Ideal Current-voltage Characteristics and Rectification Performance of Molecular Rectifier under Single Level based Tunneling and Hopping Transport

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ABSTRACT: As a fundamental unit for molecule-based electronics, molecular rectifier is one of the most widely studied molecular device. Understanding its ideal current-voltage (I-V) characteristics based on a theoretical model is of great importance for its property modulation and performance improvement. In this work, we performed a systematic and comparative theoretical model study on the I-V characteristics and rectification performance of the single level based molecular rectifier under two well-recognized transport mechanisms, tunneling and hopping, using

Landauer formula and Marcus theory respectively. We identified very distinct origin and performance of rectification by the two transport mechanisms, and found the hopping transport can afford a much higher rectification than tunneling. The influence of key physical parameters on the I-V characteristics was further extensively evaluated, like asymmetric factor, energy barrier, coupling to the electrode and temperature, which provided a baseline for the design and mechanism study of the molecular rectifier. Based the two models, we further analyzed the reported experimental data, and more detailed transport mechanisms were revealed.

INTRODUCTION

The molecular electronics was initially proposed to simulate the function of semiconducting devices by modulating charge transport at molecular scale. Inspired by p-n junction made of positive and negative doped silicon, molecular rectifier was the first molecular device designed and investigated theoretically, using an electron rich donor and poor acceptor pair molecule ¹. Current flow under one polarity of bias in the junction was favored over the other due to the misaligned molecular orbital (MO) of donor and acceptor. Experimental observations of rectification

Figure 1 Model diagram of an asymmetric molecular junction containing an active center

by this type of design have been successfully achieved, albeit a rectification ratio (**RR**) of mere ~10, significantly lower than those of inorganic semiconductor p-n junction (10^5 to 10^6).

Another type of molecular rectification was later on conceived and realized in the junction based on a single electronic state of *asymmetric* position relative to each electrode²⁻⁶. The electronic state in the junction was polarized and shifted *asymmetrically* at bias of two different polarities, so resonant tunneling of high conductance is achieved at one direction over the other one^{5, 7-10}. In the theoretical model for this system, an *asymmetric* potential division factor was introduced into the energy gap term with respect to bias in the single state transmission function, which, after being incorporated to the Landauer formula, produced rectified I-V¹¹. Experimental investigation by using redox active moieties (such as organic conjugate groups or metal complexes) as active electronic state, and inert spacer (like alkane molecule) to adjust the position have been extensively explored.^{2, 4, 5} The rectification behavior seems in line with theory, as demonstrated by Whitesides and Nijhuis et al⁹.

Theoretical investigations of the molecular rectification, as mentioned above, have been done based on tunneling transport, by which the rectification ratio is theoretically limited to hundreds with temperature independency (at least below room temperature)¹². Experimental studies, on the other hand, have again and again reached rectification ratio of more than 10^3 . Meanwhile, significant temperature dependent behaviors were observed in the molecular diode devices⁸, which is generally regarded as signature of incoherent transport with molecular relaxation and redox mediated hopping mechanism¹³. However, theoretical study on rectification under hopping transport is still very limited, except that Migliore and Nitzan ever mentioned the rectification properties in their theoretical work on redox molecular junction without detailed discussion¹⁴.

In this work, we systematically studied the rectifying properties of molecular junction based on asymmetric tunneling and hopping charge transport in a single electronic state model using Landauer formula and Marcus theory. We first analyzed the asymmetric I-V characteristics and

revealed distinct physical origins of the rectification under the two types of transports. We found significant difference in I-V characteristics of the two and the hopping transport can afford a much higher rectification ratio than tunneling. Next, the effect of key physical parameters on rectification performance under tunneling and hopping, like asymmetric factor, energy barrier, temperature and molecule-electrode coupling et al, were extensively evaluated, which provided a theoretical baseline for molecular diode design and performance modulation. At last, we further analyzed representative experimental results using the two models. We successfully reproduced the experimental results by adjusting the model parameters and revealed the coexistence of the tunneling and hopping processes in the ferrocene based molecular diode. The model method thus can work as powerful tool in mechanism analysis for the molecular rectification study.

THEORETICAL METHOD

In this section we briefly introduce single-level based tunneling and hopping transport model, and then further extend them to asymmetric polarization cases where rectification can be realized. The details of the single-level models can be found in the references^{11, 14}.

Tunneling model based on single-level model:

The electron transport based on tunneling transport was described by Landauer-Büttiker formalism¹⁵, which consider coherent transport only. The current flow in molecular junction can be given by¹⁶

$$I = \frac{2e}{h} \int dE [f_L(E) - f_R(E)] Tr(E) \quad (1)$$

In Eq.1, E is the energy of the electronic state in the electrode. f_L and f_R are the fermi function of left and right electrode, respectively and are given by

$$f_K(E) = \frac{1}{\exp\left(\frac{E - \mu_K}{k_B T}\right) + 1} \quad (2)$$

μ_K is the chemical potential of electrode and $K = L$ or R represent the left and right electrode. The bias V applied to the junction will move the chemical potential of electrode up and down to create potential difference. For convenience, we will fix μ_L and let μ_R move by eV as shown in Figure 2.

