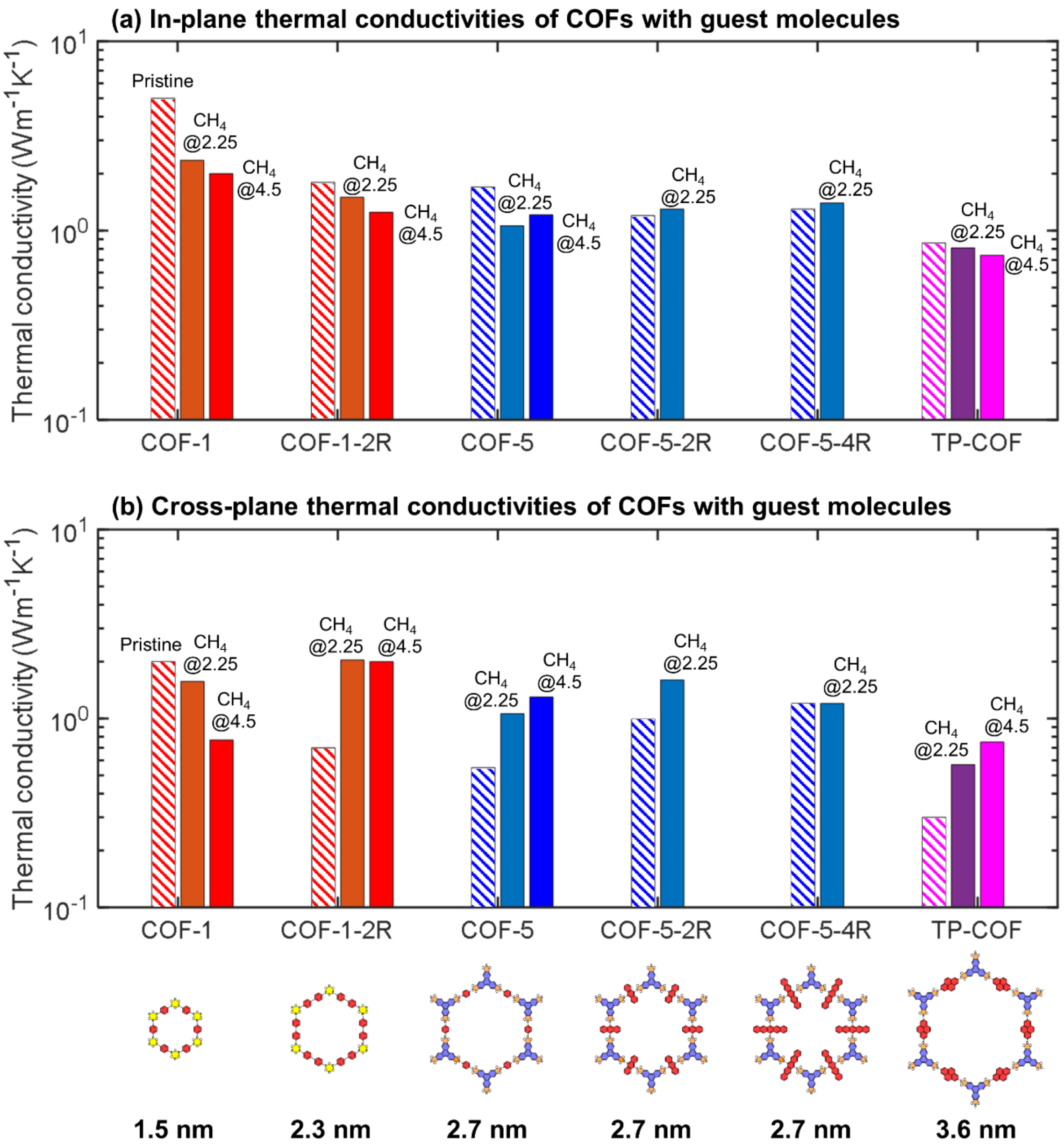

Figure. 3 The comparison of (a) in-plane and (b) cross-plane thermal conductivities between pristine and infiltrated COFs filled with gas molecules (CH_4 (Methane)) *via* MD simulations. The hatched bars indicate pristine COFs, while the filled bars denote infiltrated COFs. The concentration of CH_4 is shown with the unit of the gas density (molecules/nm^3)

Perspective for Future Directions

High thermal conductivity

In order to achieve high thermal conductivity, several important factors need to be considered, including dense structure with tiny pores, high crystallinity, and certain guest interactions.[9,14,17] A straightforward way to increase the thermal conductivity of COFs is to build a dense network with small pores or a highly interpenetrated structure with high crystallinity.[18] A denser network not only increases the density but also limits the rotational degree of freedom of the linkers and normally results in higher crystallinity.

