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Control the electronic transport properties of tetrapyrimidinyl molecule with atom modified sulfur bridge

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ABSTRACT

The effect of the modified sulfur bridge on the I - V characteristics of two-probe system of tetrapyrimidinyl molecule and Au electrodes is explored based on density functional theory with nonequilibrium Green's function. Five modified sulfur bridges with H, N or O atom are considered. The two-probe system demonstrates a switch behavior when the sulfur bridge is modified with atom H, while negative differential resistance behavior when the modified atom is N or O. The analysis for the mechanism of the various properties has been presented with the highest occupied molecular orbital, lowest unoccupied molecular orbital and the transmission spectra.

Keywords: tetrapyrimidinyl molecule; Non-equilibrium Green's function; Electronic transport; Modified sulfur bridge

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1. Introduction

With an aim to find a possible way to solve the miniaturization problem of traditional silicon based device, investigations on electronic structure and charge transfer of molecular devices are developing at an accelerating pace in recent years. In the last several years, there has been a large growth of research effort in nanotechnology, various molecular devices have been made to realize the functions existing in microelectronic devices. So far, many interesting device properties such as switching¹⁻⁴, rectifying behavior⁵⁻⁸, negative differential resistance (NDR) behavior⁹⁻¹², field effect transistor^{13,14}, and spin filter^{15,16} have been demonstrated at the real molecular level. NDR behavior is a property of electrical circuit in which current decreases with the increase in voltage over certain voltage ranges. Since discovery of Esaki in 1958¹⁷, the NDR effect has motivated a wide range of theoretical and experimental investigations from fundamental aspect of electron transport to all possible applications¹⁸⁻²¹. The different contact types also affect the characteristics of current-voltage ($I-V$) curves^{22,23}. All these facts indicate that the contact mode plays a key role in the determination of the electron-transport mechanism. Therefore, to provide a repeatable environment to make precise measurements of a wide variety of molecules is highly desirable. Unfortunately, achieving such an experimental environment is not an easy task. Here we theoretically investigate the $I-V$ curves induced with the sulfur bridge modified by H, N and O atoms. Five contact modes with different modified bridges are considered. To fully understand the electronic

transport properties, we analyze the I - V behavior with the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and transmission spectra.

2. Model and Method

Before the quantum transport properties are determined, the stable geometrical structure of tetrapyrimidinyl molecule has been optimized using the first-principles DFT method implemented in the DMol³ software package²⁴. The exchange-correlation energy is calculated by generalized gradient approximation (GGA) with parameterization of Perdew–Burke–Ernzerhof (PBE)²⁵. The energy convergence tolerance is 10^{-5} Ha, with the force on each atom at less than 5.0×10^{-4} Ha Bohr⁻¹. Frequency analysis is performed to validate the energetic stability of the molecule. Vibrational spectra are obtained in harmonic approximation using finite displacement to obtain the force constant matrix. The maximum change allowed in any Cartesian coordinate is set to 0.002 Å to obtain accurate geometries. The structure of the molecule in transport property calculations is determined by geometry optimization and vibration frequency analysis. The considered molecular architectures are illustrated schematically in Figure 1. The modified bridges are thiol (-S), hydrogen sulfur (-SH), nitrogen sulfur (-SN), oxygen sulfur (-SO). The contact modes with these bridges are represented with M1–M5, respectively. The modified atom on the sulfur bridge results in different contact modes. As shown in Figure 2, the -SH bridge

is similar to thiol. However, the -SN and -SO bridges are obviously different from that of thiol, which results in the various I - V properties. Each layer of gold electrodes is represented by a 3×3 supercell with the periodic boundary conditions so that it imitates bulk metal structures. The geometrical optimizations and the electronic transport properties are calculated by the *ab initio* code package Atomistix ToolKit (ATK)²⁶, which is based on the combination of DFT with the NEGF technique, and the method has been used by several groups for a variety of applications and is well documented. In our calculations, the exchange-correlation potential is described by the Perdew–Burke–Ernzerhof parameterization of the generalized gradient approximation (GGA.PBE). Single-zeta plus polarization (SZP) basis set for gold atoms and double-zeta plus polarization (DZP) basis set for other atoms are adopted. The Hamiltonian, overlaps, and electronic densities are evaluated in a real space grid defined with a plane wave cut off of 150 Ry to achieve a balance between calculation efficiency and accuracy.

