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pi-conjugated molecules and their electrical properties

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DOI:
[10.33612/diss.172231449](https://doi.org/10.33612/diss.172231449)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Liu, Y. (2021). *pi-conjugated molecules and their electrical properties*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.172231449>

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π -conjugated Molecules and Their Electrical Properties

Yuru Liu

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This project was carried out in the research group Chemistry of (Bio) Molecular Materials and Devices which is part of Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, The Netherlands.

This work was funded by Chinese Scholarship Council, CSC NO.201707040075

Printed by:
Front & Back:

GVO drukkers & vormgevers B.V.

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π -conjugated Molecules and Their Electrical Properties

PhD Thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

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To my dear family
致我亲爱的家人

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1

INTRODUCTION

The part of the contents in this chapter was part of our recent review paper: Charge-transport Through Molecular Ensembles: Recent Progress in Molecular Electronics, accepted by the Chemical Physics Review, AIP Publishing.

1.1. THE FIELD OF MOLECULAR ELECTRONICS

Molecular electronics (ME) describes the field of research in which single molecules or ensembles of molecules are utilized as functional elements in electronic circuits. In 1971, Kuhn and Mann successfully measured conductance through monolayers of cadmium salts of fatty acids.[1] Although not the first to measure the conductance of molecular ensembles,[2] they observed a temperature-independent, exponential decrease of conductivity with increasing thickness of the monolayers, which they ascribed to incoherent tunneling through the organic monolayers. But the modern concept of ME was introduced in 1974 when Aviram and Ratner published a theoretical paper describing tunneling charge transport through a molecule comprising donor and acceptor moieties that, when connected to two electrodes, acted as a molecular rectifier.[3] Their work provided an *ad hoc* approach to predict the charge transport through molecules, which set the stage for subsequent studies that led to modern approaches such as those combining density functional theory (DFT) with the non-equilibrium Green's function (NEGF).[4–6] In those early years, the primary experimental hurdle was the attachment of electrodes to individual molecules; while Kuhn and Mann had used Hg to contact Langmuir-Blodgett films, it was the invention and development of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) in the 1980s that laid the foundation for modern research on molecular ensemble junctions (MEJs) by allowing the interrogation of individual molecules on surfaces. Nuzzo and Allara contemporaneously demonstrated the robust self-assembly of thiols on Au,[7] which enabled simple σ -bonded (*e.g.*, alkanes) and π -bonded molecules (*e.g.*, phenylenes) bearing thiols to be trapped, as single-molecules between two electrodes[8] or contacted by a conductive tip in densely-packed monolayers, allowing the measurement of (tunneling) currents under applied bias.[9–12] These pioneering studies advanced the methodology for determining the electrical conductivity of different molecules and provided insights into their charge transport properties in experimental platforms that were readily reproducible in different laboratories. These early experiments drove the broad interest from cross-disciplinary physical scientists that has led to the acceleration of fruitful discoveries in recent decades.

1.2. MECHANISMS OF CHARGE TRANSPORT

The mechanisms of charge transport through ensembles or single-molecule junctions can be broadly divided into two phenomenological extremes: tunneling and hopping. The major differentiator is whether the charge transport process is thermally activated. Charge transport through a molecular junction can be described as the propagation of an electron wave between electrodes that is modulated by a molecule/molecular layer between them. When

the energy and phase of the charge carrier are maintained during the process, the mechanism is considered to be tunneling. At the other extreme is hopping, in which the charge relaxes inside the junction, requiring thermal activation for traversal. In general, tunneling preponderates across shorter distances (*i.e.*, molecules) and hopping across longer distances.[13, 14] Between these extremes lie hybrid tunneling-hopping processes, *e.g.*, SAMs comprising of ferrocene/pyridine/fullerene-terminated alkanethiols, which rectify current due to different mechanisms at forward and at reverse bias.[15–17] These systems are better described as more or less Landauer-like and Marcus-like, as activationless, incoherent processes become possible that are not well described by the tunneling/hopping dichotomy.[18–20]

The most commonly used theoretical model to describe temperature-independent tunneling is the simplified Simmons model,[21–23] which considers the junction formed by the molecule as an approximately trapezoidal potential barrier and is mathematically described by Equation 1.1 where J is the current density; V is the applied bias; d is the zero-bias width of the barrier, which is nominally determined by molecular-length; β is the tunneling decay coefficient and scales with the square root of the difference between the Fermi level E_f and the frontier orbitals of the molecule(s); and J_0 is the theoretical value of J when $d = 0$. This model captures the length-dependence of J in relatively simple systems such as SAMs of alkanethiols,[24–26] but its most important feature is that the values of β are highly reproducible across laboratories and experimental platforms. While the Simmons model is too simple to provide much meaningful physical insight, β and (to a lesser extent) J_0 are invaluable benchmarks for validating experimental platforms and controlling for their specific effects.[27, 28] Simmons presupposes tunneling; for thermally activated charge transport, the relationship between current density and temperature is expressed as in Equation 1.2, where E_a is the activation energy of the hopping step. In practice, β is much more commonly reported because it is easy to obtain from any platform in which at least three molecules of different lengths can be measured and it does not require variable-temperature measurements.

$$J(V) = J_0(V)e^{-\beta d} \quad (1.1)$$

$$J(V) = J_0(V)e^{-E_a/KT} \quad (1.2)$$

1.3. CHARACTERISTICS OF MOLECULAR ENSEMBLE JUNCTIONS

There are many phenomena that are specific to MEJs (as compared to SMJs), for example, intermolecular effects[29–31] and the impositions of molecular self-assembly.[32] Molecular

ensemble junctions are also very sensitive to the topography of the metal substrate (*i.e.*, the bottom electrode) and defects in molecular monolayers can not be avoided due to the ubiquity of grain-boundaries, step edges, and impurities in the substrate.[33] Weiss *et al.* fabricated junctions comprising SAMs of alkanethiolates on rough and smooth substrates using a hanging Hg-drop top electrode, observing that thin-area defects and thick-area defects cause the overall conductance to be higher and lower, respectively, than non-defect junctions, readily revealing defects by direct comparisons to benchmark MEJs.[25] These defects are defined by a change in d (from Equation 1.1) caused by substrate topography and/or the morphology of the SAM vis-à-vis deviations from ideal packing. Jiang *et al.* further observed that these defects can scale with the junction area, which can cause Joule heating in the junctions that affect J_0 rather than J .[34] Thus, J/V curves alone cannot necessarily reveal defects present in a MEJ because changes to J_0 caused by defects that are systematic or endemic to a particular experimental platform affect the accuracy of J by shifting the J/V curves uniformly. (Accuracy characterizes the distance between a measurement and its true value.) Ordered molecular ensembles like SAMs also exhibit collective effects that are independent of the substrate and that cannot be observed in SMJs, for example, odd-even effects driven by the conformation of close-packed alkyl chains[26, 35–38], the collective action of molecular dipoles affecting transport by shifting vacuum levels[39–43] and quantum interference effects correlated to molecular conformations imposed by self-assembled monolayers.[44] Although many intermolecular effects are system-specific, Dubi *et al.* showed that incorporating in-plane dephasing into transport calculations helps to address several universal transport features of ensemble junctions, such as the exponential decay of current with molecular length, the odd-even effect, and negative differential resistance.[45] Thus, some of the phenomena that are specific to MEJs are the result of practical constraints, not physical differences.

1.4. DATA-COLLECTION AND ANALYSIS

Molecular ensemble junctions are typically measured with one electrode grounded while current is recorded as a function of applied bias to produce a J/V trace. However, due to the aforementioned phenomena, J/V traces acquired from different areas on a substrate or across multiple substrates can vary by several orders of magnitude. Treating this variance correctly is integral to extracting physical insight from J/V data and reducing it is vital to potential technological applications. Moreover, tunneling currents through SAMs are often in the pA regime at low bias and can increase by many orders of magnitude over bias windows of only 1 V to 2 V. Combined, these features of MEJs can lead to noisy data, which is obviously an impediment to both research and technological applications. In some cases,

Figure 1.1 Plots of typical data acquired from a molecular ensemble junction. a) 230 raw J/V traces (blue lines), mean values (black circles) and standard deviation (black error bars). b) The histogram of $\log |J|$ at $V = 1.0$ V (blue bars) and Gaussian fit (pink line) of the raw J/V data. The dashed box in a indicates the data plotted in the histogram in b. The black circle and error bar in b approximate how the data in a are plotted from the Gaussian fit. The data marked “short” were acquired from the junction that failed, *i.e.*, an electrical short.

additional noise is intrinsic to the type of measurement,[27] because of poor experimental design or inadequate control of experimental variables. Without rigorous standards for measurement, incorrect conclusions can be drawn from, for example, improper data selection or winnowing from large numbers of failed junctions without appropriate and rigorous statistical methodology. For example, using the liquid metal eutectic Ga-In (EGaIn), the experience of the operators demonstrably impacted the precision—in practical terms, the size of the error bars—of the measurements;[26, 46] a less experienced operator is more likely to encounter a lower yield of non-shortng junctions and broader spreads in J across junctions and substrates. While the accuracy of J is not user-dependent, subtle effects can be masked by low precision. Of greater concern, defects in the substrate and the environment under which a junction is measured can have pronounced effects,[47] even concealing/revealing length-dependence entirely.[48]

Using SAM-based junctions with EGaIn electrodes as an example, data are typically collected across multiple substrates. For each substrate, at least $n \approx 10$ cycles are measured from $0 \text{ V} \rightarrow V_{\text{max}}(+)\rightarrow V_{\text{max}}(-)\rightarrow 0 \text{ V}$ such that at least $2n$ trace/re-traces are measured for each of $N \approx 10$ junctions. (Here a junction is equivalent to a single contact formed between a tip and a substrate.) Junctions that do not short over all the n cycles are considered non-shortng for computing yields. Averaged J/V curves are constructed from Gaussian fits to the log-normal distributions of J for each value of V as depicted in Figure 1.1. This method of data collection assumes that the variance in J is the result of randomly distributed defects that exponentially affect J by locally varying d from Equation 1.1. That is why it is important that the N junctions be measured at different areas of each of several substrates that are preferably prepared on different days, using different monolayer-forming solutions,

etc. The details can vary across or within laboratories but are necessarily standardized in order to produce meaningful statistics and are reliable as long as the data within a particular study were collected and analyzed using the same procedure. Simeone *et al.* observed that data collected with a non-standardized protocol—forming an arbitrary number of junctions, running arbitrary numbers of scans—can decrease precision by increasing the variance in J .^[28] They proposed a “1/3/20” protocol for collection of data: for each freshly-formed EGaIn electrode,^[49, 50] they formed three junctions in three different places on a Ag substrate supporting a SAM; for each junction, they recorded 20 $J - V$ traces/retraces. They claim that this 1/3/20 protocol can avoid the effects of adventitious impurities on the EGaIn electrode. And collecting the same number of J/V curves per EGaIn electrode ensures each freshly-prepared electrode has the same statistical weight. The 20 scans are necessary so that one does not statistically overweight instabilities of the current that can occur in the first few scans, as the electrode conforms to the topography of the SAM.^[51] Although the specifics vary with the experimental platform, for example, a Au-coated AFM tip does not oxidize in air, the statistical methods are universally applicable for ensuring precise, accurate measurements.

The choice of statistical methods used, which analyzes the large, often noisy data sets produced by MEJs, directly impacts the interpretation of the data. Since the source of error is the defects (as defined above) that are distributed randomly, population statistics can be used to distinguish between distributions of J that differ by coincidence, but belong to the same parent population (*i.e.*, measurement artifacts) and those that differ because they are representative of different parent populations (*i.e.*, that are caused by physical differences between MEJs). Reus *et al.* examined different statistical methods, summarized in [Figure 1.2](#), that are applicable to such data, specifically those produced by measurements of SAMs with EGaIn electrodes.^[51] Methods 1-3 use the data to calculate single-compound statistics; method 1 fits Gaussian functions to histograms of $\log |J|$, method 2 uses the median and interquartile range, and method 3 uses arithmetic means and standard deviations. Methods 4a and 4b proceed directly to plotting and fitting the raw data to determine trend statistics; method 4a uses an algorithm that minimizes the sum of the absolute values of the errors between the data and a fit (a “least-absolute-errors” algorithm), while method 4b employs an algorithm that minimizes the sum of the squares of those errors (a “least-squares” algorithm). They compared the accuracy and precision of these methods for individual SAMs, comparisons between two or more SAMs, and for determining β and J_0 . They concluded that methods 1, 2, and 4a are all sufficiently accurate, while methods 3 and 4b are not. Method 1 assumes informative measurements of $\log |J|$, that [Equation 1.1](#) is a valid, that the data are distributed log-normal and that any deviations of $\log |J|$ from normality

Figure 1.2 a) Deviations of $\log |J|$ from normality and their effects on method 1-3 discussed in the text; b) Schematic of different statistical methods of analyzing charge transport discussed in the referenced paper. Adapted with permission from ref. 51. Copyright (2012) American Chemical Society.

are not informative, for example, the data marked “short” in Figure 1.1. Methods 2 and 4a assume that informative measurements of $\log |J|$ represent the bulk of the data and that non-informative data comprise extreme values. They favor method 1 over method 2, but both are probably accurate enough to use in reporting single-compound statistics. Method 4a is as accurate as method 2 and about an order of magnitude more precise. They recommend method 4a for calculating trend statistics, as long as the result does not conflict with method 1 and method 2. They do not recommend methods 3 and 4b, as those methods respond too strongly to non-informative, extreme values of $\log |J|$.

In practice, most MEJ data are reported using method 1 because it is straightforward and most MEJ data fit the criteria for its use. And, although method 1 mathematically excludes extreme values of J , it remains common practice to pre-select data because of the aesthetics of digital publishing vis-à-vis the graphical representation of data. A more statistically sound approach that accomplishes the same goal is to plot the error as the confidence interval (CI) instead of the standard deviation (SD) using Equation 1.3, where z is the inverse of the cumulative distribution function for the standard normal distribution—the t -test parameter—and is based on the confidence level (usually 95 % or 99 %) and N is the number of junctions (not J/V traces) measured.[51] Data are then plotted as the Gaussian mean value of the current-density $\langle J \rangle \pm \text{CI}$ instead of $\langle J \rangle \pm \text{SD}$. This method uses the Student’s t -test because the true standard deviation of the population is not known. The practical consequence of this methodology is that one cannot say that two values of $\langle J \rangle$ whose CI overlaps come from two different populations, which is not the case for SD. In

other words, the true value of $\langle J \rangle$ is likely to reside within the CI, so overlapping error bars computed from CI's imply that $\langle J \rangle$ can differ by coincidence rather than an underlying physical difference. It is also important to distinguish between values of $\langle J \rangle$ reported with SD, CI, and standard error (of the mean). When the goal is to describe the underlying statistical distribution, as is the case with method 1, the error should be reported as SD. When reported as CI, the error reflects an estimation of the range of $\langle J \rangle$ if the measurement were repeated in the future. Both reflect the precision of the measurement, which is the definition of error bars that is typically assumed in the MEJ literature. Standard error, however, reflects the accuracy of a measurement and is more common in SMJs where the assumption is that the mean conductance reflects the most probable configuration of the junction, which has only one, true value. Statistical methods are, unfortunately, not always reported with sufficient detail to ascertain which method is being used and how error is computed, which complicates meta-analyses.

$$\text{CI} = z \frac{\text{SD}}{\sqrt{N}} \quad (1.3)$$

Sporrer *et al.* reported the use of heat maps of raw data to expose information that is otherwise concealed by statistical treatments.[52] They intentionally prepared SAMs under experimental conditions that would affect their quality and collected data via users with different levels of expertise. The raw data, without pre-selection, were plotted in both 3D and 2D formats, shown in Figure 1.3. Although informative, 3D plots can be difficult to interpret, while a 2D heat map—a planar version of the 3D data—captures the skewness and outliers in a single figure. (Skewness is indicative of a shift in the mode and median values of a population relative to its mean.) The two dominant distributions, as in the bottom figure in Figure 1.3a, suggest a skewness, which the authors hypothesized as an indication of the origin of the adjacent major distribution, with the higher $\log |J|$ values from thin-area defects and the lower $\log |J|$ values from thick-area defects. They further validated this assumption by looking at the data obtained from junctions using soft/hard contact methods that are known to induce thick/thin area defects. These data indeed showed skewness towards low/high values of current densities commensurate with the type of defect. The same authors later reported that the analysis of experimental data sets with higher statistical moments (skewness and kurtosis) reveals the dynamic nature of the MEJ.[53] (Kurtosis describes the convergence towards the mean, the “peakedness”, of a population.) They investigated MEJs comprising SAMs of molecules with two dipole moments, an internal amide and varied terminal R groups in which intramolecular Keesom (dipole-dipole) interactions were revealed by analysis of skewness and kurtosis; molecules bearing more-polarizable

Figure 1.3 a) Discrete data from unhealthy measurement of tunneling junctions; histograms of J at different values of V in terms of counts (top) and the corresponding heat map plot (bottom). Adapted with permission from ref. 52. Copyright (2015) American Chemical Society. b) Schematics of a Gaussian fit to a histogram of J and a description of first and second statistical moments: Gaussian mean and standard deviation; the third and the fourth statistical moment (skewness and kurtosis). Adapted with permission from ref. 53. Copyright (2018) American Chemical Society.

moieties exhibited an applied field-induced negative skewness in $\log|J|$ with concomitant narrowing of the tails (larger Kurtotic value), while moieties bearing fixed dipole moments did not show these correlations.

While the aforementioned methods deal with primary J/V data, Vilan used normalized differential conductance (NDC) to explore the effects of applied bias on the detailed mechanism of tunneling.[54] The author showed the power of NDC plots in revealing subtle features that are associated with specific tunneling models. Mathematical modeling of the tunneling process will differ depending on the assumptions made in the analysis. Two well-known examples are the single-level model[55–58] and the (aforementioned) Simmons model.[21] These models have very different mathematical expressions, while they yield I/V (or J/V) traces that are graphically very similar.[59] However, they exhibit subtle, characteristics features that are difficult to observe on a linear scale that can be revealed in NDC plots. Additionally, NDC analysis can be used to extract quantitative information, such as scaling bias V_0 , which is sensitive to the choice of the tunneling model. The author further showed the practical utility of NDC by analyzing the experimental data from MEJs comprising SAMs of short alkanethiols on smooth and rough Ag substrates, though NDC analysis can be used for any MEJ and is valid for tunneling charge transport, in general.

The statistical techniques described above are valid for any experimental technique that

measures molecular ensembles. While some of the specific methods are specific to EGaIn (*e.g.*, how often a tip should be regenerated), measurements on ensembles will always lead to some variance. That variance can be very narrow—in fact, that is a prerequisite of technological applications. Under-sampling, due to low yields of junctions or high fabrication overhead, can adversely affect accuracy and precision, for example, increasing the latter (small spreads in data) and decreasing the former (large junction-to-junction or device-to-device variation). In all cases, the proper application of rigorous statistics is necessary to ensure that the true population is described by the data, which is vital for reproducibility, validating theoretical models and technological applications.

1.5. THESIS OUTLINE

This thesis aims to extend the understanding of the relationship between chemical structure of π -conjugated molecules and their electrical properties. Above we briefly discuss the mechanisms of charge transport, followed by a discussion of issues that are specific to MEJs. We also touch on the interpretation of data and the statistics used to analyze primary data with the aim of clarifying differences intrinsic to types of junctions.

In [chapter 2](#) we discuss the fabrication of molecular ensemble junctions using state-of-the-art methods to solve the unique challenge of applying a top contact. There are many methods for attaching electrodes to molecules, in this chapter, the focus is on techniques that install a top contact to self-assembled monolayers. We divide the methods of making a top contact into four parts: 1) solid metallic electrodes, *i.e.*, applying solid-metal electrodes directly to a molecular ensemble supported by a conductive substrate; 2) liquid metallic electrodes; 3) hybrid electrodes, *e.g.*, using a buffer layer between the molecular layer and the top contact; 4) non-metallic electrodes.

In [chapter 3](#) we describe the conductance of self-assembled monolayers and single-molecules comprising an oligophenyleneethynylene core, functionalized with acenes of increasing length that extend conjugation perpendicular to the path of tunneling electrons. In the Mechanically Controlled Break Junction (MCBJ) experiment, multiple conductance plateaus are identified. The high conductance plateau, which we attribute to the single molecule conformation, shows an increase of conductance as a function of acene length, in good agreement with theoretical predictions. The lower plateaus are attributed to multiple molecule bridging the junctions with intermolecular interactions playing a role. In junctions comprising a self-assembled monolayer with eutectic Ga-In (EGaIn) top-contacts, the pentacene derivative exhibits unusually low conductance, which we ascribe to the inability of these molecules to pack in a monolayer without introducing significant intermolecular contacts. This hypothesis is supported by the MCBJ data and theoretical calculations show-

ing suppressed conductance through the monolayers of pentacene derivative. These results highlight the role of intermolecular effects and junction geometries in the observed fluctuations of conductance values between single-molecule and ensemble junctions, and the importance of studying molecules in both platforms.

In [chapter 4](#) we continue the study of conductance of self-assembled monolayers and single molecules comprising π -conjugated oligophenyleneethynylene core but with central phenyl ring replaced by one or two thiophene/thiazole rings. We keep the length of the molecules and the anchoring groups the same while changing the central thiophene rings by introducing heteroatoms (electronegative N atom) step by step. In this design, we keep the width of the tunneling barrier and the interface of the SAM-electrode the same while varying the height of the tunneling barrier, hence we are able single out the role of the electron withdrawing group in the electrical properties of molecular junctions. The conductance of the designed molecular wires are indistinguishable both in ensemble junctions with EGaIn top contact and in single-molecule junctions. However, we observe the decrease of the frontier orbitals when introducing electron withdrawing groups to the molecular wire. We propose that modifying the molecular wire with much stronger electron withdrawing groups would exhibit larger changes of the conductance of a molecular junction. We then test our proposal by performing transport simulations on the model junction comprising molecules with stronger electron withdrawing units. Theoretical simulations show that the lowest unoccupied π states are strongly dependent on the electron withdrawing groups and can be even lowered down to the position of the Fermi level of the electrode, which indicates high conductivity of the molecular wires.

In [chapter 5](#), we describe the design and synthesis of a series of conjugated polyions that incorporate formal positive charge into their conjugated backbones, balanced by anionic pendant groups with increasing electron-donating ability. The energy levels and the bandgap of these conjugated polyions are determined by optical absorption spectroscopy and cyclic voltammetry (CV) and are easily modulated by varying the electron donating group. The energies of occupied states increase with increasing electron-donating ability, while the energies of the unoccupied states are almost unchanged due to the presence of tritylium ions in the conjugated backbone. All conjugated polyions exhibit pristine semiconducting properties in weak protonic acids, but with sufficiently strong acids, the polymers exhibit spontaneous spin unpairing and convert to a metallic state. The requisite strength of the acids varies with electron-donating ability, with higher HOMO levels leading to more facile proton acid doping and higher electrical conductivities. The mechanism of protonic acid doping of conjugated polyions involves a spinless doping process (dehydration) followed by spontaneous spin unpairing leading to the formation of polarons. While protonic acid doping

occurs in polyaniline, conjugated polyions offer synthetic tunability and selective processing into insulating, semiconducting and metallic states simply by controlling acidity.

BIBLIOGRAPHY

- (1) Mann, B.; Kuhn, H. Tunneling Through Fatty Acid Salt Monolayers. *J. Appl. Phys.* **1971**, *42*, 4398–4405.
- (2) Race, H. H.; Reynolds, S. I. Electrical Properties of Multimolecular Films. *J. Am. Chem. Soc.* **1939**, *61*, 1425–1432.
- (3) Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
- (4) Cuevas, J. C.; Scheer, E., *Molecular Electronics*; WORLD SCIENTIFIC: 2010.
- (5) Nitzan, A. Electron transmission through molecules And molecular interfaces. *Annu. Rev. Phys. Chem.* **2001**, *52*, 681–750.
- (6) Datta, S., *Lessons from Nanoelectronics*; WORLD SCIENTIFIC: 2012.
- (7) Nuzzo, R. G.; Allara, D. L. Adsorption of Bifunctional Organic Disulfides on Gold Surfaces. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.
- (8) Xin, N.; Guan, J.; Zhou, C.; Chen, X.; Gu, C.; Li, Y.; Ratner, M. A.; Nitzan, A.; Stoddart, J. F.; Guo, X. Concepts in the Design and Engineering of Single-Molecule Electronic Devices. *Nat. Rev. Phys.* **2019**, *1*, 211–230.
- (9) Reed, M. A. Conductance of a Molecular Junction. *Science* **1997**, *278*, 252–254.
- (10) Dorogi, M.; Gomez, J.; Osifchin, R.; Andres, R. P.; Reifenger, R. Room-Temperature Coulomb Blockade From a Self-Assembled Molecular Nanostructure. *Phys. Rev. B* **1995**, *52*, 9071–9077.
- (11) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. Are Single Molecular Wires Conducting? *Science* **1996**, *271*, 1705–1707.
- (12) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenger, R. "Coulomb Staircase" at Room Temperature in a Self-Assembled Molecular Nanostructure. *Science* **1996**, *272*, 1323–1325.

- (13) Yamada, R.; Kumazawa, H.; Tanaka, S.; Tada, H. Electrical Resistance of Long Oligothiophene Molecules. *Appl. Phys. Lett.* **2009**, *2*, 025002.
- (14) 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.
- (15) Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. Molecular Rectification in Metal-Sam-Metal Oxide-Metal Junctions. *J. Am. Chem. Soc.* **2009**, *131*, 17814–17827.
- (16) Qiu, L.; Zhang, Y.; Krijger, T. L.; Qiu, X.; van't Hof, P.; Hummelen, J. C.; Chiechi, R. C. Rectification of Current Responds to Incorporation of Fullerenes Into Mixed-Monolayers of Alkanethiolates in Tunneling Junctions. *Chem. Sci.* **2017**, *8*, 2365–2372.
- (17) Yoon, H. J.; Liao, K.-C.; Lockett, M. R.; Kwok, S. W.; Baghbanzadeh, M.; Whitesides, G. M. Rectification in Tunneling Junctions: 2, 2'-Bipyridyl-Terminated N-Alkanethiolates. *J. Am. Chem. Soc.* **2014**, *136*, 17155–17162.
- (18) Migliore, A.; Schiff, P.; Nitzan, A. On the Relationship Between Molecular State and Single Electron Pictures in Simple Electrochemical Junctions. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13746.
- (19) Yuan, L.; Wang, L.; Garrigues, A. R.; Jiang, L.; Annadata, H. V.; Antonana, M. A.; Barco, E.; Nijhuis, C. A. Transition From Direct to Inverted Charge Transport Marcus Regions in Molecular Junctions via Molecular Orbital Gating. *Nat. Nanotechnol.* **2018**, *13*, 322–329.
- (20) Kang, H.; Kong, G. D.; Yoon, H. J. Solid State Dilution Controls Marcus Inverted Transport in Rectifying Molecular Junctions. *J. Phys. Chem. Lett.* **2021**, *12*, 982–988.
- (21) Simmons, J. G. Generalized Formula for the Electric Tunnel Effect Between Similar Electrodes Separated by a Thin Insulating Film. *J. Appl. Phys.* **1963**, *34*, 1793–1803.
- (22) Simmons, J. G. Electric Tunnel Effect Between Dissimilar Electrodes Separated by a Thin Insulating Film. *J. Appl. Phys.* **1963**, *34*, 2581–2590.
- (23) Matthews, N.; Hagmann, M. J.; Mayer, A. Comment: “Generalized Formula for the Electric Tunnel Effect Between Similar Electrodes Separated by a Thin Insulating Film” [*J. Appl. Phys.* *34*, 1793 (1963)]. *J. Appl. Phys.* **2018**, *123*, 136101.
- (24) Akkerman, H. B.; Blom, P. W. M.; de Leeuw, D. M.; de Boer, B. Towards Molecular Electronics With Large-Area Molecular Junctions. *Nature* **2006**, *441*, 69–72.

- (25) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO₂-Templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 9686–9694.
- (26) Thuo, M. M.; Reus, W. F.; Nijhuis, C. A.; Barber, J. R.; Kim, C.; Schulz, M. D.; Whitesides, G. M. Odd-Even Effects in Charge Transport Across Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2011**, *133*, 2962–2975.
- (27) Akkerman, H. B.; de Boer, B. Electrical Conduction Through Single Molecules and Self-Assembled Monolayers. *J. Phys.: Condens. Matter* **2007**, *20*, 013001.
- (28) Simeone, F. C.; Yoon, H. J.; Thuo, M. M.; Barber, J. R.; Smith, B.; Whitesides, G. M. Defining the Value of Injection Current and Effective Electrical Contact Area for EGaIn-Based Molecular Tunneling Junctions. *J. Am. Chem. Soc.* **2013**, *135*, 18131–18144.
- (29) Selzer, Y.; Cai, L.; Cabassi, M. A.; Yao, Y.; Tour, J. M.; Mayer, T. S.; Allara, D. L. Effect of Local Environment on Molecular Conduction: Isolated Molecule Versus Self-Assembled Monolayer. *Nano Lett.* **2005**, *5*, 61–65.
- (30) Nerngchamnong, N.; Yuan, L.; Qi, D.-C.; Li, J.; Thompson, D.; Nijhuis, C. A. The Role of Van Der Waals Forces in the Performance of Molecular Diodes. *Nat. Nanotechnol.* **2013**, *8*, 113–118.
- (31) Liu, Y.; Ornago, L.; Carlotti, M.; Ai, Y.; Abbassi, M. E.; Soni, S.; Asyuda, A.; Zharnikov, M.; van der Zant, H. S. J.; Chiechi, R. C. Intermolecular Effects on Tunneling Through Acenes in Large-Area and Single-Molecule Junctions. *J. Phys. Chem. C* **2020**, *124*, 22776–22783.
- (32) Valkenier, H.; Huisman, E. H.; van Hal, P. A.; de Leeuw, D. M.; Chiechi, R. C.; Hummelen, J. C. Formation of High-Quality Self-Assembled Monolayers of Conjugated Dithiols on Gold: Base Matters. *J. Am. Chem. Soc.* **2011**, *133*, 4930–4939.
- (33) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1170.
- (34) Jiang, L.; Sangeeth, C. S. S.; Nijhuis, C. A. The Origin of the Odd–Even Effect in the Tunneling Rates Across EGaIn Junctions With Self-Assembled Monolayers (SAMs) of N-Alkanethiolates. *J. Am. Chem. Soc.* **2015**, *137*, 10659–10667.

- (35) Jiang, L.; Sangeeth, C. S. S.; Nijhuis, C. A. The Origin of the Odd–Even Effect in the Tunneling Rates Across EGaIn Junctions With Self-Assembled Monolayers (SAMs) of N-Alkanethiolates. *J. Am. Chem. Soc.* **2015**, *137*, 10659–10667.
- (36) Yuan, L.; Thompson, D.; Cao, L.; Nerngchangnong, N.; Nijhuis, C. A. One Carbon Matters: The Origin and Reversal of Odd–Even Effects in Molecular Diodes With Self-Assembled Monolayers of Ferrocenyl-Alkanethiolates. *J. Phys. Chem. C* **2015**, *119*, 17910–17919.
- (37) Song, P.; Thompson, D.; Annadata, H. V.; Guerin, S.; Loh, K. P.; Nijhuis, C. A. Supramolecular Structure of the Monolayer Triggers Odd–Even Effects in the Tunneling Rates Across Noncovalent Junctions on Graphene. *J. Phys. Chem. C* **2017**, *121*, 4172–4180.
- (38) Chen, J.; Giroux, T. J.; Nguyen, Y.; Kadoma, A. A.; Chang, B. S.; VanVeller, B.; Thuo, M. M. Understanding Interface (Odd–even) Effects in Charge Tunneling Using a Polished EGaIn Electrode. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4864–4878.
- (39) Obersteiner, V.; Egger, D. A.; Heimel, G.; Zojer, E. Impact of Collective Electrostatic Effects on Charge Transport through Molecular Monolayers. *J. Phys. Chem. C* **2014**, *118*, 22395–22401.
- (40) Fracasso, D.; Muglali, M. I.; Rohwerder, M.; Terfort, A.; Chiechi, R. C. Influence of an Atom in EGaIn/Ga₂O₃ Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2013**, *117*, 11367–11376.
- (41) Abu-Husein, T.; Schuster, S.; Egger, D. A.; Kind, M.; Santowski, T.; Wiesner, A.; Chiechi, R.; Zojer, E.; Terfort, A.; Zharnikov, M. The Effects of Embedded Dipoles in Aromatic Self-Assembled Monolayers. *Adv. Funct. Mater.* **2015**, *25*, 3943–3957.
- (42) Kovalchuk, A.; Egger, D. A.; Abu-Husein, T.; Zojer, E.; Terfort, A.; Chiechi, R. C. Dipole-Induced Asymmetric Conduction in Tunneling Junctions Comprising Self-Assembled Monolayers. *RSC Adv.* **2016**, *6*, 69479–69483.
- (43) Kovalchuk, A.; Abu-Husein, T.; Fracasso, D.; Egger, D. A.; Zojer, E.; Zharnikov, M.; Terfort, A.; Chiechi, R. C. Transition Voltages Respond to Synthetic Reorientation of Embedded Dipoles in Self-Assembled Monolayers. *Chem. Sci.* **2016**, *7*, 781–787.
- (44) Carlotti, M.; Kovalchuk, A.; Wächter, T.; Qiu, X.; Zharnikov, M.; Chiechi, R. C. Conformation-Driven Quantum Interference Effects Mediated by Through-Space Conjugation in Self-Assembled Monolayers. *Nat. Commun.* **2016**, *7*, 1–7.

