Supporting Information

Power Factor of One Molecule-thick Films and Length Dependence

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1. Experimental Details

1.1 Materials and Characterization

All reagents including \( n \)-alkanethiols and oligophenylthiols were purchased from Sigma-Aldrich, Alfa Aesar, and TCI and used as supplied unless otherwise specified. All organic solvents including toluene were purchased from Sigma-Aldrich and Daejung. In our experiments, no unexpected or unusually high safety hazards were encountered. High purity eutectic gallium-indium (EGaIn; 99.99%) was obtained from Sigma-Aldrich and used as supplied. Gold thin films (300 nm) were deposited onto silicon wafer (100 mm in diameter; 1–10 ohm-cm, 525 ± 50 microns thick) using an e-beam evaporator (ULVAC). Glass with a thickness of 1.2 to 1.5 mm used to prepare the template-stripped gold substrates was purchased from Matsunami and cut into 1 cm × 1 cm pieces.

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker FT-NMR Advance-500 using CDCl\(_3\) as a solvent and residual solvents as an internal standard. Chemical shifts are expressed in parts per million (ppm) related to internal TMS and coupling constant (\( J \)) are in Hertz. Mass spectra of S4 molecule was recorded by the EI mode on JEOL JMS-700 magnetic sector instrument. All X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha photoelectron spectrometer with a monochromated Al Kα X-ray source (1486.6 eV) and He I source.

1.2 Synthesis

To synthesize HS(Cy)_2, we followed four synthetic steps: i) the reduction of biphenyl alcohol under high-pressure H\(_2\) atmosphere, ii) mesylation of alcohol, iii) S\(_2\)N reaction of the resulting mesyl group with thioacetate, and iv) reduction of thioacetate to thiol. Note
that there is a Walden inversion in the third step. The all trans forms are thermodynamically stable among others, which is confirmed in the literature.\textsuperscript{1,2} We confirmed the desired structures of molecules with \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopies, and high resolution mass spectrometry. In particularly, the resonance corresponding to the $\alpha$ proton of cyclohexyl derivatives and the splitting of the \textsuperscript{1}H NMR signal were highly indicative of whether the functional group (OH, OMs, SAc, and SH) was in axial or equatorial positions. In general, when the $\alpha$ proton is in an axial position (i.e., the functional group is in an equatorial position), the coupling constants are relatively large as compared to those of the equatorial-positioned $\alpha$ proton.\textsuperscript{3,4} This \textsuperscript{1}H NMR interpretation was confirmed by single crystal X-ray diffraction experiments.\textsuperscript{2} Hence, we here used \textsuperscript{1}H NMR spectra to distinguish the stereochemistry of cyclohexyl derivatives.

\begin{center}
\begin{tikzpicture}
\tikzset{>=latex}
\begin{scope}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme.png}};
\end{scope}
\end{tikzpicture}
\end{center}

**Scheme S1.** Synthetic scheme of HS(Cy)$_2$

**cis-[1,1'-bi(cyclohexan)]-4-ol (S1)**

Compound S1 was synthesized following the method modified from literature.\textsuperscript{5} A mixture of HO(Ph)$_2$ 1.70 g (10 mmol) and Ru on activated carbon as a catalyst (10 wt% of substrate) in $i$-PrOH (15 mL) in a sealed tube was stirred at the 90 °C under H$_2$ pressure (10 atm) for 24 hours. Reaction completion was indicated by a constant H$_2$ pressure after a
gradual decrease. After cooling to room temperature, the reaction mixture was diluted with CH$_3$OH (20 mL) and the catalyst was removed by filtration through a Celite and a membrane filter. The filtrate was concentrated in vacuo to give the corresponding hydrogenated product. This product was passed through a column of silica gel using 3 % ethyl acetate in hexane, afforded 621 mg (32%) as white powder. The analytical data for this compound were in excellent agreement with the reported data.$^5$

**cis-[1,1'-bi(cyclohexan)-4-yl methanesulfonate (S2)]**

Compound S2 was synthesized following the method modified from literature.$^2$ S1 206 mg (1.13 mmol) was taken in a round bottom flask equipped with balloon filled with N$_2$, followed by addition of 2.5 mL dichloromethane (DCM). The resulted clear solution was cooled to 0 °C and Et$_3$N (0.236 mL, 1.70 mmol) was added. After 10 min of stirring, a solution of methanesulfonyl chloride (0.1 mL, 1.24 mmol) in 2 mL DCM was added drop wise. Stirring was continued for 30 min and then reaction mixture was allowed to warm up to room temperature (RT). The reaction mixture was allowed to stir for 30 min at RT and checked with the TLC. After completion of reaction; the reaction mixture was diluted with 2 mL DCM. The organic phase was washed with aqueous NaHCO$_3$ and dried with MgSO$_4$. The solvent was removed under reduced pressure to yield the mesylated product as a white solid. The product was further purified with recrystallization from cyclohexane at RT, afforded 150 mg (51 %) as white powder. The analytical data for this compound were in excellent agreement with the reported data.$^2$

**trans-S-[1,1'-bi(cyclohexan)-4-yl ethanethioate (S3)]**
Compound S3 was synthesized following the method modified from literature. S2 150 mg (0.577 mmol) was dissolved in 5 mL DMF and potassium thioacetate 198 g (1.73 mmol) was added. Resulting bluish-green solution was refluxed in a two necked round bottom flask equipped with reflux condenser with balloon filled with N₂ for 2 h. Progress of reaction was monitored by ¹H NMR analysis. After the completion of reaction; DMF was evaporated and dark brown solid was dissolved in DCM followed by addition of saturated aqueous. NH₄Cl solution. The aqueous phase was extracted three times with DCM. The combined organic phases were washed with brine and dried over MgSO₄. The organic solvent was evaporated to yield light brown oil. This product was passed through a column of silica gel using 1 % ethyl acetate in cyclohexane. This unstable product was immediately used for next reaction. In this reaction inversion in configuration takes place. cis mesylate gave trans-thioacetate 55 mg (42 %). The analytical data for this compound were in excellent agreement with the reported data.

trans-S-[1,1'-bi(cyclohexane)]-4-thiol (S4)

Compound S4 was synthesized following the method modified from literature. LiAlH₄ 8.20 mg (0.217 mmol) was taken in dry two necked round bottom flask equipped with septum and N₂ filled balloon. Dry ether (2 mL) was added and the resulting suspension was stirred at 0 °C for 10 min. The solution of S3 16.5 mg (0.0722 mmol) in dry ether 1mL was added drop wise through a syringe and ice bath was removed. Stirring was continued for an additional 1 hour and checked with TLC. After completion of the reaction, mixture was cooled down to 0 °C and 0.5 mL of 2 N NaOH solution was added and filtered. The filtrate was diluted with N₂ bubbled diethyl ether. Organic phase was washed with degassed water (bubbled with N₂ for 10 min.) and dried over MgSO₄ to afford the light-yellow oil. The
crude product was further purified with flash column chromatography using cyclohexane followed by distillation using Kögel-Rhor apparatus to afford 12.2 mg (74 %) of product as light yellow oil. The analytical data for this compound were in excellent agreement with the reported data.²

1.3 SAM Preparation

The SAMs were prepared following a previously reported procedure.⁵ Briefly, toluene (anhydrous, 99.9%) solution containing a 3 mM thiol compound was added to a clean vial. A freshly prepared template-stripped gold (Au⁵) chip was rinsed with pure toluene and placed into the solution with the exposed metal faceing upwards. After 3 h of incubation at room temperature, the SAM-bound Au⁵ chip was removed from the solution and rinsed by repeatedly dipping the chip in clean toluene (3 × 1 mL). The solvent on the SAM was then evaporated in air for a few seconds.
2. Electrical Measurements

2.1 Preparation of the EGaIn Tip

An EGaIn conical tip of EGaIn was formed following a method reported in the literature. Briefly, a 10 μL gas-tight syringe was filled with EGaIn (≥99.99%, Aldrich) and a drop of EGaIn was pushed to the tip of the syringe needle, where the hanging drop was brought into contact with a surface on which the EGaIn could stick (e.g., bare Au or Ag surfaces), and the needle was gently pulled away from the drop using a micromanipulator. Upon breaking from the bulk EGaIn on the surface, a conical tip was obtained. An EGaIn conical tip for tunneling junctions was newly formed for every junction in order to eliminate any complexities that may arise from contamination of the EGaIn surface by volatile organics in air. In the cases that visible whiskers formed during tip fabrication, the tip was discarded, and a new tip was formed.

