

# Probing the Chemistry of Molecular Heterojunctions Using Thermoelectricity

Kanhayalal Baheti,<sup>†,‡,¶</sup> Jonathan A. Malen,<sup>§,¶</sup> Peter Doak,<sup>†,‡,¶</sup> Pramod Reddy,<sup>||,£</sup>  
Sung-Yeon Jang,<sup>‡,⊥,\*</sup> T. Don Tilley,<sup>†,¶</sup> Arun Majumdar,<sup>\*,‡,§,||,+</sup> and  
Rachel A. Segalman<sup>\*,‡,||,⊥</sup>

*Department of Chemistry, Department of Mechanical Engineering, Applied Science and Technology Program, Department of Chemical Engineering, Department of Materials Science and Engineering, University of California Berkeley, California 94720, and Materials Science Division, Chemical Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*

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## ABSTRACT

Thermopower measurements offer an alternative transport measurement that can characterize the dominant transport orbital and is independent of the number of molecules in the junction. This method is now used to explore the effect of chemical structure on the electronic structure and charge transport. We interrogate junctions, using a modified scanning tunneling microscope break junction technique, where: (i) the 1,4-benzenedithiol (BDT) molecule has been modified by the addition of electron-withdrawing or -donating groups such as fluorine, chlorine, and methyl on the benzene ring; and (ii) the thiol end groups on BDT have been replaced by the cyanide end groups. Cyanide end groups were found to radically change transport relative to BDT such that transport is dominated by the lowest unoccupied molecular orbital in 1,4-benzenedicyanide, while substituents on BDT generated small and predictable changes in transmission.

Metal-molecule heterostructures are a class of hybrid organic–inorganic materials that have shown promise in a variety of applications including molecular electronics, optoelectronics, photovoltaic energy conversion, and thermoelectric energy conversion.<sup>1,2</sup> The behavior of the heterostructures is dominated by the large number of interfaces that produce unique, emergent properties that are not observed in either the molecule or the metal individually. Deeper understanding of how metals and molecules interact and produce these emergent properties is therefore of fundamental interest in the design and performance of devices made from these materials.<sup>3</sup> While devices generally use an ensemble of metal-molecule heterojunctions, it is extremely difficult to probe

the interfacial structure and properties in this arrangement. Instead, valuable insight can be obtained by studying one or a few junctions at a time to avoid interference from others. Over the past decade, this has become an active area of experimental and theoretical research with emphasis on understanding the electronic structure of such junctions by investigating charge conductance.<sup>4–6</sup> While this simple two-point probe measurement has yielded some insight, many questions about the electronic structure remain unanswered and have only been partially addressed.<sup>7</sup> Perhaps the most important one is the following: What is the role of chemistry of the molecule on the electronic structure of the junction? While this issue has been addressed with some depth in bulk materials, simulations suggest that the role of the metal interfaces will significantly alter the effects in molecular junctions.<sup>8</sup> The goal of this paper is to address this issue directly by investigating the thermopower or Seebeck coefficient of such junctions.

It was theoretically proposed<sup>9</sup> that thermopower measurements offer an alternative to conductance measurements that are insensitive to the number of molecules in the junction and can uniquely distinguish whether transport is dominated by the highest occupied molecular orbital (HOMO) (if measured value is positive) or lowest unoccupied molecular orbital (LUMO) (if it is negative) level in the molecule. We recently showed experimentally that such experiments can

\* Corresponding authors. E-mail: (A.M.) majumdar@me.berkeley.edu; (R.S.) segalman@berkeley.edu..

<sup>†</sup> Department of Chemistry, University of California Berkeley.

<sup>‡</sup> Materials Science Division, Lawrence Berkeley Laboratory.

<sup>§</sup> Department of Mechanical Engineering, University of California Berkeley.

<sup>||</sup> Applied Science and Technology Program, University of California Berkeley.

<sup>⊥</sup> Department of Chemical Engineering, University of California Berkeley.

