Full Counting Statistics of Single Electron Transport in a Biological Motor

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Abstract

Full counting statistics (FCS) of single electron transport in low dimensional solid-state devices enables to quantitatively assess information on correlation effects and structure symmetry. By combining molecular dynamics (MD) simulation and master equations derived from the Marcus theory, we show that the FCS of single electron transport can also be very attractive in non-solid-state molecular systems. Depending on the symmetry of the molecular motion and electron-transfer-based or diffusion-based correlations, a Brownian motion driven redox-labeled single-strand (ss) DNA sandwiched between two electrodes evidences either full shot noise or noise suppression with Fano factors of 1/2 or 1/3. This study provides a route to better understand biological systems at the single-molecule level, and to design functional Brownian-motion driven biomolecular devices.

1. Introduction

The system under study is a 50 base pair ss-DNA sandwiched between two electrodes and tethered only at one extremity (Fig.1a). A redox ferrocene (Fc) molecule ends the free extremity of the ss-DNA. We assume that there is no direct tunneling between the two electrodes biased at +/- 0.5V vs Fc energy level, and neglect the charge transfer along the ss-DNA (TTT… sequence). MD is performed using oxDNA coarse grained code which realistically reproduces sequence-dependent DNA motion [1]. At each time step of 0.9 ps, the *z* position of the Fc molecule is tracked (Fig.1a), and the probability of charge transfer is computed to get a time-dependent Fc charging state trace (Fig.1b). The master equations are based on the Marcus kinetics theory of charge transfer, and include a reorganization energy that depends on *z* and *d*-*z*. We have first confirmed that such an approach provides a good quantitative agreement with previously published cyclic voltammetry experimental results for ss-DNA-Fc without adjustable fitting parameter (not shown here) [2]. Here, we use this combined computation method to study the full counting statistics of single-electron transfer in a biological motor. When compared to a solid state quantum dot, the motion of the Fc molecule adds another degree of freedom that is translated into time-dependent transfer rates (Fig.2a).

2. Results

First, we consider the inter-electrode gap fixed at 6 nm, and the kinetics transfer rate at z=0 as a tunable parameter (via the electronic coupling term H in the Marcus formalism). As H is increased, we observe a transition from an electron transfer limited to a diffusion limited current I. Interestingly, the transition appears at $H \approx 6\text{x}10^{-5}$ eV which is the typical value to be considered for Ferrocene electrochemical process at a gold electrode interface. As a matter of comparison, a "free" Fc following a random walk leads to similar results except that the current is enhanced in the diffusion regime due to the absence of spring force. Electron transfer always appears near the interfaces (Fig.2c). However, the probability distribution of charge transfer is reduced at z=0 and d-z=0 in the diffusion regime because the electrons transfer probability is large enough to enable charge transfer few angstroms away from the interface.

The FCS is obtained by counting the number of times the Fc is charged in a given time window (Δt) over a trace of few tens of microseconds (Fig.3a). From the FCS, the Fano Factor (FF=variance/average) and skewness, 2nd (μ_2) and third moments (μ_3) of the FCS, respectively, show noise suppression and contain high information content (Fig.3b). At low H, in the regime where diffusion has a weak contribution, we find $\mu_2 \approx 0.5$ and $\mu_3 \approx 0.25$ as in the case of a symmetric solid-state quantum dot [3]. Interestingly, as H is increased, noise is further suppressed. In the case of ss-DNA-Fc, μ_2 tends to 0.3, which corresponds to an inelastic collision-free diffusive transport in 1D wires [3]. τ_{in} and τ_{out} time constants, as described in Fig.1b, show a (sub) Poissonian distribution in both conduction regime above a critical diffusion time constant of 0.1 ns. We stress that in the case of a "free" Fc, μ_2 remains at 0.5 but μ_3 is further suppressed.

Finally, as d is increased, the z probability distribution becomes asymmetric and the FF tends to 1, as expected for an asymmetric quantum dot [3].

