Length dependence of rectification in organic co-oligomer spin rectifiers*

Gui-Chao Hu(胡贵超)†, Zhao Zhang(张朝), Ying Li(李营), Jun-Feng Ren(任俊峰), and Chuan-Kui Wang(王传奎)

School of Physics and Electronics, Shandong Normal University, Jinan 250014, *China*

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The rectification ratio of organic magnetic co-oligomer diodes is investigated theoretically by changing the molecular length. The results reveal two distinct length dependences of the rectification ratio: for a short molecular diode, the charge-current rectification changes little with the increase of molecular length, while the spin-current rectification is weakened sharply by the length; for a long molecular diode, both the charge-current and spin-current rectification ratios increase quickly with the length. The two kinds of dependence switch at a specific length accompanied with an inversion of the rectifying direction. The molecular ortibals and spin-resolved transmission analysis indicate that the dominant mechanism of rectification suffers a change at this specific length, that is, from asymmetric shift of molecular eigenlevels to asymmetric spatial localization of wave functions upon the reversal of bias. This work demonstrates a feasible way to control the rectification in organic co-oligomer spin diodes by adjusting the molecular length.

Keywords: organic spintronics, organic ferromagnet, rectification

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1. Introduction

Molecular rectification is an important concept in molecular electronics, which has been extensively investigated in the past decades.[1,2] Various designs have been involved in experimental and theoretical researches, like using asymmetric molecule-electrode interfaces[3] or asymmetric molecules.[4–6] Among these, conjugated diblock co-oligomers with a donor–acceptor (D–A) structure are particularly attractive as intrinsic molecular diodes owing to their repeatable performance and controllable rectification behaviors.[4,5] Especially, the rectifying direction in such diodes may be tuned with chemical methods such as protonation[7] or changing anchor group.[8,9]

The exploitation of the electron spin degree of freedom in spintronics also triggered a great deal of interest in pursuit of spin rectifiers.[10,11] Spin rectifiers mean the spin current (SC), defined as the difference between spin-up and spin-down currents, is asymmetric upon the reversal of bias voltage. The charge current (CC) is a scalar as the sum of spin-up and spin-down currents, and the rectification of CC is easy to understand as the asymmetric amplitude of current. However, the SC is a vector which contains two characteristics: the amplitude of the current and its spin-polarized orientation. The concept of spin-current rectification is more complicated than the normal charge-current rectification. In nature, two kinds of spin-current rectification may exist, asymmetric amplitude or different spin-polarized orientations of the spin current upon the reversal of bias, which can be called parallel spin-current rectification or antiparallel spin-current rectification, respectively.[12,13] The construction of spin rectifiers requires an asymmetric spatial structure in the spin degree of freedom. The first molecular spin rectifier was designed by Dalgleish and Kirczenow, where an organic molecule is coupled with one ferromagnetic metal and one nonmagnetic metal, where the spatial spin asymmetry comes from the external electrodes.[12] Recently, with the utilization of organic ferromagnets, we proposed an intrinsic organic spin rectifier with a magnetic/nonmagnetic co-oligomer structure,[13] where the charge-current rectification and spin-current rectification may be realized simultaneously or separately. The effects of proportion of the co-oligomer and the interfacial coupling with electrodes were also discussed.[14,15]

Upon the design of molecular spin rectifiers, a controllable rectification with a large rectification ratio is another important issue. As one of non-negligible factors, molecular length can be adjusted conveniently in experiments, which has been proved to tune the rectification in normal charge-current molecular diodes by *ab-initio* and model calculations.[16,17] Therefore, the length effect in organic spin diodes deserves to be considered, especially on the spin-current rectification. Here we will explore the length effect on the rectification in organic spin co-oligomer diodes by investigating the asymmetric evolution of the spin-dependent eigenstates under biases. The paper is organized as follows. In Section 2 the model and cal-

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†Corresponding author. E-mail: hgc@sdnu.edu.cn

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culation method will be introduced. In Section 3 the calculated results are discussed and a summary is given in Section 4.