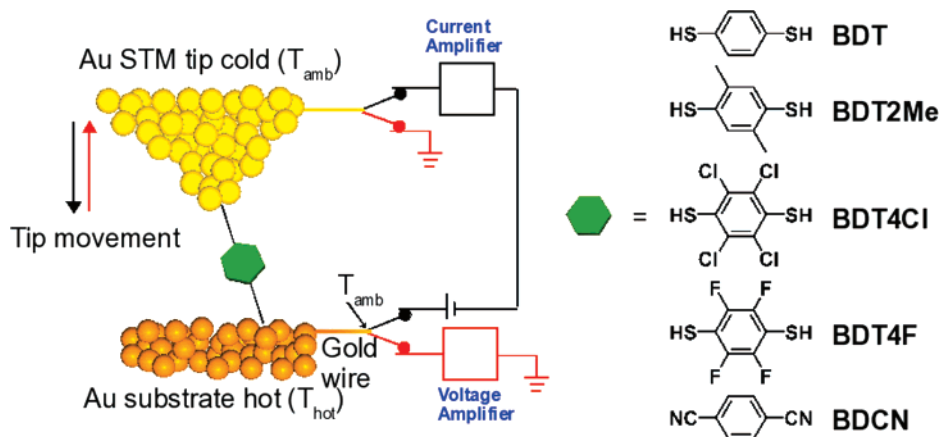
<sup>§</sup> Chemical Science Division, Lawrence Berkeley Laboratory.

<sup>+</sup> Department of Materials Science and Engineering, University of California Berkeley.

<sup>¶</sup> These authors contributed equally to this paper.

<sup>£</sup> Present address: Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

<sup>⊥</sup> Present address: Korea Institute of Science and Technology, Seoul 136-791, Korea.



**Figure 1.** Experimental setup. Schematic description of the experimental setup for measuring thermoelectric voltage based on an STM break junction. Molecules of BDT, BDT2Me, BDT4Cl, BDT4F, and BDCN are trapped between the Au STM tip kept at ambient temperature and a heated Au substrate kept at temperature  $\Delta T$  above the ambient. When the tip approaches the substrate, a voltage bias is applied and the current is monitored to estimate the conductance. When the conductance reaches a threshold of  $0.1 G_0$ , the voltage bias and the current amplifier are disconnected. A voltage amplifier is then used to measure the induced thermoelectric voltage,  $V$ , while the tip is gradually pulled away from the substrate.

indeed be performed and in particular that charge transport in Au–BDT–Au junctions is through the HOMO. We herein use this approach to explore the role of substituents and endgroups on the electronic structure of metal-molecule junctions through measurements of substituted 1,4-benzenedithiol (BDT) molecules and 1,4-benzenedicyanide (BDCN) molecules between gold contacts.

For metal-molecule junctions, one can write a general form of the Seebeck coefficient as

$$S = \frac{1}{eT} \frac{\int_0^\infty \sigma(E)(E - E_F) dE}{\int_0^\infty \sigma(E) dE} \quad (1)$$

where  $\sigma(E)$  is the energy-dependent differential electrical conductance,  $E_F$  is the Fermi level (or more accurately, the chemical potential),  $e$  is the charge of an electron, and  $T$  is the absolute temperature; the denominator in eq 1 is the electrical conductance,  $\sigma$ . The numerator in eq 1 is proportional to the asymmetry in the energy dependence of the conduction electrons with respect to the  $E_F$ . In metal-molecule junctions, this asymmetry is caused by the potential barrier between  $E_F$  and the HOMO and LUMO levels of the junction. Here,  $S$  is not an inherent property of a molecule but that of the metal-molecule heterojunction, and we therefore call it a junction Seebeck coefficient,  $S_{\text{junction}}$ . Because  $S_{\text{junction}}$  characterizes the height of an energy barrier, it is not expected to depend on the number of molecules in the junction.

