Molecular Length Dictates the Nature of Charge Carriers in Single-Molecule Junctions of Oxidized Oligothiophenes

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Contents

- 1. Experimental Details
 - a. Synthesis
 - b. Conductance measurements
 - c. Thermopower measurements

2. Additional Data

- a. Figure S1. UV-vis absorption spectra for T3 derivatives
- b. Figure S2. Cyclic voltammograms for TDOn
- c. Table S1. Values determined from CV data
- d. Figure S3. Two dimensional histograms for TDOn
- e. Figure S4. Sample Trace for Thermopower Measurement
- f. Figure S5. Thermoelectric current histograms for the TDOn
- g. Figure S6. Solvent induced conductance shifts
- 3. Additional Analysis
 - a. Single Lorenztian Model
 - b. I-V Analysis
 - c. Figure S7. I-V curves for TDO1 and TDO4
 - d. Tight binding model
 - e. Figure S8. Tight binding
- 4. References

a. Synthesis:

General Procedures: All reactions were performed in oven-dried round bottom flasks, unless otherwise noted. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon, unless otherwise noted. Anhydrous solvents were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. All column chromatography was performed on a Teledyne ISCO Combiflash RF using Redisep RF silica gel columns. Thin- layer chromatography (TLC) was performed on silica gel 60 F₂₅₄ plates (EMD). The synthesis presented here follows methods from Potash and Rozen.¹

Instrumentation. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker DRX300 (300 MHz) and a Bruker DRX400 (400 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃: δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and referenced to the carbon resonances of the solvent (CDCl₃: δ 77.0). Data are represented as follows: chemical shift, multiplicity (app = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), and integration. The mass spectroscopic data were obtained at the Columbia University mass spectrometry facility using a JEOL JMSHX110A/110A tandem mass spectrometer. Absorption spectra were taken on a Shimadzu UV-1800 spectrophotometer.

Electrochemistry.

Samples were dissolved in dichloromethane containing 0.1 M of supporting electrolyte, tetrabutylammoniumhexafluorophosphate (TBAPF₆). These solutions were used in a single cell with a CH Instruments Electrochemical analyzer potentiostat assembly for cyclic voltammetry measurements. The measurements were carried out with a glassy carbon working electrode, a platinum wire counter electrode and an Ag₊/AgCl reference electrode. The potentials were measured against a Ag₊/AgCl reference electrode and each measurement was calibrated using ferrocene/ferrocenium (Fer) redox system.

HOF •CH₃CN Setup

Fluorine is a very toxic and corrosive gas and must be used with care. Details on working with fluorine are explained in Wei et al.²

1. 2-tributylstannyl 5-thiomethyl thiophene

$$S \xrightarrow{S} SnBu_{3}$$

Br
$$S \xrightarrow{S} Br \xrightarrow{1. nBuLi, S_{2}Me_{2}}{2. nBuLi, SnBu_{3}Cl} \xrightarrow{S} SnBu_{3}$$

