First Principle Simulations of Current Flow in Inorganic Molecules: Polyoxometalates (POMs)

Paven Thomas Mathew[1], Fengzhou Fang[1], Laia Vila Nadal[2], Lee Cronin[2], Vihar Georgiev[3]
[1]Center of Micro/Nano Manufacturing Technology, University College Dublin, Dublin D04V1W8, Ireland
[2]WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK
[3]Device Modeling Group, University of Glasgow, Glasgow G128LT, UK
paven.mathew@ucdconnect.ie & vihar.georgiev@glasgow.ac.uk

***Abstract*— In this work we present a simulation study of current flow in inorganic molecular metal oxide clusters known as *polyoxometalates* (POMs). The simulations are carried out by using combination of the density functional theory (DFT) and non-equilibrium Green's function (NEGF) methods. To investigate the current flow in POMs, we investigate two possible ways to place the POM cluster between two gold (Au) electrodes – vertical and horizontal. Our results show that the position of the POM molecule and the contact between the molecule and the Au electrodes determines the current flow. Overall, the vertical configuration of the molecule between the two Au electrodes shows better current flow in comparison to the horizontal configuration. In this work we also establish a link between the underlying electronic structure and transmission spectra and conductance.**

Keywords: Polyoxometalates (POMs); Non-Equilibrium Green's Function (NEGF); Density Functional Theory (DFT); molecular electronics; simulations

I. Introduction

In recent years interest in electronic, magnetic and optical structures and devices based on inorganic, organic, hybrid and nano-materials has increased significantly. Polyoxometalates (POMs) are molecules that contain metal and oxygen atoms. They are highly ordered clusters and they exist as several structures [1]. Among them, the most notable structures are the Keggin anion ($[XM_{12}O_{40}]^{q-}$) and the Wells-Dawson anion ($[X_2M_{18}O_{62}]^{q-}$) that can be defined as 'electron sponges'. These molecular clusters could be used to develop new types of data storage devices [2] and various other applications [3]. For detailed information on polyoxometalates, we suggest readers consult some of the recent reviews [4],[5].

In our recent work we showed that the use of inorganic molecules known as polyoxometalates (POMs) could form a storage media in flash memory cells [6],[7]. This could offer several important advantages over the conventional polysilicon floating gate (FG) flash cells. In order to take our research further, in this paper, we explore correlation between the current flow and the position of POMs when they are placed between two electrodes.

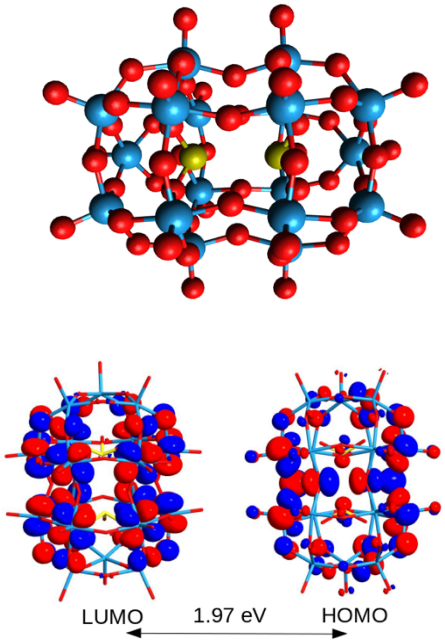

Figure 1. Top: Balls and stick structure of the Wells-Dawson clusters polyoxometalate $[W_{18}O_{54}(SO_3)_2]^{4-}$. Blue represents tungsten; red represents oxygen and yellow represents sulfur. Bottom: The LUMO and HOMO levels for the $[W_{18}O_{54}(SeO_3)_2]^{4-}$ POM cluster and energy difference between them.

Here, we study the influence of molecular contact over the electronic transport through the junction. The selected molecule is the Wells-Dawson type of POM that is shown in Fig. 1. It can be synthesised from elementary metal oxide (MO_x) molecules by self-assembly to form an elliptical shell of about 1.2 nm in length (here, M is tungsten (W) and X is 4). The shell has a cavity that can accommodate two anions in an intermediate oxidation

This work was supported in part by ESPRC (Molecular-Metal-Oxide-nanoelectronicS (M-MOS): Achieving the Molecular Limit under ref. EP/H024107/1. The work of Paven Thomas Mathew and Fengzhou Fang was supported in part by the Science Foundation Ireland (SFI) under Grant 15/RP/B3208 and in part by the National Natural Science Foundation of China under Grants 51320105009 and 61635008.