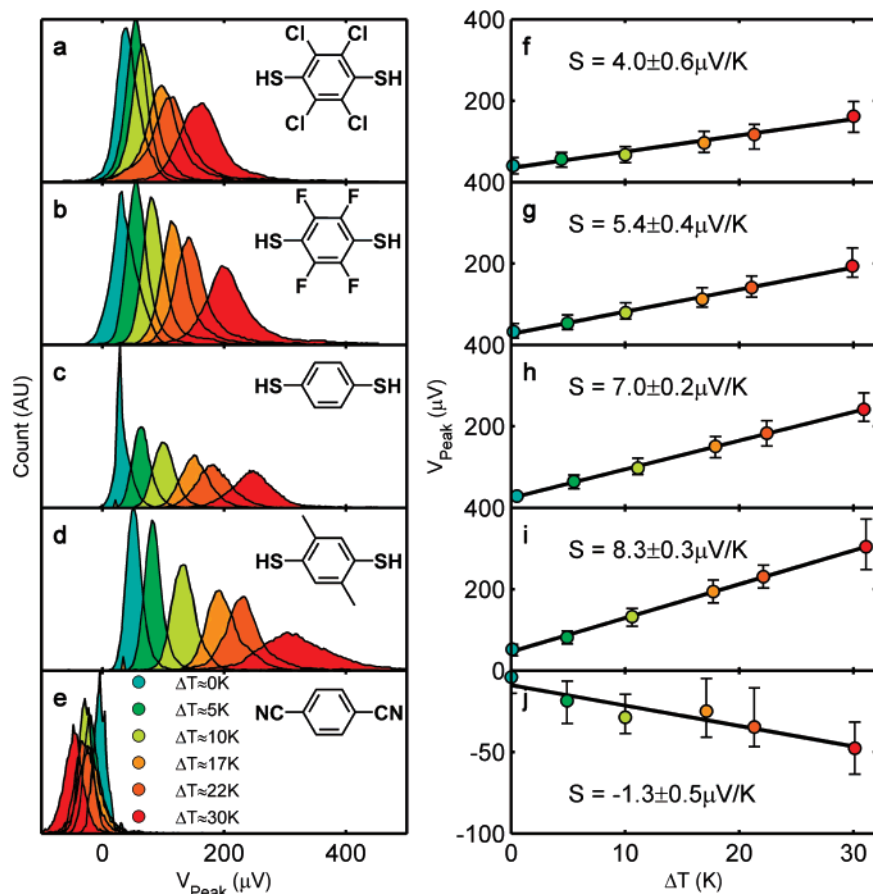
Thermopower measurements were made on BDT, 2,5-dimethyl-1,4-benzenedithiol (BDT2Me), 2,3,5,6-tetrachloro-1,4-benzenedithiol (BDT4Cl), 2,3,5,6-tetrafluoro-1,4-benzenedithiol (BDT4F), and BDCN (schemes shown in Figure 1). A modified scanning tunneling microscope (STM) was used to form a junction between an Au STM tip and the molecule-coated Au substrate<sup>10</sup> (see Materials and Methods in Supporting Information for experimental details). The

STM tip is maintained at ambient temperature while the substrate is heated<sup>11</sup> (Figure 1). We see a thermoelectric voltage,  $V$ , generated between the electrodes when molecules are trapped between the tip and the substrate. Control experiments performed on clean gold surfaces without any molecules demonstrate that no measurable  $S_{\text{junction}}$  is generated in the absence of molecules.<sup>10</sup>

