Measuring Relative Barrier Heights in Molecular Electronic Junctions with Transition Voltage Spectroscopy

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ABSTRACT Though molecular devices exhibiting potentially useful electrical behavior have been demonstrated, a deep understanding of the factors that influence charge transport in molecular electronic junctions has yet to be fully realized. Recent work has shown that a mechanistic transition occurs from direct tunneling to field emission in molecular electronic devices. The magnitude of the voltage required to enact this transition is molecule-specific, and thus measurement of the transition voltage constitutes a form of spectroscopy. Here we determine that the transition voltage for a series of alkanethiol molecules is invariant with molecular length, while the transition voltage of a conjugated molecule depends directly on the manner in which the conjugation pathway has been extended. Finally, by examining the transition voltage as a function of contact metal, we show that this technique can be used to determine the dominant charge carrier for a given molecular junction.

KEYWORDS: molecular electronics · charge transport · tunneling · transition voltage spectroscopy

The field of molecular electronics is driven by the perceived opportunity to use molecules as active elements in electronic circuits. Instances of two-state switching[1–4] and Coulomb blockading[5–7] have been demonstrated in a small number of molecule-based devices, but realization of a practical device technology will require a detailed understanding of the transport mechanisms. We have recently demonstrated that the charge transport mechanism in electronic junctions of a series of π-conjugated molecules undergoes a transition from direct tunneling (rectangular barrier) to field emission (triangular barrier) upon increasing the applied bias. The voltage at which this transition occurs (V_{trans}) is linearly correlated with the energy offset between the metal Fermi level and the highest occupied molecular orbital (HOMO),[8] a feature that allows us to probe the effective energy barrier to charge transport by measuring V_{trans} for a series of structurally distinct molecular junctions. We refer to this barrier height measurement as transition voltage spectroscopy, or TVS.

One of the most salient attributes of TVS is that V_{trans} is a measurable quantity and therefore does not require any assumptions or fit parameters for its determination. Other advantages of TVS include the following: (1) TVS is simple to implement and requires only basic mathematical transformation of the acquired data; (2) TVS is sensitive to the metal-molecule contact chemistry at each interface, and therefore inherently reflects the contact resistance; (3) the measured V_{trans} is independent of contact area, which eliminates problems associated with comparing current densities between different device architectures.[9] Though V_{trans} is a single experimental observable, its value is sensitive to the molecular topology, metal−molecule linking group, and electrode composition, as will be demonstrated within.

Understanding of TVS is facilitated by a simple barrier picture for charge tunneling in a junction, Figure 1b. While this barrier description is known to be deficient in capturing quantitative aspects of tunneling through molecules, it allows us to understand in a straightforward manner the cause of the transition in transport mechanism that we observe in molecular junctions; more sophisticated approaches based on the Landauer formalism do not readily lend themselves to prediction of a switch in mechanism. Therefore, we model the electronic structure of our metal−molecule−metal junctions as a rectangular tunneling barrier with a height (ϕ) set by the energy offset between the metal Fermi level and the closest molecular orbital, and a width (d) determined by the length of the molecule incorporated into the junction, as shown in Figure 1b. In molecular junctions incorporating thiols, a variety of spectroscopic[10,11] and electrical[12–14]

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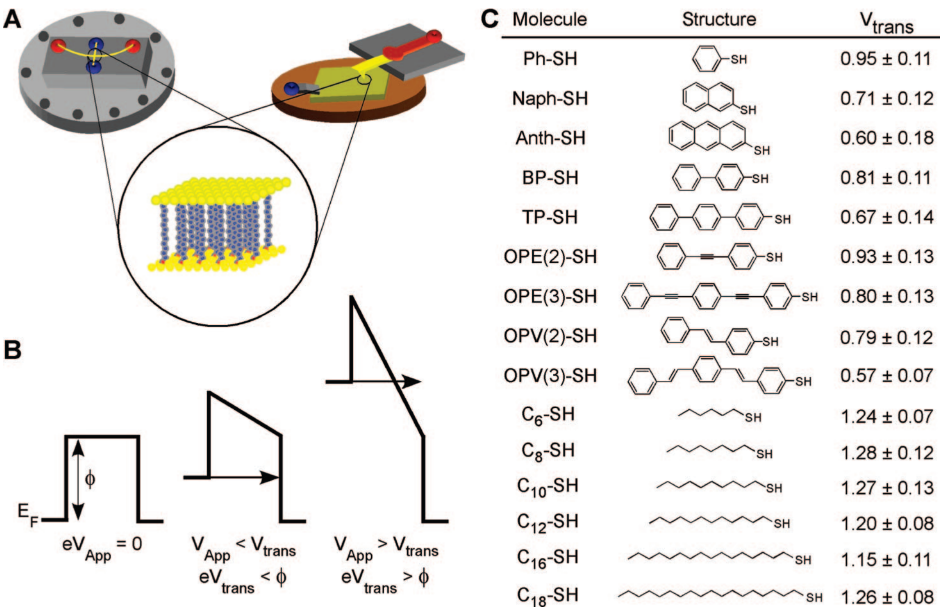