2. Model and method

The calculation is based on a quasi-one-dimensional model of magnetic co-oligomer spin rectifier. As shown in Fig. 1, the magnetic co-oligomer is sandwiched between two metallic electrodes. The electrodes are noninteracting semi-infinite one-dimensional metallic chains. The central molecule is composed of the left magnetic molecule (such as poly-BIPO (poly(1,4-bis-(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxyl)-butAdiin))[18,19] and the right nonmagnetic one (such as polyacetylene). In the magnetic moiety, magnetic side radicals hang on the even-number sites, each of which contains an unpaired electron and has an uncompensated spin $\boldsymbol{S}_{nR}$. The magnetic co-oligomer can be described with an extended SSH+Heisenberg (SSH: Su–Schrieffer–Heeger) model[20,21]

$$H_m = -\sum_{n,\sigma} t_{n,n+1}(c^+_{n,\sigma}c_{n+1,\sigma} + c^+_{n+1,\sigma}c_{n,\sigma}) + J_{\rm f}\sum_{n}^{N/2}\delta_{n,{\rm e}}\boldsymbol{S}_{nR}\cdot\boldsymbol{S}_n + \frac{K}{2}\sum_n (u_{n+1}-u_n)^2, \quad (1)$$

where $t_{n,n+1}$ is the hopping integral of the π electrons between the n-th and $(n+1)$-th sites along the main chain with total N sites, which is modulated due to a possible lattice distortion with $t_{n,n+1} = t_0 - \alpha(u_{n+1}-u_n)$. Here t_0 is the hopping integral for the uniform lattice and α is the electron–lattice coupling parameter, u_n is the lattice displacement at site n and $c^+_{n,\sigma}$ ($c_{n,\sigma}$) the creation (annihilation) operator of an electron at the n-th site with spin σ. The second term in Eq. (1) describes the spin correlation between spin $\boldsymbol{S}_n$ of the π electron and $\boldsymbol{S}_{nR}$ of the side radical R. $J_{\rm f}$ is the coupling strength and N is the number of total sites of the co-oligomer. We treat the side radical spin in a mean-field approximation as $\langle S^z_{nR}\rangle$, 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. $\delta_{n,{\rm e}}$ means that the side radicals connect and so couple only with the even number sites of the left moiety. The last term is the lattice elastic energy due to lattice distortion with elastic coefficient K as a constant through the whole chain.

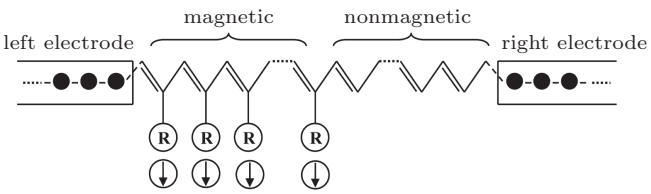


Fig. 1. Schematic structure of a metal/magnetic-nonmagnetic co-oligomer/metal spin diode.

The two metallic electrodes are symmetric and described by a one-dimensional single band tight-binding model with on-site energy $\varepsilon_{\rm f}$ and the nearest neighboring transfer integral $t_{\rm f}$. To focus on the intrinsic property of the molecule, the interfacial coupling between the electrodes and the molecule are simplified and set equally as $t_{\rm lm} = t_{\rm rm} = t_{\rm fm}$.

Under a bias V, an external field E will be generated from the bias between the two electrodes. The spatial potential is described by the following Hamiltonian:

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

with e being the electronic quantity of an electron and a the lattice constant. The first term is the electric potential energy of all π electrons and the second term is the electric potential energy of the lattice sites (ions). It is assumed that the field is uniform along the whole molecule chain and $E = V/[(N-1)a]$. This linear treatment is suitable for the case that the bias applied on the molecule is not too large.