The crystal network topologies of COFs can play a role. In the case of MOFs, it was reported that the topologies possessing 4-connected nodes exhibited surprisingly high thermal conductivity. This behavior may be attributed to the favorable alignment of strong covalent bonds along the direction of heat transfer.[19] Interestingly, COF-300 derivative that exhibited ultra-high thermal conductivity also has a 4-connected topology. Thus, leveraging a desired primitive topology of COFs can potentially enhance COFs' thermal conductivity.

Stronger bonds are generally preferred for better heat conduction.[20] (1) *Conjugation*. COFs exhibit a high degree of conjugation, which can be beneficial to achieve high thermal conductivity.[21–23] For example, π-conjugated crystalline linear[20] and 2D polymers[22,24] with large bond energy in their backbones show large thermal conductivity. In this regard, the extended conjugation in COFs can promote the propagation of phonons along the framework, leading to increased thermal conductivity. (2) *Robust Linker*. Recently, COFs with robust bonds developed by multicomponent reactions or strengthening covalent linkages to overcome their inherent chemical stability issues have been developed.[25,26] The introduction of stronger covalent linkages in robust COFs itself can enhance thermal conductivity if everything else is kept the same. However, it is essential to consider that the enhanced stability of robust COFs may come at the cost of reduced reversibility in linkage formation, which can affect error correction and defect healing processes crucial for maintaining high crystallinity in COFs.

If isotropically high thermal conductivity is desired, 3D COFs can be a good candidate because it inherently gives more isotropic heat conduction than 2D COFs. If 2D COFs are preferred, given the easier synthesis conditions, there are also ways to improve its cross-plane thermal conductivity: (1) *Backbone modification*. For example, COF-5-2R and COF-5-4R show larger cross-plane thermal conductivity by introducing additional phenyl rings into COF-5, as shown in Figure 3. These additional phenyl rings can increase the solid surface area and introduce extra π−π stacking interactions between the layers, enhancing cross-plane thermal conductivity. Meanwhile, these phenyl rings have a small impact on in-plane heat conduction. (2) *Guest filler Infiltration*. Guest molecules like methane infiltrating and diffusing along the pore channels allow additional cross-plane heat conduction. For instance, instead of using methane gas, filling the pore with crystalline polymers with high thermal conductivity may provide more efficient heat transfer pathways.[27] However, the relative difference between pore size and filler size, the filler density, the guest-host interaction strength, the intactness of the framework are all important factors to consider. (3) *2D COF Interpenetration*.[28,29] Essentially, one can build a 3D network from 2D COFs. The constructed 3D network exhibited a dramatic increase in thermal conductivity while maintaining the same mass density as traditional 3D frameworks.[29] This superior thermal conductivity was attributed to the enhanced phonon hardening and shift of heat-carrying vibrations to higher frequencies resulting from the supramolecular interactions between the 2D frameworks.

Low thermal conductivity

Opposite approaches from above can be taken to achieve low thermal conductivity, for example, developing amorphous COFs in powder form, with large pores and lower density. Besides, the wall grafting technique could be adapted to induce a gas-solid scattering effect. As shown in the COF-5 case,[12] small amounts of gas infiltration into COF-5 (*i.e.*, methane gas with 2.24 molecules/nm^3) is likely to increase the gas-solid scattering rather than create additional heat transfer paths, resulting in the reduction of in-plane thermal conductivity.

Moreover, exploiting specific polymer guests could decrease thermal conductivity. For instance, the BBO-COFs doped with poly(3-hexylthiophene) (p3HT) were reported to give lower thermal conductivity compared to undoped BBO-COFs, because the filling of p3HT polymers disrupted some of the π–π stacking between the BBO-COF layer.[16] Therefore, introducing guest molecules that are large enough to disrupt or distort the covalent network in the COFs is another strategy to create COFs with low thermal conductivity.

