Environmental gating of conductance and temperature dependence in oligothiophene single molecule junctions

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Environmental gating of conductance and temperature dependence in oligothiophene single molecule junctions

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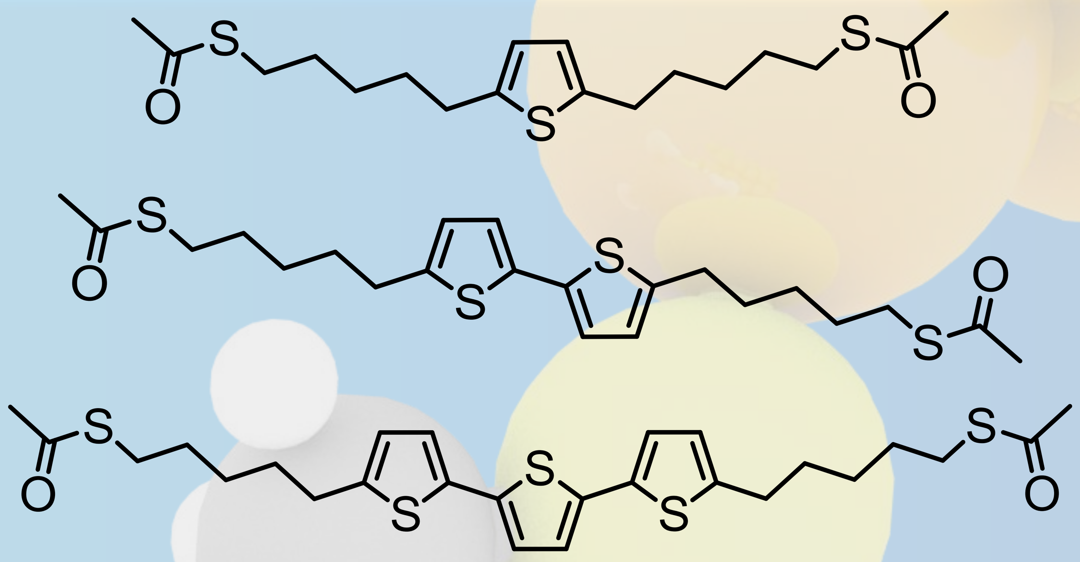
Introduction

In the last decade, many techniques [1-3] have been developed to fabricate and characterise **metal|molecule|metal** junctions. Although an isolated molecule within a junction must be affected by supramolecular interactions, this has provoked few detailed studies. We synthesised a series of **oligothiophene** molecular wires and measured their conductance as a function of temperature in different environments (air, dry argon and UHV), and found a remarkably different behaviour. The effect of ambient moisture on the conductance of oligothiophene molecular wires is known in the literature [4], and this study sheds some more light on the **mechanism of charge transport** through such systems.



5[T]5

5[2T]5

5[3T]5

Experimental

AIR – CONDUCTANCE INCREASES WITH LENGTH
UHV – CONDUCTANCE DECREASES WITH LENGTH

Molecular conductance has been determined using the non-contact *I(z)* technique [3], involving the repeated formation of molecular junctions within an STM.