- (45) Dubi, Y. Transport Through Self-Assembled Monolayer Molecular Junctions: Role of In-Plane Dephasing. *J. Phys. Chem. C* **2014**, *118*, 21119–21127.
- (46) Fracasso, D.; Valkenier, H.; Hummelen, J. C.; Solomon, G. C.; Chiechi, R. C. Evidence for Quantum Interference in SAMs of Arylethynylene Thiolates in Tunneling Junctions With Eutectic Ga–In (EGaIn) Top-Contacts. *J. Am. Chem. Soc.* **2011**, *133*, 9556–9563.
- (47) Barber, J. R.; Yoon, H. J.; Bowers, C. M.; Thuo, M. M.; Breiten, B.; Gooding, D. M.; Whitesides, G. M. Influence of Environment on the Measurement of Rates of Charge Transport Across AgTS/SAM//Ga₂O₃/EGaIn Junctions. *Chem. Mater.* **2014**, *26*, 3938–3947.
- (48) Carlotti, M.; Degen, M.; Zhang, Y.; Chiechi, R. C. Pronounced Environmental Effects on Injection Currents in EGaIn Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2016**, *120*, 20437–20445.
- (49) Chiechi, R.; Weiss, E.; Dickey, M.; Whitesides, G. Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, 142–144.
- (50) Dickey, M. D.; Chiechi, R. C.; Larsen, R. J.; Weiss, E. A.; Weitz, D. A.; Whitesides, G. M. Eutectic Gallium–Indium (EGaIn): A Liquid Metal Alloy for the Formation of Stable Structures in Microchannels at Room Temperature. *Adv. Funct. Mater.* **2008**, *18*, 1097–1104.
- (51) Reus, W. F.; Nijhuis, C. A.; Barber, J. R.; Thuo, M. M.; Tricard, S.; Whitesides, G. M. Statistical Tools for Analyzing Measurements of Charge Transport. *J. Phys. Chem. C* **2012**, *116*, 6714–6733.
- (52) Sporrer, J.; Chen, J.; Wang, Z.; Thuo, M. M. Revealing the Nature of Molecule–Electrode Contact in Tunneling Junctions Using Raw Data Heat Maps. *J. Phys. Chem. Lett.* **2015**, *6*, 4952–4958.
- (53) Chen, J.; Kim, M.; Gathiaka, S.; Cho, S. J.; Kundu, S.; Yoon, H. J.; Thuo, M. M. Understanding Keesom Interactions in Monolayer-Based Large-Area Tunneling Junctions. *J. Phys. Chem. Lett.* **2018**, *9*, 5078–5085.
- (54) Vilan, A.; Aswal, D.; Cahen, D. Large-Area, Ensemble Molecular Electronics: Motivation and Challenges. *Chem. Rev.* **2017**, *117*, 4248–4286.
- (55) Bâldea, I. Ambipolar Transition Voltage Spectroscopy: Analytical Results and Experimental Agreement. *Phys. Rev. B* **2012**, *85*, 035442.

- (56) Peterson, I. R.; Vuillaume, D.; Metzger, R. M. Analytical Model for Molecular-Scale Charge Transport. *J. Phys. Chem. A* **2001**, *105*, 4702–4707.
- (57) Huisman, E. H.; Guédon, C. M.; van Wees, B. J.; van der Molen, S. J. Interpretation of Transition Voltage Spectroscopy. *Nano Lett.* **2009**, *9*, 3909–3913.
- (58) Chen, J.; Markussen, T.; Thygesen, K. S. Quantifying Transition Voltage Spectroscopy of Molecular Junctions: Ab Initio Calculations. *Phys. Rev. B* **2010**, *82*, 121412.
- (59) Vilan, A.; Cahen, D.; Kraisler, E. Rethinking Transition Voltage Spectroscopy Within a Generic Taylor Expansion View. *ACS Nano* **2012**, *7*, 695–706.

2

RECENT PROGRESS OF ENSEMBLE JUNCTIONS: THE TOP ELECTRODE

The content in this chapter is part of our recent review paper: Charge-transport Through Molecular Ensembles: Recent Progress in Molecular Electronics, accepted by the Chemical Physics Review, AIP Publishing.

2.1. INTRODUCTION

This chapter focuses specifically on the role of molecular ensemble junctions (MEJs) in molecular electronics (ME) because they are central to both the theoretical advancements and the development of useful devices that are reflected in the two complementary goals of ME: understanding the underlying physical properties and extracting useful functionality, *i.e.*, constructing devices. These goals necessitate measuring, controlling, and understanding (tunneling) charge transport through molecules attached to electrodes in two broad and complementary experimental approaches to constructing tunneling junctions: single-molecule junctions (SMJs) [1–4] and large-area junctions comprising ensembles.[5–7] The principle goal of the former is to develop a fundamental understanding of electron transport through junctions comprising single molecules, a construct that is relatively straightforward to treat *in silico*. The principle goal of the latter is functionality on the device-level, utilizing ensembles of molecules, usually in the form of self-assembled monolayers (SAMs), to define both the function and the smallest dimension of the junction. Single-molecule techniques like break-junctions, in which the electric leads repeatedly form and rupture by the trapping and releasing of individual molecules, are primarily useful as spectroscopic tools for investigating the detailed mechanisms of charge transport; they are not (yet) useful as devices because they are transient, but they can be modeled atomistically. This chapter focuses on (large-area) junctions comprising molecular ensembles, which are potentially directly useful in technological applications, as they are intrinsically static, solid-state devices; however, they are difficult to model.

There are already several excellent reviews on the field of ME, both in MEJs and SMJs.[5, 7–9] Our goal is to review the recent progress in this field and give the reader a general idea of what has been done, with an emphasis on the types and properties of molecular junctions. We would like to present our review from the perspective of forming a molecular junction: the bottom electrode and bottom interfaces are reviewed first, next the molecular monolayers are reviewed, and then top electrode and top interfaces are reviewed. In this specific chapter, we will discuss the fabrication of MEJs from these ensembles using state-of-the-art methods to solve the unique challenge of applying a top contact. We divide the methods of making a top contact into four parts: 1) solid metallic electrodes, *i.e.*, applying solid-metals electrodes directly to a molecular ensemble supported by a conductive substrate; 2) liquid metallic electrodes; 3) hybrid electrodes, *e.g.*, using a buffer layer between the molecular layer and the top contact; 4) non-metallic electrode. There are many methods for attaching electrodes to molecules and an entire review could be devoted to the topic; here, the focus is on techniques that install a top contact to MEJs. We will not discuss techniques that form nano-gaps, such as on-wire lithography, self-aligned lithography and

on-edge molecular junction, for which there are already excellent reviews.[9, 10]

2.2. ENSEMBLE JUNCTIONS: THE TOP ELECTRODES

2.2.1. SOLID METAL ELECTRODES

CONDUCTING-PROBE ATOMIC FORCE MICROSCOPY

Originally developed by Wold *et al.* to form metal-molecule-metal junctions, conducting-probe atomic force microscopy (CP-AFM), brings a metal-coated, conductive AFM tip into contact with a surface supporting a molecular ensemble.[11] Like STM-BJs, CP-AFM forms transient junctions; Unlike STM-BJs, these junctions comprise hundreds of molecules and persist for as long as the tip is held in contact with the substrate.[12, 13] Alternatively, an AFM tip can be used to address pre-formed nano-scopic contacts such as a conductive nanoparticle pre-deposited on a SAM.[14] Since the size of the nanoparticle is well defined, the number of molecules contacted can be determined from the packing density (which can be determined from several spectroscopic techniques), thus, the per-molecule conductance can be calculated. MEJs with CP-AFM top contacts are particularly well-suited for characterizing the nuances of bottom-electrodes, interfaces, and molecular layers because they can efficiently probe per-molecule conductance in small, defect-free areas of molecular ensembles, eliminating the influences of substrate topography and disorder that are endemic to large-area MEJs. Furthermore, the mechanical and the electrical properties of the molecule/substrate can be interrogated simultaneously.[15–17] The force of the tip can also be controlled to optimize the molecule-electrode interface and study the effects of deformations or rearrangements of the molecules.[11, 18] This fine control over the molecule-interface is also ideally suited for studying the correlation between energy level alignments and the chemistry of the interface. For example, comparing aromatic thiols to aromatic isocyanides,[19] alkane-monothiols to alkane dithiols,[20, 21] and oligophenyl thiols to oligophenyl dithiols.[22, 23] CP-AFM is a widely-used technique with a large body of work that has been reviewed elsewhere.[9] Since the focus of this chapter is on MEJs with potential technological implications and MEJs formed using AFM tips are unlikely to find direct technological applications, they will not be discussed further.

CROSSED-WIRE JUNCTIONS

Although crossed-wires have been long-used to form metallic tunneling junctions,[25] Gregory *et al.* improved on the methodology enough to form MEJs and perform IETS on them.[26] Kushmerick *et al.* further improved on the technique, measuring the I/V characteristics of MEJs comprising SAMs, as shown in Figure 2.1.[27] To fabricate a crossed-wire junction, two metallic wires of $\approx 10\ \mu\text{m}$ in diameter are mounted in an orthogonal geometry. A SAM

Figure 2.1 Schematic description of a cross-wire junction. The crossed wires were mounted in a custom-built test and the spacing of wires was controlled by the Lorentz force. One wire is coated with a SAM perpendicular to the applied magnetic field B . The low current through the wire coated with a SAM generates a Lorentz force and the two wires are then gently brought together to form a junction at the contact point. Inset: $I - V$ characteristics of metal-molecule-metal junction. Reproduced with permission from ref. 24. Copyright (2003) American Chemical Society.

is grown on one of the wires and it is positioned perpendicular to an applied magnetic field. A small current through this wire uses the Lorentz force to control its deflection from the other wire, allowing them to be brought into contact sufficiently gently to avoid damage to the SAM; SAMs are both chemically and mechanically fragile. Once a MEJ is formed between the wires, a voltage is applied to measure the conductance of the junction.[28, 29] Since different metallic wires can be used, the work functions of the electrodes and junction asymmetry can also be varied.[30] Yoon *et al.* reported a device-level crossed-wire junction which enables the simultaneous measurement of I/V curves at variable temperatures while performing Raman and IETS measurements.[31] Like CP-AFM, crossed-wire junctions are transient, but form small, well-defined junctions that are ideally suited to study the details of transport through SAMs of a wide variety of molecules,[24, 27, 32, 33] revealing the vibronic contributions to transport as well as the IETS selection rules.[29, 30] As a result of the fine control over the deflection of one of the wires, the contact force between the wires can be varied precisely, allowing the junction-area to be varied *i.e.*, more molecules are contacted when the deflection current in the wire is increased.[24, 32] The number of molecules in a crossed-wire MEJ is, however, difficult to estimate because the curvature is not well-defined and the orientation of the SAM w.r.t. the wires is difficult to determine exactly. Crossed-wire junctions share many of the advantages and limitations (*i.e.*, in the

Figure 2.2 Schematic description of the nanotransfer printing procedure. a) The GaAs substrate is first etched in concentrated NH_4OH or HCl and then immediately exposed to a 1,8-octanedithiol vapor or solution for self-assembly. b) The gold-coated elastomeric PDMS stamp is brought into contact with the modified substrate. c) The stamp was removed from the substrate, then the Au on the PDMS stamp is bonded by the molecules and transferred to the molecule-coated GaAs substrate. Reproduced with permission from ref. 34. Copyright (2003) American Chemical Society.

context of technological applications) of CP-AFM junctions and thus will not be discussed further for the same reasons.

NANOTRANSFER PRINTING

Nanotransfer printing (nTP), first introduced by Loo *et al.*, [35, 36] is a technique to make MEJs with the SAMs acting as covalent ‘glue’ to transfer thin metal films from a stamp, as shown in Figure 2.2. Elastic stamps of PDMS fabricated by soft lithography are the commonly used to transfer patterned electrodes by nTP. [37, 38] Rigid stamps can be made from GaAs by locally etching the GaAs with a patterned resist layer as an etching mask. [39] The elastic properties of PDMS allow it to conform to small variation in height, mitigating the effects of substrate topography than can be detrimental to rigid stamps, however, that deformation can reduce the fidelity of the contact-patterns. In both cases, the size and ratio of the pattern determines the number of molecules contacted. An important feature of nTP is the ability to fabricate multiple electrodes with different patterns and sizes simultaneously, which is useful both in the context of potential technological applications and for the statistical analyses that are described in section 1.4. [34] Since the solid metallic films on the stamp are transferred in their entirety, the resulting structures do not suffer from short-circuits induced by filaments, which is a common failure mode with vapor-deposited metallic top electrodes. [40] Suggestive of technological applications vis-à-vis integrated circuits, nTP

Figure 2.3 Schematic description of the lift-off, float-on (LOFO) procedure. a) Lift-off process of the evaporated leaf (metal layer) from a glass slide. First, the glass slide is partly inserted into a detaching agent to induce the peeling process. Then the disjoining pressure detaches the leaf from the glass substrate. Lastly, the metal leaf floats on solvent due to the capillary interaction. b) Float-on process of the leaf onto the solid substrate. The metal pad floats on the substrate adsorbed with molecules. The solvent is rapidly removed to prevent the wrinkling of the leaf. Then the metal-SAM-substrate is completed. Reproduced with permission from ref. 49. Copyright (2008) American Chemical Society.

has been used to fabricate crossbar arrays of MEJs in high yields.[41, 42] The crossbar architecture is key to the realization of memory and logic devices based on MEJs,[43–46] as it capitalizes on the ability to include multiple functions into a single junction[47] in high-throughput, low-cost parallel fabrication. The primary disadvantage of nTP is that it requires a mechanically robust molecular layer that covalently binds to the top contact with a thiol group, restricting the class of materials that can be used[41] and precluding the investigation of weak or physisorbed contacts. However, the only physical limitation is interfacial free-energy of the stamp, which, as Niskala *et al.* reported, can be reduced significantly by the choice of elastomer, resulting in high-yields of stable junctions.[48]

LIFT-OFF, FLOAT-ON ELECTRODES

The lift-off float-on (LOFO) approach is inspired by the sample preparation for transmission electron microscopy experiments to deposit GaAs on other substrates.[50] It was developed as a soft deposition method to reduce electrical shorts in MEJs by Moons, Vilan *et al.*[51–53] The general procedure for the LOFO approach is illustrated in Figure 2.3. In this method, a thin metallic film is deposited on a sacrificial substrate and then lifted off using a detaching agent and then floated on top of a conductive substrate supporting a molecular ensemble, thus resulting in a MEJ in a sandwich-configuration. Similar to nTP, LOFO avoids filament formation from vapor deposition and avoids exposing the molecular layer

Figure 2.4 Schematics of the fabrication of nanopore devices. a) Nanopore junction: a pore is made through a Si_3N_4 membrane via reactive ion etching. The bottom Au electrode is evaporated onto the other side of the membrane, upon which a SAM is formed before completing the junction with the evaporation of the top electrode; b) Nanowell junction: a hole is drilled through a layer of SiO_2 with a focused ion beam layer to expose a bottom electrode of Au. After growing a SAM on the electrode, the junction is completed with the deposition of a Au top electrode. Reproduced with permission from ref. 9. Copyright (2016) American Chemical Society.

to vacuum, but it also mitigates physical damage to the SAM from the direct application of solid metallic contacts.[51] Unlike nTP, LOFO does not depend on chemical bonding or low surface free-energy elastomers, but it is constrained by capillary forces and requires exposure to solvent.[53] The surface supporting the molecular ensemble must be kept wet until the metal film establishes an electrical contact, which is particularly amendable to making MEJs comprising proteins.[54] Au is often used in LOFO rather than Ag, Al or Cu because detaching agents, such as hydrofluoric or acetic acid solutions, can etch or react with other metals, creating ill-defined interfaces between the top electrode and the molecular layer. To mitigate this limitation, Ikram *et al.* reported a method for forming Ag and Al electrical contacts without using chemical etching treatment.[55] Further modifications have lead to related methods such as polymer-assisted LOFO (PALO),[41, 56] wedge transfer,[57] and direct metal transfer.[58] The PALO method, developed by Shimizu *et al.*, combines the advantages of LOFO and nTP, readily forming crossbar junctions, successfully overcoming wrinkling problems and providing a potential path forward for integrated circuits of MEJs.[41]

NANOPORE JUNCTIONS

The top electrode definitionally determines the area of a MEJ because it is installed last and, in the aforementioned strategies, is smaller (in area) than the molecular layers. Shrinking the area of the top-contact is useful both to mitigate the influence of defects and to miniaturize devices comprising MEJs. While CP-AFM and crossed-wires form nanoscopic contacts, they are not static and neither LOFO nor nTP can reliably produce contacts that small.

Nanopore junctions are MEJs defined by a nanoscopic hole, *e.g.*, a nanopore or a nanowell that affords precise control over the area of static, nanoscopic top electrodes.[59–61] In general, the fabrication of a nanopore device starts with the creation of a bowl-shaped hole (~ 50 nm in diameter) on a Si_3N_4 membrane using electron beam lithography and reactive ion etching (Figure 2.4a).[60] The bottom electrode (~ 200 nm Au) is thermally evaporated onto the top side of the membrane, filling the pore. A SAM is grown on the bottom electrode and then a top electrode is evaporated such that the total area of the MEJ is defined by the diameter of the hole in the Si_3N_4 . Alternatively, a layer of SiO_2 is evaporated on a bottom electrode, a focused ion beam is used to drill a nanowell (~ 40 nm in diameter) through to the bottom electrode upon which a SAM is grown before a top electrode is deposited to complete a MEJ that is defined by the diameter of the hole etched in the SiO_2 (Figure 2.4b).[61] The essential feature of nanopore junctions is the area of the MEJ, which incorporates a small number of self-assembled molecules (~ 1000), comparable to CP-AFM, minimizing the influence of defects and disorders that are present in larger junctions. Both nanopore methods also allow the fabrication of a large number of devices for potential integration and the collection of a statistically significant amount of data.[60] Unlike CP-AFM, where the operator determines the exact placement of a junction on a large substrate, nanopore junctions exhibit unavoidable sample-to-sample variation in the electrical behaviors of junctions as a result of the multi-step fabrication process. Additionally, the yields of the nanopore and nanowell devices can be very low ($\approx 2\%$) due to the penetration of metal atoms into the SAMs during the deposition of the top electrode, though the pores are small enough that gaseous metal atoms tend to be slowed by collisions with the walls and yields can be improved by careful deposition. Another approach to mitigating damage to the SAMs and increasing yields is to insert a conductive buffer layer between the top electrode and the SAM, which will be discussed further in subsection 2.2.3.

2.2.2. LIQUID METAL ELECTRODES

HANGING MERCURY DROPS

The main disadvantage of solid metal top contacts is that they either have to be physically transferred to a molecular layer or vacuum deposited from the vapor phase. An alternative is to use metals that are liquids at room temperature, which can be physically transferred to make conformal contact to the molecular layer without vacuum deposition, resulting in the easy fabrication of high yields of MEJs.[62] Though not in the modern context of ME, the use of liquid metal top contacts for molecular layers dates back to 1939 when Race *et al.* used liquid Hg to measure the electrical properties of “multimolecular films”.[63] They tried several metals, finding that Hg was unique in not damaging the molecular layer(s). In 1971,

Mann *et al.* reported the measurement of tunneling currents through fatty acid monolayers using liquid Hg applied to Langmuir-Blodgett films supported by Al bottom electrodes.[64] Becucci *et al.* reported the use of Hg electrodes to mimic a biological membrane.[65] Slowinski *et al.* fabricated Hg/SAM//SAM/Hg and Hg/SAM/Hg junctions (where ‘/’ and ‘//’ represent covalent and van der Waal interfaces, respectively) by bringing two mercury drops, one or both of which bearing a SAM, in contact using a micromanipulator and applying a bias across the drops.[66–68] This approach exploits the ability to grow defect-free SAMs on the surface of Hg; Simply exposing a Hg drop to a solution of alkanethiols is enough to form a pinhole-free SAM, enabling the extensive study of charge-tunneling in symmetric and asymmetric alkanethiol junctions as well as the relationship between structure and stability.[69, 70] Asymmetric junctions can be formed by bringing a hanging mercury drop electrode (*i.e.*, a drop of Hg hanging from a conductive lead) into contact with a conductive substrate supporting a monolayer. One limitation of using Hg is the formation of amalgams with Au and Ag;[7, 71] a single pinhole defect can precipitate the dissolution of the entire bottom electrode. This problem is somewhat mitigated by the passivation of the Hg top electrode with an additional SAM of alkanethiols—pinhole-free because it is formed on Hg—and measuring charge transport by contacting it with a SAM-modified[72, 73] or a bare bottom electrodes,[74, 75] *e.g.*, an oxide-free silicon substrate, as shown in Figure 2.5. These methods permit measurements of a large number of tunneling junctions on the same or different substrates, which then facilitates the collection of a large sets of data for statistical analysis and interrogating reproducibility. Unfortunately, Hg has a non-zero vapor pressure at room temperature and is toxic and, although it can be handled safely in a laboratory, these properties obviate commercialization. It is also difficult to encapsulate and otherwise requires measurements to be performed in solvent baths, limiting even laboratory-scale studies on proto-devices.

Figure 2.5 Schematic of MEJs using hanging mercury drops as top electrodes: the mercury drop is first modified by octadecanethiolates (C18SH), then brought into contact with an oxide-free silicon substrate. Reproduced with permission from ref. 76. Copyright (2015) American Chemical Society.

CAPILLARY TUNNELING JUNCTIONS

Bai *et al.* fabricated MEJs inside capillary tubes in which the molecules self-assemble on Sn or In electrodes to form a capillary tunnel junction (CPT).[77, 78] These junctions are formed inside capillary fibers between solidified tin/indium electrodes, as illustrated in Figure 2.6. Both Sn and In are low-melting metals that form native oxides and are well-known in optoelectronic devices. To form a CPT, melted Sn or In is allowed to infiltrate a capillary fiber to a preferred height at temperatures that are slightly higher than their melting points. The metal is then cooled until they solidify. Second, the end of the fiber is exposed to a solution of alkanethiols or carboxylic acids to form a SAM at the metal/metal-oxide surface. Finally, the SAM-modified fiber is inserted into a larger fiber that is also filled with melted Sn or In, encapsulating the SAM between two electrodes. The MEJ is completed when the junction is cooled to room temperature. These MEJs are both stable and reproducible. Xun *et al.* also reported the use of Ga in CPTs to investigate tunneling conductance of aryl-halides.[79] The primary limitation of this method is that the contact area and the distance between the two electrodes are fixed when the MEJ is formed; liquid metal electrodes that remain liquids during measurement can accommodate changes in the molecular layer, such as photo-induced isomerization.[80] Another disadvantage of this method is that the insertion of the smaller fiber into the larger one may cause mechanical damage to the molecular layer, limiting the kinds of SAMs that can be used.

Figure 2.6 Schematic description of forming a capillary tunnel junction. a) Molten metal (tin or indium) infiltrates a capillary fiber due to capillary forces; b) after solidifying, the exposed end of the fiber is then immersed in an ethanolic solution of the target molecules to form SAMs; c) the SAM-modified fiber is inserted into another fiber with a larger diameter also filled with molten metal, encapsulating the SAM; d) a schematic of the CPT connected to an outer circuit. Reproduced with permission from ref. 78. Copyright (2004) American Chemical Society.

EUTECTIC GALLIUM-INDIUM

The liquid metal alloy, eutectic Gallium-Indium (EGaIn), was first proposed by Chiechi *et al.* as a non-toxic alternative to hanging mercury drop electrodes.[81] Although it is a liquid metal, it shares few properties with Hg; It does not form amalgams, it is easily encapsulated and measurements can be performed in ambient conditions. Moreover, it can be molded into cone-shaped tips (Figure 2.7) and used to form non-damaging contacts to SAMs that are ≈ 10 times smaller than those formed using Hg. The reversible, non-damaging nature of EGaIn also allows extensive studies in the correlation between molecular structure and electric properties in MEJs by combining electrical measurements with surface spectroscopies *in* and *ex situ*. It is also useful as an electrode for impedance spectroscopy on soft, fragile films.[82, 83] Byeon *et al.* reported a method for the *in situ* encapsulation of EGaIn microelectrodes with a photocurable polymeric scaffold that enables the untethering of the electrode and direct writing of arrays to form high-yield MEJs under ambient conditions and without masks.[84] Park *et al.* reported a method for thermoelectric measurements in MEJs using conical EGaIn tips as top electrodes.[85] They incorporated a thermocouple to monitor the *in situ* temperature change as the bottom electrode was heated to create a temperature difference across the junction and measuring the generated voltage gradient due to the thermoelectric effect (details are discussed in ref. 86).

Figure 2.7 Optical micrographs showing the formation of a conical EGaIn tip. A microliter EGaIn droplet is squeezed out of a syringe and crashed into a bare metal substrate (1st frame). As the syringe is retracted, it sticks to the substrate and, as shown in consecutive frames, forms an hourglass shape that eventually breaks off to form a sharp conical tip, as shown in the last frame.

The non-Newtonian rheology of EGaIn allows it to form stable microstructures upon injection into microfluidic channels.[87, 88] Nijhuis *et al.* described a method of fabrication that generates crossbar arrays of MEJs based on SAMs; These junctions have stabilized EGaIn top contacts in microchannels and use ultraflat (template-stripped) bottom electrodes to achieve yields of 70 % to 90 %.[89] The technique rapidly generated large sets of data ($N = 300$ -800) and allowed measurements over a broad range of temperatures (100 K to 393 K), allowing variable-temperature charge-transport experiments. They further compared the results of this method with those from conical EGaIn tips, concluding that both produce high device yields and indistinguishable results.[90] However, this method requires patterned bottom electrodes and the resulting, unavoidable, edge effects and contamination by photoresist

can influence the junction properties. Wan *et al.* solved those problems by combining filling through-holes in PDMS with EGaIn and bringing them into contact with SAMs.[91] This micropore method does not need patterned bottom electrodes and is compatible with large, ultra-flat, template-stripped surfaces. Similar to the aforementioned photocurable polymer scaffolds, it immobilizes PDMS in a polymer form, but in a barrel shape rather than a tip; A single top electrode can be used to form up to 15-25 junctions and yields highly reproducible electrical characteristics. Karuppannan *et al.* used AlO_x micropores instead of PDMS to form EGaIn MEJs on template-stripped Au surfaces, using a double-etch process to avoid contamination and unwanted etching of the Au surface and minimizing stray capacitance and leakage currents in the junction. This method enables variable-temperature measurements down to 8.5 K, has excellent current retention characteristics, and forms devices that are stable for at least 2 months.[92]

2.2.3. HYBRID TOP ELECTRODES

Hybrid top electrodes, here, refer to the use of a buffer layer between the top electrode and the molecular layer that prevents the penetration of metal atoms into the layer, reducing or eliminating electrical shorts and enabling vapor deposition and many common photolithographic techniques. These advantages facilitate the fabrication of robust and stable devices that can be integrated into standard semiconductor fab lines. Common materials for buffer layers include nanoparticles,[93–95] aluminum oxide,[96] conductive polymers,[97–99] graphene or graphene oxide sheets,[100–102] and carbon paint.[103]

Akkerman *et al.* first reported a method for fabricating high-yielding MEJs that are compatible with semiconductor fab techniques[104] that incorporates the conductive polymer blend poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as a buffer layer between the top electrode and the SAM.[97] These micropore MEJs are defined by microscale vertical interconnections — via holes photo-lithographically patterned in a photo-resist — that eliminate parasitic currents in crossbar arrays and completely encapsulate the thiol-SAMs within. The yields of working devices are $\approx 100\%$ in devices that are air-stable for at least several months without any signs of degradation, yielding identical I/V sweeps month over month that scale perfectly with the diameter of the via holes, which can be as big as $100\ \mu\text{m}$. Van Hal *et al.* demonstrated compatibility with semiconductor fabrication technology and the ability to upscale micropore MEJs integrated with silicon semiconductor devices.[104] However, the use of PEDOT:PSS imposes several limitations, such as a limited processing window (below 50°C), a poorly-defined polymer-SAM interface and a strong dependence of yields on the type of molecules used in the SAMs.[105] Neuhausen *et al.* reported the use of Aedotron P—a low-viscosity, amphiphilic conducting polymer—as a

replacement for PEDOT:PSS that allows the incorporation of SAMs with either hydrophobic or hydrophilic end-groups without changing the junction architecture.[99] The main limitation of micropore MEJs is the contact resistance of polymer buffer layers; PEDOT:PSS and its derivatives and Adeotron P all yield contact resistances that will dominate the electrical properties of junctions comprising all but the most resistive SAMs, *e.g.*, alkanethiols. The all-carbon MEJs developed by McCreery and co-workers (which are discussed below and in subsection 2.2.4) capture most of the useful properties of micropore MEJs without the contact resistance issues, though with a different set of trade-offs vis-à-vis upscaling, integration and tolerance for functional groups. In the context of laboratory-scale studies, EGaIn solves the contact resistance problem by relying on the sub-nanometer, self-limiting Ga_2O_3 as an in-built buffer layer,[106] though (as described in Figure 2.2.2) devices incorporating EGaIn top electrodes are less technologically useful than micropore or all-carbon MEJs.

The thinnest buffer layer that is physically possible is one atom-thick, *i.e.*, a single sheet of graphene. Wang *et al.* first reported the use of multilayer-graphene as a buffer layer in MEJs.[100] The graphene buffer layers were grown on Ni substrates by chemical vapor deposition (CVD) and physically transferred on top of SAMs in SiO_2 micropores. At the time, the authors were only able to produce ≈ 10 nm-thick graphene multilayers by CVD (*i.e.*, not one atom-thick sheets). Statistical analysis of the electrical properties of the MEJs showed that their graphene-based devices had very low contact resistances, comparable to the metal-molecule-metal devices without buffer layers, and could be obtained in yields of $\approx 90\%$ regardless of the (hydrophobic or hydrophilic) SAMs used. Thus, buffer layers of multilayer graphene were shown to produce excellent device durability, thermal stability, and longer lifetimes compared to other MEJs without a buffer layer and lower contact resistances than MEJs with polymer buffer layers. Li *et al.* and Seo *et al.* nearly simultaneously demonstrated the use of reduced graphene oxide (rGO) to avoid the limitations of CVD.[101, 107] In this method, graphite is exfoliated by oxidization to form suspensions of graphene oxide than are solution-proceeded into films than are then reduced (thermally or chemically) to rGO. These ≈ 5 nm-thick layers are then transferred to SAMs in Al_2O_3 micropores and a protective layer of Au installed on top by vapor deposition. Initially, rGO did not perform as well as multilayer graphene, affording higher contact resistances and introducing a defect-mediated thermally-activated hopping component, however, Kühnel *et al.* have since refined the technique to produce rGO-MEJs that operate from room temperature to below 1 K.[102] The contact resistance of these improved rGO buffer layers is similar to that of pure metal-molecule-metal junctions, however, installing the buffer layer still requires a LOFO step, which presents a challenge for upscaling and integration.

Polymer and graphene/rGO buffer layers are not innocent and do constrain the the type

and magnitude of electrical functions that are possible. Peubla-Hellmann *et al.* reported the use of Au nanoparticles (AuNPs) as top electrode to retain the advantages of buffer layers without the constraints.[95] The AuNPs are processed from solution directly onto SAMs, directly forming a metal-molecule interface that also serves as a conformal, protective layer for the installation of top electrodes by vapor deposition, as depicted in Figure 2.8a. This approach enables the fabrication of thousands of identical, room-stable metal-molecule-metal MEJs. The I/V characteristics and IETS spectra of devices comprising SAMs of alkanethiols of different lengths produced values of β commensurate with charge-transport that is dominated by the molecular layer and not strongly affected by the AuNP or metal overlayer. However, this method also has an important limitation: The AuNP layer requires SAMs that present anchoring groups to adhere to, which limits the scope of molecules that can be studied. This requirement is shared with micropore MEJs and is known to complicate the self-assembly process, often leading to lying-down or looped SAM phases that can also result in multilayer formation.[108]

Figure 2.8 a) Schematic of the fabrication of MEJs using Au nanoparticles as a buffer layer: (1) Pores of diameter d are etched into a dielectric film on a Pt electrode; (2) a SAM is grown on the platinum electrode; (3) AuNPs are deposited onto the SAM from solution; and (4) a top electrode is installed by vapor deposition. Reproduced with permission from ref 95. Copyright(2018) Springer Nature. b) Schematic showing junctions fabricated using carbon paint as buffer layer between the SAM and Au top electrode. Reproduced with permission from ref. 103. Copyright (2020) American Chemical Society.

Other carbon-based, such as electron-beam deposited carbon (eC)[109] and carbon paint, have been developed as buffer layers to form stable MEJs. Najarian *et al.* reported molecular junctions fabricated with eC between SAMs and both metal electrodes.[109] The buffer layer of eC between the Au bottom electrode and the molecular layer reduces the roughness of the substrate and prevents electromigration. The buffer layer of eC between the Au top

electrode and the molecular layer imparts long-term device stability and eliminates electro-migration and oxidation. Moreover, partial transparency of one or both contacts permit *in operando* monitoring of MEJs with optical spectroscopy as well as photocurrent electroluminescence phenomena. Karuppannan *et al.* used protective layers based on commercially available carbon paint to form high-quality, large-area MEJs with low contact resistance as shown in Figure 2.8b. This protective layer has the advantage of being solution-processable, eliminating the need for LOFO that is required by graphene and rGO. Carbon paint buffer layers also allow measurements over a wide range of temperatures (8.5 K to 340 K). The resulting MEJs are also stable, reproducible and can be fabricated with 100 % yield of non-shortening junctions. The absolute resistance of carbon paint is higher than graphene and rGO (but comparable to eC), limiting it to MEJs comprising SAMs that are more resistive than butanethiol.