We measured the  $V$  at different values of  $\Delta T$  for each Au–molecule–Au junction. Roughly 1000 consecutive approach–withdraw sequences were completed for each molecule, and histograms of the measured voltage were generated for each temperature difference. The heated substrate was attached to the voltage amplifier using gold leads, which also experience a temperature drop resulting in an additional thermoelectric voltage that must be subtracted as follows:

$$S_{\text{junction}} = S_{\text{Au}} - \frac{V}{\Delta T} \quad (2)$$

where  $S_{\text{Au}}$  is the Seebeck coefficient<sup>12</sup> of bulk Au, which is  $\sim 1.94 \mu\text{V/K}$  at 300 K, and the sign convention results from the circuit orientation described by Reddy et. al.<sup>10</sup> Histograms of  $V$  were generated without any data preselection and then normalized so that the histogram for each  $\Delta T$  contains the same number of counts. The normalized histograms for each  $\Delta T$  were plotted on a common axis and are shown in Figure 2a–e, where panel a is BDT4Cl, panel b is BDT4F, panel c is BDT, panel d is BDT2Me, and panel e is BDCN. The histograms shift right and broaden as higher temperature differences are applied. The histogram peaks, representing the most frequently measured  $V_{\text{peak}}$ , are plotted as a function of  $\Delta T$  in the adjacent figure (2f–j). Error bars at each  $\Delta T$  represent the full width half-maximum from the histogram, which increase with  $\Delta T$ . We observe that the plots are linear in behavior for all the molecules measured. Least-squares linear regression was used to fit a line to these points. The slope



**Figure 2.** Normalized histograms for each  $\Delta T$  plotted on a common axis and obtained by analyzing approximately 1000 consecutive thermoelectric voltage curves for (a) BDT4Cl, (b) BDT4F, (c) BDT, (d) BDT2Me, and (e) BDCN. Histogram peaks as a function of the temperature differential for (f) BDT4Cl, (g) BDT4F, (h) BDT, (i) BDT2Me, and (j) BDCN. The error bars represent full width half-maximum of the corresponding histograms. The measured voltage varies linearly with the temperature differential.

**Table 1.** Measured Values of  $S_{\text{junction}}$  and Calculated Values for  $E_{\text{F}} - E_{\text{HOMO}}$ ,  $G_{\text{junction}}$  (using Equations 2, 3, and 4) and Calculated Energy of HOMO (DFT)

molecule type	measured $S_{\text{junction}}$ ( $\mu\text{V/K}$ )	calculated $E_{\text{F}} - E_{\text{HOMO}}$ (eV) <sup>a</sup>	calculated $G_{\text{junction}}$ ( $\times 10^{-3} G_0$ ) <sup>a</sup>	calculated HOMO (eV) <sup>b</sup>
2,5-dimethyl-1,4-benzenedithiol	$8.3 \pm 0.3$	$1.07 \pm 0.01$	$11.9 \pm 0.3$	6.27
1,4-benzenedithiol	$7.2 \pm 0.2$	$1.16 \pm 0.02$	$10.5 \pm 0.2$	6.42
tetrafluoro-1,4-benzenedithiol	$5.4 \pm 0.4$	$1.32 \pm 0.02$	$8.7 \pm 0.2$	6.47
tetrachloro-1,4-benzenedithiol	$4.0 \pm 0.6$	$1.47 \pm 0.05$	$7.6 \pm 0.3$	6.57

<sup>a</sup> Calculation based on eqs 2, 3, and 4, where  $\tau(E)$  for Au–BDT–Au is assumed for all molecules. <sup>b</sup> Calculated using DFT (see Supporting Information).

of this line is the reported  $S_{\text{junction}}$ , and the 99% confidence interval in slope of this fit line is the reported deviation.  $S_{\text{junction}}$  of BDT4Cl, BDT4F, BDT, BDT2Me, and BDCN between gold contacts are  $4.0 \pm 0.6 \mu\text{V/K}$ ,  $5.4 \pm 0.4 \mu\text{V/K}$ ,  $7.2 \pm 0.2 \mu\text{V/K}$ ,  $8.3 \pm 0.3 \mu\text{V/K}$ , and  $-1.3 \pm 0.5 \mu\text{V/K}$ , respectively (see Table 1). All the substituted BDT molecules have positive measured thermopower values, which imply that these junctions are dominated by transport through the HOMO of the molecule. On the other hand, for BDCN the measured value is negative, and thus we conclude that the transport is through the LUMO of the molecule. The average as well as the deviation in  $S_{\text{Au–BDT–Au}}$  obtained here ( $7.2 \pm 0.2$ ) are lower than the values of  $8.7 \pm 2.1 \mu\text{V/K}$  reported

earlier,<sup>10</sup> although they still lie within the previously reported deviation. The data reported here offer a smaller deviation because measurements were performed at more values of  $\Delta T$ .