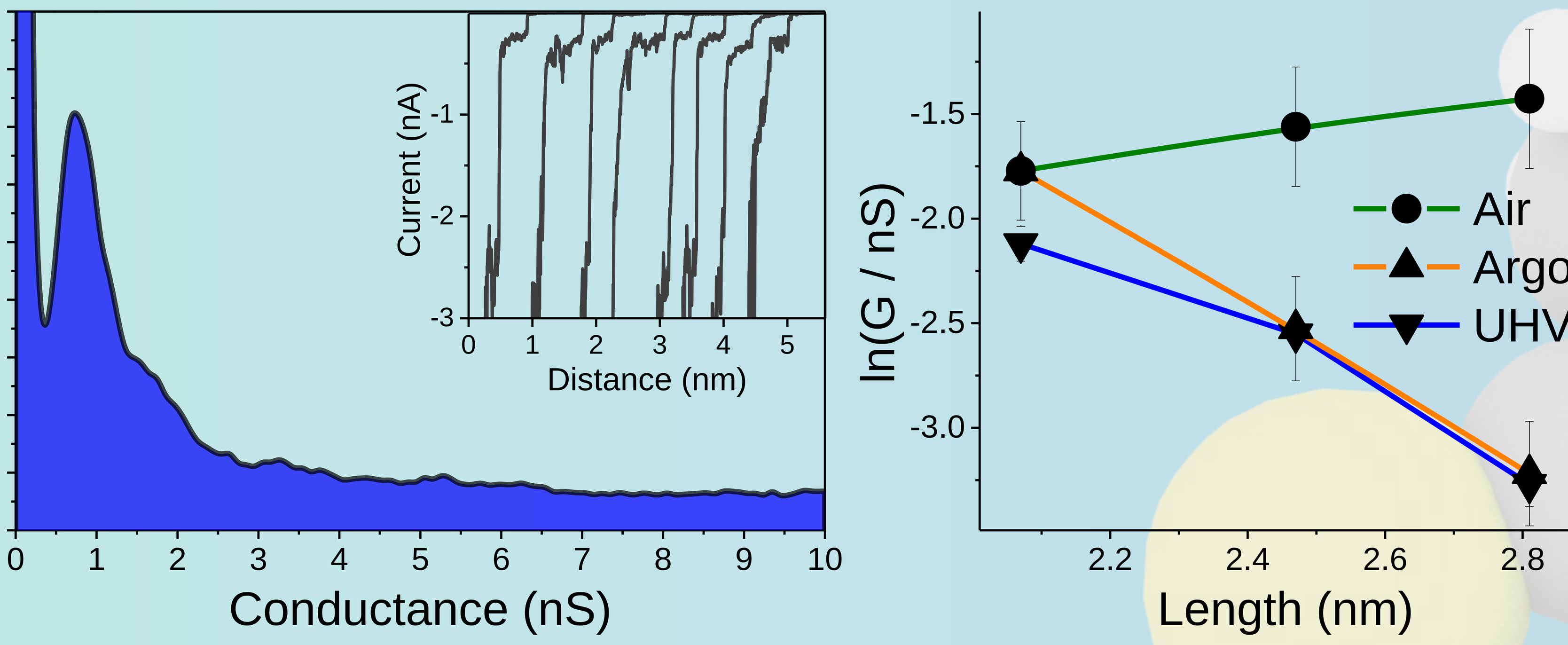


Figure 1: Left): Example of conductance histogram (5[T3]5 in air) and traces (inset). 500 such traces have been used in histogram. Right: Logarithmic plot of conductance in the three environments.