2.2.4. NON-METALLIC TOP ELECTRODES

Nanoscale metal electrodes are mechanically unstable due to the high mobility of the metal atoms. While MEJs comprising solid metal electrodes remain operational, experimental platforms based on non-metallic materials have been developed, thus leading to new possibilities for molecular-scale electronics. Carbon-based and silicon-based electrodes, in particular, have been developed to fabricate stable, high-yielding molecular devices. Carbon-based nanomaterials, including the single-walled carbon nanotubes (SWCNTs),^[110] graphene sheets,^[100, 101, 111] rGO,^[102, 107, 112] eC,^[109] and carbon paint^[103] were developed as point contacts, which are promising for progress in fabrication of electronic devices. In the above subsection, we discussed graphene, rGO, eC, and carbon paint buffer layers to form a soft contact to the SAM and to protect it from subsequent vapor deposition of a solid metal top contact.

Here, we will discuss the use of SWCNTs and graphene/rGO as the top electrode or both the electrodes in MEJ. SWCNTs and graphene have sp^2 -hybridized carbon atoms arranged in a honeycomb lattice, offering natural compatibility with organic/biological molecules.^[113] He *et al.* reported a testbed containing two oxide-free, non-metallic electrodes, silicon and SWCNTs.^[110] This metal-free testbed eliminates the issue of the metal filament formation in MEJs, avoiding fatigue induced shorts. They observed hysteretic $I - V$ curves for π -conjugated oligo-phenylenethynylene molecules in these silicon-molecule-SWCNT MEJs, which can be useful towards memory storage applications. Control devices without of π -conjugated molecules (bare Si-H or long alkane molecules) produced no hysteresis, indicating that the observed memory effect was intrinsic to the molecules (in combination with these electrodes).

Thin graphene and reduced graphene oxide sheet are optically transparent, making them good candidates for fabricating photo-switching devices. Li *et al.* reported the use of solution-processed, ultrathin rGO as a transparent, soft top-contacts to successfully fabricate solid-state switches operated by thermo-optical stimuli.[112] Seo *et al.* reported the fabrication of a MEJ between two graphene electrodes in which the two ends are chemically and physically bonded to the top and bottom graphene electrodes, respectively.[111] This configuration imparts stability and improved yields due to the soft top contact. Moreover, the transparent graphene electrodes allow stable molecular switching induced by external light stimulus.

Silicon-based materials benefit from decades of intense development in the semiconductor industry and compatibility with complementary metal oxide semiconductor technology, such as controllable conductivity and the tuning of E_f by doping.[114] The work function of silicon depends on the doping, type, and density of charge carriers, but not on the interfacial structure and the chemical binding, which allows for the independent interfacial energy alignment. This distinction is also the reason silicon materials are widely used as bottom electrodes, as was discussed in elsewhere.[86] Silicon-based nanomaterials are used as top electrodes by fabricating MEJs inside a silicon nanogap.[115–118] First, a vertical Si/SiO₂/Si structure is formed, in which the bottom and top electrodes are the heavily doped Si(111) and polycrystalline Si surfaces, respectively. The native oxide layer is then etched using NH₄F to create a nanogap. The nanogap serves as a platform for the formation of thin films or assembly of nanoparticle arrays.[116] Further, the nanogap can be scaled down to include only a few or a single molecule in the junction between the two silicon electrodes.

2.3. SUMMARY

In this chapter, we reviewed the state-of-the-art methods of applying a top contact of the fabrication of MEJs in a sandwiched configuration. Of each method, we briefly discussed its advantages and limitations. In general, the remaining difficulties in the field are the fragility of the organic molecules, the mobility of the molecules in the SAM and the understanding of the interfaces between electrode and the SAM. Creative solutions have been attempted to meet the challenges of encapsulating a defect-free molecular layers between two electrodes and forming stable devices with reproducible and reliable data. We would like to conclude here, there is no the best technique to study the electrical properties of molecules in the field of ME. The choice of which technique to use depends mainly on the motivation of the research work. Every technique for sure will provide interesting and promising results and extend the knowledge in the field of ME.

BIBLIOGRAPHY

- (1) Aradhya, S. V.; Venkataraman, L. Single-Molecule Junctions Beyond Electronic Transport. *Nat. Nanotechnol.* **2013**, *8*, 399–410.
- (2) Schwarz, F.; Lörtscher, E. Break-Junctions for Investigating Transport at the Molecular Scale. *J. Phys.: Condens. Matter* **2014**, *26*, 474201.
- (3) Metzger, R. M. Unimolecular Electronics. *Chem. Rev.* **2015**, *115*, 5056–5115.
- (4) Nichols, R. J.; Higgins, S. J. Single-Molecule Electronics: Chemical and Analytical Perspectives. *Annu. Rev. Anal. Chem.* **2015**, *8*, 389–417.
- (5) Akkerman, H. B.; de Boer, B. Electrical Conduction Through Single Molecules and Self-Assembled Monolayers. *J. Phys.: Condens. Matter* **2007**, *20*, 013001.
- (6) Zhang, Y.; Zhao, Z.; Fracasso, D.; Chiechi, R. C. Bottom-Up Molecular Tunneling Junctions Formed by Self-Assembly. *Isr. J. Chem.* **2014**, *54*, 513–533.
- (7) Vilan, A.; Aswal, D.; Cahen, D. Large-Area, Ensemble Molecular Electronics: Motivation and Challenges. *Chem. Rev.* **2017**, *117*, 4248–4286.
- (8) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1170.
- (9) Xiang, L.; Hines, T.; Palma, J. L.; Lu, X.; Mujica, V.; Ratner, M. A.; Zhou, G.; Tao, N. Non-Exponential Length Dependence of Conductance in Iodide-Terminated Oligothiophene Single-Molecule Tunneling Junctions. *J. Am. Chem. Soc.* **2016**, *138*, 679–687.
- (10) Jeong, H.; Kim, D.; Xiang, D.; Lee, T. High-Yield Functional Molecular Electronic Devices. *ACS Nano* **2017**, *11*, 6511–6548.
- (11) Wold, D. J.; Frisbie, C. D. Formation of Metal-Molecule-Metal Tunnel Junctions: Microcontacts to Alkanethiol Monolayers With a Conducting AFM Tip. *J. Am. Chem. Soc.* **2000**, *122*, 2970–2971.
- (12) Xu, B. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. *Science* **2003**, *301*, 1221–1223.

- (13) Chen, F.; Hihath, J.; Huang, Z.; Li, X.; Tao, N. Measurement of Single-Molecule Conductance. *Annu. Rev. Phys. Chem.* **2007**, *58*, 535–564.
- (14) Morita, T.; Lindsay, S. Determination of Single Molecule Conductances of Alkanedithiols by Conducting-Atomic Force Microscopy With Large Gold Nanoparticles. *J. Am. Chem. Soc.* **2007**, *129*, PMID: 17516649, 7262–7263.
- (15) Li, W.; Sepunaru, L.; Amdursky, N.; Cohen, S. R.; Pecht, I.; Sheves, M.; Cahen, D. Temperature and Force Dependence of Nanoscale Electron Transport via the Cu Protein Azurin. *ACS Nano* **2012**, *6*, 10816–10824.
- (16) Zhang, Y.; Qiu, X.; Gordiichuk, P.; Soni, S.; Krijger, T. L.; Herrmann, A.; Chiechi, R. C. Mechanically and Electrically Robust Self-Assembled Monolayers for Large-Area Tunneling Junctions. *J. Phys. Chem. C* **2017**, *121*, 14920–14928.
- (17) Xie, Z.; Bâldea, I.; Haugstad, G.; Frisbie, C. D. Mechanical Deformation Distinguishes Tunneling Pathways in Molecular Junctions. *J. Am. Chem. Soc.* **2018**, *141*, 497–504.
- (18) Song, H.; Lee, H.; Lee, T. Intermolecular Chain-To-Chain Tunneling in Metal- Alkanethiol -Metal Junctions. *J. Am. Chem. Soc.* **2007**, *129*, 3806–3807.
- (19) Kim; Beebe, J. M.; Jun, Y.; Zhu, X.-Y.; Frisbie, C. D. Correlation Between HOMO Alignment and Contact Resistance in Molecular Junctions: Aromatic Thiols Versus Aromatic Isocyanides. *J. Am. Chem. Soc.* **2006**, *128*, 4970–4971.
- (20) Xie, Z.; Bâldea, I.; Frisbie, C. D. Why One Can Expect Large Rectification in Molecular Junctions Based on Alkane Monothiols and Why Rectification Is So Modest. *Chem. Sci.* **2018**, *9*, 4456–4467.
- (21) Xie, Z.; Bâldea, I.; Frisbie, C. D. Energy Level Alignment in Molecular Tunnel Junctions by Transport and Spectroscopy: Self-Consistency for the Case of Alkyl Thiols and Dithiols on Ag, Au, and Pt Electrodes. *J. Am. Chem. Soc.* **2019**, *141*, 18182–18192.
- (22) Xie, Z.; Bâldea, I.; Smith, C. E.; Wu, Y.; Frisbie, C. D. Experimental and Theoretical Analysis of Nanotransport in Oligophenylene Dithiol Junctions as a Function of Molecular Length and Contact Work Function. *ACS Nano* **2015**, *9*, 8022–8036.
- (23) Xie, Z.; Bâldea, I.; Frisbie, C. D. Determination of Energy-Level Alignment in Molecular Tunnel Junctions by Transport and Spectroscopy: Self-Consistency for the Case of Oligophenylene Thiols and Dithiols on Ag, Au, and Pt Electrodes. *J. Am. Chem. Soc.* **2019**, *141*, 3670–3681.

- (24) Kushmerick, J. G.; Naciri, J.; Yang, J. C.; Shashidhar, R. Conductance Scaling of Molecular Wires in Parallel. *Nano Lett.* **2003**, *3*, 897–900.
- (25) Cuevas, J. C.; Scheer, E., *Molecular Electronics*; WORLD SCIENTIFIC: 2010.
- (26) Gregory, S. Inelastic Tunneling Spectroscopy and Single-Electron Tunneling in an Adjustable Microscopic Tunnel Junction. *Phys. Rev. Lett.* **1990**, *64*, 689–692.
- (27) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. Metal-Molecule Contacts and Charge Transport Across Monomolecular Layers: Measurement and Theory. *Phys. Rev. Lett.* **2002**, *89*, 086802.
- (28) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Schull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. Effect of Bond-Length Alternation in Molecular Wires. *J. Am. Chem. Soc.* **2002**, *124*, 10654–10655.
- (29) Kushmerick, J. G.; Whitaker, C. M.; Pollack, S. K.; Schull, T. L.; Shashidhar, R. Tuning Current Rectification Across Molecular Junctions. *Nanotechnology* **2004**, *15*, S489–S493.
- (30) Beebe, J. M.; Kushmerick, J. G. Nanoscale Switch Elements From Self-Assembled Monolayers on Silver. *Appl. Phys. Lett.* **2007**, *90*, 083117.
- (31) Yoon, H. P.; Maitani, M. M.; Cabarcos, O. M.; Cai, L.; Mayer, T. S.; Allara, D. L. Crossed-Nanowire Molecular Junctions: A New Multispectroscopy Platform for Conduction -Structure Correlations. *Nano Lett.* **2010**, *10*, 2897–2902.
- (32) Blum, A. S.; Kushmerick, J. G.; Pollack, S. K.; Yang, J. C.; Moore, M.; Naciri, J.; Shashidhar, R.; Ratna, B. R. Charge Transport and Scaling in Molecular Wires. *J. Phys. Chem. B* **2004**, *108*, 18124–18128.
- (33) Yu, L. H.; Gergel-Hackett, N.; Zangmeister, C. D.; Hacker, C. A.; Richter, C. A.; Kushmerick, J. G. Molecule-Induced Interface States Dominate Charge Transport in Si-alkyl-metal Junctions. *J. Phys.: Condens. Matter* **2008**, *20*, 374114.
- (34) Loo, Y.-L.; Lang, D. V.; Rogers, J. A.; Hsu, J. W. P. Electrical Contacts to Molecular Layers by Nanotransfer Printing. *Nano Lett.* **2003**, *3*, 913–917.
- (35) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. Interfacial Chemistries for Nanoscale Transfer Printing. *J. Am. Chem. Soc.* **2002**, *124*, 7654–7655.
- (36) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. Additive, Nanoscale Patterning of Metal Films With a Stamp and a Surface Chemistry Mediated Transfer Process: Applications in Plastic Electronics. *Appl. Phys. Lett.* **2002**, *81*, 562–564.

- (37) Balmer, T. E.; Schmid, H.; Stutz, R.; Delamarche, E.; Michel, B.; Spencer, N. D.; Wolf, H. Diffusion of Alkanethiols in PDMS and Its Implications on Microcontact Printing (μ CP). *Langmuir* **2005**, *21*, 622–632.
- (38) Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Willson, C. G.; Whitesides, G. M. New Approaches to Nanofabrication: Molding, Printing, and Other Techniques. *Chem. Rev.* **2005**, *105*, 1171–1196.
- (39) Hsu, J. W. P.; Lang, D. V.; West, K. W.; Loo, Y.-L.; Halls, M. D.; Raghavachari, K. Probing Occupied States of the Molecular Layer in Au-Alkanedithiol-GaAs Diodes. *J. Phys. Chem. B* **2005**, *109*, 5719–5723.
- (40) Martin, C. A.; Smit, R. H. M.; van Egmond, R.; van der Zant, H. S. J.; van Ruitenbeek, J. M. A Versatile Low-Temperature Setup for the Electrical Characterization of Single-Molecule Junctions. *Rev. Sci. Instrum.* **2011**, *82*, 053907.
- (41) Shimizu, K.; Fabbri, J.; Jelincic, J.; Melosh, N. Soft Deposition of Large-Area Metal Contacts for Molecular Electronics. *Adv. Mater.* **2006**, *18*, 1499–1504.
- (42) Sanetra, N.; Karipidou, Z.; Wirtz, R.; Knorr, N.; Rosselli, S.; Nelles, G.; Offenhäusser, A.; Mayer, D. Printing of Highly Integrated Crossbar Junctions. *Adv. Funct. Mater.* **2012**, *22*, 1129–1135.
- (43) Xia, Q.; Robinett, W.; Cumbie, M. W.; Banerjee, N.; Cardinali, T. J.; Yang, J. J.; Wu, W.; Li, X.; Tong, W. M.; Strukov, D. B.; Snider, G. S.; Medeiros-Ribeiro, G.; Williams, R. S. Memristor-Cmos Hybrid Integrated Circuits for Reconfigurable Logic. *Nano Lett.* **2009**, *9*, 3640–3645.
- (44) Borghetti, J.; Li, Z.; Straznicky, J.; Li, X.; Ohlberg, D. A. A.; Wu, W.; Stewart, D. R.; Williams, R. S. A Hybrid Nanomemristor/Transistor Logic Circuit Capable of Self-Programming. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 1699–1703.
- (45) Kim, K.-H.; Gaba, S.; Wheeler, D.; Cruz-Albrecht, J. M.; Hussain, T.; Narayan, S.; Lu, W. A Functional Hybrid Memristor Crossbar-Array/Cmos System for Data Storage and Neuromorphic Applications. *Nano Lett.* **2011**, *12*, 389–395.
- (46) Linn, E.; Rosezin, R.; Tappertzhofen, S.; Böttger, U.; Waser, R. Beyond Von Neumann—logic Operations in Passive Crossbar Arrays Alongside Memory Operations. *Nanotechnology* **2012**, *23*, 305205.
- (47) Han, Y.; Nickle, C.; Zhang, Z.; Astier, H. P. A. G.; Duffin, T. J.; Qi, D.; Wang, Z.; del Barco, E.; Thompson, D.; Nijhuis, C. A. Electric-Field-Driven Dual-Functional Molecular Switches in Tunnel Junctions. *Nat. Mater.* **2020**, *19*, 843–848.

- (48) Niskala, J. R.; Rice, W. C.; Bruce, R. C.; Merkel, T. J.; Tsui, F.; You, W. Tunneling Characteristics of Au–Alkanedithiol–Au Junctions formed via Nanotransfer Printing (nTP). *J. Am. Chem. Soc.* **2012**, *134*, 12072–12082.
- (49) Haick, H.; Cahen, D. Contacting Organic Molecules by Soft Methods: Towards Molecule-Based Electronic Devices. *Acc. Chem. Res.* **2008**, *41*, 359–366.
- (50) Yablonovitch, E.; Hwang, D. M.; Gmitter, T. J.; Florez, L. T.; Harbison, J. P. Van Der Waals Bonding of GaAs Epitaxial Liftoff Films Onto Arbitrary Substrates. *Appl. Phys. Lett.* **1990**, *56*, 2419–2421.
- (51) Moons, E.; Bruening, M.; Shanzer, A.; Beier, J.; Cahen, D. Electron Transfer in Hybrid Molecular Solid-State Devices. *Synth. Met.* **1996**, *76*, 245–248.
- (52) Vilan, A.; Shanzer, A.; Cahen, D. Molecular Control Over Au/GaAs Diodes. *Nature* **2000**, *404*, 166–168.
- (53) Vilan, A.; Cahen, D. Soft Contact Deposition Onto Molecularly Modified GaAs. Thin Metal Film Flotation: Principles and Electrical Effects. *Adv. Funct. Mater.* **2002**, *12*, 795–807.
- (54) Ron, I.; Sepunaru, L.; Itzhakov, S.; Belenkova, T.; Friedman, N.; Pecht, I.; Sheves, M.; Cahen, D. Proteins as Electronic Materials: Electron Transport Through Solid-State Protein Monolayer Junctions. *J. Am. Chem. Soc.* **2010**, *132*, 4131–4140.
- (55) Ikram, I. M.; Rabinal, M. K.; Kalasad, M. N.; Mulimani, B. G. Formation of Electronic Junctions on Molecularly Modified Surfaces by Lift-And-Float Electrical Contacts. *Langmuir* **2009**, *25*, 3305–3309.
- (56) Stein, N.; Korobko, R.; Yaffe, O.; Lavan, R. H.; Shpaisman, H.; Tirosh, E.; Vilan, A.; Cahen, D. Nondestructive Contact Deposition for Molecular Electronics: Si-Alkyl//Au Junctions. *J. Phys. Chem. C* **2010**, *114*, 12769–12776.
- (57) Krabbenborg, S. O.; Wilbers, J. G. E.; Huskens, J.; van der Wiel, W. G. Symmetric Large-Area Metal-Molecular Monolayer-Metal Junctions by Wedging Transfer. *Adv. Funct. Mater.* **2012**, *23*, 770–776.
- (58) Jeong, H.; Kim, D.; Kim, P.; Cho, M. R.; Hwang, W.-T.; Jang, Y.; Cho, K.; Min, M.; Xiang, D.; Park, Y. D.; Jeong, H.; Lee, T. A New Approach for High-Yield Metal–molecule–metal Junctions by Direct Metal Transfer Method. *Nanotechnology* **2014**, *26*, 025601.
- (59) Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L.; Tour, J. M. Nanoscale Metal/Self-Assembled Monolayer/Metal Heterostructures. *Appl. Phys. Lett.* **1997**, *71*, 611–613.

- (60) Chen, J. Large On-Off Ratios and Negative Differential Resistance in a Molecular Electronic Device. *Science* **1999**, 286, 1550–1552.
- (61) Majumdar, N.; Gergel, N.; Routenberg, D.; Bean, J. C.; Harriott, L. R.; Li, B.; Pu, L.; Yao, Y.; Tour, J. M. Nanowell Device for the Electrical Characterization of Metal–molecule–metal Junctions. *J. Vac. Sci. Technol., B: Nanotechnol. Microelectron.: Mater., Process., Meas., Phenom.* **2005**, 23, 1417.
- (62) Simeone, F. C.; Rampi, M. A. Test-beds for Molecular Electronics: Metal- Molecules -Metal Junctions Based on Hg Electrodes. *CHIMIA Int. J. Chem.* **2010**, 64, 362–369.
- (63) Race, H. H.; Reynolds, S. I. Electrical Properties of Multimolecular Films. *J. Am. Chem. Soc.* **1939**, 61, 1425–1432.
- (64) Mann, B.; Kuhn, H. Tunneling Through Fatty Acid Salt Monolayers. *J. Appl. Phys.* **1971**, 42, 4398–4405.
- (65) Becucci, L.; Moncelli, M. R.; Guidelli, R. Surface Charge Density Measurements on Mercury Electrodes Covered by Phospholipid Monolayers. *J. Electroanal. Chem.* **1996**, 413, 187–193.
- (66) Slowinski, K.; Chamberlain, R. V.; Bilewicz, R.; Majda, M. Evidence for Inefficient Chain-To-Chain Coupling in Electron Tunneling Through Liquid Alkanethiol Monolayer Films on Mercury. *J. Am. Chem. Soc.* **1996**, 118, 4709–4710.
- (67) Slowinski, K.; Chamberlain, R. V.; Miller, C. J.; Majda, M. Through-Bond and Chain-To-Chain Coupling. Two Pathways in Electron Tunneling Through Liquid Alkanethiol Monolayers on Mercury Electrodes. *J. Am. Chem. Soc.* **1997**, 119, 11910–11919.
- (68) Slowinski, K.; Slowinska, K. U.; Majda, M. Electron Tunneling Across Hexadecanethiolate Monolayers on Mercury Electrodes: Reorganization Energy, Structure, and Permeability of the Alkane/Water Interface. *J. Phys. Chem. B* **1999**, 103, 8544–8551.
- (69) Slowinski, K.; Fong, H. K. Y.; Majda, M. Mercury-Mercury Tunneling Junctions. 1. Electron Tunneling Across Symmetric and Asymmetric Alkanethiolate Bilayers. *J. Am. Chem. Soc.* **1999**, 121, 7257–7261.
- (70) Slowinski, K.; Majda, M. Mercury–mercury Tunneling Junctions. *J. Electroanal. Chem.* **2000**, 491, 139–147.
- (71) Weiss, E. A.; Kriebel, J. K.; Rampi, M.-A.; Whitesides, G. M. The Study of Charge Transport Through Organic Thin Films: Mechanism, Tools and Applications. *Phil. Trans. Royal Soc. A* **2007**, 365, 1509–1537.

- (72) Holmlin, R. E.; Haag, R.; Chabynyc, M. L.; Ismagilov, R. F.; Cohen, A. E.; Terfort, A.; Rampi, M. A.; Whitesides, G. M. Electron Transport Through Thin Organic Films in Metal-Insulator-Metal Junctions Based on Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2001**, *123*, 5075–5085.
- (73) Holmlin, R. E.; Ismagilov, R. F.; Haag, R.; Mujica, V.; Ratner, M. A.; Rampi, M. A.; Whitesides, G. M. Correlating Electron Transport and Molecular Structure in Organic Thin Films. *Angew. Chem., Int. Ed.* **2001**, *40*, 2316–2320.
- (74) Selzer, Y.; Salomon, A.; Cahen, D. The Importance of Chemical Bonding to the Contact for Tunneling Through Alkyl Chains. *J. Phys. Chem. B* **2002**, *106*, 10432–10439.
- (75) Salomon, A.; Böcking, T.; Gooding, J. J.; Cahen, D. How Important Is the Interfacial Chemical Bond for Electron Transport Through Alkyl Chain Monolayers? *Nano Lett.* **2006**, *6*, 2873–2876.
- (76) Zhu, L.; Popoff, R. T. W.; Yu, H.-Z. Metastable Molecular Metal–Semiconductor Junctions. *J. Phys. Chem. C* **2015**, *119*, 1826–1831.
- (77) Fan, X.-l.; Wang, C.; Yang, D.-l.; Wan, L.-j.; Bai, C. Molecule Rectifier Fabricated by Capillary Tunnel Junction. *Chem. Phys. Lett.* **2002**, *361*, 465–468.
- (78) Liu, Y.; Fan, X.; Yang, D.; Wang, C.; Wan, L.; Bai, C. Tunneling Characteristics of Octadecyl Derivatives on Tin and Indium Electrodes. *Langmuir* **2004**, *20*, 855–861.
- (79) Li, X.; Fan, X.; Liu, X.; Zhu, M.; Jin, H. In *2008 3rd IEEE International Conference on Nano/Micro Engineered and Molecular Systems*, IEEE: 2008.
- (80) Ferri, V.; Elbing, M.; Pace, G.; Dickey, M.; Zharnikov, M.; Samorì, P.; Mayor, M.; Rampi, M. Light-Powered Electrical Switch Based on Cargo-Lifting Azobenzene Monolayers. *Angew. Chem. Int. Ed.* **2008**, *47*, 3407–3409.
- (81) Chiechi, R.; Weiss, E.; Dickey, M.; Whitesides, G. Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, 142–144.
- (82) Wang, D.; Fracasso, D.; Nurbawono, A.; Annadata, H. V.; Sangeeth, C. S. S.; Yuan, L.; Nijhuis, C. A. Tuning the Tunneling Rate and Dielectric Response of SAM-Based Junctions via a Single Polarizable Atom. *Adv. Mater.* **2015**, *27*, 6689–6695.
- (83) Douvogianni, E.; Qiu, X.; Qiu, L.; Jahani, F.; Kooistra, F. B.; Hummelen, J. C.; Chiechi, R. C. Soft Nondamaging Contacts Formed From Eutectic Ga–In for the Accurate Determination of Dielectric Constants of Organic Materials. *Chem. Mater.* **2018**, *30*, 5527–5533.

- (84) Byeon, S. E.; Kim, M.; Yoon, H. J. Maskless Arbitrary Writing of Molecular Tunnel Junctions. *ACS Appl. Mater. Interfaces* **2017**, *9*, 40556–40563.
- (85) 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.
- (86) Liu, Y.; Qiu, X.; Soni, S.; Chiechi, R. C. Charge-transport Through Molecular Ensembles: Recent Progress in Molecular Electronics. *Chemical Physics Review* **2021** (accepted).
- (87) Dickey, M. D.; Chiechi, R. C.; Larsen, R. J.; Weiss, E. A.; Weitz, D. A.; Whitesides, G. M. Eutectic Gallium–Indium (EGaIn): A Liquid Metal Alloy for the Formation of Stable Structures in Microchannels at Room Temperature. *Adv. Funct. Mater.* **2008**, *18*, 1097–1104.
- (88) Larsen, R. J.; Dickey, M. D.; Whitesides, G. M.; Weitz, D. A. Viscoelastic properties of oxide-coated liquid metals. *J. Rheol.* **2009**, *53*, 1305–1326.
- (89) Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. Mechanism of Rectification in Tunneling Junctions Based on Molecules with Asymmetric Potential Drops. *Journal of the American Chemical Society* **2010**, *132*, 18386–18401.
- (90) Nijhuis, C. A.; Reus, W. F.; Barber, J. R.; Whitesides, G. M. Comparison of SAM-Based Junctions With Ga₂O₃/EGaIn Top Electrodes to Other Large-Area Tunneling Junctions. *J. Phys. Chem. C* **2012**, *116*, 14139–14150.
- (91) Wan, A.; Jiang, L.; Sangeeth, C. S. S.; Nijhuis, C. A. Reversible Soft Top-Contacts to Yield Molecular Junctions With Precise and Reproducible Electrical Characteristics. *Adv. Funct. Mater.* **2014**, *24*, 4442–4456.
- (92) Karuppannan, S. K.; Hongting, H.; Troadec, C.; Vilan, A.; Nijhuis, C. A. Ultra-smooth and Photoresist-Free Micropore-Based EGaIn Molecular Junctions: Fabrication and How Roughness Determines Voltage Response. *Adv. Funct. Mater.* **2019**, *29*, 1904452.
- (93) Mbindyo, J. K. N.; Mallouk, T. E.; Mattzela, J. B.; Kratochvilova, I.; Razavi, B.; Jackson, T. N.; Mayer, T. S. Template Synthesis of Metal Nanowires Containing Monolayer Molecular Junctions. *J. Am. Chem. Soc.* **2002**, *124*, 4020–4026.
- (94) Maitani, M. M.; Allara, D. L.; Ohlberg, D. A. A.; Li, Z.; Williams, R. S.; Stewart, D. R. High Integrity Metal/Organic Device Interfaces via Low Temperature Buffer Layer Assisted Metal Atom Nucleation. *Appl. Phys. Lett.* **2010**, *96*, 173109.

- (95) Puebla-Hellmann, G.; Venkatesan, K.; Mayor, M.; Lörtscher, E. Metallic Nanoparticle Contacts for High-Yield, Ambient-Stable Molecular-Monolayer Devices. *Nature* **2018**, *559*, 232–235.
- (96) Preiner, M. J.; Melosh, N. A. Creating Large Area Molecular Electronic Junctions Using Atomic Layer Deposition. *Appl. Phys. Lett.* **2008**, *92*, 213301.
- (97) Akkerman, H. B.; Blom, P. W. M.; de Leeuw, D. M.; de Boer, B. Towards Molecular Electronics With Large-Area Molecular Junctions. *Nature* **2006**, *441*, 69–72.
- (98) Milani, F.; Grave, C.; Ferri, V.; Samorì, P.; Rampi, M. A. Ultrathin π -Conjugated Polymer Films for Simple Fabrication of Large-Area Molecular Junctions. *ChemPhysChem* **2007**, *8*, 515–518.
- (99) Neuhausen, A. B.; Hosseini, A.; Sulpizio, J. A.; Chidsey, C. E. D.; Goldhaber-Gordon, D. Molecular Junctions of Self-Assembled Monolayers With Conducting Polymer Contacts. *ACS Nano* **2012**, *6*, 9920–9931.
- (100) Wang, G.; Kim, Y.; Choe, M.; Kim, T.-W.; Lee, T. A New Approach for Molecular Electronic Junctions with a Multilayer Graphene Electrode. *Adv. Mater.* **2010**, *23*, 755–760.
- (101) Li, T.; Hauptmann, J. R.; Wei, Z.; Petersen, S.; Bovet, N.; Vosch, T.; Nygård, J.; Hu, W.; Liu, Y.; Bjørnholm, T.; Nørgaard, K.; Laursen, B. W. Solution-Processed Ultrathin Chemically Derived Graphene Films as Soft Top Contacts for Solid-State Molecular Electronic Junctions. *Adv. Mater.* **2012**, *24*, 1333–1339.
- (102) Kühnel, M.; Petersen, S. V.; Hviid, R.; Overgaard, M. H.; Laursen, B. W.; Nørgaard, K. Monolayered Graphene Oxide as a Low Contact Resistance Protection Layer in Alkanethiol Solid-State Devices. *J. Phys. Chem. C* **2018**, *122*, 9731–9737.
- (103) Karuppannan, S. K.; Neoh, E. H. L.; Vilan, A.; Nijhuis, C. A. Protective Layers Based on Carbon Paint to Yield High-Quality Large-Area Molecular Junctions With Low Contact Resistance. *J. Am. Chem. Soc.* **2020**, *142*, 3513–3524.
- (104) Hal, P. A. V.; Smits, E. C. P.; Geuns, T. C. T.; Akkerman, H. B.; Brito, B. C. D.; Perissinotto, S.; Lanzani, G.; Kronemeijer, A. J.; Geskin, V.; Cornil, J.; Blom, P. W. M.; Boer, B. D.; Leeuw, D. M. D. Upscaling, integration and electrical characterization of molecular junctions. *Nat. Nanotechnol.* **2008**, *3*, 749–754.
- (105) Akkerman, H. B.; Kronemeijer, A. J.; Harkema, J.; van Hal, P. A.; Smits, E. C.; de Leeuw, D. M.; Blom, P. W. Stability of Large-Area Molecular Junctions. *Org. Electron.* **2010**, *11*, 146–149.

- (106) Cademartiri, L.; Thuo, M. M.; Nijhuis, C. A.; Reus, W. F.; Tricard, S.; Barber, J. R.; Sodhi, R. N. S.; Brodersen, P.; Kim, C.; Chiechi, R. C.; Whitesides, G. M. Electrical Resistance of AgTS–S(CH₂)_n–1CH₃//Ga₂O₃/EGaIn Tunneling Junctions. *J. Phys. Chem. C* **2012**, *116*, 10848–10860.
- (107) Seo, J. H.; Gutacker, A.; Sun, Y.; Wu, H.; Huang, F.; Cao, Y.; Scherf, U.; Heeger, A. J.; Bazan, G. C. Improved High-Efficiency Organic Solar Cells via Incorporation of a Conjugated Polyelectrolyte Interlayer. *J. Am. Chem. Soc.* **2011**, *133*, 8416–8419.
- (108) Akkerman, H.; Kronemeijer, A.; van Hal, P.; de Leeuw, D.; Blom, P.; de Boer, B. Self-Assembled-Monolayer Formation of Long Alkanedithiols in Molecular Junctions. *Small* **2008**, *4*, 100–104.
- (109) Najarian, A. M.; Szeto, B.; Tefashe, U. M.; McCreery, R. L. Robust All-Carbon Molecular Junctions on Flexible or Semi-Transparent Substrates Using “Process-Friendly” Fabrication. *ACS Nano* **2016**, *10*, 8918–8928.
- (110) He, J.; Chen, B.; Flatt, A. K.; Stephenson, J. J.; Doyle, C. D.; Tour, J. M. Metal-Free Silicon–molecule–nanotube Testbed and Memory Device. *Nat. Mater.* **2005**, *5*, 63–68.
- (111) Seo, S.; Min, M.; Lee, S. M.; Lee, H. Photo-Switchable Molecular Monolayer Anchored Between Highly Transparent and Flexible Graphene Electrodes. *Nat. Commun.* **2013**, *4*, 1920.
- (112) Li, T. et al. Ultrathin Reduced Graphene Oxide Films as Transparent Top-Contacts for Light Switchable Solid-State Molecular Junctions. *Adv. Mater.* **2013**, *25*, 4164–4170.
- (113) Chung, D. D. L. Electrical Applications of Carbon Materials. *J. Mater. Sci.* **2004**, *39*, 2645–2661.
- (114) Buriak, J. M. Organometallic Chemistry on Silicon and Germanium Surfaces. *Chem. Rev.* **2002**, *102*, 1271–1308.
- (115) Berg, J.; Che, F.; Lundgren, P.; Enoksson, P.; Bengtsson, S. Electrical Properties of Si–SiO₂–Si Nanogaps. *Nanotechnology* **2005**, *16*, 2197–2202.
- (116) Howell, S. W.; Dirk, S. M.; Childs, K.; Pang, H.; Blain, M.; Simonson, R. J.; Tour, J. M.; Wheeler, D. R. Mass-Fabricated One-Dimensional Silicon Nanogaps for Hybrid Organic/Nanoparticle Arrays. *Nanotechnology* **2005**, *16*, 754–758.

