



Oligo(ethylene glycol) and alkane: a look at charge transport

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figure 1: Top: BDT_TEG. Bottom: BDT_C10SH

Abstract

Differences between ethylene-glycol and alkyl chains are examined. Their charge transport properties and their molecular orbital energies were investigated using DFT computations. The orbitals show some overlap between oxygen p-orbitals, supporting the superexchange theory as explanation for higher charge transport in EG compared to alkyl. The charge transport calculation revealed a lack of interaction between EG and the gold electrodes, inhibiting charge transport compared to the alkyl which had a terminal thiol. However, a large peak in the transmission spectrum of EG aligns with the oxygen p-orbitals, providing more support for the superexchange theory.

Motivation

As the world demands more powerful, small-sized and energy-efficient devices, transistors have been made smaller and smaller still. So small, that conventional methods are starting to be limited by the effects of quantum tunnelling.¹ Much research is now done towards molecular electronics^{2,3}, even towards using tunnelling to our advantage in tunnelling field effect transistors.^{4,5}

In the field of molecular electronics, there is an interest in SAM based junctions. In the research group of Chiechi, SAMs based on oligo(ethylene glycol) (EG) are being investigated.² Baghbanzadeh et al. have already compared EG and alkanethiols and found that EG has a significantly higher charge transport through tunnelling compared to the alkane.⁶ They found that EG has a significantly lower attenuation factor β of the simplified Simmons equation compared to the alkane ($\beta = 0.24 \pm 0.01$ Å⁻¹ and $\beta = 0.77 \pm 0.03$ Å⁻¹ resp.) and is in fact on the same level as oligophenylenes ($\beta = 0.28 \pm 0.03$ Å⁻¹).

This attenuation factor is a simplified way of describing tunnelling resistance. Low resistance is desirable, as it enables larger currents to flow through a particular molecular wire. The much lower attenuation factor of EG compared to an alkane chain is particularly interesting, as the only difference between the two is the replacement of every third methylene ($-CH_2$ -) group with an oxygen. The latter has lone pairs available while the former has all its electrons coupled in bonding orbitals. Despite the lone pairs on oxygens in EG being separated, electrons can tunnel through EG with the same resistance as oligophenylenes, which features extensive pi-conjugation. Thus, EG makes a great candidate for a molecular wire.

Introduction

The current explanation for the high charge transport in EG is based on superexchange, of which a prominent example is manganese oxide, shown in figure 2.

Superexchange is brought forth by electrons that are close together and feel each other's spin. The MnO example shows that the 2 electrons on Mn are opposite spin, despite being separated by an oxygen. In the case of an EG chain, the lone pairs of oxygen would be used, each one feeling the previous lone pair, and influencing the next. This produces a bridge of interacting spins, that an electron on one electrode may interact with, spreading its wavefunction to the other electrode. This allows the electron to tunnel to the other side, even though none of the orbitals on the molecule in between are easily accessible.

The aim of this research then is to study the difference between EG chains and alkyl chains, in particular their charge transport and orbital properties to question superexchange as the current

explanation. To this end, molecules **6** (BDT_C10SH, alkyl) and **8** (BDT_TEG, TEG), consisting of a BDT core with on either side a phenyl, with an alkyl chain or TEG chain resp. in the para position, were studied using DFT methods.



figure 2: Manganese oxide as example for superexchange. The outer electrons are opposite spin, despite not interacting directly. Author: Melarn, taken from <u>https://en.wikipedia.org/wiki/Superexchange</u>,

For the calculations performed for this research, the AMS software suite, developed by SCM was used. ADF was used for the geometry optimizations and single point calculations, while BAND was used for the NEGF charge transport calculations.

ADF^{7,8} is a DFT program that uses Slater Type orbitals. It is useful for geometry optimizations and calculating a host of properties of the system, including orbital energies and spectra like IR, UV/Vis and H-NMR.⁹

BAND^{10,11} is a DFT program for periodic systems and employs atomic orbitals for this. A unique feature is the self-consistent approach to NEGF¹², in which the output of an NEGF calculation is compared to the input and then a new input is generated. This process continues until it converges, which sets BAND apart from other NEGF methods that are not self-consistent. However, the self-consistent approach does increase computational cost, and can be difficult to converge.¹³

Computing the transmission spectrum using BAND NEGF requires 4 steps. First, a tight binding representation is generated for the leads, which makes use of BAND's ability to deal with periodic systems as the leads are periodic in one dimension. Secondly, a program called SGF is used to calculate the Fermi energy of the tight-binding representation, which is used to reference the spectrum to. The third step is an optional alignment run, which corrects for a possible non-zero charge in the central region. The final part is the self-consistent NEGF calculation that calculates the spectrum.