$Tr(E)$ is transmission function and is related to the coupling strength Γ_L/Γ_R between the molecule and left/right electrode, can be given by

$$Tr(E) = D_\varepsilon(E) 2\pi \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \quad (3)$$

Where, $D_\varepsilon(E)$ is the broadened state density of the molecular energy level ε due to the coupling to the electrode, and its distribution is a Lorentz function centered at the energy level ε , therefore, let $\Gamma = \Gamma_L + \Gamma_R$, the broadening can express as

$$D_\varepsilon(E) = \frac{1}{2\pi} \frac{\Gamma}{(E - \varepsilon)^2 + (\Gamma/2)^2} \quad (4)$$

For convenience, we can set the chemical potential of electrode to be zero in the absence of bias so that ε can be replaced by energy barrier $\Delta\varepsilon$ that represents the difference between ε and μ . Therefore, the above process can be simply described as the process of electrons tunneling from one electrode to the other via a barrier $\Delta\varepsilon$, and mainly affected by $\Delta\varepsilon$ and Γ_K .

Hopping model based on single-level model

Charge transport in hopping mechanism is a multi-step process and can be described by consecutive charge transfer (CT) from one electrode to molecule then to the other electrode. Each transfer step at the molecule-metal electrode interface, $R_{o/r}^K$ for the rate from electrode to molecule and $R_{r/o}^K$ the rate of reverse process, can be described by Marcus theory as^{14, 17}

$$R_{o/r}^K = \int_{-\infty}^{+\infty} dE k_K(E) f_K(E) F(E - \Delta E) \quad (5)$$

$$R_{r/o}^K = \int_{-\infty}^{+\infty} dE k_K(E) [1 - f_K(E)] F(\Delta E - E) \quad (6)$$

Here, $k_K(E)$ is the electron quantum transition rate between the electronic state of electrodes and molecular state as given by Fermi golden formula.

$$k_K(E) = \frac{2\pi}{\hbar} |V_{o/r}^K|^2 \rho_K(E) \quad (7)$$

where $V_{o/r}^K$ is the coupling strength between electronic state of electrodes and molecular state, $\rho_K(E)$ is the density of states in the electrodes.

$f(\varepsilon)$ is the Fermi distribution of the electron in electrode and F is the Franck-Condon factor, and it is related to nuclear relaxation and electron-vibration coupling by^{14, 17}

$$F(x) = \frac{1}{2\sqrt{\pi\lambda k_B T}} \exp\left[-\frac{(x - \lambda)^2}{4\lambda k_B T}\right] \quad (8)$$

x here is the energy change of the electrode-molecule system before and after the CT process from the electronic state of the electrode to the redox state. Roughly speaking, it is equal to the energy difference between the electronic states of the electrode and the molecule, i.e. $E - \varepsilon$, similar to the tunneling transport. We therefore set a parameter ΔE to be the energy change of the CT from the chemical potential energy state of the electrode to the redox state, roughly equal to $\varepsilon - \mu$, which is one of the intrinsic properties of the electrode-redox state system. x is then becomes $E - \Delta E$ for CT from electrode to molecule (reduction) and $\Delta E - E$ for the reverse process. λ is the well-known reorganization energy.

At last, the steady-state current flowing through molecular junction is given by

$$I = -e(P_e R_{o/r}^L - P_m R_{r/o}^L) \quad (9)$$

where, P_e and P_m are the stationary occupations in the electrode and molecule, and they are determined by solving the steady-state master equation and normalization condition.

$$\dot{P}_m = (R_{o/r}^L + R_{o/r}^R)P_e - (R_{r/o}^L + R_{r/o}^R)P_m = 0 \quad (10)$$

$$P_m + P_e = 1 \quad (11)$$

Combining eqs 9-11, the current in molecular junction described by the rate equation can be obtained

Figure 2 (a) The schematic diagram of asymmetry molecular junction based on single-level model and the energy level shift at forward bias and reverse bias. (b) the voltage drops in the molecular junction (c) Energy level shift plotted against bias voltage, for energy barrier $\Delta\epsilon = 0.75$ eV and $\alpha=1/12$. The shaded area is the bias window. (d) Exponential dependency between coupling strength and the position of active center, for $C=0.3, \beta = 1.1$, and the parameter setting see the section of Results and discussion.

$$I = -e \frac{R_{o/r}^L R_{r/o}^R - R_{r/o}^L R_{o/r}^R}{R_{o/r}^L + R_{r/o}^L + R_{o/r}^R + R_{r/o}^R} \quad (12)$$

The transport properties of the hopping process therefore mainly depend on four parameters: (i) energy difference ΔE between electrode and molecule, (ii) reorganization energy λ due to the nuclear relaxation by redistribution of charge, (iii) the rate term k_K that related to the coupling strength, and (iv) the temperature T of the system.

