Chapter 6

Oligo-para-phenylene dithiols in large area molecular junctions at low temperatures

In this chapter, we report on conductance measurements on large area molecular junctions of oligo-para-phenylene (OPP) dithiols at low temperatures. We find that the conductance of OPP devices has a strong dependence on temperature and bias, similar to control devices without OPP molecules. However, the current through the via decreases exponentially with the length of the molecules at all temperatures and biases measured. We speculate on possible origins for these observations. We find evidence that the granular nature of the PEDOT:PSS is crucial to understand the charge transport through large area molecular junctions. ¹

6.1 Introduction: the power of conjugation

As we have discussed in chapter 5, the electronic levels of molecules can still be up to several electronvolts away from the Fermi levels of the metal electrodes. Therefore, resonant transport in 2-terminal devices is only expected to be observed at elevated biases. Electrons in flat conjugated organic molecules with contiguous sp² carbon atoms are delocalized over the molecule (see chapter 1). Therefore, they have relatively low HOMO-LUMO gaps and are good candidates to observe resonant transport.

Previously, signatures of molecular levels were observed using conjugated molecules in single molecule junction. Figure 6.1 shows two recent examples

¹This chapter will be part of a forthcoming paper.
Figure 6.1: Signatures of molecular levels in single molecule transport measurements using a conjugated molecule. (a) $I(V)$-traces of a benzenedithiol molecule, measured at 77K using the MCBJ technique. Solid lines are $I(V)$-traces and dotted lines are differential conductance measurements ($dI/dV$). The peaks in $dI/dV$ around 0.5V suggest the position of the nearest molecular orbital. Figure is courtesy of C.A. Martin and was taken from [58]. (b) Conductance map of a OPV 5 "molecular quantum dot" in a nanogap created by electromigration. The map shows the differential conductance as a function of bias ($V$) and gate voltage ($V_g$). The addition energy ($E_{add}$) indicated shows how much energy is needed to add an electron to the molecule. Figure is courtesy of E.A. Osorio and was taken from [149]. Note that in both cases the conductances measured at resonance are much lower than the quantum of conductance (77.6 $\mu$S). The conductance 'gap' reported here is two times the distance between the Fermi level and the nearest molecular orbital and not the difference between the HOMO and the LUMO. Pictures are used with permission.