Molecule	Structure	V_{trans}
Ph-SH		0.95 ± 0.11
Naph-SH		0.71 ± 0.12
Anth-SH		0.60 ± 0.18
BP-SH		0.81 ± 0.11
TP-SH		0.67 ± 0.14
OPE(2)-SH		0.93 ± 0.13
OPE(3)-SH		0.80 ± 0.13
OPV(2)-SH		0.79 ± 0.12
OPV(3)-SH		0.57 ± 0.07
C_6-SH		1.24 ± 0.07
C_8-SH		1.28 ± 0.12
C_{10}-SH		1.27 ± 0.13
C_{12}-SH		1.20 ± 0.08
C_{16}-SH		1.15 ± 0.11
C_{18}-SH		1.26 ± 0.08

Figure 1. (a) Schematic representation of crossed-wire and CP-AFM junctions. Both techniques measure an ensemble of molecules that are chemically bound to the bottom electrode and physically contacted by the top electrode (magnified region). (b) (left) At an applied bias smaller than V_{trans}, the tunneling barrier height ϕ is set by the Fermi level-molecular orbital energy offset, and the barrier width *d* corresponds to the length of the molecule in the junction. (center) For biases less than the barrier height, the shape of the barrier is trapezoidal. (right) At an applied bias greater than V_{trans}, the barrier shape becomes triangular, and the transport mechanism changes to field emission. Note that our cartoons are drawn for the case of electron transport mediated by an unoccupied orbital; hole transport mediated by an occupied orbital is equivalent. (c) Our adopted nomenclature and the chemical structure of each of the molecules used in this study, along with their corresponding V_{trans} values. Standard deviations are determined by using the 10 measured values of V_{trans} for each junction type. The overall average standard deviation is 0.11 V.

measurements predict that the occupied molecular orbitals lie closer in energy to the metal Fermi level than to the unoccupied molecular orbitals. Although the energy diagram (Figure 1b) is drawn for electron transport mediated by an unoccupied orbital, the following argument also applies for hole transport mediated by an occupied state.

When a bias is applied to the junction, the overall voltage drop across the junction is equal to the magnitude of the applied bias. The details of the electrostatic potential profile across the junction are unknown, and voltage drop can occur at both metal–molecule contacts as well as across the molecular bridge.[15,16] If the voltage is dropped only at the contacts (the weak coupling limit often achieved in scanning tunneling microscope experiments), then the barrier remains rectangular, and the electrode Fermi level can be swept through the molecular orbitals, resulting in resonant tunneling.[17,18] If, however, a significant fraction of the bias is dropped across the molecular bridge, then the barrier *shape* will change from rectangular to trapezoidal. At a threshold voltage defined by the barrier height and the distribution of voltage drops, the barrier becomes triangular (Figure 1b), and the functional dependence of current on applied voltage changes due to a change in transport mechanism. We refer to the voltage required to enact this transition as V_{trans}, which can be directly determined from a plot of ln (I/V^2) against $1/V$.[8]

As already noted, for the sake of simplicity we are referring to the potential barrier as a simple geometric shape (rectangular, trapezoidal, triangular). The true barrier of course is much more complex and is determined by the electronic structure of the molecule. Although these barriers are oversimplifications, this approximation does not affect our results because the true barrier shape is not important for TVS analysis. Rather, the important feature is the prediction of a transition from direct tunneling through a barrier (trapezoidal type) to field emission through the top of the barrier (triangular type). In more complex treatments, the true barrier shape is required as an input parameter to a series of equations that fully describe the electronic state of the junction. One of our key findings is that the simple barrier model qualitatively explains the change in the functional form of the current–voltage behavior.

