Supporting Information

Hybridization from guest-host interactions reduces the thermal conductivity of metal organic frameworks (MOFs)

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S1. XRD (400 nm Thin Films and 5.5 μm Thick Samples)

Figure S1: The pristine HKUST-1 (black), TCNQ@HKUST-1 (red), F4-TCNQ@HKUST-1 (green), H4-TCNQ@HKUST-1 (blue) XRD data for 400 nm thin films (top) and 5.5 μm thick (bottom) MOF samples. We see little evidence of excess TCNQ, F4-TCNQ and H4-TCNQ that did not diffuse into the pores.

The formation of HKUST-1 structures and the polycrystallinity are confirmed with powder X-ray diffraction (XRD) (Figure S1). The XRD data suggest a small increase in grain size upon infiltration (see Figures S1-S3). The thin films are surface anchored, where a self-assembled monolayer (SAM) is deposited on the metal side of the SiO₂/Au substrate. The MOFs are then deposited on the pretreated Au side of the substrate, resulting in highly oriented growth. In contrast, the thick MOFs are directly deposited on the metal side of the substrate without a SAM, and do not grow in an oriented fashion resulting in higher polycrystallinity than the thin films. The LPE method produces low RMS surface roughness (< 10 nm) for the thin films, while the solution shearing RMS surface roughness is quite high (~1μm), as confirmed through profilometry. Additional crystallinity and film quality
characterization are discussed in the SI with respect to SEM, Raman, FTIR, IRRAS and NMR.

We use XRD to both confirm the successful fabrication of HKUST-1 and also to understand if the morphology of the MOF upon infiltration of the guest molecule. The XRD diffractogram shows that the thin film and 5.5 μm thick samples result in polycrystalline growth of HKUST-1. We note that the XRD patterns for the thick MOF show a very slight increase in the (111) peak reflection at 2θ=5.82, which has been shown to increase monotonically with the loading amount of TCNQ.[1] This feature also appears in the pristine and TCNQ@HKUST-1 thin films, however it is not seen when F4-TCNQ is infiltrated into the thin film MOFs. The lack of a (111) peak in the thin films is likely due to the fact that we infiltrate with low concentrations of the guest molecules. In fact, our process can be thought of more as doping, where a maximum of 2% weight of TCNQ/F4-TCNQ/H4-TCNQ is introduced into the HKUST-1. Additionally, we expect the thin films to have different peak intensities compared to their thicker counterparts. This is because thin films and thick material differ from their anchoring. This causes the uptake of the guest molecule to occur differently, as the molecules can be introduced from all sides in the thick crystal (and the loaded unit cells can expand in all directions), while the thin films are blocked from the substrate side, and not all the channels are available for loading. These differences in loading characteristics will result in different strains occurring within the crystal unit cell. Further, fewer diffraction peaks are observed for the thin film MOFs due to their oriented nature.

We note here that we were not able to achieve infiltration of the H4-TCNQ molecule into the 400 nm thin films of HKUST-1. After performing the infiltration procedure, XRD data taken of the freshly infiltrated H4-TCNQ@HKUST-1 showed evidence for the lack of diffusion and adsorption of the H4-TCNQ into the MOF. Mainly, the XRD data for the 400 nm H4-TCNQ@HKUST-1 indicated the lack of the presence of the guest molecule as shown by a lack of a (111) peak, as well as major degradation of the polycrystallinity of the MOF captured by
the decrease in intensity and broadening on the (002) peak. This is likely due to the fact the H4-TCNQ is a highly volatile molecule, and the high surface area of the thin film HKUST-1 was not conducive to facilitating diffusion and adsorption into the pores. We note that although we were not able to successfully infiltrate the thin HKUST-1 with H4-TCNQ, we do not expect any thickness dependence in the thermal conductivity, which is consistent with the lack of thickness dependence among all the other infiltrated MOF samples. Generally, a reduction in thermal conductivity in materials with a decreasing thickness indicates that heat carrying vibrational mean free paths are less than the sample thickness. In general, the lower the thermal conductivity, the shorter the heat carrying vibrational mean free paths. If the thermal conductivity of a material does not change based on a change in characteristic length scale (grain size or sample thickness), this is a good indicator that the heat carrying vibrational mean free paths are much less than the characteristic length scales. Many materials that have thermal conductivities below 1 Wm⁻¹K⁻¹ (which is the case for the MOF films studied here) are well known to have thermal mean free paths that are on the order of a few nanometers, or even on the order of a unit cell or vibrational wavelength (the so called minimum limit). In fact, a prior work by one of our authors have shown that MOFs have these “minimum limit” mean free paths.[2] Thus, for us to observe any thickness dependence in our measured thermal conductivity, we would expect to have to study MOF films with thicknesses much thinner than the ones we focused on in this work.

Infiltration of the guest molecules may result in different polymorphs, as it has been shown that subtle geometrical changes for the nitrile arrangements around the Cu centers can occur.[3] Despite this, the congruency of features between the thin and thick samples indicate that the morphology is relatively consistent between samples. To understand this further, we perform a Williamson-Hall analysis on the thin and thick XRD data in order to show that the morphology of the MOF remains relatively constant upon infiltration in both systems. Here, we measure the peak broadening of the following peaks: 002, 222, 004, and 333 (because they have
high intensities in all three samples) to understand the relative effects of the size of ordered crystalline domains captured by

$$\beta_L = \frac{K\lambda}{L \cos \theta}$$  \hspace{1cm} (Eqn. S1)

where K is the dimensionless shape factor (0.9), \(\lambda\) is the x-ray wavelength (1.5406 Å), \(\beta_L\) is the XRD feature broadening at FWHM after subtracting the instrumental line broadening (for the instrument at UVA it’s 0.03575 radians) due to crystalline and strain effects, L is the mean size of the ordered domains, and \(\theta\) is the Bragg angle. See Figure S2 for the resulting Williamson Hall plots based on Eqn. S1. We find that the mean size of the ordered crystalline domains (L) increases when infiltrated (Figure S3). This is in line with what has been seen for TCNQ@HKUST-1 previously, where crystallites increase upon loading.\textsuperscript{[1]} It is expected that we would see a larger crystalline domain increase for the (F4/H4)-TCNQ, since they are larger molecules than TCNQ. We note these results are qualitative and do not put a lot of emphases on the differences calculated between the TCNQ, F4-TCNQ and H4-TCNQ.

Analysis of the XRD data indicate that the morphology of the MOF’s remains relatively unchanged upon introduction of different guest molecules.

Finally, the 5.5 \(\mu\)m thick MOFs contain additional peaks that do not appear in the XRD of the thin film MOFs. As previously mentioned, this is due to the highly oriented nature of the thin film due to the surface anchoring. The absence of diffraction peaks arising from other crystallographic orientations (422 and 331) in the thin film indicate the high quality of the LPE deposited films.

XRD characterization for the HKUST-1, TCNQ@HKUST-1 and F4-TCNQ@HKUST-1 thin films fabricated at KIT occurred on a Bruker D8 Advance. The instrument was operated with the following configurations: a Si-strip detector (PSD Lynxeye©; position sensitive detector) with Cu K\(\alpha\)1,2 radiation (\(\lambda = 0.15418\) nm) in 0–0 geometry, variable slit on primary circle. Scans were run with step width of 0.024° 2\(\theta\) and dwell times of 84 seconds. Higher order peaks were obtained with up to 336 seconds per step.
The $2\theta$ angle scanning range was 5° to 60°. XRD data for all of the 5.5 $\mu$m thick samples fabricated at UVA, were collected on a multipurpose PANalytical Empyrean diffractometer. An X-ray was generated via Cu K-alpha radiation that was accelerated by 45 kV and 40 mA. The scan width was $2\theta = 0.01432$ ° and the scanning was performed within the range 5 ° - 35 °.