6.2 Results: power law physics with a $\beta$

We will discuss the results of five wafers fabricated as discussed in section 2.3. Table 6.1 summarizes the most important wafer properties. Figure 1.1 gives the skeletal structures of all molecules measured. P1 was obtained from Sigma-Aldrich. P2-P4 were synthesized by Bert de Boer using a prescribed procedure [150]. In contrast to alkanethiols, working in an oxygen-free environment was needed to prevent polymerization of the conjugated molecules. Hence, monolayers of conjugated OPPs were grown in a N$_2$ glovebox using a 300 $\mu$M SureSeal THF solution. For the monolayers of terphenyl-dithiol (P3)
Table 6.1: Table summarizing the five wafers characterized. For drawings of the molecular structures, see figure 1.1. All wafers were fabricated using Orgacon PEDOT:PSS (ICPnew + 5% DMSO, Agfa Geveart) and negative novolak resist (Ma-N 1410, MicroResist). The calculated length $d$ of the molecule was taken from reference [150]. The thickness $t$ of the SAM was determined using spectroscopic ellipsometry. Ellipsometry was performed on two different spots on the reference samples. The spotsize of the beam was $\sim 1 \text{ mm}^2$ and the spectra were taken between 300 - 600 nm at three angles of incidence ($65^\circ$, $70^\circ$ and $75^\circ$). Both the amplitude ratio ($\Psi$) and the phase difference ($\Delta$) of the polarization parallel and perpendicular to the initial polarization were recorded. The thickness was determined by modeling $\Psi$ and $\Delta$ at all wavelengths and angles using V-VASE software. Optical constants of the bare reference sample were determined separately, also on two spots. The SAM layers were modeled as a Cauchy layer on top of the reference bottom stack. The monolayer thicknesses were calculated using an isotropic refractive index of 1.55. Absorption of the monolayers was neglected.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Wafername</th>
<th>$d$ [nm]</th>
<th>$t$ [nm]</th>
<th>$\alpha$ [$^\circ$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pedot only</td>
<td>PF233</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P1</td>
<td>PF242</td>
<td>0.90</td>
<td>0.58</td>
<td>50</td>
</tr>
<tr>
<td>P2</td>
<td>PF240</td>
<td>1.3</td>
<td>0.98</td>
<td>41</td>
</tr>
<tr>
<td>P3</td>
<td>PF236</td>
<td>1.8</td>
<td>1.5</td>
<td>34</td>
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<tr>
<td>P4</td>
<td>PF238</td>
<td>2.2</td>
<td>2.1</td>
<td>17</td>
</tr>
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and quaterphenyldithiol (P4) the acetyl-protected compounds were used. These compounds were deprotected by stirring two drops of aqueous ammonia to the 90 ml of solution. The wafers were immediately immersed in solution after deprotection and stored in the glovebox for 36 hours. In order to check the quality of the monolayer, pieces of a Si-SiO$_2$ wafer with 60 nm thermally evaporated gold were immersed in the solutions together with the wafer. After immersion and rinsing, the thickness of the SAM was measured on reference samples (Si-SiO$_2$-Au samples) using a V-VASE ellipsometer (J.A. Woollam Co., Inc, VB-400). The thicknesses found (see table 6.1) are within the length of the molecule and indicate that a monolayer of molecules has formed. More precisely, when densely packed, the thickness of the monolayer and the length of the molecule are related by $\cos(\alpha)$. Here, $\alpha$ is the angle between the long axis of the molecule and the surface normal. $\alpha \neq 0$ is due to intermolecular interactions and is expected to decrease with increasing number of phenylenes ($N$) [150]. A decrease is also apparent from our data (table 6.1) and confirms the formation of a dense layer.

After finishing device fabrication, the resistance of each via was determined by 4-probe measurements of the Kelvin structures using the auto-
mated prober machine. We will discuss the $I(V)$-traces in detail below and will first address the dependence of the resistance on molecular length. Figure 6.2 shows the average RS value of 248 vias (diameter = 5, 10, 20 and 50 $\mu$m) versus the molecular length for each wafer. RS is the resistance at 0.5V times the area of the via ($A_{\text{via}}$) in $\mu$m$^2$. Note that the resistance is plotted on a logarithmic scale. The error bar shows the standard deviation of the resistance distribution on a logarithmic scale. For both sets, the resistance scales exponentially with the number of phenylene rings of the molecule. The data can be fitted with

$$RS = 2.8 \cdot 10^3 \exp(\beta d).$$

(6.1)

Here, $d$ is the molecular length in Å. We find $\beta = 0.28 \pm 0.02$ Å$^{-1}$. Alternatively, one can use the measured thickness of the molecular layer $t$ (see table 6.1); $RS = 1.0 \cdot 10^4 \exp(\beta_t t)$. The grey points in figure 6.2 show RS versus $t$. We find $\beta_t = 0.22 \pm 0.02$ Å$^{-1}$. Using the thickness, one assumes that current follows the shortest path from electrode to electrode (through space). Using the molecular length, one assumes that current follows the backbone of the molecule (through bond). Values reported in literature usually determine $\beta$ using the molecular length. $\beta = 0.28$ Å$^{-1}$ falls just below the lower limit of previous reports ranging from 0.35 till 0.61 Å$^{-1}$ [30], [43], [151]-[155]. In the majority of these experiments, methylene groups were present between the phenyl rings and the contact [43]-[154]. Steigerwald et al. found $\beta = 0.39$ Å$^{-1}$ for OPP with amine anchor groups on both sides (-NH$_2$) [30]. Holmlin et al. found $\beta = 0.61$ Å$^{-1}$ for Hg-drop experiments with OPP thiols assembled on one drop and alkanemonothiols assembled on the second Hg-drop [151]. Theoretical calculations for $\beta$ using the molecular length predicted $\beta = 0.17 - 0.51$ Å$^{-1}$ [156]-[163].