- (117) Ashwell, G. J.; Phillips, L. J.; Robinson, B. J.; Urasinska-Wojcik, B.; Lambert, C. J.; Grace, I. M.; Bryce, M. R.; Jitchati, R.; Tavasli, M.; Cox, T. I.; Sage, I. C.; Tuffin, R. P.; Ray, S. Molecular Bridging of Silicon Nanogaps. *ACS Nano* **2010**, *4*, 7401–7406.
- (118) Ashwell, G. J.; Phillips, L. J.; Robinson, B. J.; Barnes, S. A.; Williams, A. T.; Urasinska-Wojcik, B.; Lambert, C. J.; Grace, I. M.; Cox, T. I.; Sage, I. C. Synthesis of Covalently Linked Molecular Bridges Between Silicon Electrodes in CMOS-Based Arrays of Vertical Si/SiO₂/Si Nanogaps. *Angew. Chem., Int. Ed.* **2011**, *50*, 8722–8726.

3

INTERMOLECULAR EFFECTS ON TUNNELING THROUGH ACENES IN LARGE-AREA AND SINGLE-MOLECULE JUNCTIONS

The Contents of this chapter were published in Journal of Physical Chemistry C. (doi:10.1021/acs.jpcc.0c05781). I would like to thank Dr. Yong Ai and Dr. Marco Carlotti for their preliminary observations, Dr. Marco Carlotti for EGaIn measurement, Dr. Harry T. Jonkman for the training of ARXPS, Saurabh Soni and Dr. Remco W. A. Havenith for the ADF/BAND calculations, Luca Ornago, Dr. Maria El Abbassi and Prof. Herre S. J. van der Zant for MCBJ measurement, Andika Asyuda and Prof. Michael Zharnikov for HRXPS measurement, Prof. Ryan C. Chiechi for his supervision.

3.1. INTRODUCTION

Understanding the correlation between the chemical structure of molecules and charge transport through molecular junctions is one of the biggest challenges of Molecular Electronics.[1] By chemical design, several devices with functionality, such as rectification and switching, have already been demonstrated.[2–4] The synthetic control over the structure of organic molecules makes them useful functional elements,[5] particularly π -conjugated molecules, because their electronic delocalization facilitates charge-transport in both hopping and tunneling processes. Quantum Interference (QI) effects can also be accessed readily by synthetically tuning the wave-functions of the π system.[6] These effects have been predicted theoretically and observed experimentally in π -conjugated molecules that exhibit cross-conjugation, [7–12] meta-substitution[13, 14] and non-covalent spatial overlap.[6, 15, 16]

Oligo(phenylene-ethynylene) (OPE) compounds and their derivatives are a widely-used class of functional π -conjugated molecular wires, rigid and rod-like molecules, making them the building blocks of large-area and single-molecule junctions.[16–19] Oligoacenes are another class of rigid, planar, aromatic and linear π -conjugated molecular wires. One interesting feature of oligoacene is its exponentially narrowing HOMO-LUMO band-gap,[20] which attracts lots of researches on their electronic properties.[21–23]

Figure 3.1 Chemical structures of OPE3-like Acene series.

Here, we study five OPE derivatives in which the central benzene ring is replaced by a series of oligoacenes: naphthalene (NP), anthracene (9,10-AC), tetracene (TC) and pentacene (PC). As shown in Figure 3.1, this functionalization strategy extends π -conjugation perpendicular to the long axis of the molecular wire, like in cruciforms.[24, 25] This acene series maintains the same linear conjugation pattern and length between the thiol anchors, allowing the interrogation of the effects of extended conjugation in both large-area and single-

molecule junctions without changing the width of the tunneling barrier or introducing heteroatoms.

3.2. RESULTS AND DISCUSSION

TRANSMISSION SPECTRA

We first simulated the transmission spectra of the acene series using Density Functional Theory (DFT) combined with non-equilibrium Greens function (NEGF) transport calculations using the Artaios software package.[26] Figure 3.2 shows the transmission spectra for the acene series in single-molecule, Au/molecule/Au geometry. The spectra show that the frontier orbital gap (E_g) between the highest occupied π -state (HOPS) and the lowest unoccupied π -state (LUPS) decreases as the conjugation-length increases from **OPE3** to **PC**. Large, positive resonances move towards the Fermi level E_f with increasing conjugation length, reflecting the shrinking frontier molecular orbital gap; however, based on these simulated transmission spectra, the low-bias conductance, which is determined by transmission at E_f , is not expected to change much as the transmission probability near E_f increases by only a factor of five when going from **OPE3** to **PC**. Thus, the NEGF-DFT simulation predicts the experimental trend in low-bias conductance to increase moderately and continuously from **OPE3** to **PC** as E_g decreases.

Figure 3.2 Transmission spectra for **OPE3**, **NP**, **9,10-AC**, **TC** and **PC**. The x-axis is referenced to an approximate Fermi level of $E_f = -4.3$ eV for EGaIn (see Ref. 27).

Figure 3.3 Plots of $\log|J|$ (the units of J are A cm^{-2}) versus V for SAMs using EGaIn top-contacts ($\text{Au}^{\text{TS}}/\text{SAM}/\text{EGaIn}$). Black squares for **OPE3**, blue circles for **NP**, lemon-yellow up-triangle for **9,10-AC**, red down-triangle for **TC**, and darkgreen left-triangle for **PC**. Each data point is the mean from a Gaussian fit to a histogram of $\log|J|$.

EGaIn MEASUREMENT

We measured tunneling charge-transport through large-area junctions comprising **OPE3**, **NP**, **9,10-AC**, **TC** and **PC** molecular wires using conformal eutectic Ga-In (EGaIn) contacts as top electrodes.[28] To ensure that high-quality self-assembled monolayers (SAMs) are formed, we used an *in situ* deprotection strategy that is optimized for large, π -conjugated molecules[16, 17] to grow SAMs directly on ultra-smooth Au substrates prepared by template-stripping (Au^{TS}).[29] Figure 3.3 shows the current-density versus voltage (J/V) curves from the Acene series. **OPE3**, **9,10-AC** and **TC** showed nearly the same conductance, while the conductance of **NP** was slightly higher. However, the low-bias conductance value of **PC** is significantly lower than the rest of the series, despite having the smallest E_g . While this observation could result from poor quality SAMs, spectroscopic evidence suggests that SAMs of **PC** do not differ significantly from the rest (see below). These results deviate from those predicted by the transmission spectra in Figure 3.2, suggesting that the NEGF-DFT simulations are not capturing a key physical detail that is intrinsic either to the molecules or the SAMs.

SAM CHARACTERIZATIONS

We characterized SAMs of the acene series molecules by several complementary techniques, including Atomic Force Microscopy (AFM) and synchrotron-based X-ray photoelectron spectroscopy (XPS). AFM images (Figure 3.4) show that the surface morphologies of the SAMs are similar. The effective thicknesses of the acene SAMs were measured by angle-

Figure 3.4 AFM images of the SAMs of **OPE3**, **NP**, **9,10-AC**, **TC** and **PC** on Au^{TS} .

Table 3.1 Effective thickness of SAMs of Acene molecules on Au surface (Au^{TS}) by angle-resolved XPS. Packing Density of **NP**, **9,10-AC**, **TC**, **PC** and **SC18** SAMs derived from the synchrotron-based XPS data. The **SC18** is served as reference. The accuracy of the packing density values is $\pm 10\%$

	thickness($\text{\AA}$)	packing density (molecules/ cm^2)
SC18	20.9 ± 0.2	4.63×10^{14}
OPE3	24.8 ± 2.3	3.5×10^{14} *
NP	21.0 ± 1.7	3.0×10^{14}
9,10-AC	34.9 ± 4.5	2.9×10^{14}
TC	26.4 ± 1.9	2.2×10^{14}
PC	26.8 ± 2.1	2.9×10^{14}

* This value is from our earlier work in ref. [16]

resolved XPS in a home-built machine.[30] The results are summarized in Table 3.1 along with the value for aliphatic octadecanethiol SAM, **SC18** as a reference.[31] The thickness values for all acene SAMs, except for **9,10-AC**, are comparable, but slightly higher than that for **SC18** in spite of the similar molecular lengths. On the one hand, this difference may be related to the different attenuation lengths of the photoelectrons for aliphatic and aromatic compounds. On the other hand, it can result from the sensitivity of acenes to oxidation during the unavoidable, brief exposure to air upon loading the samples into the vacuum chamber of the XPS spectrometer.[32, 33] The somewhat higher thickness of **9,10-AC** can be tentatively explained by deprotection agent contamination for this particular sample. Most important, however, is that the thickness of **PC** was very similar to those of the other SAMs.

Further, the acene SAMs, except for **OPE3** studied in detail before,[16] were characteri-

Figure 3.5 C 1s XP spectra of **NP**, **9,10-AC**, **TC**, **PC** and reference **SC18** SAMs on Au/mica substrates. The positions of the observed peak are marked by red dash lines.

zed by synchrotron-based XPS. Representative C 1s XP spectra of these SAMs, measured with an energy resolution of approximately 0.3 eV and presented in [Figure 3.5](#), show a single, nearly symmetric peak associated with the backbone of the acene molecules. As expected for such molecules,^[34] this peak is shifted to lower binding energy (284.8 eV) as compared to that for **SC18** (285.0 eV). Most important, however, is the absence of any perceptible signals associated with the presence of oxygen-containing and nitrogen-containing contaminants. In addition to this qualitative analysis, the packing density of the acene SAMs was roughly estimated. The results are presented in [Table 3.1](#). The values vary to some extent over the series but are similar to each other, including **PC**. Thus, the morphology of the SAMs alone cannot explain the abnormally low conductance of **PC**.

MCBJ MEASUREMENT

Having established that the unexpected experimental trends in conductance are most likely not due to artifacts in the SAMs, we turned to single-molecule measurements to disentangle the properties of individual molecules from intermolecular effects present in SAMs.

Figure 3.6 a) 2D conductance-displacement (left panel) and 1D conductance (right panel) histograms of **OPE3**. b) 2D conductance-displacement (left panel) and 1D conductance (right panel) histograms of the corresponding high-conductance class extracted through clustering. c) 1D conductance histograms of the high-conductance class for all molecules of the studied series. Each histogram includes all measurements from the corresponding molecule obtained after clustering. Counts were re-scaled by peak height.

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Table 3.2 Average most-probable conductance (plus-minus standard deviation) for each molecule. The values are reported for the raw data, for the high-conductance class and for the low-conductance class. In the latter case, if multiple peaks were present, only the highest one was used to compute the values in this table.

	Raw data	High-conductance class	Low-conductance class
OPE3	$7.6 \pm 1.9 \times 10^{-5}$	$9.4 \pm 0.1 \times 10^{-5}$	$3.8 \pm 2.3 \times 10^{-6}$
NP	$1.1 \pm 0.3 \times 10^{-4}$	$1.3 \pm 0.2 \times 10^{-4}$	$2.1 \pm 1.7 \times 10^{-5}$
9,10-AC	$3.1 \pm 1.0 \times 10^{-4}$	$3.6 \pm 0.8 \times 10^{-4}$	$2.8 \pm 1.0 \times 10^{-5}$
TC	$2.1 \pm 0.6 \times 10^{-4}$	$3.1 \pm 0.6 \times 10^{-4}$	$3.6 \pm 1.3 \times 10^{-5}$
PC	$3.6 \pm 0.7 \times 10^{-4}$	$5.2 \pm 0.3 \times 10^{-4}$	$8.0 \pm 3.0 \times 10^{-6}$

Thus, in parallel with SAM measurements, single molecular scale investigation of the acene-substituted OPE3s was performed using the Mechanically Controllable Break-Junction technique (MCBJ)[35, 36]. **OPE3** and their derivatives have been extensively studied in single-molecule junctions, and they show a conductance plateau at around $1 \times 10^{-4} G_0$ [37]. However, additional lower conductance features have been reported, which at least in part are thought to be caused by the formation of $\pi-\pi$ stacked dimers of which each is coupled to one electrode[18, 38]. In the measurements performed on the series of acene substituted OPE3s, a high-conductance plateau could be identified in all cases, together with low-conductance features (Figure 3.6 a). The most-probable conductance values obtained by fitting the data are reported in Table 3.2.

A reference-free clustering algorithm was used to better identify the molecular features emerging from the measurements, similar to previous reports [39, 40]. In this way, three main categories of classes were identified: the high-conductance plateau, the low-conductance features, and traces with no clear signature of a molecule (“empty” traces). An example of the resulting histograms of the high-conductance class is given in Figure 3.6 b. All measurements consistently showed this class, whose conductance at the peak in the 1D histograms follows the trend: **OPE3** < **NP** < **9,10-AC** $\approx$ **TC** < **PC** (Figure 3.6 c, Table 3.2), in agreement with the transmission calculated for this series of molecules (Figure 3.2). Note that the conductance peak in the 1D histograms is more prominent and narrower in the high-conductance class than in the unfiltered data, yielding a more accurate estimation of the most-probable molecule conductance. On the other hand, the low-conductance features do not appear to follow a clear trend (Table 3.2): sometimes they appear as slanted traces at $\approx 1 \times 10^{-6} G_0$ (as for **OPE3**), as shorter plateaus at around $1 \times 10^{-5} G_0$ (as for **TC**), as long (> 2 nm) straight plateaus in the $1 \times 10^{-5} \sim 1 \times 10^{-6} G_0$ range (mostly for **PC**), or even as combinations of the aforementioned behaviors (**NP** and **9,10-AC**).

Figure 3.7 A) Experimental MCBJ (triangles) and simulated (stars) conductances of single-molecule junctions: Up-triangles are from the high-conductance plateaux; down-triangles are from the low-conductance plateaux; and stars are conductances as $G = G_0 T(0)$ from the DFT simulations shown in Fig. 3.2. B) Conductances of SAMs of the acene series, extracted from the J/V traces of EGaIn data down in Fig. 3.3.

LOW-BIAS CONDUCTANCE: MCBJ VS. EGaIn

Figure 3.7 compares the trends in low-bias conductance for the acene series in single-molecule MCBJs and SAMs in EGaIn junctions (extracted from the low-bias region, see experimental section). While the MCBJ data show both high- and low-conductance peaks for each acene, the EGaIn data show one value per molecule. The EGaIn values are clustered together, with the exception of **PC**; the conductance of this molecule is significantly less with respect to the others. The trend in the high-conductance values in the MCBJs data are in agreement with the transmission calculations presented in Figure 3.2. In contrast, the low conductance plateau and the EGaIn data are not compatible with these calculations, suggesting that the experiments are capturing effects in addition to transport through isolated single-molecules.

RELATING PACKING TO CONDUCTANCE

LOW-BIAS CONDUCTANCE IN SAMs

In order to make it clear that conductance behavior of **PC** SAM is quite different among the Acene series, we also calculated the conductance of individual molecules at low bias by using data from EGaIn measurement and HRXPS measurement (Figure 3.8). The conductance of individual molecule is calculated by using the formula:

$$G/molecule = \frac{(dJ/dV) \times A_{eff}}{\rho \times A_{eff}} \quad (3.1)$$

dJ/dV is obtained from the EGaIn measurement at low bias, the details are stated later in the experimental section. A_{eff} is the effective contact area between EGaIn tip and the substrate.

$A_{\text{eff}} = \chi_0 \times A$ (A is the real contact area, which is defined by the diameter of the tip, χ_0 is the correction factor of effective contact area). In this case, A_{eff} can be easily leaved out as it showed up both in the numerator and denominator. Packing density ρ is obtained from XPS and is listed in Table 3.1.

Figure 3.8 Conductance of individual molecule at low bias calculated from EGaIn measurement and HRXPS measurement. The value of conductance of **PC** is lower than the other four molecules.

QUALITATIVE DESCRIPTION OF PACKING

Figure 3.9 is a top-down view showing how intermolecular interaction might develop in the Acene series on Au(111) substrate. The lattice distance a is $2.88 \text{ \AA}$ and the S-S distance is $\sqrt{3}a$. The colored circles represent axial benzene rings and the intersecting lines show the width of the perpendicular acene functionality. Based on that the value of packing density of the five SAMs shows no big difference (Table 3.1), here we arranged same amount of each molecules in the Au surface within the same-sized gold surface. We see that **OPE3**, **NP** and **9,10-AC** can be packed freely while **TC** and **PC** lost some freedoms. Figure 3.9 also shows two types of **TC** SAMs (d,e) and two types of **PC** SAMs (f,g). Type d and type f are less favored arrangement as the inter-molecule interactions between aromatic rings would be big. Type e and type g are energetically favored but defects and vacancies would be increased. Since the packing density of SAMs are similar, so we assumes that there might be a competition among the two types of arrangement within the SAMs. Aso **PC** SAMs needs more type f, as compared the needs of type d in **TC** SAMs, to compensate the defects in the type g.

Figure 3.9 A top-down view showing how intermolecular interactions might develop in the acene series Au (111). The lattice distance a is 2.88 Å and the S-S distance is $\sqrt{3}a$. The colored circles represent axial benzene rings and the intersecting lines show the width of the perpendicular acene functionality showing: a) **OPE3** SAMs, b) **NP** SAMs, c) **9,10-AC** SAMs, d) and e) two types of **TC** SAMs, f) and g) two types of **PC** SAMs.

THIN-AREA DEFECT MODEL

The assumption of the possible competition of the two types of arrangement of **TC** and **PC** molecules existing in SAMs gives us a possible explanation of why we only see significantly suppressed conductance features in **PC** but not **TC** in EGaIn measurements. A simple model for tunneling transport SAMs in which a fraction of the molecules in the SAM is less resistive to tunneling currents, is to model the total current using the simplified Simmons equation, $J = J_0 e^{-\beta d}$ where d is the effective tunneling distance, β is the tunneling decay coefficient and J_0 is the theoretical value of at $d = 0$. To describe areas of the SAM that are more conductive, d is varied to account for a change in the effective width of the tunneling barrier, while leaving β constant. These areas are, therefore, called “thin-area defects,” but can be used to describe any region of a SAM that exhibits a smaller effective tunneling distance, *i.e.*, some fraction of molecules that are more conductive than the rest of the SAM.[41, 42] Equation 3.2 is used to describe the current density J_{total} where χ is the fraction of thin-area defects (more conductive molecules) and J_i is the nominal current density of the pristine SAM.

$$J_{\text{total}} = \chi J_0 e^{-\beta d} + (1 - \chi) J_i \quad (3.2)$$

In our case we assumes that π - π stacked geometry (Figure 3.9 d,f) leads to lower conductance, while geometries lacking π - π contacts (Figure 3.9 g,e) leads to higher conductance. We took the low-conductance value from MCBJ results as J_i , values of J_0 and β from series of OPEs,[43] and d as the theoretical length of acene molecules to plot J_{total} as a function of

the percentage of J_{total} carried by $\pi - \pi$ -stacked molecules in Figure 3.10. We also varied the effective tunneling distance as a percentage of the theoretical length to consider defects and impurities in the SAM. The thin-area defect model is normally applied to SAMs that exhibit higher than expected conductances because only a small fraction of highly-conductive molecules is required to increase the total conductance of the junction. This behavior is evident in Figure 3.10, which shows that SAMs of both **TC** and **PC** require very large fractions of molecules to adopt a $\pi - \pi$ -stacked geometry to affect the total conductance of the junction because, in our case, the “thin-area defects” are molecules that are packed normally and not π -stacked. The dashed lines in Figure 3.10 are the current density values at 0.1 V from our EGaIn junctions, which predict that the observed junction conductance can only be driven by π -stacking in SAMs of **PC** and that the fraction of molecules that engage in stacking must be close to 100 %.

Figure 3.10 Plots of Equation 3.2 with x axis is $(1 - \chi)$, J_i is the low conductance value of **TC** and **PC** from MCBJ, $J_0 = 10^{-0.3} \text{ Acm}^{-2}$ and $\beta = 0.23 \text{ \AA}$ from literature.⁴³ The percentages refer to the defects or impurities as compared to the theoretical length of **OPE3** of 20.27 $\text{\AA}$. The horizontal dashed lines indicate the experimental value of J_{total} at 0.1 V from EGaIn measurements.

NDC PLOT

For more insights into the molecular interactions, we computed the normalized differential conductance (NDC) the conductance data from the acene series of EGaIn junctions, shown as heatmaps in Figure 3.11. For **OPE3**, **NP**, **9,10-AC** and **TC** a U-shaped curve is observed indicative of non-resonant tunneling. For **PC** a distinctively different shape is found, especially around zero-bias where the curve is more V shaped. The qualitative difference between **PC** and the rest of the series confirms that the suppression of conductance correlates to a difference in bias dependence, which would not be the case for multilayers or other artifacts that simply increase the tunneling distance. V-shaped curves, on the other hand, have been observed before and ascribed to destructive quantum-interference (QI) effects in

SAMs.[11, 12, 16, 44]

Figure 3.11 Normalized Differential Conductance heatmap plots of $\text{Au}^{\text{TS}}/\text{SAMs}/\text{EGaIn}$ junctions comprising of a) OPE3, b) NP, c) 9,10-AC, d) TC and e) PC. Y-axis is normalized differential conductance $\log |dJ/dV|$, X-axis is potential. The colors correspond to the frequencies of the histogram and the lighter color represents higher frequencies.

Figure 3.12 Schematic of junction geometries showing the semi-infinite, periodic electrode-left lead-molecule-right lead-semi infinite, periodic electrode configuration for single and dimer pentacene molecule.

SIMULATIONS ON SLIP-STACK GEOMETRY OF THE PC JUNCTION

This V-shaped feature is not present in the transmission curves of Figure 3.2 because those calculations are based on a single-molecule junction in vacuum. Because they are periodic,[45, 46] simulations on SAM-based junctions require highly crystalline, particularly

well-ordered SAMs—criteria that are not met by the acene series. However, atomistic simulations were performed on a metal-molecular-metal model junction comprising two molecules trapped between metallic leads and semi-infinite, periodic electrodes using ADF-BAND, implementing the Non-Equilibrium Green's Function approach with DFT [47] (See Figure 3.12). Here, we put a slip-stack geometry of two **PC** molecules between metal electrodes. Figure 3.13 shows suppressed transmission near E_f and a broadening of anti-resonances in the slip-stack geometry compared to single-molecules, suggesting that a SAM comprising **PC** molecules in contact with each other would exhibit lower conductance than a SAM comprising non-interacting **PC** molecules. Figure 3.14 shows a theoretical prediction of QI by looking at the orbital coefficients of the molecules,[48, 49] where we see QI features in the pentacene dimer geometry but not in individual pentacene molecules. Together with the trends in conductance and the NDC plots, we ascribe the suppressed conductance in junctions comprising SAMs of **PC** to a specific packing geometry involving intermolecular π - π interactions.

Figure 3.13 Transmission spectra for single and dimer pentacene molecular wires shown in black and red, respectively. The transmission of the dimer reduces all over in the energy window near the fermi level, broadening the destructive QI peaks.

3.3. CONCLUSIONS

In both the MCBJs and EGaIn measurements we find that increasing the π surface area of molecules promotes intermolecular interactions that suppress the conductance compared to the case of a single-molecule bridging the electrodes. In MCBJs, this single-molecule configuration and the configurations involving two or more molecules lead to distinct features in the conductance histograms. In EGaIn junctions, where molecules seek a thermodynamic-minimum packing, **PC** in the series shows a suppression of conductance that cannot be explained by bond topology or the formation of multilayers, suggesting the presence of molecular interactions, which is especially strong for extended pentacene cores. Differential conductance plots of this molecule are consistent with the presence of a destructive

Figure 3.14 HOMO, HOMO-1, LUMO, and LUMO+1 isoplots of single pentacene and dimer with two Au atoms attached to each of the systems on the opposite thiols. The geometry is shown on the top. These were calculated using ADF at *Hybrid:B3LYP-D3* and *TZP* level. At the bottom of the figure is a table listing the product of orbital coefficients at the terminal sulfur group for every orbital.

QI feature in the bias window, which is supported by DFT calculations. Regardless of the mechanism, further studies are needed to ascertain the generalizability of these effects beyond acenes; it should be possible to design molecules with deliberate strong, intermolecular $\pi - \pi$ interactions optimized for differences in packing across various substrates. Moreover, the static nature of SAM-based junctions means that such effects could be exploited in devices, for example, by designing molecular switches capable of forming and breaking strong intermolecular contacts reversibly.

3.4. EXPERIMENTAL DETAILS

CHEMICALS AND SYNTHESIS

The synthesis of OPE3, NP and 9,10-AC is described elsewhere.[50] All compounds were stored in nitrogen-flushed vials and in the dark. The synthesis of TC and PC are synthesized according to procedures highlighted in Figure 3.15 and Figure 3.16 respectively.

Synthesis of 5,12-dimethoxy-5,12-bis((trimethylsilyl)ethynyl)-5,12-dihydrotetracene, 2

In a dry three-neck flask under N_2 , 3.2 mL of trimethylsilylacetylene (22.3 mmol) were dissolved in 40 mL of anhydrous THF and the solution was cooled to $-70^\circ C$ with a EtOH/dry

Figure 3.15 Synthetic route for TC

ice bath. 13.8 mL of *n*-butyllithium 1.6 M in hexane (22 mmol) was added drop-wise and the solution was stirred for 30 min in the cold bath. 1 g of tetracene-5,12-quinone (**1**, 4.4 mmol) was added. It slowly dissolved to form a yellowish solution. The mixture was allowed to warm to 0 °C, then the bath was removed and reaction kept under stirring for 3 hours. MeI (5.5 mL, 88 mmol) was added and the reaction heated to 50 °C overnight. After cooling to the room temperature, the mixture was poured into a saturated NH_4Cl solution. The aqueous phase was extracted with DCM, and the organic phases combined dried over anhydrous Na_2SO_4 . Then, the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel, hexane:ethyl acetate 4:1) to obtain the product (856 mg, yield:40 %).

^1H NMR (400 MHz, CDCl_3). δ : 8.47 (s, 2H), 8.05-7.99 (m, 2H), 7.98-7.93 (m, 2H), 7.58-7.53 (m, 2H), 7.52-7.49 (m, 2H), 2.90 (s, 6H), 0.17 (s, 18H).

Synthesis of 5,12-diethynyl-5,12-dimethoxy-5,12-dihydro-tetracene, **3**

In a round bottom flask, 376 mg of K_2CO_3 (2.7 mmol) were added to a solution of **2** (856 mg, 1.8 mmol) in 100 mL of degassed methanol. The flask was stirred at room temperature under N_2 overnight. The solution was then poured into 100 mL water, extracted with DCM, and it was washed with saturated NaHCO_3 , water and finally brine. The organic phase was then dried over Na_2SO_4 and the solvent removed by rotary evaporation to provide the product **3** as a solid in (582 mg, yield: 96 %). The crude was used in next step without further purification.

^1H NMR (400 MHz, CDCl_3). δ : 8.50 (s, 2H), 8.09-8.02 (m, 2H), 8.01-7.94 (m, 2H), 7.59-7.49 (m, 4H), 2.93 (s, 6H), 2.84 (s, 2H).

Synthesis of S,S'-((tetracene-5,12-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate, TC

In a dry Schlenk, 164 mg of **3** (0.48 mmol) and 404 mg of 4-ethynyl-1-thioacetylbenzene (1.45 mmol) were dissolved in mixture of freshly distilled Et_3N (3 mL) and anhydrous THF (10 mL) and the solution was degassed with N_2 . 23 mg of $\text{Pd}(\text{PPh}_3)_4$ (0.02 mmol) and 10 mg of CuI (0.05 mmol) were added. The reaction mixture was heated to 45°C overnight. After that, 50 mL of a 10% H_2SO_4 solution containing 11 g of SnCl_2 were added into the reaction mixture and stirred for one hour in the dark. The reaction was then poured into water (100 mL) the precipitate was collected by filtering and washed with MeOH. The crude solid was purified by recrystallization from MeOH and CHCl_3 to give the pure product as a red/purple solid (856 mg, yield:40%).

^1H NMR (400 MHz, CDCl_3) δ : 9.22 (s, 2H), 8.67-8.56 (m, 2H), 8.15-8.05 (m, 2H), 7.90-7.81 (m, 4H), 7.61-7.48 (m, 8H), 2.49 (s, 6H).

Figure 3.16 Synthetic route for PC

Synthesis of 6,13-dimethoxy-6,13-bis((trimethylsilyl)ethynyl) -6,13-dihdropentacene, **5**

In a dry three-neck flask under N_2 , 1.45 mL of trimethylsilylacetylene (10.2 mmol) were dissolved in 50 mL of anhydrous THF and the solution was cooled to -78°C with a EtOH/dry ice bath. 6.25 mL of *n*-butyllithium 1.6 M in hexane (10 mmol) were added drop-wise and

the solution stirred for 45 min. 611 mg of pentacene-6,13-quinone (**4**, 2 mmol) were added, and the mixture was slowly allowed to 0 °C. The bath was removed and reaction was kept stirring for 3 hour. MeI (7.5 mL 40 mmol) was added and the reaction was heated to 50 °C for two days. After cooling to room temperature, the mixture was poured into a saturated NH₄Cl aqueous solution. The aqueous phase was extracted with DCM, and the combined organic phases dried over anhydrous Na₂SO₄. The solvent was evaporated by rotary evaporation and the obtained product purified by column chromatography (silica gel, DCM:hexane 2:1) (482 mg, yield: 45 %).

¹H NMR (400 MHz, CDCl₃) δ: 8.51 (s, 4H), 8.01-7.93 (m, 4H), 7.60-7.51 (m, 4H), 3.00 (s, 6H), 0.22 (s, 18H).

Synthesis of 6,13-diethynyl-6,13-dimethoxy-6,13-dihydropentacene, **6**

In a round bottom flask under N₂, 120 mg of K₂CO₃ were added to a degassed solution of **5** (430 mg, 0.83 mmol) in THF-methanol (25 mL:25 mL). The solution was stirred at room temperature for one hour. It was then poured in water (100 mL), extracted with DCM, and the organic phase washed with saturated NaHCO₃, water and finally brine. The organic phase was then dried over Na₂SO₄ and the solvents removed by rotary evaporation to provide the product as a solid (218 mg, yield: 68 %). The crude was used in next step without further purification.

¹H NMR (400 MHz, CDCl₃) δ: 8.54 (s, 4H), 8.01-7.93 (m, 4H), 7.60-7.51 (m, 4H), 3.03 (s, 4H), 2.93 (s, 4H).

Synthesis of S,S'-((pentacene-6,13-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate, **PC**

In a dry Schlenk flask under N₂, 125 mg of **6** (0.36 mmol) and 176 mg 4-ethynyl-1-thioacetylbenezene (1 mmol) were dissolved in mixture of fresh distilled Et₃N (5 mL) and anhydrous THF (10 mL). The solution was degassed and 58 mg of Pd(PPh₃)₄ (0.05 mmol) and 10 mg of CuI (0.05 mmol) were added. The reaction mixture was kept at 80 °C overnight. 50 mL of a 10 % H₂SO₄ solution containing 11 g of SnCl₂ were added into the reaction mixture and kept under stirring for one hour in the dark. The reaction was then poured into water (100 mL), extracted with DCM, and the organic phase washed with saturated NaHCO₃, water and finally brine. The organic phase was then dried over Na₂SO₄ and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography (silica gel, DCM:hexane 1:2) to give the product as a dark blue solid (20 mg, yield: 27 %).

¹H NMR (400 MHz, CDCl₃) δ: 9.16 (s, 4H), 8.04-7.96 (m, 4H), 7.94-7.86 (m, 4H), 7.61-7.56 (m, 4H), 7.46-7.39 (m, 4H) 2.51 (s, 6H).

SELF-ASSEMBLED MONOLAYERS

To ensure that high-quality self-assembled monolayers (SAMs) are formed, we used an *in situ* deprotection strategy that is optimized for large, π -conjugated molecules[16, 17] to grow SAMs directly on ultra-smooth Au substrates prepared by template-stripping (Au^{TS}). [29] 100 nm of Au (99.99%) were deposited by thermal deposition at 10^{-7} mbar onto a 3" Silicon wafer (without adhesion layer). Glass substrates (1 cm $\times$ 1 cm) were glued onto deposited metal by using UV-curable optical adhesive (Norland 61) with 300 s exposure of UV. All SAMs were formed by incubating the thioacetate precursors with 1 cm $\times$ 1 cm template-stripped Au surfaces (100 nm-thick) overnight in 3 mL of 50 μ m solution of the respective compound in freshly distilled toluene followed by addition of 0.05 mL of 17 mmol dm⁻³ diazabicycloundec-7-ene solution in toluene 1 h prior the measurement. The substrates were then rinsed with ethanol and let to dry for 10 min.