Experimental

Despite the current COVID-19 measures making lab work not an option, a synthesis for the compounds was prepared. All chemicals may be obtained from Sigma-Aldrich. Column chromatography is to be executed with SiO_2 as the stationary phase. The synthetic pathways are included in the appendix.

Synthesis of BDT C10SH: This synthesis consists of 6 major steps, beginning with a Friedel-Crafts acylation¹⁴ between decanoyl chloride and bromobenzene to produce product **1**. It is then used as substrate in a Willgerodt-Kindler reaction¹⁵ using elemental sulfur, morpholine and a catalyst. This reaction will move the carbonyl in 1 to the end of the alkyl chain while converting it to thioamide **2**. The third step is a conversion of the thioamide to thioester **3**, using triisopropyl silane chloride (TIPSCl), DABCO and water. We propose to use TIPSCl instead of 4-nitrobenzyl bromide¹⁶, as this eliminates an additional step necessary to protect the sulfur with TIPS^{17,18}. The fourth step is a reduction of the carbonyl part of thioester 3 to yield thioether 4, which demands a mild and selective reaction¹⁹, as the sulfur is also susceptible to reduction. This is achieved with p-tosylhydrazide and sodium borohydride. In the fifth step, 2 molecules of 4 are connected to benzo[1,2-b:4,5-b']dithiophene-4,8-dione (BDT) in a Grignard reaction²⁰. 4 is converted to a Grignard reagent before reacting with the BDT. After elimination of the remaining hydroxide, the TIPS-protected BDT_C10SH 5 remains. The final step consists of deprotection using tetrabutyl ammonium fluoride (TBAF) followed by hydrolysis to yield thiol 6, BDT_C10SH. If a thioether is desired, which may be the case as the thiol is susceptible to oxidation²¹, then an allyl bromide may be used instead of water.

Synthesis of BDT_TEG: This synthesis consists of 2 major steps, the first of which is a Williamson ether synthesis, adapted from literature procedure²⁰. 4-bromophenol is coupled to (2-(2-(2-methoxy)ethoxy)ethoxy)p-toluenesulfonate (Ts-TEG) to produce 7. This is then used in the second step, which is the same as the fifth step in the BDT_C10SH synthesis, to yield product **8**.

As mentioned before, lab work could not be performed. Instead, computational methods were used to analyze the molecules and find differences in the chains.

The first step of the computational process is to optimize the geometry of the molecules. To do this, ADF was used with the B3LYP functional, as it is known to be an accurate functional for organic chemistry. The relatively small basis set of DZP²² was chosen to keep the calculations short. Since the 2 molecules are to be compared with each other, absolute error was less of a concern, so long as the comparison is accurate. No frozen core was used for these optimizations, as this is not advisable with hybrid functionals. BDT_TEG was optimized without issues, but BDT_C10SH did not optimize easily. The alkane chains started to curl up, but the molecule should look like a SAM in a molecular junction, and there the chain would have been straight²³. This was circumvented by restricting the dihedral angle of the C-C bonds in the alkane chain to 180°, which results in a straight chain. As a result, the optimization could not find a minimum, and the molecule continued moving the chains back and forth during the optimization until the calculation reached the time limit. It was decided to choose the lowest energy conformation that could be found in the geometry optimization steps, as the last geometry in this calculation was not necessarily the optimal structure.

To place the molecules in a gold junction, the geometry of BDT_C10SH was reoptimized with a gold atom attached to each of the terminal thiols. This allows for an accurate placement of the molecule in the junction. At this point, the switch from B3LYP to PBE functional was made, as BAND, required in the next step, cannot work with hybrid orbitals, and since the single point calculations from ADF were going to be compared to the results from the BAND NEGF calculation, changing the functional only for BAND would introduce another variable. PBE was chosen as a fairly popular functional. Additionally, ZORA relativistic effects^{24–26} were included for all calculations that include gold.