Next, we address the absolute value of the resistance. Assuming all molecules of the SAM are contacted and each molecule is a single conductance channel, the RS value divided by the area per molecule ($A_{\text{mol}}$) gives the resistance per molecule. Assuming $A_{\text{mol}} = 25$ Å$^2$ [164] (for alkanes $A_{\text{mol}} = 22$ Å$^2$), we find $R_{P1} = 1.4 \cdot 10^{11}$ Ω, $R_{P2} = 3.9 \cdot 10^{11}$ Ω, $R_{P3} = 9.7 \cdot 10^{11}$ Ω, $R_{P4} = 4.8 \cdot 10^{12}$ Ω. These resistances of OPPs in LAMJs are about 2-5 orders of magnitude higher than literature results mentioned above. Note that for alkanethiols, this difference was reported to be 0-1 order of magnitude, see figure 2.11.

The observed combination of a relatively high resistance value per molecule and an almost consistent length dependence compared to the values found in literature was previously reported for LAMJs with alkanedithiols [85]. Van Hal et al. showed that the resistance in LAMJs is dependent on the type of resist and on the type of PEDOT:PSS used [86]. However, for all combinations, $\beta_{\text{alk}} \sim 0.73$ Å$^{-1}$. For a certain choice of PEDOT:PSS (Orgacon ICP new) and resist (L6000.5), the resistance per molecule was consistent with
Figure 6.2: The averaged normalized resistance at 0.5V as a function of molecular length d and molecular layer thickness t. d,t=0 corresponds to the pedot only wafer. Each data point is the average of the 5, 10, 20 and 50 μm via of 62 dies. The error bars shows the standard deviation of all vias measured. When fitting the 4 wafers containing the molecules we find that the RS values increases roughly 0.5 decades per phenyl ring \((\beta = 0.28 \text{Å}^{-1})\), see equation 6.1. The interpolated contact resistance using equation 6.1 falls within the error bar of the normalized resistance of the pedot only device: \(2.8 \cdot 10^3 \Omega \mu \text{m}^2\).

the resistance per molecule reported elsewhere in literature (see figure 2.11). Van Hal et al. suggested to describe the conductance of a single molecule junction as the product of three transmission factors: the molecules top contact \((tc)\), the molecule itself \((mol)\) and the molecules bottom contact \((bc)\) times the quantum of conductance \(2e^2/h\):

\[
G_{mol} = \frac{2e^2}{h} \cdot T_{tc} \cdot T_{mol} \cdot T_{bc}. \tag{6.2}
\]

Here, \(T_{mol} \propto \exp(\beta \cdot d)\) and contains the length dependence. The total conductance of the via is then simply given by the sum of all single molecule channels, \(G_{via} = N \cdot G_{mol}\), with \(N = A_{via}/A_{mol}\). The observed differences in the resistance of the molecule as a function of resist and PEDOT:PSS (≈ one order of magnitude), were attributed to different \(T_{tc}s\).

Applying this reasoning to the OPPs measured here, \(T_{tc}\) is several orders of magnitude lower compared to LAMJs with alkanes and single molecule experiments on OPPs. To see the influence of \(T_{tc}\), we also measured OPP monothiols (now the end group is a C-H in stead of a C-S-H). However, we found similar RS values within one order of magnitude compared to the
OPP dithiols [165]. An alternative explanation within the picture sketched by Van Hal et al. is that the number of channels contacted per area might be unequal to the packing density of the SAM. However, it seems unlikely that this can account for more than two orders of magnitude. A combination of both seems more likely. We also attempted to process the OPPs in LAMJs using the L6000.5 resist. However, THF-ammonia was found to damage this resist (for alkanes ethanol was used to dissolve the molecules). At the end of this chapter, we will leave equation 6.2 and discuss the obtained result in a different light.