SURFACE CHARACTERIZATION

ANGLE-RESOLVED XPS

Angle-resolved XPS (ARXPS) measurement were performed using a VG Microtech spectrometer with a hemispherical electron analyzer (Clam 100), and a MgK α (1253.6 eV) X-ray source. Operation of the measurement and Data analysis are following the method stated in the experimental section in a previous paper[51]. Here we only pointed out the different part from that paper. The Au 4f peaks and C 2p were acquired with the sample rotated under 0, 5, 10, 15, 20, 25, 30, 40 and 50 degrees with respect to the electron analyzer. An expression for the intensity of the peaks for different lengths of the path that through the overlayer:

$$I(\phi) = I_0 \exp\left(\frac{-L}{\phi}\right) = I_0 \exp\left(\frac{-d}{\lambda \cos(\phi)}\right) \quad (3.3)$$

with L the length of the path through the layer, d the thickness of the layer, λ the inelastic mean free path, ϕ the angle of rotation of the sample with respect to the analyzer, I_0 is the corrected peak intensity. The corrected peak intensity I^* are obtained by the $I^* = \gamma_1 I$ and can be used to determine the thickness of the layer. In the measurement, **C18SH** is used as the reference whose length is known as 20.9(2) Å [31] Then the λ value can be calculated. Next we can make a fit to the corrected intensities to find the thickness of the five Acene SAMs. Some of the samples indicated the presence of residual DBU from the *in situ* deprotection during the growth of the SAMs that increased the apparent thickness of the SAM slightly. These trace amounts of DBU do not impact the EGaIn measurements because they occur infrequently and randomly and, because we measure many junctions across many substrates, they show up as low-frequency outliers in the conductance histograms; however,

they are over-represented in the AR-XPS because we measured fewer substrates and XPS is very sensitive to small amounts of impurities. We do not know the cause of the residual DBU, as it appears to be unique to the acene series.

SYNCHROTRON-BASED X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

The measurements were performed at the HE-SGM beamline (bending magnet) of the German synchrotron radiation facility BESSY II in Berlin using a custom-designed experimental station.[52] The spectra were collected with a SCIENTA SES200 electron energy analyzer, in normal emission geometry. The synchrotron light served as the primary X-ray source. The photon energy was set either to 350 eV or 580 eV depending on the acquisition range. The energy resolution was 0.3 eV and 0.6 eV, respectively. The binding energy scale of the spectra was referenced to the Au $4f_{7/2}$ peak at 84.0 eV.[53]

The spectra were fitted by symmetric Voigt functions and a linear or Shirley-type background. The S 2p spectra were decomposed by several S $2p_{3/2,1/2}$ doublets. Each of these doublets comprised two peaks with the same full width at half-maximum, a standard[53] spin-orbit splitting of ~ 1.2 eV (verified by fit), and a branching ratio of 2 ($S2p_{3/2}/S2p_{1/2}$). The packing densities of the monolayers were calculated from the $S2p/Au4f$ intensity ratio,[54] with the thiolate signal only being taken into account. A standard exponential attenuation of the photoelectron signal was assumed[55] and the attenuation lengths typical of densely packed SAMs were used.[56] An octadecanethiolate (SC18) SAM with a well defined packing density ($4.63 \times 10^{14} \text{ cm}^{-2}$)[31] served as the reference, to determine the spectrometer-specific constants.

EGaIn MEASUREMENT

To minimize the change of oxidative damage to the compounds and SAMs, sample preparation, handling and measurement with the EGaIn setup were all performed in a nitrogen flow box with a controlled O_2 level between 1 – 3% (some O_2 is necessary to form tips of EGaIn) and humidity below 10%. At least 20 junctions were measured on each of at least three substrates per molecule (12 scans from 0 V $\rightarrow$ 1 V $\rightarrow$ -1 V $\rightarrow$ 0 V, steps of 0.05 V) for a total of at least 600 traces per SAM. A new EGaIn tip was prepared every 5-8 junctions and flattened by gently pushing it on a Si wafer few times according to the procedure reported by Simone *et al.*[57] The details of the EGaIn setup are described elsewhere.[9] The raw data acquired using EGaIn are processed using Scientific Python. The source code is available at <http://github.com/rchiechi/GaussFit> and it retained internally in accordance with the aforementioned data retention policies. J-V curves and NDC plot are obtained directly from the code stated above.

Low-bias conductance were obtained by computing the slope of EGaIn data (J vs. V)

Figure 3.17 An example: the 95% confidence band of the lowest 4 data points of J-V data of **PC** junctions

for the lowest 4 data points, *i.e.*, from -1 V to 1 V. This was done by fitting a linear equation to the linear $J - V$ data. Figure 3.17 is an example of the J/V data of **PC** junctions. The pink area is 95% confidential interval band, where the mean value and error bars of Low bias G are obtained by computing the largest value and lowest value of the slope of fitted line that is within this area.

MCBJ MEASUREMENT

In the MCBJ experiment, a lithographically fabricated nanoscale gold wire was patterned on a flexible substrate. Electrodes were first characterized without molecules to ensure that they were clean (in which case a clear peak at $1 G_0$ is observed, indicative of atomically sharp electrodes, followed by exponential decay of conductance with increasing displacement). Then, a droplet of the solution that contained the molecules was deposited on the electrodes (0.1 mM in dichloromethane, with 0.5 mM of tetrabutylammonium hydroxide to favour removal of the acetate protection). After solvent evaporation, thousands of traces are recorded consecutively. The measurements were performed in air at room temperature, using a bias voltage of 100 mV and 200 V/s piezo actuation speed. The measurements were repeated on a total of two devices (with four junctions each), measuring at least 7000 consecutive traces on a single junction for each sample. A detailed description of this technique and the experimental setup has been given previously.[36] A reference-free clustering algorithm was then used to cluster the data. The method was detailed in previous work [39]. The noteworthy difference is on the definition of the feature vector. In this work, a 25×32 pixels image of the 2D-histogram was used. The displacement range was from -0.5 nm to 3 nm, and the conductance range was from -0.5 to $-6 \log(G/G_0)$ (the -0.5 limit being the point used for trace

3. INTERMOLECULAR EFFECTS ON TUNNELING THROUGH ACENES IN LARGE-AREA AND SINGLE-MOLECULE JUNCTIONS

alignment). Additionally, the 1D conductance histogram, using 100 bins, was appended to the feature vector created from the image, for a total of 900 dimensions per trace. Each measurement was analyzed individually, and the number of clusters was chosen to be the lowest that would isolate the high-conductance class. Clusters showing only empty traces were merged together (when more than one would result from the analysis), and reported as the "empty class". All clusters showing molecular traces are reported without additional merging or sub-splitting, and in all measurement this resulted in one high-conductance class and one low-conductance class (in some cases with multiple features). Additional analysis of the molecular features may reveal clearer low-conductance features, or hidden ones. However, this lies outside the scope of this work. The logarithmically binned 1D-conductance histograms were fitted using a Normal distribution, both for the raw data and for the molecular classes resulting from clustering. The position of the maximum of the fit is reported as the most-probable conductance value (or "conductance" for short) of the plateau. In the case of the raw data, a single Gaussian was used to fit the highest conductance peak exclusively, and the same holds for the high-conductance classes. Regarding low-conductance features, two Gaussians were used for the fit in cases where two peaks/plateaus were evident in both the 1D- and 2D- histograms. Otherwise, a single Gaussian distribution was employed.

THEORETICAL METHODS

SIMULATION ON INDIVIDUAL MOLECULES

Calculations were performed using ORCA 4.10 software package[58, 59] and the ARTAIOS-030417 software package[26]. The molecules terminated with thiols were first optimized by BP/def2-SVP at gas-phase; then the molecules were attached to two pyramidal Au clusters via the terminal sulfur atoms. Single point energy calculations were performed on this model junction using B3LYP/G and LANL2DZ basis sets according to literature procedures to compute the energy levels[60]. Transmission curves were computed in ARTAIOS using outputs from B3LYP/G(LANL2DZ) calculations based on the minimized geometries.

SIMULATION ON DIMERS

Calculation were performed using the *BAND* module of Amsterdam Density Functional (ADF) quantum chemistry program for the pentacene molecular wire.[47, 61] We simulated the ideal metal-molecule-metal junctions, *i.e.*, a single wire between electrodes and two wires in slip-stack conformation. We first optimized the single and dimer pentacene molecular wire using GGA:PBE functional and TZ2P basis sets. The optimized geometries were then connected to two leads consisting of gold electrodes in Au111 arrangement. The two Au atoms that were attached to thiols in the optimized geometry served as the tip of the two

leads. The two leads and molecule formed the *extended molecule* system which is finite. The leads then connect to two semi-infinite, periodic electrodes. *Self-consistent* method for determining fermi level was used in BAND module implementing NEGF with DFT. We used *SZ* basis set and *GGA:PBE* functional with scalar ZORA relativistic effects. 5 layers of gold atoms were used in the electrodes. Calculations were also performed on systems with 3 and 4 layers of Au layers to check for convergence of transmission as suggested by the BAND authors. [62–64]

Due to the presence of the gold atoms, we used ZORA scalar relativistic effects with DZ basis sets for Au and TZ2P for the rest of the atoms. This Au atoms served as reference point for attachment to the electrodes in the NEGF calculations. We also included dispersion corrections for the dimer by using GGA:PBED3 functional instead of GGA:PBE functional to account for accurate calculation of the $\pi - \pi$ interactions between the two wires. Single-point energies of these two optimized geometries were also computed using *Hybrid B3LYP-D3* functional (to account for van der Waal interactions) and *TZ2P* (triple-zeta with two polarization functions) basis sets. We used one-component scalar ZORA relativistic effects without any frozen core approximations.

AUTHOR CONTRIBUTIONS

The content of this chapter is published and the texts are re-organized based on the original manuscript and supporting information. Full citation is: Yuru Liu, Luca Ornago, Marco Carlotti, Yong Ai, maria el abbasi, Saurabh Soni, Andika Asyuda, Michael Zharnikov, Herre S. J. van der Zant, Ryan C. Chiechi, *Intermolecular Effects on Tunneling through Acenes in Large-Area and Single-Molecule Junctions*. *The Journal of Physical Chemistry. C*, **41**, 22776, (2020)

Y.L. performed the transmission calculations using ORCA and ATAIOS, AFM measurements, ellipsometry measurements, ARXPS measurements and related data handling and interpretation. M.C. synthesized and characterized the compounds and performed the EGaIn measurements. Y.L. performed the related data handling and interpretation. Y.A. performed the STM-Break Junction measurements. A.A. and M.Z. carried out synchrotron measurements and related data handling and interpretation. L.O., M.E.A. and H.S.J.V. performed the MCBJ measurements and related data handling and interpretation. S.S. performed ADF/BAND calculations. R.C.C. supervised the whole project. All the authors contributed to preparing figures and writing the manuscript.

BIBLIOGRAPHY

- (1) Vilan, A.; Aswal, D.; Cahen, D. Large-Area, Ensemble Molecular Electronics: Motivation and Challenges. *Chem. Rev.* **2017**, *117*, 4248–4286.
- (2) Xiang, L.; Hines, T.; Palma, J. L.; Lu, X.; Mujica, V.; Ratner, M. A.; Zhou, G.; Tao, N. Non-Exponential Length Dependence of Conductance in Iodide-Terminated Oligothiophene Single-Molecule Tunneling Junctions. *J. Am. Chem. Soc.* **2016**, *138*, 679–687.
- (3) Xin, N.; Guo, X. Catalyst: The Renaissance of Molecular Electronics. *Chem* **2017**, *3*, 373–376.
- (4) Lörtscher, E. Reaction: Technological Aspects of Molecular Electronics. *Chem* **2017**, *3*, 376–377.
- (5) Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
- (6) Solomon, G. C.; Herrmann, C.; Vura-Weis, J.; Wasielewski, M. R.; Ratner, M. A. The Chameleonic Nature of Electron Transport Through Π -Stacked Systems. *J. Am. Chem. Soc.* **2010**, *132*, 7887–7889.
- (7) Markussen, T.; Stadler, R.; Thygesen, K. S. The Relation Between Structure and Quantum Interference in Single Molecule Junctions. *Nano Lett.* **2010**, *10*, 4260–4265.
- (8) Tsuji, Y.; Hoffmann, R.; Movassagh, R.; Datta, S. Quantum Interference in Polyenes. *J. Chem. Phys.* **2014**, *141*, 224311.
- (9) Fracasso, D.; Valkenier, H.; Hummelen, J. C.; Solomon, G. C.; Chiechi, R. C. Evidence for Quantum Interference in SAMs of Arylethynylene Thiolates in Tunneling Junctions With Eutectic Ga–In (EGaIn) Top-Contacts. *J. Am. Chem. Soc.* **2011**, *133*, 9556–9563.
- (10) Pedersen, K. G. L.; Borges, A.; Hedegård, P.; Solomon, G. C.; Strange, M. Illusory Connection Between Cross-Conjugation and Quantum Interference. *J. Phys. Chem. C* **2015**, *119*, 26919–26924.

- (11) Zhang, Y.; Ye, G.; Soni, S.; Qiu, X.; Krijger, T. L.; Jonkman, H. T.; Carloti, M.; Sauter, E.; Zharnikov, M.; Chiechi, R. C. Controlling Destructive Quantum Interference in Tunneling Junctions Comprising Self-Assembled Monolayers via Bond Topology and Functional Groups. *Chem. Sci.* **2018**, *9*, 4414–4423.
- (12) Carloti, M.; Soni, S.; Qiu, X.; Sauter, E.; Zharnikov, M.; Chiechi, R. C. Systematic Experimental Study of Quantum Interference Effects in Anthraquinoid Molecular Wires. *Nanoscale Advances* **2019**, *1*, 2018–2028.
- (13) Manrique, D. Z.; Huang, C.; Baghernejad, M.; Zhao, X.; Al-Owaedi, O. A.; Sadeghi, H.; Kaliginedi, V.; Hong, W.; Gulcur, M.; Wandlowski, T., et al. A Quantum Circuit Rule for Interference Effects in Single-Molecule Electrical Junctions. *Nat. Commun.* **2015**, *6*, 1–8.
- (14) Gantenbein, M.; Wang, L.; Al-jobory, A. A.; Ismael, A. K.; Lambert, C. J.; Hong, W.; Bryce, M. R. Quantum Interference and Heteroaromaticity of Para-And Meta-Linked Bridged Biphenyl Units in Single Molecular Conductance Measurements. *Sci. Rep.* **2017**, *7*, 1–9.
- (15) Stefani, D.; Weiland, K. J.; Skripnik, M.; Hsu, C.; Perrin, M. L.; Mayor, M.; Pauly, F.; van der Zant, H. S. Large Conductance Variations in a Mechanosensitive Single-Molecule Junction. *Nano Lett.* **2018**, *18*, 5981–5988.
- (16) Carloti, M.; Kovalchuk, A.; Wächter, T.; Qiu, X.; Zharnikov, M.; Chiechi, R. C. Conformation-Driven Quantum Interference Effects Mediated by Through-Space Conjugation in Self-Assembled Monolayers. *Nat. Commun.* **2016**, *7*, 1–7.
- (17) Valkenier, H.; Huisman, E. H.; van Hal, P. A.; de Leeuw, D. M.; Chiechi, R. C.; Hummelen, J. C. Formation of High-Quality Self-Assembled Monolayers of Conjugated Dithiols on Gold: Base Matters. *J. Am. Chem. Soc.* **2011**, *133*, 4930–4939.
- (18) Kaliginedi, V.; Moreno-García, P.; Valkenier, H.; Hong, W.; García-Suárez, V. M.; Buitter, P.; Otten, J. L. H.; Hummelen, J. C.; Lambert, C. J.; Wandlowski, T. Correlations Between Molecular Structure and Single-Junction Conductance: A Case Study With Oligo(phenylene-Ethynylene)-Type Wires. *J. Am. Chem. Soc.* **2012**, *134*, 5262–5275.
- (19) Frisenda, R.; Stefani, D.; van der Zant, H. S. J. Quantum Transport Through a Single Conjugated Rigid Molecule, a Mechanical Break Junction Study. *Acc. Chem. Res.* **2018**, *51*, 1359–1367.

- (20) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States. *J. Am. Chem. Soc.* **2004**, *126*, 7416–7417.
- (21) Kim; Beebe, J. M.; Jun, Y.; Zhu, X.-Y.; Frisbie, C. D. Correlation Between HOMO Alignment and Contact Resistance in Molecular Junctions: Aromatic Thiols Versus Aromatic Isocyanides. *J. Am. Chem. Soc.* **2006**, *128*, 4970–4971.
- (22) Yelin, T.; Korytár, R.; Sukenik, N.; Vardimon, R.; Kumar, B.; Nuckolls, C.; Evers, F.; Tal, O. Conductance Saturation in a Series of Highly Transmitting Molecular Junctions. *Nat. Mater.* **2016**, *15*, 444–449.
- (23) Cirera, B.; Sánchez-Grande, A.; de la Torre, B.; Santos, J.; Edalatmanesh, S.; Rodríguez-Sánchez, E.; Lauwaet, K.; Mallada, B.; Zbořil, R.; Miranda, R.; et al Tailoring topological order and π -conjugation to engineer quasi-metallic polymers. *Nature Nanotechnology* **2020**, *15*, 437–443.
- (24) Klare, J. E.; Tulevski, G. S.; Sugo, K.; de Picciotto, A.; White, K. A.; Nuckolls, C. Cruciform π -Systems for Molecular Electronics Applications. *J. Am. Chem. Soc.* **2003**, *125*, 6030–6031.
- (25) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. Organization of Acenes With a Cruciform Assembly Motif. *J. Am. Chem. Soc.* **2006**, *128*, 1340–1345.
- (26) Deffner, M.; Gross, L.; Steenbock, T.; Voigt, B. A.; Solomon, G. C.; Herrmann, C. ARTAIOS - a transport code for postprocessing quantum chemical electronic structure calculations, <https://www.chemie.uni-hamburg.de/ac/herrmann/software/index.html>, 2009-2017.
- (27) Nerngchamnong, N.; Yuan, L.; Qi, D.-C.; Li, J.; Thompson, D.; Nijhuis, C. A. The Role of Van Der Waals Forces in the Performance of Molecular Diodes. *Nat. Nanotechnol.* **2013**, *8*, 113–118.
- (28) Chiechi, R.; Weiss, E.; Dickey, M.; Whitesides, G. Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, 142–144.
- (29) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO₂-Templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 9686–9694.

- (30) Krijger, T. L. The Soft Molecular Landing Machine Ultra-High Vacuum Deposition of Non-Volatile Solution Processable Organic Materials and Polymers, PhD dissertation, University of Groningen, 2018.
- (31) Schreiber, F. Structure and Growth of Self-Assembling Monolayers. *Prog. Surf. Sci.* **2000**, 65, 151–257.
- (32) Hutt, D. A.; Leggett, G. J. Influence of Adsorbate Ordering on Rates of UV Photooxidation of Self-Assembled Monolayers. *J. Phys. Chem.* **1996**, 100, 6657–6662.
- (33) Schoenfish, M. H.; Pemberton, J. E. Air Stability of Alkanethiol Self-Assembled Monolayers on Silver and Gold Surfaces. *J. Am. Chem. Soc.* **1998**, 120, 4502–4513.
- (34) Nilsson, D.; Watcharinyanon, S.; Eng, M.; Li, L.; Moons, E.; Johansson, L. S. O.; Zharnikov, M.; Shaporenko, A.; Albinsson, B.; Mårtensson, J. Characterization of Self-Assembled Monolayers of Oligo(phenyleneethynylene) Derivatives of Varying Shapes on Gold: Effect of Laterally Extended π -Systems. *Langmuir* **2007**, 23, 6170–6181.
- (35) He, J.; Sankey, O.; Lee, M.; Tao, N.; Li, X.; Lindsay, S. Measuring Single Molecule Conductance With Break Junctions. *Faraday Discuss.* **2006**, 131, 145–154.
- (36) Martin, C. A.; Smit, R. H. M.; van Egmond, R.; van der Zant, H. S. J.; van Ruitenbeek, J. M. A Versatile Low-Temperature Setup for the Electrical Characterization of Single-Molecule Junctions. *Rev. Sci. Instrum.* **2011**, 82, 053907.
- (37) Frisenda, R.; Perrin, M. L.; Valkenier, H.; Hummelen, J. C.; van der Zant, H. S. Statistical Analysis of Single-Molecule Breaking Traces. *Phys. Status Solidi B* **2013**, 250, 2431–2436.
- (38) Wu, S.; González, M. T.; Huber, R.; Grunder, S.; Mayor, M.; Schönenberger, C.; Calame, M. Molecular Junctions Based on Aromatic Coupling. *Nat. Nanotechnol.* **2008**, 3, 569.
- (39) Cabosart, D.; El Abbassi, M.; Stefani, D.; Frisenda, R.; Calame, M.; Van der Zant, H. S.; Perrin, M. L. A Reference-Free Clustering Method for the Analysis of Molecular Break-Junction Measurements. *Appl. Phys. Lett.* **2019**, 114, 143102.
- (40) Abbassi, M. E.; Zwick, P.; Rates, A.; Stefani, D.; Prescimone, A.; Mayor, M.; van der Zant, H. S. J.; Dulić, D. Unravelling the Conductance Path Through Single-Porphyrin Junctions. *Chem. Sci.* **2019**, 10, 8299–8305.

- (41) Weiss, E. A.; Chiechi, R. C.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Duati, M.; Rampi, M. A.; Whitesides, G. M. Influence of Defects on the Electrical Characteristics of Mercury-Drop Junctions: Self-Assembled Monolayers Ofn-Alkanethiolates on Rough and Smooth Silver. *J. Am. Chem. Soc.* **2007**, *129*, 4336–4349.
- (42) Pourhossein, P.; Vijayaraghavan, R. K.; Meskers, S. C.; Chiechi, R. C. Optical Modulation of Nano-Gap Tunnelling Junctions Comprising Self-Assembled Monolayers of Hemicyanine Dyes. *Nat. Commun.* **2016**, *7*, 1–9.
- (43) Carloti, M.; Degen, M.; Zhang, Y.; Chiechi, R. C. Pronounced Environmental Effects on Injection Currents in EGaIn Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2016**, *120*, 20437–20445.
- (44) Guédon, C. M.; Valkenier, H.; Markussen, T.; Thygesen, K. S.; Hummelen, J. C.; van der Molen, S. J. Observation of Quantum Interference in Molecular Charge Transport. *Nat. Nanotechnol.* **2012**, *7*, 305–309.
- (45) Dubi, Y. Transport Through Self-Assembled Monolayer Molecular Junctions: Role of In-Plane Dephasing. *J. Phys. Chem. C* **2014**, *118*, 21119–21127.
- (46) Obersteiner, V.; Egger, D. A.; Heimel, G.; Zojer, E. Impact of Collective Electrostatic Effects on Charge Transport through Molecular Monolayers. *J. Phys. Chem. C* **2014**, *118*, 22395–22401.
- (47) Philipsen, P. et al. BAND 2019.3, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>, 2019.
- (48) Yoshizawa, K.; Tada, T.; Staykov, A. Orbital Views of the Electron Transport in Molecular Devices. *J. Am. Chem. Soc.* **2008**, *130*, 9406–9413.
- (49) Solomon, G. In *Handbook of single-molecule electronics*, Moth-Poulsen, K., Ed.; CRC Press: 2015, pp 341–369.
- (50) Valkenier, H.; Guédon, C. M.; Markussen, T.; Thygesen, K. S.; van der Molen, S. J.; Hummelen, J. C. Cross-Conjugation and Quantum Interference: A General Correlation? *Phys. Chem. Chem. Phys.* **2014**, *16*, 653–662.
- (51) Qiu, L.; Zhang, Y.; Krijger, T. L.; Qiu, X.; van't Hof, P.; Hummelen, J. C.; Chiechi, R. C. Rectification of Current Responds to Incorporation of Fullerenes Into Mixed-Monolayers of Alkanethiolates in Tunneling Junctions. *Chem. Sci.* **2017**, *8*, 2365–2372.
- (52) Nefedov, A.; Wöll, C. In *Surface Science Techniques*; Springer Berlin Heidelberg: 2013, pp 277–303.

- (53) Moulder, J.; Stickie, W.; Sobol, P.; Bomben, K. Handbook of X-Ray Photoelectron Spectroscopy ed J Chastain (Eden Prairie, MN: Perkin-Elmer Corporation). **1992**.
- (54) Gärtner, M.; Sauter, E.; Nascimbeni, G.; Petritz, A.; Wiesner, A.; Kind, M.; Abu-Husein, T.; Bolte, M.; Stadlober, B.; Zojer, E.; Terfort, A.; Zharnikov, M. Understanding the Properties of Tailor-Made Self-Assembled Monolayers With Embedded Dipole Moments for Interface Engineering. *J. Phys. Chem. C* **2018**, *122*, 28757–28774.
- (55) Ratner, B. D.; Castner, D. G. In *Surface Analysis– The Principal Techniques*; John Wiley & Sons, Ltd, pp 47–112.
- (56) Lamont, C. L. A.; Wilkes, J. Attenuation Length of Electrons in Self-Assembled Monolayers Ofn-Alkanethiols on Gold. *Langmuir* **1999**, *15*, 2037–2042.
- (57) Simeone, F. C.; Yoon, H. J.; Thuo, M. M.; Barber, J. R.; Smith, B.; Whitesides, G. M. Defining the Value of Injection Current and Effective Electrical Contact Area for EGaIn-Based Molecular Tunneling Junctions. *J. Am. Chem. Soc.* **2013**, *135*, 18131–18144.
- (58) Neese, F. The ORCA Program System. *Sci. China, Ser. F: Info. Sci.* **2011**, *2*, 73–78.
- (59) Neese, F. Software Update: The ORCA Program System, Version 4.0. *Sci. China, Ser. F: Info. Sci.* **2017**, *8*, e1327.
- (60) Herrmann, C.; Solomon, G. C.; Subotnik, J. E.; Mujica, V.; Ratner, M. A. Ghost Transmission: How Large Basis Sets Can Make Electron Transport Calculations Worse. *J. Chem. Phys.* **2010**, *132*, 024103.
- (61) Baerends, E. et al. ADF 2019.3, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>, Accessed: 2019, 2019.
- (62) Te Velde, G.; Baerends, E. J. Precise Density-Functional Method for Periodic Structures. *Phys. Rev. B* **1991**, *44*, 7888–7903.
- (63) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry With ADF. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (64) Verzijl, C. J. O.; Thijssen, J. M. DFT-Based Molecular Transport Implementation in ADF/BAND. *J. Phys. Chem. C* **2012**, *116*, 24393–24412.

4

INTRODUCING ELECTRON WITHDRAWING GROUPS TO MOLECULAR WIRES IN TUNNELING JUNCTIONS

I would like to thank Dr. Gang Ye for the synthesis, UV-Vis measurements of the molecules, and all the discussions;
Prof. Ryan C. Chiechi for his supervision.

4.1. INTRODUCTION

One of the goals in molecular electronics is to correlate the structure of the molecules sandwiched between two electrodes with the rate of charge tunneling through the molecular junction.[1–3] Researchers have synthesized molecular wires with various functional groups to explore how the intrinsic structure would influence the electric properties.[4] Theoretical simulations may also provide insights into the nature of electron tunneling through the molecular junctions. The first theoretical discussion of charge transport through a single molecule was reported by Arieh Aviram and Mark Ratner, who proposed the potential possibility of a molecular rectifier.[5] Further theoretical work has been evolved later to understand the nature of electron transport through a molecular junction.[6] Experimental and theoretical efforts cooperate with each other and provide impressive results, which allows a better understanding of the charge transport properties.

The most commonly used theoretical model is the simplified Simmons model, which considers the junction formed by the molecule as an approximately rectangle tunneling barrier (see Equation 1.1 in chapter 1.) The values of β can be obtained by measuring at least three molecules of different length while keeping the molecule-electrode interface the same. Researchers have reported the values of β among different molecular systems, including SAMs of alkanethiols,[7–9] oligothiophenes,[10] oligoacenes,[11] oligophenyls[12–14] and other long π -conjugated systems.[15] The values of β vary among different systems because β is related to the average height of tunneling barrier ϕ , which is related to the offset between the Fermi level (E_f) of the electrode and the dominated frontier orbitals [16] (see Equation 4.1 and Figure 4.1a). The energies of the molecular orbitals can be synthetically controlled by adding functional groups and heteroatoms,[10, 17, 18] therefore allows a deeper understanding of the correlation with molecular structure and electrical properties.

$$J(V) = J_0(V)e^{-\beta d} \quad (1.1)$$

$$\beta = \frac{4\pi}{h} \sqrt{2m\phi} \quad (4.1)$$

For this chapter, we synthesized three π -conjugated molecular wires, **BT**, **TTz** and **BTz** which are shown in Figure 4.1b. We keep the length of the molecules and the anchoring group the same while changing the central bithiophene rings by adding a heteroatom (in our case N) step by step. The thiazole unit is an electron-deficient heterocycle and is attractive for the development of organic and polymeric semiconductors due to molecular features that impart significant differences in electronic characteristics as compared with bithiophene.[19–22] The presence of the sp^2 hybridized N atom increases the electron affinity and lowers

Figure 4.1 a) A schematic representation of the electronic structure of a molecular junction. Frontier orbitals are presented: shaded parabolic shape denotes the occupied state and non-shaded parabolic shape denotes the unoccupied state. The average barrier height ϕ denotes the energy offset with the dominated frontier orbitals which can be either occupied states or unoccupied states. b) The structure of the target molecular wires synthesized.

the energy of the frontier orbitals as compared to the thiophene rings, while maintaining the planarity. In our molecular design, we keep the width of the tunneling barrier (d) and the interface between electrode and SAM (J_0) the same while varying the height of the tunneling barrier (β), which allows us to single out the role of electron withdrawing moiety in the electrical properties of the molecular junction. Our work aims to answer the following questions: (i) Will the heteroatoms affect the electrical properties of a molecular junction? (ii) What role of the heteroatom play in the tunneling process? (iii) How will this rationalize the future design of new molecules?

4.2. RESULTS AND DISCUSSION

CONDUCTIVITY MEASUREMENTS

To explore the conductivity of these molecular wires, we used two testbeds for measurement, in ensemble and single-molecule junction. Firstly, we measured the tunneling current through $\text{Au}^{\text{TS}}/\text{SAM}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ junctions (where ‘/’ denotes an interface defined by chemisorption and ‘//’ denotes an interface by physisorption).[23] Figure 4.2a shows the plots of logarithmic value of current-density versus voltage ($\log |J|/V$), in which the values of $\log |J|$ are nearly identical at low bias window whereas there is a slightly difference at larger bias window. Overall, the current density is indistinguishable among the three molecular wires. This observation might result from the molecular interactions in the SAM, where in-plane dephasing of the molecular orbitals happens, thus the change of conductivity caused by energy level shifts is suppressed.[24] Therefore it is worthwhile to measure these molecular wires in the single-molecule junctions.

Figure 4.2 a) Plots of log current-density versus voltage ($\log |J|/V$) for Au^{TS}/SAM//Ga₂O₃/EGaIn junctions, where SAM denotes self-assembled monolayer comprising **BT**, **TTz** or **BTz**, TS denotes for template stripped. Values of $|\log J|$ at 0 V are omitted for clarity. Error bars represent 95% confidential interval. b) 2D histogram of counts vs. conductance from STM-BJ measurements on **BT**, **TTz** and **BTz**. The conductance peaks for **BT**, **TTz** and **BTz** were located at approximately $4.74 \times 10^{-5} G_0$, $6.15 \times 10^{-5} G_0$ and $7.95 \times 10^{-5} G_0$ respectively.

The tunneling current rate was then measured in single-molecule junctions using the scanning tunneling microscopy break junction (STM-BJ) technique.[25] The experiment was operated in ambient conditions and dilute 1 mM mestlyene solutions of the molecules were prepared. A single-molecular junction was formed when a molecule was trapped at the end of the Au contact as it was being pulled away from the substrates through the solution. The molecular conductance was measured by repeatedly forming and breaking Au point contacts at a fixed bias (0.1 V). Thousands of traces were collected to allow for detailed statistical analysis.[26] Figure 4.2b shows the histograms of counts *vs.* conductance. The conductance peaks for **BT**, **TTz** and **BTz** were located at approximately $4.74 \times 10^{-5} G_0$, $6.15 \times 10^{-5} G_0$ and $7.95 \times 10^{-5} G_0$ respectively, where G_0 is the quantum conductance, $G_0 = 2e^2/h$. Considering the width of the histograms (the gaussian mean value of the peak), the values obtained indicate the conductivity of the three molecular wires were insignificant from one another.

MOLECULAR ORBITALS

To further understand the results from the conductivity measurements, we looked at the energy levels of each molecule both experimentally and theoretically. In Figure 4.3, the UV-Vis spectra of the three molecules and the frontier orbitals of HOMO and LUMO obtained from DFT calculation by the ORCA program are shown.[27, 28] The results are also summarized in Table 4.1. The optical gap extracted by UV-vis spectroscopy is in good agreement with the HOMO-LUMO gap obtained by DFT simulations. Both gaps show a trend of slightly increasing from **BT** to **TTz** and to **BTz**. Additionally, the values of the

Table 4.1 Optical properties, thickness of the self-assembled monolayers, and energy levels calculated by DFT

Molecular Wires	optical gap ^a (eV)	Thickness ^b (Å)	Length ^{c,d} (Å)	E _{HOMO} ^d (eV)	E _{LUMO} ^d (eV)	Gap ^d (eV)
BT	2.70	14.90	23.52	-5.36	-2.51	2.84
TTz	2.72	14.66	23.48	-5.58	-2.68	2.89
BTz	2.74	11.50	23.47	-5.95	-3.02	2.93

a. Determined from the onsets of the UV-Vis absorption spectra of the molecules.

b. Determined by ellipsometry measurements.

c. The distance from S to S atom.

d. Results obtained from DFT calculations.

Figure 4.3 a) UV-vis spectra of **BT**, **TTz** and **BTz** in chloroform (10^{-5} M); b) Molecular orbital diagrams of HOMO and LUMO from DFT calculations.

HOMO and LUMO are both decreasing. Therefore it is reasonable to say that the introduction of electron-withdrawing sp^2 nitrogens to the thiophene cores do impact the molecular orbitals of the molecule, however the effect seems not enough to cause big differences in the charge transport rate in electrical measurements.