After lining the gold atoms, attached to the thiol, up with the X-axis and with the junction already lined up with the X-axis, the distance between the electrodes was adjusted such that the gold atom attached to sulfur overlapped with a gold atom of the electrode. One of the overlapping gold atoms was then deleted, leaving the molecule at the optimized distance to the gold surface.

Optimization of BDT_TEG in the presence of gold atoms was attempted but failed. On multiple attempts, the Self-Consistent Field (SCF) calculation required for every geometry step failed to converge, cancelling the process. The interactions between the terminal methoxy group and the surface of gold are primarily van der Waals interactions, in contrast to the covalent bond between gold and sulfur on the alkyl chain. Likely, this makes it difficult for the SCF calculation to find a minimum, taking many steps to converge to the required 10⁻⁶ absolute error, often crossing the default of 300 SCF cycles with an absolute error in the range of 10⁻¹ or 10⁻², at which point the software recognizes a failed optimization and cancels the calculation. BDT_TEG was instead optimized without gold atoms and subsequently placed into the junction by eye.

Notable about the second round of geometry optimizations is that the alkyl chain with gold and the TEG chain were first optimized with one phenyl group. This optimization did not need any restrictions. Then, the chain was attached on either side of a BDT unit to give the full molecule, and the geometry of the aromatic rings was optimized again while keeping the chains frozen. The resulting structure was checked to be similar to the geometry of the first optimization.

With both BDT_TEG and BDT_C10SH placed inside gold junctions, created with the BAND NEGF software from the 3x3 gold lead template included with the software, the charge transport could be calculated. An initial calculation was performed with SZ basis set, to observe the performance of the calculation. Then a calculation was attempted with DZP basis set. It was expected that this would take longer, and a 30-fold increase in the time required for a step of the alignment run was observed. Together with slower convergence on the alignment run, completing the calculation with DZP became unfeasible. It was also attempted to perform the calculation with SZ for gold atoms and DZP for the other atoms which was unsuccessful, due to lack of support from the program.

The geometry used for the charge transport calculation was then used in a single point calculation to obtain the orbital energies. This was done with the PBE functional and the DZP basis set.

Results

Based on previous research, it is expected to find the charge transport for TEG to be higher than that of the alkyl. The main contribution towards charge transport comes from the Fermi level. The data, visualized in figure 3, shows that at the Fermi level, the alkyl has higher transmission than the TEG. This contradiction of the expectation may be contributed to the placement of TEG in the junction, but more generally, to the lack of a thiol on the TEG chain to bind it to the surface. The lack of interaction with the surface makes it difficult for electrons to tunnel, and as the alkyl does have this thiol group with strong interaction, it achieves higher transmission at the Fermi level.

Another explanation for the unexpected result is that BAND does not take the orbitals on oxygen and the superexchange effect into account.

However, TEG has high peaks around -6.0 eV, indicating that electron tunnelling is much easier at that level. To see if this has any correlation with the orbitals of oxygen on the TEG chain, the transmission graph from the BAND NEGF calculation was combined with a graph of the orbital energies, shown in figure 4 and figure 5. The height of the orbital peaks is irrelevant, they are only used to show at which energy an orbital exists.

Keeping in mind that the single point calculations, which produced the orbital energies, did not include the gold junction of the charge transport calculation, and that this may cause orbital energies to shift a little, there is a correlation between the transmission graphs and the orbital energies. Certain orbitals appear at the same or similar energies as main features in the charge transport graphs. For both compounds, the HOMO aligns very well, and the LUMO's orbital energy is a little higher than in the transmission spectrum. For the TEG compound, the high peaks around -6.0 eV appear slightly shifted to the right, away from a set of orbitals. These orbitals were examined and some are shown as figure 6.



figure 3: Computed transmission spectrum. The dashed grey line shows the Fermi energy of -4.642 eV, as calculated by the SGF step



figure 4: Transmission spectrum and the orbital energies of TEG.



figure 5: Transmission spectrum and the orbital energies of the alkyl.