Asymmetric case of two mechanisms

Next, we extend above two types of transport to asymmetric case. The schematic diagram of asymmetry molecular junction is shown in **Figure 2** where a molecule containing one active electronic state and two spacers of different lengths is sandwiched between two electrodes. In the nanogap of the two electrodes, the energy of the electronic state will change following the potential profile across the gap space upon the bias, which, in the case of asymmetric position of the state in the junction, leads to the asymmetric energy variation of the state and the current of the junction in response to the applied bias. As shown in Figure 2b, the potential drop in the nanogap consists of three parts:

$$\Delta V = \Delta V_L + \Delta V_R + \Delta V_A \approx \Delta V_L + \Delta V_R \quad (13)$$

where, $\Delta V_{L,R}$ is the voltage drop between active center and right or left electrode, ΔV_A is the voltage drop at active center which can be neglected by considering active center as equipotential surface. The degree of asymmetry (symmetry) of the molecular junction is parameterized into the voltage division factor α_R depending on the potential drops at two sides of the state:

$$\alpha_R = \frac{\Delta V_L}{\Delta V} = \frac{\Delta V_L}{\Delta V_L + \Delta V_R} \quad (14)$$

For the active center located at different positions in the nanogap, potential drops and voltage division factor α_R varies following the potential profile in the junction. For convenience, and also for more illuminative results, we will discuss the I-V characteristics by applying linear profile first^{10, 18}. The actual potential profile is a complex function of molecular screening length and the device geometry¹⁹⁻²¹, and the results and discussion of the non-linear potential profile can be found in the **Supporting information**, which did not change our main conclusion. We also incorporated the non-linear potential profile later on when applying our model method to the experimental

results. For the linear potential profile, the voltage-drop and the position of the state defined by the length of the spacer is linearly related, then the voltage division factor can be defined as

$$\alpha = \frac{\Delta V_R}{\Delta V} = \frac{L_R}{L_L + L_R} \quad (15)$$

Where L_L and L_R represent the length of spacer. The larger α , the closer the active center is to the left electrode. **Figure 2(a. b. c)** shows the position of molecular energy levels under different bias polarities and the shift of energy level with bias in the asymmetric system.

Furthermore, the coupling to the two electrodes changes as well with the position of the active state. It has been well recognized, based on the study on CT dynamics in the electrode-bridge-acceptor system, the coupling decrease exponentially with the length of the spacer²². In Landauer formula, this relation can be expressed as

$$\Gamma_K = Ce^{-\beta L_K} \quad (16)$$

where C is contact coupling constant (coupling at zero spacer length), and β is the attenuation coefficient and is the measure of decay rate with respect of the length of the bridge molecule²². In the Marcus charge transfer theory, the exponential decay rule works on $V_{o/r}^K$, the coupling between electronic state of electrodes and molecular electronic state over the length of the spacer, and the two types of coupling are related by¹⁷.

$$\Gamma_K = \pi |V_{o/r}^K|^2 \rho_K(E) \quad (17)$$

Therefore, electron quantum transition rate k in Marcus theory can be written as

$$k_K = \frac{2\Gamma_K}{\hbar} \quad (18)$$

Then, we introduce the asymmetric factors discussed above into the models. To make the point of view clearer, we fixed the energy level of the left electrode and allowed the energy level of right electrode and the molecular energy state to move as shown in **Figure 2(a)**.

First, for the right electrode, the relationship between the Fermi distribution and applied bias voltage V can be expressed as

$$f_R(E, V) = \frac{1}{\exp\left(\frac{E + eV - \mu_R}{k_B T}\right) + 1} \quad (19)$$

Then, for tunneling transport, combining **eqs 3-4** and considering the relationship between the transmission function and the bias voltage in an asymmetric system and the change in coupling strength with the position of the active center, the transmission function can be expressed as

$$Tr(E, V, L_L, L_R) = \frac{\Gamma_L(L_L)\Gamma_R(L_R)}{(E - \varepsilon + \alpha_R eV)^2 + \left[\frac{\Gamma(L_L, L_R)}{2}\right]^2} \quad (20)$$

Substituting **eqs 19-20** into **eq 1**, the tunneling current as a function of bias and the voltage division factor can be obtained.