3. Conclusions

Noise suppression related to single-electron transport in a biological motor provides quantitative information on biomolecule motion. The developed simulation tool could be exploited for the development of a wide variety of biomolecular devices and electrochemical imaging tools [4].

References

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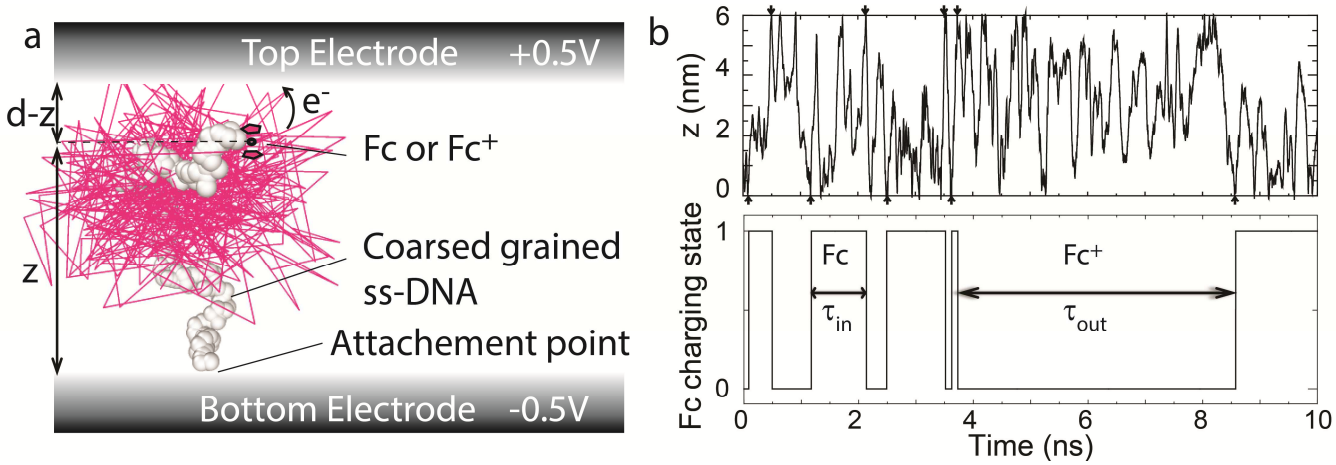

Fig. 1 a Schematic representation of the device composed of a ss-DNA attached at one electrode and free at the other Fc-labelled extremity. Distance to the electrodes are indicated as z, d-z. b Time dependent fluctuation of the Fc molecule z position obtained by MD and Fc charging state computed at each MD time step with the Master equations, when $H=6x10^{-5}$. z at which charge transfer occurs are indicated with a small arrow.

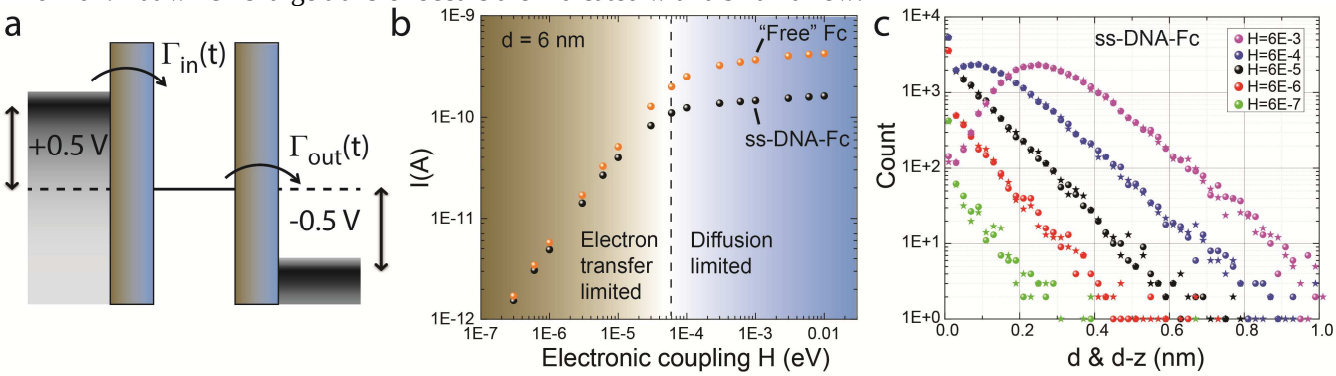

Fig. 2 Time-dependent energy band diagram (a), estimated current (b) and extracted electron transfer z position (c).