2.2 Electrical Measurements and Data Analysis

Junction formation and measurements were carried out following the method reported in the literature. All of the junction formations formation and measurements were carried out under ambient conditions. Briefly, a SAM was first gently brought into contact first with a tungsten metal electrode. Then using a micromanipulator, an EGaIn conical tip was gently brought into contact with the surface of the SAM. The SAM-bound bottom electrode was grounded, and the EGaIn top electrode was biased.

The diameter of the contact area was measured at high magnification (~ ×480). Assuming a circular contact, the area was derived from the measured diameter from which the current densities ($J$, A/cm$^2$) were calculated. The contact and presence of a SAM was confirmed by running a single $J$-$V$ scan after which 20 scans were run if there was
indication of contact and tunneling. A trace is based on the following voltage sweep sequence: 0 V → +0.5 V → 0 V → -0.5 V → 0 V, with a step size of 0.05 V. Therefore, one trace corresponds to two scans. The total number of working junctions versus those that shorted was used to calculate the yield (%) of working junctions. Shorts were usually excluded prior to analysis. Shorts clearly do not give information about the SAM and can bias distributions of current density toward high values. Thus, when operations are carried out on the raw distribution of the log-current density (log|J|), the values corresponding to shorts can be discarded. Shorts are defined as values of current that reach the compliance limit of the electrometer used (± 0.105 A in this case). To generate histograms, the bin-size of the histograms was kept constant (the width of each bin is 0.2 for J values and 0.1 for r values on the log-scale).

2.3 Determination of the Electric Field

Because of the use of the ultra-flat AuTS as a bottom electrode, it is assumed that the electric field formed by a SAM-based molecular junction is a field with a constant electric field at all points. The electric field value can be approximated by maintaining the voltage (electric potential difference) between the gold as a bottom electrode and the EGaIn as a top electrode. Assuming an infinite surface, the magnitude of field $E$ can be defined as follows:

$$E = \frac{v}{d} \text{ (GV/m)}$$  \hspace{1cm} (Eq. S1.)

where $V$ is the applied voltage between the electrodes and $d$ is the distance separating the two electrodes. The value of $d$ was determined using two methods. First, the length of ideal molecule (e.g. fully extended trans forms for $n$-alkanethiolates) was used to estimate the $E$
value. If the value of \( d \) is linearly translated into the vertical distance between the electrodes, this approximation is valid. Consequently, the \( E \) values were determined using the two methods.

Second, the vertical distance between the electrode was estimated by considering the tilt angle of the molecule with respect to the surface normal (Figure S14). The tilt angles of \( n \)-alkanethiolates (SC\(_n\)) and oligophenyleneethiolates (S(Ph)\(_n\)) on gold have been well defined in many studies using various analytical techniques.\(^6,7\) Commonly accepted values are \( \theta = 32^\circ, 22^\circ, \) and \( 49^\circ \) for \( SC_n \), S(Ph)\(_n\) (\( n=2 \) and 3), and S(Ph)\(_n\) (\( n=1 \)), respectively. The tilt angle value was used to calculate the value of \( d \cdot \cos \theta \) which corresponds to the vertical distance between the electrodes as shown in Figure S14. In this case, \( E = V/d \cdot \cos \theta \) and the SI unit is gigavolts per meter (GV/m).

### 2.4 Determination of the Tunneling Conductivity and Power Factor

Electrical conductivity, \( \kappa \), is the inverse of resistivity (\( \rho \)):

\[
\kappa = \frac{1}{\rho} \text{ (}\mu\text{S/cm)} \quad \text{(Eq S2.)}
\]

Conductivity has the unit of “microsiemens per centimeter” (\( \mu\text{S/cm} \)). Generally, the resistivity at a particular point is defined as the ratio of the electric field to the density of the current it creates at that point:

\[
\rho = \frac{E}{J} \text{ (cm/}\mu\text{S)} \quad \text{(Eq S3.)}
\]

where \( \rho \) (\( \mu\text{S/cm} \)) is the resistivity of the conductor material, \( J \) (A/cm\(^2\)) is the magnitude of the current density and \( E \) (GV/m) is the magnitude of the electric field.
Conductivity is the inverse (reciprocal) of resistivity, and thus given by:

\[ \kappa = \frac{1}{\rho} = \frac{J}{E} \text{ (}\mu\text{S/cm)} \quad \text{(Eq S4.)} \]

Using the calculated \( \kappa \) value and the measured Seebeck coefficient (\( S \)), the power factor (PF) value was obtained according to the following relationship:

\[ \text{Power factor (PF)} = \kappa S^2 \text{ (}\mu\text{Wm}^{-1}\text{K}^{-2}) \quad \text{(Eq S5.)} \]

where, \( S \) has the unit of “microvolts per kelvin” (\( \mu\text{V/K} \)) and the product (\( \kappa S^2 \)) has the unit of "microwatts per meter kelvin square" (\( \mu\text{Wm}^{-1}\text{K}^{-2} \)).

### 2.5 Determination of the ZT (Figure of Merit)

Using the PF value calculated in Section 2.4, thermal conductivity (\( \lambda \)), and average temperature (\( T \)) between the hot and cold surfaces, the value of Figure of merit (ZT) could be determined according to the following equation:

\[ ZT = \frac{\kappa S^2 T}{\lambda} \quad \text{(Eq S6.)} \]

where, \( \kappa S^2 \) has the unit of “microwatts per meter kelvin square” (\( \mu\text{Wm}^{-1}\text{K}^{-2} \)), \( \lambda \) has the unit of microwatts per meter kelvin (\( \mu\text{Wm}^{-1}\text{K}^{-1} \)), and the product (\( \frac{\kappa S^2 T}{\lambda} \)) is dimensionless considering the unit of temperature as \( K \).

Most of thermal transport studies on a molecular scale have reported the ability of material to conduct thermal energy as thermal conductivity (\( \lambda \), \( \mu\text{Wm}^{-1}\text{K}^{-1} \)), thermal
conductance ($G, \mu\text{WK}^{-1}$), or interfacial thermal conductance ($G_i, \mu\text{Wm}^{-2}\text{K}^{-1}$). Yu et al.\cite{Yu2004} reported the measurement of the thermal conductivity of C$_{60}$. They found the value of $\lambda_{C_{60}}$ was 0.4 Wm$^{-1}$K$^{-1}$ ($= 4.0 \times 10^5 \mu\text{Wm}^{-1}\text{K}^{-1}$). Recently, Cui et al.\cite{Cui2005} have measured the $G$ of single-molecule junctions using calorimetric scanning thermal microscopy (denoted as C-SThM). They reported the $G$ value of Au-SSC$_{10}$S-Au single-molecule junction as 30 pWK$^{-1}$ ($= 30 \times 10^{-6} \mu\text{WK}^{-1}$). Considering the molecular length (~1.4 nm), we could infer the value of $\lambda$ for SSC$_{10}$S ($\lambda_{SSC_{10}}$) as $2.1 \times 10^4 \mu\text{Wm}^{-1}\text{K}^{-1}$.

