Redox-Dependent Franck–Condon Blockade and Avalanche Transport in a Graphene–Fullerene Single-Molecule Transistor

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Supporting Information

ABSTRACT: We report transport measurements on a graphene–fullerene single-molecule transistor. The device architecture where a functionalized C\textsubscript{60} binds to graphene nanoelectrodes results in strong electron–vibron coupling and weak vibron relaxation. Using a combined approach of transport spectroscopy, Raman spectroscopy, and DFT calculations, we demonstrate center-of-mass oscillations, redox-dependent Franck–Condon blockade, and a transport regime characterized by avalanche tunnelling in a single-molecule transistor.

KEYWORDS: Single-molecule electronics, Franck–Condon blockade, avalanche transport, electron-vibron coupling, graphene

C
pling between electronic and vibrational degrees of freedom in single-molecule devices can lead to transport properties very different from those of metal/semiconductor nanostructures.\(^6\) Charge transfer can excite vibrational modes,\(^3\) or vibrons, and strong electron–vibron coupling leads to suppression of tunnel current at low bias.\(^3,4\) Theory further predicts super-Poissonian current noise, characterized by giant Fano factors, for molecular junctions with weak vibron-relaxation owing to avalanche-type charge transfer.\(^5\) Here, we demonstrate a device architecture of a single-molecule transistor where a functionalized fullerene binds to graphene nanoelectrodes via π–π interactions. The stability and weak vibron-relaxation of our system enables us to investigate redox-dependent electron–vibron coupling and avalanche transport.

We perform transport measurements of graphene–fullerene single-molecule transistors fabricated using feedback-controlled electroburning.\(^6\) The molecule bridging the graphene nanogap is a pyrene functionalized C\textsubscript{60} bisadduct synthesized through a 1,3 dipolar cycloaddition using 1-pyrene carboxaldehyde and N-methylglycine (Supporting Information Section 1.1).\(^7\) While the functionalization results in different isomers, steric considerations mean only the cis-2 and cis-3 isomers are expected to bridge the graphene nanogap. Density functional theory (DFT) calculations of the relaxed graphene–fullerene–graphene structure confirm that the cis-3 isomer forms the most stable configuration without steric hindrance, as shown in Figure 1a. Iso-surfaces of the frontier orbitals of gas phase cis-3 isomer are shown in Figure 1b.\(^8\) The wave function of the lowest unoccupied molecular orbital (LUMO) level is mostly localized in the central C\textsubscript{60} whereas for the highest occupied molecular orbital (HOMO) level, the wave function is extended to the pyrene anchors. Comparison of the iso-surfaces of frontier orbitals for cis-2 and cis-3 isomers further show that the wave function delocalization of the HOMO levels are more pronounced in the cis-3 isomer, indicating that it has a better π–π interaction with the graphene electrodes and is therefore more likely to bridge the junction (Supporting Information Figure S12). In pristine C\textsubscript{60}, DFT predicts LUMO dominated transport that was verified with thermoelectric experiments.\(^9\) In contrast, our DFT calculations predict that charge transport in the bisadduct is more likely to be HOMO dominated.\(^10,11\)

Figure 1c shows the current I as a function of bias V\textsubscript{g} and gate voltage V\textsubscript{g} of a single-molecule transistor (device A), measured at 20 mK. The addition energies between adjacent redox states, measured from the height of the Coulomb diamonds, are E\textsubscript{add} \sim 160 meV for all charge-state transitions. We attribute the absence of odd/even oscillations of E\textsubscript{add} previously observed for two-fold spin shell systems,\(^6,12\) to orbital degeneracies of the C\textsubscript{60} molecule.\(^13\) Calculations have shown that the interactions within each shell in C\textsubscript{60} are almost constant with only a slight increase of the electron–electron on-site Coulomb interaction in the middle of each shell where electrons with opposite spins begin to fill.\(^13\) We observe a small increase of \sim 10 meV per electron added from charge state N to N + 2 which we attribute to the on-site Coulomb interactions. In the constant interaction model E\textsubscript{add} is given by the sum of the charging energy E\textsubscript{C} due to Coulomb interactions of the electrons in the molecule, and the energy gap Δ\textsubscript{HL} between the HOMO and LUMO.\(^14\) For a two-fold degenerate system, E\textsubscript{add} oscillates between E\textsubscript{C} and E\textsubscript{C} + Δ\textsubscript{HL} while for systems with higher degeneracies, E\textsubscript{add} = E\textsubscript{C} until a level is completely filled.

