Single $C_{59}N$ Molecule as a Molecular Rectifier

Jin Zhao, Changgan Zeng, Xin Cheng, Kedong Wang, Guanwu Wang, Jinlong Yang,* J. G. Hou,† and Qingshi Zhu
Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China,
Hefei, Anhui, 230036 People's Republic of China

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We report a new kind of experimental realization of a molecular rectifier, which is based on a single azafullerene $C_{59}N$ molecule in a double-barrier tunnel junction via the single electron tunneling effect. An obvious rectifying effect is observed. The positive onset voltage is about 0.5–0.7 V, while the negative onset voltage is about 1.6–1.8 V. Theoretical analyses show that the half-occupied molecular orbital of the $C_{59}N$ molecule and the asymmetric shift of the molecular Fermi level when the molecule is charged are responsible for the molecular rectification.

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As a basic component in molecular electronics, the molecular rectifier has been explored extensively in recent years [1]. The most widely designed and experimentally synthesized molecular rectifiers are based on the Aviram and Ratner proposal, which suggested a donor-insulator-acceptor-type molecule connected with two electrodes would behave as molecular rectifier under a bias voltage [2]. Recently, the Aviram-Ratner mechanism for the rectification has been debated [3], and an alternative mechanism is suggested and demonstrated, where a single electroactive unit is positioned asymmetrically with respect to electrodes, and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are positioned asymmetrically with respect to the Fermi level [4]. In this Letter, we report a new kind of experimental realization of molecular rectifier, which is based on a single azafullerene $C_{59}N$ molecule in a double-barrier tunnel junction (DBTJ) via the single electron tunneling (SET) effect.

Dimer $(C_{59}N)_2$ was prepared according to the reported procedure in Refs. [5,6]. The green color of $(C_{59}N)_2$ in solution, the longer high performance liquid chromatography (HPLC) retention time (about 17.0 min. of $(C_{59}N)_2$ versus 7.6 min. of C_{60} on a Cosmosil Buckyprep column (4.6 mm × 250 mm) with toluene as the eluent indicating its apolar character, and absorptions at 442, 593, 717, and 800 nm in the UV-vis spectrum are all consistent with those reported before and thus confirm its identity. The small amount of solid powder of $(C_{59}N)_2$ dimers was obtained in a crucible by evaporation of solvent in a dry box. The substrate was prepared by self assembling high-quality monolayer alkanethiols on Au(111) surface, and the detailed process and characterization were reported in our previous work [7]. Less than 0.01 monolayer of $C_{59}N$ was deposited on the alkanethiol self-assembled monolayer (SAM) surfaces by *e*-beam evaporation in vacuum chamber at room temperature, and then the sample was quickly transferred to the low temperature sample holder at 5 K in an OMICRON scanning tunneling microscope (STM) chamber with a base pressure below 2.0×10^{-11} Torr. Because $C_{59}N$ sublimes in monomer form and the molecules are unable to diffuse and redimerize on the substrate at low temperature 5 K [8], we observed single $C_{59}N$ on the substrate from the STM topology images [Fig. 1(a)]. In the Fig. 1, the lattice of the SAM can be seen clearly and used to calibrate the scale of image. The line profile along the line AB shows the image of a $C_{59}N$ on the SAM is a protrusion with the width of about 2 nm and height of 0.8 nm. As a comparison, we performed the same experiment for C_{60} molecules. The STM image of a single C_{60} on the SAM [Fig. 1(b)] is quite similar to that of a $C_{59}N$ in size, showing the $C_{59}N$ is really in monomer form on the SAM. We notice that while the STM detects the valance charge distribution of a molecule, the abnormally large width of molecules in STM images may be due mainly to convolution with the finite size of the STM tip.