In order to further study the OPPs, we studied $I(V)$-traces as a function of temperature. To cool down, we used the dipstick setup described in section 2.3. Figure 6.3 compares the $I(V)$-traces and the $dI/dV(V)$-trace (2-probe, dipstick) of a 2 $\mu$m pedot only via and a 2 $\mu$m P2 via at three different temperatures in vacuum. $I(V)$-traces are symmetric with respect to voltage and non-linear. The current through the monolayer scales linear with the via area, resulting in similar current densities for all device areas. The conductance at zero bias of both devices drops approximately a factor of 4 between 300 K and 77 K and more than a factor of 100 in going from 77 K to 5 K. Also, the non-linear character of both the pedot only and the P2 via increases dramatically when cooling down. The strong temperature dependence for the P2 via comes as a surprise, since we expected molecular devices to be characterized by temperature independent tunneling [85].

It should be noted that the evacuation of air has a direct effect on the resistance of the LAMJ via. The effect of pumping on LAMJ devices was previously attributed to the presence of water in the PEDOT:PSS [85]. We compared the zero bias conductance of a P2 via before and after evacuation of air. We found that the conductance increased by $\sim 20\%$ when evacuating the dipstick for 1-2 hours using a turbo molecular pump. To verify that the vias are not irreproducibility damaged by a cooling cycle, we also compared the zero bias conductance before and after cooling. After a cycle of pumping and cooling to 4.2 K the zero bias conductance returned to its initial zero bias conductance within 10 %. To investigate the charge transport in more detail, we repeated the experiment for a 10 $\mu$m via of each wafer between 5 and 45 K. Figure 6.4 compares two differential conductance measurements of a pedot only via and a P2 via at 5±0.5, 15±1, 25±2, 35±3 and 45±3 K. For both vias, a strong conductance dip is observed at zero bias. For the molecular device, the dip extends over a larger voltage range as compared to the pedot only device.

Akkerman et al. described the charge transport mechanism through LAMJs of alkanes as temperature independent tunneling. Therefore, we expected that the conductance of OPPs would be temperature independent down to the point where the PEDOT:PSS series resistance has a higher resistance than the molecular layer. From that point on, the conductance is
Figure 6.3: The current and differential conductance of a 2 \( \mu m \) via of wafer P2 (left) and of a 2 \( \mu m \) via of the pedot only wafer for three different temperatures; 300K (upper), 77K (middle) and 5K (lower). When cooling down, the conductance at zero bias drops and the \( I(V) \)-traces become more non-linear. Note: the saturation around zero bias at 5K is not an artefact of the electronics.
expected to drop. We made a sketch of our hypothesis in figure 6.5a on a log-log plot. Figure 6.5b shows the experimental results on a log-log scale. Here, \( dI/dV(V = 0) \) (2-probe, V-bias) divided by the via area \( A \) is plotted versus temperature. The conductance of the pedot only vias indeed decreases at low temperatures. However, the molecular vias show a similar temperature dependence. \( dI/dV(V = 0) \) roughly has a power law dependence on temperature,

\[
dI/dV(T, V = 0) \propto T^\alpha. \tag{6.3}
\]

We find \( \alpha \) ranging between 2.4 and 3.1. The value of \( \alpha \) used for each fit is listed in figure 6.5b. Note that previously, PEDOT:PSS was modeled by variable range hopping (VRH) between PEDOT:PSS particles [84, 166, 167]. If the hopping occurs in three dimensions, a plot of \( \log(G) \) vs. \( T^{-1/3} \) should result in a straight line [168]-[170]. The inset of figure 6.5b shows that instead of a power law, we also could have chosen this VRH representation. However, since \( \log(G) \) vs. \( T^{-1/2} \) and \( T^{-1/3} \) also give reasonable fits, we prefer a log-log representation.