AIR – THERMALLY ACTIVATED CONDUCTANCE
UHV – ACTIVATIONLESS CONDUCTANCE

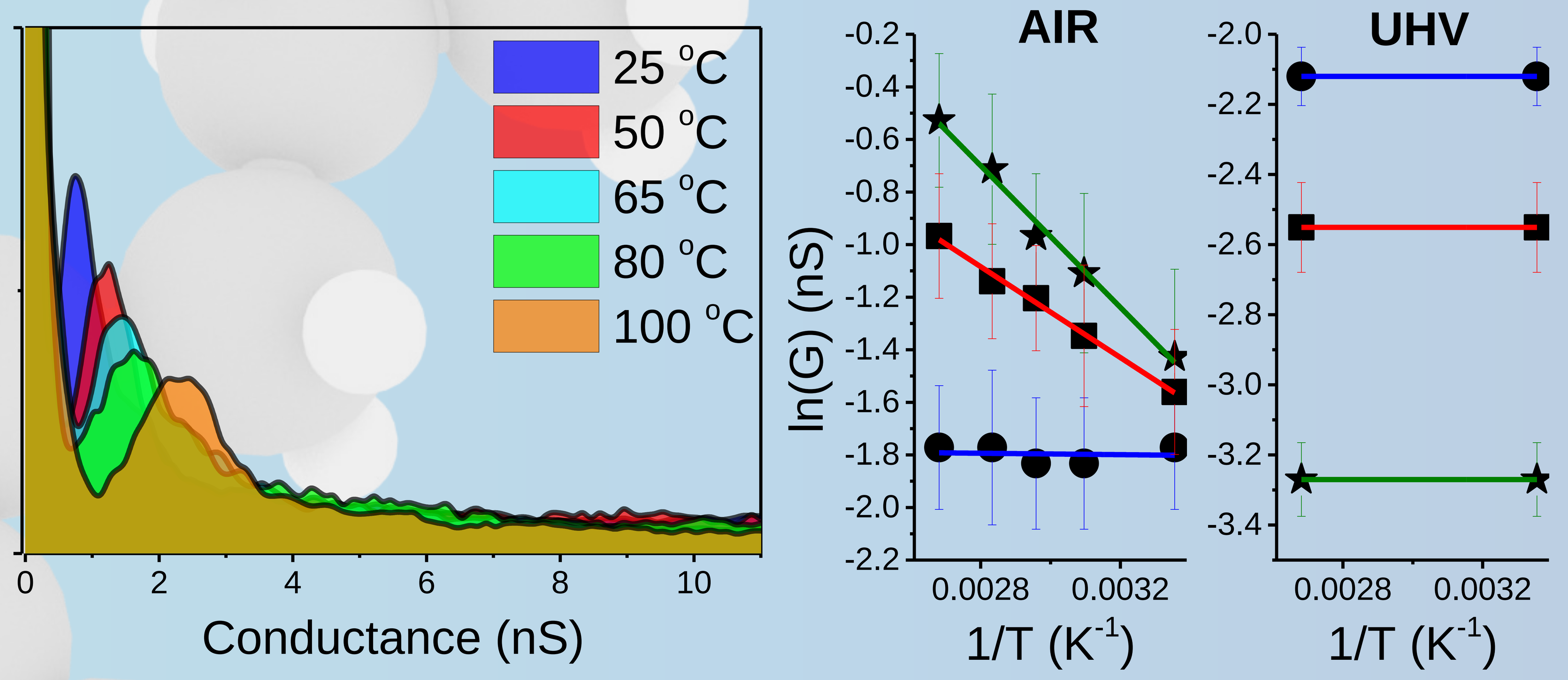


Figure 2: Left: Conductance histograms for 5[T3]5 in air over a range of temperatures. 300-600 current-distance scans have been used to construct each histogram. Right: Arrhenius plot for the three oligomers employed in this study in air and UHV. Activation energies in air are 0.13 eV for 5[T3]5 (green) and 0.08 eV for 5[T2]5 (red). 5[T]5 (blue) showed an activationless mechanism in both environments.

While a temperature dependent conductance is generally taken as sign of **incoherent hopping** charge transport, it has been previously demonstrated that thermal broadening of transport resonances can explain such behaviour within a **coherent tunnelling** mechanism [5].

Calculations

NEGF and DFT calculations have been used to understand the observed behaviour: in air, the presence of **ambient moisture** shifts LUMO resonance towards the Fermi level.

As the number of thiophene rings increase, the resonances are moved further, resulting in an **increasing** boost in conductance along the oligothiophene series.

The observed temperature dependence can be explained *via* **thermal broadening** of transport resonances. In vacuum the resonances are far from the Fermi level of the electrodes and there is no thermal activation. In air, **5[T2]5** and **5[T3]5** have resonances shifted close enough to the Fermi level for their thermal broadening to promote a temperature dependent conductance.