The current through the device with spin σ is calculated with the Landauer–Büttiker formula[22]

$$I_\sigma(V) = \frac{e}{h}\int_{-\infty}^{+\infty} T_{\sigma\sigma}(E,V)[f_{\rm l}(E) - f_{\rm r}(E)]{\rm d}E. \quad (3)$$

Here, $T_{\sigma\sigma}(E,V)$ is the spin-dependent transmission probability determined from the lattice Green's function through the Fisher–Lee relation[22]

$$T_{\sigma\sigma}(E,V) = {\rm Tr}[\Gamma_{\rm l}G_{\sigma\sigma}(E,V)\Gamma_{\rm r}G^+_{\sigma\sigma}(E,V)],$$

where $G_{\sigma\sigma}(E,V)$ is the spin-related single-particle Green's function of the central molecule and $\Gamma_{\rm l(r)}$ denotes the broadening matrix due to coupling to the electrodes. $f_{\rm l(r)}(E) = 1/\{1+\exp[(E-\mu_{\rm l(r)})/k_{\rm B}T]\}$ is the Fermi function of the metal electrode with chemical potential $\mu_{\rm l(r)} = E_{\rm F} \pm eV/2$ and Fermi energy $E_{\rm F}$. Then both the CC and SC through the device can be obtained with $I_{\rm c} = I_\uparrow + I_\downarrow$ and $I_{\rm s} = \frac{\hbar}{2e}(I_\uparrow - I_\downarrow)$.

The calculation is performed as follows. First, the ground state of an isolated co-oligomer (poly-BIPO + polyacetylene) molecule is obtained by a self-consistent iteration method.[20,23] It is found that, in the ground state or under a low temperature, the radical spins in poly-BIPO form a ferromagnetic order.[20,23] Then, the spin-dependent Green function and the transmission probability are calculated. Finally, the spin-dependent current is obtained from Eq. (3).

We carry out numerical calculations by taking the values of the above parameters as those generally adopted.[13,20,23] For the magnetic co-oligomer, we use the parameters of poly-BIPO and polyacetylene with $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, and $J = J_{\rm f}/t_0 = 1.0$. The elastic constant of the carbon atom chain is $K = 21.0$ eV/Å^2. The parameters of the electrodes are taken as $\varepsilon_{\rm f} = 0$, $t_{\rm f} = 2.5$ eV, and $E_{\rm F} = 0.3$ eV. The coupling between

the molecule and electrodes is $t_{fm} = 1.0$ eV. A low temperature of $T = 10$ K is chosen to avoid the spin fluctuation in the electron-transport process.

3. Results and discussion

To clarify the length effect on the rectification, we start our calculations from several specific cases by taking $N = 12$, 16, 24, and 30, respectively. The CC and SC through each device are calculated and displayed in Fig. 2. Obviously, in each case both the CC and SC are asymmetric upon the reversal of bias, which means that the charge-current rectification and spin-current rectification are realized simultaneously. The spin-current rectification takes the form of parallel spin-current rectification, where only the amplitude of the SC is asymmetric.[13] Meanwhile, an obvious length-dependent rectification can be observed. For example, in the two shorter cases, $N = 12$ and 16, the current in the negative bias region is larger than the positive bias region. However, in the longer cases, $N = 24$, 30, the rectifying direction is opposite with a larger current in the positive bias region. Besides the rectifying direction, the rectification ratio is also length dependent. Here we define the rectification ratio as $\mathrm{RR} = -I_c(+V)/I_c(-V)$ for the charge-current rectification and as $\mathrm{SRR} = -I_s(+V)/I_s(-V)$ for the spin-current rectification. For $N = 12$ and 16, the inversion of SRR achieves about 10 at +1.0 V, but the inversion of RR is much smaller with the value below 3.5. The magnitude of RR is close to that of some single-molecule co-oligomer diodes measured in experiments.[5,24] For the two longer molecules, the SRR follows the RR to increase with the bias, where the maximum value of RR (SRR) achieves 4.5 (3.0) for $N = 24$ and 7.3 (5.7) for $N = 30$.