THF, -78°C, 12 hr

An oven-dried 100 mL round bottom flask and stir bar were cooled under Ar. 2,5 dibromothiophene (1 g, 4.13 mmol, 1 eq) was added and dissolved in 50 mL THF. The solution was cooled to -78 °C. n-Butyllithium (2.4M in hexanes, 1.89 mL, 4.5 mmol, 1.1 eq) was added dropwise by syringe and the solution was stirred for 30 minutes at -78 °C. Dimethyl disulfide (0.39 g, 4.13 mmol, 1 eq) was added dropwise by syringe and the solution was allowed to warm to room temperature and stirred for one hour. The solution was then cooled back down to -78 °C. n-Butyllithium (2.4M in hexanes, 1.89 mL, 4.5 mmol, 1.1 eq) was added dropwise by syringe and the solution was stirred for 30 minutes at -78 °C. Tributyl tin chloride (1.34 g, 4.13 mmol, 1 eq) was added dropwise by syringe and the solution was allowed to warm to room temperature and stirred overnight. The mixture was added to 25 mL water. The organic layer was extracted with diethyl ether (2 x 50 mL), and the combined organic layers were washed with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. After filtration, the organic layer was concentrated under reduced pressure to yield the product as a dark brown oil (1.6 g, 92 % yield). The crude product was used in the next step without further purification. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 7.15 \text{ (d, } J = 3.3 \text{ Hz}, 1\text{H}), 7.02 \text{ (d, } J = 3.3 \text{ Hz}, 1\text{H}), 2.50 \text{ (s, } 3\text{H}), 1.56$ (m, 8H), 1.34 (m, 8H), 1.09 (m, 8H), 0.90 (m, 12H), 13 C NMR (400 MHz, CDCl₃) δ 141.85, 140.18, 135.51, 131.07, 28.76, 26.99, 21.76, 13.48, 10.70. HRMS (ESI+) calculated for C₁₇H₃₂S₂Sn 419.28, found 419.28.

2. 2,5-dibromothiophene-1,1-dioxide



An oven-dried 100 mL round bottom flask and stir bar were cooled under Ar. 2,5 dibromothiophene (400 mg, 1.65 mmol, 1 eq) was added and dissolved in 10 mL DCM. The solution was cooled to 0 °C. HOF•CH₃CN (55 mL, 0.15 M, 8.27 mmol, 5 eq) was added dropwise. The solution was allowed to warm to room temperature and stirred for 2 hours. The reaction was quenched by adding 30 mL of saturated NaHCO₃ dropwise. The organic layer was extracted with DCM (2 x 50 mL), and the combined organic layers were washed with NaHCO₃ (100 mL) and water (100 mL) and dried over magnesium sulfate. After filtration, the organic layer was concentrated under reduced pressure to yield the product as a white powder (355 mg, 78% yield). The crude product was used in the next step without further purification. ¹H NMR (400 MHz, CDCl₃) 6.86 (s, 2H). ¹³C NMR (400 MHz, CDCl₃) δ 128.16, 119.46. LRMS (APCI+) calculated for C₄H₂O₂SBr₂ 273.93, found 274.00.

3. 5,5"-bis(methylthio)-[2,2':5',2"-terthiophene] 1',1'-dioxide (**TDO1**)



An oven-dried 5 mL round bottom flask and stir bar were cooled under Ar. 2 mL of DMF was added and sparged with Ar for 15 minutes. **2** was added (30 mg, 0.11 mmol, 1 eq) together with tetrakis(triphenylphosphine)palladium (6.4 mg, 0.0055 mmol, 0.05 eq). The solution was heated under Ar to 80 °C for 5 minutes. **1** was added (92 mg, 0.22 mmol, 2 eq) and the solution was stirred at 80 °C under Ar for 5 hours, during which time it turned from yellow to a deep red color. The crude mixture was cooled and then passed through a

SUPPLEMENTARY INFORMATION

silica plug with DCM and 2% triethylamine. The solution was then washed with water (3 x 75 mL) and dried over magnesium sulfate. After filtration, the organic layer was concentrated under reduced pressure. Purification by column chromatography in 20% ethyl acetate in hexanes ($R_f = 0.32$) yield the product as a deep red/bronze solid (29 mg, 71% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 3.9 Hz, 2H), 7.00 (d, J = 3.9 Hz, 2H), 6.65 (s, 2H), 2.57 (s, 6H). ¹³C NMR (500 MHz, CDCl₃) δ 142.76, 135.29, 130.37, 129.87, 128.36, 117.92, 20.77. LRMS (APCI+) calculated for C₁₄H₁₂O₂S₅ 372.57, found 371.94.

4. 5,5'-dibromo-4,4'-dihexyl-[2,2'-bithiophene] 1,1,1',1'-tetraoxide



The above compound was synthesized according to published procedures.¹ ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, *J* = 6.6 Hz, 6H), 1.34 (m, 12H), 1.62 (m, 4H), 2.47 (t, *J* = 7.8 Hz, 4H), 7.12 (s, 2H).