Our experiments are conducted on a DBTJ formed by positioning a STM Pt-Ir tip above a $C_{59}N$ which resides on top of the SAM on Au(111). In such a DBTJ configuration [Fig. 2(a)], the SAM layer acts as the insulating barrier between the $C_{59}N$ molecule and gold substrate, and there is no charge transfer and bond formation between the molecule and supporting SAM. The current-voltage (I-V) curves for a DBTJ show the Coulomb blockade (CB) and Coulomb staircases behavior due to the discreteness of the charge, its associated charging energy, and molecular energy levels. Figure 2(b) shows a typical set of tunneling I-V curves for individual $C_{59}N$ molecules measured at various setting parameters. Pronounced I-V asymmetry is observed, and this rectifying effect is repeatable for all measurements we made. We find that although the detailed feature of each curve is varied slightly due to the different setting parameters, the positive onset sample bias voltage (V_+) is always about 0.5–0.7 V while the negative onset sample bias voltage (V_-) is about 1.6–1.8 V. We also find that the decrease of the distance between the tip and molecule (via increasing the setting point current while remaining the setting point voltage unchanged) can decrease V_- and keep V_+ to a constant. By contraries, we did not observe the distinct asymmetry in the I-V curve of

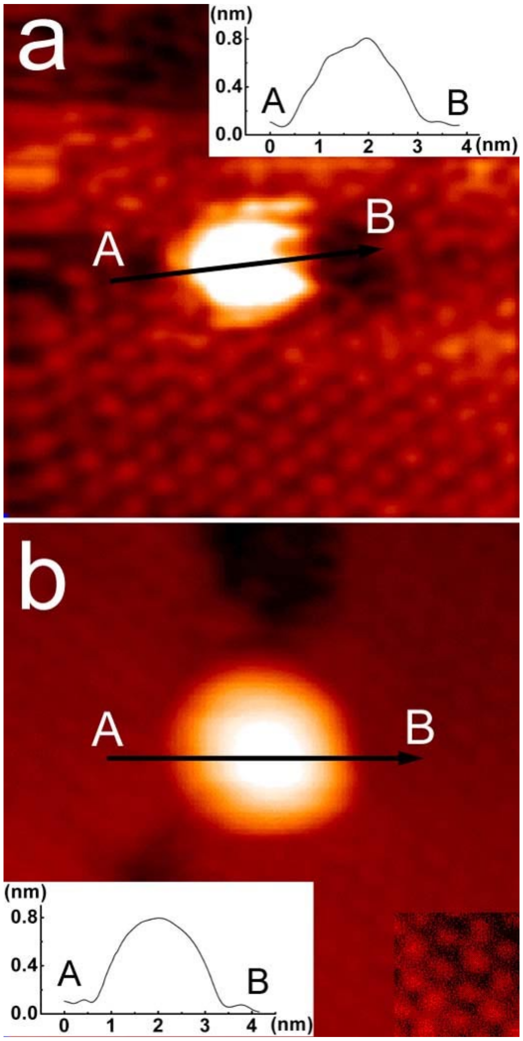


FIG. 1 (color online). The STM images of $C_{59}N$ (a) and C_{60} (b) on SAM at 5 K. Image size: 8 nm × 8 nm, scanning parameters: 1.86 V/0.1 nA. The line profiles along the line AB are shown in the insets, and the right inset in (b) is a high-contrast STM image of the SAM substrate.

the STM tip over the SAM background which shows a symmetrically metallic behavior, or over a C_{60} molecule on the SAM which shows a symmetrically CB behavior [inset in Fig. 2(b)].

The mechanism of rectifying effect of a single $C_{59}N$ molecule in a DBTJ can be qualitatively understood by the orthodox theory [9] for the SET effect and the electronic structure of $C_{59}N$. As it is well known in the orthodox theory, to add (+) [remove (−)] an electron to (from) the quantum dot through one junction of the DBTJ system, work has to be done against the electric field of excess electrons (ne) which already reside on the quantum dot:

$$E_C^{\pm}(n) = e^2\left(\frac{1}{2} \pm n\right)/(C_1 + C_2), \tag{1}$$

where C_1 and C_2 are the capacitances of the two junctions, respectively. This charging energy induces the zero current gap—CB in the I-V curve. To simplify discussions below, we assume that $C_1 < C_2$. This means that the first tunneling electron will always span the first junction. The CB thresholds of the negative and positive voltages are deduced from the law of partial voltage:

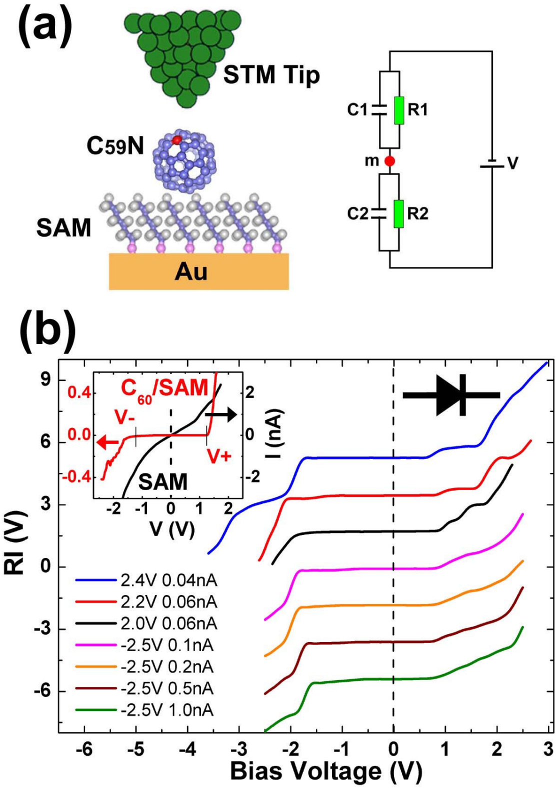
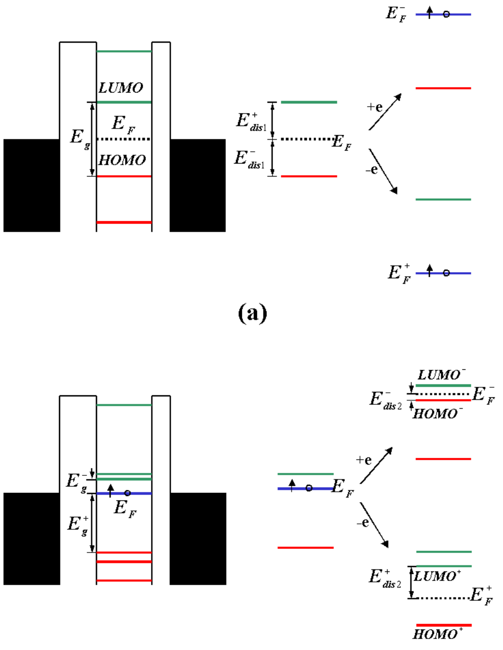


FIG. 2 (color online). (a) The diagram and equivalent circuit of the experimental system. (b) A set of I-V curves for individual $C_{59}N$ molecules measured at 5 K and at various setting parameters. For clarity, we use RI, instead of using I, as the vertical axis, and shift the curves vertically, where R is the asymptotic resistance and estimated from the slope of the I-V curve. The inset shows the I-V curves for the SAM substrate and individual C_{60}.

$$V_+ = V_- = \frac{C_1 + C_2}{C_2 e} E_C(0). \tag{2}$$

In this model, the quantum dot is considered to have a continuous energy band around the Fermi level (E_F). For a single molecule, however, there is a discrete energy level structure, so additional work due to the discrete level effect should be taken into account: $E_{\rm tot}^{\pm} = E_C^{\pm} + E_{\rm dis}^{\pm}$, where $E_{\rm tot}^{+}$ ($E_{\rm tot}^{-}$) is the required energy for the addition (reduction) of an electron to (from) the molecule, $E_C^{\pm}$ are the charging energies in Eq. (1), and $E_{\rm dis}^{\pm}$ are the accessional energies required by the discrete level effect. With the quasiparticle approximation, $E_{\rm dis}^{\pm}$ can be expressed as the energy difference between the Fermi level and the energy level in which the tunneling will occur.