Tunable thermal conductivity

To achieve tunable thermal conductivity, a contrast between the initial and final states through structural or interaction change is needed. The gas-solid interaction in COFs offers one way to develop tunable thermal conductivity. Based on the MD simulations, the infiltrated methane gas can either decrease or increase thermal conductivity. The infiltration ratio of guest materials could be controlled to regulate thermal conductivity. Further investigations into the complexities of guest-host interactions are still needed to understand the effect of different types of guest-host chemistries on thermal transport. Moreover, the inclusion of solvent molecules as guests could be considered. Solvent molecules typically have larger sizes and greater molecular weights compared to gas molecules, which can lead to distinct effects on phonon propagation within COFs. The presence of solvent molecules can induce structural changes, converting the COF framework from a robust system to a more dynamic one, as observed in MOF-5.[30,31] Additionally, solvent-COF interactions may influence vibrational lifetimes and alter the character of vibrational modes, promoting the emergence of localized incoherent modes over a broad range of frequencies, as exemplified by the HKUST-1 system.[32] Considering these factors, the thermal conductivity of COFs in the presence of solvent molecules may significantly deviate from that in the dry state. Further investigation is needed to gain insights into the solvent effect on the thermal conductivity of COFs and to optimize their performance in specific environments.

The second strategy to achieve tunable thermal conductivity is to integrate stimuli-responsive units into a rigid COF matrix as a part of the COF backbone, whose phase transition could disrupt the structural order and thereby alter thermal transport in response to external stimuli.[4] Similar to the case of photo-switchable MOFs,[33] the framework built by stimuli-responsive units, such as photoisomerization of azobenzene,[34], or magnetic stimuli with mesogen[35], could achieve controllable morphology and thus tunable thermal conductivity. One can also introduce stimuli-responsive units to graft or modify the COF walls. For instance, adsorbed species and functional attachments of stimuli-responsive units on the pore walls of COFs could alter the free space volume of the pores through contraction or expansion of the functional moieties, changing the porosity of the COFs and thus the thermal transport properties. We envision that the thermal conductivity of COFs can be switched on demand using different stimuli, including electrical, magnetic, thermal, and optical.

Current Challenges and Potential Solutions

Even though the previous COF studies have demonstrated their great potential for a broad range of thermal applications, only a few COF structures have been investigated so far. Moreover, most of the results are based on the MD simulations, and there is still a lack of experimental verifications. For the MD simulations, it is still challenging to describe all the atomic interactions in COFs, and describing interactions between guests and COFs is even harder. The experimental efforts to study the thermal transport processes in COFs are limited by the difficulty in synthesizing high-quality crystalline COFs with large sizes. In addition, no experimental data on in-plane thermal conductivity have been reported so far because of the technical challenges. These challenges in MD simulations, COF synthesis, and thermal property measurements are mutually complementary, as illustrated in Figure 4, and should be addressed in the future for a better understanding of the thermal transport mechanisms in COFs.