For the substituted BDT molecules, we observe that the thermopower of the molecular junction decreases for electron-withdrawing substituents (fluorine and chlorine) and increases for electron-donating substituents (methyl). To understand this trend, it is useful to look at the relative position of the HOMO and LUMO levels of the junction with respect to  $E_{\text{F}}$ . The Landauer<sup>13</sup> formula can be used to relate  $S_{\text{junction}}$  to the transmission function  $\tau(E)$  of the junction<sup>14</sup> as follows:

$$S_{\text{junction}} = - \frac{\pi^2 k_B^2 T}{3e} \frac{\partial \ln(\tau(E))}{\partial E} \bigg|_{E=E_F} \quad (3)$$

where  $e$  is the charge of a proton,  $k_B$  is the Boltzmann constant, and  $T$  is the average absolute temperature of the junction. The conductance of a junction can also be related to the transmission function as follows

$$G_{\text{molecule}} \approx \frac{2e^2}{h} \tau(E)|_{E=E_F} = \tau(E)|_{E=E_F} G_0 \quad (4)$$

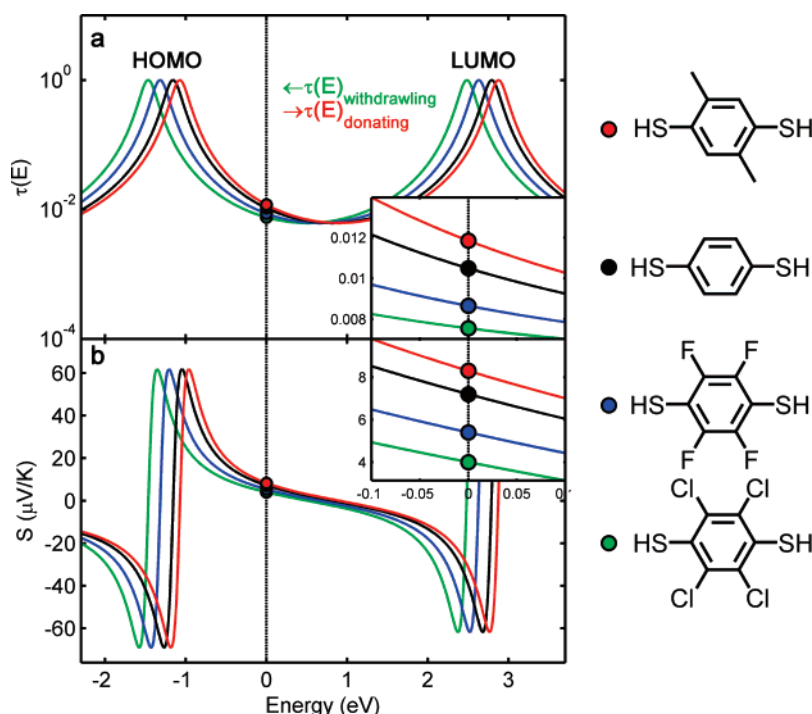
where  $G_0$  is the quantum of conductance. Paulsson and Datta<sup>9</sup> derived the transmission function of Au–BDT–Au using nonequilibrium Green's function formalism (NEGF) in conjunction with extended Huckel theory. They generated an analytical expression for  $\tau(E)$  by fitting Lorentzians to the HOMO and LUMO found by the NEGF calculation

