Supporting Information:

Heat transfer mechanisms and tunable thermal conductivity anisotropy in two-dimensional covalent organic frameworks with adsorbed gases

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As pictorially represented in Fig. S1a, the scattering of gas adsorbates with solid framework can increase the thermal conductivity via providing additional channels for energy transfer, or could lead to phonon scattering, which lowers the thermal conductivity. This work unravels these phenomena in gas infiltrated two-dimensional covalent organic frameworks (2D COFs). We note that a recent experimental measurement of cross-plane thermal conductivity on 2D COF-5 thin film (> 0.8 W m⁻¹ K⁻¹) shows that these materials are relatively more thermally conductive as
compared to other porous solids with similar densities.\textsuperscript{1} Even though our EMD-predicted thermal conductivity of $\sim 0.55 \text{ W m}^{-1} \text{ K}^{-1}$ does not exactly replicate the experimentally measured thermal conductivity at room temperature most probably due to limitations of our interatomic potential used in the simulations, our calculations do confirm the relatively higher thermal conductivity of these materials as compared to other porous solids with similar densities (such as aerogels with thermal conductivities $\sim 0.01 - 0.1 \text{ W m}^{-1} \text{ K}^{-1}$).\textsuperscript{2} In terms of the effect of adsorbates on thermal transport, a recent experimental work on infiltrated MOFs has shown that thermal conductivity decreases with liquid infiltration.\textsuperscript{3} However, due to the dissimilarities in the chemical and structural makeups of COFs as compared to MOFs (such as the unique 1D laminar pores in COFs), we cannot make an “apples-to-apples” comparison on the effect of adsorbates on heat conduction in these porous framework materials. Therefore, to realize the unique thermal properties of COFs and the prospect of anisotropic control of thermal conductivity in 2D COFs with gas infiltration, future studies should focus on how infiltration with gas adsorbates influence the vibrational scattering mechanisms dictating the anisotropic thermal properties of 2D COFs. For example, investigation of heat transfer processes across 2D COFs exposed to CH$_2$, nitrogen (lighter gases) and chlorine (heavier gas) environments could shed light on the effect of varying gas diffusivities in dictating heat conduction in these materials.

\textbf{Simulation details}

The initial computational domain are equilibrated under the Nose-Hoover thermostat and barostat,\textsuperscript{4} which is the NPT integration with the number of atoms, pressure and temperature of the simulation cell held constant for a total of 2 ns at 0 bar pressure with a time step of 0.5 fs. An NVT integration (with constant volume and number of particles) is implemented to further equilibrate the COF-5 structures with (or without gas adsorbates) at the desired temperature following the NPT simulations. Note, for all simulations periodic boundary conditions are applied in all directions. During the equilibration process, the pressure for all our computational domains are prescribed at
ambient to remove the effect of pressure on the thermal transport properties of our gas infiltrated and pristine COF-5 structures. Therefore, the interlayer separation of the 2D COF layers remain at 3.41 Å as prescribed in the AIREBO potential. Schematic representations of our equilibrated computational domains at 300 K for COF-5 and COF-5 infiltrated with gas adsorbates are shown in Fig. S1b and Fig. S1c, respectively. Figure S2 shows the top view of the computational domain equilibrated at a temperature of 50 K showing aggregation of gas molecules on the pore walls at low temperatures.

After equilibration, the thermal conductivities of the COF-5 structures (pristine and with adsorbates) are predicted via the Green-Kubo (GK) approach under the equilibrium molecular dynamics (EMD) framework. In this formalism, the thermal conductivities of our COFs along the zig-zag (zz-), arm-chair (ac-) and cross-plane (z-) directions are calculated as,

\[ \kappa_{zz,ac,z} = \frac{1}{k_B T^2} \int_0^\infty \langle J_{zz,ac,z}(t)J_{zz,ac,z}(0) \rangle dt. \]  

Here \( t \) is time, \( T \) and \( V \) are the temperature and volume of the systems, respectively, and \( \langle J_{zz,ac,z}(t)J_{zz,ac,z}(0) \rangle \) is the component of the heat current autocorrelation function (HCACF) in the prescribed direction and is given as,

\[ J = \frac{1}{V} \left( \sum_i v_i \epsilon_i + \sum_i S_i \cdot v_i \right), \]  

where, \( v_i, \epsilon_i \) and \( S_i \) are the velocity, energy and stress of atom \( i \). The first term of the equation is the convective part of the heat flux and the second term is the “virial” or the “interaction” term. By separately grouping the atoms into their respective gas or solid framework subsystems in Eq. 2, we can calculate the contributions to the total heat flux from the gas molecules separately from that of the solid framework.

