Single-molecule junctions:
Towards new frontiers for next-generation electronics

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Electronics have become an indispensable aspect of modern life, shaping communication, work, education, entertainment, and access to transportation and healthcare. The semiconductor industry has fueled this transformation over the past five decades by pushing the boundaries of Moore's Law, continually moving to smaller and more powerful technological nodes. Despite recent breakthroughs in EUV photolithography, the industry faces new challenges as progress stalls with the commercialisation of the 3 nm node. With the potential end of Moore's Law on the horizon and the escalating costs of top-down fabrication approaches, coupled with the demand for highly integrated and performing, low-power systems, there is a pressing need to shift towards Beyond-CMOS technologies.
To address the current challenges hindering top-down manufacturing in the rapid development of modern information technology, adopting a bottom-up approach for electronic device development is a promising alternative.
Molecular technologies, which utilise bottom-up fabrication approaches and self-assembly techniques, offer significant potential, particularly with single-molecule junctions (SMJs) that enable sub-nanometer precise engineering. Single-molecule junction technology could extend Moore's Law further, allowing for unprecedented integration at lower costs, with finely-tuned electronic properties achieveble through chemical synthesis, providing a level of control unmatched by current solid-state technology.

This dissertation showcases the potential of SMJ-based devices for the next generation electronics. It emphasizes that, after 50 years of progress and technological advancement the field of Single-Molecule Electronics (SME) is now technologically sound and ready to thrive, demanding increased attention not only from the fundamental science community but also from engineers and technologists.
By providing a comprehensive examination of SME fundamentals and literature, necessary for understanding and interpreting the reported results, this dissertation discusses case studies spanning various applications in electronics, from nanocomputing to chemical sensors and nano-electromechanical systems.
In particular, theoretical proof-of-concept or experimentally verified SMJ devices are meticulously characterised and engineered in terms of their electronic structure and transport properties, employing density functional theory coupled with Non-equilibrium Green's function formalism and/or with Scanning Tunneling Microscopy Break-Junction (STM-BJ) experiments.
Specifically, the thesis is structured as follows:

- **Chapter 1**, provides context and outlines the motivations behind the work presented in this thesis alongside a brief overview of Molecular Electronics.
- **Chapter 2**, offers a comprehensive overview of the fundamentals of Single-Molecule Junctions (SMJs), which are the primary focus of investigation in this thesis. It covers various aspects of SMJs, including their structure-charge transport properties, applicable external stimuli, and nanofabrication methods. This detailed overview is primarily intended for beginners and novices in the field who, like myself at the start of this doctoral journey, may lack a strong background in physical chemistry. The topics in this chapter are presented in a pedagogical and informative manner, making them accessible to readers from diverse scientific backgrounds. Experienced readers may find it valuable primarily for updating their knowledge of the current state-of-the-art literature.
- **Chapter 3**, provides the theoretical and experimental background necessary for understanding and interpreting the results delineated in Chapters 5, 6, 7, 8. It particularly focuses on the theoretical methodologies and experimental techniques employed across this thesis.
- **Chapter 4**, discusses the exploited methodology throughout this thesis, in terms of computational models, approximations and parameters used for the theoretical calculations and in terms of materials, samples, procedures and protocols used for the experiments.

- **Chapter 5**, offers an in-depth investigation into destructive quantum interference and Fano effects in SMJs. It explores how these phenomena can be manipulated through various structure-property relationships, including anchoring groups, electrode materials, molecular lengths, heteroatom substitutions, and incorporation of pendant groups, to enhance the performance of SMJ devices. The guidelines derived from this study are finally employed to design and engineer, through density-functional theory calculations, a high-performance paracyclophane-based SMJ transistor, achieving unprecedented performance metrics not previously reported in the literature, including an ON/OFF current ratio of almost 10^6 and a subthreshold slope of approximately 180 mV/dec.

- **Chapter 6**, discusses a preliminary theoretical study on electronic structure and transport properties of endohedral fullerene C_{28} encapsulating a Chromium cation. This study, performed through density-functional theory calculations, explores the feasibility of using C_{28} for implementing a single-molecule memory cell, which holds promise for Logic-in-Memory applications.

- **Chapter 7**, explores the sensing capability of a pyrrole-based SMJ device, designed to function as a single-molecule sensor for detecting the carcinogenic aflatoxin B1 through amperometric detection. This investigation employs density functional theory calculations to assess how modifications in the structural properties of the SMJ can influence the sensitivity of the sensor.

- **Chapter 8**, presents the research project performed during my Ph.D. visiting period at the University of Liverpool. This study employ STM-BJ experiments complemented by density functional theory (DFT) theoretical calculations to explore the mechanoresistive properties of two series of cyclometalated organoplatinum(II) complexes for nano-electromechanical systems applications. The investigated device exhibits an unprecedented level of conductance modulation, with a 2700-fold increase per just 1 nm compression.

- **Chapter 9**, provides a brief introduction to a circuital look-up-table model developed for evaluating the performance of circuits implemented with SMJ devices. The chapter also presents a few applications of this model.

- **Chapter 10**, concludes this thesis by summarising the key findings that showcase the potential of SMJ devices for future next-generation electronic. Future perspectives are also delineated.

Finally, the appendices at the end of the thesis offer additional information about theoretical and experimental results, as well as additional details of STM-BJ experiments and the experimental setup.

The research presented in this doctoral dissertation, through a comprehensive exploration and novel contributions from the discussed case studies, not only demonstrates the significant potential of single-molecule electronics in future next-generation electronic devices but also expands the theoretical and experimental toolkit for the design and functionality of SMJ devices. While substantial challenges remain on the path to final applications and commercialisation, yet this work offers a small but valuable contribution to the field's progress and hopefully provide a foundation and inspiration for future studies.
