Chemistry in a Nanoscale Gap

Albert C. Cortijos, Nadim Darwish, Simone Ciampi, Michelle

Coote, Katrin F. Domke, <u>Ismael Díez-Pérez</u>^a

Affiliation: a Chemistry Department, King's College London, Britannia House, 7 Trinity St, London SE1 1DB

Email: ismael.diez_perez@kcl.ac.uk

Abstract: In the realm of the Single-Molecule Electronics, a suite of advanced electrical characterization approaches have emerged allowing measuring charge transport in an electric contact made out of an individual molecule[1]. The field has (and is still) drawn(ing) an scenario where individual molecules can be chemically modified to deliver a particular electrical function in a nanoscale circuit, e.g. variable resistors[2], diodes[3], switches[4], etc. Along this excursion, we have observed that single molecules trapped in a nanoscale tunneling junction experience conformational structural changes and changes in molecule/electrode contact geometries, which are usually accompanied by large conductance variations and can be easily detected electrically[1]. Such changes are induced by the imposed forces fields experienced by the molecules within the nanoscale gap, namely, a mechanical force and/or an electric field. In the past decade, we have learnt that under certain force field conditions, the individual molecules wired in a nanoscale junction undergo chemical transformations. Here, we will present a couple of illustrative examples of the use of single-molecule junction to study and control reactivity at the nanoscale using electric fields, a concept that is inherent in the natural enzymatic molecular machinery[5]. Tunable, welloriented electric fields can be easily delivered along the main junction axis of a nanoscale electrical device[6]. We exploited the latter to study; (1) a simple monomolecular cis-trans isomerization reaction[7], and (2) a bi-molecular Diels-Alder reaction[8]. Along with the experimental design and fundamental chemistry aspects, we will discuss the advantages these examples can bring to possible technological applications.

References:

- [1]. L. Sun et al. Chem. Soc. Rev., 2014,43, 7378-7411.
- [2]. A. C. Aragones et al. Chem. Eur.J.2015, 21,7716 -7720.
- [3]. I. Diez-Perez et al. Nature Chemistry 1, 635-641 (2009).
- [4]. N. Darwish et al. Nano Lett. 2014, 14, 12, 7064-7070.
- [5]. Stephen D. Fried et al. Annu Rev Biochem. 2017; 86: 387–415.
- [6]. N. Darwish *et al.* "Principles of Molecular Devices Operated by Electric Fields" in Effects of Electric Fields on Structure and Reactivity: New Horizons in Chemistry, Royal Society of Chemistry, Ed. Sason Shaik.
- [7]. C. S. Quintans et al. Appl. Sci. 2021, 11(8), 3317.
- [8]. A. C. Aragones et al. Nature 531, 88-91 (2016).

Biography: Dr. Díez-Pérez obtained his degree in Chemistry from the University of Barcelona in 2000. He completed his Master's degree in Electrochemistry at the Physical Chemistry department of the same university, and continued with his PhD project trying to deepen into the fundamental aspects controlling Passivation and Corrosion processes at metal/electrolyte interfaces. An essential part of his PhD training was conducted in several international renowned institutions such as the Lawrence Berkeley National Lab in USA and the University Pierre Marie-Curie in France. His PhD research resulted in the development of a novel electrochemical tunneling spectroscopy approach to interrogate meta/electrolyte interfaces at the nanoscale; work that was awarded with the ISE-prize Hans-Jürgen-Engell in 2008. After graduating in 2006, he enjoyed a Marie-Curie fellowship to develop his postdoctoral project in Arizona State University under the supervision of Prof. Nongjian Tao. There, he explored fundamental aspects of charge transport of metal/molecule interfaces and immersed in the field of Molecular Electronics. He actively helped in the development of new single-molecule junction methods and was able to demonstrate several basic electrical behaviors in a single-molecule wire, namely, diode effect, transistor behavior and electromechanical effects. In 2011, he received an European Reintegration grand to work as a senior researcher at the Institute for Bioengineering for Catalonia, where he created a new research line in BioMolecular Electronics. In 2012, he got his assistant professor position at the Physical Chemistry department of the University of Barcelona, and tenured associate Prof in 2015. In 2017, he obtained a prestigious ERC Consolidator award focused on studying the effects of force fields in Biology. The same year, he moved to the department of Chemistry at King's College London, where he currently supervises a wide variety of projects involving the study of fundamental charge transport in (bio)molecules, spanning from simple synthetic backbones to complex biomolecular moieties with the aim of understanding the underlying mechanisms of bioelectricity.