We set the total correlation time period to integrate the HCACF to 50 ps so that the HCACF decays to zero completely as shown in the inset of Fig. S3. The HCACF is computed every 10 time steps with a time step of 0.5 fs during the data collection period followed by integration.
of the HCACF t to calculate the converged thermal conductivity for our COF-5 structures. The converged thermal conductivity is averaged from the integration from 10 ps to 50 ps as shown in Fig. S3 (dashed line) for the case of the pristine COF-5 computational domain. Note, the thermal conductivities in the $zz$- and $ac$-directions are similar within uncertainties for all our structures, so we report an average in-plane thermal conductivity for the two directions. We vary the total cross-plane thickness, $d$, and length of the computational domain, $L$, to check for system size effects for our nonequilibrium and equilibrium MD simulations to predict the thermal properties as detailed below. We find that the thermal conductivities of structures with cross-sections of $15\times13$ nm$^2$ and $30\times26$ nm$^2$ are comparable within uncertainties. Similarly, the thermal conductivities of structures with computational domain sizes of $15.1\times13.1\times34$ nm$^3$, and $15.1\times13.1\times68$ nm$^3$ are also similar within uncertainties. Therefore, we use the former for all of our simulations.

The uncertainties in our EMD calculations are determined from three independent simulations and averaging the thermal conductivity from 10 to 50 ps correlation time as mentioned above. As noted above, the contributions from each atom in the simulation domain to the total heat flux can be calculated with Eq. 2 and the contributions to thermal conductivity from the covalent solid framework and the gas constituents can be easily separated. This is shown in Fig. 1b and Fig. 1c of the main manuscript for our COF-5 structure with 3.7 molecules nm$^{-3}$ in the pores. The in-plane thermal conductivity dominated by the contribution from the solid framework as shown in Fig. 1b, whereas, the addition of the gas adsorbates enhances the cross-plane thermal conductivity as shown in Fig. 1c. Since temperature increases the diffusivities of the gas molecules and increases gas-framework collisions, increasing the temperature leads to higher contributions from the gas adsorbates as shown in Fig. S6.

Figure S5 shows the temperature dependent thermal conductivities in the in-plane (red squares) and cross-plane (blue circles) directions for the COF-5/CH$_4$ computational domain with methane gas at 0.5 molecules/nm$^3$. We also plot the temperature trends for the pristine COF-5 computational domain in the two directions for comparison. In comparison to the pristine case, the temperature dependent cross-plane thermal conductivity for the low gas density case is similar to that of the
pristine case while the temperature dependence is greatly reduced for the in-plane direction with the addition of 0.5 molecules/nm\(^3\). This shows that while the cross-plane thermal conductivity is not drastically enhanced at higher temperatures (at these low gas densities), the in-plane vibrational scattering due to gas infiltration can drastically reduce the temperature dependence of thermal conductivity along the 2D COF layers (even at such low gas densities).

Table I shows our calculated gas densities, mass densities, in-plane (\(\kappa_{ip}\)) and cross-plane (\(\kappa_{cp}\)) thermal conductivities, contributions from the gas and solid framework to the cross-plane thermal conductivity of our different 2D COF/methane computational domains.