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From the fact that $E_{\text{add}}$ here is constant for three charge-state transitions, we infer that electrons are filling exclusively an orbital that is at least four-fold degenerate. We conclude that charge transport is HOMO dominated based on two independent observations: (i) DFT calculations predict that the Fermi energy of the graphene leads are closer aligned to the HOMO than to the LUMO and, (ii) the experimentally observed level degeneracy is compared to DFT calculations of the Kohn–Sham energy levels, which indicate that the HOMO ($-4.59$ eV) and HOMO$-1$ ($-4.60$ eV) are nearly degenerate whereas the LUMO ($-3.12$ eV) and LUMO$+1$ ($-2.86$ eV) are well separated in energy (Supporting Information Section 2.3).

Figure 2 shows a map of the differential conductance $G$ of charge transition $N+1$ to $N+2$ of device A taken with a higher resolution (P3 in Figure 1c). The gate potential for the charge transition is different for repeated measurements due to a common hysteretic effect likely related to charge traps in the oxide. The effect occurs when the gate potential is swept quickly across a large range but is otherwise stable when swept slowly. We observe lines corresponding to excited state transitions at energies $\geq 33$ meV (white arrows) that are in excellent agreement with the intrinsic vibrational modes of pristine C$_{60}$, as summarized in Table 1. We also observe excited states at energies $<33$ meV (green arrows), below the lowest vibrational mode of the pristine C$_{60}$. The asymmetry of the excited states on the bias polarity can be explained through a rate equation model involving asymmetric tunnelling barriers, which was previously observed in the orbital excited state spectrum of a single donor in silicon. When the excited state relaxations are fast compared to the tunneling rates, an electron can tunnel on to the molecule through any number of excited states that lie within the bias window but only leave through the...
ground state as the molecule relaxes. In the limit where the molecule-electrodes coupling is very asymmetric, current steps are not expected for one bias polarity.\(^6\)

A comparison of the transport spectroscopy and Raman spectra of pristine C\(_{60}\) and bisadduct (Table 1) indicates that these excited state transitions have a vibrational nature. To identify the mechanical motion of these additional low-lying vibrational modes, we use DFT results where we analyze the mechanical degrees of freedom of the bisadduct in the limit where the atomic mass of the pyrene anchor groups approach infinity (Supporting Information Section 2.6). In this limit, the anchor groups are effectively clamped and the modes corresponding to internal vibrations of the pyrene are filtered from the vibrational spectrum. DFT calculations in this limit reveal six vibrational modes at energies \(<33\) meV with two sets of three modes each corresponding to the translational and rotational center-of-mass (CM) motion of the central C\(_{60}\) with respect to the anchor groups (Figure S14a, animations in Supporting Information).

Figure 3 shows low energy excitations observed for all four charge transitions (P1\(\sim\)4 in Figure 1c) with spacings of 1.7 meV (P1), 1.5 meV (P2), 1.7 meV (P3), and 1.5 meV (P4) (white arrows). Low energy excitations are similarly observed in measurements of device B (~2 meV, Supporting Information Figure S8a). Lines with different slopes, corresponding to different capacitive couplings, are probably not related to the energy spectrum of the molecule. They can be from a different Coulomb diamond related to a separate quantum dot located close to the device or associated with density of states fluctuations in the graphene electrodes. Similar fluctuations have also been observed in silicon SETs.\(^7\) To account for the nature of the low energy excitations (~2 meV), we analyze the vibrational modes of the bisadduct using DFT where all the mechanical degrees of freedom of the atoms are allowed (Supporting Information Section 2.6). The lowest nonzero mode is at 1.7 meV, consistent with our measurements (Supporting Information Figure S14b). This mode is due to the combined center-of-mass motions of the central C\(_{60}\) and pyrene anchors moving perpendicularly relative to each other with the central C\(_{60}\) moving out-of-plane while the anchors move in-plane (animation in Supporting Information). Our findings are consistent with a previous report that the binding energy of pyrene to graphene is much stronger out-of-plane compared to in-plane, such that the pyrene anchors can more easily slide on the graphene electrodes.\(^8\)