The value of $\lambda$ has also been determined using the value of interfacial thermal conductance ($G_i$) by Losego et al.\cite{Losego2006} They measured $G_i$ value for the Au/SAM/Quartz structure with time-domain thermoreflectance (TDTR) technique, which uses a pulsed laser to monitor temperature decay by thermoreflectance with a picosecond resolution. Since acoustic waves travel at a few nanometers per picosecond, the depth resolution of TDTR is approximately the same as the SAM thickness (~1 nm). Thus, the SAM layer is treated as one-molecular thick interface. The thermal conductance per unit area of the interface $G_i$ is defined as follows:

$$G_i = \frac{J}{\Delta T} \quad (\mu\text{Wm}^{-2}\text{K}^{-1})$$

(Eq S7.)

where $J$ is the heat flux normal to the interface and $\Delta T$ is the temperature drop at the interface. The ratio of thermal conductivity $\lambda$ divided by $G_i$ can be used to define the Kapitza length\cite{Kapitza1937} $L_k$,

$$L_k = \frac{\lambda}{G_i} \quad (\text{m})$$

(Eq S8.)
The Kapitza length is a characteristic length in which the thermal resistance is the same as the interfacial thermal conductance. Therefore, $\lambda$ in the layer with the Kapitza length can be described as follows:

$$\lambda = G_i \times L_k \ (\mu \text{Wm}^{-1}\text{K}^{-1}) \quad \text{(Eq S9.)}$$

We could derive the $\lambda$ value from the $G_i$ value assuming the length of molecule to be $\sim 1 \text{ nm}^{10}$, and $\lambda_{SC_{12}} = 3.6 \times 10^4 \mu \text{Wm}^{-1}\text{K}^{-1}$. The value of $\lambda_{C_{60}} \ (4.0 \times 10^5 \mu \text{Wm}^{-1}\text{K}^{-1})$ is an order of magnitude higher than that of $\lambda_{SC_{10S}} \ (2.1 \times 10^4 \mu \text{Wm}^{-1}\text{K}^{-1})$ value. The value of $\lambda_{SC_{12}}$ is similar to that of $\lambda_{SC_{10S}}$. This indicates that our calculations of thermal conductivity are correct.

3. Thermoelectric Measurements

3.1 Junction Formation and Thermoelectric Measurements

While molecular tunneling junctions have been long established with various testbeds and molecules, molecular thermoelectric junctions are relatively unexplored. A few testbeds have been devised to measure Seebeck coefficient at the molecular level. Ludoph et al. first demonstrated the measurement of Seebeck coefficient over a single atom in mechanically controlled break junction (MCBJ) in 1999. In 2007, Reddy et al. measured the first Seebeck coefficient of single molecules in scanning tunneling microscopy-break junction (STM-BJ). In 2011, Tan et al. presented small-area junctions formed with thermoelectric atomic force microscopy (ThAFM) to determine Seebeck coefficient of hundreds molecules per junction. Recently, Park et al. demonstrated the large-area
thermoelectric junctions with Ga$_2$O$_3$/EGaIn electrode. Soft top-contact of EGaIn makes it possible to form non-damaging tunneling and thermoelectric contacts with delicate surface of SAMs in ambient conditions.$^{21,22}$

An EGaIn conical tip was fabricated following the procedures detailed for the tunneling current measurements. A SAM was placed on a hot chuck, and the rest of the area was covered with glass to block or minimize heat transfer to the EGaIn tip. The SAM was then gently brought into contact with a tungsten ground electrode. To measure the temperature of the bottom electrode, a thermocouple was placed and secured onto the electrode. Note that the substrate required glass and optical adhesive (organic polymer), the thermal conductivities of which are $\sim 1$ and $\sim 0.2$ W/mK, respectively.$^{23}$ These values are approximately one or two orders of magnitude larger than the thermal conductivity of air (0.02 W/mK). Once the temperature of the substrate was monitored by the thermocouple, we found the heat transfer from the hot chuck to the SAM on gold was sufficient enough to carry out the desired experiments. To create a temperature difference, the temperature of the hot chuck was varied from 290 to 302 K. At each temperature, a few seconds were allowed to pass before the temperature measured at the bottom-electrode thermocouple was stabilized. Then using a micromanipulator, an EGaIn conical tip was gently brought into contact with the surface of the SAM, and the output voltage was measured. 76 traces were measured per junction. At each temperature, 8 – 10 junctions were measured per sample, and at least three samples were used. A freshly prepared EGaIn conical tip was used for measuring 3 – 5 junctions, and thereafter a new tip was generated. Usually, measurement for a sample took a few hours: $\sim 100$ data points were collected in 0.5 min and thus, in principle, 6000 data points could be collected in $\sim 5$ h. The yields of the working junctions were calculated using the ratio of non-shorting junctions to all measured junctions.
Shorting junctions were defined as the junction showing a value of $S_{\text{EGaIn}}$ (3.4 μV/K), which was measured from the shorting junction of the EGaIn conical tip with bare AuTS.

### 3.2 Temperature Gradient in EGaIn-based Junctions

Tan et al. discussed thoroughly the temperature gradient across a molecular junction formed with a SAM-bound gold and a gold-coated silicon cantilever of conductive atomic force microscopy (CAFM) as bottom and top electrodes, respectively. This junction was formed and used for measuring thermopower in ambient conditions, which were the same as our experimental condition. Using one-dimensional heat conduction equation, they reasoned that, when the cantilever tip was brought into contact with the SAM, the temperature at the very end of the tip was less than $T_{\text{ambient}} + 0.05(T_{\text{substrate}} - T_{\text{ambient}})$, where $T_{\text{ambient}}$ and $T_{\text{substrate}}$ were the temperatures of reservoir and substrate, respectively. That is, the increase in tip temperature was less than 5 % of the temperature differential applied across the junction. The insignificant temperature increase at the end of tip was attributed to the high thermal conductivity (~150 W/m·K) of silicon cantilever and the short length of the cantilever (~125 μm), which minimized the heat flow from the substrate to the cantilever. Thermal conductivities of Ga$_2$O$_3$ and EGaIn are ~20 and ~26 W/m·K. Given that these values do not significantly differ from that of silicon (the difference less than an order of magnitude), we assumed that the uncertainty of temperature differentials applied to our junctions was similar to the Si cantilever-based system.

We assumed the top-electrode’s skin region being in contact with SAM feels $\Delta T$ while the bulk region is in equilibrium with room temperature; the same assumption has been
previously used for single-molecular junction systems.\textsuperscript{26-28} Note that the desired $\Delta T$ across junctions would not be exactly identical with the real $\Delta T$. Precisely measuring the small temperature difference between the electrodes is a separate challenge, and the level of precision we used was enough to measure the thermopower of oligophenylenethiolates and $n$-alkanethiolates-based large-area junctions.

3.3 Thermopower Analysis of the Junctions

To analyze the thermopower of the junctions, a previous method reported by Segalman and Majumdar research groups was used.\textsuperscript{16, 27} The thermopower reflects the slope of $\Delta V$ vs. $\Delta T$, and $\Delta T$ occurs across the junction. Hung \textit{et al.}\textsuperscript{29} showed via molecular dynamics (MD) calculations that $\Delta T$ is usually created at the organic-electrode interfaces in the SAM to junctions. When a SAM is not present, $\Delta T$ occurs across the EGaIn tip and the tungsten (W) ground electrode. When a SAM is present, $\Delta T$ occurs across the molecule and the W electrode. Thus, using the equations in the Figure S13, the thermopower of the SAMs was estimated. For the Seebeck coefficients of EGaIn and Ga$_2$O$_3$, previously measured values were used.\textsuperscript{21}
4. Further Discussions on Characterization

4.1 XPS Measurements

The XPS measurements were carried out on a Thermo Scientific K-Alpha photoelectron spectrometer with a monochromated Al Ka (1486.6 eV) source. The binding energies were calibrated by setting Au 4f of bulk metals to values 84.0 eV. The peak shapes of the core level photoelectron spectra were analyzed with a XPS Peak Fit program. A Shirley-type background correction was used. The XPS Au4f, C1s, and S2p lines were detected to study the SAMs. The single binding energies of C1s were observed at 284 – 285 eV for our SAMs. The S2p signal has a doublet peak present at 162 eV and 163 eV, which confirms the formation of a S-Au bond and the ordered structure in monolayers. The XPS spectra for each molecule are shown in Figure S18-S25.
5. Supplementary Figures and Tables

