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Electrochemically-gated single-molecule electrical devices

Shaoyin Guo[c], Juan Manuel Artés[b], Ismael Díez-Pérez[a,b,*]

[a] *Physical Chemistry Department, University of Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain*
[b] *Institute for Bioengineering of Catalonia (IBEC), Baldiri Reixac 15-21, 08028 Barcelona, Spain*
[c] *Center for Bioelectronics and Biosensors, Biodesign Institute at Arizona State University, Tempe, AZ 85287, USA*

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ABSTRACT

In the last decade, single-molecule electrical contacts have emerged as a new experimental platform that allows exploring charge transport phenomena in individual molecular blocks. This novel tool has evolved into an essential element within the Molecular Electronics field to understand charge transport processes in hybrid (bio)molecule/electrode interfaces at the nanoscale, and prospect the implementation of active molecular components into functional nanoscale optoelectronic devices. Within this area, three-terminal single-molecule devices have been sought, provided that they are highly desired to achieve full functionality in logic electronic circuits. Despite the latest experimental developments offer consistent methods to bridge a molecule between two electrodes (source and drain in a transistor notation), placing a third electrode (gate) close to the single-molecule electrical contact is still technically challenging. In this vein, electrochemically-gated single-molecule devices have emerged as an experimentally affordable alternative to overcome these technical limitations. In this review, the operating principle of an electrochemically-gated single-molecule device is presented together with the latest experimental methodologies to built them and characterize their charge transport characteristics. Then, an up-to-date comprehensive overview of the most prominent examples will be given, emphasizing on the relationship between the molecular structure and the final device electrical behaviour.

1. Introduction

Back in 1974, Aviram and Ratner firstly proposed a theoretical single-molecule device with one molecule connected between two metallic beads that could rectify the current as in a standard diode configuration [1]. This was the kickoff of the single-molecule transport studies in the rapidly growing field of Molecular Electronics and, since then, large efforts were put in experimentally realizing a single-molecule electrical contact. The beginning of last decade brought us the first experimental examples [2–8], and to date, different strategies have been designed to reproducibly obtain single-molecule conductance signatures [6,9–11]. Among all these methodologies, Scanning Tunnelling Microscopy (STM) has been proven to be a powerful tool to *in situ* create and analyze thousands of single-molecule contacts and come out with statistically meaningful values for the conductance of the single-molecule device [9]. Generally, in order to reliably bridge a molecule between two electrodes and characterize its charge transport, several conditions have to be met: (i) provide stable chemical anchoring between the two electrodes and the molecule [11–21], (ii) identify signatures linked to the formation of a single-molecule bridge [9,22,23] and (iii) design experimental protocols to statistically analyze the observed single-molecule conductance signatures [9,24–26]. Points (i) and (iii) have been particularly decisive for the advance of this field; on the one hand, different anchoring chemistry has allowed to stably held molecules between two macroscopic electrodes through strong covalent chemical bonds such as metal-S [12,13] and, more recently, metal-C [20]. On the other hand, statistically meaningful results of single-molecule conductance values have been provided, which is a requirement in view of the observed dispersion in conductance results from device to device [9,24]. The dispersion mainly stems from the uncertainty in the atomic details of the molecule–electrode contact geometry [27]. The improved statistical methodologies in measuring single-molecule conductance have prompted extensive studies regarding how charge transport in single molecular devices is affected by molecular chemistry [28–33] and conformation [25,34–36]. These measurements, together with theoretical efforts, have provided the bulk of our current knowledge about electron transport in molecules. For further revision on single-molecule charge transport characterization on simple two-terminal devices, we address the reader to recent comprehensive reviews [37–41] and books [42–44].

The main block of experimental work on single-molecule transport has been developed in two-terminal device configurations,

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* Corresponding author at: Physical Chemistry Department, University of Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain. Tel.: +34 93 4033707.
E-mail address: isma_diez@ub.edu (I. Díez-Pérez).

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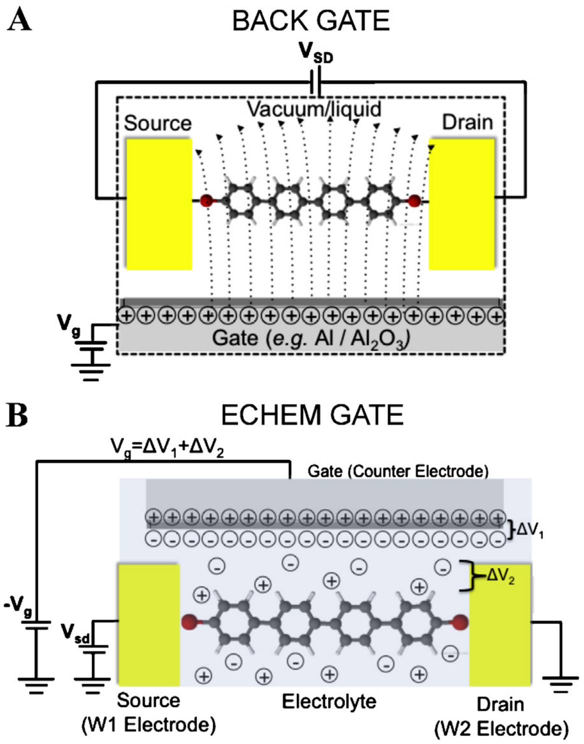