RESULTS AND DISCUSSION

We employ two distinct but complementary test structures to measure the current–voltage properties of molecules: conducting probe atomic force microscopy (CP-AFM)[19,20] and crossed-wire tunnel junctions[21,22] (Figure 1a). Each technique features a soft, physically placed top electrical contact, which avoids potential damage from evaporated metal sources.[23,24] In both test structures, a self-assembled monolayer of a molecule of interest is formed on the bottom (Au) contact. The top (Au) electrode is then brought into physical contact with the molecular layer. Voltage is swept at the top contact, the bottom electrode is held at ground, and the current through the junction is measured.

To begin, we will look at two series of molecules which have been carefully chosen such that the contact chemistry remains constant throughout a given molecular series. For all molecules in these two series, the bottom contact is Au–S, and the top contact is Au/phenyl for the π-conjugated molecules and Au/methyl for the alkanes. Measurement of V_{trans} in a Au/C_8–SH/Au junction is illustrated in Figure 2. To generate Figure 2, the average of 20 current–voltage traces (as shown in Figure 2, inset) is transformed to axes of

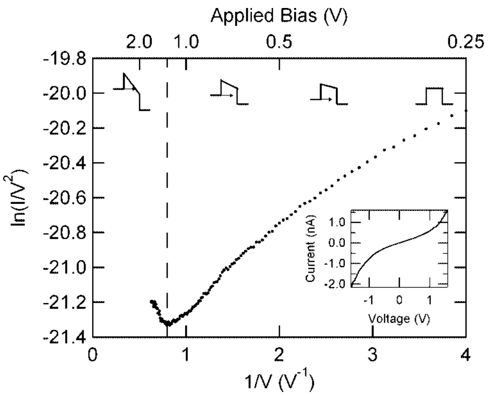

Figure 2. Solid circles represent the average of 20 *I*−*V* curves for a Au/C$_8$−SH/Au junction measured by CP-AFM. The dashed line corresponds to the voltage required to change the functional dependence of current on applied voltage (V_{trans}). Also shown are representations of the barrier shape at various values of applied bias. The inset shows current−voltage data on standard axes. Note that only a small portion of the field emission regime can be sampled in molecular junctions contacted directly by electrodes on both sides because field-dependent breakdown of the junction occurs at biases ranging from ∼1.5−2.0 V, depending on the length of a given molecule.

ln (I/V^2) against $1/V$. To arrive at a composite V_{trans} for each molecule, 10 separate metal−molecule−metal junctions are formed, generating 10 spectra of the type found in Figure 2. The average value of the inflection point voltage across these junction formations is then used as V_{trans} for a given molecule. The results across each molecular series are summarized numerically in Figure 1c and graphically in Figure 3 (alkanethiols) and Figures 4 and 5 (π-conjugated thiols). The alkanethiols constitute an important control series in molecular electronic experiments, because their HOMO−LUMO gap remains effectively constant as the number of methylene repeat units is increased, and it has been unambiguously determined that nonresonant tunneling is the transport mechanism for small applied biases.[12]

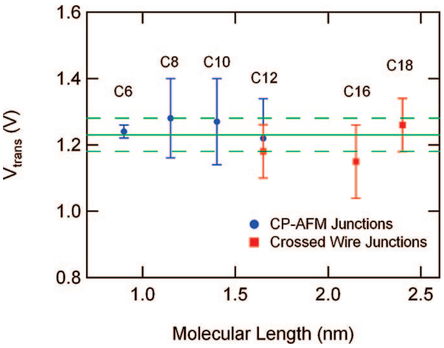

Figure 3. V_{trans} as a function of molecular length for a series of alkanethiols. Shorter molecules were measured using CP-AFM (blue circles) because the small contact areas enabled measurement of current at higher bias than was attainable in the crossed-wire geometry (red squares). The solid line represents the mean alkanethiol barrier height, and the dashed lines show the standard deviation across the seven individual measurements. The numbers above each data point display the number of carbon atoms in each molecule.