**Comparison of thermal conductivity predictions from the Green-Kubo and the direct methods**

Recently, the use of several many-body interactions have been in contention for accurately predicting the stress of individual atoms for calculation of heat flux as implemented in the LAMMPS package.\(^5,6\) Therefore, to gain confidence in our GK-predicted thermal conductivities of our COF-5 structures, we compare the in-plane thermal conductivity prediction of our pristine COF-5 from the GK method to that determined from the direct (or the nonequilibrium molecular dynamics) method. The results from the direct method are shown in Fig. S4. For the direct method, a steady-state temperature gradient is established by adding and subtracting equal amounts of energies from the hot and cold baths as shown in Fig. S4a. We then obtain the temperature profile along the direction of the applied temperature gradient by averaging the temperature of the atoms along 100 equally spaced bins for a total of 8 ns. We invoke the Fourier’s law to calculate the thermal conductivities by ignoring the initial \(\sim3\) ns of data to create time-averaged steady-state temperature profiles as shown in Fig. S4a. As there is considerable size effects on the prediction of thermal conductivity with the direct method, we determine the thermal conductivity for an infinite length simulation domain by first plotting \(1/\kappa\) vs. \(1/d\) and then taking the reciprocal of the \(y\)-intercept value as the length-converged thermal conductivity (see Fig. S4b). This method predicts \(\sim2\pm0.5\) W m\(^{-1}\) K\(^{-1}\) for the in-plane thermal conductivity of a pristine COF-5 structure, which agrees well
with our GK-predicted value of \( \sim 1.8 \text{ W m}^{-1} \text{ K}^{-1} \) providing confidence to our GK-predictions. Note, the large uncertainty associated with the direct method arises from the linear fitting routine (with 95 % confidence level) to obtain the length converged thermal conductivity from the NEMD results as shown in Fig. S4b.

Gas diffusivity calculations, comparison to bulk gas and mass modified methane/COF-5 systems

To show that collisions between the gas-solid framework is the reason behind the increase in cross-plane thermal conductivity with increasing gas densities, we calculate the thermal conductivity of a bulk gas (without the solid framework) at a very high density of 6 molecules nm\(^{-3}\) (see Fig. S7a). Separate contributions from the convective and virial part of the Green-Kubo predicted thermal conductivity of bulk gas at 6 molecules nm\(^{-3}\) shows that the thermal conductivity is dominated by the convective term in the calculation of the heat flux for bulk gas unlike for gases diffusing in the COF-5 pores. Figure S7b shows the contribution of the solid framework to the total thermal conductivity in the cross-plane direction for COF-5 structure with gas density of 3.7 molecules nm\(^{-3}\). The addition of gas increases the thermal conductivity by \( \sim 0.7 \text{ W m}^{-1} \text{ K}^{-1} \), which is much higher than the thermal conductivity of the bulk gas at an almost double the gas density; the virial component of thermal conductivity for bulk methane at 6 molecules nm\(^{-3}\) is \( \sim 0.05 \text{ W m}^{-1} \text{ K}^{-1} \), which is much lower than the contribution of methane gas inside the pores of 2D COF-5 (see Fig. S7). This suggests that gas-gas collisions is not the dominant heat transfer mechanism and rather it is the gas-solid collisions that increase the thermal conductivity in the cross-plane direction for our gas infiltrated COFs. The drastically varying thermal conductivity of the gas in the bulk phase and inside the COF pores also suggests that predicting the thermal conductivity of gas infiltrated COFs cannot be accurately made with a simple ‘rule of mixtures’ type of calculation.

Calculations of mean-squared displacements (MSD) of the gas molecules is conducted to investigate their diffusivities. The MSDs as a function of simulation time for the COF-5 with gas density of 3.7 molecules nm\(^{-3}\) at 50 K and 300 K is shown in Figs. S8a and S8b, respectively. As
the temperature increases, the diffusivities of the gas molecules increase as well. At temperature below 150 K, the gas molecules adsorb to the pore walls as shown by the top view of the computational domain for COF-5 with gas density of 3.7 molecules nm\(^{-3}\) at 50 K in Fig. 4c of the main manuscript. Mean square displacements in the in-plane directions are also shown to highlight the limited diffusivities of gas molecules along the more constrained in-plane direction. The slope of the MSD is directly proportional to the diffusivities of the gas molecules. Following this, the diffusivities of the gas molecules at different gas densities is shown in Fig. S10. The diffusivities are calculated to be \(\sim 10^{-3} \text{ cm}^2 \text{ s}^{-1}\) for the gases inside the COF-5 pores, which is three orders of magnitude smaller than the diffusivities of bulk gas. This implies that the diffusion of gas molecules is described by Knudsen diffusion dominated by collisions with the solid framework rather than gas-gas collisions. We note that the slope of the MSD vs. time (and therefore the calculated diffusivities) for our COF-5/CH\(_4\) systems are independent of the length of simulation time as shown in Fig. S9.

