Modulation of the spin transport properties of the iron-phthalocyanine molecular junction by carbon chains with different connection sites

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ABSTRACT

Based on the non-equilibrium Green's function method combined with the density functional theory, the spin transport properties of an iron-phthalocyanine (FePc) molecule connected to two Au electrodes by carbon chains are investigated, and three kinds of connecting position between FePc molecule and carbon chains are considered. It is found that the spin filtering effect and the negative differential resistance (NDR) behavior in these systems can be achieved in the calculated bias region. However, the efficiency and the bias region of spin filtering are affected significantly by the connecting positions. The above results are explained by the spin-resolved transmission spectrum, electron transmitting path, molecular projected self consistent Hamiltonian state, and the local density of states (LDOS) analyses. Our calculations demonstrate a promising modification for developing molecule spintronic devices.

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1. Introduction

In recent years, the single-molecule device has been an interesting topic due to the progress in experimental techniques for manipulating individual molecules [1–3] and the availability of first-principles method to describe the electrical properties of devices [4–6]. Many novel and promising physical properties have been demonstrated in various kinds of molecular systems, including rectifying [7,8], switching [9,10], negative differential resistance (NDR) [11,12], field effect transistors [13,14], and spin filtering [15,16]. Of particular interests among the large number of single-molecule devices are the molecule spintronic device due to its importance in next-generation electronics systems, and the search for suitable spintronic materials is a basic but crucial task. The metal phthalocyanines (MPcs) and its derivatives display a surprising variety of functions due to their tunable electronic and magnetic properties by changing the central transition metal atom. The spin transport properties of MPcs (M = Mn, Fe, Co, Ni, Cu, and Zn) sandwiched between two single-walled carbon nanotubes were investigated, but only MnPc and FePc can act as nearly perfect spin filters [17].

The symmetry-matched interaction between CuPc and the electrodes is important to enhance the electron transmission [18], Liu et al. found that the adsorbed small molecules show diverse effects which depend on the connecting position between the metalloporphyrin and the electrodes [19]. Generally, the single-molecule magnet as stated above was set to be connected to gold electrodes with sulfur atoms [20,21], also connected to carbon nanotube (ACNT) electrodes or graphene nanoribbons (GNR) electrodes by carbon atoms [22,23]. In addition, carbon atomic chains have been achieved recently via chemical methods [24] and studied widely [25–28], and the magnetic and electronic properties of the carbon chain complex system with GNRs can be tuned by the shape of graphene edges (armchair or zigzag) [25] and hybrid structures [26]. Zeng et al. proposed that carbon chain bridging GNR electrodes can be as a good spin-filter, but the bias region for such spin-filtering is less than 0.2 V [27]. On the other hand, the connection between chain and electrode such as paralinkage and meta-linkage in benzene also can lead to different conductance and spin effect [28].

In this paper, we examine the spin transport properties of FePc molecule sandwiched between two gold electrodes through carbon chain by employing the non-equilibrium Green's function method combined with the density functional theory, and three kinds of connect position between FePc molecule and carbon chain are

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considered. Our calculated results clearly reveal that the efficiency and the bias region of spin filtering are affected significantly by the connecting position between the FePc and carbon chain.

2. Model and method

The molecular device we study is illustrated schematically in Fig. 1, where the FePc molecule is bridged between two Au (111) electrodes through the carbon chain consisting of nine carbon atoms. Three models, M1 ~ M3, are considered depending on the connecting position between the FePc and the carbon chain. For M1, the left and right carbon chains are symmetrically connected to the two carbon atoms of the left and right benzenes of FePc, respectively, but connected to its one carbon atom of the upper and lower benzenes for M2. For M3, the left carbon chain is connected to two carbon atoms of the left benzene, and but the right carbon chain is connected to one carbon atoms of the lower benzene. The device composes of the left electrode, scattering region, and right electrode, marked by L, C, and R, respectively, and a 15 Å vacuum slab is used to eliminate an interaction between Au electrodes and neighboring cells. The optimization and calculations of electronic structure of geometry are performed by using the density functional theory (DFT) combined with the non-equilibrium Green's function (NEGF) method as implemented in latest version of Atomistix ToolKit (ATK) [29,30]. We employ Troullier-Martins norm-conserving pseudopotential to present the atom core and linear combinations of atom orbitals to expand the valence state of electrons. The spin generalized gradient approximation (SGGA) is used as the exchange-correlation functional, and the wave functions of all atoms are expanded by double-zeta polarized (DZP) basis set. The k-point sampling is 1, 1, and 150 in the x, y, and z directions, respectively, and the cut off energy is set to 150 Ry.

The current I in systems as a function of the applied external bias V, can be calculated from the Landauer-like formula [31]: $I_\sigma = (e/h) \int_{-V/2}^{V/2} T_\sigma(E, V) dE$, where $\sigma = \uparrow$ (spin up) and $\downarrow$ (spin down). The region of the bias window is $[-V/2, +V/2]$, $T_\sigma(E,V)$ is the bias-dependent transmission coefficient. In our calculations, the average Fermi level, an average value of the chemical potential of the left and right electrodes, is set as zero.

