Effect of proportion on rectification in organic co-oligomer spin rectifiers*

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The rectification behaviours in organic magnetic/nonmagnetic co-oligomer spin rectifiers are investigated theoretically. It is found that both the charge current and the spin current through the device are rectified at the same time. By adjusting the proportion between the magnetic and nonmagnetic components, the threshold voltage and the rectification ratio of the rectifier are modulated. A large rectification ratio is obtained when the two components are equal in length. The intrinsic mechanism is analysed in terms of the asymmetric localization of molecular orbitals under biases. The effect of molecular length on the rectification is also discussed. These results will be helpful in the future design of organic spin diodes.

Keywords: organic spintronics, rectification, co-oligomer, proportion

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1. Introduction

Molecular rectification, which manifests an asymmetric current-voltage characteristic on the scale of a single molecule, has attracted a lot of attention in the past decade.[1,2] Experiments have shown that molecular rectification may be realized by designing a device with asymmetric molecule–electrode interfaces or using asymmetric molecule.[3−6] Among these, organic diblock co-oligomers are particularly attractive as efficient rectifiers where the rectifying direction is controlled by the molecular orientation.[4,5] Importantly, such rectification is believed to arise from the intrinsic asymmetry of the molecule, which is advantageous to avoid the uncontrollable molecule–electrode interface and offers the possibility of being integrated into a molecular circuit.

The new field of spintronics,[7] which builds functional devices based on electronic spin, has also triggered a large interest in designing spin rectifiers. A charge current (CC), which is the sum of currents with different spins $I_c = I_\uparrow + I_\downarrow$, is a scalar and the charge-current rectification means an asymmetric magnitude of current. But a spin current (SC), defined as $I_s = \frac{\hbar}{2e}(I_\uparrow - I_\downarrow)$, contains both the amplitude of the current and its spin-polarized orientation. Thus the spin-current rectification may emerge in two possible forms, the asymmetric magnitude of the current and the reversal of its spin-polarized orientation. A spin rectifier requires an asymmetric device structure or potential field in the electron spin degree of freedom, for example, a semimagnetic semiconductor heterostructure and a quantum wire (dot) sandwiched between a ferromagnetic and a normal-metal lead or in an asymmetric magnetic field.[8−12] The utilization of organic molecules in spintronics, which led to the emergence of the field of organic spintronics or molecular spintronics,[13−15] generates the idea to design molecular spin rectifiers. Dalgleish and Kirczenow proposed a molecular spin diode by sandwiching a molecule between ferromagnetic and nonmagnetic contacts.[16] With the help of *ab-initio* calculations they found that both the CC and SC may be rectified simultaneously through the device. Other than the above extrinsic devices, in which an external magnetic field or two asymmetric electrodes are necessary, we also proposed a prototype of intrinsic organic spin rectifier with the form of a magnetic/nonmagnetic co-oligomer structure.[17] It has been demonstrated that the two kinds of spin-current rectification mentioned above can be realized through the device.

Beyond the design of molecular rectifiers, the

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search for a proper structure with a large rectification ratio is important for further applications. The structural asymmetry of a molecular rectifier is the key point in determining its rectification property. For a co-oligomer spin rectifier with a magnetic/nonmagnetic structure, the structural asymmetry is decided by the different materials of the magnetic and nonmagnetic moieties and the proportion between them. It has been known that adopting a magnetic molecule with large spin splitting in the co-oligomer is advantageous to obtain a large rectification ratio.[17] However, the effect of the proportion on the rectification still remains unclear. The proportion of a co-oligomer may be adjusted by changing the length of the two components in experiments, which will further modulate the molecular orbitals as well as their response to the bias. A detailed study is necessary for a comprehensive understanding of the rectification behaviour in the related structure. In this paper, we calculate the spin-dependent transport through a magnetic co-oligomer with different proportions to find out the relation between the rectification ratio and the proportion. The effect of molecular length on the rectification is also discussed. The paper is organized as follows: the model and the formulas are described in Section 2. In Section 3, we give the numerical calculation and the results are analysed. Finally, in Section 4, a summary is given.