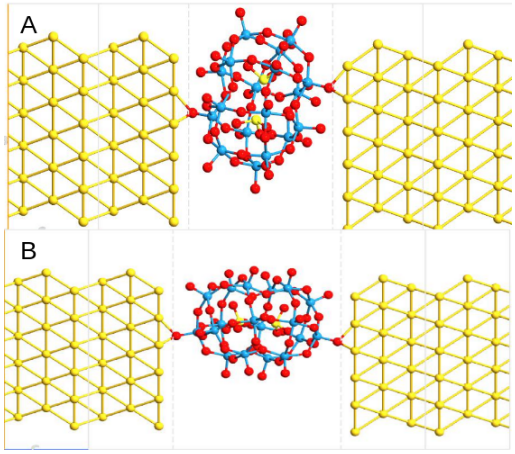

Figure 3. a) The vertical configuration and b) The horizontal configuration of the POM between two Au [111] electrodes.

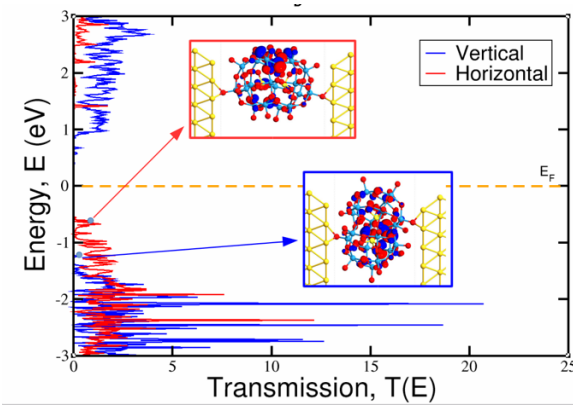

Figure 2. The transmission analysis for vertical and horizontal configurations at zero drain voltage.

state, here $[S^{IV}O_3]^{2-}$, making them highly redox active [8]. Redox-active molecules can store a multiple number of electrons making them very attractive candidates for a novel class of molecular devices for low-power, high-density and high-reliability non-volatile memory applications [6].

II. Simulation Mehtodology and Design

Density functional theory (DFT) is by far the most widely used simulation method for simulating the structural, electronic and magnetic properties of a molecule. In our work all calculations are carried out using the DFT and non-equilibrium Green's function (NEGF) methods implemented in the Synopsys QuantumWise ATK software [9]. The exchange-correlation functionals of Becke and Perdew are used with a generalised gradient approximation (GGA). Single-ζ polarisation basis sets are used to explain the valence electrons of W, O and S. The POMs molecular cluster is geometrically optimised using the same functionals and basis set as mentioned above.

To be able to calculate the current flow through the POM, the molecule is placed between two bulk gold electrodes on either end of the molecule. The gold leads are cleaved in the [111] surface (Fig. 2). The distance between the terminal gold surface and the POM molecule is 1.8 Å and the Au-Au bond length is 2.9 Å.

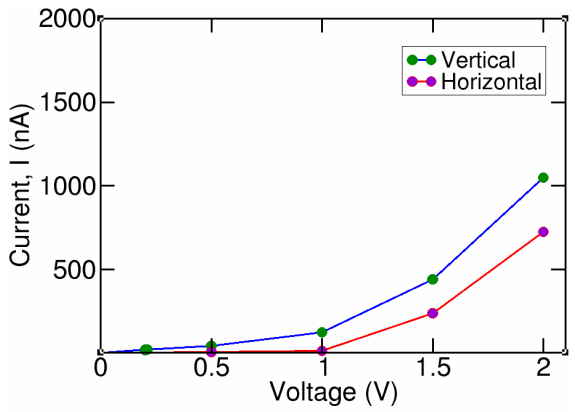

Figure 4. The current-voltage (I-V) characteristics for the vertical and horizontal POM configurations at zero drain bias.

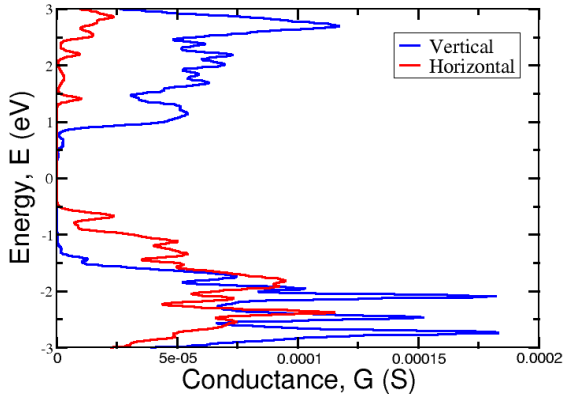

Figure 5: The conductance analysis for the vertical and horizontal POM configurations at zero drain bias.