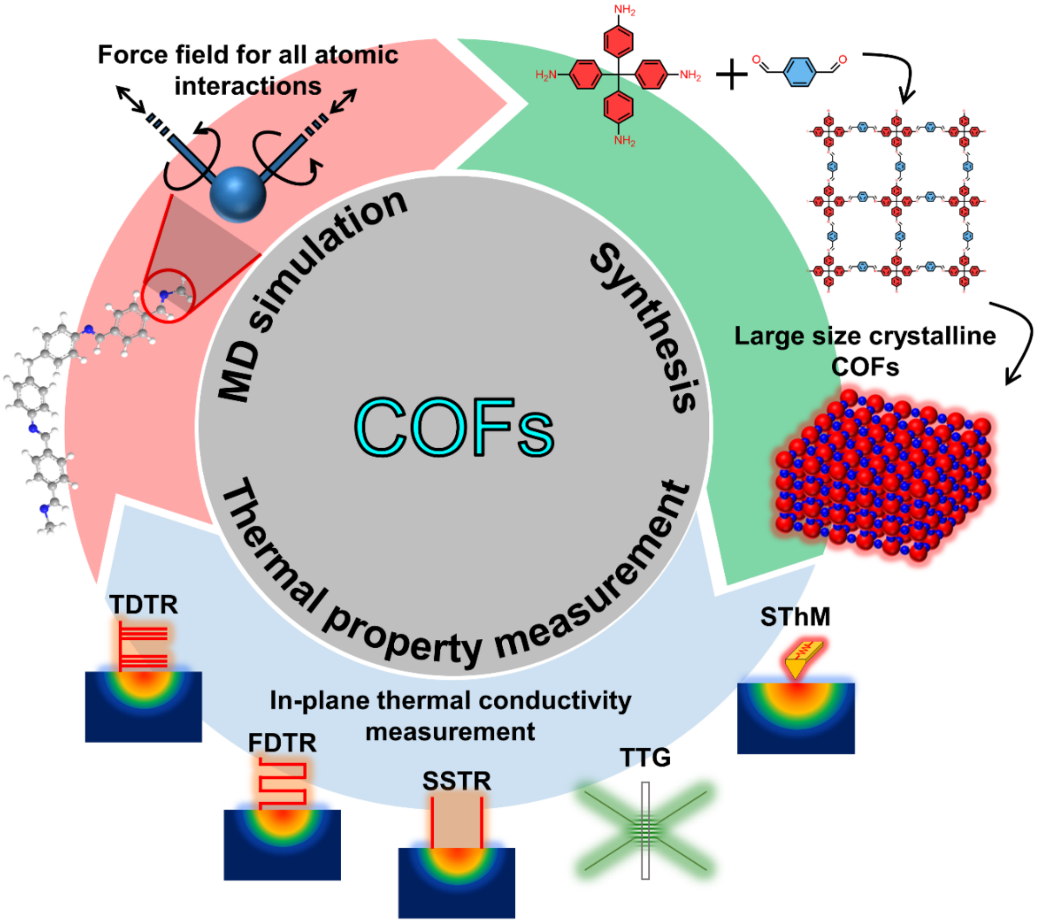

Figure. 4 Schematic of current challenges of investigating thermal transport mechanism in COFs

MD simulations

As discussed above, MD simulations have already provided crucial insights into the heat transfer mechanisms in various 2D and 3D COFs. There are ample opportunities where MD simulations can help guide the design of COFs from a thermal perspective. One of the advantages of MD over methods such as density functional theory (DFT) calculations is the ability of MD simulations to intrinsically account for full-order anharmonicity. For polymeric materials such as COFs that have large unit cells, DFT-based methods involving calculations of higher-order anharmonic interatomic force constants become computationally infeasible. As such, MD simulations where one can efficiently study large supercells (required to accurately model the vibrational physics) become the practical choice to gain atomistic- and spectral-level insights into the thermal transport properties of COFs. However, one critical limitation of MD simulations is the lack of interatomic potentials for COFs that are able to accurately describe all the atomic interactions and replicate their correct vibrational physics.

In general, classical interatomic potentials such as the universal force field (UFF) and polymer consistent force field (PCFF) have had considerable success in correctly describing a range of physical phenomena for several polymeric materials.[36,37] In fact, PCFF has already been employed to understand the role of pore size on the thermal transport properties of COF-300 and its derivatives.[14] However, these force fields still lack some appropriate parameters to fully describe both the long- and short-range interactions for various COFs. For example, although some classical all-atom force fields, such as the widely used UFF, are able to describe a monolayer sheet of 2D COF, they are not able to fully replicate the 2D stacked structure with columnar pore geometries in various 2D COFs. This is mainly because the force fields lack key parameters (such as the π-π interactions) that are necessary to keep the columnar pores and the stacked layers intact. In addition, although PCFF can handle nonbonded interactions such as π-π interactions and hydrogen bonds,[38] it cannot describe some complicated covalent bonds or interactions between multiple atoms. Therefore, lacking some key parameters required to correctly model all interactions in COFs, these potentials are not fully equipped to study the fundamental thermal transport processes for a wide array of COF structures.

Recent MD simulations utilizing reactive bond order potentials, such as the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential, have had some success in correctly describing the layered 2D structures for some idealistic COFs.[12,17,39] These studies have shed light on some crucial heat transfer mechanisms in idealized 2D COFs. However, insights gained from these toy models are still limited, and there is plenty of room for advancements in modeling the correct chemistries and architectures for a range of 2D and 3D COFs. For accurate thermal conductivity predictions and to gain atomistic insights into the thermal transport characteristics of COFs, machine learning-based interatomic potentials could be pivotal in accounting for all the diverse interatomic interactions necessary to correctly replicate the intricate chemistries and geometries of COFs. These machine learning potentials also provide the prospect of acquiring DFT-level accuracies in MD simulations that are critically important for replicating the correct vibrational physics in COFs.

