Cooperative Molecular Behavior Enhances the Thermal Conductance of Binary Self-Assembled Monolayer Junctions

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Supporting Information

ABSTRACT: The effect of the local molecular environment on thermal transport through organic–inorganic heterojunctions is investigated using binary self-assembled monolayer (SAM) junctions built from a mixture of alkanethiol and alkanedithiol species sandwiched between gold leads. Thermoreflectance measurements and molecular dynamics simulations demonstrate that the thermal conductances of the binary SAM junctions vary with molecular composition and are greater than predictions of a parallel resistance model. The enhancement results from increased thermal transport through the alkanethiols, whose terminal methyl groups are confined by the anchored alkanedithiols. This confinement effect extends over length scales that are more than twice the range of the van der Waals interactions between molecules and are commensurate to the sizes of experimentally observed molecular domains. Conversely, for a partially packed (i.e., submonolayer) alkanedithiol unary SAM, increasing the molecular packing density decreases the per molecule thermal conductance. This finding indicates that thermal transport measurements of SAMs cannot be used to predict the thermal transport properties of single molecules.

KEYWORDS: Nanoscale, molecular junctions, binary monolayers, thermal transport, thermoreflectance, molecular dynamics

Devices based on molecular junctions have garnered widespread interest for their potential application in electronics,1−4 LEDs,5−7 and thermoelectric.8−14 The interfaces between the organic and inorganic components in these devices play a critical role in their electrical and thermal performance. By modifying the substrates (leads), the type and length of the molecules, and the end-groups, both the electronic and thermal transport properties of these heterojunctions can be tuned.15−20

Electronic transport studies on systems ranging from single molecules to ensembles of molecules arranged in self-assembled monolayers (SAMs) have shown that the local molecular environment affects the transport physics.21−27 Selzer et al. measured electrical conductances for Au-[1-nitro-2,5-di-(phenylethynyl-4′-mercapto)benzene]-Au junctions that contained a single isolated molecule or a SAM.21 Under increasing bias voltage, they found that the electrical conductance of a single molecule junction increased, while the per molecule electrical conductance of a SAM junction remained unchanged. Using alkane-based binary SAMs, Katsouras et al.22 also showed that the individual molecules in a SAM exhibit different electrical conductances depending on their local environment. Nernghamnong et al. measured the rectifying current through a ferrocene alkanethiolate SAM-based diode.28 They found that stronger intermolecular van der Waals interactions, which were created by decreasing the molecular tilt angle, increased the ability to rectify current and device efficiency. First-principles and tight-binding calculations predict that the per molecule electrical conductance is a function of the direct electronic (i.e., dipole) coupling between molecules,24,25 the interaction between the molecular energy levels and the substrates,26 and electrostatic effects within the molecules.27 These experimental and modeling results all point to cooperative electronic effects between the molecules in organic–inorganic heterojunctions.

Because the thermal conductance of a single molecule has yet to be measured, insight into cooperative effects on thermal transport in organic–inorganic heterojunctions has come from molecular dynamics (MD) simulations. Sasikumar et al. predicted the junction thermal conductance of two polyethylene molecules between silicon substrates.28 They found that the per molecule thermal conductance increased nonlinearly as the mean distance between the two molecules increased, even when they were too far apart to directly interact with each other. In contrast, Luo and Lloyd studied partially packed Au−decanedithiol−Au SAM junctions and reported a linear decrease in junction thermal conductance as they reduced the number of molecules in their simulation cell (i.e., increased the mean distance between molecules).29

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Experimental investigations of thermal transport through heterojunctions have focused on SAM junctions containing a single species of organic molecule. The vibrational overlap and interfacial bond strength between the organic molecules and the inorganic substrates have been leveraged to tune SAM junction thermal conductances from 10 to 300 MW/m²·K. In a standalone study, Losego et al. measured the variation of junction thermal conductance for binary SAMs composed of thiol- and methyl-terminated alkanes sandwiched between gold and quartz substrates. Both molecular species had equal lengths, and they found that the thermal conductance decreased as the concentration of the weaker methyl-terminated molecule in the SAM-forming solution increased. The role of the local molecular environment on thermal transport through SAMs has not yet been experimentally investigated.