As shown in Fig. 3(a), for a molecule such as C_{60}, with a fully occupied HOMO, its E_F locates between the HOMO



(a)

(b)

FIG. 3 (color online). A schematic diagram for the changes of the Femi level of a molecule with a fully occupied HOMO (a), and with a half-occupied HOMO (b) in the DBTJ. The red lines denote the occupied levels, blue lines denote the half-occupied levels, and green lines denote the unoccupied levels.

and LUMO when the molecule is neutral. When the first tunneling electron spans the first junction, the LUMO (HOMO) will be occupied (unoccupied). Therefore, the accessional energies required by the discrete level effect for the addition (reduction) of one electron to (from) the molecule through the first junction are: $E^+_{\text{dis1}} = E_{\text{LUMO}} - E_F$, $E^-_{\text{dis1}} = E_F - E_{\text{HOMO}}$. After getting or losing one electron, the molecule will be ionized with a partially occupied level. The E_F will shift up/down to coincide with this partially occupied level. Therefore, there is no accessional energy required by the discrete level effect for the tunneling of the second junction: $E^+_{\text{dis2}} = E^-_{\text{dis2}} = 0$. Although the precise position of the E_F shows some randomness in the measurements, it locates near the middle of the HOMO and LUMO generally when the molecule is neutral. If we assume that the position of the Fermi level lies in the middle of HOMO and LUMO, the CB thresholds of the negative and positive voltages are:

$$V_+ = V_- = \frac{C_1 + C_2}{C_2 e}\left(E_C(0) + \frac{E_g}{2}\right), \qquad E_g = E_{\text{LUMO}} - E_{\text{HOMO}}. \tag{3}$$

Thereby, there are no regular and significant rectifying effects.

For a molecule with a half-occupied HOMO, the Fermi level of the molecule coincides with this half-occupied level when the molecule is neutral. Accordingly, there is no accessional energy required by the discrete level effect for the tunneling of the first junction: $E^+_{\text{dis1}} = E^-_{\text{dis1}} = 0$. Then the CB thresholds of the first junction are deduced to be:

$$V^1_+ = V^1_- = \frac{e}{2C_2}. \tag{4}$$

After receiving or losing one electron, the molecule will have fully occupied HOMO and unoccupied LUMO. For the tunneling of the second junction, therefore, the accessional energies required by the discrete level effect are: $E^-_{\text{dis2}} = E^-_F - E^-_{\text{HOMO}}$ and $E^+_{\text{dis2}} = E^+_{\text{LUMO}} - E^+_F$, where E^-_F and E^-_{HOMO} are the Fermi level and HOMO energy position after the molecule gets an electron, E^+_F and E^+_{LUMO} are the Fermi level and LUMO position after the molecule loses one electron. And the CB thresholds of the second junction are:

$$\begin{aligned} V^2_+ &= [E^-_{\text{dis2}} + E^-_C(1)]\frac{C_1 + C_2}{eC_1}, \\ V^2_- &= [E^+_{\text{dis2}} + E^+_C(-1)]\frac{C_1 + C_2}{eC_1}. \end{aligned} \tag{5}$$

The precise positions of E^-_F and E^+_F also show some randomness. Nevertheless, E^-_F (E^+_F) generally lies near the middle of the HOMO and LUMO of the negative (positive) ionic molecule [as shown in Fig. 3(b)]:

$$\begin{aligned} E^-_{\text{dis2}} &\approx \frac{E^-_{\text{LUMO}} - E^-_{\text{HOMO}}}{2} \equiv \frac{E^-_g}{2} \\ E^+_{\text{dis2}} &\approx \frac{E^+_{\text{LUMO}} - E^+_{\text{HOMO}}}{2} \equiv \frac{E^+_g}{2}. \end{aligned} \tag{6}$$