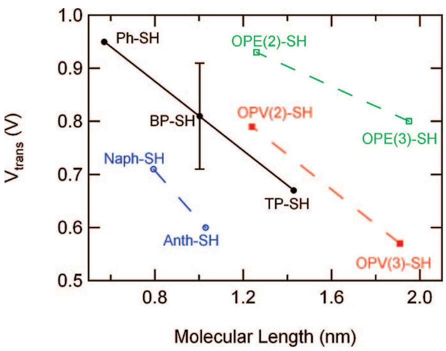

Figure 4. V_{trans} as a function of molecular length for four different pathways for extending conjugation. Dashed lines connecting molecules within the OPE series (open green squares), OPV series (filled red squares), and acene series (open blue circles) have been added to guide the eye. The solid black line is a linear fit to the three points in the phenylene series (filled black circles). The standard deviation in V_{trans} for each molecule is given in Figure 1, for clarity only the uncertainty in the BP-SH measurement is shown here.

Similarly, ultraviolet photoelectron spectroscopy measurements have shown that the $E_F - E_{HOMO}$ offset for alkanethiols is nearly independent of molecular length.[25,26] Therefore, we expect that V_{trans} would also be constant across the alkanethiol series. The average value of V_{trans}, represented by the solid green line in Figure 3, falls within the standard deviation of measured values for each of the molecules, thereby illustrating that V_{trans} is indeed independent of molecular length in alkanethiols. Another important feature of Figure 3 is the excellent agreement between V_{trans} as determined by CP-AFM and V_{trans} obtained from the crossed-wire geometry. We have previously observed similar cross-platform agreement for acenes (Naph-SH, Anth-SH) and phenylenes (BP-SH, TP-SH).[8] Here, one junction, Au/C$_{12}$−SH/Au, was chosen for measurement in both test structures. As shown in Figure 3, the measured values of V_{trans} agree within 5%, demonstrating the independence of V_{trans} on junction area. We note that one must be careful when performing this type of analysis in junctions with evaporated metal contacts, as the metal evaporation step likely perturbs the physical structure of the molecules[23] and therefore the electronic structure of the resulting junction.[24]

In contrast to the alkane series, the HOMO−LUMO gap of π-conjugated molecules is known to decrease with an increase in conjugation length.[27] We would therefore expect longer conjugated molecules to exhibit a smaller value of V_{trans} than shorter conjugated molecules. However, as shown in Figure 4, V_{trans} does not decrease monotonically with molecular length for all aromatic thiols. Rather, V_{trans} is observed to decrease with molecular length within a given molecular series (*i.e.*, $V_{trans,OPV(2)\text{-}SH} < V_{trans,OPV(3)\text{-}SH}$). The molecules explored here represent four distinct ways of extending conjugation within a molecular series. The solid black line in Figure 4 is a linear least-squares fit to the molecules in the phenylene series. The second (BP-SH) and

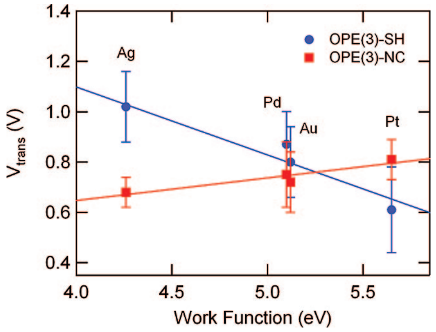

Figure 5. V_{trans} as a function of work function for thiol and isocyanide OPE(3) molecules on Ag, Pd, Au, and Pt electrodes. V_{trans} decreases (increases) as the work function increases for thiol (isocyanide)-coupled molecules, suggesting that hole (electron) transport is dominant. Values of the work function for the metal electrodes used are from ref 34.

third (TP-SH) molecules in this series have a structural repeat unit that is strikingly similar to benzenethiol, and therefore it is unsurprising that V_{trans} exhibits a monotonic dependence on length for this series. All other aromatic families have a repeat structure that does not neatly reduce to benzenethiol. The OPV and OPE series have repeat structures that are longer than benzenethiol, while the molecules in the acene series (Naph-SH, Anth-SH) have a repeat unit that is smaller than benzenethiol by two carbon atoms, and therefore extrapolation of V_{trans} for these molecular families down to a single repeat unit results in a barrier that is larger and smaller respectively than that measured for benzenethiol. The scaling of V_{trans} with molecular conjugation is demonstrated in Figure S1 where V_{trans} is plotted *versus* the calculated HOMO−LUMO gap. This scaling is supported by prior experimental examinations of the efficiency of charge transport through aromatic bridges.[21,28−30]