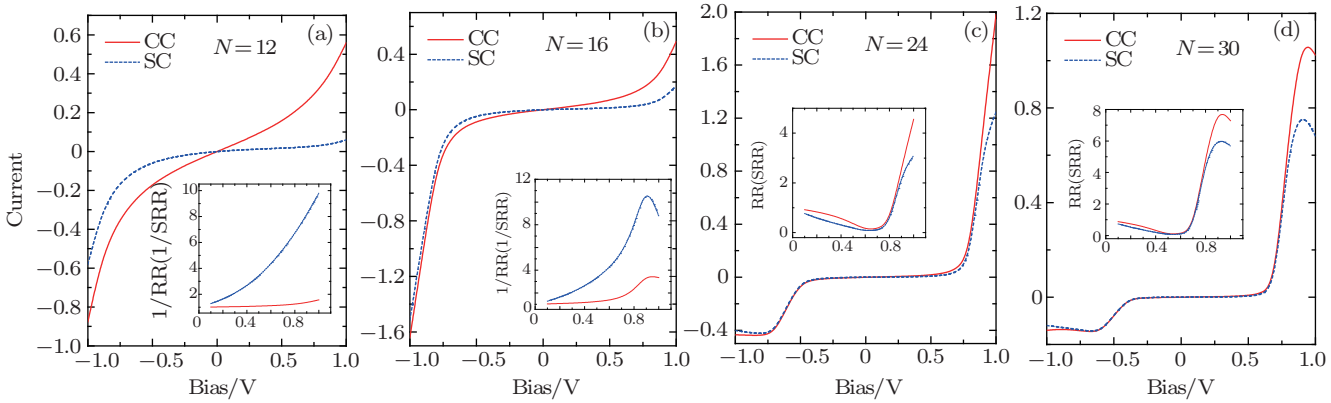


Fig. 2. (color online) Calculated charge current and spin current as a function of bias voltage with (a) $N = 12$, (b) $N = 16$, (c) $N = 24$, (d) $N = 30$. Solid (red) lines correspond to charge current in units of μA, and dashed (blue) lines indicate spin current in units of $\hbar/2e$. The inserts are bias-dependent rectification ratios.

To get a clear view of the dependence of the rectification ratio on the molecular length, we calculate the rectification ratio at $|V| = 1.0$ V as a function of the molecular length. The result is shown in Fig. 3. The length effect on the rectification can be concluded into the following three terms: firstly, the rectification ratio remains fractional until $N = 20$ and then exceeds 1.0, which means that the rectifying direction is reversed from along the negative bias to along the positive bias; secondly, for a shorter length less than 20, the inverse RR in the inserted plot increases little with the length, i.e., from about 1.0 to about 3.0, but the inverse SRR drops sharply from 70 to about 5.0. Thirdly, when the length is over 20, both the RR and SRR are enhanced obviously by the length, which achieves 8.5 and 7.3 at $N = 32$. The above results indicate that the molecular length can be used as a valid method not only to control the rectifying direction but also to adjust the rectification ratio. For example, a shorter molecule is advantageous to obtain a large spin-current rectification, but a longer molecule is beneficial for a large charge-current rectification.

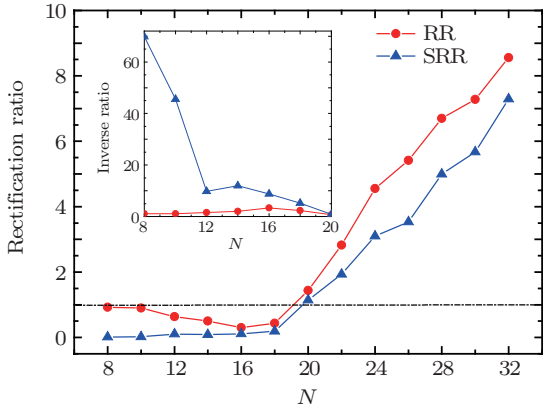


Fig. 3. (color online) Dependence of charge-current rectification ratio and spin-current rectification ratio on the molecular length at $|V| = 1.0$ V. The insert is the inverse ratio at short length.

Next, let us try to understand the mechanism of the length effect on the rectification. Firstly, the length-induced inversion of the rectification can be explored by comparing the spin-dependent transmission of $N = 16$ and $N = 30$. Figure 4

shows the spin-dependent transmission at 0 V and ±1.0 V. At zero bias, one can find that the transmission is spin split for the two cases, and the spin-up transmission spectrum is closer to the Fermi energy than the spin-down one. By examining the molecular eigenstates, we find that the nearest transmission peak to the Fermi level is mainly contributed by the spin-up lowest unoccupied molecular orbital (LUMO). Applying a bias, one can find that for the short molecule the transmission peak of the spin-up LUMO enters the bias window at a negative bias of −1.0 V. However, it is excluded outside the bias window under a positive bias of +1.0 V. Thus, the device rectifies the (spin) current along the direction of negative bias. For the long molecule of $N = 30$, the spin-up LUMO lies in the bias window no matter whether applying a positive bias of +1.0 V or a negative bias of −1.0 V. However, the transmission peak at the positive bias is much higher than that at the negative bias. As a result, the rectifying direction is reversed with respect to the case of $N = 16$.