COF Synthesis

There are still many obstacles in synthesizing high-quality COFs, preparing uniform thin films, and growing crystals suitable for single-crystal X-ray analysis and thermal conductivity measurements. As mentioned in the introduction, the COF preparation is a compromise between formation of highly robust chemical bonds (ensuring chemical and thermal material stability) and maintenance of high COF crystallinity (relying on formation of dynamic bonds and self-correction mechanisms).[25,26] The solvothermal method is a classical approach commonly used to synthesize COFs, but it has various shortcomings, including strict temperature and pressure controls, a longer reaction time, harmful organic solvents, and a complex operating procedure. Alternative growth mechanisms based on non-traditional heating methods and reaction media have been developed. For example, microwave synthesis methods and ionic liquid-mediated synthesis offer faster, simpler, and more environmentally friendly routes to COF synthesis.[40–42] As an attractive alternative to existing direct synthetic routes of COF preparation is their post-synthetic modification, *i.e.* a reliable method allowing for tailoring material properties after material synthesis. Currently, reconstruction routes for enhancement of framework crystallinity and porosity and on-surface COF synthesis attract significant attention of the broader scientific community.[6,7] Despite significant progress in understanding COF formation mechanisms, current studies are largely limited to COFs linked by borate and imine.[42] A clear elucidation of the process of COF growth and nucleation is needed to synthesize other types of COFs. Furthermore, current synthesis strategies are primarily applied to 2D COFs, while the field of 3D COFs has shown a slower growth trajectory due to two main reasons. Firstly, organic building blocks with multiple reactive groups possessing suitable geometry are less accessible for 3D COFs.[43] Secondly, the orientation of organic building blocks in 3D frameworks is more flexible due to the absence of layered structures and strong π-π interlayer interactions observed in 2D COFs. As a result, the synthesis of 3D COFs is more challenging and can lead to multiple crystalline structures or even amorphous phases, which are typically less stable than 2D COFs. The combination of these factors exhibits a profound influence on the process of crystallization of 3D scaffolds, thereby contributing to the scarcity of 3D COF single-crystal structures reported in the literature to date. To overcome these challenges, further thermodynamics and kinetic studies on COF growth under various reaction conditions are essential, given that the development of 3D COFs is still in its early stages.

Larger than micrometer-sized COF single crystals are desired for thermal characterization. Fortunately, there have been synthesis efforts to pursue larger COF crystals, and they have shown promising results. For example, a large single crystal of 3D imine COF with the size of tens of microns was obtained by dynamic control during crystal growth.[44] 2D COF single crystals with sizes up to 0.2 mm were produced within 2~5 min *via* the growth in supercritical CO_2.[45] Nevertheless, the synthesis of large-scale COF single crystals as well as formation of highly uniform thin films are still in its early stages and requires further development to fulfill the requirements of large-scale production that is necessary for thermal measurements and eventually practical applications in industry.

Thermal Conductivity Measurement of COFs

The anisotropic thermal conductivity of 2D COFs gives the potential for exceptional heat-spreading solutions on the nanoscale. However, the computationally predicted high in-plane thermal conductivity has never been experimentally validated. This, in part, is due to limitations in the current thin film thermal conductivity metrologies coupled with growth considerations for highly ordered COFs.

Pump-probe thermoreflectance techniques (TDTR, FDTR, and SSTR)

Standard implementations of the pump-probe thermoreflectance techniques, such as time-domain thermoreflectance (TDTR), frequency-domain thermoreflectance (FDTR), and steady-state thermoreflectance (SSTR), are ideal for measurements of cross-plane thermal conductivity. However, their standard implementations make them relatively insensitive to in-plane thermal conductivity for COF thin films due to the fact that while COFs are strongly anisotropic, the magnitude of their in-plane thermal conductivity is still relatively low and thus will not influence the in-plane heat spreading of the deposited heat from the focused laser spot. Further, the high-quality COF thin films synthesized to date are typically on graphene-templated thin thermal oxides (~100's nm of SiO_2 on Si wafer) or metals; these substrates dominate the in-plane heat spreading relative to the thin COFs, thus preventing any sensitivity to the in-plane thermal conductivity of the COFs. One possibility to accurately measure the in-plane thermal conductivity of thin COF films would be to use much thicker thermally insulating layers as substrates so that the majority of heat spreading in the measurement volume of a thermoreflectance experiment would be in the COF. This sample configuration would be ideal for a standard SSTR measurement,[46] which operates in the low frequency, steady state regime and thus is inherently more sensitive to in-plane heat transfer or a beam-offset thermoreflectance measurement.[47] In principle, however, even with current COF sample geometries that are fabricated on thermally conductive substrates or very thin insulating layers, implementing pump-probe thermoreflectance-based measurements with diffraction- or sub-diffraction limited spot size and/or beam offset approaches could enhance the measurement sensitivity to in-plane transport.[48] In addition, using oblong beam or patterned transducers, such as 1D metallic grating on sample surface, may offer a possibility to directly control directional sensitivity of pump-probe thermoreflectance -based measurements.[49,50]