For hopping transport, we introduce asymmetric factor (eq 14), bias V , and quantum transition rate k (eq 16) into **eqs 5-6** and obtained the 4 following equations. At last these 4 equations were put into **eq 12** to get the current.

$$R_{o/r}^L(V) = \int_{-\infty}^{+\infty} dE k_L(E) f_L(E) F(E - \Delta E - \alpha_L eV) \quad (21)$$

$$R_{r/o}^L(V) = \int_{-\infty}^{+\infty} dE k_L(E) [1 - f_L(E)] F(\Delta E + \alpha_L eV - E) \quad (22)$$

$$R_{o/r}^R(V) = \int_{-\infty}^{+\infty} dE k_L(E) f_R(E, V) F(E - \Delta E + (1 + \alpha_R) eV) \quad (23)$$

$$R_{r/o}^R(V) = \int_{-\infty}^{+\infty} dE k_L(E) [1 - f_R(E, V)] F(\Delta E - (1 + \alpha_R) eV - E) \quad (24)$$

Again, the Fermi distribution of the left electrode f_L does not depends on the bias voltage in our model. By now we have given a full description of the two mechanisms of charge transport in asymmetric molecular junction. The modelling was done in MATLAB and the integrations were conducted numerically.

RESULT AND DISCUSSION

Hopping VS Tunneling

Using above models, we ran the simulation of current-voltage response of tunneling and hopping transport. The molecular structure is shown in **Figure S3**. The parameters are selected based on reported experimental results on ferrocene as the electroactive group and alkane as spacer. In tunneling transport, energy gap $\Delta\epsilon$ was set to 0.75 eV, the voltage division factor $\alpha_R=1/12$, as reported by Nijhuis et al², and temperature $T=298\text{K}$. In hopping transport, we need to consider the redox properties of active center, including redox potential (relative to electrode chemical potential) ΔE and reorganization energy λ . Based on experimental reports²³⁻²⁵, the parameters was set as follows: $\Delta E = 0.5\text{eV}$, $\lambda = 0.5\text{eV}$, the voltage division factor and temperature were kept the same as tunneling transport, i.e. $\alpha_R=1/12$, $T=298\text{K}$. Attenuation coefficient is set to 1.1 per carbon atom, which is a typical value for alkane group^{26, 27}.

Figure 3 The I-V characteristics of tunneling (a) and hopping (b) in linear scale (blue line) and semi-log scale (red line) for rectification.

The simulated I-V curves by the two models are shown in **Figure 3**. It can be seen that the I-Vs of the two mechanisms exhibit quite different characteristics. Firstly, similar to our previous study

Figure 4 The transmission spectrum of tunneling transport shift with voltage and the gray region is bias window.

on symmetric models, the current in hopping transport can span a much higher range than the tunneling transport. The current in hopping is near exponentially dependent on voltage, therefore in the semi-logarithm scale plot, the $\text{Lg}(I)$ -V curve is more linear²⁸. The other important characteristic is that the rectification ratio of hopping transport is much higher than tunneling transport. In order to get more insight into the origin of the difference, we proceed to investigate key functions of the two transports. For tunneling, the properties of charge transport determined by transmission function that described by **eq 3**. Due to the asymmetric polarization of the electronic state, the transmission area, i.e. the part of the transmission function that falls into bias window, which is directly proportional to the current, at two opposite bias polarities will be different. **Figure 4** showed the transmission area in the bias window at shade area for $\alpha_R = 1/12$. It can be seen that at negative, the transmission area is large because the resonance transmission peak is in the bias window. In contrary, the bias window covers only the tail part of the

Figure 5 Electron transfer step in hopping transport under negative bias (a) and positive bias (b). Electron transfer rate of each step plotted against bias voltage (c) at the parameters $\Delta E=0.5\text{eV}$, $\lambda=0.5\text{eV}$, $\gamma=1/12$, and $T=298\text{K}$.

transmission function at positive bias. Therefore, we see large current at negative bias over positive bias. Different from tunneling transport, charge transport in hopping mechanism is a sequential stepwise process so that the transport properties are determined by the CT rate of each step. We have given the variation in the CT rates of different steps as a function of bias voltage in **Figure 5**. Similar to tunneling transport, at negative bias (**Figure 5(a)**), the redox state gradually falls into the bias window and the rate of rightward flow $R_{o/r}^L$ and $R_{r/o}^R$ dominate in the junction, resulting into a large current. While at positive bias, due to the voltage division effect, the redox state is outside the bias window even at high bias. The leftward charge flow is then limited by the slow $R_{o/r}^R$, and the rightward $R_{r/o}^L$ (being the largest rate) played an additional negative effect for the leftward charge flow. These altogether results into a small current in the positive bias. **Figure 5(c)** also indicates that the elementary CT rates are all exponentially dependent on bias voltage based on Marcus rate equation, and this is the origin of the exponential dependence of the current on bias and high rectification ratio of hopping transport than tunneling. We further looked into the effects of different parameters of the two types of transport on the rectification properties, shown in **Figure 6**.

Figure 6 The I-V characteristic of tunneling transport for (a) voltage division factor and (b) energy barrier and hopping transport for (c) voltage division factor, (d) reorganization energy, (e) energy barrier and (f) temperature in semi-log scale.