Binary SAM junctions are a convenient system to probe intermolecular cooperative effects since they create a heterogeneous bonding environment at one or both substrate–SAM interfaces that can be systematically tuned. In this letter, we measure, predict, and interpret the junction thermal conductance for binary SAMs composed of thiol- and methyl-terminated alkanes sandwiched between gold and quartz substrates. Both molecular species had equal lengths, and they found that the thermal conductance decreased as the concentration of the weaker methyl-terminated molecule in the SAM-forming solution increased. The role of the local molecular environment on thermal transport through SAMs has not yet been experimentally investigated.

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behavior between the three binary SAMs in Figure 1b is due to differences in the adsorption rates of the molecules.\textsuperscript{32,37}

The contact angle measurements were fit to a first-order adsorption model using the expression\textsuperscript{32}

\[
\cos \theta_{\text{SAM}} = \cos \theta_{\text{a,1S}} + \left( \frac{1}{k_{\text{rel}} R_{\text{soln}} + 1} \right) \left( \cos \theta_{\text{a,2S}} - \cos \theta_{\text{a,1S}} \right)
\]

(1)

where \( \cos \theta_{\text{a,1S}} \) is the cosine of the contact angle for a fully monothiol SAM, \( \cos \theta_{\text{a,2S}} \) is the cosine of the contact angle for a fully dithiol SAM, and \( k_{\text{rel}} \) is the ratio between the adsorption rate constants of the monothiol and the dithiol (details in Section S2 of the SI). We performed a nonlinear least-squares fit to extract \( k_{\text{rel}} \) for each SAM and used these values with eq 1 to plot the dashed lines in Figure 1b. The fitted values of \( k_{\text{rel}} \) are 0.56 \( \pm \) 0.04 for C\textsubscript{10}S\textsubscript{2}:C\textsubscript{6}S, 0.39 \( \pm \) 0.01 for C\textsubscript{10}S\textsubscript{2}:C\textsubscript{11}S, and 0.05 \( \pm \) 0.01 for C\textsubscript{10}S\textsubscript{2}:C\textsubscript{14}S, indicating that the adsorption rate for all the monothiols is lower than the dithiol, in agreement with measurements performed by Kathrena et al.\textsuperscript{38} The origin of this result may be that the dithiol has twice the number of adsorption sites (i.e., thiol groups) as compared to the monothiols.

The correlation between \( R_{\text{soln}} \) and the composition of the SAM itself is derived from eq 1 as\textsuperscript{32}

\[
\chi_{\text{1S,SAM}} = \frac{k_{\text{rel}} R_{\text{soln}}}{k_{\text{rel}} R_{\text{soln}} + 1}
\]

(2)

where \( \chi_{\text{1S,SAM}} \) is the mole fraction of the monothiol in the SAM. The mole fraction of the monothiol in the solution with respect to the total amount of dissolved thiols, given by \( \chi_{\text{1S,soln}} = \frac{R_{\text{soln}}}{(R_{\text{soln}} + 1)} \), is plotted in Figure 2a as a function of \( \chi_{\text{1S,SAM}} \). For all three data sets, the mole fraction of monothiols on the surface is smaller compared to their fraction in the solution. \( \chi_{\text{1S,SAM}} \) also decreases with increasing molecular length for all values of \( \chi_{\text{1S,soln}} \). This observation is consistent with previous findings, where it was attributed to the increased solubility of shorter alkanethiols in ethanol.\textsuperscript{32,37}

The thermal conductances (\( G \)) of the SAM junctions were measured at a temperature of 296 K using frequency domain thermoreflectance (FDTR), a noncontact laser-based measurement technique that is ideal for measuring thermal properties of interfaces and thin films.\textsuperscript{16,39,40} In an FDTR measurement, the phase lag between the temperature modulation of the sample surface (532 nm probe laser) and the imposed periodic heat flux (488 nm pump laser) is fit with an analytical solution to the heat diffusion equation to extract \( G \).\textsuperscript{41} The phase lag data and the associated fit for three Au–C\textsubscript{10}S\textsubscript{2}:C\textsubscript{11}S–Au junctions of different composition are plotted in Figure 1c as a function of the modulation frequency (100 kHz–3 MHz). The three data sets give fitted \( G \) values of 60 \( \pm \) 7, 49 \( \pm \) 6, and 36 \( \pm \) 4 MW/m\(^2\)K with \( R_{\text{soln}} = 0.50 \pm 0.07 \), 1.00 \( \pm \) 0.14, and 1.60 \( \pm \) 0.85, indicating that FDTR is sensitive to the binary SAM composition. We could not successfully measure samples having >80% C\textsubscript{6}S or >50% C\textsubscript{14}S in the solution, possibly due to defects in the SAM that enable metallic shorts between the gold leads. We prepared at least two samples for every binary SAM composition and measured at five different laser spot locations on each sample. The fitted values of \( G \) were consistent within the single measurement uncertainty for all samples.