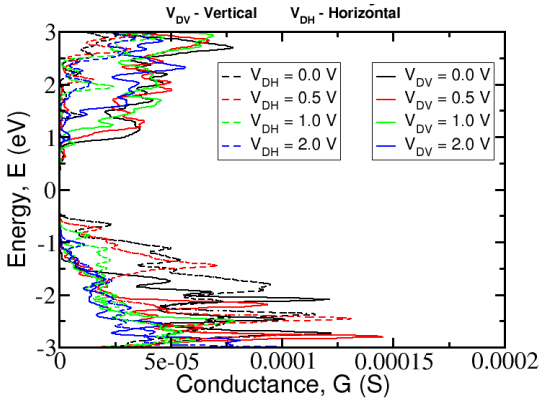

Figure 6: The conductance analysis for the vertical and horizontal POM configurations for different drain voltages.

III. Results and Discussions

Bottom part of Fig. 1 shows the HOMO and the LUMO electronic levels based on the DFT simulations of the insolated molecule. From the symmetry of the levels it is clear that molecular orbitals are delocalised along the outer shell of the molecule. Moreover, the HOMO and LUMO orbitals are constructed from the d-type atomic orbitals that come from the W atoms. Also, the HOMO-

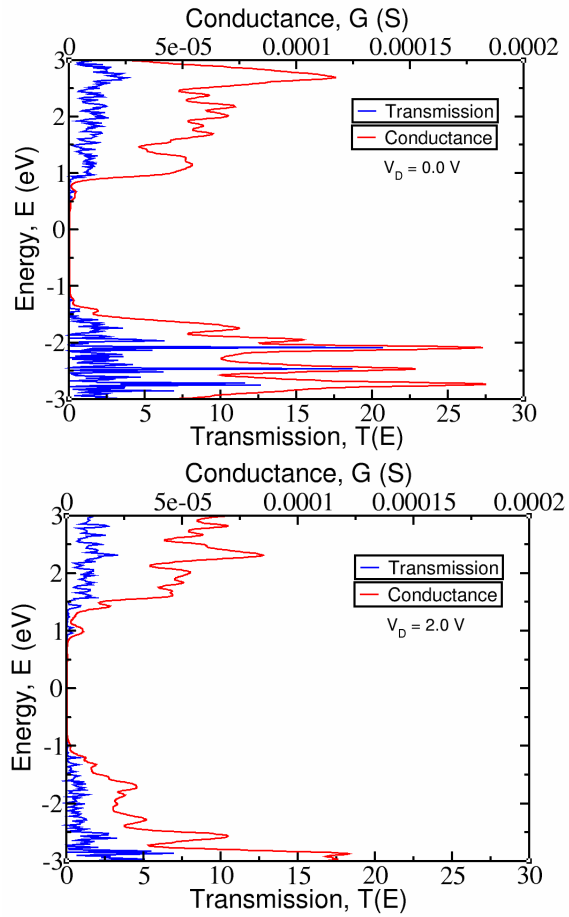

Figure 7. The transmission and conductance peaks of the vertical POM configuration for different drain voltages.

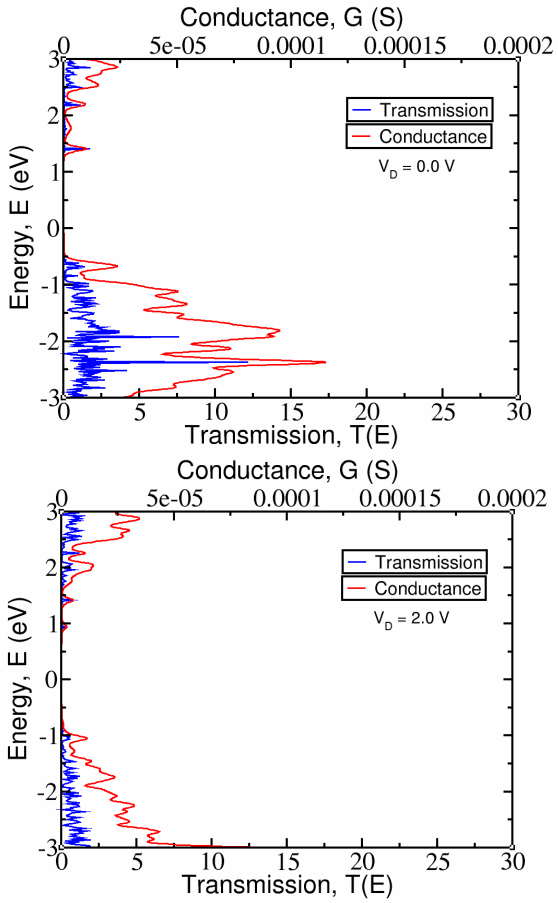

Figure 8. The transmission and conductance peaks of the horizontal POM configuration for different drain voltages.