For tunneling, since the coupling Γ and the voltage division factor can be correlated by **Eq. 15** and **16**, we have the division factor α and the energy barrier $\Delta\epsilon$ leftover as independent variables. As shown in **Figure 6(a)**, as α deviating from the symmetric value (6/12), asymmetric I-V and the rectification start to appear. However, the rectification did not increase monotonically following α , it reaches maximum when α is around 4/12 to 5/12. This is the result of the balance between the voltage division factor and the coupling strength. When α become smaller and smaller, Γ_R increases and Γ_L decrease exponentially, and the transmission function become low and broad (see **Figure S5**). As a result, the transmission areas covered by the bias window at two opposite polarities are less different and so the rectification decreases. For the energy barrier (**Figure 6(b)**), as $\Delta\epsilon$ increase, the negative saturated current did not change, while positive leaking current decrease. This originate from the fact the energy barrier did not change the shape neither the area

of Tr , rather, it shifts its position relative to the Fermi energy level of the electrode only. Therefore, the negative saturated current, which is proportional to the full area of the Tr covered by the negative bias window (resonance), won't change with $\Delta\epsilon$. In contrast, the tail part of the Tr covered by positive bias window will decrease as Tr shift away from the Fermi energy level of the electrode following increase of $\Delta\epsilon$. Meanwhile, energy barrier affects the bias limit at which the molecular orbital will fall into the bias window, which also determines the turn-on voltage. As the energy barrier increases, the voltage required to resonant tunneling increases gradually. To see the overall effect of voltage division factor α and energy barrier $\Delta\epsilon$ on rectification ratio, we plot the maximum ratio as a function of α and $\Delta\epsilon$ as a 2-D map, see the **Figure 7(a)** (the results of nonlinear voltage drop was shown in **Figure S6**). We can find the maximum rectification ratio need a proper position of the electroactive group in the junction and big enough energy barrier². It is worth mentioning that, although in theory, the rectification ratio increases with the increase of the energy barrier, in reality, it is necessary to consider whether the loading capacity of the molecule to the voltage can meet the bias requirement to achieve the maximum rectification ratio before the junction getting short at high bias²⁹. This is also a limitation to the improvement of tunneling molecular junction performance.

For hopping transport, we have four independent variables: energy barrier ΔE , temperature T , reorganization energy λ and division factor α . The I-V results of these parameters are displayed in **Figure 6(c-f)**. Unlike the tunneling transport, the rectification ratio of hopping transport changes monotonically with α , that is, the more asymmetric the voltage division, the stronger the rectification. This is because the CT rates at two electrodes have monotonical relation to the current, unlike tunneling. The ΔE plays a similar role as the barrier in tunneling and the rectification ratio increases as it increases. We also made the 2-D map of the rectification ratio versus α and ΔE

Figure 7 Variation of maximum rectification ratio with energy barrier and active center position. (a) tunneling transport, (b) hopping transport. This position represents the number of carbon atoms spaced between the active center and the right electrode.

(**Figure 7(b)**). The result again stresses the fact that, unlike the tunneling mechanism, the influence of different parameters on hopping rectification is a monotonical trend. In Marcus equation, ΔE and λ determine the activation energy required for the reaction. However, unlike ΔE , λ only affects the I-V shape but has little influence on the change of the rectification ratio. Most pronounced, the rectification behavior of the hopping is significantly temperature dependent. As shown in Figure 6f, as the temperature decrease, the saturated negative current kept the same while the low bias and positive current decreased dramatically, which is quite typical for hopping transport, resulting into a significant increase in rectification ratio.

Putting all the results together, it suggests that hopping and tunneling transports have significantly different I-V characteristics and rectification behavior. Hopping transport might afford much higher rectification ratio than tunneling and is quite temperature dependent. It is deserved to mention that the current suppression at low bias caused by Frank-Condon blockade is unique in the hopping process, which made the main contribution to the high rectification ratio. However, in reality, such a low conductance is hardly possible in molecular scale electronic device where the junction gap size is in the range of nanometer. In such small gap, charge can go across the molecule

by tunneling instead of being tarped due to Frank-Condon blockade effect. This is probably one of the reasons why such high rectification was hardly observed experimentally in single level based molecular device. The problem for the two simplified models is that they cannot tell whether the charge transport in a real molecular device will proceed by coherent tunneling or incoherent hopping transport. The tunneling and hopping transports are actually two extremes in the whole coherent-incoherent picture of the charge transport process, which is determined by the charge-molecule and charge-environment interactions³⁰. In addition, the hopping and tunneling mechanisms can switch between each other depending on bias and temperature, and they can also coexist^{31, 32}. A full theoretical description of the tunneling-hopping transition and coexist is still a difficult task, though several attempts have been made in recent years, and is beyond the topic of this study^{30, 33}. Nevertheless, for general cases the two model methods can still be used, for the study of charge transport mechanism on experimental molecular rectification devices. We are going to show several examples below.