According to NEGF formulas, the current in the two-probe system can be obtained with the Landauer–Büttiker formula,

$$I = \frac{2e}{h} \int_{\mu_l}^{\mu_r} T(E, V) [f(E - \mu_l) - f(E - \mu_r)] dE, \quad (1)$$

Where $\mu_{l(r)}$ is the chemical potential of the left (right) electrode, $f(E - \mu_{l(r)})$ is the Fermi distribution function of electrons in the left (right) electrode, and $T(E, V)$ is the transmission coefficient at energy E and bias V , which can be obtained by the following formula,

$$T(E, V) = \text{Tr} \left[\Gamma_l(E) G^R(E) \Gamma_l(E) G^A(E) \right], \quad (2)$$

where $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's functions of the central scattering region, $\Gamma_{l(r)} = i \left[\sum_{l(r)}^R(E) - \sum_{l(r)}^A(E) \right]$ is the line width function, $\sum_{l(r)}^R(E)$ and $\sum_{l(r)}^A(E)$ are the self-energies of the central scattering region, which contain all the effects of the electrodes. The transmission coefficient $T(E)$ can be decomposed into the contribution of n eigenchannels,

$$T(E) = \sum_n T_n(E). \quad (3)$$

For the system in equilibrium state, the equilibrium conductance can be obtained by the transmission coefficient $T(E)$ at the Fermi level E_f ,

$$G = G_0 T(E_f) = G_0 \sum T_n \quad (4)$$

where $G_0 = 2e^2/h$ is the conductance quantum ($7.748091733 \times 10^{-5} \text{S}$). More details for the method can be found elsewhere^{27, 28}.

3. Results and Discussion

The current-voltage characteristics of tetrapyrimidinyl molecule with contact modes of M1-M5 are presented in Figure 3. From the figure, it can be found that the transport properties of the molecular devices are strongly dependent on the contact modes. It is noted that the contact mode of M1 tetrapyrimidinyl molecule connects to the two Au electrodes with two unmodified sulfur bridges. The I - V curve of the contact mode displays symmetry for both the positive and the negative biases. It will be used for a reference to analyze the effect of the other modified bridges with

different atoms.

To show the characteristic of the I - V curves, we calculated the rectification ratios and presented them in Figure 4. The rectification effects of the M2 and M3 and the NDR behaviors of M4 and M5 can be obviously displayed in the figure. It is helpful for us to discuss them in detail the following sections.

3.1 Switch behaviors caused by H-modified sulfur bridge

The current of M2 is very small until -1.5V start rise steadily with the negative bias, and small all the time on the positive bias. Carefully check the I - V curve with M3, one can find it is an approximate mirror symmetry image of that with M2 although tetrapyrimidinyl molecule is not symmetry in the axes direction. As a result, the current occur on the larger positive bias. This result shows that the present characteristic of I - V curve is mainly determined by the bridge but not by the molecule itself. The both cases can be used molecular switches, and the only difference is that the close status depends on different direction of bias. Comparing the results with that of M1, one can recognize the effect of the modified atom is responsible for the change of the I - V curves.

The new characteristic of I - V curve for M2 can be understood with the transmission spectra shown in Figure 4. In the range of low bias, the transmission peak under positive bias has not entered the bias window, therefore does not appear current. The transmission peak began to enter bias window after -1.4V under positive bias, so current start to rise. Figure 4 shows that the main part of a transmission peak is outside of the right threshold of the bias window, therefore the current can continue

to increase if the bias keeps increasing. So, the currents of M2 and M3 in Figure 3 show no threshold.

This phenomenon can be understood through molecular projected self-consistent Hamiltonians (MPSHs) shown in Figure 6. It is known that the coupling between the electrodes and molecule are especially important to the electronic transport properties, therefore, the present MPSHs include not only the molecule but also two surface layers of electrodes (the first layer of left and right electrodes). The LUMO of M2 has a high level of localization above the Fermi level and no delocalized electronic density; the electrons can not tunneling through LUMO. From Figure 6, one can find that the localization of HOMO remains at a low level below -1.4V. However, the delocalization is obvious at -1.4V, which makes the electrons can easily tunneling through HOMO, therefore, the current increase sharply. Moreover, the delocalization keeps with the bias increase, so the current remains at a high level. As for M3 which the H modified S bridge is placed between the molecule and other electrode, the similar HOMO and LUMO can be found from Figure 7. We omit the similar explanation to avoid repetition. Because of the structure of tetrapyrimidinyl is not symmetrical therefore the I - V curves of M2 and M3 is not absolute mirror symmetrical distribution, but it has obviously demonstrates the effect of the H modified bridge on I - V curve.