To conclude this section, we would like to emphasize that at each temperature and all voltages measured, the conductance still decreases exponentially with the length of the molecule. To further illustrate this, we also plotted the differential conductance versus voltage for all five wafers on a log-log scale.
Figure 6.5: (a) Expected temperature dependence of the conductance on temperature for OPP wafers on a log-log scale. (b) Measured temperature dependence of the conductance on temperature on a log-log scale. The normalized differential conductance at 0 mV between 5-290 K is plotted. The points on the left are measured using the dipstick setup (5-45 K). Here, each point is a single measurement of a 10 μm via. The points on the right are measured using the Janis system. Here, each point is an average of a 3, a 5 and a 10 μm via (110-290K). The data can be fitted using equation 6.3. The α values used are listed in the figure. The inset shows that the data can also be fitted using a VRH model [168].

for two different temperatures in figure 6.6a,b. Strikingly, parallel $dI/dV(V)$-traces are observed for both temperatures,

$$dI/dV(V,T) \propto V^{\gamma(T)}$$  

(6.4)

beyond a threshold voltage. $\gamma(T)$ increases when T decreases. Even more surprisingly is that data sets of different temperatures can be collapsed on a single ‘master’ curve when plotting the conductance as a function of $eV/k_b T$. Figure 6.5c shows such a master curve for the pedot only wafer and the P2 wafer. The differential conductance in this plot is scaled by dividing it by $T^{\alpha}$ using the $\alpha$ obtained in figure 6.5. When $eV > k_b T$, $dI/dV(T) \propto V^{\gamma(T)}$. For $eV < k_b T$, $\gamma$ approaches zero.

6.3 Interpretation: granular PEDOT

In the remainder of this chapter we propose a tentative model to explain the observations. Our data suggest that the molecular devices can be roughly described by: $G_{via} = \exp(-\beta \cdot d) \cdot G_{pedotonly}(V,T)$. We consider four possible
Figure 6.6: (a), (b), The differential conductance as a function of bias voltage of a 10 μm via of all five wafers on a log-log scale at 25 K and 298 K. The current scales with a power of the voltage beyond a threshold voltage. (c) Plot of scaled differential conductance versus $eV/k_bT$. The differential conductance was scaled by dividing through $dI/dV(V)$ by $T^\alpha$. $\alpha$ was obtained from figure 6.5. The plots shows 6 different data sets (5, 15, 25, 35, 45 and 300K, 4-probe) collapsed onto one master curve for a 20 μm pedot only via and for a 20 μm P2 via. The 300K data set was measured on a 10μm via and multiplied by 4 to correct for the size difference. Representing data in this way was obtained from references [172, 174, 175].
explanations. (i) Molecules act as insulating particles, simply reducing the contact area between the polymer and the metal, thereby lowering the current. (ii) The charge transport through molecules is described by tunneling coherently through multiple layers (equation 6.2). (iii) The devices classify as a Lüttinger liquid. (iv) The molecules modify the hopping transport of PEDOT:PSS.

Although (i) is appealingly simple, we find it rather unlikely that the contact area decreases exponentially with the length of the molecule. Also, comparing phenylenes with alkanes, the exponential decay depends on the type of molecule. Furthermore, previously capacitance measurements confirm the presence of a closed molecular layer [85]. Therefore we find this explanation unlikely.

Within the coherent transport picture (explanation ii), the transmission through two pieces of material in series can only be multiplied if the there is phase coherence of the electrons while they travel through the two pieces. If this is not the case, the total resistance of the two pieces of material in series is simply given by: 

\[ R_{\text{tot}} = R_1 + R_2 \]  

[171]. Our data suggest that one of the transmission factors is temperature and voltage dependent. Since both the pedot only and molecular vias show a similar temperature and voltage dependence, this transmission factor needs to appear in both. Hence, \( T_{\text{mol}} \) and \( T_{\text{bc}} \) are excluded (equation 6.2). Therefore, \( T_{\text{tc}} \) remains. Several physical pictures can give rise to a temperature dependent interface transmission, e.g. a Schottky barrier or a temperature dependent occupation of the density of states of the PEDOT:PSS. With such a temperature dependent \( T_{\text{tc}} \), we can explain the observed temperature dependence. However, we do not see how it can account for the observed power law voltage dependence.