Figure S1. (a) Log$J$-$V$ traces. Histograms of (b) log$|r^+|$, (c) log$|J (-0.5 \text{ V})|$, and (d) log$|J (+0.5 \text{ V})|$ of the Au$^{\text{TS}}$/S(Ph)$_1$/Ga$_2$O$_3$/EGaIn junctions. Mean and standard deviation values of log$|J|$ and log$|r^+|$ are shown in the plots.
Figure S2. (a) Log-$J$-$V$ traces. Histograms of (b) log|$r^+$|, (c) log|$J (-0.5 \text{ V})$|, and (d) log|$J (+0.5 \text{ V})$| of the AuTS/ S(Ph)$_3$/Ga$_2$O$_3$/EGaIn junctions. Mean and standard deviation values of log|$J$| and log|$r^+$| are shown in the plots.
Figure S3. (a) Log-$J$-$V$ traces. Histograms of (b) log|$r^+$|, (c) log|$J (-0.5\, V)$|, and (d) log|$J (+0.5\, V)$| of the Au$^{TS}/\text{S(Ph)$_3$/Ga}_2\text{O}_3$/EGaIn junctions. Mean and standard deviation values of log|$J$| and log|$r^+$| are shown in the plots.
**Figure S4.** (a) Log-$J$-$V$ traces. Histograms of (b) log|$r^\dagger$|, (c) log|$J$ (-0.5 V)|, and (d) log|$J$ (+0.5 V)| of the Au$^{TS}$/SC$\delta$/Ga$_2$O$\delta$/EGaIn junctions. Mean and standard deviation values of log|$J|$ and log|$r^\dagger$| are shown in the plots.
Figure S5. (a) Log-$J$-$V$ traces. Histograms of (b) log|$r^+$|, (c) log|$J(-0.5\, V)$|, and (d) log|$J(+0.5\, V)$| of the AuTS/SC8/Ga2O3/EGaIn junctions. Mean and standard deviation values of log|$J$| and log|$r^+$| are shown in the plots.
Figure S6. (a) Log-$J$-$V$ traces. Histograms of (b) log|$r^+|$, (c) log|$J$ (-0.5 V)|, and (d) log|$J$ (+0.5 V)| of the AuTS/SC12/Ga$_2$O$_3$/EGaIn junctions. Mean and standard deviation values of log|$J$ and log|$r^+|$ are shown in the plots.
**Figure S7.** (a) Log\(|J|\)-\(V\) traces, and histograms of (b) log\(|r^+|\), (c) log\(|J(-0.5\, V)|\), and (d) log\(|J(+0.5\, V)|\) of the AuTS/\(S(Cy)_1\)/Ga\(_2\)O\(_3\)/EGaIn junctions. Mean and standard deviation values of log\(|J|\) and log\(|r^+|\) are shown in the plots.
Figure S8. (a) Log$|J| - V$ traces, and histograms of (b) log$|r^*|$, (c) log$|J| (-0.5 \, V)$, and (d) log$|J| (+0.5 \, V)$ of the Au$^{TS}/S(Cy)_2//Ga_2O_3/EGaIn$ junctions. Mean and standard deviation values of log$|J|$ and log$|r^*|$ are shown in the plots.
Figure S9. Plots of (a) $\log|J(\pm 0.5 \, \text{V})|$ and (b) $\log|J(\pm 0.1 \, \text{V})|$ as a function of the molecular length ($\text{Å}$).\textsuperscript{32}

| Molecule | $\beta$ or $\log|J_0|$ | Our values | Ref [32] |
|----------|------------------------|-------------|---------|
| $\text{S(Ph)}_n$ | $\beta$ at $+0.5\, \text{V}$ | $0.26 \pm 0.01 \, (\text{Å}^{-1})$ | $0.28 \pm 0.03 \, (\text{Å}^{-1})$ |
| | $\log|J_0|$ at $+0.5\, \text{V}$ | $2.5 \pm 0.1$ | $2.7 \pm 0.1$ |
| $\text{SC}_m$ | $\beta$ at $+0.5\, \text{V}$ | $0.76 \pm 0.03 \, (\text{Å}^{-1})$ | $0.76 \pm 0.03 \, (\text{Å}^{-1})$ |
| | $\log|J_0|$ at $+0.5\, \text{V}$ | $3.8 \pm 0.2$ | $4.2 \pm 0.2$ |
| $\text{S(Cy)}_k$ | $\beta$ at $+0.5\, \text{V}$ | $0.57 \pm 0.0 \, (\text{Å}^{-1})$ | |
| | $\log|J_0|$ at $+0.5\, \text{V}$ | $2.9 \pm 0.0$ | |
Figure S10. Histograms of thermoelectric voltage measured at the Au^{TS}/S(Ph)_n/Ga_2O_3/EGaIn junctions, and estimated mean and sigma (standard deviation) values from Gaussian fitting curves.
Figure S11. Histograms of thermoelectric voltage measured at the Au$^{TS}/$SC$_n$/Ga$_2$O$_3$/EGaIn junctions, and estimated mean and sigma (standard deviation) values from Gaussian fitting curves.
**Figure S12.** Histograms of thermoelectric voltage measured at the Au$^{TS}$/S(Cy)$_2$/Ga$_2$O$_3$/EGaIn junctions, and estimated mean and sigma (standard deviation) values from Gaussian fitting curves.
Figure S13. Thermopower analysis of the Au$^{TS}$/SAM//Ga$_2$O$_3$/EGaIn junction.
**Figure S14.** Illustration of the two methods that can be used to calculate the distance between the bottom- and top- electrodes. Tilt angles ($\theta$) with respect to the surface normal were taken from the literature involving the identical SAMs on gold.

\[ E = \frac{V}{d} \quad \text{(Table S2)} \quad \text{or} \quad E = \frac{V}{d \cdot \cos \theta} \quad \text{(Table S3)} \]

**Method I**

**Method II**
Figure S15. Plot of PF-molecular length trends according to $\beta$ and $\beta^S$ of molecules (1-9) in Figure 4 (a). The values in y-axis are corrected PF values (with a $10^6$ correction factor to reflect effective contact area).
**Figure S16.** Plot of PF-molecular length trends according to the change of $\beta$ (Å$^{-1}$) at 45 Å for oligothiophene (the derivative of molecule 9) in Figure 4a. The value of $\beta$ changes with and without changing the sign at the point where the transition from tunneling to hopping occurs. The value of $\beta^S$ does not change with length. The values in y-axis are non-corrected PF values.
**Figure S17.** Plot of PF-molecular length trends according to the change of $\beta (\text{Å}^{-1})$ at 45 Å for oligothiophene (the derivative of molecule 9) in Figure 4a. The value of $\beta$ changes without changing the sign at the point where the transition from tunneling to hopping occurs. The value of $\beta$ does not change with length. The values in y-axis are non-corrected PF values.
**Figure S18.** XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for SC₄ SAM on Au⁹.
Figure S19. XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for SC$_8$ SAM on Au$^{TS}$. 
**Figure S20.** XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for SC$_{12}$ SAM on Au$^{TS}$. 
Figure S21. XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for S(Ph)$_1$ SAM on Au$^{TS}$. 
Figure S22. XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for S(Ph)$_2$ on Au$^{TS}$. 
**Figure S23.** XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for S(Ph)$_3$ on Au$^{TS}$. 