LUMO gap, which can be considered a band gap, is 1.97 eV and this is in agreement with the previously reported simulations based again on DFT but using the ADF simulation software [2].

In this work we investigate two possible configurations of the molecule to be connected to the metal electrodes. Fig. 2 shows the two possible geometrical configurations that are considered in this work – vertical and horizontal. The POM molecule is incorporated between two 6 x 6 layers of gold electrodes, both in their vertical and horizontal configurations as shown in Fig. 2.

Based on the DFT and NEGF simulations described in the previous section it is possible to obtain a transmission spectrum that provides information about electronic transport across the molecular junction. Fig. 3 presents transmission spectra of both configurations (horizontal and vertical) at zero drain bias. Fig. 3 also shows the molecular orbitals that correspond to the first peaks below the Fermi Level. Those are the HOMO levels for each configuration. From Fig. 3 it is clear that the transmission spectra for both configurations are very different and the vertical system has more and higher transmission peaks in comparison to the horizontal one. Also, the molecular orbitals (HOMO) have slightly different and distorted symmetry in comparison to the HOMO and LUMO levels for the insolated molecule. These are presented in Fig. 2. For example, the HOMO levels are significantly less delocalised in comparison to the HOMO in Fig. 2 and the main electron density is concentrated in the middle W atoms. There is also absence of electron density at the oxygen atoms which connect the molecule to the Au leads.

In our simulations, the transmission spectra are directly proportional to the current in our DFT-NEFG simulation formalism. The current flow through the molecule is calculated by using the Landauer-Buttiker formula

$$\mathrm{I\ (V)} = \frac{e}{h} \int T\ (E,V)[f(E-\mu_L) - f(E-\mu_R)]\, dE$$

where e is the charge of electron, h is the Plank's constant, T(E,V) is the transmission and $f\left(E-\mu_{L\ (R)}\right)$ is the Fermi-Dirac function for the left and right electrodes with the chemical potential $\mu_{L(R)}$. Hence, the current is directly proportional to the transmission (T), where higher transmission means higher current.

Fig. 4 shows the current-voltage characteristics for both POM configurations. The current for the vertical configuration is higher than the horizontal one and this is

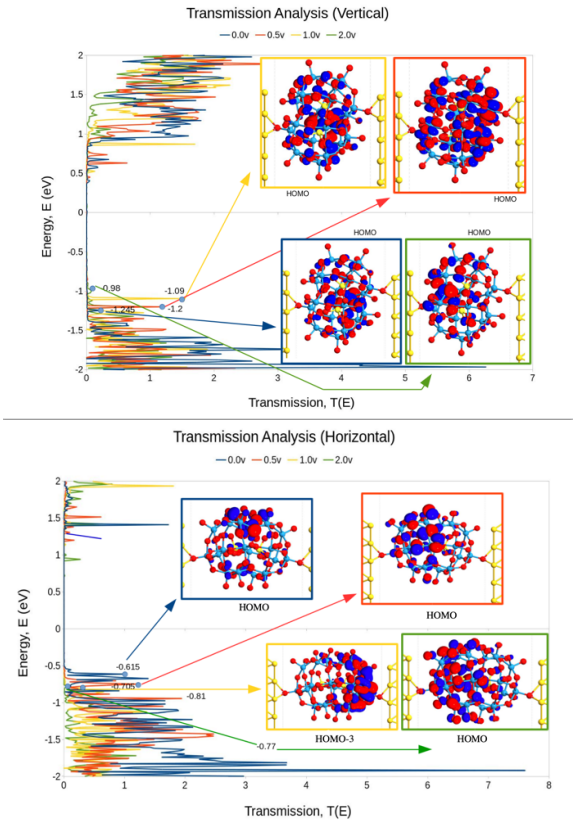

Figure 9. Top: Transmission curves for a vertical POM configuration at 4 different drain biases. Bottom: Transmission curves for a horizontal POM configuration at 4 different drain biases.

due to the fact that the current is directly proportional to the area under the peaks in the transmission spectra. The vertical system has more and higher peaks, which leads to a higher area under the curve, in comparison to the horizontal system. Another property which can be obtained from our simulation is the conductance. Fig. 5 reveals that the conductance for the vertical device is higher in comparison to the data for the horizontal device. This is consistent with the results for the I-V curves presented in Fig. 4.