Another possibility would be to create suspended COF films for electrothermal-based measurement methods allowing a more direct assessment of in-plane thermal conductivity without obfuscation from cross-plane diffusion.

Transient thermal grating techniques (TTG)

The laser-based transient thermal grating (TTG) technique is a pump-probe method for measuring the thermal diffusivity of various types of materials, such as bulk crystals, thin films, liquid samples, *etc*.[51–53] It is sensitive to in-plane thermal diffusivity, as demonstrated in 2D hybrid perovskite.[53] In the TTG system, the two pulsed pump laser beams overlap and create the thermal gratings on the sample surface by interference. The gratings are transient, as they disappear quickly due to the short pulse of the pump laser, and their decay rate can be detected by the diffracted probe laser. This non-destructive, non-contact approach provides an accurate measurement of the in-plane thermal diffusivity, which when multiplied by density and specific heat capacity, results in the in-plane thermal conductivity. We have performed preliminary TTG studies on COF thin films, and it is feasible. Previous works that applied TTG to other types of porous materials, such as nanoporous silicon membranes and disordered porous silicon, also demonstrate the potential of TTG.[54,55]

Scanning Thermal Microscopy (SThM)

SThM is a scanning probe-based technique that enables measurements of the thermal properties of materials at the nanoscale.[56] The technique utilizes a specialized probe, which is equipped with a resistance temperature detector (RTD). The probe is sensitive to the heat flow between the probe and the sample, which can be monitored by measuring the change in resistance of the probe. SThM offers several advantages, one of which is its exceptional spatial resolution that goes beyond the diffraction limit. Because the SThM probe can be highly localized, it allows for establishing precise structure-property relationships experimentally and a more direct comparison with MD simulations. AFM has been applied to characterize the structures and orientation of COFs,[57–59] highlighting the potential to investigate heat transfer at the nanometer-scale that other thermal reflectance methods cannot achieve. Another advantage of SThM is its versatility.[60] It can be combined with various scanning probe microscopy (SPM) modes, such as electrical or mechanical measurements, as well as topography. This enables comprehensive characterization by integrating multiple types of data simultaneously. Considering these advantages, SThM holds promise for observing local thermal phenomena with significantly higher spatial resolution than other techniques, unraveling the intricate structure-property relationships of COFs.

Conclusion

In summary, COFs offer a great platform for a broad range of thermal applications. Thermal conductivities of 2D and 3D COFs are related to density, pore size, and crystallinity, as well as crystal network topologies, robust bonds, and degree of conjugation in COFs. The effect of guest-host interactions on the thermal conductivity of COFs depends on their pore size and the type of guest molecules. Incorporating stimuli-responsive moieties as either a guest or a building unit could also be explored to tune the thermal conductivities of COFs. Despite previous efforts to study the thermal behavior of COFs, obtaining a comprehensive understanding of COFs remains challenging due to limitations in atomistic simulations, COF synthesis, and thermal conductivity measurement techniques. We expect that the development of MD simulations incorporating machine learning interatomic potentials, advancements in large-scale crystalline COF synthesis, and in-plane measurement techniques will provide greater insight into the underlying thermal transport mechanisms in COFs. A comprehensive understanding of the thermal transport mechanisms of COFs will contribute to the fundamental understanding of COFs for their thermal applications.

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Author Contributions

The final version of the manuscript has received approval from all authors. All authors have participated in the discussions and agreed on the content. Jinha Kwon was responsible for writing the draft, while Hao Ma and Natalia Shustova contributed information on COF synthesis and reviewed the draft. Ashutosh Giri provided insights on guest-host interactions and MD simulation in the challenges section and reviewed the manuscript. Patrick Hopkins contributed information on measurement in the challenges section and reviewed the draft. Zhiting Tian conceived the idea of this perspective, led the discussion, and reviewed and revised the manuscript.

Notes

The authors declare no competing financial interest.

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