![XPS spectra](image-url)
Figure S24. XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for S(Cy)$_1$ on Au$^{TS}$. 
Figure S25. XPS survey spectrum and high resolution spectra (C 1s, S 2p and Au 4f) for S(Cy)₂ on Au^{TS}. 
Table S1. Summary of calculations to estimate molecular length and thickness of SAMs using ChemDraw software.

| Molecule | Fully extended molecular length (Å) | Molecular length considering tilt angle (Å) |
|----------|------------------------------------|-------------------------------------------|
| SC₄      | 6.2                                | 5.2                                       |
| SC₈      | 10.2                               | 8.7                                       |
| SC₁₂     | 15.2                               | 13.0                                      |
| S(Ph)₁   | 5.7                                | 3.7                                       |
| S(Ph)₂   | 9.8                                | 9.1                                       |
| S(Ph)₃   | 14.0                               | 13.0                                      |
| S(Cy)₁   | 5.7                                | 4.8                                       |
| S(Cy)₂   | 10.2                               | 8.7                                       |
Table S2. Summary of the tunneling conductivity ($\kappa$), Seebeck coefficient ($S$), and power factor (PF) values estimated assuming that the distance between the electrodes corresponds to the length of fully extended molecule ($d$, Å) (that is, the method I in Figure S14).

| Molecule | $|j(+0.1\text{V})|$ (A/cm$^2$) | $E$ (GV/m) | $\kappa$ ($\mu$S/cm) | $S$ ($\mu$V/K) | PF ($\mu$Wm$^{-1}$K$^{-2}$) |
|----------|-------------------------------|------------|----------------------|----------------|-----------------------------|
| SC$_4$   | 7.9                           | $1.6 \times 10^{-1}$ | 4.8                  | 6.4            | $2.0 \times 10^{-8}$       |
| SC$_8$   | $4.6 \times 10^{-1}$          | $9.8 \times 10^{-2}$ | $4.7 \times 10^{-1}$ | 3.5            | $5.7 \times 10^{-10}$      |
| SC$_{12}$| $5.8 \times 10^{-3}$          | $6.6 \times 10^{-2}$ | $8.9 \times 10^{-3}$ | 3.0            | $8.0 \times 10^{-12}$      |
| S(Ph)$_1$| 7.9                           | $1.8 \times 10^{-1}$ | 4.5                  | 7.8            | $2.7 \times 10^{-8}$       |
| S(Ph)$_2$| 3.8                           | $1.0 \times 10^{-1}$ | 3.7                  | 9.8            | $3.6 \times 10^{-8}$       |
| S(Ph)$_3$| 1.1                           | $7.2 \times 10^{-2}$ | 1.6                  | 12.9           | $2.6 \times 10^{-8}$       |
| S(Cy)$_1$| 6.5                           | $1.8 \times 10^{-1}$ | 3.7                  | 7.3            | $2.0 \times 10^{-8}$       |
| S(Cy)$_2$| $4.1 \times 10^{-1}$          | $9.8 \times 10^{-2}$ | $4.2 \times 10^{-1}$ | 4.3            | $7.7 \times 10^{-10}$      |
**Table S3.** Summary of the tunneling conductivity (κ), Seebeck coefficient (S), and power factor (PF) considering the tilt angle (alkyl: 32°, aromatic S(Ph)2, S(Ph)3: 22°, and S(Ph)1: 49°) (that is, the method II in Figure S14).

| Molecule | \( |J(+0.1\text{V})| \) (A/cm²) | \( E \) (GV/m) | \( \kappa \) (µS/cm) | \( S \) (µV/K) | PF (µWm⁻¹K⁻²) |
|----------|-----------------|-------------|-------------|-------------|-------------|
| SC₄      | 7.9             | 1.9 \times 10^-1 | 4.1         | 6.4         | 2.0 \times 10^-8 |
| SC₈      | 4.6 \times 10⁻¹ | 1.2 \times 10⁻¹ | 4.0 \times 10⁻⁴ | 3.5         | 4.9 \times 10⁻¹⁰ |
| SC₁₂     | 5.8 \times 10⁻³ | 7.1 \times 10⁻² | 8.2 \times 10⁻² | 3.0         | 7.4 \times 10⁻¹² |
| S(Ph)₁   | 7.9             | 1.9 \times 10⁻¹ | 4.2         | 7.8         | 2.5 \times 10⁻⁸ |
| S(Ph)₂   | 3.8             | 1.1 \times 10⁻¹ | 3.5         | 9.8         | 3.3 \times 10⁻⁸ |
| S(Ph)₃   | 1.1             | 1.1 \times 10⁻¹ | 1.0         | 12.9        | 1.7 \times 10⁻⁸ |
| S(Cy)₁   | 6.4             | 2.1 \times 10⁻¹ | 3.1         | 7.3         | 1.7 \times 10⁻⁸ |
| S(Cy)₂   | 4.1 \times 10⁻¹ | 1.2 \times 10⁻¹ | 3.5 \times 10⁻¹ | 4.3         | 6.6 \times 10⁻¹⁰ |
Table S4. Summary of the tunneling conductivity ($\kappa$), Seebeck coefficient ($S$), and power factor (PF) for $J$ values at various voltages. In the main text, we used the value $J(+0.1V)$.

The units for $J$, $E$, and PF are A/cm$^2$, GV/m, and $\mu$Wm$^{-1}$K$^{-2}$, respectively.

| Molecule | $J(+0.1V)$ | $J(+0.2V)$ | $J(+0.3V)$ | $J(+0.4V)$ | $J(+0.5V)$ |
|----------|------------|------------|------------|------------|------------|
|          | $E$        | $E$        | $E$        | $E$        | $E$        |
|          | PF         | PF         | PF         | PF         | PF         |
| SC$_4$   | 7.9        | $1.6 \times 10^1$ | $2.5 \times 10^1$ | $3.5 \times 10^1$ | $4.7 \times 10^1$ |
|          | 1.6 $\times 10^{-1}$ | $3.2 \times 10^{-1}$ | $4.9 \times 10^{-1}$ | $6.5 \times 10^{-1}$ | $8.1 \times 10^{-1}$ |
|          | 2.0 $\times 10^{-8}$ | $2.1 \times 10^{-8}$ | $2.1 \times 10^{-8}$ | $2.2 \times 10^{-8}$ | $2.4 \times 10^{-8}$ |
| SC$_8$   | 4.5 $\times 10^{-1}$ | $9.9 \times 10^{-1}$ | 1.3 | 2.4 | 3.3 |
|          | 9.8 $\times 10^{-2}$ | $2.0 \times 10^{-1}$ | $2.9 \times 10^{-1}$ | $3.9 \times 10^{-1}$ | $4.9 \times 10^{-1}$ |
|          | 5.7 $\times 10^{-10}$ | $6.2 \times 10^{-10}$ | $5.6 \times 10^{-10}$ | $7.5 \times 10^{-10}$ | $8.3 \times 10^{-10}$ |
| SC$_{12}$ | 5.8 $\times 10^{-3}$ | $1.3 \times 10^{-2}$ | $2.1 \times 10^{-2}$ | $3.2 \times 10^{-2}$ | $5.0 \times 10^{-2}$ |
|          | 6.6 $\times 10^{-2}$ | $1.3 \times 10^{-1}$ | $2.0 \times 10^{-1}$ | $2.6 \times 10^{-1}$ | $3.3 \times 10^{-1}$ |
|          | 8.0 $\times 10^{-12}$ | $9.1 \times 10^{-12}$ | $9.8 \times 10^{-12}$ | $1.1 \times 10^{-11}$ | $1.4 \times 10^{-11}$ |
| S(Ph)$_1$ | 7.9 | $1.6 \times 10^1$ | $2.5 \times 10^1$ | $3.5 \times 10^1$ | $6.8 \times 10^1$ |
|          | 1.8 $\times 10^{-1}$ | $3.5 \times 10^{-1}$ | $5.3 \times 10^{-1}$ | $7.0 \times 10^{-1}$ | $8.8 \times 10^{-1}$ |
|          | 2.7 $\times 10^{-8}$ | $2.8 \times 10^{-8}$ | $2.8 \times 10^{-8}$ | $3.1 \times 10^{-8}$ | $4.7 \times 10^{-8}$ |
| S(Ph)$_2$ | 3.8 | 8.0 | $1.3 \times 10^1$ | $1.9 \times 10^1$ | $2.6 \times 10^1$ |
|          | 1.0 $\times 10^{-1}$ | $2.0 \times 10^{-1}$ | $3.1 \times 10^{-1}$ | $4.1 \times 10^{-1}$ | $5.1 \times 10^{-1}$ |
|          | 3.6 $\times 10^{-8}$ | $3.8 \times 10^{-8}$ | $4.0 \times 10^{-8}$ | $4.4 \times 10^{-8}$ | $4.9 \times 10^{-8}$ |
| S(Ph)$_3$ | 1.1 | 2.4 | 4.1 | 5.9 | 8.1 |
|          | 7.2 $\times 10^{-2}$ | $1.4 \times 10^{-1}$ | $2.1 \times 10^{-1}$ | $2.9 \times 10^{-1}$ | $3.6 \times 10^{-1}$ |
|          | 2.6 $\times 10^{-8}$ | $2.6 \times 10^{-8}$ | $3.1 \times 10^{-8}$ | $3.4 \times 10^{-8}$ | $3.8 \times 10^{-8}$ |
| S(Cy)$_1$ | 6.5 | $1.3 \times 10^1$ | $2.2 \times 10^1$ | $3.3 \times 10^1$ | $3.6 \times 10^1$ |
|          | 1.8 $\times 10^{-1}$ | $3.5 \times 10^{-1}$ | $5.3 \times 10^{-1}$ | $7.0 \times 10^{-1}$ | $8.8 \times 10^{-1}$ |
|          | 2.0 $\times 10^{-8}$ | $2.0 \times 10^{-8}$ | $2.2 \times 10^{-8}$ | $2.5 \times 10^{-8}$ | $2.2 \times 10^{-8}$ |
| S(Cy)$_2$ | 4.1 $\times 10^{-1}$ | $9.0 \times 10^{-1}$ | 1.5 | 2.2 | 3.0 |
|          | 9.8 $\times 10^{-2}$ | $2.0 \times 10^{-1}$ | $2.9 \times 10^{-1}$ | $3.9 \times 10^{-1}$ | $4.9 \times 10^{-1}$ |
|          | 7.7 $\times 10^{-10}$ | $8.4 \times 10^{-10}$ | $9.3 \times 10^{-10}$ | $1.0 \times 10^{-9}$ | $1.1 \times 10^{-9}$ |
Table S5. Summary of thermoelectric measurements over AuTS/S(Ph)n/Ga2O3/EGaIn junctions.