To investigate the influence of gas diffusivity on the overall thermal transport, we perform additional simulations by varying the mass of the carbon atoms in the CH\(_4\) molecules (in the 2 to 40 g mol\(^{-1}\) range) for our computational domain with a gas density of 3.7 molecules nm\(^{-3}\). As shown in Fig. S12a, increasing the mass results in a decrease in the diffusivities of the gas molecules at room temperature. Overall, as shown in Fig. S12b, the total cross-plane thermal conductivities of the computational domains for the entire mass range of the gas adsorbates are similar. With increasing mass, however, the thermal conductivity contributions from the solid framework increases; the thermal conductivity of the solid framework is lowered by \(\sim 40\%\) for the 2 g mol\(^{-1}\) case with the highest value for the gas diffusivity (see Fig. S12a). This suggests that with higher number of collisions with the solid framework (due to higher gas diffusivities), the solid framework thermal conductivity is lowered for the 2 g mol\(^{-1}\) as compared to that in the pristine case. We attribute this to reduced number of solid-gas collisions and the increase in thermal boundary conductance with decreasing diffusivity. For these simulations, although the relative contributions from the guest and the host are different, the overall cross-plane thermal conductivities with varying mass of the
gas adsorbates are similar due to the fact that the contributions to the total cross-plane thermal conductivity from the gas adsorbates decrease with increasing mass. Modifications to the internal pore geometry to restrict the motion of the gas adsorbates and concomitantly their diffusivities can also impact the cross-plane heat conduction in these systems as shown in Fig. 4 of the manuscript.

**Density of states and spectral heat flux calculations**

To understand these mechanisms of heat transfer in more detail, we conduct density of states (DOS) calculations and spectral heat flux calculations as detailed in our previous work. The vibrational density of states (DOS) are calculated by outputting the velocities of the atoms in the computational domain every 10 time steps for a total of 2 ns. The density of states, \( D(\omega) \), is obtained from the fourier transform (\( \mathcal{F} \)) of the velocity correlation function (VACF) by the Welch method of power spectral density estimation,

\[
D(\omega) = \frac{1}{2} m \mathcal{F}(VACF) \frac{1}{k_B T \rho}
\]

where \( m \) is the atomic mass of the different species, \( k_B \) is the Boltzmann constant, \( T \) is the local temperature, and \( \rho \) is the atomic density.

The spectral heat flux calculations are based on the analysis as described in our previous work in Ref. 7. Briefly, the heat current between atoms \( i \) and \( j \) is proportional to the correlation between the force, \( \mathbf{F}_{ij}^* \), and the velocities of the two atoms, \( q_{i,j}(\omega) \propto \langle \mathbf{F}_{ij}^* \cdot (\mathbf{v}_i^* + \mathbf{v}_j^*) \rangle \), where \( \langle \rangle \) denotes a steady-state nonequilibrium ensemble average. To determine the spectral heat flux for our computational domains, we tabulate the forces and velocities of a group of atoms in the solid framework for a total of 5 ns with 5 fs time intervals under the microcanonical ensemble.
Table S1: Gas densities, mass densities, in-plane ($\kappa_{ip}$) and cross-plane ($\kappa_{cp}$) thermal conductivities, contributions from the gas and solid framework to the cross-plane thermal conductivity of our different 2D COF/methane computational domains.

<table>
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<th>COF structure</th>
<th>gas density (molecules nm$^{-3}$)</th>
<th>mass density (g cm$^{-3}$)</th>
<th>$\kappa_{cp}$ (W m$^{-1}$ K$^{-1}$)</th>
<th>gas contribution (%)</th>
<th>solid contribution (%)</th>
<th>$\kappa_{ip}$ (W m$^{-1}$ K$^{-1}$)</th>
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Figure S1: (a) Schematic illustration of different mechanisms that could be responsible for heat transfer in two-dimensional covalent organic frameworks with gas adsorbates. The scattering of gas molecules with the laminar pore walls in the covalent organic framework could potentially lead to an increase or decrease in thermal conductivity depending on whether the scattering will lead to additional heat pathways or additional vibrational scattering. Equilibrated computational domains used in our molecular dynamics simulations showing (b) an empty COF-5 structure and (c) one where methane gas molecules are added at a density of 3.7 molecules nm\(^{-3}\).