Let us consider Lüttinger liquid (LL) behavior as an explanation for our observations (explanation iii). Systems that have previously been characterized as LLs include carbon nanotubes [172], atomic wires [173], inorganic crystalline nanowires [174] and a bulk polycrystalline organic conductor [175]. For a LL, indeed a power law dependency of the current as a function of voltage and temperature is expected [176]. In three of these reports the collapse of temperature and voltage dependence conductance measurements on a single curve was used as an important piece of evidence to identify the LL behavior [172, 174, 175]. A prerequisite for LL behaviour is one dimensional confinement of electrons. For most systems reported thus far, one dimensionality is rather obviously present [172, 173, 174]. However, we do not see direct evidence for structural one dimensionality in our system. Furthermore, we do not think that the collapsing seen in figure 6.6c itself is a proof of the existence of a LL. Therefore, we will not further evaluate the LL explanation.

For a commentary on LL behavior a bulk polycrystalline organic conductor [175] we refer to reference [177].

In the last part of this chapter we will discuss how the molecules can
Figure 6.7: Tentative model to explain the experimental observations of the OPP LAMJs. (a) Schematic representation of a PEDOT:PSS colloid as a Coulomb island between two tunnel junctions. The island region between the junction is the PEDOT:PSS colloid. The lower junction represents the molecular layer with a resistance $R \propto \exp(\beta \cdot d)$ and a capacitance $C$. The upper junction represents all other connections to the PEDOT island. When $R \gg r$ the total current through the double junction is solely determined by $R$ [184]. This explains why we still observe $R_{\text{via}} = \exp(\beta \cdot d)$. (b) PEDOT:PSS represented as an array of Coulomb islands. Each cross represents a PEDOT:PSS colloid and $r$ represents the effective resistance of the PSS between two colloids. When molecules are present, this resistance will increase, as observed experimentally, $R = r \cdot \exp(-\beta \cdot d)$. For $d = 0$, $R = r$. Judging from the measured PEDOT:PSS layer thickness and the colloid size, the number of colloids in the $z$ direction is limited to $\sim 2$. (c) Schematic representation of the PEDOT:PSS islands (white circles) embedded in the PSS (grey area). In reality the sizes of the pedot islands are probably not homodisperse, such that Coulomb islands of different $c$ and $r$ will be present. Part of the PEDOT islands will probably fuse with neighboring islands. (d) After having entered the array of Coulomb islands, the charges have to meander over PEDOT:PSS islands to reach the other electrode. To enter an island, an energy $E_C$ has to be paid. 1 and 2 depict two different charge paths. The ‘ladders’, in between the electrodes depict the Coulomb energy levels for each islands (level spacing = $E_C$). When ladders of different islands are not exactly aligned, the charge carriers lose energy while traveling through the network.
modify the hopping transport in the PEDOT:PSS (explanation iv). We will put forward a tentative model, in which we model the PEDOT:PSS as a network of 'Coulomb islands'. The first indication for considering Coulomb blockade is the size of the PEDOT:PSS colloids. Small metallic particles have a small capacitance $C$. Therefore, the Coulomb charging energy $E_C = e^2/2C$ can become of importance. For a sphere, the capacitance is given by $e_0\varepsilon_r2\pi d$.

Where $e_0 = 8.8510^{-12}F/m$ is the static relative permittivity and $\varepsilon_r$ is the dielectric constant of the insulating layer. For the PEDOT:PSS used here, we estimate that the colloids have an average diameter of $\sim 50$ nm [178]. Assuming $\varepsilon_r = 2$ and $d = 50$ nm, we find a capacitance of 5.6 aF. In general, two requirements need to be fulfilled to observe Coulomb blockade. The first requirement is $k_B T << E_C$; the thermal energy needs to be much lower than the Coulomb charging energy. For $C = 5.6$ aF, we find $E_C = 14$ meV and the requirement is fulfilled at temperatures below 162 K. Secondly, the total charge 'leakage' from an island should be less than the quantum of conductance, $G < 2e^2/h$ [44]. It is more difficult to judge whether this requirement is fulfilled in the case of PEDOT:PSS. However, taking into account that the outer shell of the PEDOT:PSS colloids is insulating (PSS) and the inter particle contact area is small, it is certainly not unlikely.