3.2 Negative differential resistance behavior with N (or O) -modified sulfur bridge

Figure 3 shows that the current for M4 reaches a peak value at 1.38V, then

decrease suddenly along with the bias further increase. While for M5, the peak values appear at 1.14V although the peak is lower than that of M4. That is, obvious NDR behaviors are demonstrated for the both bridges, and the strongest NDR behavior appears in M4.

Transmission spectra from 1.1 V to 1.6 V for M4 are shown in Figure 8. There is a transmission peak in the bias window at 1.1V, and the peak strengthens gradually with the increase of the applied positive bias. However, when the bias reaches 1.6V, the resonance peak in the bias window keeps broadening but lowering drop to the peak value. As a result, the current drops a lower value, and a NDR behavior appears. Therefore the NDR behavior is less obvious. To quantitatively demonstrate the NDR effect, we have calculated the peak-to-valley ratio parameter (PVR) for the I - V curves of the M4 and M5 where NDR is obvious. The PVRs are 5.21 for M4 and 1.84 for M5, which shows that the NDR effect are sensitive to the modified atom. Figure 8 shows that no transmission peak out of the bias window, therefore the current cannot increase despite the bias keep increasing. So, the currents of M4 and M5 in Figure 3 show threshold.

We show the HOMO of M4 in Figure 9. It is found that the delocalization of HOMO becomes obvious after 1.4V, where the current also increases obviously as shown in Figure 2. However, the delocalization begins weakening after 1.6V, which decreases the transmission ability of M4. Carefully checking the MPSH in Fig.9, one can find that the LUMO always has no contribution to the charge transmission. The NDR behavior only depends on the variation of charge distribution on the HOMO. So,

we can conclude that the mechanism of the NDR behavior is the effect of bias voltage on HOMO, but not the additional effect of LUMO as the case of the twisty diphenyldipyrimidinyl system²⁹. M5 demonstrates the similar situation to that of the M4. However, the peak shows less significant changes. The mechanism is also similar to that of M4 and we omit the repeat explanation and figure.

Compared the I - V s of M4 and M5 with those of M2 and M3, one can find that the modified bridges –SN and –SO perform more impact on the I - V properties. Carefully examining Figure 2, we find the N atom is closer to the electrode than the S atom, implying it completely change the contact mode when compared with the –S bridge. Therefore, the NDR behavior of the I - V is the most obvious. In the case of –SO bridge, both the O and S atoms are close to the electrode, and contribute to the charge transmission. Therefore the change of I - V of M5 is less strong than that of the M4. One also can find from Figure 2 that the H atom varies a little the contact mode of S bridge. So that, the changes of I - V of M2 and M3 are much smaller in comparison with those of the M4 and M5. It means the geometries of the sulfur bridge significantly effect on the transmission properties of the two-electrode systems, as the geometrical torsions between molecular rings play significant roles in the rectification properties.²⁹

4. Conclusions

We have obtained the I - V characteristics for the tetrapyrimidinyl molecule with

different bridge radicals based on density functional theory and non-equilibrium Green's function method. It is found that the two-probe system of tetrapyrimidinyl molecule appears a switching effect when the sulfur bridge modified with H atom, while significant NDR behavior when the bridge modified with N or O atom. These results show that the I - V characteristics of the two-probe system can be controlled with the modified atoms on the sulfur bridge. The delocalization changes of HOMO, which are resulted by the modified atoms, are responsible for the various the I - V characteristics of the two-probe system. These findings can contribute to design various functional molecular devices using the idea to modify the sulfur bridge with atoms.

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FIGURE CAPTIONS

Figure 1. The two-probe system of tetrapyrimidinyl molecule with the modified sulfur bridges. M1–M5 represent the different contact modes. The modified atoms on sulfur atom have not been shown in the figure (the light yellow represents the anchoring points). The white, gray, blue and golden spheres represent H, C, N and Au atoms.

Figure 2. The snapshots for the bridging position. (a) only S atom; (b) modified with H atom; (c) modified with N atom; (d) modified with O atom.

Figure 3. Calculated I – V curves for each contact mode.

Figure 4. The calculated rectification ratios for each contact mode.