The junction thermal conductance is plotted as a function of \( \chi_{\text{1S,SAM}} \) in Figure 2b for the three binary SAM compositions. The fitting parameters and uncertainty calculations are described in Section S3 of the SI. The extreme cases, relating to \( R_{\text{soln}} = 0 \) and \( R_{\text{soln}} \to \infty \), are plotted as horizontal lines with shaded uncertainty (65 \( \pm \) 7 MW/m\(^2\)K for Au–C\textsubscript{10}S\textsubscript{2}:Au–C\textsubscript{11}S and 34 \( \pm \) 3 MW/m\(^2\)K for Au–C\textsubscript{11}S–Au). The thiol–Au interaction is stronger than the methyl–Au interaction, which leads to higher \( G \) for a fully dithiol SAM junction as compared to a fully monothiol SAM junction.\textsuperscript{16,20}

Junction thermal conductance decreases with increasing \( \chi_{\text{1S,SAM}} \) (i.e., an increasingly methyl-Au dominated top interface) for all binary SAM compositions. The C\textsubscript{10}S\textsubscript{2}:C\textsubscript{14}S data bridges the two extremes of fully dithiol and fully monothiol junctions. For any value of \( \chi_{\text{1S,SAM}} \), \( G \) for C\textsubscript{10}S\textsubscript{2}:C\textsubscript{14}S is equal to or consistently higher than that for C\textsubscript{10}S\textsubscript{2}:C\textsubscript{6}S. We hypothesize that this behavior is due to the shorter distance between the terminal methyl group of the monothiol (C\textsubscript{11}S versus C\textsubscript{6}S) and the transfer-printed gold surface, which leads to a stronger interaction. The \( G \) values for C\textsubscript{10}S\textsubscript{2}:C\textsubscript{11}S and C\textsubscript{10}S\textsubscript{2}:C\textsubscript{14}S are comparable, which we attribute to bending of the longer C\textsubscript{14}S molecules. These two hypotheses are supported by our MD simulations, as described in Section S8 of the SI.
To further probe the nature of thermal transport in a binary SAM and to explore the effects of intermolecular cooperation, we now turn to MD simulations, which can resolve the atomic-level detail up to length scales of \( O(10 \text{ nm}) \). Before doing so, we note that binary SAMs created through adsorption from solution have nanoscale domains of the individual molecular species.\(^{42-50}\) Purely random (i.e., homogeneous) mixing between two molecular species, even for those with equal lengths and similarly sized end-groups, has not been observed except in a standalone study by Kakiuchi et al.\(^{51}\) Typically, domains with areas of \( 15\text{–}100 \text{ nm}^2 \) have been detected, corresponding to linear dimensions of \( 4\text{–}10 \text{ nm} \).\(^{52-50}\) These domain sizes are orders of magnitude smaller than the FDTR laser spot diameter (\( 5.8 \pm 0.2 \mu \text{ m} \)) and the water droplet diameter (\( \sim 1 \text{ mm} \)) used for contact angle measurements. The repeatability of our FDTR and contact angle measurements across different locations on the same sample indicates their insensitivity to the molecular domains.