There are three more important arguments to consider Coulomb blockade. First, figure 6.4 shows a so called zero bias anomaly (ZBA) [179]. ZBA showing a minimum in the conductance have been observed in a variety of systems, including disordered point contacts [180] and disordered metallic films described by hopping conduction at low temperatures at low voltages [181]. Coulomb blockade is one of the pictures explaining ZBA. Second, the observed power law voltage dependence beyond a threshold $V_t$;

$$I \propto (V - V_t)^\eta$$

has been predicted [182] and measured [183] for 2D arrays of Coulomb blockade arrays. Note, $\eta = \gamma + 1$, see equation 6.4. Third, the observed 'factorization' of the current by the presence of molecules can be explained by considering a Coulomb island coupled two metal leads via two different tunnel barriers.

Let us consider the third argument in more detail. Figure 6.7a shows a schematic representation of a Coulomb island connected by two different tunnel junctions. As long as one of the barriers has a much higher resistance than the other, the high resistance barrier will determine the total current flowing through the island [184]. The insertion of the molecular layer possibly forms the high resistive barrier, whereas the connections between the PEDOT:PSS island and other PEDOT:PSS islands might form the low resistive barrier. Therefore, as long as the molecular layer acts as a lead to a PEDOT:PSS island with a relative high resistance compared to the other connections to the island, the molecules will limit the current and determine
Table 6.2: For arrays of Coulomb islands, $I(V)$-traces at zero temperature are given by $I \propto (V - V_t)^\eta$ [182]. $\eta$ and $V_0$ were determined for all five wafers using the methodology proposed by [186].

<table>
<thead>
<tr>
<th>Wafer</th>
<th>$\eta(= \gamma + 1)$</th>
<th>$V_t(0)$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pedot only</td>
<td>2.9</td>
<td>26</td>
</tr>
<tr>
<td>P1</td>
<td>3.5</td>
<td>45</td>
</tr>
<tr>
<td>P2</td>
<td>3.9</td>
<td>62</td>
</tr>
<tr>
<td>P3</td>
<td>4.1</td>
<td>106</td>
</tr>
<tr>
<td>P4</td>
<td>4.2</td>
<td>127</td>
</tr>
</tbody>
</table>

Before being able to proceed, we have to make a guess how PEDOT:PSS layer looks like. When spinning the suspension of PEDOT:PSS colloids on a substrate, layers of $\sim 100$ nm thickness form (see figure 2.9). This layer thickness corresponds to about two times the estimated average colloid size. To proceed we will assume that the PEDOT:PSS remains its colloidal structure in the spincoated layer [185]. Figure 6.7b gives an idealized model for a the structure of the PEDOT:PSS layer. In this picture, the PEDOT:PSS colloids forms a three dimension network of Coulomb islands with only a few islands ($\sim 2$) in the Z direction. Each cross denotes a PEDOT:PSS colloid. The colloids are interconnected by a resistor, $r$, representing the PSS layer. The resistance between the bottom gold and the first layer of colloids is depicted by $R$. Figure 6.7c shows a more realistic cross section of how the PEDOT:PSS layer might look like. In reality, part of the colloids probably fuse and the colloids will have a particle size distribution.

To check the validity of our idea, we will revisit the data and verify whether $I(V)$-traces are indeed of the form presented in equation 6.5. We follow a procedure found in literature [186]-[188]. A problem in determining $V_t$ is that above a temperature $T^\dagger$, charges can already meander through the network, giving rise to an Ohmic background. This background linearly shifts $V_t$ as a function of temperature $V_t(T) = V_t(0) - xT$. $T^\dagger$ is then defined as the temperature for which $V_t(T^\dagger) = 0$. An elegant way of determining the power, $\eta$ and the threshold, $V_t(T)$, is to plot $dV/dI \cdot I$ versus $V$ [188]. For equation 6.5, this results in $dV/dI \cdot I = \eta^{-1}(V - V_t(T))$, a straight line of slope $1/\eta$ and $V_t(0)$ at $y=0$.