Figure 5. Transmission spectra from 1.3 V to 1.8 V for M2. The red dotted line indicates positive bias, and the black solid line indicates native bias. The region between two blue dotted lines represents the bias window.

Figure 6. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) corresponding to an applied bias of -1.2 V to -1.6V of M2.

Figure 7. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) corresponding to an applied bias of 1.2 V to 1.6V of M3.

Figure 8. Transmission spectra from 1.1 V to 1.6 V for M4. The black solid line indicates negative bias. The region between two blue dotted lines represents the bias window.

Figure 9. The highest occupied molecular orbital (HOMO) corresponding to an applied bias of 1.3 V to 1.8V of M4.

Figure 1.

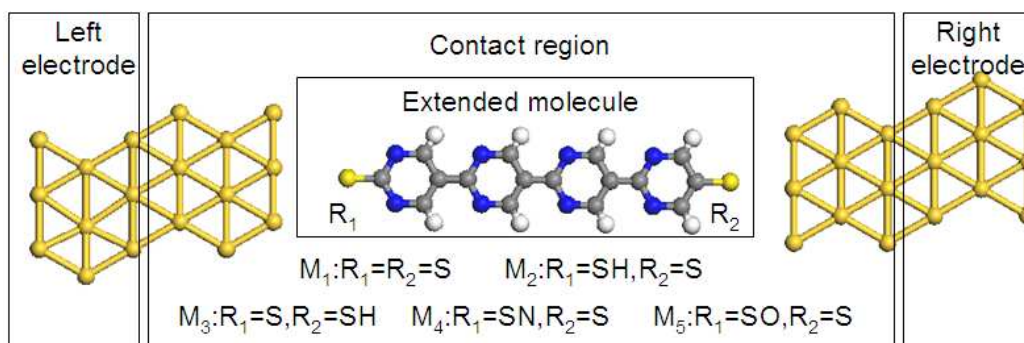


Figure 2.

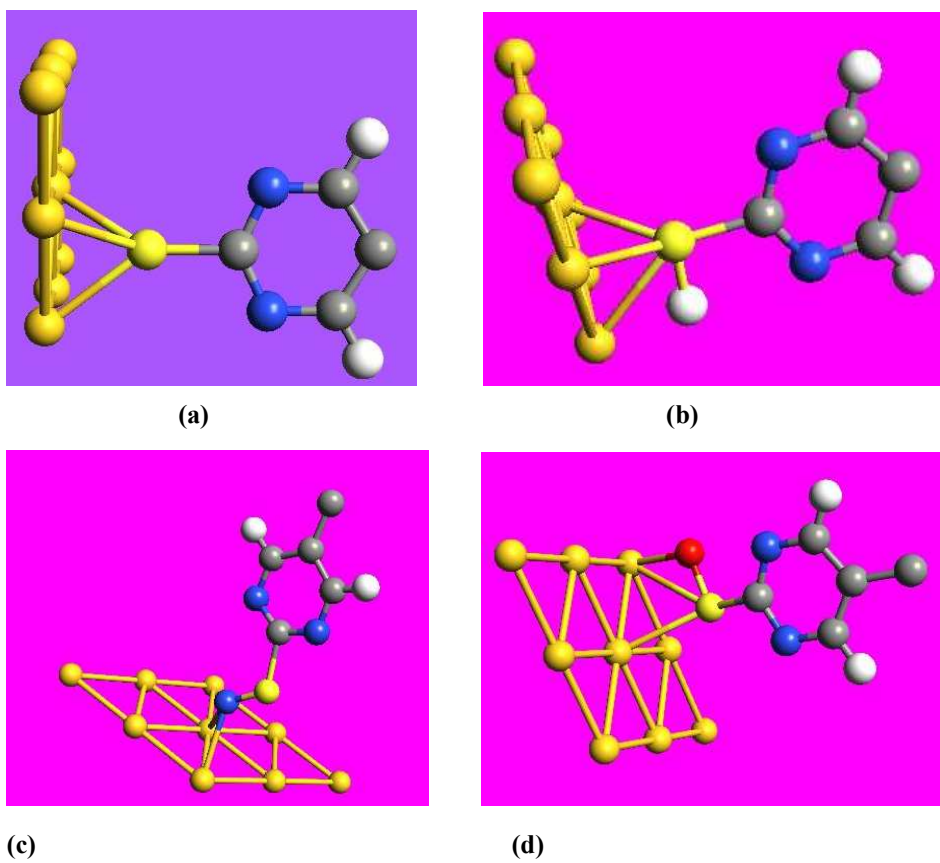


Figure 3.

