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# Large rectification ratio induced by nitrogen (boron) doping in graphene nanoribbon electrodes for OPE junctions

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## ABSTRACT

Using nonequilibrium Green's function method combined with density functional theory, we present electronic transport properties for a molecular device constructed by an oligomeric phenylene ethynylenes (OPE) molecule between two zigzag-edge graphene nanoribbon (zGNR) electrodes. Nitrogen and boron dopants are introduced into one electrode, which makes the molecular junctions to have obvious rectifying behaviors. The conductance properties are closely related to the position and the kind of impurity atoms in electrodes. Moreover, the *I*–*V* curve of the junction, which is boron doping at the edge, displays unidirectional features in the studied bias region, and large rectification ratios up to $10^3$ are obtained. The mechanism of the performance is analyzed in terms of transmission spectra combined with molecular projected self-consistent Hamiltonian and electrode band structures under different bias voltages. Symmetry analyses of the Bloch wave functions of the corresponding subbands and the frontier molecular orbitals are also applied to reveal the rectifying behavior.

## 1. Introduction

Since Aviram and Ratner first proposed a molecular rectifier in 1974 [1], molecular rectifiers have been attracting considerable attention because they could lead to new miniaturization strategies in electronic devices [2]. As one knows, asymmetry in molecular devices is a key factor to induce rectification [3]. Thus, when one builds molecular diodes, either an asymmetric molecule or asymmetric arrangement of electrodes is necessary to display rectifying behavior. To study the effect of the asymmetric electrodes, we choose the symmetric phenylene ethynylene oligomer (OPE) molecule which has been demonstrated to have a favorable conducting property due to $\pi$-conjugated delocalized frontier orbitals [4,5]. Thus, OPE is taken to be an attracting building block for molecular electronic components [6–8].

As one knows, how to link between molecule and electrodes is a dominant issue to determine charge transport properties for molecular devices [4,9,10]. The metallic electrodes are often used to construct molecular junctions [11,12]. Recently, as one kind of graphene nanostructures, graphene nanoribbons (GNRs) fabricated by various approaches are potentially building blocks for molecular devices [13]. Edge geometry of a GNR is found to determine its electrical property [14–17]. A GNR with zigzag edge (zGNR) has metallic properties, which has been experimentally formed through tailoring nanotubes or etching graphene layers [18,19]. Nitrogen and boron dopants in GNRs are demonstrated to be feasible methods for modifying their electronic properties that depend on the doping sites [20–26].

Considering the perfect conductance of OPE molecules and interesting properties of doped GNRs, in present work, we explore the electronic transport properties of OPE molecules anchored with a carbon atom sandwiched between a pristine zGNR electrode and a periodic N- or B-doped zGNR electrode, by applying density functional theory (DFT) in combination with nonequilibrium Green's function (NEGF) method. It is noticed that the *I*–*V* curves present obvious rectifying characteristics that the currents at negative bias are much larger than those at positive bias. The analysis of the transmission spectra, the central region's molecular projected self-consistent Hamiltonian eigenvalues and the band structures of electrodes reveal an underlying mechanism of the observed rectification. The conductance and rectifying behaviors of the molecular junction are observed to be dependent on the doping element and doping site of zGNR electrodes. Therefore asymmetric doped zGNR electrodes can be taken into account to design molecular rectifiers.

## 2. Model and method

As shown in Fig. 1, the molecular junctions consist of an OPE molecule and two zGNR electrodes, where M1 and M2 have nitrogen dopants at the center and the edge of right zGNR electrode,