Fig. 6 shows the conductance for both types of configurations at four different drain biases. From Fig. 6 it can be pointed out that the conductance for both devices is different. Below the Fermi levels, which is a position at 0 eV, the conductance for the horizontal configuration is higher in comparison to the vertical set-up. However, for energies above the 0.0 eV the vertical set-up has higher configuration in comparison to the horizontal device.

Fig. 7 and Fig. 8 show the transmission and the conductance at two drain biases for the vertical and horizontal configurations, correspondingly. From both figures it can be concluded that overall the conductance and the transmission for the vertical configuration are higher in comparison to the horizontal system. Also, the peaks for the transmission and the conductance show a very similar profile, where the peaks at the transmission are at the same energies with the peaks at the conductance. Hence, higher transmission means higher conductance and, hence, higher current at this energy level.

Fig. 9 shows the transmission spectra and the molecular orbital, where peaks are linked to the symmetry of the molecular orbitals. From the figure it can be concluded that each peak corresponds to a different type of delocalised molecular orbital. For example, HOMO is mainly localised in the middle belt created by the W atoms but HOMO-3 is mainly localised at the drain site. Indeed, the difference in the symmetry provides different transmission and conductance values and the peak height.

IV. Conclusions

In concussion, in this work we provide a detailed study of the electronic transport in POM molecules. In order to evaluate the current flow in such inorganic molecules, the POM cluster is placed between two Au electrodes. We assume two possible positions of establishing a contact between the POM and the Au electrodes – vertical and horizontal. It has been shown that the position of the POM molecule and the contact with the electrodes determine the current flow through the junction. We have also shown that the transmission peaks, current-voltage characteristics and the conductance peaks are higher for the vertical configuration, which shows that the vertical configuration is a better current conductor in comparison to the horizontal system. Moreover, in this work we have established a link between the current transport, conductance, transmission and the underlying electronic structure of the molecule. Our work can contribute to better understanding of the current flow not only in inorganic molecules but also in the field of molecular electronics in general.

V. References

[1] M. Hutin, M. H. Rosnes, D.-L. Long, and L. Cronin, “Polyoxometalates: Synthesis and Structure – From Building Blocks to Emergent Materials,” in *Comprehensive Inorganic Chemistry II*, vol. 2, Oxford: Elsevier, 2013, pp. 241–269.

[2] L. Vilà-Nadal *et al.*, “Towards Polyoxometalate-Cluster-Based Nano-Electronics,” *Chem. - Eur. J.*, vol. 19, no. 49, pp. 16502–16511, Dec. 2013.

[3] D. E. Katsoulis, “A Survey of Applications of Polyoxometalates,” *Chem. Rev.*, vol. 98, no. 1, pp. 359–388, Feb. 1998.

[4] K. Y. Monakhov, M. Moors, and P. Kögerler, “Perspectives for Polyoxometalates in Single-Molecule Electronics and Spintronics,” in *Advances in Inorganic Chemistry*, vol. 69, Elsevier, 2017, pp. 251–286.

[5] J. Zhang, Y. Huang, G. Li, and Y. Wei, “Recent advances in alkoxylation chemistry of polyoxometalates: From synthetic strategies, structural overviews to functional applications,” *Coord. Chem. Rev.*, vol. 378, pp. 395–414, Jan. 2019.

[6] H. Zhu and Q. Li, “Redox-Active Molecules for Novel Nonvolatile Memory Applications,” in *Redox - Principles and Advanced Applications*, M. A. A. Khalid, Ed. InTech, 2017.

[7] C. Busche *et al.*, “Design and fabrication of memory devices based on nanoscale polyoxometalate clusters,” *Nature*, vol. 515, no. 7528, pp. 545–549, Nov. 2014.

[8] V. P. Georgiev, S. Markov, L. Vila-Nadal, C. Busche, L. Cronin, and A. Asenov, “Optimization and Evaluation of Variability in the Programming Window of a Flash Cell With Molecular Metal–Oxide Storage,” *IEEE Trans. Electron Devices*, vol. 61, no. 6, pp. 2019–2026, Jun. 2014.

[9] *Atomistix Toolkit*. Synopsys QuantumWise.