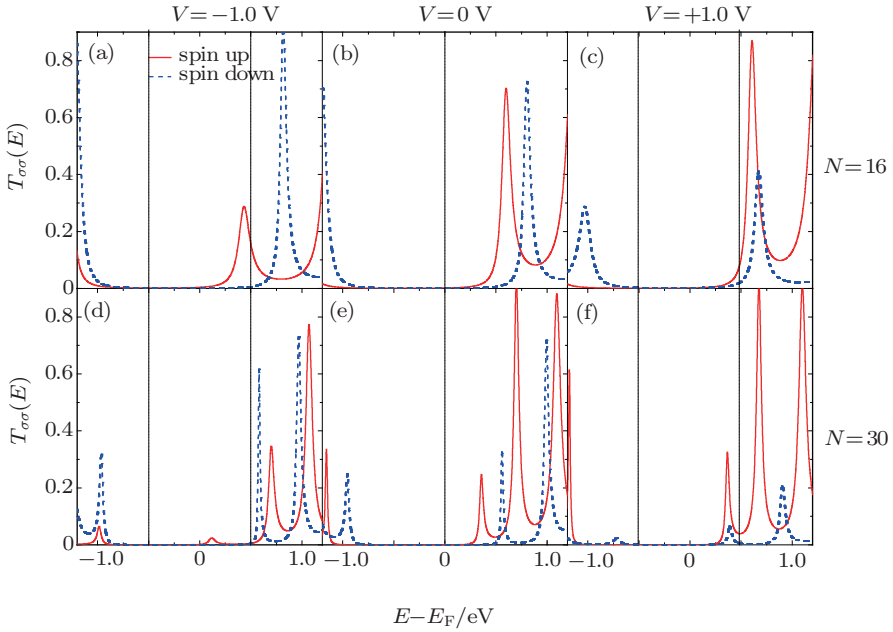


Fig. 4. (color online) Spin-dependent transmission near the Fermi energy at $V = 0$, ±1.0 V for the different lengths $N = 16$ (a)–(c) and $N = 30$ (d)–(f). The vertical dash-dot lines indicate the chemical potentials of electrodes, and the window between them is the conducting bias window.

The mechanism of the length-induced inversion of rectification in magnetic co-oligomer diodes can be deeply understood in reference to that of D/A type co-oligomer charge-current diodes.[17] In D/A type co-oligomer diodes, there exist two kinds of mechanisms for the rectification: bias-induced asymmetric shift of molecular eigenlevels and bias-induced asymmetric spatial localization of wave functions of the conducting orbitals. The two kinds of mechanisms are very common in molecular rectifiers or even in graphene nanoribbon rectifiers, where the asymmetric evolution of the electronic states may originate from the asymmetric built-in structure of the central molecules or from the asymmetric interfacial contacts with the electrodes.[25,26] In D/A type diodes, the two mechanisms lead to different rectifying directions, and the dominant mechanism of rectification may exchange with molecular length. The magnetic co-oligomer is not a D/A type diode since there is not obvious structural asymmetry of charge density. However, due to the spin splitting of eigenlevels in the left magnetic moiety, the magnetic co-oligmer can be seen as a combination of an A/D type diode for spin-up channels and a D/A type diode for spin-down channels. In the present case, the spin-up channel dominates the transport. Hence, a similar length-induced inversion of rectification is observed for the spin diode. This can be verified by checking the evolution of the spin-dependent eigenstates under bias, which is shown in Fig. 5. Here the electronic localization of