Model study on experimental results

Charge transport mechanism distinguished by I-V characteristics: In the first part, we show the I-V characteristics can be used to distinguish the charge transport mechanism of molecular rectifier. In our previous study, we ever found decent rectification behavior of ferrocene-undecanethiol SAM on gold substrate with $\sim 2\text{nm}$ roughness³⁴. As shown in Figure 8a, we can find the I-Vs have a quite broad distribution, which can be divide into three regions through the current histogram at -0.3V , see **Figure8(c)**. We then averaged the I-Vs in each group and found three types of I-V behavior. As shown in Figure 8d of the semi-log plot, the group III (blue one) has the highest rectification and has the characteristics of hopping transport, i.e. linear shape in semi-log plot. In contrast, group I and II (red and black) take on the characteristics of tunneling with much higher

Figure 8 (a) Schematic representation of molecular junction consisting of Au bottom electrodes, SAM of SC₁₁Fc and Ga₂O₃/EGaIn top electrodes. (b) Heat image of I-V curve in semi-log scale (c) The histogram of current at -0.3V. (d) The average I-V curve for three regions. (e) and (f) are the fitting result for tunneling and hopping, respectively.

current at low bias than group III. According to our previous study²⁸, we attribute the three groups to leaking current (group I) by defects of monolayer^{35, 36}, tunneling (group II)⁷ and hopping (group III) through ferrocene-undecanethiol monolayer. We further applied the asymmetric tunneling and hopping model to fit the three group respectively, and the results are displayed in **Figure 8(e, f)** and **Figure S9**. For group I and II, the tunneling model fit the current pretty well and hopping model reproduce group III better than tunneling model. The parameters of fitting results are given in **Table S3-S4**, which are well consistent with the experimental results. This case study told us that the tunneling and hopping transport coexist in the rectification behavior of the ferrocene monolayer and the hopping can afford higher rectification than tunneling. The I-V characteristics

in semi-log plot can be used to make an instant judgement on the transport mechanism and the fitting can be used further for quantitative analysis.

Control on the direction of molecular rectification

Yuan and Nijhuis et al² reported the control of the direction of rectification by the spatial position of electroactive ferrocene center in the junction, which is similar to the scenario we assumed in our model. Similar single-level tunneling model was also applied to explain the experimental result by Garrigues et al¹¹. Here we attempt to give more generic results and detailed analysis through our tunneling and hopping models to check further the applicability of the two models.

We first attempted to fit the I-Vs of the junctions using the two models to tell the transport in the rectifier is through tunneling or through hopping mechanism. In the fitting, we open all the

Figure 9 Fitting results by single-level tunneling rectification model for ferrocenyl-alkanethiol self-assembled monolayer, (a)SC2FcC11, (b)SC6FcC7, (c)SC11FcC2. And parameters exacting from fitting result compared with experimental results: (d) total coupling strength, (e) energy barrier and (f) voltage division factor $\alpha_L=1-\alpha$

restrictions on the parameters. As shown in **Figure 9**, the main characteristics of the I-V plots can

be captured by tunneling model better than hopping, indicating a tunneling based rectification (the fitting results for all the junctions are in supporting information). Furthermore, as can be found in panel d, e and f in Figure 9, the parameters, including energy barriers, voltage division factors and coupling strengths, obtained from fitting generally agree with the trend of the experimental study, though the absolute values of energy barrier and coupling are lower than those ones deduced from UPS measurement on SAM in absence of second electrode^{11, 37, 38}. Overall, the asymmetric tunneling model can be used to fit the experimental results to obtain important physical parameters. On the other hand, however, the fitting process itself still suffered from problems. First, all the parameters, which are enveloped into the complex mathematics of **eq 1-4**, are unable to isolate. How sensitive of the I-V characteristics to the combination of all the physical parameters is still questionable and the parameters obtained from fitting may be not unique. Second, the simple algorithm used in fitting by looking for the smallest errors equally weighted for all the I-V data may lead to overfitting where the main physical factors can be contaminated by side effects. Indeed, as shown by Vilan et al³⁹ that care must be taken in drawing conclusion from the fitting result using the featureless I-V data.