3. Results and discussion

Fig. 2 demonstrates the magnetism for M1~M3 with the isosurface of spin density ($\nabla\rho = \rho_{up} - \rho_{down}$) at zero bias. The cyan and magenta colors stand for the up-spin and down-spin components, respectively. One can see that all the Fe atoms for three models are strong spin-polarized, which shows an antiparallel feature as compared with the adjacent nitrogen (carbon) atoms. In other
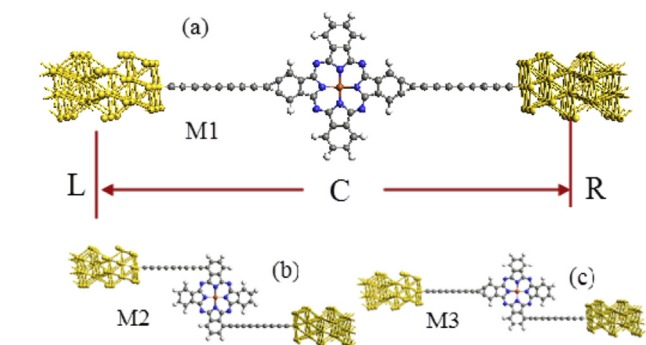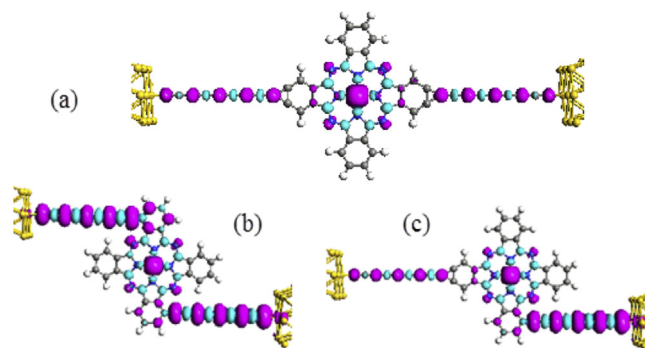

Fig. 2. The isosurface of spin density ($\Delta\rho = \rho_{up} - \rho_{down}$) for M1~ M3.

word, the magnetism of FePc molecule mainly origins from Fe atom and carbon atoms of the carbon chain which are strong spin-polarized for M2 compared with M1. In fact, the magnetism of chain atoms after relaxation completely depends on the presence of unsaturated carbon bonds, which is responsible for magnetism in all carbon nanostructures. For 9C chain of M2, it has 8 C—C bonds and the exact alternation of single and triple bonds cannot thus be achieved. Therefore, the bond type switches from single/triple (at the chain ends) to double/double (in the middle of the chain), resulting in some uncompensated charge delocalized on the chain. But For 9C chain of M1, the end of chain is connected to two carbon atoms of benzene on FePc, and the double/double except for the carbon atom connected to the Au electrode, the uncompensated charge delocalized on the chain is one half of M2 chain. For M3, the left (right) carbon chain shows a weak (strong) magnetism.

We calculate the spin-polarized current−voltage (I−V) characteristics for M1 ~ M3, as shown in Fig. 3(a) ~ (c). For M1 ~ M3, the current of the down-spin state increases quickly at lower bias and then decreases with increasing the bias, indicating the interesting negative differential resistance (NDR) behavior, which is very important in the field of electronic technology. However, the up-spin current keeps only a very small value within the whole bias region for M3, moderate for M1, the larger value for M2. To study spin-filter effects, we define the spin-filter efficiency (SFE) at finite bias as $\eta = \left|\frac{I_{up}-I_{down}}{I_{up}+I_{down}}\right| \times 100\%$, and the SFE at zero bias can be obtained based on the equation $\eta = \left|\frac{T_{up}-T_{down}}{T_{up}+T_{down}}\right| \times 100\%$. As we know, the high spin-filter ability is very important for designing spintronic devices. Fig. 3(d) demonstrates the SFE for M1 ~ M3 from zero to 1.0 V. It is notable that the spin-filter efficiency is very large when the bias is less than 0.7 V, then decrease significantly to zero at 1.0 V for M1. M2 shows the unstable SFE between 17% and 85% in the whole bias range. However, M3 exhibits a perfect spin-filtering effect in the largest bias range and the smallest spin filter efficiency is found to be 90%.

To give a better explanation of the spin filtering effect, the spin-dependent transmission spectra for M1 ~ M3 at zero bias are shown in Fig. 4(a) ~ (c). The transmission spectrum of two spin channels is obviously different. The spin-up transmission coefficients are very tiny near the Fermi level for M1 and M3. In contrast, pronounced transmission peaks for the spin-down electron are observed in the vicinity of the Fermi level, which contributes to the current. Therefore the spin-down current is much bigger than the spin-up one, leading to a robust spin filtering effect. While for M2, up-and down-spin broad transmission peaks appear below and above the Fermi level, resulting in the increase of the current for up- and down-spin states at low bias and thus a weak SFE. We now turn to investigate the electron transmission pathway, which gives a clear

Fig. 1. The geometric structures, (a)–(c) correspond to models M1~ M3. L, R, and C mean the left and right electrodes, and the central scattering region, respectively.