The measured transition voltage for a molecular junction is also sensitive to the nature of the metal−molecule linkage. For example, the value of V_{trans} is bias polarity-dependent in molecular junctions incorporating asymmetric metal−molecule contacts such as afforded by monothiols, but is polarity-independent in symmetric junctions incorporating dithiols.[8] This behavior illustrates that V_{trans} simultaneously probes both the barrier height and the voltage drop or spectral overlap at each metal−molecule contact. While a number of studies have examined how contact asymmetry can lead to charge transport rectification[22,31] or how the chemistry of the metal−molecule contact can affect the contact resistance,[14,32] TVS can provide added insight into these investigations. By measuring the transition voltage for OPE(3) moieties attached through thiolate and isocyanide linkages on four different metal electrodes (Ag, Pd, Au, and Pt), we are able to explore how the metal−molecule contact influences the so-called "band lineup" problem.[33] Band lineup refers to the position of the metal electrodes Fermi level with respect to the occupied and unoccupied molecular orbitals. In its simplest form if the Fermi level is energetically closer to an unoccupied orbital, electron tunneling would be the dominate conduction channel. Conversely for a band lineup in which occupied orbitals are closer to the Fermi level hole conduction is expected.

Figure 5 plots V_{trans} *versus* electrode work function[34] for the systems measured. Focusing first on the OPE(3)-SH system, we see that V_{trans} decreases as the electrode work function increases. As the work function of a metal increases, the energy difference between the Fermi level and the HOMO decreases, and therefore the observed correlation suggests that charge transport in these aromatic thiol systems is modulated by charge carriers interacting with an occupied molecular level (hole tunneling). Hole conduction for aromatic thiols has been previously suggested by a number of experimental and theoretical studies,[32] and recently confirmed by thermoelectric measurements.[35] What is more interesting is the dependence of V_{trans} for isocyanide-coupled OPE(3) across the metal series. The fact that V_{trans} for OPE(3)-NC monolayer junctions increases as the electrode work function increases clearly suggests that LUMO-mediated tunneling is the dominant channel in these systems. The reason for the difference in the absolute value of the slopes of the thiol and isocyanide data is not immediately apparent, but likely occurs due to the manner in which each functional group influences the energy level alignment when adsorbed to a metal. In general, the alignment caused by a molecular adsorbate on a metal surface will lie somewhere between the Schottky−Mott limit (vacuum level alignment) and Fermi-level pinning, depending on the contact chemistry between metal and molecule.[36] At the Schottky−Mott limit the offset between the molecular orbitals and the Fermi level will shift rigidly with the metal work function, while Fermi-level pinning would produce a constant offset regardless of metal work function. Since for both the thiol and isocyanide linkages the change in V_{trans} is smaller than the change in work function it is clear that some extent of charge transfer occurs forming a dipole at the interface and thus causing a deviation from the Schottky−Mott limit. The fact that the magnitude of the slopes is different—V_{trans} of the thiol junctions is more strongly coupled to the metal work function than the isocyanide junctions—suggests that there is a difference in how this interface dipole changes with metal type for the two linkages.[37,38]

The idea that different charge carriers (holes for thiols and electrons for isocyanides) are dominant is also supported by photoemission measurements of the orbital alignment in aromatic thiol and isocyanide systems.[32,37] On the basis of these measurements, one should choose either the Pt−S or Ag−CN to minimize the barrier to charge transport for holes or electrons, respectively, in a molecular device. This is in some conflict with theoretical calculations that suggest that the Pd−S and Pd−CN should be the best linkage pairs.[39] The fact that an experimentally simple test method can provide us with information on the charge carrier in molecular electronic junctions and determine which contact chemistry provides the lowest barrier to charge transport highlights the utility and power of transition voltage spectroscopy.