The Coulomb diamond edges do not intersect at zero bias for P1\(\sim\)3 (Figure 3a\(\sim\)c) and in device C (Supporting Information Figure S8b). The current suppression at low bias remain unchanged with the application of a magnetic field, ruling out a magnetic origin (Supporting Information Figure S7)\(^9\) and the size of the gaps correspond to an integer spacing of the energy excitations. We attribute these features to Franck-Condon (FC) blockade that occurs for strong electron-vibron coupling, illustrated in Figure 5a. Electrons tunnelling onto the molecule shifts the equilibrium coordinates of the harmonic oscillator wave functions for charge states N and N + 1 by an amount proportional to the dimensionless electron-vibron coupling constant \(\lambda\). For strong coupling, \(\lambda \gg 1\), the equilibrium coordinates of the N + 1 charge state is greatly displaced from that of the N charge state (Figure 5a). As a result, the transition rate between the vibronic ground states of charge states N and N + 1, determined by the overlap of the vibron wave functions, is exponentially reduced with \(\lambda\), leading to current suppression at low bias. The FC blockade is lifted when the applied bias is sufficiently large for transitions from the vibronic ground state to higher excited states (Figure 5c), where the transition rates are higher from increased overlap of the vibronic wave functions. When electrons are added to the molecule, we observe a decrease of the FC gap from P2 to P4, such that for P4 (Figure 3d), the FC blockade is completely lifted. The FC gap, that is, the threshold voltage at which the FC blockade is lifted when it matches a multiple of the vibrational quantum \(\hbar\omega\), is proportional to \(\lambda^2\). Additional electrons on the molecule shift the equilibrium positions of the harmonic oscillator wave functions, leading to a smaller displacement of the equilibrium coordinates between charge states N + 2 and N + 3, that is, a smaller \(\lambda\). The higher transition rate for the vibronic ground states from the increased wave function overlap allows for current in the previously FC blockade region. Redox-dependent electron-vibron coupling is possibly due to Jahn-Teller (JT) distortion of the molecule,\(^9\) which is particularly strong in molecules with a large orbital degeneracy and high spatial symmetry such as C\(_{60}\).\(^21\) The geometrical JT distortion lowers the overall ground state energy, which is directly proportional to \(\lambda\), as derived in ref 23. Our observation of HOMO degeneracy and a charge state dependent \(\lambda\) is in line with these predictions.

Using the set of evenly spaced excitations of P3 (Figure 3c) and fitting them to the rate equation model,\(^7\) we determine \(\lambda = 3.0\) for the charge transition N + 1 to N + 2 (Supporting Information Section 1.5). We simulate the stability diagram for an asymmetric molecule-electrode tunnel coupling, dependent on the contact geometry of the molecule to the electrodes, \(t_L = 0.24t_b\) (Figure 4b), which shows good qualitative agreement with our measurements (Figure 4a). The electroburnt graphene nanoelectrodes are not likely to be symmetric on the atomic scale, which can lead to asymmetric positioning of the molecule.
across the junction. Furthermore, our DFT calculations show that the pyrene anchors are not symmetric relative to the central C_{60} (Supporting Information Section 2.2).

At elevated temperatures, T, the thermal equilibrium population of vibrational excited states with exponentially greater transition rates are increased,3,4 and transitions at low bias can now proceed via these states. In device A, the FC gap is lifted at 3 K. Transitions due to vibron absorption are described by Bose–Einstein statistics, such that $I_{\text{trap}} \propto 1/k_BT \times 1/(\exp(\hbar\omega/k_BT) - 1)$. We extract and fit the temperature dependence of $I$ at $V_{\text{g}} = 7$ V and $V_S = 7.2$ mV in Figure 3c and obtained a value of $\hbar\omega = 1.7$ meV, consistent with our experimentally determined value.

To characterize the current fluctuations, we extract the 0 ↔ 2 escape and return rates by fitting a current–time trace of device A measured at $V_S = 12$ mV and $V_g = 10.15$ V to a Hidden Markov Model (HMM) assuming a two state stochastic process (orange line in Figure 5e).24 We obtain an escape rate of $15 \pm 4$ s$^{-1}$, which corresponds to a FC matrix element $W_{0 \rightarrow 2} \sim 0.002$ and $\lambda \sim 4$ (Supporting Information Section 1.9), and a return rate of $22 \pm 2$ s$^{-1}$. These rates place an upper-bound of $\sim 10^{-1}$ s$^{-1}$ on the dissipative relaxation rate. The observation of such a slow relaxation rate, compared to values measured in time-resolved spectroscopy ($\sim 1$ ps$^{-1}$),25 is indeed surprising. However, those measurements are usually performed in a solvent where dissipation to solvent ions is possible. Low temperature and vacuum conditions suppresses the dissipation rate,26 which is mostly dependent on dissipation to the electrodes in single-molecule junctions.10,27 Fits of the conductance peaks (Supporting Information Section 1.5) show that the pyrene anchors form weak $\pi$–$\pi$ stacking interactions with the graphene electrode (molecule–electrode coupling $t_b \sim 1$ meV). While the in-plane thermal conductivity of graphene is exceptionally large, its out-of-plane thermal conductivity is limited by weak van der Waals interactions between adjacent planes and substrates and can possibly suppress vibron dissipation to the graphene electrodes.28 Vibrationally induced conformational changes where an anharmonic potential with local minima suppress dissipation is another possibility.1 Metastable molecular conformation can be long-lived on the order of milliseconds, consistent with the return rates in our system, and can be accessed through a vibrational excited state.29 Dissipation to the electrodes is