5. 3',4"-dihexyl-5,5"'-bis(methylthio)-[2,2':5',2":5",2"'- quaterthiophene]1',1',1",1"- tetraoxide (**TDO2**)



¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 4.0 Hz, 2H), 7.17 (s, 2H), 7.07 (d, *J* = 4.0 Hz, 2H), 2.71 – 2.64 (t, 4H), 2.59 (s, 6H), 1.72 – 1.58 (m, 4H), 1.47 – 1.21 (m, 12H), 0.97 –

0.81 (m, 6H). ¹³C NMR (500 MHz, CDCl₃) δ 143.93, 134.72, 132.03, 129.83, 129.51, 129.13, 128.14, 127.84, 31.44, 30.37, 29.27, 27.30, 22.49, 20.77, 14.01. LRMS (APCI+) calculated for C₃₀H₃₈O₄S₆ 655.01, found 654.15.

6. 5,5"-dibromo-3',4'-dihexyl-[2,2':5',2"-terthiophene] 1,1,1',1'',1",1"-hexaoxide



The above compound was synthesized according to published procedures.^{1 1}H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 5.4 Hz, 2H), 7.01 (d, J = 5.3 Hz, 2H), 2.86 – 2.77 (t, 4H), 1.62 (m, 4H), 1.34 (m, 12H), 0.91 – 0.85 (m, 6H).

7. 3",4"-dihexyl-5,5""-bis(methylthio)-[2,2':5',2":5",2"':5",2"''-quinquethiophene] 1',1',1",1",1"',1"''-hexaoxide (**TDO3**)



¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 3.9 Hz, 2H), 7.49 (d, J = 5.5 Hz, 2H), 7.00 (d, J = 4.0 Hz, 2H), 6.69 (d, J = 5.6 Hz, 2H), 2.93 – 2.83 (m, 4H), 2.60 (s, 6H), 1.65 (m, 4H), 1.35 (m, 12H), 0.90 (m, 6H). LRMS (APCI+) calculated for C₃₄H₄₀O₆S₇ 769.13, found 768.3.

8. 5,5"'-dibromo-3',4,4",4"'-tetrahexyl-[2,2':5',2":5",2"'-quaterthiophene]

1,1,1',1',1",1"',1"'-octaoxide



The above compound was synthesized according to published procedures.¹ ¹H NMR (400 MHz, CDCl₃) δ 0.89 (m, 12H), 1.29-1.38 (m, 20H), 1.42-1.46 (m, 4H), 1.59-1.67 (m, 8H), 2.57-2.65 (m, 8H), 7.16 (s, 2H), 7.39 (s, 2H). ¹³C NMR(100 MHz, CDCl₃) δ 13.99, 14.06, 22.47, 22.55, 27.19, 28.90, 29.25, 29.44, 29.49, 30.37, 31.40, 31.51, 114.55, 127.88, 128.05, 128.24, 130.10, 131.76, 135.35. 143.75.

9. 3',3",4"',4""-tetrahexyl-5,5""'-bis(methylthio)-[2,2':5',2":5",2"':5"',2"'':5"'',2"'''-sexithiophene] 1',1',1"',1"'',1"'',1"''-octaoxide (**TDO4**)



¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 5.5 Hz, 2H), 7.39 (s, 2H), 7.26 (s, 2H), 7.07 (d, J = 5.4 Hz, 2H), 2.98 (t, 4H), 2.68 (t, 4H), 2.60 (s, 6H), 1.69 (m, 8H), 1.36 (m, 8H), 1.33 (m, 8H), 1.26 (m, 8H) 0.90 (m, 12H) ¹³C NMR (500 MHz, CDCl3) δ 144.76, 141.32, 133.35, 132.29, 131.65, 130.58, 130.26, 129.75, 129.42, 129.25, 128.89, 126.82, 31.62, 31.48, 31.46, 30.23, 29.71, 29.26, 29.21, 28.78, 27.26, 22.49, 20.59, 14.01. LRMS (MALDI) calculated for C₅₀H₆₆O₈S₈ 1051.57, found 1050.59.