SUMMARY

We have demonstrated that the measurement of V_{trans} for a molecular junction—a technique we term transition voltage spectroscopy—can be used as a direct probe of charge transport in molecular systems, even in the absence of more traditional spectroscopic measurements. Further, because the magnitude of V_{trans} does not depend on junction area, information about the charge transport properties, namely, the effective barrier height, of a molecule can be garnered without specific knowledge of the number of molecules in the junction. The most direct application of transition voltage spectroscopy is to measure the effective barrier to charge transport across a molecular junction. We have shown that the effective barrier height is constant across the alkane series and decreases with the extent of electron delocalization across π-conjugated molecules. We have also demonstrated how transition voltage spectroscopy can be used to investigate metal–molecule contacts, and in the specific case of OPE(3)-SH *versus* OPE(3)-NC, provide information on the dominant charge carrier. In future work, our goal is to develop a more complete theoretical framework for transition voltage spectroscopy so that this formalism can find wider use in understanding charge transport in molecular electronic systems.

MATERIALS AND METHODS

Monolayer Deposition and Characterization. The method of assembly and monolayer characterization for the molecules examined in this paper have been previously described.[22,32,40,41] Briefly, the self-assembled monolayers were prepared on commercially available 10-μm diameter wires. Prior to monolayer deposition, the wires were cleaned in 30% H_2O_2 for at least 10 min to remove any adsorbates; ~1 mM solutions of each of the molecules were prepared in an Ar glovebox from suitable solvents (ethanol for the alkanes and CH_2Cl_2/EtOAc for the aromatic molecules). Monolayers were allowed to assemble overnight, and the resulting monolayer-coated wires were rinsed by placing them in a vial of ethanol (for alkanes) or CH_2Cl_2 (for aromatics) to remove any physisorbed molecules.

Current−Voltage Measurements. For each molecule used in this study, a total of 200 $I-V$ traces were collected using either the crossed-wire or the CP-AFM junction geometry. In both cases, a voltage is swept at the top (bare) electrode, the bottom (monolayer-containing) electrode is held at ground, and the current through the junction is measured. For each molecule, the top electrode was brought into contact with the molecular monolayer, 20 $I-V$ traces were collected, and the top contact was removed from the monolayer surface. The inherent noise in the current−voltage data can make it somewhat difficult to determine V_{trans} for an individual current−voltage trace. Twenty $I-V$ traces per junction formation were averaged together to provide a more robust value of V_{trans} that was less influenced by current fluctuations. This process was repeated 10 times for each molecule, thereby providing a statistical sampling across various spatial regions of the monolayer.

Transition Voltage Determination. Each 20-trace data set was geometrically averaged, and transformed onto axes of ln (I/V^2) against $1/V$. The position of the transition voltage was determined manually for each data set. The mean value of the 10 data sets was then reported as V_{trans} for that molecule. This process was then repeated for each of the 15 molecules used in this study. The standard deviation in V_{trans} measured across 10 data sets is approximately 0.1 V. Two types of data were rejected during V_{trans} analysis. One exclusion criterion was any junction that resulted in a short circuit. Because the top electrode is placed into soft contact with the monolayer, only a very small number of junctions (<5%) exhibited this condition. A second rejection criterion was for cases where we were unable to unambiguously determine V_{trans}. Ambiguity in V_{trans} occurs for junctions with a higher level of noise in the $I-V$ data, which causes the appearance of multiple possible V_{trans} values. Rather than arbitrarily choosing between these values, we simply made an extra set of measurements in cases where this problem occurred. With the exception of these exclusion criteria, no data selection was performed.

Transition Voltage as a Function of Metal Electrode. For the investigation of metal−molecule contact effects, monolayers of OPE(3)-SH and OPE(3)-NC were deposited on 10 μm diameter wires of the different metals. The crossed-wire apparatus was then used with a Au top electrode to measure the I−V characteristics and transition voltage as described above. Because H_2O_2 oxidizes the Ag wires (and potentially the Pt wires), a change in preparation technique was required for this set of experiments. Wires were first affixed to a stainless steel block inside an Ar plasma chamber that was located inside an Ar glovebox. Wires were cleaned *via* exposure to a 25-W Ar plasma for 10 min. After plasma cleaning, wires were placed into molecule-containing solutions inside the glovebox, and thus the wires were never exposed to ambient conditions after plasma exposure. For consistency, wires of all metal types involved in this series of experiments were cleaned using the Ar plasma method.

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Supporting Information Available: Plot of V_{trans} *versus* calculated HOMO−LUMO gap for the aromatic molecules studied and complete current−voltage data set for the OPE(3)-SH molecular junction including the method for determining V_{trans} and its related uncertainty. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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