**Figure 4.** (a) Current stability diagram of P3 at 20 mK. (b) Simulated current stability diagram using the rate equation model with $t = 3$ and $t_b = 0.2t_b$, showing good qualitative agreement with (a). Conductance stability diagrams of P3 at 1 K (c) and 3 K (d). The FC gap is lifted at 3 K. Transitions due to vibron absorption are described by Bose–Einstein statistics, such that $I_{\text{trap}} \propto 1/k_BT \times 1/(\exp(\hbar\omega/k_BT) - 1)$. We extract and fit the temperature dependence of $I$ at $V_{\text{g}} = 7$ V and $V_S = 7.2$ mV in Figure 3c and obtained a value of $\hbar\omega = 1.7$ meV, consistent with our experimentally determined value.

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dependent on the atomistic details of the vibron density of states at the molecule−electrode interface. The nonequilibrium distribution of vibrons is nontrivial and requires a self-consistent calculation of electron−vibron dynamics.

Electron avalanche transport is characterized by giant Fano factors on the order of $10^2$−$10^3$ occurring in steps over the bias window ($\hbar \omega / \beta e$) corresponding to a vibron transition. The zero frequency Fano factor $F(0) = S(0)/2e\langle I \rangle$ for the excess noise $S_0 = S(0)$ indicates the deviation from Poissonian noise, where $F = 1$. The noise power density $S(\omega)$ is defined as the Fourier transform of the current−current correlation

$$S(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \delta I(t) \delta I(t') \rangle e$$

In Figure 5h, we determine the zero frequency Fano factors as a function of $V_g$ (Supporting Information Section 1.9), taken at $V_b = 10.15$ V indicated by the vertical green line in Figure 3c. At $10 \leq V_b \leq 13$ mV, the Fano factors increase to an order of $\sim 10^2$, reflecting the current fluctuations due to avalanche transport. These giant Fano factors likewise persist over an applied bias corresponding to $\hbar \omega / \beta e$. When $V_b = 13.4$ mV, the Fano factors decrease to $\sim 1$ in accordance with sequential tunnelling.

We have demonstrated a device architecture, using functionalized C$_{60}$ bisadduct and graphene electrodes to create single-molecule transistors, that enables the observation of redox-dependent FC blockade and avalanche transport. We observe HOMO dominated transport. While doping-induced variations in the Fermi-level of the graphene electrodes and offset charges in the oxide can influence the alignment of the electrochemical potential of the molecule with the Fermi-level of the graphene electrodes, we show that the functionalization of C$_{60}$ with pyrene anchors groups can modify electron delocalization and energy levels leading to HOMO dominated transport, which is in contrast to previous reports of LUMO dominated transport in C$_{60}$ transistors. Calculations have suggested that the modification of electron delocalization and energies via the inclusion of side groups can be used to tune the thermopower of single-molecule junctions. Furthermore, thermoelectric efficiency is maximized when charge transport across a junction occurs through a single level with low vibrational heat conductance. Therefore, the observation of an extremely long vibron lifetime not only offers unique

![Figure 5](image-url)
potential for the fundamental study of quantized motion and thermal transport on the nanoscale but is also promising for practical applications in single-molecule energy-conversion devices.32

Methods. Device Fabrication and Measurements. The molecular devices are fabricated on a heavily doped silicon chip with a 300 nm thick oxide that also serves as a back gate to modulate charge transport through the junction. First, graphene is synthesized on liquid copper supported on a tungsten substrate using chemical vapor deposition.33 Using a wet transfer technique, the graphene is transferred to the silicon substrate with prepatterened gold electrodes. The graphene electrodes are fabricated based on the method of feedback-controlled electroburning.34 Fabricated nanogaps are typically between 1 to 2 nm. The devices are next immersed in a 10 μM chloroform solution containing the C_{60} bisadducts for 30 min. We wirebond the devices to our sample puck and transfer them to our dilution fridge with a base temperature of 20 mK. All electrical measurements are performed using low noise, battery operated electronics, while the gate voltage was modulated with a Keithley 2400 sourcemeter.

Theoretical Methods. To calculate the vibrational modes of the bisadducts, we use the Harmonic approximation method to construct the Dynamical Matrix $D$. The xyz coordinates of the two isomers of the bisadducts were constructed and the geometry relaxation was performed with Siesta35 implementation Section 2.1).36 The electronic structure and transport calculations are performed using GOLLUM as described in ref 8.

ASSOCIATED CONTENT

Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b03434.

Further details about molecular synthesis and characterization, magnetic and temperature dependence measurements, rate equation model, current noise analysis, DFT calculations. (PDF)

Animations of the electronic vibrations. (ZIP)

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Notes
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