TRANSMISSION SPECTRA

Next we simulated the transmission spectra of the single-molecule junctions. The model junction is shown in Figure 4.4a, where one molecule with optimized geometry is sandwiched between two Au electrodes with the numbers of atoms of $3 \times 3 \times 2$. We optimized the isolated **BT**, **TTz** and **BTz** molecules with terminal thiol groups using ORCA 4.10 [27, 28] and then chemisorbed them on the face centered cubic (FCC) hollow sites of the two Au electrodes with a binding distance 1.75 Å taken from the literature.[29] Figure 4.4b shows the transmission spectra at zero-bias of the model junctions with **BT**, **TTz** and **BTz** molecules. Transmission spectra show the features that control the magnitude of the current through the molecules, thus provide useful insights into the correlation between the frontier orbitals and the electrical properties. The x-axis is shifted with respect to Fermi level (E_f) of bare Au

Figure 4.4 a) A schematic representation of the model junction comprising the optimized geometry of **BT** molecules that sandwiched between two electrode comprising Au atoms with the size $3 \times 3 \times 2$. b) Transmission curves at zero bias for single-molecule junctions comprising **BT**, **TTz** and **BTz**. The x-axis is the energy offset of the molecular states with respect to E_f (where $E_f = -4.3$ eV). The gray line where $E = E_f$, colored bars above the plot indicate the resonances of the frontier orbitals and the tunneling process.

metal (where $E_f = -4.3$ eV). The choice of the E_f is somewhat arbitrary as it shifts when the metal is modified with molecules, however the transmission plots would maintain their shape if referenced to the vacuum level and the true value of E_f should be located between the HOMO and LUMO of the model junction. The transmission spectra clearly show that the LUMO shifts towards the E_f while the HOMO shifts away from the E_f .

Figure 4.5 presents a much better visualization of how the molecular orbitals shift with respect to the E_f (where $E_f = -4.3$ eV). The values of the HOMO/LUMO were extracted from the single point energy calculations of thiol terminated **BT**, **TTz** and **BTz** molecules. HOPS denotes highest-occupied π state and LUPS denotes lowest-unoccupied π state. The values of the HOPS/LUPS were extracted from the molecular orbitals where the electron mainly stays on the backbone of the molecule rather than on the gold electrode or the anchor groups of the model junction. In the plot, even though the HOMO/HOPS shifts away from E_f and the LUPS shifts closer to E_f , the HOPS dominates the tunneling process as it is much closer to E_f . This result agrees with the observation in previous STMBJ measurements: the conductivity is decreasing as the electron withdrawing sp^2 N atom is introduced to the thiophene cores.

DESIGN & TRANSPORT CALCULATIONS

The experimental and theoretical results above inform our future design for making new molecular wires. In our previously designed molecules, the N atom has a trivial contribution to orbital alignments to the E_f . We attributed this to the weak electron-withdrawing ability of the sp^2 N in the thiophene ring. For the design of new molecules in the future, we propose

Figure 4.5 Orbital alignment with respect to E_f . Y-axis shows the energy value with respect to E_f (where $E_f = -4.3$ eV). The value of HOMO/LUMO was extracted from the single point energy calculation of thiol terminated **BT**, **TTz** and **BTz** molecules. HOPS denotes highest occupied π states and LUPS denotes lowest unoccupied π states. The value of HOPS/LUPS was extracted from the single molecular energy calculations of model junction of **BT**, **TTz** and **BTz** molecules.

molecules with stronger electron withdrawing groups. The assumption here is if the electron withdrawing group is strong enough to bring the frontier orbital closer to E_f , then the LUPS would dominate the process of electron tunneling, hence it could increase the conductivity of a molecular wire. Here we choose strong electron withdrawing groups to functionalize our previous molecules: fluoride ($-F$) substituted thiophene or thiazole, or changing the thiol in thiophene or thiazole to 1,1-dioxide thiophene or thiazole. Figure 4.6 shows the proposed molecular structures: the top row are the molecules that are modified **BT** with electron withdrawing group (*i.e.*, the **BT** series) and below are the molecules that are modified **BTz** with strong electron withdrawing groups (*i.e.*, the **BTz** series).

We further tested our proposals by transport simulations on the model junctions with the same method discussed previously. Figure 4.7 shows the transmission spectra of the model junction of designed molecules. Colored bars above each plot indicate where there are frontier orbitals resonances occur. Both of the plots show that the HOPS shifts away from the E_f while the LUPS shifts close to the E_f . The extent of the changes in the LUPS are more significant than those of the HOPS. The role of strong electron withdrawing groups in a molecular wire is to shift the LUPS closer to E_f , which assists the process of electron tunneling. Additionally, the influence of sulfoxide groups ($-\text{SO}_2$) is much stronger than fluoride ($-F$) groups. The LUPS of sulfoxide groups locate nearly at E_f , which indicates that the 1,1-dioxide thiophene/thiazole functionalized molecular wires are highly conductive and would be a good candidate for design in future molecular wires.

Figure 4.6 A schematic representation of chemical structure of the designed molecules. Above is the **BT** series, below is the **BTz** series.

Figure 4.7 a) Transmission spectra for the modified **BT** molecules with additional electron withdrawing groups: BT-monoSO, BT-biSO, BT-biF and BT-biF-biSO; b) Transmission spectra for the modified **BTz** molecules with additional electron withdrawing groups: BTz-monoSO, BTz-biSO, BTz-biF and BTz-biF-biSO. The x-axis is aligned with respect to the E_f of Au ($E_f = -4.3$ eV). Colored bars above the plot indicate where the resonances of the frontier orbitals and the electron tunneling occur.

4.3. CONCLUSIONS

We explored the electrical properties of tunneling junctions comprising of **BT**, **TTz** and **BTz**. In our design, we keep the length of the molecules and the anchoring group the same while changing the central thiophene rings by introducing a heteroatom (electronegative N atom) step by step. In this way, we keep the tunneling barrier width (d) and the interface between electrode and SAM (J_0) the same while varying the tunneling barrier height (β). We tested the charge transport properties in both ensemble junctions using EGaIn top electrode and single-molecule junctions using STMBJ technique. We observed insignificant difference in charge tunneling rate from both testbeds. Optical gaps obtained from the UV-vis spectra and HOMO-LUMO gaps from DFT calculations show subtle differences. The transmission spectra show slight differences between the three molecular wires as well. However, the frontier orbitals of the molecule or model junction do provide insights in understanding the electrical results. The diagram of energy level alignment shows that the HOPS dominates in the tunneling process for the three molecular wires. Both HOMO/HOPS and LUMO/LUPS are lower due to the electronically N atom. The distance between HOPS and E_f is large while the change in HOPS is comparatively small, thus it does not make big difference to the conductance of a tunneling junction. We attributed this insignificant difference of charge tunneling rate to the weak electron-withdrawing property of the sp^2 N atom in the molecular wires. The role of the electron withdrawing moiety in our molecular wire is to lower both HOPS and LUPS of the molecular junction. We assume that if the electron withdrawing group is strong enough, it could bring the LUPS even closer to E_f , hence LUPS would dominate the tunneling process. We confirmed our assumptions by performing transmission simulations on molecules with functional groups such as fluoride group and sulfoxide groups. It is worth noting that sulfoxide group (*i.e.*, 1,1-dioxide thiophene or 1,1-dioxide thiazole) could be a good candidate of molecular wires with high conductivity.

4.4. EXPERIMENTS DETAILS

SYNTHESIS AND CHARACTERIZATION

SYNTHESIS OF **BITHIOPHENE (BT)**

5,5'-bis((trimethylsilyl)ethynyl)-2,2'-bithiophene

5,5'-dibromo-2,2'-bithiophene 10 (1002 mg, 3.11 mmol) and trimethylsilylacetylene (880 mg, 9 mmol) were dissolved in a mixture of fresh distilled Et_3N (10 mL) and anhydrous THF (20 mL). After degassing with dry N_2 , the catalysts $\text{Pd}(\text{PPh}_3)_4$ (80 mg, 0.07 mmol) and CuI (15mg, 0.08 mmol) were added. The reaction mixture was stirred at room temperature overnight under N_2 . The reaction mixture was poured into water, then the product was

4. INTRODUCING ELECTRON WITHDRAWING GROUPS TO MOLECULAR WIRES IN TUNNELING JUNCTIONS

Figure 4.8 Synthetic route for **Bithiophene (BT)**.

extracted with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography to give product (870 mg, 78 %).

^1H NMR (400 MHz, CDCl_3) δ : 7.11 (d, $J = 3.8$ Hz, 1H), 6.99 (d, $J = 3.8$ Hz, 1H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ : 138.17, 133.68, 123.96, 122.73, 100.72, 97.39, 0.04.

5,5'-diethynyl-2,2'-bithiophene

To a solution of trimethylsilyl derivative 5,5'-bis((trimethylsilyl)ethynyl)-2,2'-bithiophene (180 mg, 0.5 mmol) in THF-methanol (10 mL : 3 mL), aqueous KOH (170 mg, 0.5 mL H_2O) was added to deprotect the trimethylsilyl group. The reaction solution was stirred at room temperature under N_2 for 1 h. The reaction was quenched by adding water (5 mL), then the product was extracted with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents removed by rotary evaporation to provide 5,5'-diethynyl-2,2'-bithiophene as a yellow solid in 95 % yield. The crude was used in the next step without further purification.

^1H NMR (400 MHz, CDCl_3) δ : 7.16 (d, $J = 3.8$ Hz, 2H), 7.02 (d, $J = 3.8$ Hz, 2H), 3.41 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ : 138.26, 134.13, 124.08, 121.63, 82.85, , 76.83, 68.14.

S,S'-((2,2'-bithiophene)-5,5'-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate

5,5'-diethynyl-2,2'-bithiophene (107 mg, 0.5 mmol) and 4-iodophenylthioacetate (280 mg, 1 mmol) were dissolved in mixture of fresh distilled Et_3N (5 mL) and anhydrous THF (15 mL). After degassing with dry N_2 , the catalysts $\text{Pd}(\text{PPh}_3)_4$ (40 mg, 0.04 mmol) and CuI (20 mg, 0.1 mmol) were added. The reaction mixture was stirred at room temperature overnight under N_2 . The reaction mixture was poured into water, then the product was extracted with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents removed by rotary evaporation. The

Figure 4.9 ¹H NMR spectrum of molecular wire Bithiophene (BT).

Figure 4.10 ¹³C NMR spectrum of molecular wire Bithiophene (BT).

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crude solid was purified by recrystallization from toluene to give product (75 mg, 30%).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.4$ Hz, 4H), 7.40 (d, $J = 8.4$ Hz, 4H), 7.20 (d, $J = 3.8$ Hz, 2H), 7.10 (d, $J = 3.8$ Hz, 2H), 2.44 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.60, 138.62, 134.46, 133.48, 132.11, 128.63, 124.38, 124.16, 122.52, 94.10, 84.40, 30.53.

HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{19}\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$: 515.02624, found: 515.02734.

Figure 4.11 HRMS spectrum of molecular wire **Bithiophene (BT)**. Top is experimental data, bottom is calculation data.

SYNTHESIS OF THIOPHENETHIAZOLE (TTz)

Figure 4.12 Synthetic route for **Thiophenethiazole (TTz)**.

2-(thiophen-2-yl)thiazole

2-Bromothiazole (1160 mg, 7.1 mmol), 2-(tributylstannyl)thiophene (2200 mg, 5.9 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (60 mg) were added into (30 mL) toluene under N_2 . The reaction mixture was heated at reflux for overnight, then cooled to room temperature. To the reaction was added water, then the mixture was extracted with dichloromethane (DCM). The organic layer was washed with brine and then concentrated under reduced pressure. The residue was purified by column chromatography (eluent: Hexane:DCM = 5:1) to give a colorless liquid as the product (187 mg, 19%).

^1H NMR (400 MHz, CDCl_3) δ : 7.64 (d, J = 3.2 Hz, 1H), 7.37 (d, J = 3.6 Hz, 1H), 7.23 (d, J = 5.0 Hz, 1H), 7.08 (d, J = 3.2 Hz, 1H), 6.92 (t, J = 4.45 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ : 161.49, 142.86, 136.94, 127.57, 127.28, 126.26, 117.92.

5-bromo-2-(5-bromothiophen-2-yl)thiazole

Compound 2-(thiophen-2-yl)thiazole (1340 mg, 8.02 mmol) was dissolved into 40 mL DMF, and then to the reaction mixture was added NBS (3320 mg, 18.46 mmol) in one portion. After stirred at 60 °C for 4 h, After the reaction mixture cooled to room temperature. 100 mL H_2O was added, then the mixture was extracting with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents was concentrated under reduced pressure. The residue was purified by column chromatography (eluent: Hexane:DCM = 5:1) to give a white solid as the product (2200 mg, 84%).

^1H NMR (400 MHz, CDCl_3) δ : 7.60 (s, 1H), 7.15 (d, J = 3.7 Hz, 1H), 7.01 (d, J = 3.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ : 162.41, 144.89, 138.48, 131.23, 127.07, 116.44, 108.48.

5-((4-(tert-butylthio)phenyl)ethynyl)-2-(5-((4-(tert-butylthio)phenyl)ethynyl)thiophen-2-yl)thiazole

5-bromo-2-(5-bromothiophen-2-yl)thiazole (100 mg, 0.31 mmol) and 1-tert-butylthio-4-ethynylbenzene (176 mg, 0.92 mmol) were dissolved in mixture of fresh distilled Et_3N (5 mL) and anhydrous THF (20 mL). After degassing, the catalysts $\text{Pd}(\text{PPh}_3)_4$ (20 mg) and CuI (10 mg) were added. The reaction mixture was refluxed overnight under N_2 . After the reaction mixture cooled to room temperature. 100 mL H_2O was added, then the mixture was extracting with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography (eluent: CH_2Cl_2 :Hexane = 1:3) to give product (120 mg, 71 %).

^1H NMR (400 MHz, CDCl_3) δ : 7.89 (s, 1H), 7.54 (dd, J = 8.3, 2.1 Hz, 4H), 7.48 (dd, J = 8.1, 3.9 Hz, 4H), 7.43 (d, J = 3.9 Hz, 1H), 7.24 (d, J = 3.9 Hz, 1H). 1.31 (s, 18H).

S-(4-((5-(5-((4-(acetylthio)phenyl)ethynyl)thiazol-2-yl)thiophen-2-yl)et- -hynyl)phenyl)

Figure 4.13 ^1H NMR spectrum of molecular wire **Thiophenethiazole (TTz)**.

ethanethioate [30]

TiCl_4 (0.3 mL, 0.3 mmol) was added drop-wise to a solution of compound **5-((4-(tert-butylthio)phenyl)ethynyl)-2-(5-((4-(tert-butylthio)phenyl)ethynyl)thiophen-2-yl)thiazole** (60 mg, 0.1 mmol) and $\text{CH}_3\text{C}(\text{O})\text{Cl}$ (0.1 mL) in CH_2Cl_2 at 0°C . The resulting mixture was stirred at room temperature for 60 min and the conversion was monitored by TLC (Hexane/ CH_2Cl_2 2:1). Upon completion the reaction was quenched with water (10 mL). Then the mixture was extracting with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography (eluent: CH_2Cl_2 :Hexane = 1:2) to give **TTz** (20 mg, 38 %).

^1H NMR (400 MHz, CD_2Cl_2) δ : 7.93 (s, 1H), 7.59 (dd, J = 8.2, 1.6 Hz, 4H), 7.51 – 7.40 (m, 5H), 7.31 (d, J = 4.0 Hz, 1H), 2.44 (s, 6H).

^{13}C NMR (101 MHz, cdcl_3) δ : 195.89, 195.82, 163.93, 150.37, 140.60, 136.93, 136.91, 135.76, 134.67, 134.63, 131.69, 131.45, 129.52, 128.42, 126.28, 126.00, 120.98, 105.00, 99.17, 97.60, 86.55, 83.20, 32.98, 32.97.

HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{17}\text{N}_2\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$: 516.02022, found: 516.02149.

Figure 4.14 ^{13}C NMR spectrum of molecular wire **Thiophenethiazole (TTz)**.

Figure 4.15 HRMS spectrum of molecular wire **Thiophenethiazole (TTz)**. Top is experimental data, bottom is calculation data.

SYNTHESIS OF BITHIAZOLE (BTz)

Figure 4.16 Synthetic route for Bithiazole (BTz).

2,2'-bithiazole

2-bromothiazole (4 g, 24.4 mmol), Pd(OAc)₂ (280 mg, 1.24 mmol), N,N-Diisopropylethylamine (DIPEA, 4.26 mL, 24.4 mmol) and n-Bu₄NBr (3.94 g, 12.2 mmol) were dissolved into 40 mL toluene under N₂. The reaction mixture was heated at reflux for overnight, then cooled to room temperature. 100 mL H₂O was added to the reaction mixture, then the mixture was extracted with dichloromethane (DCM). The organic layer was washed with brine and then concentrated under reduced pressure. The residue was purified by column chromatography (eluent: Hexane:DCM = 3:1 to 2:1 to 1:2) to give a white solid as the product (660 mg, 16%).

¹HNMR (400 MHz, CDCl₃) δ: 7.86 (d, J=3.2Hz, 2H), 7.41 (d, J=3.2Hz, 2H).

¹³CNMR (101 MHz, CDCl₃) δ: 161.58, 143.87, 120.95.

5,5'-dibromo-2,2'-bithiazole

5,5'-dibromo-2,2'-bithiazole was synthesised according to the literature.[31]

¹HNMR (400 MHz, CDCl₃) δ: 7.75 (s, 2H).

¹³CNMR (101 MHz, CDCl₃) δ: 162.37, 145.63, 112.47.

5,5'-bis((4-(tert-butylthio)phenyl)ethynyl)-2,2'-bithiazole

5,5'-dibromo-2,2'-bithiazole (100 mg, 0.306 mmol) and 1-tert-butylthio-4-ethynylbenzene (175 mg, 0.92 mmol) were dissolved in mixture of fresh distilled Et₃N (5 mL) and anhydrous THF (20 mL). After degassing, the catalysts Pd(PPh₃)₄ (20 mg) and CuI (10 mg) were added. The reaction mixture was refluxed overnight under N₂. After the reaction mixture cooled to room temperature, 100 mL H₂O was added, then the mixture was extracting with CH₂Cl₂, washing with saturated NaHCO₃, water and then brine. The organic phase was then collected and dried over Na₂SO₄ and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography to give product (160 mg, 89 %).

¹HNMR (400 MHz, CDCl₃) δ: 7.99 (s, 2H), 7.52 (q, J = 8.2 Hz, 8H), 1.31 (s, 18H).

¹³CNMR (101 MHz, CDCl₃) δ: 160.82, 148.02, 137.39, 134.84, 131.57, 122.35, 121.54, 97.96, 80.32, 46.89, 31.18.

S,S'-((2,2'-bithiazole)-5,5'-diylbis(ethyne-2,1-diyl))bis(4,1-phenylene) diethanethioate

Figure 4.17 ^1H NMR spectrum of molecular wire **Bithiazole (BTz)**.

TiCl_4 (0.25 mL, 0.25 mmol) was added drop-wise to a solution of compound **5,5'-bis((4-(tert-butylthio) phenyl) ethynyl) -2,2'-bithiazole** (45 mg, 0.082 mmol) and $\text{CH}_3\text{C(O)Cl}$ (0.03 mL, 0.18 mmol) in CH_2Cl_2 at 0°C . The resulting mixture was stirred at room temperature for 60 min and the conversion was monitored by TLC (hexanes/ CH_2Cl_2 2:1). Upon completion (6 hours) the reaction was quenched with water (10 mL). Then the mixture was extracting with CH_2Cl_2 , washing with saturated NaHCO_3 , water and then brine. The organic phase was then collected and dried over Na_2SO_4 and the solvents removed by rotary evaporation. The crude solid was purified by column chromatography (eluent: CH_2Cl_2) to give **BTz** (25 mg, 59 %).

^1H NMR (400 MHz, CDCl_3) δ : 8.01 (s, 2H), 7.58 (d, $J = 8.3$ Hz, 4H), 7.43 (d, $J = 8.3$ Hz, 4H), 2.45 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ : 193.56, 148.56, 134.76, 132.55, 129.83, 123.56, 121.72, 102.82, 97.96, 30.82.

HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{17}\text{N}_2\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$: 517.01552, found: 517.01674.

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Figure 4.18 ¹³CNMR spectrum of molecular wire Bithiazole (BTz).

Figure 4.19 HRMS spectrum of molecular wire Bithiazole (BTz). Top is experimental data, bottom is calculation data.

SAMS PREPARATION

To ensure that high-quality self-assembled monolayers (SAMs) are formed, we used an *in situ* deprotection strategy that is optimized for large, π -conjugated molecules[32, 33] to grow SAMs directly on ultra-smooth Au substrates prepared by template-stripping (Au^{TS}). [8] 100 nm of Au (99.99%) were deposited by thermal deposition at 10^{-7} mbar onto a 3" Silicon wafer (without adhesion layer). Glass substrates (1 cm $\times$ 1 cm) were glued onto the deposited metal by using UV-curable optical adhesive (Norland 61) with 300s exposure of UV light. All SAMs were formed by incubating the thioacetate precursors with 1 cm $\times$ 1 cm template-stripped Au surfaces (100 nm-thick) overnight in 3 mL of 50 μM solution of the respective compound in freshly distilled toluene followed by addition of 0.05 mL of 17 mmol dm^{-3} diazabicycloundec-7-ene solution in toluene 1 h prior the measurement. The substrates were then rinsed with ethanol and left to dry for 10 min.

EGaIn MEASUREMENTS

To minimize the change of oxidative damage to the compounds and SAMs, sample preparation, handing and measurement with the EGaIn setup were all performed in a nitrogen flow box with a controlled O_2 level between 1 – 3% (some O_2 is necessary to form tips of EGaIn) and humidity below 10%. At least three substrates were prepared for each molecule, on each substrate 12 junctions were measured, and for every junction 10 scans (from 0 V $\rightarrow$ 1 V $\rightarrow$ -1 V $\rightarrow$ 0 V, steps of 0.05 V) were performed, thus for a total of at least 360 traces per SAM. A new EGaIn tip was prepared every six junctions and flattened by gently pushing it on a Si wafer few times according to the procedure reported by Simone et al.[34] The details of the EGaIn setup are described elsewhere.[35] The raw data acquired using EGaIn are processed using Scientific Python. The source code is available at <http://github.com/rchiechi/GaussFit> and it retained internally in accordance with the aforementioned data retention policies. J-V curves and NDC plot are obtained directly from the code stated above.

STMBJ MEASUREMENTS

The STM break-junction experiments were performed with a Molecular imaging system using PicoScan software. The STM tip was prepared by cutting a 0.25 mm gold wire (99.999%). The STM cell was cleaned with piranha solution (98% H_2SO_4 :30% H_2O_2 =3:1 v/v) and then sonicated three times in MilliQ water. We carried out the conductance measurements in a 0.1 mM mesitylene solution of the different compounds. Prior to the measurement, a small amount of NEt_3 was added to the solution in order to cleave the thioacetate group.[32] Then the tip was precisely driven by the piezo, leading to a repeatedly in and out

of contact with the substrate. During such movements, the molecules may bridge both the tip and the substrate electrodes. Meanwhile, current versus tip travel distance (I/S) curves are recorded under a fixed bias (0.1 V in our case).[26] Thousands of traces were recorded to allow statistical analysis. Single molecular conductance is determined by the current plateau as well as the conductance histogram constructed from large number of individual events.

TRANSPORT CALCULATIONS

All DFT calculations were performed using ORCA 4.10 software package[27, 28]. The molecules terminated with thiols were first optimized by BP/def2-SVP in the gas-phase. Single point energy calculations were performed on this model junctions using B3LYP/G and LANL2DZ basis sets according to literature procedures to compute the energy levels[36]. Single-molecule junction were constructed by attaching the minimized structures to 12-atom Au(111) surface by the terminal sulfur atoms at hexagonal close-pack hollow sites at a distance of 1.75 Å from the center of the hollow site. Transmission spectra were computed in ARTAIOS using outputs from B3LYP/G(LANL2DZ) calculations based on the minimized geometries[37].

AUTHOR CONTRIBUTIONS

The content in this chapter is not published in any journal. Authors contributed to this chapter are Yuru Liu, Gang Ye, Ryan C. Chiechi.

Y.L. performed EGaIn measurement, STM-BJ measurement, transport calculations. G.Y. synthesized and characterized the molecules, performed the measurements of UV-vis spectra, and related data handling and interpretation. R.C.C. supervised the whole project. All the authors contributed to preparing figures and writing the manuscript.

BIBLIOGRAPHY

- (1) Zhang, Y.; Zhao, Z.; Fracasso, D.; Chiechi, R. C. Bottom-Up Molecular Tunneling Junctions Formed by Self-Assembly. *Isr. J. Chem.* **2014**, *54*, 513–533.
- (2) Vilan, A.; Aswal, D.; Cahen, D. Large-Area, Ensemble Molecular Electronics: Motivation and Challenges. *Chem. Rev.* **2017**, *117*, 4248–4286.
- (3) Xiang, L.; Hines, T.; Palma, J. L.; Lu, X.; Mujica, V.; Ratner, M. A.; Zhou, G.; Tao, N. Non-Exponential Length Dependence of Conductance in Iodide-Terminated Oligothiophene Single-Molecule Tunneling Junctions. *J. Am. Chem. Soc.* **2016**, *138*, 679–687.
- (4) McCreery, R. L.; Yan, H.; Bergren, A. J. A critical perspective on molecular electronic junctions: there is plenty of room in the middle. *Phys. Chem. Chem. Phys.* **2013**, *15*, 1065–1081.
- (5) Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
- (6) Solomon, G. C.; Herrmann, C.; Vura-Weis, J.; Wasielewski, M. R.; Ratner, M. A. The Chameleonic Nature of Electron Transport Through Π -Stacked Systems. *J. Am. Chem. Soc.* **2010**, *132*, 7887–7889.
- (7) Akkerman, H. B.; Blom, P. W. M.; de Leeuw, D. M.; de Boer, B. Towards Molecular Electronics With Large-Area Molecular Junctions. *Nature* **2006**, *441*, 69–72.
- (8) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO₂-Templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 9686–9694.
- (9) Thuo, M. M.; Reus, W. F.; Nijhuis, C. A.; Barber, J. R.; Kim, C.; Schulz, M. D.; Whitesides, G. M. Odd-Even Effects in Charge Transport Across Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2011**, *133*, 2962–2975.
- (10) Dell, E. J.; Capozzi, B.; Xia, J.; Venkataraman, L.; Campos, L. M. Molecular length dictates the nature of charge carriers in single-molecule junctions of oxidized oligothiophenes. *Nat. Chem.* **2015**, *7*, 209–214.

- (11) Kim; Beebe, J. M.; Jun, Y.; Zhu, X.-Y.; Frisbie, C. D. Correlation Between HOMO Alignment and Contact Resistance in Molecular Junctions: Aromatic Thiols Versus Aromatic Isocyanides. *J. Am. Chem. Soc.* **2006**, *128*, 4970–4971.
- (12) Fracasso, D.; Muglali, M. I.; Rohwerder, M.; Terfort, A.; Chiechi, R. C. Influence of an Atom in EGaIn/Ga₂O₃ Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2013**, *117*, 11367–11376.
- (13) Xie, Z.; Bâldea, I.; Smith, C. E.; Wu, Y.; Frisbie, C. D. Experimental and Theoretical Analysis of Nanotransport in Oligophenylene Dithiol Junctions as a Function of Molecular Length and Contact Work Function. *ACS Nano* **2015**, *9*, 8022–8036.
- (14) Carlotti, M.; Degen, M.; Zhang, Y.; Chiechi, R. C. Pronounced Environmental Effects on Injection Currents in EGaIn Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2016**, *120*, 20437–20445.
- (15) Choi, S. H.; Kim, B.; Frisbie, C. D. Electrical Resistance of Long Conjugated Molecular Wires. *Science* **2008**, *320*, 1482–1486.
- (16) Song, H.; Kim, Y.; Jang, Y. H.; Jeong, H.; Reed, M. A.; Lee, T. Observation of Molecular Orbital Gating. *Nature* **2009**, *462*, 1039–1043.
- (17) Xie, Z.; Bâldea, I.; Oram, S.; Smith, C. E.; Frisbie, C. D. Effect of Heteroatom Substitution on Transport in Alkanedithiol-Based Molecular Tunnel Junctions: Evidence for Universal Behavior. *ACS Nano* **2016**, *11*, 569–578.
- (18) Rodriguez-Gonzalez, S.; Xie, Z.; Galangau, O.; Selvanathan, P.; Norel, L.; Dyck, C. V.; Costuas, K.; Frisbie, C. D.; Rigaut, S.; Cornil, J. HOMO Level Pinning in Molecular Junctions: Joint Theoretical and Experimental Evidence. *J. Phys. Chem. Lett.* **2018**, *9*, 2394–2403.
- (19) Guo, X.; Quinn, J.; Chen, Z.; Usta, H.; Zheng, Y.; Xia, Y.; Hennek, J. W.; Ortiz, R. P.; Marks, T. J.; Facchetti, A. Dialkoxybithiazole: A New Building Block for Head-to-Head Polymer Semiconductors. *J. Am. Chem. Soc.* **2013**, *135*, 1986–1996.
- (20) Usta, H.; Sheets, W. C.; Denti, M.; Generali, G.; Capelli, R.; Lu, S.; Yu, X.; Muccini, M.; Facchetti, A. Perfluoroalkyl-Functionalized Thiazole–Thiophene Oligomers as N-Channel Semiconductors in Organic Field-Effect and Light-Emitting Transistors. *Chem. Mater.* **2014**, *26*, 6542–6556.
- (21) Fu, B.; Wang, C.-Y.; Rose, B. D.; Jiang, Y.; Chang, M.; Chu, P.-H.; Yuan, Z.; Fuentes-Hernandez, C.; Kippelen, B.; Brédas, J.-L.; Collard, D. M.; Reichmanis, E. Molecular Engineering of Nonhalogenated Solution-Processable Bithiazole-Based Electron-Transport Polymeric Semiconductors. *Chem. Mater.* **2015**, *27*, 2928–2937.

- (22) Yuan, Z.; Fu, B.; Thomas, S.; Zhang, S.; DeLuca, G.; Chang, R.; Lopez, L.; Fares, C.; Zhang, G.; Bredas, J.-L.; Reichmanis, E. Unipolar Electron Transport Polymers: A Thiazole Based All-Electron Acceptor Approach. *Chem. Mater.* **2016**, *28*, 6045–6049.
- (23) Chiechi, R.; Weiss, E.; Dickey, M.; Whitesides, G. Eutectic Gallium–Indium (EGaIn): A Moldable Liquid Metal for Electrical Characterization of Self-Assembled Monolayers. *Angew. Chem., Int. Ed.* **2008**, *47*, 142–144.
- (24) Dubi, Y. Transport Through Self-Assembled Monolayer Molecular Junctions: Role of In-Plane Dephasing. *J. Phys. Chem. C* **2014**, *118*, 21119–21127.
- (25) Xu, B. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. *Science* **2003**, *301*, 1221–1223.
- (26) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. Single-Molecule Circuits with Well-Defined Molecular Conductance. *Nano Lett.* **2006**, *6*, 458–462.
- (27) Neese, F. The ORCA Program System. *Sci. China, Ser. F: Info. Sci.* **2011**, *2*, 73–78.
- (28) Neese, F. Software Update: The ORCA Program System, Version 4.0. *Sci. China, Ser. F: Info. Sci.* **2017**, *8*, e1327.
- (29) Bilić, A.; Reimers, J. R.; Hush, N. S. The structure, energetics, and nature of the chemical bonding of phenylthiol adsorbed on the Au(111) surface: Implications for density-functional calculations of molecular-electronic conduction. *J. Chem. Phys.* **2005**, *122*, 094708.
- (30) Pijper, T. C.; Robertus, J.; Browne, W. R.; Feringa, B. L. Mild Ti-Mediated Transformation of T-Butyl Thio-Ethers Into Thio-Acetates. *Org. Biomol. Chem.* **2015**, *13*, 265–268.
- (31) Usta, H.; Sheets, W. C.; Denti, M.; Generali, G.; Capelli, R.; Lu, S.; Yu, X.; Muccini, M.; Facchetti, A. Perfluoroalkyl-functionalized thiazole–thiophene oligomers as n-channel semiconductors in organic field-effect and light-emitting transistors. *Chem. Mater.* **2014**, *26*, 6542–6556.
- (32) Valkenier, H.; Huisman, E. H.; van Hal, P. A.; de Leeuw, D. M.; Chiechi, R. C.; Hummelen, J. C. Formation of High-Quality Self-Assembled Monolayers of Conjugated Dithiols on Gold: Base Matters. *J. Am. Chem. Soc.* **2011**, *133*, 4930–4939.
- (33) Carlotti, M.; Kovalchuk, A.; Wächter, T.; Qiu, X.; Zharnikov, M.; Chiechi, R. C. Conformation-Driven Quantum Interference Effects Mediated by Through-Space Conjugation in Self-Assembled Monolayers. *Nat. Commun.* **2016**, *7*, 1–7.

- (34) Simeone, F. C.; Yoon, H. J.; Thuo, M. M.; Barber, J. R.; Smith, B.; Whitesides, G. M. Defining the Value of Injection Current and Effective Electrical Contact Area for EGaIn-Based Molecular Tunneling Junctions. *J. Am. Chem. Soc.* **2013**, *135*, 18131–18144.
- (35) Fracasso, D.; Valkenier, H.; Hummelen, J. C.; Solomon, G. C.; Chiechi, R. C. Evidence for Quantum Interference in SAMs of Arylethynylene Thiolates in Tunneling Junctions With Eutectic Ga–In (EGaIn) Top-Contacts. *J. Am. Chem. Soc.* **2011**, *133*, 9556–9563.
- (36) Herrmann, C.; Solomon, G. C.; Subotnik, J. E.; Mujica, V.; Ratner, M. A. Ghost Transmission: How Large Basis Sets Can Make Electron Transport Calculations Worse. *J. Chem. Phys.* **2010**, *132*, 024103.
- (37) Deffner, M.; Gross, L.; Steenbock, T.; Voigt, B. A.; Solomon, G. C.; Herrmann, C. ARTAIOS - a transport code for postprocessing quantum chemical electronic structure calculations, <https://www.chemie.uni-hamburg.de/ac/herrmann/software/index.html>, 2009-2017.