Figure S2: Williamson-Hall plots based on the XRD data taken at UVA for the thick MOFs. The analysis was performed for the four peaks of highest intensity corresponding to the 002, 222, 004/400 and 333 crystallographic directions. The symbols correspond to the broadening of the four XRD peaks selected, and the red line is the linear best fit to the data.
Figure S3: The mean size of the ordered (crystalline) domains normalized to the pristine HKUST-1 for the 400 nm and 5.5 micron thick MOF samples resulting from the Williamson-Hall analysis. These results are presented as a qualitative measurement represented as the percent increase compared to the pristine activated HKUST-1 sample.
Figure S4: Planar SEM images for the a) 5.5 μm thick pristine HKUST-1 and b) 5.5 μm thick TCNQ@HKUST-1 fabricated using solution shearing at UVA. Planar SEM images of thin film MOFs fabricated by LPE from KIT for the c) 400 nm pristine HKUST-1 and d) 400 nm TCNQ@HKUST-1 films.

The HR-SEM planar measurements collected for the thin film MOFs originated from a Zeiss HR-SEM (Gemini Class) at 3-5 kV. These data allowed for the confirmation of continuous, compact, and homogeneous films in loaded and pristine form. The SEM for the thick solution sheared MOFs were collected at UVA using a FEI Quanta 650 scanning electron microscope. Before the measurement, 120 Å thickness of the Au/Pd mixture was coated on the bulk MOFs to prevent the charging effect of the HKUST-1.
S3. TDTR Data and Analysis

Table S1: Measured SiO$_2$ thermal conductivity and thermal boundary conductance between the Au/SiO$_2$ layer for each substrate that the MOF’s were deposited on. These measurements were taken before any pretreatment (addition of the SAM layer), prior to the MOF deposition onto the substrate. The measured thermal conductivity and RMS error of the deposited MOF are also reported (refer to Fig. 2 in the main manuscript). The MOF’s deposited on Al were used for pump probe Brillouin scattering measurements. The thermal conductivity results for sample 3 (300 nm pristine HKUST-1) were published in our previous work and replicated here for comparison.\,[4]

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<th>Transducer</th>
<th>Transducer thickness (nm)</th>
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Figure S5: Raw TDTR data (symbols) and the model that is fit to the data (line) at room temperature for (a) 400 nm thin film MOFs in activated pristine form, and infiltrated with TCNQ and F4-TCNQ and (b) 5.5 µm thick MOFs in activated pristine HKUST-1, and infiltrated with TCNQ, F4-TCNQ, and H4-TCNQ.
Time domain thermoreflectance (TDTR) is an optical, non-contact, thermometry technique that was used to measure the thermal conductivities of the thin film and bulk MOFs.\textsuperscript{5–8} In this work, 65-80 nm of Au, or 80 of Al was electron-beam evaporated onto bulk amorphous SiO$_2$ substrates at a base pressure of 1x10\textsuperscript{-6} Torr. This metal layer served to transduce the optical energy from the pump pulse into thermal energy which propagated through the sample of interest. This created a transient, frequency-dependent heating event within the sample, that we then measure in the form of a temporal thermal decay with a probe pulse.

We used a Ti:Sapphire femtosecond Spectra Physics Tsunami oscillator operating at a repetition rate of 80 MHz and a wavelength centered at 800 nm (bandwidth of 10.5 nm) to perform the TDTR measurements. This output was split into two paths (pump and probe). The pump path was electro-optically modulated with a square wave at 8.8 MHz, the result of which passed through the transparent SiO$_2$ substrate and heated the gold layer and the MOF. It is important to note that the heat transfers to both the silica and MOF layer in this sample geometry, and therefore this must be accounted for properly within the thermal model that is used to fit the data. The temperature dependent reflectivity of the transducer layer was then monitored temporally by the probe beam. Specifically, the probe was delayed in time by a translational mechanical delay stage up to 5.5 ns, and the reflected intensity was measured by a photodetector (Det10A). The change in the probe’s reflectivity due to the modulated heating event is small enough that a lock-in amplifier is required to measure the signal. We use a Zurich lock-in which demodulates the signal and provides the amplitude and phase which we plot as a thermal decay curve. We then fit this decay curve with a multilayered thermal model to derive the thermal properties of interest. The TDTR raw data and model are shown in Figure S5.

Specifically, for the sample geometry employed in this study, where the laser pulse propagates through the SiO$_2$ substrate first, we consider bi-directional heat flow in our
multilayer analysis.\textsuperscript{[8]} The heat conduction model requires knowledge of each layer’s heat capacity, thermal conductivity, thickness, and the thermal boundary conductance (TBC) between each layer. Literature values were assumed for the heat capacity of the gold and silica\textsuperscript{[9]} and the TCNQ@HKUST-1 which had been reported in our previous study.\textsuperscript{[10]} Further, the heat capacity for F4-TCNQ@HKUST-1 and H4-TCNQ@HKUST-1 used in the TDTR analysis were calculated from lattice dynamics, and since TCNQ (204.19 g/mol) and H4-TCNQ (208.22 g/mol) are similar molecules with molecular weights differing by \textasciitilde2\%, we apply effective medium theory to calculate the required density to derive the volumetric heat capacity with the assumption of one guest molecule per pore. We experimentally measure the heat capacity for the pristine HKUST-1, the details of which are provided below. Error! Reference source not found. shows the heat capacities that were used for all the TDTR samples. We experimentally measured the room temperature thermal conductivity of the SiO\textsubscript{2} and the TBC between the 65-80 nm Au and SiO\textsubscript{2} (G\textsubscript{Au/SiO2}) on each substrate before the MOF’s were deposited using the standard TDTR sample geometry (where the laser pulse is incident on the air/metal side of the metal/glass sample). We find that our measurements are not sensitive to the thermal boundary conductance between either the Al/SiO\textsubscript{2} and the metal/MOF (because it is so large). The measured values that were used in the room temperature analysis of the MOF data are shown in Table S1 and the sensitivities are plotted in Figure S7, and described in further detail below. Note, the MOFs deposited on Al were used for the pump-probe Brillouin scattering measurements. The thermal conductivity of the 300 nm pristine HKUST-1 deposited on Al was published in our previous work, and shown for comparison here.\textsuperscript{[4]} Additionally, the heat model is very sensitive to the thickness of the metal film transducer. We measured the thickness via profilometry. The room temperature thermal conductivity of the Au was obtained using four-point probe ($\kappa_{\text{Au}} = 312 \text{ Wm}^{-1}\text{K}^{-1}$). Finally, the thicknesses of the thin film MOFs were confirmed through SEM after deposition onto the substrates.
Figure S6: Volumetric heat capacity for the samples measured via TDTR. The TDTR measured heat capacities for the pristine and TCNQ@HKUST-1 match up quite well. The TCNQ@HKUST-1 heat capacity was obtained from Erickson et al.\textsuperscript{[10]}

![Graph showing volumetric heat capacity for different guest molecules](image.png)
Figure S7: Sensitivity of the thermal parameters (heat capacity ($C_v$), thermal conductivity ($\kappa$), and thermal boundary conductance ($G$)) to the (a) ratio and (b) in plane ($-V_{in}$) signal for the thin
films and (c) ratio and (d) in plane (-V\textsubscript{in}) signal for the 5.5 micron thick samples of HKUST-1 and TCNQ@HKUST-1. These data are modeled at a modulation frequency of 8.8 MHz at room temperature (300 K). (a) Shows that TDTR is sensitive to both heat capacity and thermal conductivity at a single modulation frequency, (c)-(d) show that we are in an effusive regime where there is equal sensitivity to thermal conductivity and heat capacity.