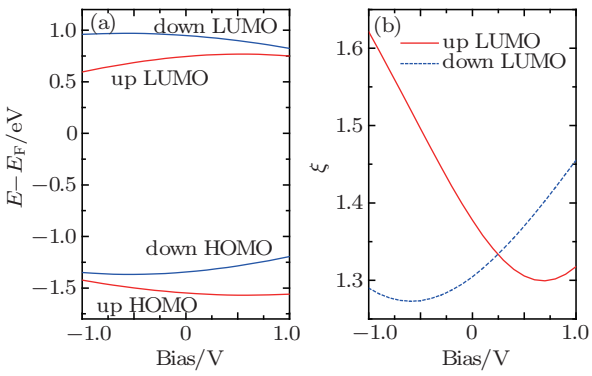


Fig. 5. (color online) (a) Bias-dependent eigenvalues near the Fermi energy. (b) Evolution of the electronic localization of the spin-up LUMO and spin-down LUMO under biases. Here the molecular length is $N = 12$.

the orbital is defined as[23]

$$\xi_{\mu,\sigma}(V) = N\sum_{n}\left|\varphi_{\mu,\sigma,n}(V)\right|^4,$$

where $\varphi_{\mu,\sigma,n}(V)$ is the wave function of the eigenstate μ with spin σ in the Wannier representation. A larger electronic localization means a more localized orbital. It can be found that at negative biases the spin-up LUMO turns closer to the Fermi level accompanied with enhanced electronic localization, and goes far away from the Fermi level with weakened electronic localization. Such evolution of eigenstates corresponds to the change of transmission shown in Fig. 4, which is similar to that in co-oligomer charge-current diodes. The evolution of the spin-down LUMO is opposite to the spin-up LUMO.

Now we are in the position to clarify the reason of the different length dependence of the rectification ratio in each rectifying direction. Before that, one should make it clear about the length-induced change of molecular eigenstates. In Fig. 6, we plot the length-dependent eigenvalues and electronic localization of the spin-up LUMO at $\pm$1.0 V. Obviously, with the increase of length, the spin-up LUMO becomes closer to the Fermi energy, while the electronic localization is enhanced at the same time. The change of this eigenstate looks similar at $\pm$1.0 V. However, one can still get some qualitative understanding about the length effect on the rectification ratio by comparing the evolution at $+1.0$ V and -1.0 V. From Fig. 6(b), we notice that the difference between the electronic localization at $+1.0$ V and -1.0 V turns larger and larger with length. The electronic localization is usually related to the height of transmission peak. Thus, a larger difference of the transmission height will be generated with length. For a longer chain ($N > 20$), the spin-up LUMO has been included in the bias window at both $+1.0$ V and -1.0 V, and the magnitude of transmission dominates both the values of CC and SC. This is why the RR and SRR increase with length in this region.

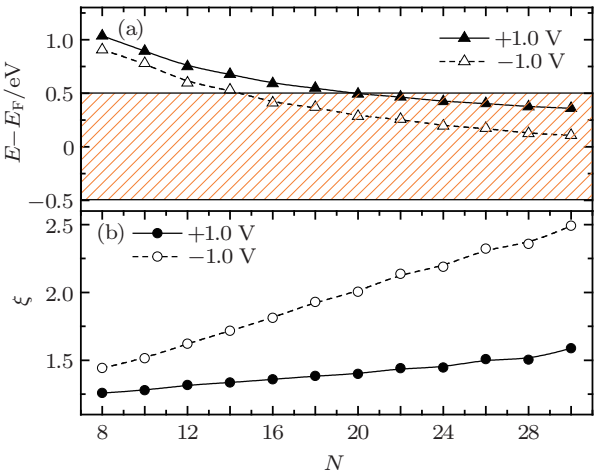


Fig. 6. (color online) Length dependence of (a) the eigenvalue and (b) the electronic localization of the spin-up LUMO. The results at both $+1.0$ V and -1.0 V are given. The rectangle in panel (a) indicates the bias window.