$$\tau(E) = \sum_{i=1}^2 \frac{\Gamma_1 \Gamma_2}{(E - E_i)^2 + (\Gamma_1 + \Gamma_2)^2/4} \quad (5)$$

where  $E_i$  is the energy of the HOMO and LUMO levels, and  $\Gamma_1$  and  $\Gamma_2$  are the broadenings due to contacts 1 and 2. It is clear that  $\tau(E) \sim 1$  when the  $E_F$  aligns with either the HOMO or the LUMO levels and decreases rapidly in

between (see Figure 3). Values of  $\Gamma_1 = \Gamma_2 = 0.11$  eV and  $E_{\text{LUMO}} - E_{\text{HOMO}} = 3.95$  eV were used for all calculations as per previous publications.<sup>9</sup> This analytical expression for  $\tau(E)$  can be used with the measured value of  $S_{\text{junction}}$ , to determine the location of  $E_F$ . Although debate remains as to the exact shape of  $\tau(E)$ , Paulsson and Datta's analytical expression is consistent with measured values of  $S_{\text{junction}}$  and  $G_{\text{junction}}$  for BDT.<sup>10,15</sup>

Intuitively, the broadening of the HOMO and LUMO due to coupling with the semi-infinite contacts should be similar for all the substituted BDT molecules because the sulfur–Au bonding is not significantly affected by substituents. Thus, to illustrate the effect of substituents we assume that  $\tau(E)$  for substituted BDT will be similar in shape to that of BDT but simply shifted in position relative to the  $E_F$  (see Figure 3A). Electron-withdrawing groups remove electron density from the  $\sigma$ -orbital of the benzene ring allowing the rings high energy  $\pi$ -system to stabilize. Because the HOMO has a largely  $\pi$ -character, its energy is therefore decreased, shifting it further away from  $E_F$ . Indeed the calculated values suggest that the HOMO level has moved further away from  $E_F$  by  $\sim 0.15$  eV in the case of BDT4F and  $\sim 0.3$  eV in case of BDT4Cl (See inset of Figure 3b and Table 1). Alternatively, the addition of electron-donating groups increases the  $\sigma$ -orbital electron density in the benzene ring, leading to an increase in the energy of the  $\pi$ -system and thereby shifting the HOMO closer to  $E_F$ . The estimated value for BDT2Me



**Figure 3.** Relation between the measured Seebeck coefficients of substituted BDT junctions to the position of  $E_F$ . (a) Theoretical prediction<sup>9</sup> of the transmission function of a Au–BDT–Au junction plotted as a function of the relative position of  $E_F$  of the Au electrodes with respect to the HOMO and LUMO levels. It is assumed that the transmission function has the same shape for the substituted molecules, but it is shifted with respect to  $E_F$ . (b) The predicted<sup>9</sup> Seebeck coefficient of the junctions as a function of the relative position of the  $E_F$  with respect to the HOMO and LUMO levels. The HOMO and LUMO are shifted relative to  $E_F$  such that  $S_{\text{junction}}$  crosses  $E_F$  at the measured value of  $S_{\text{junction}}$ . When the measured value of  $S_{\text{Au–BDT4Cl–Au}} = +4 \pm 0.6$  (green band),  $S_{\text{Au–BDT4F–Au}} = +5.4 \pm 0.4$  (blue band),  $S_{\text{Au–BDT–Au}} = +7.2 \pm 0.2$  (black band), and  $S_{\text{Au–BDT2Me–Au}} = +8.3 \pm 0.3$  (red band) are used in this figure, it is clear that the  $G_{\text{junction}} = \tau(E) * G_0$  is  $\sim 0.008 G_0$ ,  $0.009 G_0$ ,  $0.011 G_0$ , and  $0.012 G_0$  respectively.



suggests that the HOMO has moved closer to  $E_F$  by  $\sim 0.1$  eV. This picture is supported by calculations of the HOMO level using density functional theory (DFT) on the molecules with terminal gold atoms. The calculated values are listed in Table 1. This trend is also in agreement with the calculated values obtained for substituted benzenediamines.<sup>7</sup>