In order to understand the limitations of our TDTR measurement, we perform a sensitivity analysis to simulate the expected data/thermal model under different, tunable, experimental parameters such as: the pump and probe spot size, pump modulation frequency, and the mathematical construct of the TDTR signal (magnitude, ratio, in-phase (-V\textsubscript{in}), out of phase (V\textsubscript{out})). This sensitivity analysis sheds light on the ability for TDTR to measure a given thermal parameter (thermal conductivity, heat capacity, thermal boundary conductance) based on the physical constraints of the sample. We perform a sensitivity analysis using a modulation frequency of 8.8 MHz, a radial pump spot size of 8.5 µm, a radial probe spot size of 5 µm (which is what we use experimentally), fit to the ratio and in-phase (-V\textsubscript{in}) TDTR signal (Figure S7). For the pristine sample, the different magnitude and slopes of the heat capacity (C\textsubscript{V}) and thermal conductivity (κ) in both the ratio and in-phase signal indicates that our TDTR signal is independently sensitive to both parameters at a single modulation frequency; therefore, they can be measured simultaneously. We measure a volumetric heat capacity of 8.1x10\textsuperscript{5} ± 1.62x10\textsuperscript{5} JK\textsuperscript{-1}m\textsuperscript{-3} for the 250 nm thick pristine activated HKUST-1 MOF. We provide more detail about our sensitivity and measurement of the heat capacity and thermal conductivity of the 250 nm pristine MOF in the proceeding section. The TDTR signal for the loaded MOF’s have equal sensitivity to the heat capacity and thermal conductivity (similar magnitudes and slopes) in both the ratio and in plane signal (Figure S7 (a)(b)); therefore, we can only measure a single parameter at that modulation frequency, and choose to propagate a 10% uncertainty into the LD derived heat capacities for the loaded MOFs to account for uncertainties in the MOF density, and fit for the thermal conductivity. The total uncertainty for the reported thermal conductivity measurements is calculated as the mean square deviation from ± 3 nm of uncertainty in the Au film thickness, differences in the MOF
sample thicknesses (RMS surface roughness for LPE thin films is < 10 nm, and ~1 µm for the thick solution sheared samples according to profilometry measurements) as TDTR scans were rastered across the surface, uncertainty in the volumetric heat capacity, and the residual (the model fit compared to the measured thermal decay curve) of the TDTR signal.

Heat Capacity (Thin Films and Bulk Samples)

![Contour plot showing residual for single TDTR scan fit to either the V_{in} (in phase) signal and the ratio at 300 K. The plots show that the V_{in} signal is insensitive to heat capacity. The thick black and red contour lines represent an error of 3% which indicates a good fit of the thermal heat transport model to the TDTR data. The area shaded in green shows the uncertainty of our measurement/analysis technique to the parameters of interest. We can therefore measure both the heat capacity and thermal conductivity from a single scan with uncertainties defined by the shaded green polygon.](image)

Figure S8: Contour plot show the residual (the model fit compared to the obtained thermal decay curve) for a single TDTR scan fit to either the V_{in} (in phase) signal (red contour lines) and the ratio (black contour lines) at 300 K. The plots show that the V_{in} signal is insensitive to heat capacity. The thick black and red contour lines represent an error of 3% which indicates a good fit of the thermal heat transport model to the TDTR data. The area shaded in green shows the uncertainty of our measurement/analysis technique to the parameters of interest. We can therefore measure both the heat capacity and thermal conductivity from a single scan with uncertainties defined by the shaded green polygon.

By careful tuning of experimental parameters (modulation frequency, spot size, and film thickness), we can take advantage of TDTR’s experimental configuration to measure both the thermal conductivity and heat capacity of the thinnest pristine HKUST-1 film (250nm). This is accomplished by performing TDTR measurements at a pump modulation frequency of 8.8
MHz, where the signal is sensitive to both the heat capacity and thermal conductivity, and analyzing both the in-phase and the ratio of the in-phase to out-of-phase components of the probe thermoreflectivity generated by the lock-in amplifier.\textsuperscript{[11]} Figure S8 overlays two contour plots that show the TDTR signal sensitivity to the thermal conductivity and heat capacity of a 250 nm activated pristine HKUST-1 MOF film at a pump modulation frequency of 8.8 MHz. Here, the normalized residuals ($Z_n$)\textsuperscript{[12]} are displayed resulting from the model’s fit relative to the obtained thermal decay curve ($r$) for a single TDTR scan from SiO$_2$/Au/HKUST-1 given perturbations in alternative parameters of the thermal conductivity ($k$) and volumetric heat capacity ($C_v$).

$$Z = \left( \frac{\sum_x r(x; k_{exact}C_v,exact) - r(x; k_{perturbed}; C_v,perturbed)}{\sum_x r(x; k_{exact})^2} \right)^{1/2}$$  \hspace{1cm} (Eqn. S2)

The contour plot indicates the range of values that would receive a good fit given the value used for the heat capacity or thermal conductivity. The thick black and red contour lines represent a 3% residual error,\textsuperscript{43} where all values inside those contour lines represent the acceptable range of thermal conductivities based on a single heat capacity value resulting from a good fit of the thermal model to the data. Further, the green polynomial that is captured by the 3% residual error lines shows the uncertainty to which we can measure both the thermal conductivity and heat capacity at a single modulation frequency. Figure S8 shows that the in-phase component (red contour lines) of the signal is insensitive to the heat capacity. Therefore by performing an iteration procedure where we first fit the in-phase component of the TDTR signal for the thermal conductivity (where the input value for the heat capacity will not affect the result for the thermal conductivity) and then use that value as an input to the model and fit the ratio for both thermal conductivity and heat capacity, allows for the simultaneous measurement of the thermal conductivity and heat capacity at a single modulation frequency. The ability to measure both the thermal conductivity and heat capacity of a material is extremely
important because it validates the accuracy of the thermal model for characterizing the thermal properties of a new material. We assume a size independent heat capacity and therefore use the measured heat capacity value from the 250 nm pristine MOF for all of the pristine MOF samples.

It is important to quantitatively assess the steady state temperature rise induced by the pump pulses in TDTR when measuring low-thermal conductivity materials. This is because if the steady state temperature rise is large, the thermal properties of the material can drastically vary and result in large errors of the fitted parameters. We calculate the steady state temperature rise in the 400 nm pristine and TCNQ infiltrated HKUST-1 using the method outline by Braun et al. [13] Specifically, we calculate the upper bound at 300 K with a pump power of 100 mW, which is the upper limit of the pump power used in the experiments (Table S2). We see that we do not exceed a 1 K steady state temperature rise in our samples. Although the MOFs have low thermal conductivities, the gold transducer has a high heat capacity and large thermal conductivity which allow the heat to dissipate radially without creating a significant temperature rise. This confirms that the temperature dependent material properties do not need to be altered for our temperature dependent measurements.