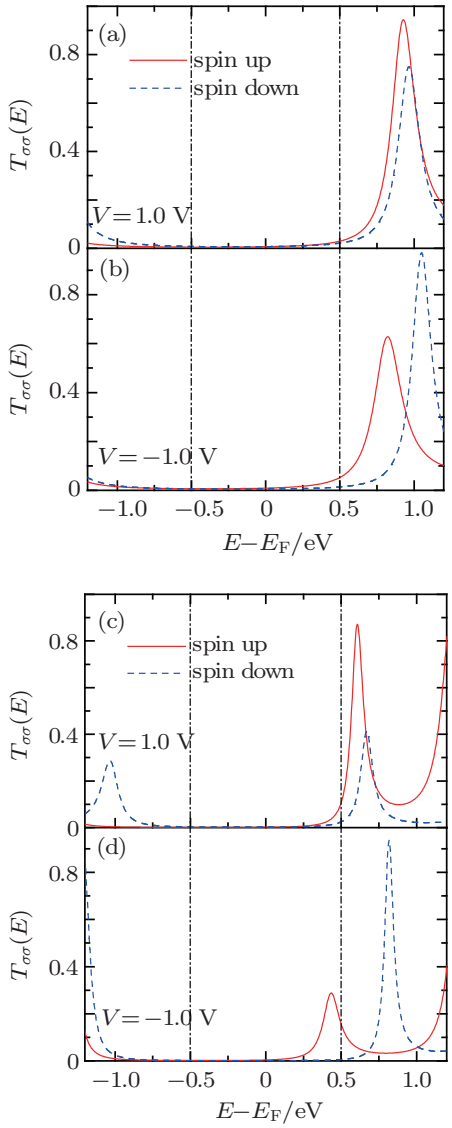


Fig. 7. (color online) Spin-dependent transmission near the Fermi energy at $V = \pm 1.0$ V with (a), (b) $N = 10$ and (c), (d) $N = 16$. The window between the vertical dash-dot lines is the conducting bias window.

In the short-length region ($N < 20$), we notice from Fig. 6(a) that the spin-up LUMO at -1.0 V is closer to the Fermi level than that at $+1.0$ V. With the increase of length (from 12 to 20), at -1.0 V this orbital enters the bias window gradually, while it is still excluded out the bias window at $+1.0$ V. Thus, more efficient transmission is contributed at -1.0 V and the charge current is increased. Hence, the RR will be increased, whose value relies on the portion of the transmission in the bias window at $\pm$1.0 V. However, the drop of the SRR cannot be understood easily from this picture. Then we plotted and compared the spin-dependent transmission spectrum at $N = 10$ and 16 (see Fig. 7). It is found that at a very short length of $N = 10$, the conducting orbitals are far away from the Fermi energy at $+1.0$ V, and the current is only contributed by the tails of the transmission peaks of spin-up LUMO and spin-down LUMO. The spin splitting is not obvious in the tails, and thus the SC is extremely small at

+1.0 V. This leads to an extremely high inverse SRR at very short length. When the length is increased to $N = 16$, the spin splitting of the transmission involved in the bias window at +1.0 V becomes very obvious. Thus, the SC at +1.0 V of $N = 16$ is much more enhanced than that of $N = 10$, as shown in Fig. 7(b). This is the reason for the sharp drop of the inverse SRR. The spin splitting of the transmission peaks from spin-up and spin-down LUMO at +1.0 V may be even larger with the increase of length (see Fig. 4(f) for $N = 30$).

4. Summary

In summary, we have investigated the length effect on organic co-oligomer spin rectifiers. The results show that both the rectifying direction and the rectification ratio may be strongly affected by the molecular length. There exists a critical length where the rectifying direction is reversed. In each rectifying direction, the length dependence of the rectification ratio is quite different. For short co-oligomers below the critical length, the inverse RR increases little, while the inverse SRR drops sharply with the length. For long co-oligomers, both the RR and SRR are increased quickly with the length. By analyzing the spin-dependent transmission and the asymmetric evolution of molecular eigenstates, we demonstrate that the origin for the different length dependence of the rectification ratio comes from two different rectification mechanisms, that is, asymmetric shift of molecular eigenlevels and asymmetric spatial electronics localization of the conducting orbitals upon the reversal of bias. This work indicates a possible way to control the rectification in organic spin diodes by molecular length and deserves to be tested by future experiments.

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