b. Conductance Measurements

Additional Conductance Data: For each molecule in the TDOn series, 20,000 conductance verses displacement traces (Figure 3a) are collected. Molecules are introduced to the STM break-junction in a solution of 1-octylbenzene, and conductance measurements are carried out at an applied bias of 10mV. The conductance traces are then compiled into 1-dimensional logarithmically binned histograms (100 bins/decade, Figure 3b) which preserve junction displacement information. The 2-dimensional histograms below were created by aligning individual conductance traces just after the gold-point contact rupture (after the 1G₀ conductance plateau) and then overlaying all conductance traces without data selection.³ It can be clearly seen that the conductance feature scales with molecular length.

c. Thermopower Measurements

We use a modified break junction procedure in order to derermine the Seebeck coefficients of single-molecules.⁴ Instead of simply retracting the STM tip after it is driven into the substrate, we now incorporate a 150ms hold into the piezo ramp after the tip has been pulled a distance of 2.2nm. As before, we apply a 10mV bias during the pullout and during the first and last 25ms of the hold, but we now apply a 0mV bias during the middle 100ms of the hold. We collect thousands of such traces with a 0K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate and with a 16K temperature difference between the tip and the substrate. The data collected at 0K is to ensure that that we have no thermoelectric current flowing when there is no temperature gradient (and no bias voltage) applied (Figure S5).

In order to analyze this data, we only consider traces where a molecule is present in the junction during the hold. In order to select out these traces, the conductance at the start and end of the hold (where the 10mV bias is applied) is averaged; traces where this conductance falls within the molecular conductance range (as determined from conductance histograms in Figure 3a) are kept. For such traces, the thermoelectric current measured during the middle portion of the hold is averaged. Thermocurrent histograms are provided in Figure S6, where the thermocurrent at $\Delta T=0K$ and $\Delta T=16K$ are provided for all four molecules. For $\Delta T=0K$, there is a narrow distribution peaked about 0pA for all TDO molecules. As the ΔT is increased, this thermocurrent distribution broadens and shifts to negative values for TDO1 and TDO2, while it shifts to a positive value for TDO4; this is indicative of a change in the sign of the dominant charge carrier.

The thermocurrent values are then used in conjunction with the average molecular conductance before and after the hold to compute the average Seebeck coefficient of the given molecular junction. These Seebeck coefficients are then compiled into the histograms shown in Figure 3d.

Additional Data:

UV-vis absorption spectra for T3 derivatives



Figure S1. Normalized UV-vis absorption spectra measured in dichloromethane for T3 derivatives with varying degrees of oxidation.

Cyclic Voltammetry Data for the TDOn series



Figure S2. Cyclic voltammograms for TDOn performed in dichloromethane with Ag/AgCl reference electrode, 0.1M tetrabutyl ammonium hexafluorophosphate as the electrolyte and a scan rate of 50 mVs⁻¹.

	$E_{ox^{1/2}}(V)$	$E_{red^{1/2}}(V)$	E _{HOMO} (eV)	E _{LUMO} (eV)
TDO1	1.12	-1.03	5.5	3.4
TDO2	1.13	-0.72	5.5	3.7
TDO3	1.12	-0.51	5.5	3.9
TDO4	1.12	-0.34	5.5	4.1

Table S1. $E_{ox\frac{1}{2}}$, $E_{red\frac{1}{2}}$, E_{HOMO} and E_{LUMO} determined from CV data. $E_{ox\frac{1}{2}}$ and $E_{red\frac{1}{2}}$ are the midpoints of the first oxidation and reduction peaks respectively in the cyclic voltammograms. E_{HOMO} and E_{LUMO} are determined^{5,6} using $E_{HOMO} = E_{ox\frac{1}{2}} + 4.4$ and $E_{LUMO} = E_{red\frac{1}{2}} + 4.4$.