2. Model and method

As proposed in Ref. [17], the structure of our calculated organic spin rectifier is shown in Fig. 1. The whole device is modeled as a quasi-one-dimensional chain. A magnetic co-oligomer is sandwiched between two semi-infinite one-dimensional metallic electrodes. The central molecule is composed of a left ferromagnetic molecule and a right nonmagnetic one, for example, poly-BIPO+polyacetylene. The poly-BIPO is a ferromagnetic molecule, which is synthesized by replacing the H atom of polyacetylene alternately with a heterocycle containing an unpaired electron. There is spin correlation between the residual spins in the side radicals and the π-electron spins in the conjugated main chain. As a result, all the radical spins will try to form a ferromagnetic order, as shown by the arrows in Fig. 1. The central magnetic co-oligomer can be well described with an extended SSH+Heisenberg (SSH=Su-Schrieffer-Heeger) model,[17−19]

$$\begin{aligned} H_{\rm m} = & -\sum_{n,\sigma}[t_0 - \alpha(u_{n+1}-u_n)] \\ & \times (c^+_{n,\sigma}c_{n+1,\sigma} + c^+_{n+1,\sigma}c_{n,\sigma}) \\ & + \frac{K}{2}\sum_n (u_{n+1}-u_n)^2 \\ & + J_{\rm f}\sum_n^{N_1} \delta_{n,{\rm e}} \boldsymbol{S}_{n{\rm R}} \cdot \boldsymbol{S}_n. \end{aligned} \tag{1}$$

Here, t_0 is the hopping integral of the π electrons between the n-th and $(n+1)$-th sites in the main chain for the uniform lattice; α is the coupling parameter between the π electrons and the lattice atoms, and u_n is the lattice displacement at site n. $c^+_{n,\sigma}$ ($c_{n,\sigma}$) denotes the creation (annihilation) operator of an electron at the n-th site with spin σ. The second term on the right-hand side of Eq. (1) is the lattice elastic energy due to lattice distortion where K is the elastic coefficient between the lattice carbon atoms, and the last term describes the spin correlation between the spin $\boldsymbol{S}_n$ of the π electron and $\boldsymbol{S}_{n{\rm R}}$ of the side radical R, which only exists in the magnetic segment with N_1 sites. $J_{\rm f}$ stands for the spin coupling strength, and $\delta_{n,{\rm e}}$ means that the side radicals connect and so couple only with the even number sites of the main chain. For simplicity, the radical spin is further treated in a mean-field approximation as $\langle S^z_{n{\rm R}}\rangle$,[15] where $\langle\cdots\rangle = \langle G|\cdots|G\rangle$ is the average with respect to the ground state $|G\rangle$ of the side radical R.

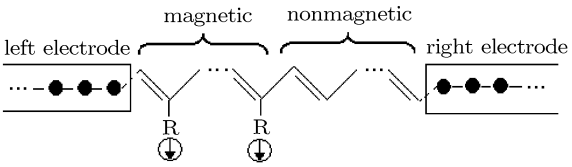


Fig. 1. Schematic structure of a metal/magnetic-nonmagnetic co-oligomer/metal spin rectifier.

The two metallic electrodes are symmetric, which is described by a one-dimensional single band tight-binding model with the on-site energy $\varepsilon_{\rm f}$ and the nearest neighbouring transfer integral $t_{\rm f}$. The interfacial coupling between the electrodes and the molecule is assumed to take place only at the nearest connecting atoms. To avoid the asymmetric effect caused by the interfaces, the coupling parameters are set equally and denoted by a hopping integral $t_{\rm fm}$, which is simplified by neglecting the spin-related scattering at the interfaces.