**Table S2: Calculated steady-state temperature rise (degree K) resulting from 100 mW of pulsed laser heating of the multilayer SiO_2/Au/MOF films measured with TDTR using the method outlined by Braun et al. [13]**

<table>
<thead>
<tr>
<th>Sample</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine HKUST-1</td>
<td>0.67 K</td>
</tr>
<tr>
<td>TCNQ@HKUST – 1</td>
<td>0.74 K</td>
</tr>
</tbody>
</table>

We also performed a time series of measurements on a 400 nm HKUST-1 pristine film that was activated according to the activation procedure described in the manuscript. We find that the change in thermal conductivity is useful for monitoring the MOF as it transitions to a deactivated state as water vapor adsorbs into the pores in ambient conditions. We use the active pristine heat capacity to perform our analysis for all data points. The results indicate that the
400 nm thin film HKUST-1 remains in its activated form up to five hours after it has been exposed to ambient conditions. Upon deactivation, water vapor is adsorbed into the pores and causes a reduction in the thermal conductivity.

Figure S9: The thermal conductivity of a 400 nm pristine activated sample vs. time (in minutes) as it is exposed to ambient conditions and becomes ‘deactivated’. Note that the first data point has been shifted to 12 min in order to use a log scale, but is representative of the MOF immediately after activation.
S4. Electrical Conductivity

Designing materials with optimum ZT is always complicated by the relationship between thermal and electrical conductivities. The goal is to maximize the electrical conductivity while minimizing the total thermal conductivity, however this is difficult to do since the total thermal conductivity is the sum of lattice thermal conductivity ($\kappa_l$) and the electronic thermal conductivity ($\kappa_e$)

$$\kappa_{total} = \kappa_l + \kappa_e.$$ 

The relationship between the electrical conductivity and the electrical component of the thermal conductivity is captured by the Wiedemann-Franz law,

$$\frac{\kappa_e}{\sigma} = LT$$ 

where the Lorenz number $L=2.44 \times 10^{-8} \text{W} \Omega \text{K}^2$, and $\sigma$ is the electrical conductivity. In the manuscript, we report that the infiltration of electrically conductive guest molecules (TCNQ, F$_4$-TCNQ, H$_4$-TCNQ) drastically decreases the total thermal conductivity ($\kappa_{total}$) of the material system. Previous works have shown that infiltration with the guest electrically conductive guest molecules investigated here increases the electrical conductivity. [14–16]

Therefore, we provide a quantitative comparison of the contribution of the electrical conductivity to the total thermal conductivity to reinforce the result that the contribution of the electrical conductivity to the total thermal conductivity is negligible, and the large reduction in total thermal conductivity stems from minimizing the lattice component of the thermal conductivity; the mechanisms of which are discussed in detail in the manuscript. We refer to curious reader to previous works that go into detail discussing the charge transport in TCNQ, F4-TCNQ, and H4-TCNQ loaded HKUST-1. [14–16] Notably, our co-authors (Xin et al.) report on the electrical conductivity of pristine and TCNQ infiltrated HKUST-1 thin films that were fabricated by the same liquid phase epitaxy/layer by layer technique used to fabricate the thin films in this study. [16]
In total, previous investigations into the electrical conductivity of pristine and loaded HKUST-1 show that pristine non-loaded HKUST-1 films are electrical insulators (their conductivity is below the signal-to-noise limit of the instrument), while infiltration with TCNQ results in the largest measurable conductivity change of the guests considered here, that is at least a factor of 10^7 higher than the pristine MOF. Further, it has been shown that the extent of electronic coupling can be tuned through the use of TCNQ-derivative guests, where the fluorinated analogue (F_4-TCNQ) and the fully hydrogenated (H_4-TCNQ) results in subsequently decreasing electrical conductivities due to the reduction of the electronic coupling matrix through fluorination and disruption of the conjugated \( \pi \)-orbitals upon hydrogenation, respectively. **Table S3** shows the calculated contributions of the measured electrical conductivity to the total thermal conductivity, measured from Chen et al.\cite{16} and Talin et al.\cite{15} for pristine HKUST-1 and TCNQ@HKUST-1 (which exhibits the highest electrical conductivity). We see that the contribution of the electrical thermal conductivity to the total thermal conductivity is negligible, and that the role adsorbate is to drastically reduce the lattice contribution of the thermal conductivity.

**Table S3**: Calculated contribution of the electrical component of the thermal conductivity from measurements of the electrical conductivity provided by Chen et al.\cite{16} and Talin et al.\cite{15}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \kappa_{total} ) (Wm(^{-1})K(^{-1}))</th>
<th>( \kappa_e ) (Wm(^{-1})K(^{-1}))</th>
<th>( \sigma ) (Sm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>0.70</td>
<td>7.32x10(^{-11})</td>
<td>10(^{-6})</td>
</tr>
<tr>
<td>TCNQ@HKUST-1</td>
<td>0.25</td>
<td>1.10x10(^{-6}) - 5.12x10(^{-5})</td>
<td>0.15 - 7</td>
</tr>
</tbody>
</table>
S5. Raman (Thick Samples)

Figure S10: Raman spectra (not normalized) for the activated thick HKUST-1, TCNQ@HKUST-1, F4-TCNQ, and H4-TCNQ samples. The peaks with black lines are peaks occurring in all the samples, the peaks with red lines are peaks that occur in only the HKUST-1 and TCNQ@HKUST-1 the peaks with green lines are unique to the F4-TCNQ@HKUST-1 and the peaks with blue lines are unique to the H4-TCNQ@HKUST-1 sample.

Raman spectra were acquired at the University of Virginia using a Renishaw inVia spectrometer with 532 nm incident light with 120 times/s exposure time, 50 x objective, and the laser power set to 1% (max power is 50 mW). The cut-on for the Rayleigh filter was approximately 100 cm$^{-1}$. The Raman spectra from 500-1800 cm$^{-1}$ range are dominated by modes associated with the organic part of the MOF framework, while the modes at lower wavenumbers involve vibration modes from Cu(II). The nitrile Raman peak occurring in the guest molecules is expected at ~2229 cm$^{-1}$ and is not resolved in these spectra.$^{[17]}$
The shifts that occur in the Raman peak for the samples allow for the assessment of structural changes in the form of chemical bonds (bond length) and symmetry of molecules. The modes at 181 cm\(^{-1}\) and 502 cm\(^{-1}\) in the pristine MOF are useful to judge the activation quality (amount of water in the pores). The amplitude of the 502 cm\(^{-1}\) peak will decrease while the 181 cm\(^{-1}\) peak amplitude will increase as higher concentrations of water infiltrate the pores.\(^{[18]}\) We see evidence of successful activation within the bulk pristine sample, validating the activation procedure used for this study. The spectral peaks shown with black lines running through them are peaks that appear in all three spectra. We note, in particular, the aromatic alkene stretches at 1617, 1544, and 1617 cm\(^{-1}\). No shift occurs between the pristine and the TCNQ@HKUST aromatic alkene peaks. The H\(_4\)-TCNQ shows red shifts in comparison to the pristine alkene aromatic peaks, and the aromatic peaks in the F\(_4\)-TCNQ are dampened in comparison to the other guest@HKUST-1. The dampening is likely due to the highly electronegative fluorine atoms, which are much more electron withdrawing than the hydrogen atoms and lower the reduction potential. The presence of these features helps to confirm the presence of the F\(_4\)-TCNQ and H\(_4\)-TCNQ molecules within the pore, which are very volatile, and can easily escape. Additionally, several new bands appear in the F\(_4\)-TCNQ@HKUST-1 sample (1394, 1241, 1100, and 771 cm\(^{-1}\)). We see slight shifts occurring for the C=C wing stretch at 1462 cm\(^{-1}\) for all three adsorbates. We note that the TCNQ and pristine spectra look very similar from 500-1800 cm\(^{-1}\), where spectral modes from the organic part of the MOF are present. This indicates that the intrinsic bonding of the MOF is unchanged. The F4-TCNQ and H4-TCNQ show the presence of completely unique peaks that are not necessarily indicative of new bonding, but rather are due to the F4-TCNQ and H4-TCNQ molecules themselves. The Raman data also shows that infiltration with all three adsorbate molecules suppresses the C=C symmetric stretch that occurs at 1048 cm\(^{-1}\) in the pristine MOF.
Figure S11: FTIR of activated bulk HKUST-1, and TCNQ@HKUST-1. The important functional groups are identified.