5

PROTONIC ACID DOPING OF LOW BAND-GAP CONJUGATED POLYIONS

The Content of this chapter is published in Materials Chemistry Frontiers. (doi:10.1039/d0qm00278j). I would like to acknowledge Dr. Gang Ye for the synthesis, UV-vis, CV and EPR measurements of the molecules, Dr. Jian Liu and Prof. dr. L. Jan Anton Koster for the conductivity measurement of the film, Dr. Xinkai Qiu for AFM measurements, Prof. dr. Ryan C. Chiechi for his supervision.

5.1. INTRODUCTION

Conjugated polymers combine the utility of organic synthesis and the intrinsic properties of soft materials with the utility of semiconductors. However, the best-performing conjugated polymers tend to require processing from solvents that difficult or expensive to scale. Conjugated polyelectrolytes (CPEs) address this problem by decorating the π -conjugated backbone with pendant ionic functionalities, enabling processing from polar, protic solvents such as water or ethanol. Although they retain their semiconducting properties, the mismatch in polarity between the backbone and pendant groups tends to drive unfavorable morphologies for bulk charge-transport.[1] We have taken a different approach, installing closed-shell charges into the π -conjugated backbone to balance the charged pendant groups, forming conjugated polyions (CPIs).[2, 3]

Conjugated polymers that can be processed from green solvents, which tend to be polar and protic, have played a key role in a range of applications in organic electronics.[4] The most widely-used of such polymers is poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), which is a polymer blend in which the charges of doped PEDOT are balanced by PSS. It is used, for example, as a hole-collection layer in organic solar cells or as an active material in thermoelectric devices.[5] However, PEDOT:PSS is prepared in the doped, metallic state and is processed from an aqueous suspension. Self-doped PEDOT-based conjugated polyelectrolytes eliminate the need to blend PEDOT with a separate polyelectrolyte and can be used as hole-collection layers in organic solar cells or as an active material organic electrochemical transistors.[6–10] These and other CPEs are semiconducting polymers defined by π -conjugated backbones with pendant ionic functionalities.[4, 11–15] They are primarily used as interfacial modifiers in optoelectronic devices because of the aforementioned morphology issues.[4, 11, 16] We are developing a new type conjugated polymer that combines the beneficial properties of CPEs and PEDOT:PSS. By introducing formal, closed-shell charges into the backbones of conjugated polymers in a process we call “spinless doping”, we can combine charged backbones with ionic pendant groups to avoid unfavorable aggregation while preserving the semiconducting properties of the backbone.[1, 3, 17, 18] As such, they can be processed from highly polar, protonic solvents to give smooth, semiconducting thin-films that serve as active layers in photovoltaic devices.[2]

The donor-acceptor strategy is a powerful tool to tune the bandgap and energy levels of conventional conjugated polymers; through the delicate modification and combination of different strengths of donor or acceptor building blocks, many polymeric materials have been designed and synthesized for applications in organic electronics.[19, 20] When applied to CPEs, donor-acceptor backbone engineering can cause pristine CPEs to become self-doped, in which the ionic pendant groups stabilize polarons in the backbone.[21–25]

Here, we apply the donor-acceptor strategy to the synthesis of a series of conjugated polymers that undergo spinless doping by protonic acids to generate CPIs. We find that the bandgap and energy levels of CPIs are easily modulated by increasing the strength of donor building block and that, surprisingly, the resulting CPIs can be further doped by protonic acids effecting conversion to the metallic state. While the aforementioned PEDOT-based CPEs become self-doped by the proximity of the ionic pendant groups to the neutral backbone,[26] CPIs are zwitterionic and the pendant groups balance the closed-shell cations already present in the backbones even in the pristine, semiconducting state. Optical absorption, electron paramagnetic resonance spectroscopy and electrical conductivity measurements reveal that this spontaneous spin-unpairing occurs more easily in CPIs with higher-lying occupied states, suggesting an internal redox process following the initial spinless doping.

5.2. RESULTS AND DISCUSSIONS

SYNTHESIS AND CHARACTERIZATION

Figure 5.1 Synthesis of conjugated polyions via a three-component, random Stille copolymerization. The Zwitterionic form is favored in the solid-state by the loss of H_2O .

Figure 5.1 shows the synthetic route and corresponding chemical structures of three CPIs, **PIIZ-T**, **PIIZ-TT** and **PIIZ-TT-DEG**. The monomers were synthesized according to literature procedures,[27–31] which are described in detail in the Supporting Information. To use the donor-acceptor strategy for controlling the band gap (E_g) and balance the cationic and anionic groups, we employed a three-component, palladium-catalyzed Stille polymer-

ization in DMF. Monomer 1 provides the anionic pendant groups in the form of carboxylic acids, Monomer 2 is a carbocation precursor and Monomer 3 is a aromatic distannyl compound with increasing electron-donating units, depicted as Ar, that differentiates the three CPIs. The polymers are prepared in their neutral, insulating forms by refluxing the mixture of monomers overnight. As synthesized, all three polymers are insoluble in non-polar solvents and only sparingly soluble in polar solvents, allowing the removal of impurities and low-molecular-weight fractions by dialysis in water.

PHOTOPHYSICAL PROPERTIES

Figure 5.2 a) Absorption spectra of the as-prepared conjugated polyions, **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG**, dissolved in either slightly basic H₂O or DMF (10⁻⁵ M) solutions, showing a decrease in the optical gap with increasing donor strength. b) Absorption spectra of the same conjugated polyions in glacial CH₃COOH (10⁻⁵ M), showing a large bathochromic shift associated with the formation of cations in the backbone, which induce a transition to the semiconducting form and increase the conjugation length.

The UV-Vis absorption spectra for polymers of **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** before and after spinless doping are shown in Figure 5.2. The spectra of **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** exhibit one, main $\pi - \pi^*$ transition, located from 350 nm to 500 nm, reflecting a decrease in the band-gap (E_g) with increasing donor strength. Since spinless doping is effected by the generation of closed-shell cations from the loss of H₂O, the degree of doping scales with the strength of the acid from which the CPI is processed. In solution, this process is in equilibrium, with weakly acidic solutions like CH₃COOH ($pK_a = 4.76$) disfavoring the dehydrated, cationic form such that the degree of conjugation, which is defined by the average number of consecutive monomers in the cationic form, scales with acidity. The commensurate decrease in E_g also scales with the strength of the donor because of the emergence of a charge-transfer band that forms because of the acceptor nature of tritylium. This relationship can be seen in Figure 5.2b; in acidic solutions, charge-transfer

Figure 5.3 a) Absorption spectra of **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** in pure HCOOH. corresponding to the formation of delocalized cations. b) Absorption spectra of **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** in pure CF₃COOH.

bands appear that follow a trend of decreasing energy with increasing donor-strength. Based on the absorption band edge, the E_g of the CPIs in the cationic form are 1.82 eV for **CPIZ-T** and 1.66 eV for **CPIZ-TT**, 1.29 eV for **CPIZ-TT-DEG**, respectively.

Figure 5.3a shows the absorption spectra of **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** dissolved in the strong acid HCOOH ($pK_a = 3.77$). As discussed above, the expectation is that the conjugation lengths would increase compared to CH₃COOH, following the same trend in donor-strengths; however, an unexpected, low-energy transition at 1200 nm is present in the **CPIZ-TT-DEG** spectrum that is absent in both the **CPIZ-T** and **CPIZ-TT** spectra. Figure 5.3b shows that, the spectrum of **CPIZ-TT-DEG** in the even stronger acid CF₃COOH ($pK_a = -0.25$) exhibits a further bathochromic shift in λ_{max} , while the low-energy transition increases in intensity without shifting in energy. The spectra of **CPIZ-T** and **CPIZ-TT** show the appearance of a very weak transition at the band edge, revealing a trend with increasing donor-strength.

To compare the effects of increased acidity directly, we re-plotted the absorption spectra of **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** separately in the three different acids in Figure 5.4. Although there is a small shoulder in CF₃COOH, the low-energy transition is not present in **CPIZ-T** in CH₃COOH or HCOOH. The same trend is apparent in **CPIZ-TT**, with a slightly higher intensity creating a resolvable transition near 1000 nm. Although these spectra are all in solution, the trends in λ_{max} coupled with the changing intensity of the transition at 1200 nm (for **CPIZ-TT-DEG**) are reminiscent of the appearance of polarons in redox-doped conducting polymers.

For further insight into the low-energy transition, we measured the absorption spectra of thin films of the CPIs cast from different acidic solutions. Figure 5.5 shows the UV-

Figure 5.4 a) Absorption spectra of **CPIZ-T** in basic or different acidic solutions (10^{-5}M). b) Absorption spectra of **CPIZ-TT** in basic or different acidic solutions (10^{-5}M). c) Absorption spectra of **CPIZ-TT-DEG** in basic or different acidic solutions (10^{-5}M).

Figure 5.5 a) Absorption spectra of thin films of the **CPIZ-TT** cast from different acidic solutions (10^{-5} M). b) Absorption spectra of thin films of the **CPIZ-TT-DEG** cast from different acidic solutions (10^{-5} M).

Vis-NIR spectra of these films for **CPIZ-TT** and **CPIZ-TT-DEG**; the spectra of **CPIZ-T** is reported in our previous work.[2] The spectra of **CPIZ-T** and **CPIZ-TT** are featureless above ~ 1000 nm, indicating the absence of polarons or bipolarons. The spectra of thin films of **CPIZ-TT-DEG** cast from CH_3COOH are also featureless above ~ 1000 nm; however, when cast from either HCOOH or CH_3COOH , a broad absorption past 1000 nm appears, indicating the likely formation of polarons.

Unlike the closed-shell cations that form via spinless doping, polarons comprise both spin and charge; they are delocalized radical cations. Thus, we acquired electron paramagnetic resonance (EPR) spectra for **CPIZ-T**, **CPIZ-TT** and **CPIZ-TT-DEG** in the strong acid solutions to investigate the possibility that radical cations form spontaneously in sufficiently strong acids with sufficiently strong donors. The resulting spectra, shown in Figure 5.6, reveal that **CPIZ-T** and **CPIZ-TT** are EPR-silent in HCOOH , in agreement with the absorption spectra in solution and the solid-state. While, even in HCOOH , **CPIZ-TT-DEG** shows a strong resonance, confirming that the low-energy transition observed in absorption spectra correspond to polarons / radical cations. In CF_3COOH , all three CPIs show a resonance, but it is much stronger in **CPIZ-TT-DEG** than in **CPIZ-TT** or **CPIZ-T**, suggesting that the shoulder in the absorbance spectra correspond to the formation of very dilute polarons / radical cations. The slightly lower intensity of the EPR signal of **CPIZ-TT** compared to **CPIZ-T** contradicts the trend in the absorption intensities, but those may be affected by their aggregation states in CF_3COOH . In any case, **CPIZ-TT-DEG** shows the strongest signal intensity by far and intensity of the EPR signals broadly correlates with the optical band at NIR regions of the absorption spectra, indicating that these optical transitions are indeed proportional to the concentration of radical species, which is commensurate with the degree of redox doping in the solid-state. The overall trend indicates that the spontaneous

Figure 5.6 EPR spectra of solutions of CPIZ-T, CPIZ-TT, and CPIZ-TT in HCOOH and CF₃COOH.

formation of polarons correlates to the donor-strength much more significantly than to the strength of the acid from which films are cast.

ELECTROCHEMICAL PROPERTIES

Figure 5.7 Cyclic voltammograms of a thin film of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG** versus Fc/Fc^+ on a glassy carbon working electrode immersed in 0.1 mol L^{-1} $n\text{-Bu}_4\text{NPF}_6$ acetonitrile solution at 100 mV s^{-1} . (a) The fully reversible reduction waves are indicative of traditional redox doping/de-doping of the band structure of a semiconducting state conjugated polymer. (b) Oxidative waves are irreversible.

While spinless doping is a two-electron processes, eliminating an equivalent of H_2O to form a closed-shell cation in the backbone and corresponding pendant carboxylate the formation of unpaired electrons implies the existence of a subsequent redox process. Thus, we used cyclic voltammetry (CV) to gain insight into the redox behavior of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG**. The results are shown in the Figure 5.7. All three polymers exhibit fully reversible reduction waves, corresponding to the reduction of tritylium moieties. Although electrochemical reduction normally leads to n-doping, in the case of CPIs, it forms positive polarons (by reducing closed-shell cations) and is, therefore, p-doping. All three polymers exhibit irreversible oxidation curves because CPIs in their semiconducting form are already fully cationic such that the removal of additional electrons corresponds to over-oxidation in traditional conjugated polymers, however, **CPIZ-TT-DEG** is arguably quasi-reversible. The onset oxidation potentials ($E_{\text{onset}}^{\text{Ox.}}$) of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG** are 0.86, 0.68, and -0.1 V, respectively. The energy levels of the polymers calculated from these data are summarized in Table 5.1. Both the occupied (HOMO/valence band) and unoccupied (LUMO/conduction band) levels of the polymers increase gradually with increasing donor-strength; however, the unoccupied states show less sensitivity than the occupied states, presumably because the effects of the donor are swamped by those of the cationic tritylim units. As predicted from the relative strengths of the donors, **CPIZ-TT-DEG** exhibits the highest-lying occupied states, making it both more energetically favorable to form cations in acidic

solutions and for subsequent oxidation.

Table 5.1 Summary of the photophysical properties and electrochemical properties of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG**.

Physical Properties	CPIZ-T	CPIZ-TT	CPIZ-TT-DEG
λ_{onset} solution ^a (nm)	680	745	960
E_g optical ^b (eV)	1.82	1.66	1.29
E_g CV (eV)	1.81	1.66	1.05
$E_{onset}^{Red.}$ (V)	−0.54	−0.58	−0.62
$E_{onset}^{Ox.}$ (V)	0.86	0.68	−0.10
Conduction Band from CV ^c (eV)	−4.54	−4.48	−4.44
Valence Band from CV ^d (eV)	−5.92	−5.74	−4.96

^a CPIs in CH₃COOH solution.

^b $E_g^{opt.} = 1240/\lambda_{onset}$.

^c Calculated from CV: $E_{conduction} = -(5.06 + E_{onset}^{red.})$ eV.

^d Calculated from CV: $E_{valence} = -(5.06 + E_{onset}^{ox.})$ eV.

CONDUCTIVITY

Redox doping, whether chemical or electrochemical, causes a transition in conjugated polymers from the semiconducting state to the metallic state, which is defined by the presence of free charge carriers (*i.e.*, polarons).[32] This property is vital to their performance when either high conductivity or carrier density is required. Thus, changes in conductivity are an indirect measure of the formation of free carriers and the transition to a metallic state. To probe the differences in conductivity across the series of CPIs, we used a two-point probe to measure the current-voltage response of thin films of **CPIZ-TT** and **CPIZ-TT-DEG** that were spin cast from HCOOH or CF₃COOH. **CPIZ-TT** was spin-coated from 5 mg mL^{−1} in HCOOH or CF₃COOH while **CPIZ-TT-DEG** was spin-coated from 10 mg mL^{−1} in HCOOH or CF₃COOH. The results are shown in Figure 5.8. The highest recorded conductivity was 5.5×10^{-3} S m^{−1} in **CPIZ-TT-DEG** cast from CF₃COOH, which is four orders of magnitude higher than that of **CPIZ-TT**. (Device channel-lengths had a negligible effect, as shown in Figure 5.9.) The conductivity of films of **CPIZ-TT-DEG** cast from CF₃COOH were three orders of magnitude higher than those case from HCOOH, while the difference between films of **CPIZ-TT** cast from CF₃COOH and HCOOH were negligible. This difference could reflect a non-linear relationship between donor-strength and protonic acid-induced doping or a difference in aggregation, but in either case the conductivities of thin films correlates well to the EPR signal-strengths in solution. The conductivity and carrier mobility of **CPIZ-T** is reported in our previous work; as expected, it is the least conductive of the series.[2]

Figure 5.8 Current-voltage plots of thin film of **CPIZ-TT** and **CPIZ-TT-DEG** cast from **HCOOH** and **CF₃COOH**.

FILM MORPHOLOGY

The putative advantage of CPIs, in general, over traditional conjugated polymers—and especially CPEs—is that they are directly solubilized by polar, protonic solvents rather than forming aggregates or suspensions; their zwitterionic nature, in which opposing charges exist in the backbone and pendant groups, means that the polymer chains are completely solvated, leading to smooth, homogeneous films. Figure 5.10 shows height images of **CPIZ-TT-DEG** films on bare glass substrates measured by atomic force microscopy (AFM). Films cast from 10 mg mL^{-1} in **HCOOH** are smoother than that from 10 mg mL^{-1} in **CF₃COOH** with RMS roughness values of 0.56 nm and 2.44 nm, respectively.

SEEBECK COEFFICIENT

The low thermal conductivity of conjugated polymers makes them ideally suited for use in organic thermoelectric devices, but since electric currents are driven by the migration of carriers along a thermal gradient, they must be used in their doped form. One possible application of doped CPIs is as p-type thermoelectric materials that can be cast from green solvents and that do not require any additional doping. In order to test the viability of doped **CPIZ-TT-DEG** and study the polarity of the doping, we determined the Seebeck

Figure 5.9 a) Channel length dependence of **CPIZ-TT-DEG** conductivity cast from CF_3COOH . b) Channel length dependence of **CPIZ-TT-DEG** conductivity cast from HCOOH .

Figure 5.10 Surface topographic AFM image of **CPIZ-TT-DEG** spun cast from a) HCOOH and b) CF_3COOH on bare glass surface ($25 \mu\text{m}^2$). The RMS values are 0.56 nm and 2.44 nm for cast from a) HCOOH and b) CF_3COOH

coefficient of films cast from CF_3COOH to be $111 \mu\text{V K}^{-1}$, from the data shown in Figure 5.11. Using the electrical conductivity and Seebeck coefficient, we also calculated the power factors of films of **CPIZ-TT-DEG**. Films cast from CF_3COOH give a power factor of $6.8 \times 10^{-5} \mu\text{W m}^{-1} \text{ K}^{-2}$. The positive sign of the Seebeck coefficient further indicates that the doped **CPIZ-TT-DEG** is a p-type polymer, in agreement with the hypothesis that positive polarons form spontaneously from the closed-shell cations.

DENSITY FUNCTIONAL THEORY CALCULATIONS

To gain insight into the electronic and donor/acceptor character of **CPIZ-T** and **CPIZ-TT**, and **CPIZ-TT-DEG**, we carried out density functional theory (DFT) calculations at the B3LYP/6-311G(d,p) level using Gaussian 16.[33] To simplify the calculation, we considered only one repeat-unit comprising two cations, which is sufficient to reveal any anomalies

Figure 5.11 Time evolution of the thermal voltage of the reference constantan wire (the black symbols) and **CPIZ-TT-DEG** thin films cast from the CF_3COOH . The corresponding plots of thermal V_{sample} versus thermal V_{ref} with the linear fits.

in the frontier orbitals. As can be seen in Figure 5.12, the HOMOs are delocalized over the neutral fluorene and thiophene moieties, while the LUMOs are localized on the cationic tritylium moieties, reflecting their strong acceptor nature. The only variation is in **CPIZ-TT-DEG**, where the HOMO density clearly extends to the cationic tritylium moieties, leading to some spacial overlap of the frontier orbitals. These results show that the electronic structure of the CPIs does not differ significantly from that of a typical donor-acceptor polymer, despite the presence of cations in the backbone. They also suggest that the donor and acceptor units are the most strongly coupled in **CPIZ-TT-DEG**, which is reflected in the small bandgap (1.05 eV electrochemically, 1.29 eV optically).

PROTON-INDUCED SPIN UNPAIRING

The exact mechanism by which CPIs form polarons from protonic acid doping cannot be determined unambiguously, but we can formulate a plausible explanation from the experimental data described above. Protonic acids as non-oxidizing dopants for conventional conjugated polymers such as poly(phenylenevinylene) and polyaniline have been systemati-

Figure 5.12 DFT-optimized molecular orbitals of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG**.

cally investigated.[34] But the mechanism for the proton-induced spin unpairing mechanism (PISUM) was first proposed by Wudl and et al. in 1987.[35] In principle, the PISUM in CPIs is no different than for ordinary conjugated polymers, since the CPIs are pristine semiconductors, even though they bear charges. We observed that the PISUM of CPIs is such that, the lower in energy the occupied states, the stronger the acid required to induce a signal by EPR. This trend is consistent with conventional conjugated polymers for which protonic acid doping scales with ionization potential.[34] Therefore, we proposed the PISUM shown in Figure 5.13 based on the results above and PISUM in conventional conjugated polymers. The first step is spinless doping, in which protonation converts an insulating CPI precursor (P-1) into a pristine semiconductor (P-2).[1–3, 17] This step is always exergonic and becomes more favorable with increasing donor-strength. To gain more insights into this step, we performed the DFT calculations of the CPI units both in a neutral state (with OH group attached to the tritylium ion, see P-1 in Fig. 5.13) and in cationic state (refer P-2 and P-3 in Fig. 5.13). The values in Table 5.2 are very large because of the lack of solvation, however, the trend is in good agreement with the experimental results. There is redox imbalance between donor and acceptor units, but that is true for all donor/acceptor copolymers; for homopolymers like PANI, this redox imbalance develops when part of a polymer chain is protonated, but in the case of CPIs, the first protonation effects spinless doping, before which the polymer backbone is not conjugated.

Thus, we propose that the second protonation of the donor unit of one polymer chain widens the redox imbalance sufficiently to drive the redox reaction and an electron transfer

Figure 5.13 Proposed proton-induced spin unpairing mechanism (PISUM) for conjugated polyions (CPIs). The protonation is assumed to take place on a thiophene ring, but the exact position is uncertain.

Table 5.2 Summary of the total energy difference of **CPIZ-T**, **CPIZ-TT**, and **CPIZ-TT-DEG**.

	CPI-(OH) ₂ (kcal mol ⁻¹)	+ 2 H ⁺ (kcal mol ⁻¹)	→	CPI-cation (kcal mol ⁻¹)	+ 2 H ₂ O (kcal mol ⁻¹)	ΔE (kcal mol ⁻¹)
CPIZ-T	-2475474.11	0		-2380019.17	-95942.92	-487.99
CPIZ-TT	-3168091.483	0		-3072642.05	-95942.92	-493.49
CPIZ-TT-DEG	-3455615.491	0		-3360174.83	-95942.92	-502.26

from the one P-2 chain to another protonated P-2 chain (or another segment of the same chain), resulting in formation of polaron segments P-3 and P-3'. According to this mechanism, PISUM in CPIs would become more favorable as the occupied state increases in energy both because it is driven by a redox imbalance between the donor and acceptor (which may also be facilitated by the spatial overlap of the HOMO and LUMO revealed by the DFT calculations) and because it depends on the protonation of the donor moiety, which is more energetically favorable in more electron-rich donors.

5.3. CONCLUSIONS

Our previous studies on CPIs has focused on their semiconducting properties and the ability to cast them into smooth, homogeneous films from green solvents. The serendipitous discovery that **CPIZ-TT-DEG** spontaneously forms polarons in acidic solutions extends the utility of CPIs to applications that require doped polymers or free charge-carriers. The cationic nature of CPIs is such that, in their semiconducting form, the backbone contains positive charges, yet electrochemical reduction leads to p-doping; because the PISUM in traditional conjugated polymers forms p-doped polymers via oxidation, one would not expect to find it in CPIs. The fact that we observed a PISUM further underscores the otherwise ordinary nature of CPIs; they are intrinsic semiconducting polymers that exhibit a transition to the metallic state upon doping, except that they are completely soluble in polar, protonic solvents and can be deposited in their semiconducting or doped forms simply by controlling the acidity of the solution from which they are processed.

5.4. EXPERIMENTS DETAILS

SYNTHESIS

GENERAL

All reagents and solvents were commercial and were used without further purification unless otherwise indicated. Monomer 1 and monomer 2 were synthesized according to literature procedures.[27–31]

Figure 5.14 Synthetic route for **Monomer T2DEG**.

Measurement and characterization. ^1H NMR and ^{13}C NMR were performed on a Varian Unity Plus (400 MHz) instrument at 25 °C, using tetramethylsilane (TMS) as an internal standard. NMR shifts are reported in ppm, relative to the residual protonated solvent signals of CDCl_3 ($\delta = 7.26$ ppm) or $\text{DMSO}-d_6$ ($\delta = 2.50$ ppm) and at the carbon absorption in CDCl_3 ($\delta = 77.23$ ppm) or $\text{DMSO}-d_6$ ($\delta = 39.52$ ppm). Multiplicities are denoted as: singlet (s), doublet (d), triplet (t) and multiplet (m). FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. EPR spectra were recorded on a Magnetech MiniScope MS400 using a quartz capillary at a concentration of 0.5–1 mg mL^{-1} in HCOOH or CF_3COOH . UV-vis-NIR measurements were carried out on a Shimadzu UV 3600 spectrometer in 1 cm fused quartz cuvettes with concentrations of 0.01 mg mL^{-1} . Cyclic voltammetry (CV) was carried out with a Autolab PGSTAT100 potentiostat in a three-electrode configuration where the working electrode was a glassy carbon, the counter electrode was a platinum wire, and the pseudo-reference was an Ag wire that was calibrated against ferrocene (Fc/Fc^+).

MONOMERS

3-(2-(2-methoxyethoxy)ethoxy)thiophene 2

In a dry three-neck round-bottom flask, 60 % NaH (1200 mg, 30 mmol) was mixed with anhydrous DMF (20 mL) under a nitrogen atmosphere. Triethylene glycol monomethyl ether (12 g, 11.68 mL, 100 mmol) was added drop-wise over a period of 30 minutes at 0 °C. The solution was allowed to stir for additional one hour. To this reaction mixture, 3-bromothiophene (3.2 g, 1.84 mL, 20 mmol) and CuBr (280 mg, 2 mmol) were added. The ice bath was replaced with an oil bath and the solution was heated up to 110 °C for another one hour. After cooling to the room temperature, the mixture was then poured into NH_4Cl aqueous solution and stirred for 10 minutes. The organic phase was extracted with *n*-hexane, dried over anhydrous Na_2SO_4 . Then, the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel) by using ethyl

acetate:hexane (1:2) as eluent to give pure target product **2** (3.6 g, 90 %).

^1H NMR (400 MHz, CDCl_3): δ : 7.15 (dd, $^3J_{\text{H,H}} = 5.3$ Hz, $^4J_{\text{H,H}} = 3.2$ Hz, 1H), 6.76 (dd, $^3J_{\text{H,H}} = 5.3$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 1H), 6.24 (dd, $^4J_{\text{H,H}} = 3.2$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 1H), 4.11 (t, $^3J_{\text{H,H}} = 4.8$ Hz, 2H), 3.83 (t, $^3J_{\text{H,H}} = 4.8$ Hz, 2H), 3.69 (t, $^3J_{\text{H,H}} = 4.8$ Hz, 2H), 3.56 (t, $^3J_{\text{H,H}} = 4.8$ Hz, 2H), 3.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ : 157.4, 124.5, 119.4, 97.3, 71.8, 70.5, 69.5, 69.4, 58.9.

3,3'-bis(2-(2-methoxyethoxy)ethoxy)-2,2'-bithiophene **3**

To a solution of 3-(2-methoxy- -ethoxy)thiophene **2** (1.8 g, 8.91 mmol) in anhydrous THF (20 mL) at ice bath, the *n*-BuLi (8.91 mmol, 5.57 mL, 1.6M in Hexane) were added dropwise over 10 min at 0 °C under N_2 condition. The mixture was kept stirring at this temperature for 2 hours before the solution was transferred to another dry flask with $\text{Fe}(\text{acac})_3$ (3.15 g, 9.8 mmol) in THF (70 mL), the reaction mixture was then heated under reflux for 3 hours. After cooling to room temperature, the precipitate was filtered off through short silica plug eluting with 5 % CH_3OH in CH_2Cl_2 . The filtrate was washed with saturated NH_4Cl solution and the aqueous phases were combined and extracted with CH_2Cl_2 . The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated by rotary evaporation. The crude solid was purified by column chromatography (silica gel) by using ethyl acetate:hexane (1:1) as eluent to give target product **3** with a little red color impurities. The crude product was then purified by recrystallization in Et_2O to give pure product **3** (900 mg, 50 %). ^1H NMR (400 MHz, CDCl_3): δ : 7.05 (d, $^3J_{\text{H,H}} = 5.2$ Hz, 2H), 6.83 (d, $^3J_{\text{H,H}} = 5.2$ Hz, 2H), 4.24 (t, $^3J_{\text{H,H}} = 4.8$ Hz, 4H), 3.89 (m, 4H), 3.72 (m, 4H), 3.55 (m, 4H), 3.37 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ : 144.0, 121.9, 116.5, 114.7, 72.0, 71.4, 70.8, 70.0, 59.1.

Monomer T2DEG (3,3'-bis(2-(2-methoxyethoxy)ethoxy)-[2,2'-bithiophene]-5,5'-diyl)bis-(trimethylstannane)

Compound **3** (402 mg, 1 mmol) was dissolved in anhydrous THF (10 mL) under an atmosphere of N_2 , cooled to -78 °C and *n*-butyllithium (2.15 mmol, 1.35 mL, 1.6 M in hexane) was added dropwise. The solution was stirred for 2 hours in the cold bath at -78 °C before being warmed to room temperature and stirred for an additional 15 minutes. The mixture was cooled to -78 °C again. Then, trimethyltin chloride (3 mL, 3 mmol, 1.0 M in THF) was added. After that, the solution was stirred at room temperature overnight. Water was added to quench the reaction, and the solution was extracted with *n*-hexane. The organic phase was dried over Na_2SO_4 and the solvent was removed by rotary evaporation leading to the crude compound as a yellow oil which was purified by recrystallization in isopropanol. The pure monomer **T2DEG** (518 mg) was obtained in 71 % yield.

^1H NMR (400 MHz, CDCl_3): δ : 6.90 (s, 1H), 4.28 (t, $^3J_{\text{H,H}} = 4.8$ Hz, 2H), 3.92 (t, $^3J_{\text{H,H}}$

= 4.8 Hz, 2H), 3.76 (t, $^3J_{H,H}$ = 4.8 Hz, 2H), 3.57 (t, $^3J_{H,H}$ = 4.8 Hz, 2H), 3.39 (s, 3H), 0.36 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ : 153.8, 134.1, 124.4, 120.9, 72.3, 71.7, 71.1, 70.4, 59.3, -8.1.

POLYMERS

General synthetic procedures for polymers

To a dry three-neck flask, Monomer 1 (1 eq), Monomer 2 (2 eq) and Distannyl derivatives (3 eq) were added under N_2 followed by Tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) (10 %mol). The flask and its contents were subjected to 3 pump/purge cycles with N_2 followed by addition of anhydrous oxygen-free DMF (5 mL) via syringe. The reaction mixture was vigorously stirred at 110 °C for three days. After cooling to room temperature, the reaction mixture was poured into 200 mL vigorously stirred acetone. The precipitated solid was collected by filtration. The solid polymers were suspended in milipore water, and transferred into a dialysis tube (MWCO:3500). The dialysis tube was placed into a large beaker with water (2 L) stirring for 3 days, and the water was changed every 12 hours. After the dialysis, the solid was collected and dried under vacuum overnight.

CPIZ-T: Synthesis according to the general polymerization procedure: monomer 1 (44 mg, 0.1 mmol), monomer 2 (92 mg, 0.2 mmol) and 2,5-bis(trimethylstannyl)thiophene (123 mg, 0.3 mmol). The polymers were obtained as a yellow solid (81 mg, 72 %).

^1H NMR (400 MHz, TFA-d): δ : 8.4–6.7 (m, Ar-H, 36H), 4.5–2.7 (m, N-CH₃ + CH₂, 16H).

IR (cm^{-1}): 695, 741, 759, 798, 905, 946, 973, 1016, 1153, 1187, 1350, 1405, 1443, 1495, 1518, 1563, 1607, 3356.

CPIZ-TT: Synthesis according to the general polymerization procedure: monomer 1 (22 mg, 0.05 mmol), monomer 2 (46 mg, 0.1 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (74 mg, 0.15 mmol). The polymers were obtained as a yellow-orange solid (60 mg, 87 %).

^1H NMR (400 MHz, TFA-d): δ : 8.83–7.71 (m, Ar-H, 42H), 4.88–3.50 (m, N-CH₃ + CH₂, 16H).

IR (cm^{-1}): 668, 689, 741, 794, 854, 927, 948, 1064, 1107, 1196, 1348, 1394, 1440, 1519, 1563, 1599, 2917, 3384.

CPIZ-TT-DEG: Synthesis according to the general polymerization procedure: monomer 1 (22 mg, 0.05 mmol), monomer 2 (46 mg, 0.1 mmol) and T2DEG (110 mg, 0.15 mmol). The polymers were obtained as an orange solid (60 mg, 58 %).

^1H NMR (400 MHz, TFA-d): δ : 8.88–6.88 (m, Ar-H, 36H), 5.29–3.54 (m, N-CH₃ + -CH₂- + O-CH₃, 82H).

IR (cm⁻¹): 691, 741, 813, 927, 1066, 1105, 1197, 1348, 1387, 1436, 1503, 1520, 1567, 1601, 2895, 3395.

CHARACTERIZATION

THIN FILM ABSORPTION

We prepared CPIs thin film for absorption measurements by drop cast from difference acidic solutions (**CPIZ-TT** in 5 mg mL⁻¹ HCOOH or CF₃COOH and **CPIZ-TT-DEG** in 10 mg mL⁻¹ HCOOH or CF₃COOH) on glass. The measurements were carried out on a Shimadzu UV 3600 spectrometer.