Thus,

$$\begin{aligned} V^2_+ &= \left(1 + \frac{C_2}{C_1}\right)\frac{E^-_g}{2e} - \frac{e}{2C_1}, \\ V^2_- &= \left(1 + \frac{C_2}{C_1}\right)\frac{E^+_g}{2e} - \frac{e}{2C_1}, \end{aligned} \tag{7}$$

and

$$V_+ = \text{Max}\,(V^1_+, V^2_+), \qquad V_- = \text{Max}\,(V^1_-, V^2_-). \tag{8}$$

From the formula above, one can see that if E^-_g and E^+_g are significantly different, V_+ and V_- will be remarkably different generally. This is the main reason of the novel rectifying effect.

In our DBTJ, the capacitance C_1 of junction 1 between the STM tip and $C_{59}N$ molecule is estimated to be 0.012–0.015 aF by considering the tip as a semisphere [10]. Using that the thickness of the SAMs is about 9.68 Å [11], and the dielectric constant for SAMs on Au(111) is about 2.6 [12], we have calculated the capacitance C_2 of junction 2 between the $C_{59}N$ molecule and Au substrate to be about 0.15 aF [10]. Figure 4(a) shows the energy level diagram of a free $C_{59}N$ molecule, which is calculated using the density functional theory with local density approximation implemented with the Dmol^3 package [13]. The HOMO orbital of

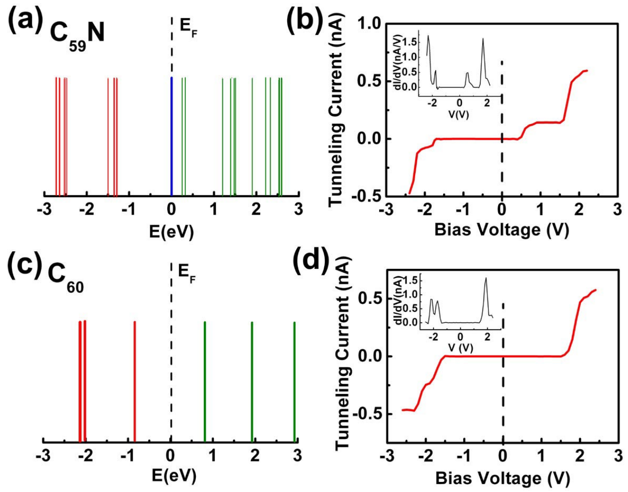


FIG. 4 (color online). The energy level structures of $C_{59}N$ (with the half-occupied HOMO being denoted by the blue line) (a) and C_{60} (c). And the calculated I-V curves of $C_{59}N$ (b) and C_{60} (d) using the parameters as $C_1 = 0.014$ aF, $C_2 = 0.15$ aF, $R_1 = 150$ MΩ, $R_2 = 50$ MΩ.

$C_{59}N$ is half occupied with one electron. The E_g^- and E_g^+ of $C_{59}N$ are 0.25 and 1.29 eV, respectively, and are consistent with previous calculations [14]. If we substitute these parameters to our deduced formula, it can be obtained easily that:

$$V_+ = \mathrm{Max}\,(V_+^1, V_+^2) = V_+^1 = \frac{e}{2C_2} = 0.53 \text{ V},$$

$$V_- = \mathrm{Max}\,(V_-^1, V_-^2) = V_-^2 = \left(1 + \frac{C_2}{C_1}\right)\frac{E_g^+}{2e} - \frac{e}{2C_1} \qquad (9)$$

$$= 1.76\text{–}2.04 \text{ V}.$$

These CB thresholds agree with the experimental ones. The simulated I-V curve is shown in Fig. 4(b), which is obtained by using the orthodox theory and the electronic structure of $C_{59}N$. One can find that it reproduces the experimental result very well. As a comparison, we also used the electronic structure of C_{60} [Fig. 4(c)] and the same junction parameters to simulate the I-V curve of C_{60} on the SAM; the result in Fig. 4(d) is in a good agreement with the measured one in Fig. 2(b). It should be pointed out that the orthodox model with a fractional residual charge Q_0 could produce an asymmetric CB behavior for a DBTJ, and the dipole moment of the molecule could also cause this kind of asymmetry. By the simulations and measurements on different $C_{59}N$ molecules, we rule out the possibility that the Q_0 or dipole moment effect is the main mechanism of the CB asymmetry for the $C_{59}N$ molecule.