To investigate the role of domain size on \( G \) and to assess the suitability of MD simulations for modeling our experimental system, we built a series of segregated C\(_{10}\)S\(_2\):C\(_{11}\)S binary SAM structures that have periodic ribbons of monothiols and dithiols of equal widths (i.e., \( \chi_{\text{SAM}} = 0.5 \)), as shown in Figure 3a. The system setup is described in ref 16 and in Section S4 of the SI. We take the ribbon width to be representative of the domain size. The \( G \) predictions (after placing a second gold lead on top of the SAM) are plotted in Figure 3a, where they are compared to predictions (i) for a binary SAM junction with randomly mixed molecules and (ii) based on a linear combination of the fully dithiol (\( G = 113 \pm 9 \text{ MW/m}^2\text{-K} \)) and fully monothiol (\( G = 17 \pm 2 \text{ MW/m}^2\text{-K} \)) systems. The \( G \) prediction for the randomly mixed SAM matches the prediction for the segregated SAM having a ribbon width of 1 nm (the smallest domain size in this study). When the ribbon width is increased from 1 to 4 nm, the latter being comparable to the experimentally measured domain sizes in binary SAMs having equal length molecules,\(^{45,47}\) \( G \) decreases by 10%. These predictions are all above (27–42%) the \( G \) values calculated from the linear combination model. This finding highlights that thermal transport through the individual molecular species is not independent at these length scales and that cooperative effects between the molecules may be influencing the \( G \) of the binary SAMs. Furthermore, the \( G \) predictions for the randomly mixed systems do not vary with increasing simulation size (details in Section S4 of the SI). Since the prediction for the randomly mixed binary SAM system is within 10% of the segregated SAM systems, we use the randomly mixed system in the subsequent analyses to maintain reasonable computational time.

A direct comparison between the MD predictions and FDTR measurements of \( G \) of the binary SAMs, as plotted in Figure 3b, reveals that the predictions are higher for all the configurations. The MD prediction for the Au–C\(_{10}\)S\(_2\)–Au SAM junction is \( 113 \pm 9 \text{ MW/m}^2\text{-K} \) and the FDTR measurement is \( 65 \pm 7 \text{ MW/m}^2\text{-K} \). We previously showed that this difference is due to incomplete areal contact between the SAM and the transfer-printed gold lead, leading to under-predictions of \( G \) in experimental measurements.\(^{52}\) Interpretation of the experimental results alone to probe cooperative effects is therefore inappropriate since they include the effects of incomplete areal contact, which are present in both the unary and binary SAM systems. The MD simulations have perfect contact. To validate the MD data, we must correct for the percentage contact area between the SAM and the transfer-printed gold lead using a rough-surface contact model for SAM junctions (details in Section S5 of the SI).\(^{16,52}\) The area-corrected MD predictions are plotted in Figure 3b. For \( \chi_{\text{SAM}} < 0.5 \) the area-corrected MD predictions agree with the FDTR measurements. They underpredict the FDTR measurements for \( \chi_{\text{SAM}} > 0.5 \), where the weak methyl–Au interaction dominates. This underprediction suggests that the methyl–Au LJ potential obtained using standard mixing rules to describe van der Waals interactions\(^{53}\) is too weak to describe the surface interaction. Creating and validating a new empirical potential from first-principles calculations is an involved process and is beyond the scope of this study. The agreement in magnitude and trend of the area-corrected MD predictions with the FDTR measurements indicates that MD simulations can be used to analyze thermal transport at the atomic level in binary SAM junctions and to investigate possible intermolecular cooperative effects.

We now focus on the MD simulations to systematically investigate how cooperative behavior between molecules...
influences $G$. The variation of $G$ from MD for C$_{10}$S$_2$:C$_{11}$S as a function of $\chi_{\text{SSAM}}$ is plotted again in Figure 4, but now with a linear horizontal axis. If each molecule acted as an independent heat channel (i.e., in parallel with the other molecules), $G$ would linearly decrease from the fully diethiol case to the fully monothiol case, as indicated by the red dashed line. The MD predictions are greater (13–83%) than the parallel-channel model, which is clear evidence that cooperative behavior enhances thermal transport in the binary SAMs. Such a nonlinear behavior of $G$ was also observed by Acharya et al.$^{54}$ for the interface between water and a binary SAM. The SAM molecules were differentiated by the hydrophilicity of their end groups and the deviations from a parallel-channel model were 3–17%.

To probe how molecular mixing gives rise to the cooperative behavior that enhances the $G$ of binary SAMs, we built atomistic models of SAM junctions having partial coverage of either C$_{10}$S$_2$ or C$_{11}$S molecules. The empty adsorption sites on the gold surface where molecules could have resided are referred to as voids. Cooperative behavior between the C$_{10}$S$_2$ and C$_{11}$S molecules that can exist in the partially packed structures. The values of $G$ for the partially packed C$_{10}$S$_2$ and C$_{11}$S SAM data and the C$_{11}$S parallel-channel model (blue circles). The number of data points shown here for the C$_{10}$S$_2$:C$_{11}$S binary SAM has been reduced from Figure 3b to avoid crowding.