Figure 6.8a shows these plots for a 20 $\mu$m pedot only device measured in a 4-probe configuration at 5, 15, 25, 35 and 45 K. 4-probe measurements were chosen, since the maximum current measured in 2-probe measurements is limited by series resistances present in the dipstick. Indeed, we find parallel lines of $\eta = 2.9$. The inset shows a plot of $V_t(T)$ versus temperature, from
Figure 6.8: By plotting the differential resistance times the current versus the voltage, power law $I(V)$-traces will yield a straight line of slope $1/\eta$ through $V = V_i(T)$ at $y=0$ [188]. (a) A pedot only via (20 µm 4-probe) measured at 45, 35, 25, 15 and 5 K (from left to right). The inset shows that $V_i(0)$ can be found by interpolating the $T$ versus $V_i(T)$ to $T=0$. (b) A P4 via (20 µm 2 probe) measured at 45, 35, 25, 15 and 5K (from left to right). The inset shows that $V_i(0)$ can be found by interpolating the $T$ versus $V_i(T)$ to $T=0$. 
which we deduce $V_t(0) = 26 meV \sim 2E_C$ of a single PEDOT:PSS particle (14meV). Note that in general, for an array of Coulomb islands $eV_t(0) > E_C$. This can be understood by considering the two current paths in figure 6.7c,d. When the Coulomb ladders are not exactly aligned, even for the shortest current paths, the charging energy has to be paid several times before reaching the other electrode [182].

To the best of our knowledge, the theory of Middleton and Wingreen [182] has not yet been extended to three dimensions. For two dimensional networks a theoretical slope of $\eta=5/3$ is expected. However, in experiment, values around 2.25 are found [183]. For three dimensions, $\eta$ is expected to increase. Recently, $\eta = 2.7 - 3.0$ was found for 3D gold colloid networks in experiment [189]. The value found for the pedot only is in agreement with this observation.

We also performed the same analysis for 20 $\mu$m molecular vias. Figure 6.8b shows the analysis for a P4 via and table 6.2 summarizes the results for all wafers. For the analysis for pedot only, P1 and P2, 4-probe measurements were used, such that the current is not limited by the series resistance present in the dipstick. For P3 and P4, 2-probe measurements were used. Strikingly, both $V_t(0)$ and $\eta$ increase. We cannot fully judge whether these results can be related to a physical picture. For the molecular device, the capacitance of the coupling between molecule and the island might also contribute to the total capacitance. In that case the total capacitance indeed diminishes for thicker tunnel barriers (longer molecules) and $V_t(0)$ is increased.

Finally, we would like to emphasize that the reasoning above has a rather tentative character. Many questions remain. We will end this chapter with three critical remarks. First, Efros and Shklovskii have previously predicted that in the presence of a Coulomb gap, the density of states at the Fermi energy will not be constant [191] (for an instructive experimental example, see reference [181]). We cannot fully oversee whether the observed temperature dependence is fully in agreement with this statement, see equation 6.3. A recent review on conduction in granular electronic materials with many connections between subjects touched in this chapter can be found in literature [192]. Secondly, the presence of power law $I(V)$-traces is certainly not unique to Coulomb blockade systems. Power law $I(V)$-traces are also very common in conductive polymers. For example space charge limited currents (SCLC) give rise to a power of $\eta = 2$ [193]. We are unaware of a connecting theories between SCLC and Coulomb blockade. Third, obviously, the network presented in figure 6.7b needs further evaluation.

6.4 Conclusion

In this chapter we electrically characterized large area molecular junctions of oligo-para-phenylene dithiols. The resistance of the molecular junctions
was found to exponentially increase with the length of the molecule: \( R \propto \exp(\beta \cdot L) \), with \( \beta = 0.28 \pm 0.02 \text{Å}^{-1} \). By studying the charge transport as a function of temperature, we found a similar behavior for polaronic devices and devices with molecules. Both devices showed a strong temperature dependence. Also, a strong dependence on the bias was observed for temperatures between 5-45 K. However, at all temperatures and voltages measured, a dependence on molecular length is observed. In order to understand the observations, we believe it is necessary to take into account the granular nature of the PEDOT:PSS. Our results indicate that it is not directly obvious to regard LAMJs as a metal-molecule-metal junction. Its electronic behavior will be largely dependent on the properties of the PEDOT:PSS.