In conclusion, we have demonstrated the rectifying effect of a single $C_{59}N$ molecule in a DBTJ using the SET effect. The half-occupied HOMO and the asymmetric shift of the Fermi level when the molecule is charged (i.e., the HOMO-LUMO gaps of $C_{59}N^-$ and $C_{59}N^+$ are distinctly different) are found to be responsible for the molecular rectification. Our study expands the application field of the SET devices for which the SET transistor [15] and negative differential-resistance diode have already been realized [7]. The realization of the $C_{59}N$ molecular rectifier also suggests a new direction to design the fullerene molecular devices [16] based on the on-ball doped fullerene molecules.

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*Author to whom correspondence should be addressed. Electronic address: jlyang@ustc.edu.cn

†Author to whom correspondence should be addressed. Electronic address: jghou@ustc.edu.cn

[1] R. L. Carroll and C. B. Gorman, Angew. Chem., Int. Ed. **41**, 4378 (2002); R. M. Metzger, Chem. Rev. **103**, 3803 (2003).
[2] S. Datta, A. Aviram, and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).
[3] S. Datta *et al.*, Phys. Rev. Lett. **79**, 2530 (1997); V. Mujica, M. A. Ratner, and A. Nitzan, Chem. Phys. **281**, 147 (2002); M. L. Chabinyc *et al.*, J. Am. Chem. Soc. **124**, 11730 (2002); M.-K. Ng, D.-C. Lee, and L. Yu, J. Am. Chem. Soc. **124**, 11862 (2002); K. Stokbro, J. Taylor, and M. Brandbyge, J. Am. Chem. Soc. **125**, 3674 (2003).
[4] C. Krzeminski *et al.*, Phys. Rev. B **64**, 85405 (2001); P. E. Kornilovitch, A. M. Bratkovsky, and R. S. Williams, Phys. Rev. B **66**, 165436 (2002); P. K. Hansma, Phys. Rep. **30**, 145 (1977); *Tunneling Spectroscopy: Capabilities, Applications, and New Techniques*, edited by P. K. Hansma (Plenum, New York, 1982), .
[5] T. Grosser *et al.*, Angew. Chem., Int. Ed. Engl. **34**, 1343 (1995).
[6] B. Nuber and A. Hirsch, Chem. Commun. (Cambridge) **1996**, 1421 (1996).
[7] C. Zeng *et al.*, Appl. Phys. Lett. **77**, 3595 (2000).
[8] M. J. Butcher *et al.*, Phys. Rev. Lett. **83**, 3478 (1999).
[9] D. V. Averin and K. K. Likharev, in *Mesoscopic Phenomena in Solids*, edited by B. Al'tshuler, P. Lee, and R. Webb (Elsevier, New York, 1991).
[10] B. Wang *et al.*, Phys. Rev. B **63**, 35403 (2001).
[11] N. Camillone III *et al.*, Langmuir **12**, 2737 (1996).
[12] M. D. Porter *et al.*, J. Am. Chem. Soc. **109**, 3559 (1987).
[13] Dmol^3 is a density-function-theory-based package with atomic basis distributed by Accelrys. [B. Delley, J. Chem. Phys. **92**, 508 (1990)].
[14] W. Andreoni, F. Gygi, and M. Parrinello, Chem. Phys. Lett. **190**, 159 (1992); F. Chen, D. Singh, and S. A. Jansen, J. Phys. Chem. **97**, 10958 (1993).
[15] M. Devoret and C. Glattli, Phys. World **11**, 29 (1998).
[16] H. Park *et al.*, Nature (London) **407**, 57 (2000).