The value of  $\tau(E)$  at  $E_F$  allows us to estimate the conductance of these molecules through eq 4. Using the value from  $E_F$  obtained from our thermopower experiments, we predict  $\sim 0.011$  for BDT,  $\sim 0.009$  for BDT4F,  $\sim 0.008$  for BDT4Cl, and  $\sim 0.012 G_0$  for BDT2Me (see inset Figure 3A and Table 1). These calculations suggest that the addition of electron-withdrawing groups (F, Cl) reduces the conductance and the addition of electron-donating groups increases the conductance of the junction. This trend is in agreement with experimental results obtained for substituted benzenediamines by Venkataraman et. al.<sup>7</sup> where they found that electron-withdrawing groups decreased the conductance and electron-donating groups increased the conductance. As previously reported,<sup>16</sup> it is very difficult to obtain direct conduction measurements on BDT and other such substituted thiols, and so no experimental results on conductance could be independently obtained for these molecules. One possible reason for this could be that while thermopower is expected to be insensitive to the value of  $\Gamma$ , the conductance depends strongly on it. Thus, conductance would vary widely in such junctions upon small changes in  $\Gamma$ .

While the substituents in BDT move the relative position of HOMO and LUMO with respect to  $E_F$  in the range 0.1–0.3 eV such that  $S_{\text{junction}}$  ranges from 4 to 8  $\mu\text{V/K}$ , changing the end groups on the benzene ring from thiol to cyanide induces a large change in  $S_{\text{junction}}$ . We observe that the histograms of  $\Delta V$  versus  $\Delta T$  are distorted (see Figure 2e,j) especially at higher  $\Delta T$ , which suggests that the bond between the N and Au in BDCN is not as strong as the bond between S and Au in BDT and its derivatives. One reason for this could be that the CN–Au bond is expected to have a more ionic character than the S–Au bond, which is believed to be more covalent. We also observe a change in the sign of the thermopower from positive to negative, which implies that electron transport in Au–BDCN–Au junction is primarily through the LUMO. This is supported by prior calculations of the transmission function for BDCN with Au contacts.<sup>8</sup> Thus, endgroups are key to controlling electron transport, but substituents can be used to induce small changes in the metal-molecule junction. By varying endgroups and substituents, one can engineer metal-molecule heterostructures with targeted properties.

Junction Seebeck coefficient measurements can not only provide insight about the electronic structure of the molecular heterojunction, but the results also have bearing on an as yet unexplored field of thermoelectric energy conversion based on molecules. Our measurements show that we can tune the thermoelectric properties of such junctions in a controllable way by the addition of substituents. This data in conjunction with a calculated transmission function imply a simultaneous increase in the thermopower and conductance in a methyl-substituted benzene, which has hitherto been

impossible to attain in simple bulk thermoelectric materials.<sup>17</sup> While we observe an increase of  $\sim 50\%$  in the power factor, defined as  $S^2\sigma$ , of the junction upon substitution of benzene dithiol with electron-donating groups, the value is still quite low in comparison to other material systems.<sup>18,19</sup> Further simultaneous improvement of  $S_{\text{junction}}$  and  $G_{\text{junction}}$  may be achieved by the use of molecules with narrowed transmission peaks (increased  $d\tau(E)/dE$ ) and HOMO or LUMO levels that are more precisely aligned with  $E_F$ . Such molecules would more aptly represent single energy level transport, which has been analytically proven to afford the best thermoelectric efficiency.<sup>18,19</sup> One promising direction for future work would be investigating contact materials other than Au that already exhibit good thermoelectric properties. Hence, a ground up approach to building thermoelectric materials from an endless array of possible organic–inorganic heterostructures evokes hope for efficient thermoelectric energy conversion.

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**Supporting Information Available:** Experimental details and additional details of analysis method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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