| n in S(Ph)n | ∆T (K) | # of samples | # of tips | # of junctions | counts | ∆Vmean ± σV | SSAM (µV/K)a | yield (%) |
|-------------|---------|--------------|-----------|----------------|--------|--------------|---------------|-----------|
| n = 1       |         |              |           |                |        |              |               |           |
|             | 5       | 5            | 17        | 43             | 3744   | −25 ± 7     | 7.8 ± 0.4     | 81        |
|             | 9       | 5            | 14        | 55             | 4869   | −55 ± 14    | 97            | 95        |
|             | 13      | 3            | 8         | 51             | 3227   | −78 ± 14    | 95            | 93        |
| n = 2       |         |              |           |                |        |              |               |           |
|             | 5       | 3            | 9         | 55             | 4960   | −41 ± 10    | 9.8 ± 0.2     | 96        |
|             | 9       | 4            | 11        | 68             | 6697   | −77 ± 19    | 93            | 92        |
|             | 13      | 4            | 12        | 77             | 6415   | −111 ± 25   | 92            | 90        |
| n = 3       |         |              |           |                |        |              |               |           |
|             | 5       | 4            | 12        | 73             | 6533   | −91 ± 30    | 12.9 ± 1.5    | 90        |
|             | 9       | 4            | 11        | 71             | 6644   | −132 ± 30   | 90            |           |
|             | 13      | 4            | 13        | 59             | 5403   | −192 ± 54   |               |           |

a SSAM was estimated by a Gaussian mean-based statistical method.
Table S6. Summary of thermoelectric measurements over Au\textsuperscript{TS}/SC\textsubscript{m}/Ga\textsubscript{2}O\textsubscript{3}/EGaIn junctions.

| n in SC\textsubscript{m} | $\Delta T$ (K) | # of samples | # of tips | # of junctions | counts | $\Delta V_{mean}$ ± $\sigma_{AV}$ | $S_{SAM}$ (µV/K)$^a$ | yield (%) |
|--------------------------|---------------|--------------|-----------|----------------|--------|-------------------------------|----------------|----------|
| m = 4                    | 4             | 3            | 6         | 25             | 1900   | $-28 \pm 5$                  | 6.4 ± 0.7      | 78       |
|                           | 8             | 3            | 6         | 25             | 1672   | $-53 \pm 11$                  |                | 65       |
|                           | 12            | 3            | 7         | 20             | 1520   | $-68 \pm 17$                  |                | 61       |
| m = 8                    | 4             | 3            | 7         | 31             | 2356   | $-27 \pm 6$                  | 3.5 ± 0.2      | 86       |
|                           | 8             | 3            | 7         | 36             | 2736   | $-36 \pm 12$                  |                | 84       |
|                           | 12            | 3            | 8         | 36             | 2736   | $-48 \pm 11$                  |                | 84       |
| m = 12                   | 4             | 3            | 6         | 33             | 2280   | $-23 \pm 7$                  | 3.0 ± 0.1      | 91       |
|                           | 8             | 3            | 6         | 27             | 2052   | $-31 \pm 7$                  |                | 89       |
|                           | 12            | 3            | 6         | 30             | 2052   | $-39 \pm 6$                  |                | 89       |

$^a$ $S_{SAM}$ was estimated by a Gaussian mean-based statistical method.
Table S7. Summary of thermoelectric measurements over Au$^{TS}$/$S(Cy)_k$//Ga$_2$O$_3$/EGaIn junctions.

| n in $S(Cy)_k$ | $\Delta T$ (K) | # of samples | # of tips | # of junctions | counts | $\Delta V_{mean}$ ± $\sigma_{AV}$ | $S_{SAM}$ (µV/K)$^a$ | yield (%) |
|----------------|----------------|--------------|-----------|----------------|--------|-----------------------------------|----------------------|-----------|
| k = 1          | 4              | 2            | 4         | 12             | 912    | $-69 \pm 7$                       | 7.3 ± 0.6           | 80        |
|                | 8              | 2            | 4         | 12             | 912    | $-95 \pm 14$                      | 75                   |           |
|                | 12             | 2            | 4         | 17             | 1292   | $-119 \pm 14$                     | 74                   |           |
| k = 2          | 4              | 2            | 8         | 18             | 1368   | $-44 \pm 12$                      | 81                   |           |
|                | 8              | 2            | 7         | 21             | 1596   | $-55 \pm 12$                      | 81                   |           |
|                | 12             | 2            | 7         | 23             | 1748   | $-71 \pm 16$                      | 82                   |           |

$^a$ $S_{SAM}$ was estimated by a Gaussian mean-based statistical method.
Table S8. Summary of electrical conductivity measurements over AuTS/S(Ph)n/Ga2O3/EGaIn junctions at +0.5 V.

| n in S(Ph)n | # of samples | # of tips | # of junctions | traces | μJ(+0.5 V) | σJ(+0.5 V) | yield (%) |
|-------------|--------------|-----------|----------------|--------|------------|------------|-----------|
| n = 1       | 2            | 10        | 10             | 200    | 1.8        | 0.13       | 42        |
| n = 2       | 2            | 11        | 11             | 220    | 1.4        | 0.24       | 73        |
| n = 3       | 2            | 11        | 11             | 220    | 0.91       | 0.20       | 92        |
Table S9. Summary of electrical conductivity measurements over AuTS/SCₘ//Ga₂O₃/EGaIn junctions at +0.5 V.

| n in SCₘ | # of samples | # of tips | # of junctions | traces | $\mu_J(+0.5\,\text{V})$ | $\sigma_J(+0.5\,\text{V})$ | yield (%) |
|----------|--------------|-----------|----------------|--------|-----------------------|------------------------|-----------|
| m = 4    | 2            | 10        | 10             | 200    | 1.7                   | 0.24                   | 46        |
| m = 8    | 2            | 11        | 9              | 180    | 0.52                  | 0.23                   | 79        |
| m = 12   | 2            | 11        | 11             | 220    | -1.3                  | 0.22                   | 85        |
Table S10. Summary of electrical conductivity measurements over $\text{Au}^{TS}/\text{S(Cy)}_k/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junctions at +0.5 V.

| $n$ in S(Cy)$_k$ | # of samples | # of tips | # of junctions | traces | $\mu_J$ (+0.5 V) | $\sigma_J$ (+0.5 V) | yield (%) |
|------------------|--------------|-----------|----------------|--------|-----------------|-------------------|-----------|
| $k = 1$          | 2            | 10        | 10             | 318    | 1.6             | 0.16              | 70        |
| $k = 2$          | 2            | 12        | 12             | 240    | 0.48            | 0.24              | 67        |
Table S11. Summary of length dependence of electrical conductance in molecular junctions.