Infrared spectra (IR) were recorded for the bulk samples only, at UVA, on a Nicolet is5 from Thermo Scientific. Samples were measured as a glaze on the spectrometer fitted with a horizontal attenuated total reflectance (HATR) accessory. We use FTIR to understand the molecular fingerprint of HKUST-1 and TCNQ@HKUST-1, where chemical bonds are directly probed. The spectra allow for the identification of specific functional groups and a better understanding of the bonding environment. FTIR is not suitable for detecting the Cu-N bond that occurs between the MOF and adsorbate because metals do not absorb infrared light (vibrational frequency is beyond the measuring range of the FTIR). We note the C=O symm feature occur at 1640 cm\(^{-1}\), the cyclic alkene features at 1591, 1442 cm\(^{-1}\) and the Ar=C-C at...
1363 cm$^{-1}$. There is evidence of the C=C alkene modes disappearing upon infiltration with the TCNQ molecule (1591 cm$^{-1}$). The absence of those modes maybe due to $\pi - \pi$ stacking interactions between the aromatic rings of the TCNQ within the pores.$^{[19]}$ Additionally, the C-O alkyl stretch at 1277 cm$^{-1}$ disappears in the TCNQ@HKUST-1
S7. IRRAS (Thin Films)

Figure S12: IRRAS spectra of 400 nm thin film pristine HKUST-1 and TCNQ@HKUST-1 confirming their composition.

Infrared reflection absorption spectroscopy (IRRAS) were obtained for the 400 nm thin film MOFs fabricated at KIT using a Bruker VERTEX 80 infrared spectrometer purged with dried air. The spectra were recorded in grazing incidence reflection mode at a fixed angle of incidence of 80° relative to the surface normal using a mercury cadmium telluride (MCT) detector. Predeuteratedhexadecanethiol SAM on Au/Ti/Quartz substrates were used for reference measurements. These data confirm the successful fabrication of HKUST-1 and TCNQ@HKUST-1 using the layer by layer LPE methodology.
S8. NMR (Bulk Samples)

NMR offers a means to probe the local structure of organic materials and can provide valuable information on the dynamics of linkers. For example, previous reports have shown that in MOF-5 at low temperatures, the aromatic rings in the organic linkers were stationary, whereas at high temperatures (>373 K) the aromatic rings exhibited π flips about their para axes which would impact the effective size of the windows between pores and can greatly influence the performance of the MOF.[20] The role of NMR becomes even more useful for studying guest molecule interactions within the pores of MOFs because the detected chemical shifts can indicate how the guest interacts with the host (i.e. Van der Waals vs. strong hydrogen bonds).[21] We use it to understand the local ligand structure of the BTC linker and the effects of the TCNQ guest molecule.

In NMR, the external magnetic field experienced by the hydrogen is affected by the electronegativity of the atoms attached to them. The effect of this is that the chemical shift of the hydrogen increases near a highly electronegative atom (like oxygen). The highly electronegative oxygen pulls electrons away from the hydrogen, leaving it more exposed to any external magnetic field. This results in a smaller external magnetic field needed to bring the nucleus into the resonance condition than if it was near a less electronegative atom. The smaller the magnetic field needed, the higher the chemical shift ($\delta$).

$$\delta = \frac{\nu_{\text{nucleus}} - \nu_{\text{standard}}}{\nu_{\text{spectrometer}}}$$

(Eqn. S3)

Where $\nu_{\text{nucleus}}$ is the frequency of the absorbed electromagnetic radiation by the MOFs nucleus in Hz, $\nu_{\text{standard}}$ is the frequency of the absorbed EM radiation by the standard (usually TMS) in Hz, and $\nu_{\text{spectrometer}}$ is the frequency of the NMR spectrometer in MHz which account for the magnet strength. Note that the chemical shift ($\delta$) is reported as parts per million (ppm) shift downfield from the TMS standard. So, a nuclei that is surrounded by less electron density will be shifted to the right (lower ppm) and a nuclei surrounded by a higher
electron density will be shifted to the left (higher ppm). H-NMR can only see the hydrogen nuclei. The HKUST-1 is made up of Cu dimers and a BTC ligand linker which is shown in Figure S13. There are two unique hydrogen atoms within the linker, which are labeled in the figure. H1 is located on the carboxylic acid and H2 is the sp² alkenyl hydrogen occurring in the aromatic. Additionally, there is one unique hydrogen in the TCNQ and is labeled H3 and is also an alkenyl hydrogen located on a sp² aromatic carbon. The local environment of these identified nuclei can be distinguished within the H-NMR spectra and are labeled accordingly in Figure S14.

![Figure S13: Schematic of the BTC ligand (left) and TCNQ guest molecule (right). The unique hydrogen nuclei are labeled H1, H2, H3 and are referenced in the NMR spectra.](image)

The presence of the paramagnetic Cu (unpaired electrons) within HKUST-1 greatly complicated the interpretation of NMR. Paramagnetism introduces complication where, in addition to the normal interactions (chemical shift anisotropy, internuclear dipolar and J-coupling) interactions with the unpaired electrons add complexity into the spectra.[22] This interaction can be observed as a large isotropic shift, the magnitude of which decreases rapidly as the length of the bonding pathway between the unpaired electron and the nucleus in
question increases. Luckily, previous works have investigated this in detail, and have properly identified the proper corresponding NMR peaks in the paramagnetic HKUST-1 system.\textsuperscript{[18]}

Figure S14 shows room temperature H-NMR data collected on pristine activated HKUST-1 and TCNQ infiltrated HKUST-1. We note that H1 will not appear in the HNMR spectrum because the samples are dissolved in deuterium oxide (deuterated water). In this environment, the hydrogen on the alcohol transfers to one of the lone pairs on the oxygen of the deuterated water molecule so that the -OH group turns into an -OD group which does not produce a peak in the same region of an NMR spectrum as ordinary hydrogen peaks. Figure S14 shows that there is a small chemical shift (0.012 ppm) of the H2 peak in the representative of the MOF linker, after the incorporation of the TCNQ into the pore, suggesting that there exists some strong hydrogen and pi bonding (not just weak Van der Waals interactions) between the guest and host. The doublet corresponding to H3 occurring around ~3.28 ppm is due to the aromatic hydrogens within the TCNQ (alkenyl hydrogen). The doublet (two peaks) stem from the two asymmetric unit cells which TCNQ is constructed (Figure S15). The other features within the HNMR spectra are due to trace amounts of solvents that were left over after fabrication (methanol) and infiltration (acetonitrile).
Figure S14: H-NMR data for pristine and TCNQ@HKUST-1 (a) full spectrum, (b) zoom in of the singlet belonging to H3, (c) zoom in of the doublet belonging to H3 and singlet for H1.