Besides the electron tunnelling behaviour of the molecules, their orbitals were investigated. The orbitals were calculated with ADF using a single point calculation with PBE and DZP, with the structures taken out of the junction. The HOMO and LUMO of both molecules are located on the aromatic structure in the middle of the molecules and show pi-conjugation. As the interest is on the chains, the deeper-lying occupied orbitals were looked at. On the TEG chain, a set of orbitals primarily localized on the oxygen in the chain were found (figure 6). Each has 1 oxygen p-orbital providing the largest contribution, with a secondary contribution from a neighbouring oxygen. This suggests that the oxygen lone pair electrons do have some interaction with each other. Since the electrons spend time in the same location, they may feel each other's spin, which can lead to superexchange throughout the molecule.



figure 6: From top to bottom: BDT_TEG HOMO-4, HOMO-6 and HOMO-9, at -6.092, -6.297 and -6.520 eV resp. There are degenerate mirror images on the other chain.

The deeper lying orbitals of BDT_C10SH were also investigated.

On the alkyl chain, orbitals were found resembling those found on TEG. The main difference is the orbital energy level. On the alkyl chain, the orbitals are located between 1.4 and 1.9 eV lower than on TEG. This is significantly further down in energy. Thus, it seems that the O is increasing the orbital energy of such orbitals and that DFT takes this effect into account. As high energy valence electrons in atoms are typically important in chemistry, and low energy electrons are typically ignored, perhaps the same can be said of molecules, and the higher TEG orbitals would have a larger contribution to charge transport. Furthermore, the difference between the orbitals on the TEG and alkyl chains suggests that the software recognizes the difference that the oxygen provides compared to methylene. This supports the idea that the terminal thiol lacking from the TEG chain was the cause for the lower transmission at the Fermi level.



figure 7: From top to bottom: BDT_C10SH HOMO-13 and HOMO-15, at -7.943 and -7.994 eV resp. There are degenerate mirror images.

Conclusion

The oxygen in oligo(ethylene glycol) has a large impact on the properties of the molecule compared to an alkyl chain. The orbitals of the lone pairs have some overlap, which allows for the spin interactions that lie at the basis of superexchange, which would explain the high rate of charge transport found in the literature. Notably, those orbitals are at significantly higher energy compared to similar orbitals on alkyl chains.

The charge transport calculation showed unexpected results, with the transmission of BDT_TEG orders of magnitude lower than BDT_C10SH at the Fermi level. This can be attributed to the lack of a thiol at the end of the TEG chain, which introduces a tunnelling barrier that the alkyl chain does not have. However, at -6 eV, TEG outperforms alkyl, and this is around the energy of the oxygen lone pairs. While this supports the theory of superexchange, it does not prove it.

For future research, the TEG chain could be modified to have a thiol as the terminal group. This would address the unexpected result from the charge transport calculation. Higher accuracy charge transport calculations may be attempted, by changing to a different functional and by increasing the basis set. Lastly, the research done here would have been greatly enhanced by the availability of laboratory experiments. As an example, X-ray or other techniques may be used to reveal the structure of BDT_TEG and BDT_C10SH bound to the gold surface in the junction. This can then be used as the structure of the molecules in the junction and obtain more accurate charge transport calculation results.

The findings of this research support EG as an interesting group of molecules, particularly useful as a wire in molecule-sized devices. The properties of EG are well worth researching to benefit the field of molecular electronics, and eventually, consumer electronics.

Experimental

1-(4-bromophenyl)decan-1-one (1)

Decanoyl chloride (1 equiv.) is to be added to bromobenzene (2 equiv.) and aluminium chloride (1.2 equiv.), followed by stirring at 50 °C for 1.5h, cooling to room temperature and pouring into ice-water. Then follows an extraction with dichloromethane, washing of the organic layer with 2M HCl and brine, and drying with MgSO₄. After evaporation of the solvent, product **1** may be used without further purification.¹⁴

10-(4-bromophenyl)-1-morpholinodecane-1-thione (2)

Compound **1** (1 equiv.) is to be mixed with sulfur (1.2 equiv.), morpholine (1 equiv.) and the catalyst HBF_4 -SiO₂ (0.05 equiv.), which should be prepared from literature procedure.¹⁵ After stirring at 80 °C for several hours, with completion indicated by TLC, the mixture should be diluted with ethanol and the filtrate washed with ethanol. The resulting organic layer should be concentrated under vacuum followed by recrystallization from ethanol.