On the other hand, the significance of the simplified models, however, are the ideal behavior and general trend, which can work as guideline in predicting the I-V character and in performance enhancement of the molecular rectifier. To this point, we take another strategy. We set the parameters of the model according to the experimental observed values and observe the rectification ratio changes with the position of the electroactive molecule in the junction. By adjusting the physical parameters like energy barrier, coupling strength and the parameters in the nonlinear potential voltage profile until we get the rectification ratio closest to experimental results, we can obtain the physical quantities that reflect the overall situation of the system and avoid

Figure 10 the rectification as a function of position of (a) ferrocene at full bias range. (b) the rectification ratio changed as a function of position of ferrocene at 1.0V compared with the experimental results. (c) compared with DFT-NEGF results of ferrocene at 1.0V. Parameter setting: $\varepsilon = 0.6\text{eV}$, the coupling constant of molecule-bottom electrode $C_{Bottom} = 0.35\text{eV}$ and molecule-top electrode $C_{Top} = 0.05\text{eV}$. The X axis represents the number of carbon atoms under the ferrocene

overfitting problem in the local results. In this study, we disregard the barrier change with the position of Fc and employ the average value of the experimental results^{2, 11}. We also took nonlinear potential profile considering it is more reasonable in molecular junction^{11, 21, 40} relative to linear potential profile to obtain theoretical voltage division factors, with adjustable variables to tune the nonlinear shape. At last, considering the contact of the molecule with the bottom and top electrode are different, i.e. chemical bond versus physical contact, the contact coupling will be different and set as adjustable variables. The decay coefficient is set to be the same as before based on the experimental study of alkane linker.

Figure 10(a) showed the 2D map of RR versus position of the electronic state and bias and the parameters used are shown in **Table S2**. As can be seen, similar to our model study results in **Figure 7**, two RR peaks was observed, indicating again the importance of the balance between coupling and voltage division. The two RR peaks are asymmetric with respect to the middle of the junction space, which is due to asymmetric contact coupling with the two electrodes. We further extract the RRs at 1.0V bias versus position of the electronic sate and plotted into **Figure 10(b)**.

We can see the model results fit the experimental results pretty well, which suggests that our model can give a good description for experimental system. It deserves mentioning that we were not able to reproduce the flat area in the middle of the rectification ratio curve, which Yuan et al propose is caused by the non-linear potential profile.¹¹ While our study suggested it may not be the case because we already included non-linear potential profile into our model.

We further compared our model results that applied same parameters as above to the ab initio calculation results to see whether this model can capture most of the physical details that are included in the ab initio calculation. Zhang et al^{41, 42} theoretically calculated the molecular rectification performance by employing non-equilibrium Green's function (NEGF) method in conjugation with density functional theory (DFT) when the active center (ferrocene and bipyridyl group) fixed at different positions. We compared their ab initio results with our model results at 1.0V in **Figure 10(c)** (the results of bipyridyl group are presented in **Figure S8**) and found a good agreement, which indicates that the model is a good approximation of the single electroactive group bridged by different alkane spacers and the model method is much simpler and faster in predicting the rectification properties of the junction.

Above results confirm the applicability of the tunneling model from two aspects, that is, important parameters can be extracted by this fitting method, which is appropriate for most tunneling junction, and simple parameter settings for the model can provide a generally prediction for rectification performance in molecular tunneling junction, which also supports the rationality of our proposed hopping rectification model, that employed similar assumptions, for rectification performance prediction.

Temperature-dependence of molecular rectification: The temperature dependence of charge transport in molecular junctions is often considered as evidence of hopping transport⁴³⁻⁴⁵. For

Figure 11 (a) A semi-log plot of the I-V cures of different component at 300K, (b) the I-V curves at different temperature, (c) Arrhenius plot of current at different negative bias as a function of temperature. Model parameter values of tunneling: $\varepsilon = 0.75\text{eV}$, $C_{\text{Bottom}} = 0.35\text{eV}$, $C_{\text{Top}} = 0.05\text{eV}$ and values of hopping $\lambda = 0.5\text{eV}$. In addition, we make the voltage drop localized in molecule.

molecular rectifier, hopping mechanism has been proposed based on temperature dependent I-V characters. Nijhuis and Whitesides et found in the ferrocene-based rectifier that the high current beyond the threshold bias is temperature dependent while the leaking current at low bias and opposite bias polarity is temperature independent⁴⁶. They therefore proposed that there is a bias dependent hopping-tunneling transition in the molecular rectifier. As mention above, the two simplified model cannot provide a full description on the transition of the tunneling and hopping transport. However, both Skourtis et al⁴⁷ and our previous work²⁸ have shown that a simple linear combination of the tunneling and hopping current can be used to provide useful insight into the charge transport when both channels are present. In this model, the current in junction can be described as

$$I_{\text{tot}} = n_t I_t + n_h I_h \quad (23)$$

where I_{tot} is the total current, n_t n_h are the number of molecules involved in the two mechanisms. I_t and I_h are the current of tunneling and hopping respectively. We adopt this expression to our rectification models, and attempt to reproduce the characteristics observed by experimental study by Nijhuis and Whitesides et al⁴⁶.