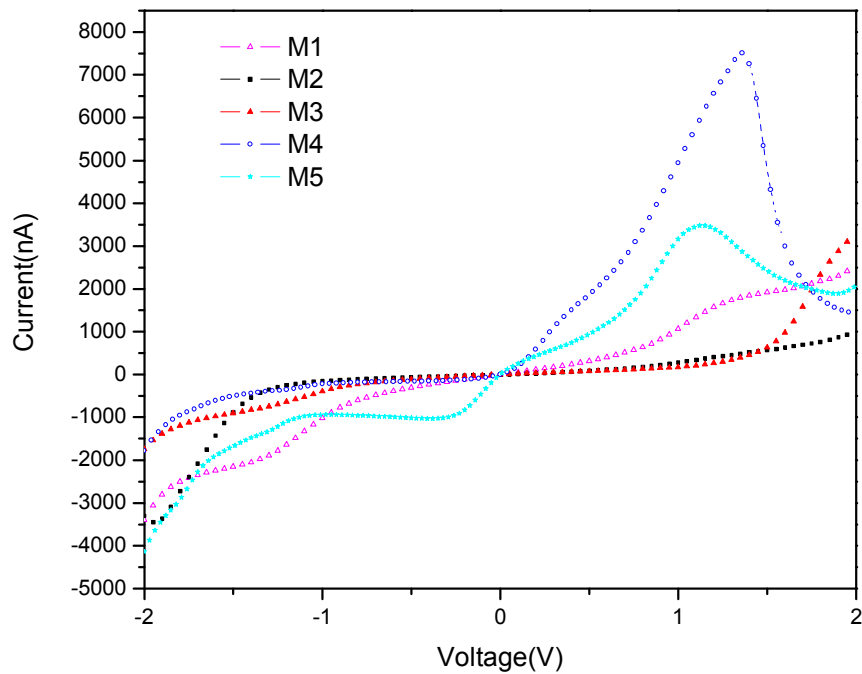


Figure 4.