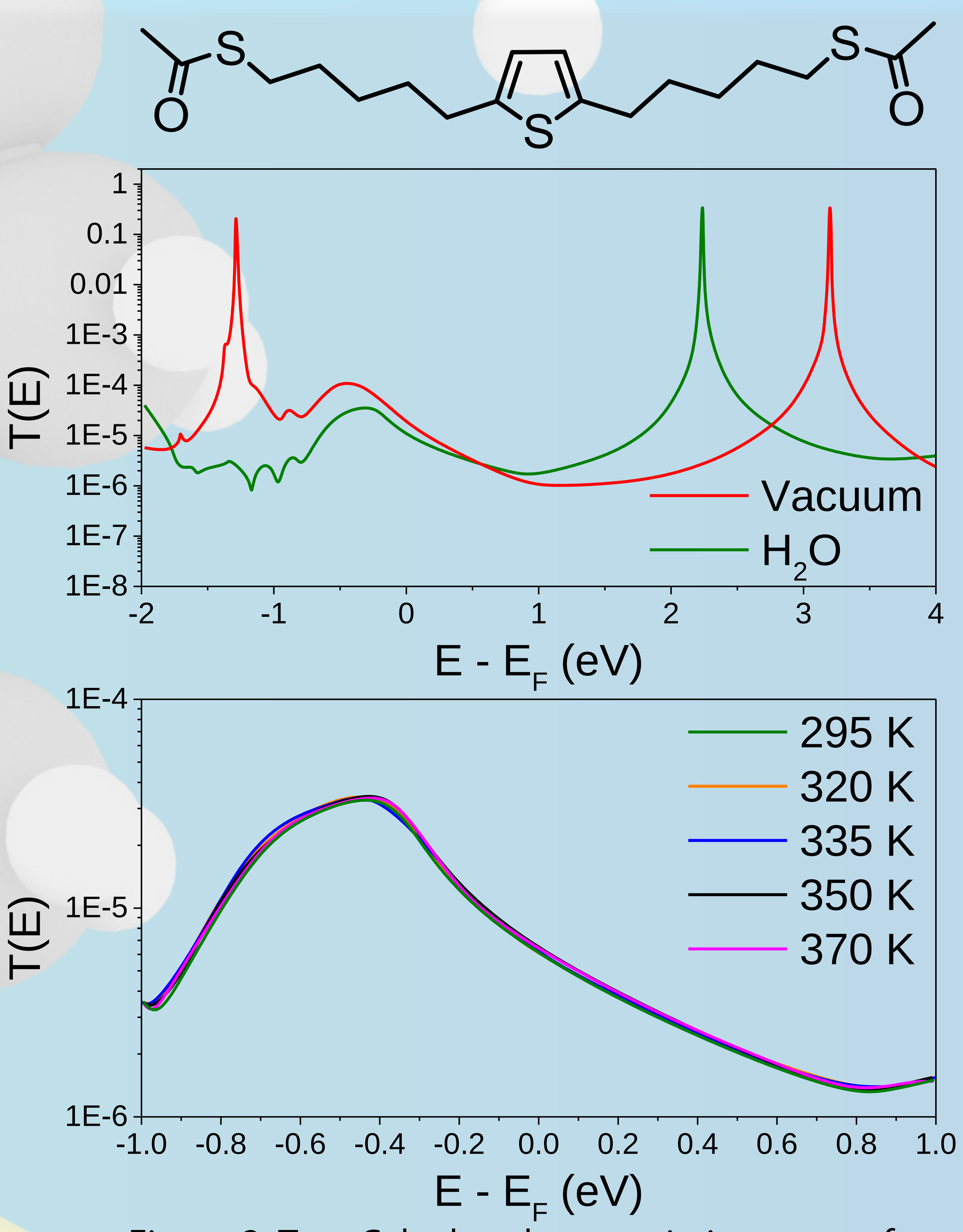


Figure 3: Top: Calculated transmission curves for 5[T]5 in vacuum and in the presence of water. Bottom: Close-up of calculated transmission curves at different temperatures near the Fermi level of the electrodes.