As such, a meaningful comparison between the MD predictions and the parallel-channel model is not possible for the C$_{11}$S case.

To investigate if cooperative behavior between the C$_{10}$S$_2$ molecules alone can account for the enhanced $G$ of the C$_{10}$S$_2$:C$_{11}$S binary SAM as compared to the parallel-channel model, we added the values of $G$ for the partially packed C$_{10}$S$_2$ from MD and the partially packed C$_{11}$S from its parallel-channel model. The results are plotted as blue circles in Figure 4. This effective $G$ underpredicts the MD values of $G$ (red triangles) by 3–32%. The data plotted in Figure 4 thus clearly indicate that cooperative behaviors must exist between the diethiol and monothiol species. Possible mechanisms for intermolecular cooperation include: (i) nonbonded (i.e., van der Waals) dispersive interactions directly between the molecules, and (ii) indirect interactions mediated by the metal leads. Each of these mechanisms can be explored using MD simulations and are represented schematically in Figure 5a.

We probed the effect of the nonbonded interactions by reducing the well-depth of the LJ potentials ($\epsilon_{\text{ff}}$) between the thiol, CH$_2$, and methyl groups to 10% of their nominal values for $\chi_{\text{SSAM}} = 0.5$ for each binary SAM. The methyl–gold interaction, which is also described by an LJ potential, was not modified. As shown in Table 1, the predicted $G$ values are unchanged when compared to those using the full well-depth. This finding indicates that the nonbonded interactions are too weak to affect thermal transport across the junction and do not contribute to the cooperative behavior.

The indirect interactions between the molecules depend on the structure of the interface formed when the metal lead is brought in contact with the binary SAM. The SAM molecules are bonded to the leads by thiol and methyl groups. The strong thiol–Au bonds anchor the diethiols to the templated gold lead upon which they were grown and to the transfer-printed top gold lead. However, the monothiols are anchored to the templated gold lead by their thiol groups but interact weakly with the transfer-printed gold lead through their methyl groups. We hypothesize that enhanced thermal transport in the binary SAMs is a result of the C$_{10}$S$_2$ molecules stabilizing the C$_{11}$S molecules. This mechanism is schematically represented in Figure 5b, where the halos represent the extent of thermal motion of the individual molecules (red for diethiols, blue for monothiols). This hypothesis would explain the data plotted in Figure 4, where $G$ increases by 44 MW/m$^2$K between $\chi_{\text{SSAM}}$ values of 1.00 and 0.83 for the MD case (red triangles) as compared to an increase of 24 MW/m$^2$K for the linear combination case (blue circles), where no interactions between diethiol and monothiol species are included.

We tested the hypothesis that dithiols confine the monothiol motion in the binary SAMs by calculating the root mean-squared (RMS) displacement of the terminal methyl groups of the C$_{11}$S molecules in the binary and partially packed SAMs (details in Section S6 of the SI). The results are plotted in Figure 5c versus $\chi_{\text{SSAM}}$. The methyl-group RMS displacements for the partially packed SAMs are a factor of 2–7 greater than their values in the fully packed binary SAMs for all values of $\chi_{\text{SSAM}}$. This result suggests a high frequency of bond breakage and formation between the methyl groups and the gold atoms in the partially packed SAMs, which is reduced in the binary SAM due to confinement by the C$_{10}$S$_2$ molecules. This confinement leads to higher per molecule conductance of the C$_{11}$S molecules in the binary SAM and is a direct result of the cooperative behavior between the molecular species mediated by the metal leads. The RMS displacement of the terminal thiol...
groups do not vary between the fully packed binary and partially packed C_{10}S_{2} structures (details in Section S6 of the SI), confirming that the thermal conductance enhancement in the binary SAMs results from the confinement of the weakly bonded monothiols. We probed the spatial extent of the monothiol confinement mechanism by calculating the RMS displacements of the terminal methyl groups in the segregated systems (Figure 3a) as a function of their distance from the dithiol–monothiol interface. For a ribbon width of 4 nm, only 65% of the fully monothiol RMS displacement is realized in the molecules furthest (i.e., 1.95 nm) from the interface. This separation is more than twice the value of the cutoff (0.9 nm) of the van der Waals interactions between molecules. The overall RMS displacement of all the methyl groups in the ribbon is within 15% of the prediction for the randomly mixed binary SAM plotted in Figure 5b (details in Section S6 of the SI). This result corroborates our observation from Figure 3a of a modest decrease (10%) in the predicted $G$ values as the ribbon width increases and establishes the long-range extent of the monothiol confinement, which enhances $G$ even for segregated systems.