Figure S2: Top view of the computational domain for COF-5 with gas density of 3.7 molecules nm\(^{-3}\) at 50 K showing aggregation of the gas molecules around the pore walls.
Figure S3: Green-Kubo predicted thermal conductivity of COF-5 structure as a function of the integration time in the zig-zag, arm-chair and cross-plane directions. (inset) HCACF vs. time for COF-5 showing that the integration time of 50 ps is enough to provide a converged thermal conductivity.

Figure S4: (a) Nonequilibrium molecular dynamics predicted in-plane thermal conductivity of pristine COF-5 structured. A hot bath and a cool bath at the domain boundaries in the arm chair direction imposes a steady-state heat flux. The thermal conductivity is calculated by invoking the Fourier’s law. (b) By plotting $1/\kappa$ vs. $1/d$ we can determine the length independent thermal conductivity from the y-intercept of the linear fit. We predict an in-plane thermal conductivity of $\sim 2 \pm 0.5$ W m$^{-1}$ K$^{-1}$ for our pristine COF-5 which agrees well with our GK-predicted thermal conductivity of $\sim 1.8 \pm 0.2$ W m$^{-1}$ K$^{-1}$ (within uncertainties).
Figure S5: Temperature dependent thermal conductivities in the in-plane (red squares) and cross-plane (blue circles) directions for the computational domain with 0.5 molecules/nm$^3$. For comparison, the temperature trends for the pristine COF-5 computational domain in the two directions are also shown. The temperature dependent cross-plane thermal conductivity for the low gas density case is similar to that of the pristine case while the temperature dependence is greatly reduced for the in-plane direction with the addition of 0.5 molecules/nm$^3$ in comparison to the pristine case.
Figure S6: (a) Contribution to the cross-plane thermal conductivity by the addition of gas adsorbates at different temperatures for COF-5 structure with gas adsorbates at a density of \( \sim 4 \) molecules nm\(^{-3}\). (b) As the temperature increases, the diffusivity of the gas increases monotonically. The similar trends of monotonically increasing diffusivities and thermal conductivity contributions from the gas molecules suggest that the linear dependence is most likely the result of increasing mobilities of gas molecules, which leads to more collisions with the solid framework and the concomitant monotonic increase in thermal conductivity.

Figure S7: (a) Separate contributions from the convective and virial part of the Green-Kubo predicted thermal conductivity of bulk gas at 6 molecules nm\(^{-3}\). In the bulk, thermal conductivity is dominated by the convective term in the calculation of the heat flux. (b) Contribution of the solid framework to the total thermal conductivity in the cross-plane direction for gas density of 3.7 molecules nm\(^{-3}\). The addition of gas increases the thermal conductivity by \( \sim 0.7 \) W m\(^{-1}\) K\(^{-1}\), which is much higher than the thermal conductivity of the bulk gas at an almost double the gas density.
Figure S8: Mean square displacement as a function of simulation time of the gas molecules in COF-5 with gas density of 3.7 molecules nm\(^{-3}\) at (a) 50 K and (b) 300 K. Mean square displacements in the in-plane directions are also shown to highlight the limited diffusivities of gas molecules along the more constrained in-plane direction.

Figure S9: Mean square displacement as a function of short and long simulation times of the gas molecules in COF-5 with gas density of 3.7 molecules nm\(^{-3}\). The calculation of diffusivities from the slope of the MSD vs. time plots are independent of the length of simulation time for our systems.
Figure S10: Diffusivities of the gas as a function of gas density inside the pores of the COF-5 structure.

Figure S11: Comparison of density of states calculated for methane gas inside 2D COF-5 pores and in the bulk case with 6 molecules/nm$^3$. Methane gas inside the 2D COF-5 pores have larger density of states in the 0 to 3 THz range in comparison to that in the bulk phase signifying additional heat transport pathways inside the laminar nanopores.
Figure S12: (a) Artificially varying the mass of carbon atoms in the methane gas (in the 2 - 40 g mol$^{-1}$ range) leads to drastically varying contributions from the solid framework to the total cross-plane thermal conductivity. Increasing the mass leads to reduced diffusivities of the gas molecules, which ultimately leads to higher contributions from the solid framework. (b) The total thermal conductivity of the mass perturbed systems are similar due to the lower contributions from the gas adsorbates as the mass is increased. As is clear, higher mass facilitates thermal boundary conductance between the solid and the gas but reduces the heat transfer pathways through the gas molecules leading to no change in the total thermal conductivity of the COF-5/mass perturbed methane systems.
References


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