When a bias V is applied, an external field E will be generated from the bias between the two electrodes. If the bias is not too large, the field is assumed to be uniform along the whole molecule chain with $E = V/[(N-1)a]$, where N is the total number of sites in the molecule and a is the lattice constant. The

spatial potential is described by the following Hamiltonian:

$$H_{\rm E} = -\sum_{n,\sigma} |e|\, E \left[\left(n - \frac{N+1}{2}\right) a + u_n\right] c^{+}_{n,\sigma} c_{n,\sigma} + \sum_{n} |e|\, E \left[\left(n - \frac{N+1}{2}\right) a + u_n\right]. \quad (2)$$

Here, the first term on the right hand side of Eq. (2) is the electric potential energy of all π electrons, where e is the electronic quantity of an electron; the second term is the electric potential energy of the lattice sites (ions). Then, the ground state of the magnetic co-oligomer under the electric field can be obtained self-consistently by solving the electronic eigenequation and minimizing the total energy of the molecule.[17,18]

The spin-dependent current through the device is calculated with the Landauer–Büttiker formula as[20,21]

$$I_\sigma(V) = \frac{e}{h}\int_{-\infty}^{+\infty} {\rm Tr}[\boldsymbol{\Gamma}_{\rm l} G_{\sigma\sigma}(E,V) \boldsymbol{\Gamma}_{\rm r} G^{+}_{\sigma\sigma}(E,V)] \times [f_{\rm l}(E) - f_{\rm r}(E)]\,{\rm d}E. \quad (3)$$

Here, the trace term in the integrand is the spin-dependent electron transmission coefficient function $T_{\sigma\sigma}(E,V)$. $G_{\sigma\sigma}(E,V)$ is the spin-related single electron Green's function in the form of

$$G_{\sigma\sigma}(E,V) = \frac{1}{E - H^{\sigma}_{\rm m} - H^{\sigma}_{\rm E} - \Sigma_{\rm l} - \Sigma_{\rm r}},$$

where $\Sigma_{\rm l}$ and $\Sigma_{\rm r}$ are the self-energy operators due to coupling to the left and right electrodes, $H^{\sigma}_{\rm m}$ and $H^{\sigma}_{\rm E}$ correspond to the electron Hamiltonian with spin σ in Eqs. (1) and (2), $\Gamma_{\rm l(r)} = {\rm i}[\Sigma_{\rm l(r)} - \Sigma^{+}_{\rm l(r)}]$ denotes the broadening matrix, $f_{\rm l(r)}(E) = 1/\{1 + \exp[(E - \mu_{\rm l(r)})/k_{\rm B}T]\}$ is the Fermi distribution function of the metal electrode with chemical potential $\mu_{\rm l(r)} = E_{\rm F} \pm \frac{1}{2}$ eV and Fermi energy $E_{\rm F}$. Note that the spin-flip transport is not considered here since the spin–orbit coupling and hyperfine interaction in organic materials are usually very weak, which will result in a large spin relaxation length.[22,23]

The values of the parameters in a numerical calculation for the magnetic co-oligomer are taken as $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21.0$ eV/Å^2, and $J = J_{\rm f}/t_0 = 1.5$. These values have been generally adopted for the ferromagnetic molecule poly-BIPO and normal molecule polyacetylene.[17,18,24] The parameters of the electrodes are taken as $\varepsilon_{\rm f} = 0$, $t_{\rm f} = 2.5$ eV. The interfacial coupling between the molecule and the electrodes is $t_{\rm fm} = 1.0$ eV. The calculation is performed at a low temperature of $T = 10$ K to avoid spin fluctuation in the electron-transport process.

3. Results and discussion

To investigate the role of proportion, the length of the magnetic co-oligomer is fixed with $N = 30$. The proportion between the magnetic segment and the nonmagnetic one is denoted by their length with $P = N_1/N_2$. We firstly calculate the CC and SC through the device in three representative cases, $P = 0.5$, $P = 1.0$ and $P = 2.0$. The results are shown in Fig. 2. Obviously, both the CC and SC are rectified for all the three cases in the bias range of [−1.0 V, +1.0 V]. The current in the positive bias region is much larger than that in the negative bias region. The spin-current rectification appears in the form of the asymmetric amplitude of the SC upon the reversal of bias while the spin polarized orientation remains unchanged.[17] However, for the three cases one can find that both the threshold voltages and the magnitude of currents are modulated by the proportion. The largest current appears in the case of $P = 1.0$, where the device begins to conduct when $V > +0.6$ V and the magnitude of CC (SC) reaches about 1.7 (1.9) at +0.9 V. Increasing the proportion to $P = 2.0$, a much smaller threshold voltage of +0.25 V is observed and the current is slightly suppressed. When the proportion is decreased to $P = 0.5$, we find that the device begins to conduct current at a larger threshold voltage of +0.7 V and the magnitude of the CC (SC) is reduced to 1.0 (0.7) at +0.9 V. Usually the rectification efficiency of a diode is labeled by the rectification ratio.[25] Here, we define the charge-current rectification ratio (RR) and the spin-current