First, we need to determine the parameters used in the model: the coupling strength setting is same as previous section, and the energy barrier can set as 0.75eV^{11} . The reorganization energy is we roughly set it as $0.5\text{eV}^{24, 48}$. The parameters used in the model are also shown in **Table S2**. Then we display the results of simulated I-V of different components at semi-log and total current of different temperature at linear scale in **Figure 11(a, b)**. We can see that we can reproduce the general characteristics of the rectification reported in the experimental study by these parameters i.e. temperature dependence changes with bias, where high current is temperature dependent while low current is independent. Furthermore, since the contribution of the two transport channels has an important effect on the characteristics of the total current, especially in temperature-dependence, we should discuss the rationality of the number of channels (n_t and n_h) involved in the mixed model, which is $n_t=1$ and $n_h=100$. The channels involved in hopping is significantly larger than tunneling, we thus speculate that for densely packed monolayer, the charge transport mechanism of densely packed monolayer is more likely to hopping, while there is still chance that the charge transport can go through tunneling mechanism, due to, for example, defects in the monolayer or some of the charge may not get enough chance to relax and be trapped on the ferrocene. However, even the less than 1% of tunneling can increase the leaking current and decrease the rectification significantly. For the fact that different mechanisms dominate the transport process at different bias, we can interpret it by the fact that the hopping transport is large suppressed at low bias voltage because of lack of activation energy, which is also the origin of the Frank-Condon blockade⁴⁹, and the tunneling is more efficient here. As the molecular energy level and the fermi energy level approach, the probability of the thermal activation process gradually increases, manifested as an increase in the hopping component, which makes the transport more temperature dependent.

Meanwhile, the increase of the hopping component under high bias is also beneficial to the improvement of molecular rectification performance.

We want to emphasize again that the above description of the mixed model is quite phenomenological and may unintentionally misguide people into the idea that two mechanisms coexist in two independent channels, i.e. tunneling channel and hopping channels work in parallel all the time. In fact, as we have mentioned before, the real situation is much more complex. The coherent-incoherent transports are always accompanying with each other, coexisting and interacting, depending on the dynamics of the charge propagation and its interaction with the molecule and environment^{30, 31}. A unified theoretical framework are being developed based on for example, quantum master equation^{30, 50}, Redfield theory⁵¹ or Landauer–Büttiker probe method⁵² etc.

CONCLUSIONS

This paper has mainly focused on the rectifying properties of two charge transports mechanisms: tunneling and hopping, and discussed their differences in molecular rectifiers. The main features can be summarized as follows, 1) The molecular rectifier of hopping mechanism can reach a rectification ratio much higher than tunneling mechanism. 2) The I-V of molecular rectifiers that are dominated by two charge transports have different linear shape, which are consistent with our previous work. The results obtained by single-level model confirmed the generality of these features. The reason for the difference between the two mechanisms is due to the different process behind charge transport. For tunneling, it is a coherent transport process that can be described by Landauer–Büttiker formalism. The limitation of its rectification ratio is mainly caused by the change of transmission function that is affected by the balance among energy barrier, potential distribution and the broadening density of state caused by the coupling strength. For hopping, it is

dominated by charge transfer between the molecule and electrodes, which is described by Marcus theory. Therefore, the rectification ratio of the hopping mechanism described by the rate equation is subject to potential barriers, reorganization energies, and voltage division factors that change monotonically, while the coupling strength only affects the magnitude of the current.

We also need to realize the limitation of our work. Landauer-Büttiker formalism ignores the electron-vibrational coupling so that seemingly mismatch the transport process in the actual molecular junction, and Marcus theory is semi-classical results, which is usually applicable to high temperature and inadequate in describing the transport behavior at low temperature. However, the effect of electronic vibration coupling on the overall transport properties is limited in many tunneling molecular junctions, while the model based on Marcus theory may inadequately catch the transport behavior at low temperature, it is still suitable for describing the general characteristics of hopping process of most experimental results and guiding the improvement of device performance. Another dilemma is that such a high rectification ratio of hopping transport as demonstrated by the model has not been observed in the experiment even though the molecular junction contains redox active centers and the transport show temperature-dependent. Our analysis suggested that tunneling transport, which is more efficient than hopping at low bias, increased the leaking current. Therefore, the effective suppression of the tunneling current at low bias by decoherent charge transport should be beneficial in improving the rectification, and the conditions to achieve this is still to be explored theoretically and experimentally. At last, in our simplified model, many factors, such as the dependence of the coupling strength on energy and bias⁵³⁻⁵⁵ were ignored, which will vanish some specific information of I-V characteristic but still retain the main features.

Our work gives a reasonable explanation of the experimental results through this simple and low-cost method, and the results produced by this method show that charge transport dominated by the hopping mechanism is a feasible solution to improve the molecular rectification performance. The I-V characteristics of the two we pointed out are helpful for the study of the charge transport mechanism in the molecular junction, and provide a simple but reliable basis for judging potential molecules with hopping transport properties. Consequently, the simplicity and generic nature of our work provides a useful framework for further investigations on molecular rectifiers.

METHODS

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