The $\beta_t$ ($\beta$ in a tunneling regime) is conductance decay constant in tunneling regime and $\beta_h$ ($\beta$ in a hopping regime) is conductance decay constant in in hopping regime.

| Molecule$^a$ | Junction Technique$^b$ | Molecular Length$^c$ (Å) | $\beta_t$ (Å$^{-1}$)$^d$ | $\beta_h$ (Å$^{-1}$) | Transition Length (Å) | ref. |
|--------------|--------------------------|---------------------------|------------------------|-----------------|------------------------|-----|
| Amine terminated OPEs
$n = 0,1,2,3$ $m = 1,2$ (OPE1 ~ 4) (OPE5, 7) | STM-BJ | 9.8 – 51.1 | 0.202 | 0.030 | 27.5 | Lu et al.33 |
| Fluorene backbone n-mer dithiol wire $n = 1,2,3,4$ | STM-BJ | 31 – 94 | 0.206 $\sim$0.01 | 52 – 73 (3-mer) | Hines et al.34 |
| DBA system oligomer (D=tetracene, B= p-phenylene vinylene (wire), A=pyromellitimide) | FPPS | - | - | - | 25 | Davis et al.35 |
| OPI 1 ~10 ($n=0,1,2,3,4$) | CP-AFM | 15 – 73 | 0.3 | 0.09 | 40 | Choi et al.36 |
| ONI 2 ~10 ($n=0,1,2,3,4$) | CP-AFM | $\sim$25 – $\sim$100 | 0.25 | $\sim$0.05 | $\sim$40 (ONI 4) | Choi et al.37 |
| (2 + 3n) mer T-di-SCN (n=1 ~ 7) | STM-BJ | 22 – 90 | 0.14 | ~0.05 | 56 – 68 | Yamada et al. 38 |
|--------------------------------|--------|---------|------|------|-------|----------------|
| OPTI 1–12 (n=0 ~ 5) | CP-AFM | 14 – 74 | 0.34 | ~0.07 | 40 – 50 | Smith et al. 39 |
| OAE 1–12 (n=0 ~ 7) | MCBJ | 16 – 58 | 0.33 | 0.016 | 30 | Zhao et al. 40 |
| OTPI 1–12 (n=0 ~ 5) | CP-AFM | 25 – 202 | 0.25 | 0.02 | ~60 | Choi et al. 41 |
| DNA | STM-BJ | 27.2 ~ 54.4° | - | ~0.08 | - | Li et al. 42 |
| DNA | STM-BJ | 27.2 ~ 54.4° | 0.203 | ~0 | ~41 | |

a. OPE = oligo(p-phenylene ethynylene)s, DBA = donor bridge acceptor, OPI = oligophenyleneimine, ONI = oligonaphthalene-fluoreneimine, T-di-SCN = thiophene backbone-dithiocyanate, OPTI = oligophenylene-naphthaleneimine, OAE = oligo(aryleneethynylene), OTPI = oligo-tetraphthalifulvalene-pyromellitic diimide-imine

b. STM-BJ = scanning tunneling microscope based break junction, CP-AFM = conducting probe atomic force microscopy, FPPS = femtosecond optical pump-probe spectroscopy, MCBJ = mechanically controlled break junction. The STM-BJ, CP-AFM and MCBJ techniques used gold top and bottom (or left and right) electrodes.

c. The range of length for the molecules studied.

d. Each β value was estimated based on the length dependence of electrical resistance, conductance, or photoinduced electron transfer.

e. The value is calculated assuming 1 base pair length = ~3.4 Å.
Table S12. Summary of length dependence of thermopower in molecular junctions. The $\beta_t^S$ is the rate of change of $S$ in a tunneling regime and $\beta_h^S$ is the rate of change of $S$ in a hopping regime.

| Molecule$^a$ | Junction Technique$^b$ | Molecular Length$^c$ (Å) | $\beta_t^S$ (µV·(K·Å)$^{-1}$) | $\beta_h^S$ (µV·(K·Å)$^{-1}$) | Transition Length (Å) | ref. |
|--------------|------------------------|---------------------------|-------------------------------|-------------------------------|------------------------|------|
| 1 DNA A(CG)$_n$T (n=3 ~7) | STM-BJ | 27.2 ~ 54.4 | - | -0.03 | - | Li et al.$^{42}$ |
| 2 DNA ACGC(base)GCGT base= A, AT, ATA, (AT)$_2$ ⋯ (AT)$_4$ | STM-BJ | 30.6 ~ 54.4 | ~0.29 | ~0 | ~41 | |

a. A, C, G, T = the four DNA bases, adenine, cytosine, guanine and thymine
b. STM-BJ= scanning tunneling microscope based break junction. The STM-BJ, CP-AFM and MCBJ techniques used gold top and bottom (or left and right) electrodes.
c. The value is calculated assuming 1 base pair length = ~3.4 Å.
6. References

1. Kwon, C. K.; Kim, M. S.; Kim, K., Raman Spectroscopy of Cyclohexanethiol Adsorbed on a Silver Surface. *J. Raman spectros.* **1989**, *20*, 575-580.

2. Waske, P. A.; Meyerbröker, N.; Eck, W.; Zharnikov, M., Self-Assembled Monolayers of Cyclic Aliphatic Thiols and Their Reaction toward Electron Irradiation. *J. Phys. Chem. C* **2012**, *116*, 13559-13568.

3. Höfner, D.; Lesko, S. A.; Binsch, G., Dynamic Proton Magnetic Resonance Studies on Complex Spin Systems. Non-Mutual Three-Spin Exchange in Four 1-Substituted Cyclohexanes-2, 2, 3, 3, 4, 4, 5, 5-d$_8$ and Mutual Four-Spin Exchange in Cyclohexane-1, 1, 2, 2, 3, 3, 4, 4-d$_8$. *Org. Magn. Reson.* **1978**, *11*, 179-196.

4. Jensen, F. R.; Bushweller, C. H.; Beck, B. H., Conformational Preferences in Monosubstituted Cyclohexanes Determined by Nuclear Magnetic Resonance Spectroscopy. *J. Am. Chem. Soc.* **1969**, *91*, 344-351.

5. Liu, C. Y.; Lu, L. H.; Rong, Z. M.; Liang, C. H.; Wang, Y.; Qu, Q. P., Carbon Supported Pd Nanocrystals as High Efficient Catalyst for Regioselective Hydrogenation of $p$-Phenylphenol to $p$-Cyclohexylphenol. *Catal. Lett.* **2012**, *142*, 1321-1329.

6. Yourdshahyan, Y.; Rappe, A. M., Structure and Energetics of Alkanethiol Adsorption on the Au (111) Surface. *J. Chem. Phys.* **2002**, *117*, 825-833.

7. Frey, S.; Stadler, V.; Heister, K.; Eck, W.; Zharnikov, M.; Grunze, M.; Zeysing, B.; Terfort, A., Structure of Thiaaromatic Self-Assembled Monolayers on Gold and Silver. *Langmuir* **2001**, *17*, 2408-2415.

8. Yu, R.; Tea, N.; Salamon, M.; Lorents, D.; Malhotra, R., Thermal Conductivity of Single Crystal C$_{60}$. *Phys. Rev. Lett.* **1992**, *68*, 2050.
9. Cui, L.; Hur, S.; Akbar, Z. A.; Klöckner, J. C.; Jeong, W.; Pauly, F.; Jang, S.-Y.; Reddy, P.; Meyhofer, E., Thermal Conductance of Single-Molecule Junctions. Nature 2019, 572, 628-633.

10. Losego, M. D.; Grady, M. E.; Sottos, N. R.; Cahill, D. G.; Braun, P. V., Effects of Chemical Bonding on Heat Transport across Interfaces. Nat. Mater. 2012, 11, 502-506.

11. Ge, Z.; Cahill, D. G.; Braun, P. V., Thermal Conductance of Hydrophilic and Hydrophobic Interfaces. Phys. Rev. Lett. 2006, 96, 186101.