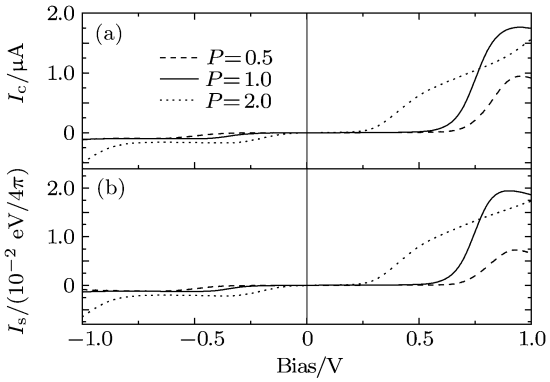


Fig. 2. (a) Calculated charge current and (b) spin current as a function of bias voltage at three proportions of $P = 0.5$, 1.0, 2.0, respectively.

rectification ratio (SRR) as $r_1 = -I_{\rm c}(+V)/I_{\rm c}(-V)$ and $r_2 = -I_{\rm s}(+V)/I_{\rm s}(-V)$, respectively. At the bias of $V = \pm 0.9$ V, it is found that an RR (SRR) of about

18:1 (16:1) is obtained for $P = 1.0$. The RR (SRR) decreases to about 11:1 (7:1) at $P = 0.5$ and 5:1 (5:1) at $P = 2.0$.

Further understanding can be achieved by investigating the spin-dependent transmission coefficients and their response to the bias for the above different proportions. The results at $V = 0$, ± 0.9 V are shown and compared in Fig. 3. It is found that the electronic transmission spectrum is spin-split due to the spin correlation in the magnetic molecule. At the bias voltages of ± 0.9 V, the (spin) current is dominated by the nearest spin-up transmission peak to the Fermi energy, which is contributed by the spin-up LUMO (lowest unoccupied molecular orbital) by examining the molecular eigenstates. This spin-up transmission peak is enhanced by the positive bias voltage and reduced by the negative bias voltage, which results in rectification. The intrinsic mechanism has been explained in a previous study as the bias-induced asymmetric electronic localization of the molecular orbital.[17] The change of the transmission spectrum caused by the proportion can be observed in two terms. One is that the spin splitting of transmission peaks is enhanced when the proportion P becomes larger. It is easy to understand that the increase of the magnetic segment will enhance the spin correlation in the magnetic co-oligomer. As a result, the spin-up LUMO becomes closer to the Fermi energy, which leads to a smaller threshold voltage for the device. Besides the spin splitting, the heights of spin-dependent transmission peaks are also modulated by the proportion, which is further modified by the applied bias. For example, at zero bias, the transmission peak of the spin-up LUMO at $P = 0.5$ is a little higher than that for other cases, but it becomes the lowest in the three proportions at the bias voltage of -0.9 V.