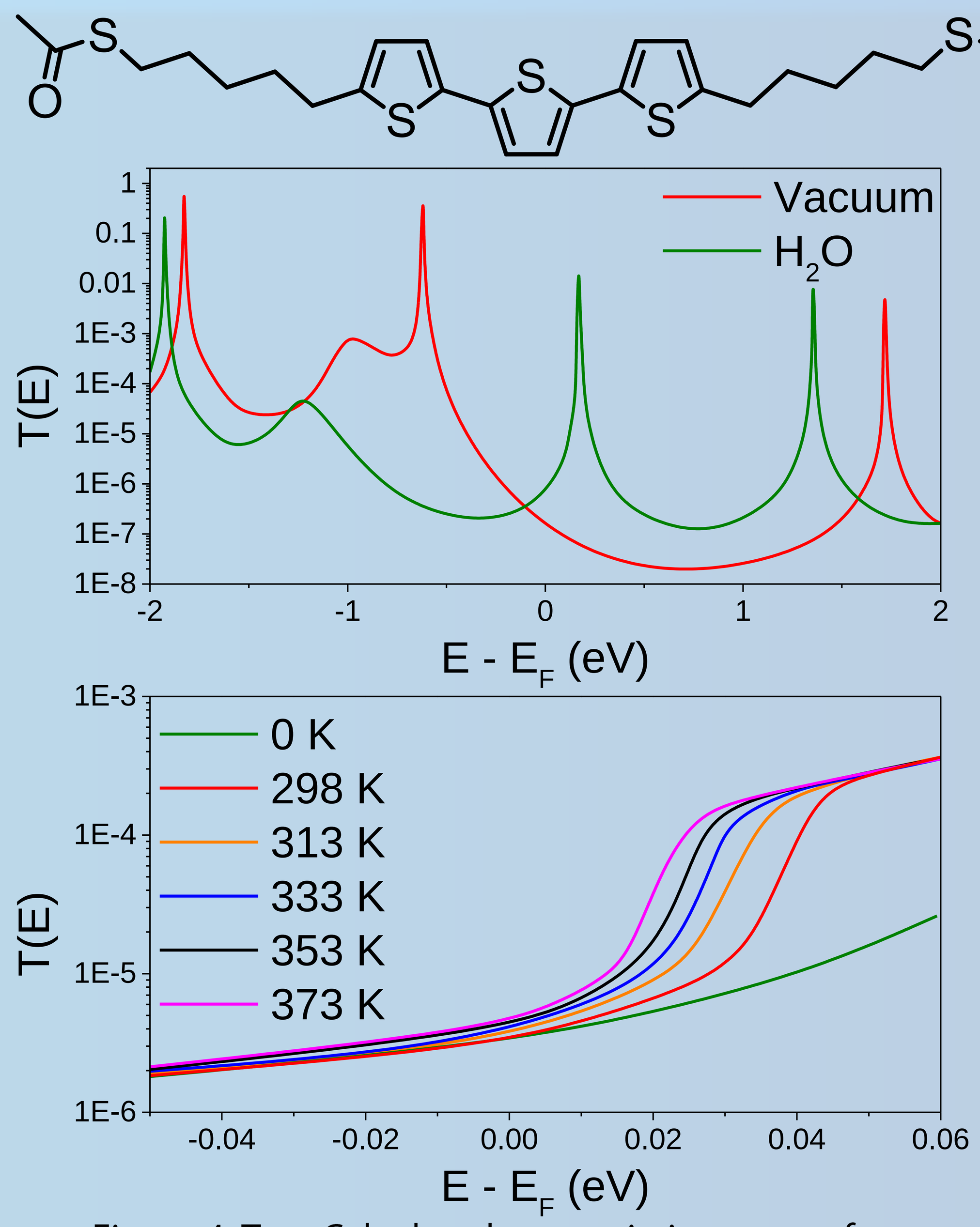


Figure 4: Top: Calculated transmission curves for 5[T]5 in vacuum and in the presence of water. Bottom: Close-up of calculated transmission curves at different temperatures near the Fermi level of the electrodes.

Conclusions

We synthesised and measured the conductance of a series of thiol-capped α-ω dialkyl **oligothiophenes** in different environments and over a range of temperatures. We found that the longer oligomers have **increased conductance** and **thermal activation** upon coordination with water (as ambient moisture). NEGF and DFT calculations explained this behaviour within a coherent tunnelling theory: water coordination shifts transport resonances closer to the Fermi level of the electrodes, and the temperature dependence of conductance can be ascribed to their thermal broadening.

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