Figure S15: The two asymmetric unit cells which TCNQ is constructed. This asymmetry results in a doublet peak in the H-NMR spectrum.
S9. Pump-Probe Brillouin Scattering

Pump-probe Brillouin scattering is an ultrafast laser pump-probe thermometry technique that is very similar to TDTR, and creates a unique opportunity to study the mechanical properties within a thin film system. Specifically, the picosecond temporal resolution of TDTR is used to generate and detect ultra-short acoustic pulses in order to measure the group velocity and relate that to the bulk modulus of the samples.\textsuperscript{[23]} By using the standard TDTR experiment and flipping the sample around so that the laser beam passes through the sample first (instead of the transparent substrate), the signal is composed of not only the temperature rise created by the ultrafast laser heating, but also the strain wave that is produced in the sample, in the form of coherent lattice motion.\textsuperscript{[24]} Here, the initial deposition of energy by the pump pulse into the transducer creates both a temperature rise and a coherent acoustic wave that propagates within the sample media and reflects at any interface. The coherent acoustic wave causes a subtle change in the refractive index associated with the pressure gradient that it creates as it propagates through the media. The probe beam monitors the change in reflection due to the constructive and destructive interference between the pressure gradient wave front associated with the acoustic wave propagation and the thermo-reflection. The constructive and destructive interference leads to periodic oscillations in the temporal reflected signal, whose intensity can be described via

\[
I(t, T) = A \cdot \exp(-\Gamma t) \cdot \cos \left( \left( \frac{2\pi}{T} \right) t - \delta \right) - B \cdot \exp \left( - \frac{t}{\tau} \right) \tag{Eqn. S4}
\]

where A, B, and δ are scaling factors, \( \Gamma \) is the damping term for the acoustic wave front due to the energy dissipation, and T is the period of the pressure front. The first term of the equation describes the damping of the acoustic wave front, the second term captures the period of the pressure front, and the third term in the equation (\( \exp \left( - \frac{t}{\tau} \right) \)) is the thermal decay associated with traditional thermoreflectance at the surface of the metal transducer. An
example of the experimental data of the 300 nm pristine activated HKUST-1 MOF and the fitted model (Eqn. S4) is shown in Figure S16.

![Figure S16](image)

**Figure S16:** Example data of Brillouin scattering signal and fit (Eqn. S4). The sample geometry needed for pump-probe Brillouin scattering measurements is shown in the inset. The periodic oscillations are depicted visually within the Al transducer layer, the blue arrow shows where in the sample the measurement takes place.

At normal incidence, the inverse of the period (or frequency, \( f \)) can be related to the sound speed of the partially transparent material via,

\[
\frac{1}{T} = f = \frac{2rv}{\lambda}
\]  

(Eqn. S5)

where \( r \) is the index of refraction, \( \lambda \) is the wavelength of the probe, and \( v \) is the velocity of the coherent wave-front (or group velocity). The bulk modulus \( (B) \) is related to the group velocity \( (v^2) \) and density of the film \( (\rho) \) as defined by Ledbetter,\(^{[25]}\)

\[
B = v^2 \rho
\]  

(Eqn. S6)

From here, the frequency of the acoustic wave probed by Brillouin scattering is given by\(^{[26]}\)

\[
v_B = \left( \frac{2rv}{\lambda_\omega} \right) \sin \frac{\psi}{2}
\]  

(Eqn. S7)

Where \( r \) is the refractive index of the MOF, \( v \) is the sound velocity (which we measure), \( \lambda_\omega \) the light wavelength, and is the \( \psi \) scattering angle. Using the values listed in Table S4 and a
scattering angle 60 degrees, this means we measure the near zone center acoustic longitudinal mode at about 6 GHz.

Pump-probe Brillouin scattering measurements allow for the indirect measurements of mechanical properties of thin films (as long as the materials are somewhat transparent to the probe wavelength),\cite{27} which can be helpful in further understanding the thermal trends.

Since pump-probe Brillouin scattering is an indirect technique for measuring the mechanical properties of the MOFs, the uncertainties for the measurement consist of random errors introduced by uncertainties in the index of refraction, film density, Poisson ratio, and also the goodness of fit of the model defined in Eqn. S4 to the data ($R^2$) and corresponding residuals. It is important to consider both the $R^2$, and the residuals because the $R^2$ provides a measure of the precision of the model, whereas the residuals provide a means to assess the accuracy. We find that the largest source of error comes from the residuals. Also, since the Poisson ratio is only needed to calculate the Young’s Modulus, the uncertainty introduced by this value is only realized in the reported Young Modulus values and not the Bulk Modulus. Together, these sources of error produce approximately 40\% uncertainty for the Youngs Modulus results, and 30\% uncertainty for Bulk Modulus in all samples.

Table S4: Parameters used for the pump-probe Brillouin scattering measurement analysis. Note parameters are reported in the literature at room temperature for HKUST-1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>MOF</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$</td>
<td>Index of refraction</td>
<td>1.39</td>
<td>\cite{28}</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of probe</td>
<td>nm 808.5</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (pristine/TCNQ@HKUST-1)</td>
<td>g/cm$^3$ 0.88/1.22</td>
<td>\cite{4,29}</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Poisson Ratio</td>
<td>0.433-0.490</td>
<td>\cite{29}, LD</td>
</tr>
</tbody>
</table>
Table S5: Measured and calculated group velocity obtained through pump-probe Brillouin scattering (BS) measurements and lattice dynamics (LD) for a 300 nm activated pristine and 400 nm TCNQ@HKUST-1 deposited on Al/SiO₂ substrates. The Bulk/Youngs Modulus are derived from the measured group velocity using Eqns. S5-S6 and the LD derived Bulk Modulus is included for reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brillouin scattering group velocity (m/s)</th>
<th>Lattice dynamics group velocity (m/s)</th>
<th>Young's Modulus (GPa)</th>
<th>Bulk Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 nm Pristine HKUST-1</td>
<td>3716</td>
<td>2136</td>
<td>12.2 ± 3.6/4.9 ± 2.0</td>
<td>21.13</td>
</tr>
<tr>
<td>400 nm TCNQ@HKUST-1</td>
<td>3342</td>
<td>2126</td>
<td>9.8 ± 2.9/4.0 ± 1.6</td>
<td>21.13</td>
</tr>
</tbody>
</table>

S10. Nanoindentation

Nanoindentation measurements were taken at UVA following the procedure outlined by Oliver and Pharr,[30] on the ~5.5µm thick, solution sheared pristine and infiltrated HKUST-1 samples. The tip of the indenter was calibrated from 200-400 nm, with the 400 nm cutoff chosen to make sure we did not see substrate effects, which start to play a role as the indentation depth approaches 10% of the total film thickness. The data are an average of at least 15 different spots on each sample. Note, these data are calculated with a Poisson ratio = 0.46, which was derived from averaging the Poisson ratio derived from our LD calculations (γ = 0.49), with that which has been previously reported in literature (γ = 0.43).[31] We note that the large error bars for the reported Youngs Modulus correspond to high RMS surface roughness of the samples (~1µm). The results show, that within error, the mechanical properties of the activated pristine, un-activated pristine, and infiltrated MOFs do not change.

In order to more fully capture the effects of long wavelength propagons that could be occurring, we turn to mechanical measurements of the elastic constants of pristine and TCNQ infiltrated HKUST-1 using nanoindentation and pump-probe Brillouin scattering, which is directly related to thermal conduction. Nanoindentation, provides a direct method for measuring the elastic modulus of the thick MOF samples. Brillouin scattering, on the other hand, provides an indirect method that measures the near-zone center group velocity of the longitudinal acoustic phonon mode (~6 GHz), which is then related to the elastic modulus of the material.[25]
We note that the mode that is probed by the Brillouin scattering is a non-thermal mode. Indeed, the LD results (Figure 3 (g) in the main manuscript) show that a reduction in thermal conductivity can be achieved in these systems without modification to the elastic modulus. Therefore, this approach reveals if a loading-dependent structural change also contributes to the large change in thermal conductivity upon adsorption (where the sound velocity is proportional to the square root of the modulus), and provides insight about the carriers that the A-F analysis could not capture.