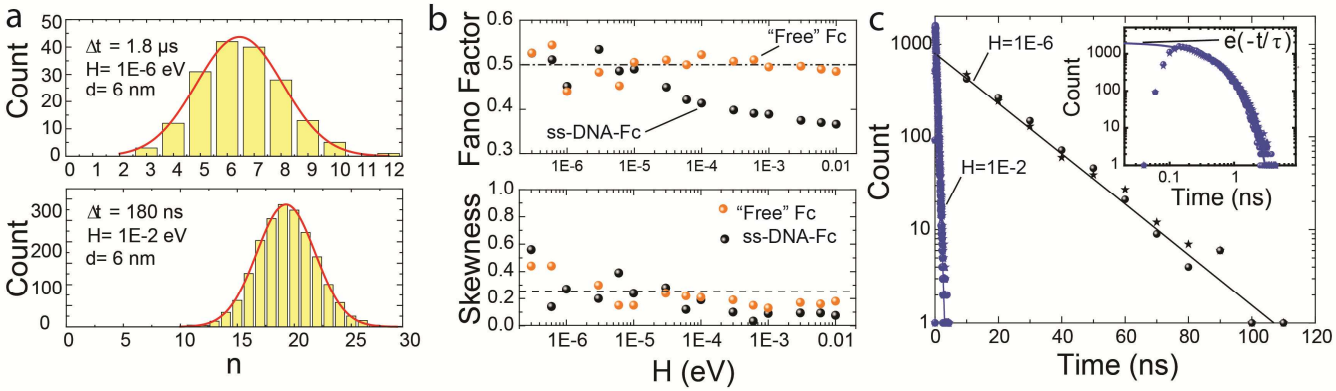

Fig. 3 FCS of Fc charging state (a), 2nd and 3rd moments of the FCS (b), and extracted τ_{in} (ball) and τ_{out} (star) (c).

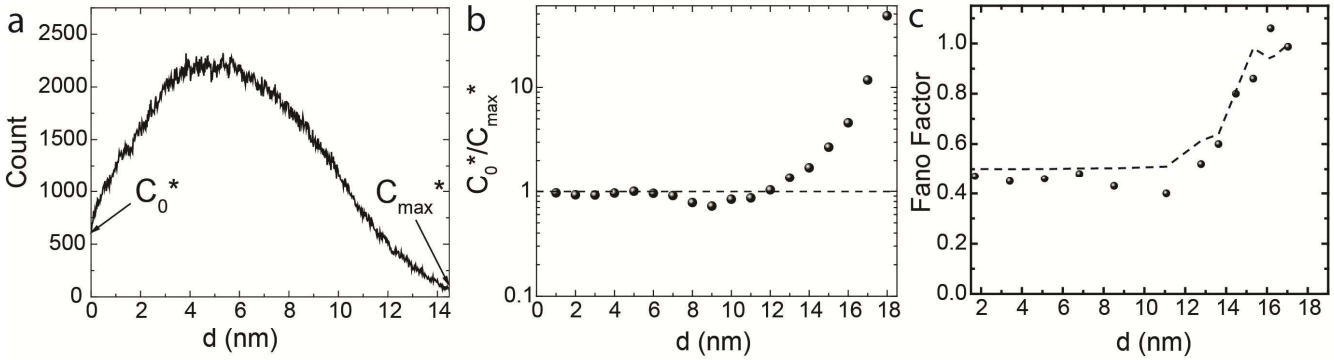

Fig. 4 z distribution of Fc position (z), normalized z distribution (b) and evolution of the Fano Factor with d (c).