12. Vilan, A.; Aswal, D.; Cahen, D., Large-Area, Ensemble Molecular Electronics: Motivation and Challenges. Chem. Rev. 2017, 117, 4248-4286.

13. Xiang, D.; Wang, X. L.; Jia, C. C.; Lee, T.; Guo, X. F., Molecular-Scale Electronics: From Concept to Function. Chem. Rev. 2016, 116, 4318-4440.

14. Sun, L.; Diaz-Fernandez, Y. A.; Gschneidtner, T. A.; Westerlund, F.; Lara-Avila, S.; Moth-Poulsen, K., Single-Molecule Electronics: From Chemical Design to Functional Devices. Chem. Soc. Rev. 2014, 43, 7378-7411.

15. Park, S.; Kang, H.; Yoon, H. J., Structure–Thermopower Relationships in Molecular Thermoelectrics. J. Mater. Chem. A 2019, 7, 14419-14446.

16. Reddy, P.; Jang, S.-Y.; Segalman, R. A.; Majumdar, A., Thermoelectricity in Molecular Junctions. Science 2007, 315, 1568-1571.

17. Rincón-García, L.; Evangeli, C.; Rubio-Bollingerac, G.; Agraït, N., Thermopower Measurements in Molecular Junctions. Chem. Soc. Rev. 2016, 45, 4285-4306.

18. Cui, L.; Miao, R.; Jiang, C.; Meyhofer, E.; Reddy, P., Perspective: Thermal and Thermoelectric Transport in Molecular Junctions. J. Chem. Phys. 2017, 146, 092201.

19. Ludoph, B.; Ruitenbeek, J. M. v., Thermopower of Atomic-Size Metallic Contacts. Phys. Rev. B 1999, 59, 12290.
20. Tan, A.; Balachandran, J.; Sadat, S.; Gavini, V.; Dunietz, B. D.; Jang, S.-Y.; Reddy, P., Effect of Length and Contact Chemistry on the Electronic Structure and Thermoelectric Properties of Molecular Junctions. *J. Am. Chem. Soc.* **2011**, *133*, 8838–8841.

21. Park, S.; Yoon, H. J., New Approach for Large-Area Thermoelectric Junctions with a Liquid Eutectic Gallium–Indium Electrode. *Nano Lett.* **2018**, *18*, 7715–7718.

22. Kang, S.; Park, S.; Kang, H.; Cho, S. J.; Song, H.; Yoon, H. J., Tunneling and Thermoelectric Characteristics of N-Heterocyclic Carbene-Based Large-Area Molecular Junctions. *Chem. Commun.* **2019**, *55*, 8780-8783.

23. Macdonald, F.; Lide, D. R., Crc Handbook of Chemistry and Physics: From Paper to Web. *Abstr. Pap. Am. Chem. Soc.* **2003**, *225*, U552-U552.

24. Yu, S.; Kaviany, M., Electrical, Thermal, and Species Transport Properties of Liquid Eutectic Ga-In and Ga-In-Sn from First Principles. *J. Chem. Phys.* **2014**, *140*, 064303.

25. Santia, M. D.; Tandon, N.; Albrecht, J., Lattice Thermal Conductivity in B-Ga2O3 from First Principles. *Appl. Phys. Lett.* **2015**, *107*, 041907.

26. Baheti, K.; Malen, J. A.; Doak, P.; Reddy, P.; Jang, S.-Y.; Tilley, T. D.; Majumdar, A.; Segalman, R. A., Probing the Chemistry of Molecular Heterojunctions Using Thermoelectricity. *Nano Lett.* **2008**, *8*, 715–719.

27. Yee, S. K.; Malen, J. A.; Majumdar, A.; Segalman, R. A., Thermoelectricity in Fullerene–Metal Heterojunctions. *Nano Lett.* **2011**, *11*, 4089–4094.

28. Kim, Y.; Jeong, W.; Kim, K.; Lee, W.; Reddy, P., Electrostatic Control of Thermoelectricity in Molecular Junctions. *Nat. Nanotechnol.* **2014**, *9*, 881-885.

29. Hung, S. W.; Kikugawa, G.; Shiomi, J., Mechanism of Temperature Dependent Thermal Transport across the Interface between Self-Assembled Monolayer and Water. *J. Phys. Chem. C* **2016**, *120*, 26678-26685.
30. Kong, G. D.; Yoon, H. J., Influence of Air-Oxidation on Rectification in Thiol-Based Molecular Monolayers. *J. Electrochem. Soc.* **2016**, *163*, G115-G121.

31. Jiang, L.; Yuan, L.; Cao, L.; Nijhuis, C. A., Controlling Leakage Currents: The Role of the Binding Group and Purity of the Precursors for Self-Assembled Monolayers in the Performance of Molecular Diodes. *J. Am. Chem. Soc.* **2014**, *136*, 1982-1991.

32. Bowers, C. M.; Rappoport, D.; Baghbanzadeh, M.; Simeone, F. C.; Liao, K. C.; Semenov, S. N.; Zaba, T.; Cyganik, P.; Aspuru-Guzik, A.; Whitesides, G. M., Tunneling across Sams Containing Oligophenyl Groups. *J. Phys. Chem. C* **2016**, *120*, 11331-11337.

33. Lu, Q.; Liu, K.; Zhang, H.; Du, Z.; Wang, X.; Wang, F., From Tunneling to Hopping: A Comprehensive Investigation of Charge Transport Mechanism in Molecular Junctions Based on Oligo (p-Phenylene Ethynylene). *ACS Nano* **2009**, *3*, 3861-3868.

34. Hines, T.; Diez-Perez, I.; Hihath, J.; Liu, H.; Wang, Z.-S.; Zhao, J.; Zhou, G.; Müllen, K.; Tao, N., Transition from Tunneling to Hopping in Single Molecular Junctions by Measuring Length and Temperature Dependence. *J. Am. Chem. Soc.* **2010**, *132*, 11658-11664.

35. Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R., Molecular-Wire Behaviour in *p*-Phenylenevinylene Oligomers. *Nature* **1998**, *396*, 60-63.

36. Choi, S. H.; Kim, B.; Frisbie, C. D., Electrical Resistance of Long Conjugated Molecular Wires. *Science* **2008**, *320*, 1482-1486.

37. Choi, S. H.; Risko, C.; Delgado, M. C. R.; Kim, B.; Brédas, J.-L.; Frisbie, C. D., Transition from Tunneling to Hopping Transport in Long, Conjugated Oligo-Imine Wires Connected to Metals. *J. Am. Chem. Soc.* **2010**, *132*, 4358-4368.

38. Yamada, R.; Kumazawa, H.; Tanaka, S.; Tada, H., Electrical Resistance of Long Oligothiophene Molecules. *Appl. Phys. Express* **2009**, *2*, 025002.
39. Smith, C. E.; Odoh, S. O.; Ghosh, S.; Gagliardi, L.; Cramer, C. J.; Frisbie, C. D., Length-Dependent Nanotransport and Charge Hopping Bottlenecks in Long Thiophene-Containing Π-Conjugated Molecular Wires. J. Am. Chem. Soc. 2015, 137, 15732-15741.

40. Zhao, X.; Huang, C.; Gulcur, M.; Batsanov, A. S.; Baghernejad, M.; Hong, W.; Bryce, M. R.; Wandlowski, T., Oligo (Aryleneethynylene)s with Terminal Pyridyl Groups: Synthesis and Length Dependence of the Tunneling-to-Hopping Transition of Single-Molecule Conductances. Chem. Mater. 2013, 25, 4340-4347.

41. Choi, S. H.; Frisbie, C. D., Enhanced Hopping Conductivity in Low Band Gap Donor-Acceptor Molecular Wires up to 20 nm in Length. J. Am. Chem. Soc. 2010, 132, 16191-16201.

42. Li, Y.; Xiang, L.; Palma, J. L.; Asai, Y.; Tao, N., Thermoelectric Effect and Its Dependence on Molecular Length and Sequence in Single DNA Molecules. Nat. Commun. 2016, 7, 11294.