The results from the nanoindentation and pump probe Brillouin scattering compared to our harmonic LD calculations are shown in Figure 3 (g) in the main manuscript. Additionally, nanoindentation results from 1 μm surface-anchored HKUST-1 film prepared using LPE from Bundschuh et al.[32] are also plotted for reference. The experimental and LD results indicate that no discernable change in the elastic modulus is observed between the pristine HKUST-1 and infiltrated TCNQ@HKUST-1 within uncertainty.[33] We note comparisons of the mechanical results between the thin film SURMOFs and thick HKUST-1 samples should be done cautiously due to the role of size effects on the mechanical properties of thin polycrystalline films on substrates due to dislocation densities, grain size, textural effects, etc.[34] Indeed, previously reported nanoindentation measurements on 80 - 135 nm thin films of LPE fabricated HKUST-1 measure a much higher elastic modulus of 22.0 ±0.5 GPa.[33]

We note that both an increase in the density of the system due to the presence of guest molecules, and an increase in guest/host bonding would typically lead to an increased degree of resistance toward deformation (increased elastic constants). Instead, no measurable change is observed, suggesting that the unit cell deformation upon infiltration/adsorption may compete with density and bonding effects. We conclude from these measurements that mechanical softening upon infiltration of HKUST-1 is negligible, and therefore a loading dependent structural change can be ruled out from contributing to the reduction in the thermal conductivity.
Figure S17: Nanoindentation data taken at UVA on the thick 5.5 micron HKUST-1, and TCNQ@HKUST-1 samples. The full range of indenter displacements is plotted, however only the unshaded region was used for analysis.

Figure S18: (a) Bulk Modulus for thin HKUST-1 and TCNQ@HKUST-1 indirectly measured with Brillouin scattering (squares) and calculated from LD (thin symbols) for HKUST-1, TCNQ@HKUST-1 and F, -TCNQ@HKUST-1. Note the LD shows a constant Bulk Modulus for all systems. (b) Young’s Modulus for 300 nm HKUST-1 and 400 nm TCNQ@HKUST-1 films measured via Brillouin scattering (squares) compared to nanoindentation measurements.
(triangles) from the 5.5 μm (opaque left triangles) thick HKUST-1, TCNQ@HKUST-1. The measured Young’s Modulus is also compared to nanoindentation results from literature for HKUST-1 from Heinen et al. (open left triangles)[35] and Bundschuh et al. (open upright triangle).[32]

Figure S18 shows our data compared to temperature dependent Young’s modulus measurements from Heinen et al.[35] We note that in total, this temperature dependent trend in the elastic constant is quite interesting. A decrease in the elastic modulus with increasing temperature implies that the MOF becomes more elastic (deformable) at higher temperatures. The temperature dependent trend in modulus is then a bit counter-intuitive paired with the fact that HKUST-1 exhibits negative thermal expansion (NTE),[36] where it undergoes contraction (and phonon softening) with increasing temperature. Typical NTE materials mechanically harden as they contract, and instead we see evidence of mechanical softening with contraction during increasing temperatures. The mechanism for the counterintuitive mechanical softening and contraction is unknown, however we hypothesize that the ligands likely adopt a contorted configuration (i.e. the carboxylic acid carbon moves closer to the Cu dimer, and the aromatic carbons move into the pore) that serves to simultaneously soften and reduce the volume of the material.
S11. Molecular Dynamics (MD)

For the interactions between atoms in HKUST-1, we used the force field developed by Zhao et al..\cite{37} HKUST-1 has a simple cubic structure with 624 atoms in the unit cell and a lattice constant of 2.63 nm. HKUST-1 contains large pores of diameter 10 Å connected by channels of diameter 3.5 Å to smaller tetrahedral pores of diameter 5 Å. For intramolecular interactions in TCNQ molecules, CVFF\cite{38} force field was used which is also the basis for the force field used for HKUST-1. For the unknown bonding potentials between TCNQ and HKUST-1, the UFF\cite{39} force field was used. Lorentz–Berthelot mixing rules\cite{40} were used to model van der Waals interactions between the adsorbate and the framework atoms. The MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)\cite{41} software with a time step of 0.5 fs and with periodic boundary conditions applied in all directions.

We applied the Green–Kubo method to predict thermal conductivity,\cite{42,43} which is based on calculating the instantaneous heat flux in an equilibrium MD simulation. All simulations were carried out at a temperature of 300 K. For determining thermal conductivity, a system size of 2×2×2 unit cells was used. The systems were initially equilibrated under NVT conditions at a temperature of 300 K for 300,000 time steps and further equilibrated for 300,000 time steps under NVE conditions. Finally, NVE simulations were run for an additional 1,000,000 time steps where the heat current was calculated every 10 time steps. For all cases, we performed this procedure for eight simulations starting from random velocity distributions. The HCACFs were calculated using a correlation time of 50 ps and then averaged and integrated for the thermal conductivity prediction. Thermal conductivity values were obtained from the plateau region of the HCACF integral that corresponded to 20 ps (the 20–40 ps time window) for the pristine MOF and less than 40 ps (the last 40 ps) for the loaded MOFs.
For TCNQ loading, different number of molecules (1, 2 and 10) per unit cell were considered. In addition, the bonding of TCNQ molecules to HKUST-1 framework is not well-known.\cite{38-40} Consequently, we also considered different scenarios for the bonding between nitrogen atoms in TCNQ molecules and the copper atoms in HKUST-1 and different concentrations to investigate the effect of morphology of the guest molecule on the thermal properties. We simulate the TCNQ in four different absorbed states using the nomenclature ‘TCNQ\textit{n=x,b=x}@HKUST-1’, which indicates the adsorbed bonding conditions, where ‘\textit{n}’ is the number of TCNQ molecules per pore and ‘\textit{b}’ is the number of covalent bonds formed (\textit{b}=0 indicates unbound, free state): one molecule per pore where the TCNQ chemically binds via all four terminal nitrile groups to neighboring metal nodes on opposite sides of the TCNQ molecule, forming a bridge across the pore (\textit{n}=1, \textit{b}=4) (Figure S19 (a)), one molecule per pore with a two covalent bonds occurring between two terminating nitrile groups on the same side of the TCNQ molecule to a Cu site (\textit{n}=1, \textit{b}=2) (Figure S19 (b)), two molecules per pore bonded by two terminating nitrile group on the same side of TCNQ to the CUS (\textit{n}=2, \textit{b}=2) (Figure S19 (c)), and two (\textit{n}=2, \textit{b}=0) (Figure S19 (d)) and ten (\textit{n}=10, \textit{b}=0) (Figure S19 (e)) molecules per pore in an unbonded ‘free state’.
Figure S19: Molecular dynamics results showing the five different TCNQ bonding environments examined: A) (n=1, b=4) one TCNQ molecule per pore bonded by four nitrile groups on both sides of the TCNQ to four Cu sites, B) (n=1, b=2) One TCNQ molecule per pore bonded by two nitrile groups on one side to two Cu site, C) (n=2, b=2) Two TCNQ molecules per pore bonded by two nitrile groups on one side of the TCNQ to two Cu sites, D) (n=2, b=0) Two molecules per pore in an unbound state, and E) (n=10, b=0) ten molecules per pore in an unbound state.