S-(triisoporpylsilyl) 10-4-bromopheyl)decanethiolate (**3**)

After stirring **2** (1 equiv.) with the TIPSCl (1 equiv.) at 110 °C for 75 min without solvent, DABCO (0.05 equiv.) in water (13 equiv.) is to be added, followed by heating for 15 min. After cooling to room temperature and allowing the oily residue to solidify, the solid is to be filtered, washed with water and recrystallized from methanol.

((10-(4-bromophenyl)decyl)thio)triisopropylsilane (4)

Thioester **3** (1 equiv.) and *p*-tosylhydrazide (1.4 equiv.) are to be dissolved in methanol and refluxed for 3 hours before cooling to room temperature. The addition of sodium borohydride (22 equiv.) to the mixture in small portions over one hour follows, then reflux for 8 hours, cooling to room temperature and solvent removal under reduced pressure. The residue is to be dissolved in diethyl ether, washed in succession with water, dilute aqueous sodium carbonate, 2 M hydrochloric acid and water again, before the organic phase is dried over MgSO₄ and evaporated under reduced pressure. The residue is to be purified with column chromatography using 7/3 (v/v) cyclohexane/ethyl acetate, and after evaporation of the solvent under reduced pressure, may be recrystallized from aqueous methanol.

4,8-bis(4-(10-((triisopropylsilyl)thio)decyl)phenyl)benzo[1,2-b:4,5-b']dithiophene (5)

Compound **4** (3 equiv.) is to be added dropwise to magnesium turnings (3.6 equiv.) in anhydrous THF under protected atmosphere and vigorous stirring, with I₂ (0.4 mol%) as catalyst. After reflux for 5 h, the magnesium should be consumed, and the mixture may be refluxed for another hour before cooling down and slowly adding to benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (1 equiv.) in THF. SnCl₂·2H₂O (6.4 equiv.) dissolved in 10% aqueous HCl (5.8 equiv. HCl) is to be added dropwise, followed by stirring for 1 h at 50 °C and cooling to room temperature. Workup should consist of pouring the mixture into water, extracting with DCM, washing the organic layer with water and sodium bicarbonate solution twice, drying the organic phase with MgSO₄ and evaporation. Purification consists of column chromatography using pure hexane.²⁰

4,8-bis(4-(10-thiodecyl)phenyl)benzo[1,2-*b*:4,5-*b*']dithiophene (6)

TBAF is to be added to **5** in THF and stirred for 1 h at room temperature. To yield thiol **6**, the thiolate intermediate should be hydrolyzed. If a thioether is desired, which may be the case as the thiol is susceptible to oxidation²¹, then an allyl bromide may be used instead of water, followed by column chromatography using hexane to separate the TIPSF resulting from deprotection.

1-bromo-4-(2-(2-(2-methoxy)ethoxy)ethoxy)benzene (7)

4-bromophenol (1 equiv.) and K_2CO_3 (1.2 equiv.) are to be dissolved in DMF under protected atmosphere, followed by dropwise addition of (2-(2-(2-methoxyethoxy)ethoxy)ptoluenesulfonate (Ts-TEG) (1 equiv.). The mixture should be left overnight in the dark at 150 °C, before cooling to room temperature, adding to water and extracting three times with chloroform. Washing of the organic phase should occur with saturated KOH solution and water, twice each, followed by drying over MgSO₄ and evaporation of the solvent under vacuum. Purification should be performed by column chromatography using petroleum ether as eluent.

4,8-bis(4-(2-(2-(2-methoxy)ethoxy)ethoxy)phenyl)benzo[1,2-*b*:4,5-*b*']dithiophene (8)

This step is the same as the synthesis of **5**.

Appendix



figure 8: BDT_TEG, HOMO, -4.988 eV



figure 9: BDT_TEG, LUMO, -2.367 eV



figure 10: BDT_C10SH, HOMO, -5.156 eV



figure 11: BDT_C10SH, LUMO, -2.400 eV



figure 12: Synthesis of BDT_C10SH, step 1 and 2



figure 13: Synthesis of BDT_C10SH, step 3 and 4



figure 14: Synthesis of BDT_C10SH, step 5 and 6



figure 15: Synthesis of BDT_TEG, steps 1 and 2

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