FILM MORPHOLOGY

The characterization of the surface morphology was performed on a Bruker AFM multi-mode MMAFM-2 equipped with a PeakForce TUNA application module (Bruker). Peak-Force tapping AFM was performed with a ScanAsyst-Air probe (resonant frequency 70 kHz, spring constant 0.4 N m⁻¹, Bruker) at a scan rate of 0.8 Hz and 800 samples per line. The data were analyzed with Nanoscope Analysis 1.5 (provided by Bruker).

MEASUREMENT OF ELECTRICAL CONDUCTIVITY

For the electrical conductivity measurements of the CPIs polymers, parallel line-shape Au electrodes with a width (w) of 13 mm and a channel length (L) of 100 μm to 300 μm were deposited as the bottom contact before spin-coating. Voltage-sourced two-point conductivity measurements were conducted with a probe station in a N₂ glovebox. The electrical conductivity (σ) was calculated according to the formula: $\sigma = (J/V) \times L/(w \times d)$.

SEEBECK COEFFICIENT MEASUREMENT

The Seebeck coefficient of **CPIZ-TT-DEG** polymers thin-film samples were measured in a home-built setup reported previously.[36–38] Two pairs of Au line electrodes (width: 1 mm and length: 7 mm; width: 1 mm and length: 4 mm) were deposited on a glass substrate with a distance of 7 mm. A thin film was spin-cast on the area (7 mm × 7 mm) defined by the two longer Au electrodes (the part of the substrate beyond that area was covered by scotch tape before coating). A standard constantan wire (with a diameter of 127 μm from Omega) was attached on the other Au line electrodes (width: 1 mm and length: 4 mm) with silver paste (ELECTRODAG 1415). The temperature difference across the sample was set by a thin film heater (KFR-5-120-C1-16, KYOWA), which was attached on top of a small copper block (3 mm × 14 mm × 2 mm) that sits in front of the active area parallel to the Au lines. The heater was controlled by Keithley 2635. The generated thermal voltages from constantan wire (reference, V_{ref}) and thin-film sample (V_{sample}) were probed by four probes

at the same time and corresponding data were recorded by Keithley 2000 with a scanning card. A step-by-step increased temperature method was used and a home-made filter (cut-off frequency = 1 Hz) was used for reducing the noise. The substrate temperature was obtained by a T-type thermocouple (Omega, the cold junction was connected on the chamber, whose temperature was detected by Pt100 sensor). The system is controlled by Labview software. The Seebeck coefficient (S) of sample was obtained by the formula:

$$S = \frac{V_{sample}}{V_{ref}} S_{const} + \left(\frac{V_{sample}}{V_{ref}} - 1 \right) S_{Au} \quad (5.1)$$

where S_{const} and S_{Au} are the Seebeck coefficient of Constantan wire and Au layer. At room temperature, $S_{const} = -39 \mu\text{V/K}$ and $S_{Au} = 1.49 \mu\text{V/K}$, respectively.

DFT CALCULATIONS

Density functional theory (DFT) calculations at the B3LYP/6-311G(d,p) level were performed using Gaussian 16[33] to gain further insights into the mechanism of proposed doping process. To simplify the calculation, we used only one repeat-unit comprising two cations, which is sufficient to reveal any anomalies in the frontier orbitals. For each molecule, we first optimized the geometry at ground state or excited state, then performed single point energy calculations with the optimized geometries at the same level.

AUTHOR CONTRIBUTIONS

The content of this chapter is published and the texts are re-organized based on the original manuscript and supporting information. Full citation is: Gang Ye, Yuru Liu, Jian Liu, Xinkai Qiu, L. Jan Anton Koster, Ryan C. Chiechi, *Protonic acid doping of low band-gap conjugated polyions*, *Materials Chemistry Frontiers*, **12**, 9, (2020)

Y.L. performed DFT calculations and related data handling and interpretation. G.Y synthesized and characterized the molecules, performed the measurements of UV-vis spectra, CV spectra, and EPR spectra, and related data handling and interpretation. J.L. and L.J.A.K. performed the measurement of conductivity of films comprising of CPIs and related data handling and interpretation. X.Q carried out AFM measurements and related data handling and interpretation. R.C.C. supervised the whole project. All the authors contributed to preparing figures and writing the manuscript.

BIBLIOGRAPHY

- (1) Voortman, T. P.; Chiechi, R. C. Thin Films Formed From Conjugated Polymers With Ionic, Water-Soluble Backbones. *ACS Appl. Mater. Interfaces* **2015**, *7*, 28006–28012.
- (2) Ye, G.; Doumon, N. Y.; Rousseva, S.; Liu, Y.; Abdu-aguye, M.; Loi, M. A.; Hummelen, J. C.; Koster, L. J. A.; Chiechi, R. C. Conjugated Polyions Enable Organic Photovoltaics Processed From Green Solvents. *ACS Appl. Energ. Mater.* **2019**, *2*, 2197–2204.
- (3) Voortman, T. P.; de Gier, H. D.; Havenith, R. W. A.; Chiechi, R. C. Stabilizing Cations in the Backbones of Conjugated Polymers. *J. Mater. Chem.* **2014**, *2*, 3407–3415.
- (4) Duan, C.; Zhang, K.; Zhong, C.; Huang, F.; Cao, Y. Recent Advances in Water/Alcohol-Soluble P-Conjugated Materials: New Materials and Growing Applications in Solar Cells. *Chem. Soc. Rev.* **2013**, *42*, 9071–9104.
- (5) Xu, B.; Hou, J. Solution-Processable Conjugated Polymers as Anode Interfacial Layer Materials for Organic Solar Cells. *Adv. Energy Mater* **2018**, 1800022.
- (6) Cai, W.; Musumeci, C.; Ajjan, F. N.; Bao, Q.; Ma, Z.; Tang, Z.; Inganäs, O. Self-doped conjugated polyelectrolyte with tuneable work function for effective hole transport in polymer solar cells. *J. Mater. Chem. A*, **2016**, *4*, 15670–15675.
- (7) Musumeci, C.; Vagin, M.; Zeglio, E.; Ouyang, L.; Gabrielsson, R.; Inganäs, O. Organic electrochemical transistors from supramolecular complexes of conjugated polyelectrolyte PEDOTS. *J. Mater. Chem. C*, **2019**, *7*, 2987–2993.
- (8) Persson, K. M.; Gabrielsson, R.; Sawatdee, A.; Nilsson, D.; Konradsson, P.; Berggren, M. Electronic control over detachment of a self-doped water-soluble conjugated polyelectrolyte. *Langmuir* **2014**, *30*, 6257–6266.
- (9) Zeglio, E.; Vagin, M.; Musumeci, C.; Ajjan, F. N.; Gabrielsson, R.; Trinh, X. T.; Son, N. T.; Maziz, A.; Solin, N.; Inganäs, O. Conjugated Polyelectrolyte Blends for Electrochromic and Electrochemical Transistor Devices. *Chem. Mater.* **2015**, *27*, 6385–6393.

- (10) Zeglio, E.; Eriksson, J.; Gabrielsson, R.; Solin, N.; Inganäs, O. Highly Stable Conjugated Polyelectrolytes for Water-Based Hybrid Mode Electrochemical Transistors. *Adv. Mater.* **2017**, *29*, 6–11.
- (11) Chueh, C. C.; Li, C. Z.; Jen, A. K. Recent Progress and Perspective in Solution-Processed Interfacial Materials for Efficient and Stable Polymer and Organometal Perovskite Solar Cells. *Energ. Environ. Sci.* **2015**, *8*, 1160–1189.
- (12) Henson, Z. B.; Zhang, Y.; Nguyen, T.-q.; Seo, J. H.; Bazan, G. C. Synthesis and Properties of Two Cationic Narrow Band Gap Conjugated Polyelectrolytes. *J. Am. Chem. Soc.* **2013**, *135*, 4163–4166.
- (13) Seo, J. H.; Gutacker, A.; Sun, Y.; Wu, H.; Huang, F.; Cao, Y.; Scherf, U.; Heeger, A. J.; Bazan, G. C. Improved High-Efficiency Organic Solar Cells via Incorporation of a Conjugated Polyelectrolyte Interlayer. *J. Am. Chem. Soc.* **2011**, *133*, 8416–8419.
- (14) Lee, W.; Seo, J. H.; Woo, H. Y. Conjugated polyelectrolytes: A new class of semi-conducting material for organic electronic devices. *Polymer* **2013**, *54*, 5104–5121.
- (15) Houston, J. E.; Richeter, S.; Clément, S.; Evans, R. C. Molecular design of interfacial layers based on conjugated polythiophenes for polymer and hybrid solar cells. *Polymer International* **2017**, *66*, 1333–1348.
- (16) He, Z.; Xiao, B.; Liu, F.; Wu, H.; Yang, Y.; Xiao, S.; Wang, C.; Russell, T. P.; Cao, Y. Single-Junction Polymer Solar Cells With High Efficiency and Photovoltage. *Nat. Photonics* **2015**, *9*, 174–179.
- (17) Voortman, T. P.; Bartesaghi, D.; Koster, L. J. A.; Chiechi, R. C. Cross-Conjugated N-Dopable Aromatic Polyketone. *Macromolecules* **2015**, *48*, 7007–7014.
- (18) Chiechi, R. C.; Sonmez, G.; Wudl, F. A Robust Electroactive N-Dopable Aromatic Polyketone. *Adv. Funct. Mater.* **2005**, *15*, 427–432.
- (19) Dou, L.; Liu, Y.; Hong, Z.; Li, G.; Yang, Y. Low-Bandgap Near-Ir Conjugated Polymers/Molecules for Organic Electronics. *Chem. Rev.* **2015**, *115*, 12633–12665.
- (20) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. Synthesis of Conjugated Polymers for Organic Solar Cell Applications. *Chem. Rev.* **2009**, *109*, 5868–5923.
- (21) Mai, C.-k.; Zhou, H.; Zhang, Y.; Henson, Z. B.; Nguyen, T.-q.; Heeger, A. J.; Bazan, G. C. Facile Doping of Anionic Narrow-Band-Gap Conjugated Polyelectrolytes During Dialysis. *Angew. Chem., Int. Ed.* **2013**, *52*, 12874–12878.

- (22) Mai, C.-K.; Schlitz, R. A.; Su, G. M.; Spitzer, D.; Wang, X.; Fronk, S. L.; Cahill, D. G.; Chabiny, M. L.; Bazan, G. C. Side-Chain Effects on the Conductivity, Morphology, and Thermoelectric Properties of Self-Doped Narrow-Band-Gap Conjugated Polyelectrolytes. *J. Am. Chem. Soc.* **2014**, *136*, 13478–13481.
- (23) Mai, C.-K.; Arai, T.; Liu, X.; Fronk, S. L.; Su, G. M.; Segalman, R. A.; Chabiny, M. L.; Bazan, G. C. Electrical properties of doped conjugated polyelectrolytes with modulated density of the ionic functionalities. *Chem. Commun.* **2015**, *51*, 17607–17610.
- (24) Cao, D. X.; Leifert, D.; Brus, V. V.; Wong, M. S.; Phan, H.; Yurash, B.; Koch, N.; Bazan, G. C.; Nguyen, T.-Q. The importance of sulfonate to the self-doping mechanism of the water-soluble conjugated polyelectrolyte PCPDTBT-SO₃K. *Mater. Chem. Front.* **2020**, *4*, 3556–3566.
- (25) Tsokkou, D.; Peterhans, L.; Cao, D. X.; Mai, C.-K.; Bazan, G. C.; Nguyen, T.-Q.; Banerji, N. Excited State Dynamics of a Self-Doped Conjugated Polyelectrolyte. *Adv. Funct. Mater.* **2019**, *30*, 1906148.
- (26) Patil, A.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. Self-doped conducting polymers. *Synthetic Metals* **1987**, *20*, 151–159.
- (27) Chen, X.; Chang, G. Synthesis and Photosensitive Properties of Poly (Aryl Imino) Containing Azobenzene Group (PAI-A). *Chin. J. Chem.* **2009**, *27*, 2093–2096.
- (28) Qin, C.; Wu, X.; Tong, H.; Wang, L. High Solubility and Photoluminescence Quantum Yield Water-Soluble Polyfluorenes With Dendronized Amino Acid Side Chains: Synthesis, Photophysical, and Metal Ion Sensing Properties. *J. Mater. Chem.* **2010**, *20*, 7957–7964.
- (29) Bartholome, D.; Klemm, E. Novel Polyarylene-Triarylmethane Dye Copolymers. *Macromolecules* **2006**, *39*, 5646–5651.
- (30) Guo, X.; Watson, M. D. Conjugated Polymers From Naphthalene Bisimide. *Org. Lett.* **2008**, *10*, 5333–5336.
- (31) Song, C. K.; Eckstein, B. J.; Tam, T. L. D.; Trahey, L.; Marks, T. J. Conjugated Polymer Energy Level Shifts in Lithium-Ion Battery Electrolytes. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19347–19354.
- (32) *Handbook of Conducting Polymers, Fourth Edition - 2 Volume Set*; Reynolds, J. R., Thompson, B. C., Skotheim, T. A., Eds.; CRC Press: 2019.
- (33) Frisch, M. J. et al. Gaussian~16 Revision C.01, Gaussian Inc. Wallingford CT, 2016.

- (34) Han, C. C.; Elsenbaumer, R. L. Protonic Acids: Generally Applicable Dopants for Conducting Polymers. *Synth. Met.* **1989**, *30*, 123–131.
- (35) Wudl, F.; Angus, R. O.; Liu, Z. X.; Heeger, A. J.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M. Poly(p-Phenyleneamineimine): Synthesis and Comparison to Polvaniline. *J. Am. Chem. Soc.* **1987**, *109*, 3677–3684.
- (36) Liu, J.; Qiu, L.; Portale, G.; Koopmans, M.; ten Brink, G.; Hummelen, J. C.; Koster, L. J. A. N-Type Organic Thermoelectrics: Improved Power Factor by Tailoring Host-Dopant Miscibility. *Adv. Mater.* **2017**, *29*, 1701641.
- (37) Liu, J.; Qiu, L.; Alessandri, R.; Qiu, X.; Portale, G.; Dong, J. J.; Talsma, W.; Ye, G.; Sengrrian, A. A.; Souza, P. C.; Loi, M. A.; Chiechi, R. C.; Marrink, S. J.; Hummelen, J. C.; Koster, L. J. A. Enhancing Molecular N-Type Doping of Donor–Acceptor Copolymers by Tailoring Side Chains. *Adv. Mater.* **2018**, *30*, 1704630.
- (38) Liu, J.; Ye, G.; van der Zee, B.; Dong, J.; Qiu, X.; Liu, Y.; Portale, G.; Chiechi, R. C.; Koster, L. J. A. N-Type Organic Thermoelectrics of Donor-Acceptor Copolymers: Improved Power Factor by Molecular Tailoring of the Density of States. *Adv. Mater.* **2018**, *30*, 1804290.

SUMMARY

Molecular electronics describes the field of research in which molecules are utilized as functional elements in electronic circuits. This thesis aims to extend the understanding of the relationship between chemical structure of π -conjugated molecules and their electrical properties. In [chapter 1](#), we briefly discuss the mechanisms of charge transport, followed by a discussion of issues that are specific to molecular ensemble junctions (MEJs). We also touch on the interpretation of data and the statistics used to analyze primary data with the aim of clarifying differences intrinsic to these types of junctions.

In [chapter 2](#) we discuss the fabrication of molecular ensemble junctions using state-of-the-art methods to solve the unique challenge of applying a top contact. There are many methods for attaching electrodes to molecules, in this chapter, the focus is on techniques that install a top contact on SAMs. We divide the methods of making a top contact into four parts: 1) solid metallic electrodes, *i.e.*, applying solid-metal electrodes directly to a molecular ensemble supported by a conductive substrate; 2) liquid metallic electrodes; 3) hybrid electrodes, *e.g.*, using a buffer layer between the molecular layer and the top contact; 4) non-metallic electrodes.

In [chapter 3](#) we describe the conductance of self-assembled monolayers and single-molecules comprising an oligophenyleneethynylene core, functionalized with acenes of increasing length that extend conjugation perpendicular to the path of tunneling electrons. In the Mechanically Controlled Break Junction (MCBJ) experiment, multiple conductance plateaus were identified. The high conductance plateau, that we attribute to the single molecule conformation, shows an increase of conductance as a function of acene length, in good agreement with theoretical predictions. The lower plateaus are attributed to multiple molecule bridging the junctions with intermolecular interactions playing a role. In junctions comprising a self-assembled monolayer with eutectic Ga-In (EGaIn) top-contacts, the pentacene derivative exhibits unusually low conductance, which we ascribe to the inability of these molecules to pack in a monolayer without introducing significant intermolecular contacts. This hypothesis is supported by the MCBJ data and theoretical calculations showing suppressed conductance through the monolayers of pentacene derivative. These results highlight the role of intermolecular effects and junction geometries in the observed fluctuations of conductance values between single-molecule and ensemble junctions, and the

importance of studying molecules in both platforms.

In [chapter 4](#) we continue the study of conductance of self-assembled monolayers and single molecules comprising π -conjugated oligophenyleneethynylene core but with the central phenyl ring replaced by one or two thiophene/thiazole rings. We keep the length of the molecules and the anchoring groups the same while changing the central thiophene rings by introducing heteroatoms (electronegative N atoms) step by step. In this design, we keep the width of the tunneling barrier and the interface of the SAM-electrode the same while varying the height of the tunneling barrier, hence we are able single out the role of the electron withdrawing group in the electrical properties of molecular junctions. The conductance of the designed molecular wires are indistinguishable both in ensemble junctions with EGAIn top contact and in single-molecule junctions. However, we observed the decrease of the frontier orbitals when introducing electron withdrawing groups to the molecular wire. We proposed that modifying the molecular wire with much stronger electron withdrawing groups would exhibit larger changes of the conductance of a molecular junction. We tested our proposal by performing transport simulations on the model junction comprising molecules with stronger electron withdrawing units. Theoretical simulations show that the lowest unoccupied π states are strongly dependent on the electron withdrawing groups and can be even lowered down to the position of the Fermi level of the electrode, which indicates high conductivity of the molecular wires.

In [chapter 5](#), we describe the design and synthesis of a series of conjugated polyions that incorporate formal positive charge into their conjugated backbones, balanced by anionic pendant groups with increasing electron-donating ability. The energy levels and the bandgap of these conjugated polyions were determined by optical absorption spectroscopy and cyclic voltammetry (CV) and are easily modulated by varying the electron donating group. The energies of occupied states increase with increasing electron-donating ability, while the energies of the unoccupied states are almost unchanged due the presence of tritylium ions in the conjugated backbone. All conjugated polyions exhibit pristine semiconducting properties in weak protonic acids, but with sufficiently strong acids, the polymers exhibit spontaneous spin unpairing and convert to a metallic state. The requisite strength of the acids varies with electron-donating ability, with higher HOMO levels leading to more facile proton acid doping and higher electrical conductivities. The mechanism of protonic acid doping of conjugated polyions involve a spinless doping process (dehydration) followed by spontaneous spin unpairing leading to the formation of polarons. While protonic acid doping occurs in polyaniline, conjugated polyions offer synthetic tunability and selective processing into insulating, semiconducting and metallic states simply by controlling acidity.

NEDERLANDSE SAMENVATTING

Moleculaire elektronica beschrijft het onderzoeksveld waarin moleculen worden gebruikt als functionele elementen in elektronische circuits. Dit proefschrift poogt om het begrip van de relatie tussen chemische structuur van π -geconjugeerde moleculen en hun elektrische eigenschappen uit te breiden. In [hoofdstuk 1](#) bespreken we kort de mechanismen van ladingsvervoer, gevolgd door een bespreking van kwesties die specifiek zijn voor moleculaire ensembleverbindingen (MEJs). We gaan ook in op de interpretatie van gegevens en de statistieken die worden gebruikt om primaire gegevens te analyseren met als doel verschillen te verduidelijken die inherent zijn aan dit soort moleculaire aansluitingen.

In [hoofdstuk 2](#) bespreken we de fabricage van MEJs met behulp van de nieuwste methoden om de unieke uitdaging van het toepassen van een topcontact op te lossen. Er zijn veel methoden om elektroden aan moleculen te bevestigen, in dit hoofdstuk ligt de focus op technieken waarbij een topcontact op SAMs wordt geïnstalleerd. We verdelen de methoden om een topcontact te maken in vier delen: 1) massief metalen elektroden, d.w.z. het rechtstreeks aanbrengen van massief metalen elektroden op een moleculair ensemble dat wordt ondersteund door een geleidend substraat; 2) vloeibare metalen elektroden; 3) hybride elektroden, bijvoorbeeld met behulp van een bufferlaag tussen de moleculaire laag en het bovenste contact; 4) niet-metalen elektroden.

In [hoofdstuk 3](#) we beschrijven de geleiding van zelf gemonteerde monolagen en enkele moleculen; bestaande uit een oligo phenyleenethynyleenkern kern die gefunctionaliseerd is met acenen van toenemende lengte, dit de conjugatie verlengen loodrecht op het pad van tunnelende elektronen. In het experiment Mechanically Controlled Break Junction (MCBJ) werden meerdere geleidingsplateaus geïdentificeerd. Het hoge geleidingsplateau, dat we toeschrijven aan de enkele molecuul-exterieur, toont een toename van geleiding als functie van acenen lengte, in goede overeenstemming met theoretische voorspellingen. De onderste plateaus worden toegeschreven aan meerdere moleculen die de verbindingen overbruggen met intermoleculaire interacties die een rol spelen. In moleculaire aansluitingen bestaande uit een zelf gemonteerde monolaag met eutectische Ga-In (EGaIn) topcontacten vertoont het pentaceenderivaat een ongewoon lage geleiding, die we toeschrijven aan het onvermogen van deze moleculen om een monolaag in te pakken zonder significante intermoleculaire contacten te introduceren. Deze hypothese wordt ondersteund door de MCBJ-gegevens en

theoretische berekeningen die onderdrukte geleiding vertonen via de monolagen van penta-ceenderivaat. Deze resultaten benadrukken de rol van intermoleculaire effecten en moleculaire vaansluitings-geometrieë in de waargenomen fluctuaties van geleidingswaarden tussen enkele-moleculen en MEJs en tevens het belang van bestuderen van moleculen in beide platformen.

In [hoofdstuk 4](#) we zetten de studie voort van geleiding van zelf gemonteerde monolagen en enkele moleculen bestaande uit π -geconjugeerde oligo phenyleenethynyleen kern, maar waarbij de centrale fenylring vervangen door één of twee thiofeen/thiazolringen. We houden de lengte van de moleculen en de verankeringsgroepen hetzelfde terwijl we de centrale thiofeenringen veranderen door stap voor stap heteroatomen (electronegatief N-atomen) te introduceren. In dit ontwerp houden we de breedte van de tunnelbarrière en de interface van de SAM-elektrode hetzelfde terwijl we de hoogte van de tunnelbarrière variëren, waardoor we de rol van de elektronen zuigende groep in de elektrische eigenschappen van moleculaire aansluitingen kunnen onderscheiden. De geleiding van de ontworpen moleculaire draden is niet van elkaar te onderscheiden, zowel in MEJs met EGaIn topcontact als in enkel-molecuul aansluitingen. We zagen echter de afname van de grens orbitalen bij het introduceren van elektronen zuigende groepen in de moleculaire draad. We stelden voor dat het aanpassen van de moleculaire draad met veel sterkere elektronen zuigende groepen grotere veranderingen van de geleiding van een moleculaire aansluiting zou kunnen vertonen. We hebben ons voorstel getest door transportsimulaties uit te voeren op de modelaansluiting bestaande uit moleculen met sterkere elektronen zuigende eenheden. Theoretische simulaties tonen aan dat de laagste onbezette π niveaus sterk afhankelijk zijn van de elektronen zuigende groepen en zelfs kunnen worden verlaagd tot de positie van het Fermi-niveau van de elektrode, wat een indicatie is van een hoge geleidbaarheid van de moleculaire draden.

In [hoofdstuk 5](#) beschrijven we het ontwerp en de synthese van een reeks geconjugeerde polyionen die formele positieve lading opnemen in hun geconjugeerde koolstofketen, in evenwicht gebracht door anionische hangende groepen met een toenemend elektronen donerend vermogen. De energieniveaus en de bandgap van deze geconjugeerde polyionen werden bepaald door optische absorptiespectroscopie en cyclische voltammetrie (CV) en zijn gemakkelijk te moduleren door de elektronenschonkende groep te variëren. De energieën van bezette toestanden nemen toe met een toenemend elektronen donaerend vermogen, terwijl de energieën van de onbezette toestanden vrijwel onveranderd zijn als gevolg van de aanwezigheid van trityliumionen in de geconjugeerde koolstofketen. Alle geconjugeerde polyionen vertonen zuivere halfgeleidende eigenschappen in zwakke protonische zuren, maar met voldoende sterke zuren vertonen de polymeren spontane spin-ontkoppeling en zetten ze om in een metaalachtige toestand. De vereiste sterkte van de zuren varieert met

elektrondonerend vermogen, met hogere HOMO-niveaus die leiden tot meer facile protonzuurdoping en hogere elektrische geleidbaarheid. Het mechanisme van protonzuurdoping van geconjugeerde polyionen omvat een spinloos dopingproces (uitdroging) gevolgd door spontane spin-ontkoppeling die leidt tot de vorming van polarons. Terwijl protonzuurdoping voorkomt in polyaniline, bieden geconjugeerde polyionen synthetische afstembaarheid en selectieve verwerking in isolerende, halfgeleidende en metaalachtige toestanden door simpelweg de zuurgraad te regelen.

PUBLICATIONS

1. Jian Liu, Gang Ye, Bas van der Zee, Jingjin Dong, Xinkai Qiu, **Yuru Liu**, Giuseppe Portale, Ryan C. Chiechi, L. Jan Anton Koster, *N-Type Organic Thermoelectrics of Donor-Acceptor Copolymers: Improved Power Factor by Molecular Tailoring of the Density of States*, *Advanced Materials* **44**, 1804290, (2018)
2. Gang Ye, Nutifafa Y. Doumon, Sylvia Rousseva, **Yuru Liu**, Mustapha Abdu-Aguye, Maria A. Loi, Jan C. Hummelen, L. Jan Anton Koster, Ryan C. Chiechi, *Conjugated Polyions Enable Organic Photovoltaics Processed from Green Solvents*, *ACS Applied Energy Materials*, **3**, 2197, (2019)
3. Gang Ye, **Yuru Liu**, Mustapha Abdu-Aguye, Maria A. Loi, Ryan C. Chiechi, *Synthesis, Optical and Electrochemical Properties of High-Quality Cross-Conjugated Aromatic Polyketones*, *ACS Omega*, **9**, 4689, (2020)
4. Gang Ye, **Yuru Liu**, Jian Liu, Xinkai Qiu, L. Jan Anton Koster, Ryan C. Chiechi, *Protonic acid doping of low band-gap conjugated polyions*, *Materials Chemistry Frontiers*, **12**, 9, (2020)
5. **Yuru Liu**, Luca Ornago, Marco Carlotti, Yong Ai, maria el abbasi, Saurabh Soni, Andika Asyuda, Michael Zharnikov, Herre S. J. van der Zant, Ryan C. Chiechi, *Intermolecular Effects on Tunneling through Acenes in Large-Area and Single-Molecule Junctions*, *The Journal of Physical Chemistry. C*, **41**, 22776, (2020)
6. Gang Ye, Jian Liu, Xinkai Qiu, Sebastian Stäter, Li Qiu, **Yuru Liu**, Xuwen Yang, Richard Hildner, L. Jan Anton Koster, Ryan C. Chiechi, *Controlling n-Type Molecular Doping via Regiochemistry and Polarity of Pendant Groups on Low Band Gap Donor–Acceptor Copolymers*, *Macromolecules*, **8**, 3886, (2021)
7. **Yuru Liu**, Xinkai Qiu, Saurabh Soni, Ryan C. Chiechi, *Charge-transport Through Molecular Ensembles: Recent Progress in Molecular Electronics*, *Chemical Physics Review*, accepted, (2021)

ACKNOWLEDGMENTS

Completing a PhD is quite an unforgettable journey with both joy and stress. It has been quite a different experience living and working here in Groningen, especially for me who have never been abroad before. I value this experience as much as obtaining the PhD certificate. I would like to take a chance here to acknowledge the people I encountered who make this journey happen and come to this nice end.

The whole story of my PhD program dates back to the workshop hosted by Zhengzhou University and Chinese Scholarship Council when I was at the final year of my master program. There are many professors or delegations from different universities. Somehow I had a chance to talk with Prof. Petra Rudolf. And Petra, thank you for the talk and later recommending me to Ryan.

Ryan, thank you for applying this PhD program together and being my supervisor. You are a very kind supervisor and never put too much pressure on your students. I think I take quite a long time being unsure about myself and worrying about research. You are very patient and guide me to think what is research and how to solve problems. I love the stories you told about you and your former students. Our monthly meeting during last two years is very helpful. I am more willing to express my opinions with you. Overall, I enjoyed working with you. I know you are also very busy recently and thanks again for taking time to read my thesis and give comments.

Shirin, thank you being my second supervisor. At the first year of my PhD, I was shy and very insecure of the whole new environment, I was not used to talk with you because you are very direct. But I am very appreciate that once you told me to be strong especially being a woman in science. Now I am being more secure to this environment and I think I am now much stronger. I also remember your nice words about my presentation at Vileland conference. Thanks for that.

Egbert, Marxim, Tibor, thanks for being my assessment committees, taking time to read my thesis and sharing your valuable comments.

Gang, thank you for being very helpful during the whole PhD journey. When I first arrived at Groningen, you and your wife Ping, offered a lot useful information on renting the houses and buying furniture. You and Ping are like big brother and sister to me. It is also nice to work with you. Looking at my publication list, most of my publications are

with collaborations with you. I got a lot experience in performing DFT calculations of your molecules. I think the most valuable experience you give me is how you get your ideas for designing new molecules and how you interpret your data. I am very happy for you that you got several nice papers published recently and there will for sure be more. Wish you good luck with your career in the future.

Sylvia, thank you for being my paranymph. You are so nice and always being helpful to the people around. I remember at the first year I always got lost in the conversation in our coffee room. You will explain to me what they are talking about if you are also there. One thing I am so proud of is that we made the trip to Spain to visit Ani a real deal. Another thing is with your help I am now being an independent baker. We had many memories here. Thanks for the fun. It is also funny that we had a lot of serious discussions about random topics, which I enjoyed a lot. Hope our current collaboration turn out to be nice. Wish you good luck in your final year of you PhD.

Minpeng, thank you as well for being my paranymph. It is nice to have you in company. We had a lot of fun exploring either the nature or the food in the weekends. I also love to discuss with you the problems I meet because your perspective is sometimes quite different from mine, which most of the time I found it very helpful. Thanks a lot for that. You are now also in your final year and I wish you good luck with your research.

Many thanks to all my collaborators: Yong, Marco, Saurabh, Remco, Luca Ornago, Maria El Abbassi, Prof. Herre S. J. van der Zant, Andika Asyuda, Prof. Michael Zharnikov, Gang, Jian, Xinkai, Prof. L. Jan Anton. It is with the collaborations with all of you that the papers in this thesis could be published on journals. Harry, thanks for your help with the training of XPS and UPS. Teo, thanks for your help with the training of Ellipsometry. Tommaso, Siva, Selim and Remco, thanks for the discussions and help on theoretical related topics.

Many thanks to all the rest of my former and current colleagues in the "CMMD + RC-CLab" group: Andrew, Yanxi, Gongbao, Difei, Viktor, Sumit, Ani, Sri, Jane, Kristin, Nahid, Kees, Renate, Bouke, Natalia, Racheal, Donato, Lungani, Micheal. With all of you, my life at work is not just with research projects. I love the interesting debates and funny discussions happened in the coffee room, the cakes at Pi time, our secret Santa plus Christmas events together, the BBQ time, the cycling time, the house warming dinner, *et al.*.

Many thanks to the Chinese friends and acquaintances that I meet in Groningen: Wen Li, Min Wang, Fan Xu, Shaoyu Chen, Qian Wang, Jieying Wang, Ping Zhang, Luo Ge, Yafei Guo, Jiuling Li, Xingchen Yan, Chengtao Ji, Yuzhen Qin, Shanshan Ge, Fan Yang, Yanfei Li, Jing Zhao, Zhiwen Wang, Xiaocui Wang, Feng Yan, Yangyang Guo, Xiaotian Zhu, Siwei Chen, Xiang Tang, Heng Zhang, Qi Chen, Xinyu Zhou, Chongnan Ye, Bohuan

Lin, Jing Wang, Sunyi Zheng, Zizhao Wu, Xiaoli Peng, Ying Wang, Puhua Wan, Le Zhang. My colleagues sometimes joke that I know every Chinese in Groningen, which is definitely not true. But I do meet a lot of nice Chinese people here. Sometimes a simple hotpot together would make me feel satisfied when I miss the time back home, let alone the big dinner event with lots of Chinese cuisines. Also special thanks to those friends with whom I traveled together to other cities in Netherlands and cities or countries abroad like Paris, Hamburg, Hanover, Bulgaria, Morocco, Porto, Japan. Those trips would not happen with you. Thanks again for making my life here more exciting and memorable here.

My family has been a great support to me all these years. I would like to thank them in Chinese here. 感谢亲爱的爸爸妈妈，谢谢你们对我的无私的爱，对我的信任与支持，让我从来不用操心除了学业之外的事情，能够毫无负担地完成博士学业。感谢整个大家庭的所有人，感谢你们周末的视频电话，你们的关心，让我在异国他乡不感觉孤单。感谢飘洋过海来荷兰游玩的露露，小任，二姨，佳鑫和开心，非常高兴你们能来。

Lastly, thank you all for reading my thesis.

Yuru Liu
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June 3, 2021