Two-Dimensional Histograms for the TDOn series

Figure S3. Two-dimensional conductance versus displacement histograms for TDOn.

Sample Trace for Thermopower Measurements



Figure S4. Top Panel: Sample piezo ramp used in collecting thermopower data. The hold is shown in the gray shaded area. Bottom Panel: Sample current vs. displacement trace (red) and voltage vs. displacement trace (blue) for TDO3.

Thermoelectric Current Histograms



Figure S5. Thermoelectric current histograms for the TDOn series. Histograms in black correspond to a ΔT of 0K, while colored histograms correspond to a ΔT of 16K. At ΔT =0K, the number of traces selected (following the procedure above) is 264 for TDO1, 520 for TDO2, 586 for TDO3 and 1,141 for TDO4. At ΔT =16K, the number of traces selected is 793 for TDO1, 891 for TDO2, 1,346 for TDO3, and 468 for TDO4.

Solvent Induced Conductance Shifts



Figure S6: a. TDO1 conductance histogram measured from a 1 mM solution in bromobenzene and phenyloctane. The peak shifts to a higher conductance in bromobenzene implying HOMO dominated transport b. TDO4 shows a decrease in conductance upon changing the solvent from phenyloctane to bromobenzene, implying LUMO transport.⁷

Single-Lorentzian Model

Charge transport through a single-molecule junction can be analyzed in terms of a transmission function which details the probability that an electron incident on the molecular barrier is transmitted through the junction. Often, when one molecular orbital is dominant in this tunneling process, the transmission function, T(E), can be approximated by a single Lorentzian of the form:⁸

$$T(E) = \frac{\Gamma^2 / 4}{\left(E - \Delta E\right)^2 + \Gamma^2 / 4}$$

Here, ΔE is the electronic molecular level alignment ($\Delta E = E_{resonance} - E_F$) and Γ is the coupling strength of the conducting orbital to the leads. Using this form of transmission, along with the definitions of conductance (*G*) and the Seebeck coefficient (*S*), expressions for ΔE and Γ can be obtained as:

$$\Delta E = -2\frac{S_0}{S} \left(1 - \frac{G}{G_0} \right) \qquad \Gamma = 4\frac{S_0}{S} \sqrt{\frac{G}{G_0} \left(1 - \frac{G}{G_0} \right)}$$

where $G_0 = 7.74 \times 10^{-5} / \Omega$ and $S_0 = 7.25 \text{ eV} \times 10^{-6} \text{ V/K}$ at 300K.⁸

From our thermopower measurements, we conclude that transmission through TDO1 and TDO4 is dominated by HOMO and LUMO respectively, and assume that the transmission can be approximated by the Lorentzian function described above. (TDO2 and TDO3 have significant contributions from both orbitals, and therefore their transmission cannot be approximated by a single Lorentzian.) Using the above equations, we determine ΔE and Γ for TDO1 and TDO4 (Table S2).

	ΔE(eV)	Γ(eV)
TDO1	-2.0	0.13
TDO4	0.7	0.01

Table S2. ΔE and Γ for TDO1 and TDO4 as determined from conductance and Seebeck measurements, assuming a single-Lorentzian as representative of transmission.

I-V Measurements & Analysis

In order to test whether our ΔE and Γ values are reasonable, we perform I-V measurements on TDO1 and TDO4 in 1,2,4-trichlorobenzene. The measurement procedure has been described before.⁹ Briefly, after contact, the Au tip is retracted from the substrate for 150 ms, before being held at constant displacement for another 150 ms. During this hold, a saw-tooth voltage ramp is applied, ranging from -1 to +1V. After, the tip is retracted further in order to rupture the molecular junction.