We now investigate variation of the MD-predicted $G$ for the partially packed C_{10}S_{2} SAM as a function of $\chi_{1S,SAM}$ plotted in Figure 4 as green squares. The magnitude of the slope of $G$ increases as $\chi_{1S,SAM}$ increases, indicating that the per molecule thermal conductance increases as the SAM becomes less dense. Using the values of $G$ for which $\chi_{1S,SAM}$ is 0 (fully packed SAM) and 0.97 (not plotted, corresponding to one molecule in the simulation cell, details in Section S7 of the SI), the corresponding per molecule thermal conductances are 24 $\pm$ 2 pW/K and 39 $\pm$ 3 pW/K. We checked if nonbonded interactions could account for this effect by reducing $\epsilon_{ij}$ to 10% of its nominal value (as we did for the binary SAMs) for $\chi_{1S,SAM} = 0.5$, but there was no change in the predicted $G$ value. Intermolecular cooperation thus reduces the thermal conductance of the individual dithiol molecules as their mean intermolecular distance decreases, an observation similar to that of Sasikumar et al. for a two-molecule polyethylene junction. It is therefore not possible to predict single molecule thermal transport behavior from measurements on SAMs and vice versa. Molecular confinement cannot be used to explain the MD predictions of the partially packed C_{10}S_{2} systems. A deeper understanding of the mechanisms of energy transfer between SAM molecules as a function of their local environment is an important direction for future research. The development of computational and/or experimental methods that can probe the energy transfer pathways will help to elucidate the effects of molecular mixing and confinement. For example, extending spatially dependent density of states calculations, such as those used by Jin et al., to resolve nonuniformities with lengths scales of $O$ (0.1 nm) may provide insight into the role played by the metal leads.

In summary, we investigated the effects of local molecular environment and cooperative behavior between molecules on the thermal conductance of binary SAM junctions. FDTR measurements and MD predictions of the junction thermal conductance showed a nonlinear change from a fully dithiol to a fully monothiol SAM, confirming the presence of cooperative interactions between the molecules. The origin of the cooperative behavior was found to be influenced by the

Table 1. $G$ Predicted from MD Simulations for the Three Binary SAMs Using Standard LJ Interactions and Weaker Interactions Having 10% of the Nominal Well-Depth for All Pairs of Nonbonded Atoms in the SAM Alone [i.e., the SH (Thiol), CH$_2$, and (CH$_3$) Methyl Groups]; All SAMs Have $\chi_{1S,SAM} = 0.5$

<table>
<thead>
<tr>
<th></th>
<th>$G$ (MW/m$^2$K)</th>
<th>$\epsilon_{ij}$</th>
<th>$0.1\epsilon_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{10}S_{2}:C_{8}S_{8}</td>
<td>77 $\pm$ 4</td>
<td>78 $\pm$ 5</td>
<td></td>
</tr>
<tr>
<td>C_{10}S_{2}:C_{6}S_{7}</td>
<td>85 $\pm$ 5</td>
<td>81 $\pm$ 5</td>
<td></td>
</tr>
<tr>
<td>C_{10}S_{2}:C_{11}S</td>
<td>95 $\pm$ 7</td>
<td>93 $\pm$ 6</td>
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confinement of monothiols by dithiols, which enhances the rate of thermal energy transmission through the methyl–Au sites. In contrast, MD simulations of partially covered SAMs suggested that intermolecular cooperation decreases the per molecule thermal conductance in a unary SAM with decreasing intermolecular distance, the origin of which remains unclear. Investigations into how such cooperative behavior can influence the electronic, mechanical, optical, and chemical properties of unary and binary SAM junctions are important for the development of molecular devices.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b03894.

More detailed information regarding the contact angle measurements, FDTR measurements, contact mechanics model, and MD simulations (PDF)

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Author Contributions

S.M. synthesized the SAM junctions, conducted the FDTR experiments and MD simulations, performed the contact mechanics analysis, and wrote the paper. All authors edited the paper, discussed the data, and commented on the results in the paper.

Notes

The authors declare no competing financial interest.

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