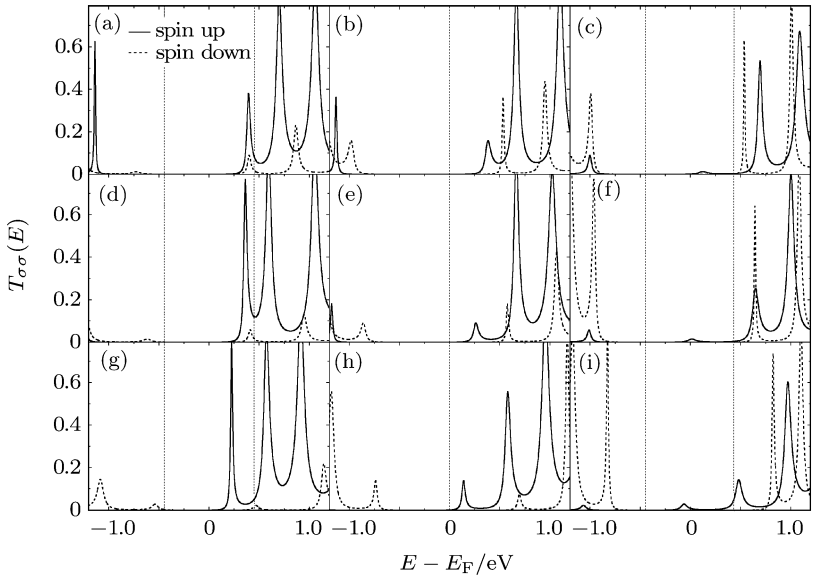


Fig. 3. Spin-dependent transmission near the Fermi energy at V=0, ± 0.9 V for different proportions. The vertical dash-dot lines indicate the chemical potentials of the electrodes, and the window between them is the conducting bias window. (a) $V = 0.9$ V, $P = 0.5$; (b) $V = 0$ V, $P = 0.5$; (c) $V = -0.9$ V, $P = 0.5$; (d) $V = 0.9$ V, $P = 1.0$; (e) $V = 0$ V, $P = 1.0$; (f) $V = -0.9$ V, $P = 1.0$; (g) $V = 0.9$ V, $P = 2.0$; (h) $V = 0$ V, $P = 2.0$; (i) $V = -0.9$ V, $P = 2.0$.

The magnitude of the transmission peak is related to the electronic localization of the molecular orbital. In Fig. 4 we calculate the electronic localization of the spin-up LUMO with bias for different proportions. The electronic localization of a molecular orbital at a bias is defined as[26] $\xi(V) = \sum_n |\varphi_n(V)|^4$, where $\varphi_n(V)$ is the wave function of the spin-up LUMO in Wannier representation. $\xi = 1/N$ stands for an extended state, while $\xi = 1$ denotes a completely localized orbital. We find that the localization increases with the positive bias and decreases with the negative bias, which is responsible for the rectification in nature. It is also found that the evolution of localization with bias depends on the proportion. The localization is sensitive to the bias at the proportion of $P = 0.5$ while it changes slowly at the proportion of $P = 2.0$. The

largest difference of localization between +0.9 V and −0.9 V is obtained at the proportion of $P = 1.0$, which induces a large rectification ratio.

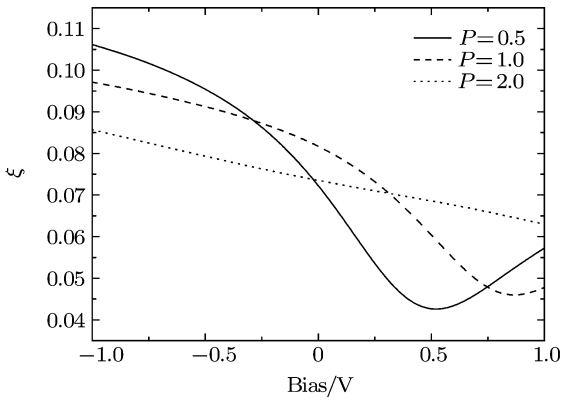


Fig. 4. Evolution of electronic localization of the spin-up LUMO with bias for different proportions.

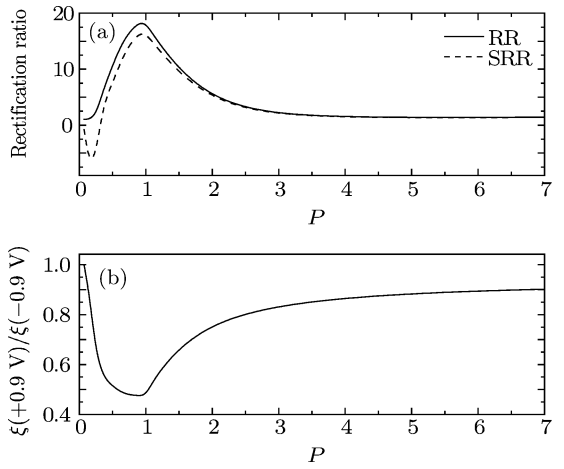


Fig. 5. (a) Dependence of rectification ratio on the proportion. The bias is taken as $V = \pm 0.9$ V. (b) Comparison of electronic localization for the spin-up LUMO between $V = +0.9$ V and $V = -0.9$ V.