We only consider traces which have a molecular feature present during the entirety of the voltage ramp. We select out approximately 1,400 such I-V traces for TDO1, and 3600 traces for TDO4. These are then compiled into logarithmically binned two dimensional current-voltage (2D IV) plots as shown in Figure S7a,b. In order to determine an average I-V curve for the two molecules, we fit each vertical line slice of the 2D IV with a Gaussian, and plot the peak value. We then plot these I-V curves on a linear scale (colored curves) in Figure S7c,d. We qualitatively compare the measured average I-V curve with I-V curves that have been generated from our single-Lorentzian transmission functions by integrating the area under the transmission curve, assuming a symmetric bias window and T=0K. Visually comparing the measured IV curve with the IV curve

SUPPLEMENTARY INFORMATION

generated from our model Lorentzian transmission functions, we find excellent agreement between the two at low biases. The model IV curves underestimate the measured current at voltages greater than 0.5V, but at high biases there are multiple physical effects which cause deviations of the junction transmission from its low bias form. These effects include (a) a Stark shift that moves the resonances closer to E_F at high biases, (b) the polarizability of the molecular orbitals under bias, (c) bias induced changes in the junction geometry and (d) Coulomb blockade effects.

IV Curves



Figure S7. a. 2D current voltage plot for TDO1. b. 2D current voltage plot for TDO4. c. Average measured IV compared with single Lorenztian model IV for TDO1. d. Average measured IV compared with single Lorenztian model IV for TDO4.

Tight Binding Model

We seek to show that an exponential decay in conductance with molecular length can arise even when one orbital does not remain dominant across a molecular series. In order to demonstrate this, we use a tight binding model to determine a Hamiltonian matrix and then use a non-equilibrium Green's Function formalism in order to qualitatively model transmission through the molecular junctions.¹⁰ We use an n-site model in which each site is represented by two orbitals of energy $\varepsilon_{\rm H}$ and $\varepsilon_{\rm L}$ (an occupied and an unoccupied orbital). Nearest neighbors have occupied orbitals coupled by $\tau_{\rm H}$ and unoccupied orbitals coupled by $\tau_{\rm L}$ (Figure S8a). Terminal sites have their occupied and unoccupied orbitals each coupled to the leads by an imaginary, energy independent, self-energy term $-i\Gamma_{\rm H}/2$ (and $-i\Gamma_{\rm L}/2$). In order to compute molecular transmission functions, we turn to the nonequilibrium Green's Function formalism. The retarded Green's function for the molecular junction is defined as $G(E) = [EI-H]^{-1}$, and transmission is then given as T(E)= $Tr(\Gamma_L G\Gamma_R G)$, which is computed numerically. Here, $\Gamma_{\rm L}$ and $\Gamma_{\rm R}$ are coupling matrices coupling the molecule to the left and right leads, respectively.

Using the model, we calculate transmission functions for molecular junctions where N ranges 2 sites to 5 sites, and show representative transmission functions in Figure S8b. To calculate these transmission functions, we choose $\varepsilon_H = -2.5 \text{eV}$, $\varepsilon_L = 3 \text{eV}$, $\tau_H = -0.4 \text{eV}$, $\tau_L = -1.2 \text{eV}$, $\Gamma_H = -0.25 \text{eV}$, and $\Gamma_L = 0.1 \text{eV}$. We plot conductance versus T(E=E_F) versus number of sites in Figure S8c. The straight line relationship (on a log-scale) observed in Figure S8c demonstrates that an exponential decay in conductance is possible even with two contributing orbitals. We find that generally conductance decays exponentially with increasing length as long as the Fermi energy is not close to any resonance despite a

SUPPLEMENTARY INFORMATION

change in the dominant transport channel going from N=2 to N=5 in this model. However, we expect to see a deviation from this clear exponential dependence especially if either resonance gets closer to E_F .



Figure S8. a. Schematic of tight binding model showing the Fermi level in relation to each site's HOMO and LUMO and the coupling between them. b. Computed transmission functions using parameters described in text. c. Transmission vs site number, along with an exponential fit to the values.

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