Temperature dependent results for the MD calculations are shown in Figure S20 compared to the Leibfried and Scholman (L-S) model for thermal conductivity. This model was chosen because it considers the effects of crystal anharmonicity above the Umklapp peak. [46] The L-S thermal prediction for thermal conductivity is

\[ \kappa_{L-S} = B_1 \left( \frac{k_B \theta_D}{h} \right)^3 \frac{M a_o}{\gamma^2 \alpha}, \]  

(Eqn. S8)

where \( B_1 \) is a constant, \( k_B \) is Boltzmann constant, \( \theta_D \) is the Debye temperature of the MOF, \( M \) is the average atomic mass of the unit cell, \( a_o \) is the lattice constant, \( T \) is temperature and \( \gamma \) is the Gruneisen parameter (derived from our pump-probe Brillouin scattering measurements). Table S6 shows the parameters that were used to calculate \( \kappa_{L-S} \). We see that the MD derived temperature dependent results show a slight decrease in thermal conductivity with increasing temperature, however the L-S model does not quite capture the trend. The MD indicates anharmonicity may be paying a role in the temperature dependent trend, implying that heat transfer in the system is a combination of the complex interaction between propagating phonons and localized molecular modes.
Table S6: Parameters used to calculate the Leibfried and Scholmann prediction ($\kappa_{L-S}$). All other parameters are taken from literature. We note that the fit resulting from Eqn. S8 is intended to allow for comparison between the experimental data and L-S trend, and not as a prediction for $\gamma$.

<table>
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<td>$\gamma$</td>
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</table>

Figure S20: Temperature dependent MD results compared to the Leibfried and Scholman model for thermal conductivity.
Harmonic lattice dynamics (LD) was performed in order to derive the phonon dispersions (Figure 4 (a)-(c)) for HKUST-1, TCNQ@HKUST-1, and F4-TCNQ@HKUST-1. The LD calculations were performed using the GULP software package. The LD vibrational density of state are also plotted in Figure S21. We also plot the phonon group velocities for the gamma wave vector for HKUST-1 and the guest@HKUST-1 molecules in Figure S22. We note that we see an increase in the group velocities at ~90 THz upon infiltration. This is expected as it captures the change induced by the guest molecules where the Hydrogen atoms in the aromatic TCNQ molecule and the Fluorine atoms in the F4-TCNQ. From 0-55 THz, the group velocity between all three systems are relatively constant.

Additionally, we calculate the diffusivities of the modes for HKUST-1, TCNQ@HKUST-1 and F4-TCNQ@HKUST-1, using the Allen-Feldman theory, to understand the contribution of diffusons to the thermal conductivity. The contribution of diffusons upon infiltration of the guest molecules contribute more to the total thermal conductivity of the material as shown in Figure S23, where the diffusivities over the full spectrum of modes increase upon infiltration. Notably, there exist a number of modes with high diffusivities occurring at 4.65 THz that are responsible for the large increase in thermal conductivity shown in Figure 6 (c).
Figure S21: (a) Phonon dispersions for HKUST-1 (black), TCNQ@HKUST-1 (blue) and F4-TCNQ@HKUST-1 (orange). The asterisk and circles in the dispersions in (b) and (c) highlight the avoided crossings and resonant bands respectively, that are introduced by the guest and lead to flat bands characteristic of localized modes that are responsible for reducing the thermal conductivity. (d) The vibrational density of states (DOS) plotted from 1-100 THz on a log scale, which captures all of the thermal frequencies at room temperature for the three HKUST-1 systems. We see a reduction in the population of modes in the infiltrated cases from 1-10 THz, and the emergence of new modes from ~9.5-14.5 THz upon infiltration indicating increased scattering of low frequency phonon modes. (e) Zoom in of the DOS showing the appearance of
localized modes as delta functions, and evidence of hybridization due to peak broadening occurring in the TCNQ infiltrated MOF.

Figure S 22: Phonon group velocities for pristine HKUST-1 (black squares), TCNQ@HKUST-1 (red circles) and F4-TCNQ@HKUST-1 (green triangles) for the gamma wave vector.
Figure S 23: LD calculated mode diffusivities using the Allen-Feldman method for pristine HKUST-1 (black squares), TCNQ@HKUST-1 (red circles) and F4-TCNQ@HKUST-1 (green triangles) for the gamma wave vector.
S13. Spectral Energy Density (SED)

In addition to MD, we perform SED calculations\[51\] which provide further evidence on phonon scattering due to the presence of TCNQ molecules. In this method, the SED is calculated from

\[ \Phi(K, \omega) = \frac{1}{4\tau_0 \pi} \sum_{\alpha, \beta} \frac{m_b}{N} \int_0^{\tau_0} \sum_l u_\alpha(l, t) \exp(iK \cdot r_l - i\omega t) dt \]

where \( K \) and \( \omega \) are the wave vector and frequency. \( \tau_0 \) is the integration time, which should be larger than the largest mode lifetime, \( N \) is the number of unit cells in the supercell, \( m_b \) is the mass of atom \( b \) in the unit cell, \( u_\alpha(l, t) \) is the \( \alpha \)-th component of velocity of atom \( b \) in unit cell \( l \) which is taken from MD simulations, and \( r_l \) is the position vector for unit cell \( l \).

The calculated SED for each \( K \) contains a number of peaks that is equal to the number of phonon branches in the dispersion curve (3 times the number of atoms in the unit cell). The lifetime of each phonon mode is equal to the inverse of the full-width at half-maximum (FWHM) of a Lorentzian function fit to its peak. In all SED calculations, we saved the velocities of all atoms every 5 fs in production EMD simulations run for 1,000,000 time steps (time step=0.5 fs).

SED evaluates phonon lifetimes, where the phonon lifetimes are inversely proportional to the width of the SED peak – sharper peaks indicate longer lifetimes. SED is performed for pristine HKUST-1, and two cases of TCNQ loaded HKUST-1 (TCNQ bonded on two sides in the pore (n=1, b=2) and an unbounded free state (n=1, b=0)). The plots are associated with the phonon wave-vector of \( \frac{2\pi}{4L} \). Figure 6 in the manuscript shows that the high-frequency modes are relatively unaffected by adsorption, however the lifetimes for the low-frequency phonon modes are greatly affected by the presence of TCNQ. Phonon lifetimes in the TCNQ bonded on two sides is shorter than in the pristine MOF and the effects on the free TCNQ molecule case are so drastic that the peaks disappear. Figure S24 shows the SED results from 1-15 THz.
The high number of modes in this region makes the distinction of individual peaks highly inaccurate, so that the phonon lifetimes cannot be calculated. In total, these calculations are useful in showing the direct effect of TCNQ on the decreased lifetimes of low frequency phonon modes in the MOFs.

Figure S24: Zoom in of the SED calculation spanning the region from 1-15 THz showing the high density of modes which prohibits the derivation of phonon lifetimes in this region because individual modes cannot be accurately resolved. Note, SED calculations were performed for the [100] crystallographic plane, where Φ is a representation of the phonon energy in the frequency domain. The SED calculations for pristine HKUST-1 and two variations of TCNQ@HKUST-1 (bonded and free). The lifetimes of high frequency phonon modes are relatively unchanged by the presence of an adsorbate, while the lifetimes of low frequency modes are drastically shortened in the presence of TCNQ.
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S14. References