To clarify the dependence of the rectification ratio on the proportion, we calculate the rectification ratio of the CC and SC under the bias of $V = \pm 0.9$ V. The result is shown in Fig. 5(a). Obviously, in the limit of $P \to 0$ the molecule is only composed of the nonmagnetic segment. The spatial asymmetry vanishes and there is no rectification. With the increase of P, the rectification appears due to the structural asymmetry. The RR (SRR) increases quickly with P and reaches a maximum value of about 18:1 (16:1) at the proportion of $P = 1.0$. Note that a little tip in the dashed line with a negative SRR is visible when $P < 0.3$, which means that the spin-polarized orientation of SC is reversed. This is because spin-down transmission is involved in the conducting bias windows and dominates the current under that condition. After the proportion exceeds 1.0, the RR (SRR) decreases with P and tends to unity when the proportion is above 3. This result indicates that it is favorable to obtain a large rectification ratio when the two moieties of co-oligomer are equal in length. To understand the dependence of the rectification ratio on the proportion, we also calculated the electronic localization of the spin-up LUMO versus the proportion, which is found to be the main conducting channel. To show the bias-induced asymmetry of the localization, we give the ratio of $\xi(+0.9\text{ V})/\xi(-0.9\text{ V})$ in Fig. 5(b). Obviously, the asymmetry of the electronic localization increases with P firstly and then drops when $P > 1$. The largest difference of the electronic localization appears at $P = 1.0$. This result is consistent with the change of rectification ratio shown in Fig. 5(a).

The dependence of the rectification ratio on the molecular length is also calculated, as shown in Fig. 6. Here, the proportion is fixed at $P = 1.0$ and the rectification ratio is calculated under the bias of $V = \pm 1.0$ V. It is found that the RR (SRR) increases almost linearly with the molecular length and then reaches a platform when $N > 30$. The rectification ratio is enhanced from about one at $N = 18$ to about 16 at $N = 34$. By examining the transmission we found that the platform is induced by the opening of more conducting channels at the negative bias of voltage. This result indicates that a relative long co-oligomer is advantageous to realize a strong rectification, which is consistent with other *ab-initio* calculations involving a co-oligomer molecular diode.[27]

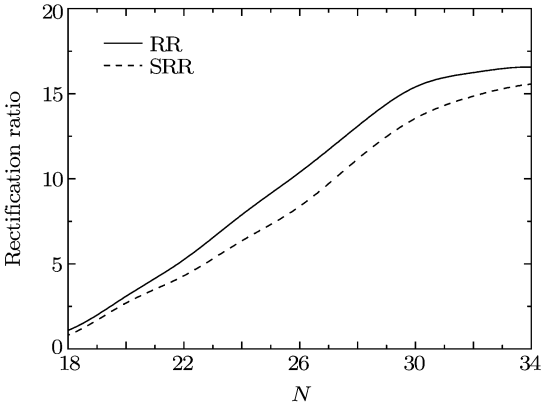


Fig. 6. Dependence of rectification ratio on the molecular length. The proportion is fixed at $P = 1.0$ and the rectification ratio is calculated under the bias of $V = \pm 1.0$ V.

4. Summary

To conclude, we have investigated the rectification behaviours of charge current and spin current in organic magnetic/nonmagnetic co-oligomers based

on different proportions between the magnetic moiety and the nonmagnetic one. The results indicate that a strong rectification effect tends to appear when the lengths of the two components are equal. The threshold voltage of the device may be reduced by increasing the magnetic segment. Further orbital analysis shows that the rectification comes from the asymmetric electronic localization of the spin-up LUMO under bias, which is further modulated by the proportion. We also find that a relatively long molecule is useful to obtain a large rectification ratio. It should be mentioned that although our calculations are based on a magnetic co-oligomer model, the results remain meaningful for normal donor–acceptor type co-oligomer molecular diodes because of their similar mechanism for rectification.[28] These results will be helpful to the further design of an efficient organic molecular rectifier in the fields of molecular electronics and organic spintronics.

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