Fig. 1. Schematic representations of three-terminal single-molecule devices with (A) a solid-state back gate and (B) an electrochemical gate. Dot lines in (A) represent electric field lines and encircled signs in (B) represent solvated anions (negative sign) and cations (positive sign) in a polar solvent. EDLs at the source-drain/electrolyte interfaces in (B) are omitted for simplicity.

meaning devices with one unique molecule bridging between two biased (V_{bias}) electrodes. Although a huge advance in the field has been achieved with such a simple configuration, three-terminal devices (Fig. 1A) are highly desirable when it comes to the requirements of the actual technological applications; not only active molecular components generating specific electrical behaviours, but also logic device functionalities [45]. To date, measurements on single-molecule three-terminal devices are limited, owing to the experimental difficulty of placing a third electrode in close proximity to a single-molecule electrical contact. In this vein, pioneer works performed at cryogenic temperatures by Park [8] and Bjørnholm [46] demonstrated the experimental feasibility of adding a third electrode into a single-molecule electrical device and measuring gate-dependent transport. Despite the experimental advances in designing solid-state three-terminal single-molecule devices during the last decade [47–49], their microfabrication involves fairly complex clean room processes, which significantly diminishes the success rate of fabrication. Moreover, an important limitation of solid-state three-terminal single-molecule devices is their low gate efficiency (α), being α defined as the ratio between the molecular orbital energy shift ($E_{\mathrm{HOMO/LUMO}}$) and the actual applied gate voltage (V_g). By measuring α, one can evaluate the *amount of electric field* from the gate electrode that is actually felt by the confined molecule (Fig. 1A). α is typically evaluated from the slope of the transition voltage (V_{trans}) as a function of V_g (Fig. 2B, bottom panel), where V_{trans} is extracted from the minimum in the Transition Voltage Spectroscopy (TVS, Fig. 2A) [50,51]. TVS plots display a minimum (V_{trans}) that represents an electron transfer transition from tunnelling to a Fowler-Nordheim or field emission regime (Fig. 2B, top panel) [50]. Fig. 2B shows α values of 0.25, which means that 25% of the gate field only reaches the single molecule device, *i.e.* to shift the molecular energy levels involved in charge transport by 250 mV, at least 1 V of gate voltage is needed. This constitutes one of the largest reported α values in such devices, which typically hits much lower values in the order of ≤ 0.1 [52].

Electrochemically-gated three-terminal single-molecule devices (Fig. 1B) offer an alternative to overcome previous difficulties in the fabrication and operation of their solid-state homologues. In such devices, the molecular junction is immersed in an electrolyte and the gate potential is applied through the electrochemical double layer developed at the different electrodes/electrolyte interfaces. In the present review, we will introduce the main operating parameters of an electrochemically-gated single-molecule device and will illustrate the most recent advances through the latest reported examples.

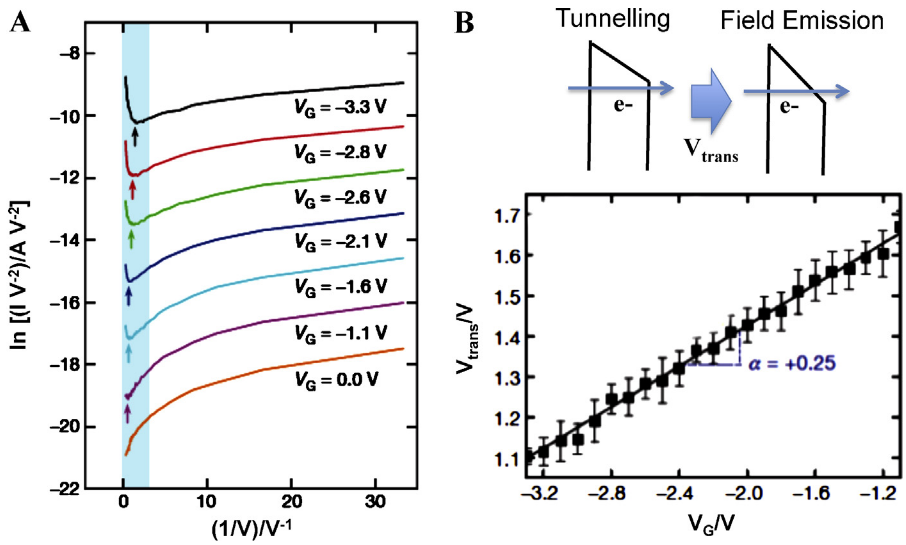

Fig. 2. Transition voltage spectroscopy (TVS) to evaluate gate efficiency in three-terminal single-molecule devices: (A) TVS plots at different gate voltages. The minima marked by arrows represent the transition bias voltage V_{trans}. (B) Top panel represents simplified band diagrams of the electron transfer process through a square tunnelling barrier at V_{trans}. Bottom graph shows the linear relationship between the transition and gate voltages. The slope α is the gate efficiency.

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