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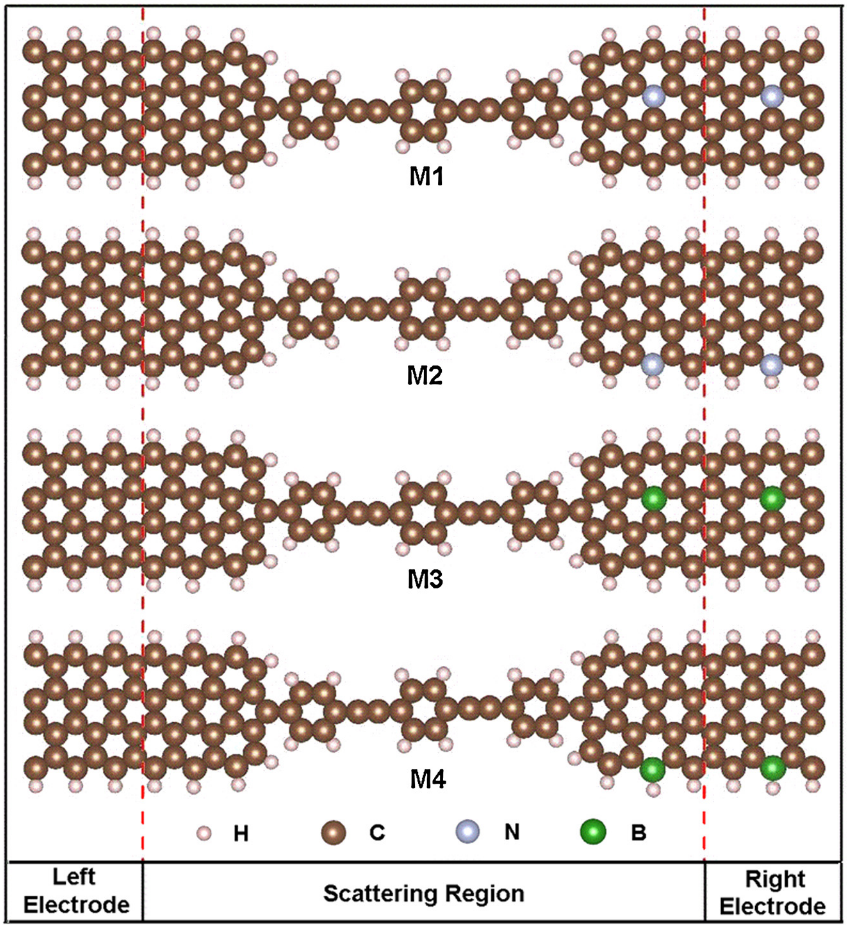

**Fig. 1.** Schematic structures of OPE molecular junctions with zGNR electrodes. Right electrodes of M1, M2, M3, and M4 are periodic center N-doped, edge N-doped, center B-doped, and edge B-doped, respectively.

respectively, while M3 and M4 dope boron atoms in the same way. In our calculation, the molecular junctions are divided into three regions, a left electrode, a central scattering region, and a right electrode. Six layer atoms on each electrode are included in the scattering region to screen the potential effect of the embedded molecule to the electrodes, and the rest parts of zGNRs serve as the left and the right semi-infinite electrodes. Edge carbon atoms of zGNRs are saturated by hydrogen atoms to eliminate the dangling bonds. Furthermore, OPE molecule connects electrodes through a five-membered ring [27–29], which forms a steady interface to reduce contact resistance.

The geometries are optimized in SIESTA package [30] with the maximum force on each atom is smaller than 0.02 eV/Å, which are based on the *ab initio* calculation. Optimization results show that the benzene connecting the left (right) electrode has an approximate 20° dihedral angle with the electrode plane, which is caused by the hydrogen steric hindrance between OPE and electrode, while the middle benzene is parallel to electrode plane. Improved Troullier–Martins type norm-conserving pseudopotentials [31] represent the core electrons and the local-density approximation (LDA) is used for the exchange–correlation potential. The transport properties are calculated by nonequilibrium Green's function method within TranSIESTA package [32]. In our calculations, a single-$\zeta$ plus single polarization (SZP) basis set is employed for all atoms, and the self-consistency was controlled by a numerical tolerance of $10^{-4}$ eV. The Brillouin zone has been sampled with $1 \times 1 \times 100$ points within the Monkhorst–Pack $\kappa$-point method. The transmission spectrum, which represents the transmission probability, can be calculated by the following equation:

$$T(E,V_b) = Tr\left[\Gamma L(E,V_b)G(E,V_b)\Gamma R(E,V_b)G^{\dagger}(E,V_b)\right], \qquad (1)$$

where $G(E,V_b)$ is the retarded Green's function of scattering region, and $\Gamma_{L/R}$ is the coupling matrix of left/right electrode, respectively. The current through the junctions is calculated by the Landauer–Büttiker formula [33],

$$I(V_b) = \frac{2e}{h}\int T(E,V_b)\left[f_L(E-\mu_L) - f_R(E-\mu_R)\right]\mathrm{d}E, \qquad (2)$$

where $f_{L/R}(E) = 1/\left[1 + e^{(E-\mu_{L/R})/K_B T}\right]$ is the Fermi–Dirac distribution function, and $\mu_{L/R}$ is the electrochemical potential of the left/right electrode.

## 3. Results and discussion

We first investigate the transport properties of those junctions mentioned above. Fig. 2 shows the calculated current–voltage (*I*–*V*) curves for the devices within bias range (−1.4 V, 1.4 V). The current values at negative bias voltages are obviously larger than those at positive counterparts, displaying significant rectification in these junctions. For the purpose of characterizing the rectifying properties, we define the bias-dependent rectification ratio as $RR(V) = |I(-V)/I(V)|$, which is shown in the inset of Fig. 2. For M1, the current values rise moderately before −0.8 V, but following with a sharp increase from 0.1 μA to 1.6 μA within the negative voltage range (−0.8 V, −1.4 V). However, the current values at positive voltages are quite small before 1.0 V. The maximum