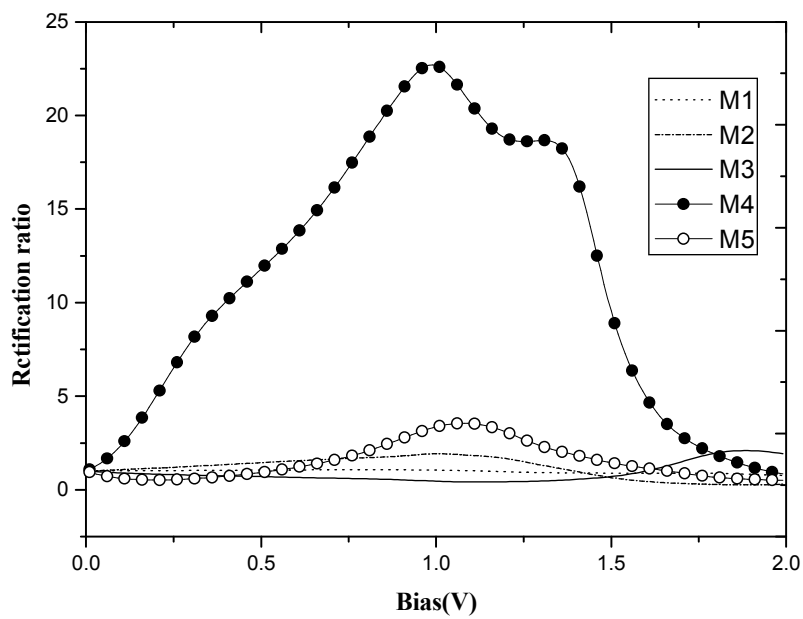


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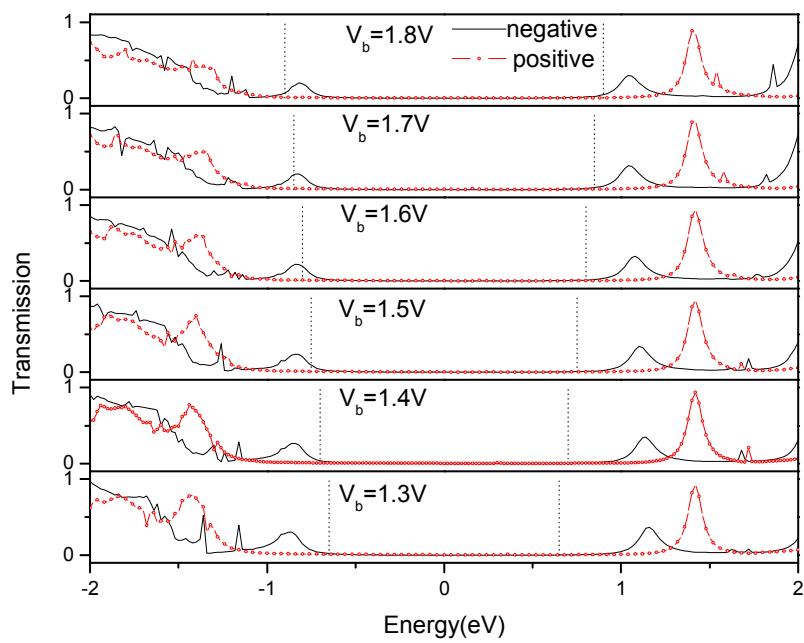


Figure 6.

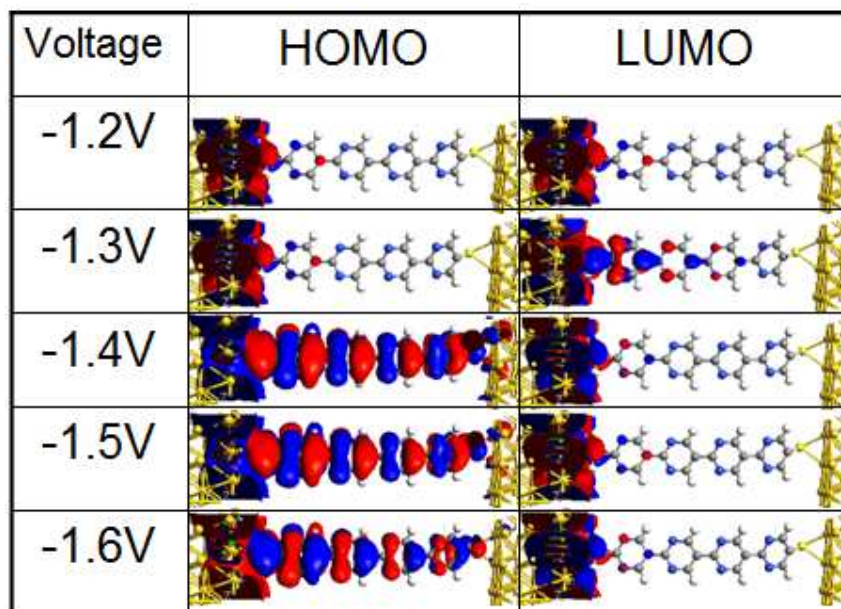


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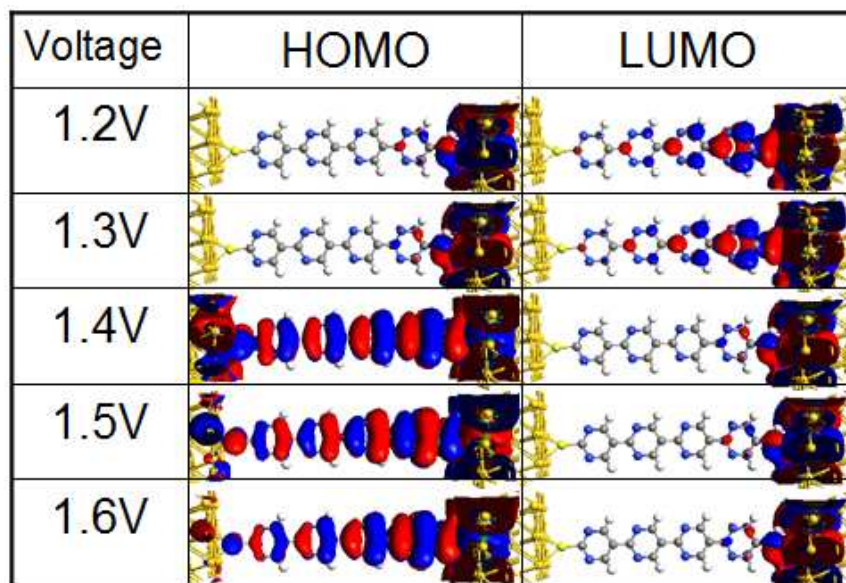


Figure 8.

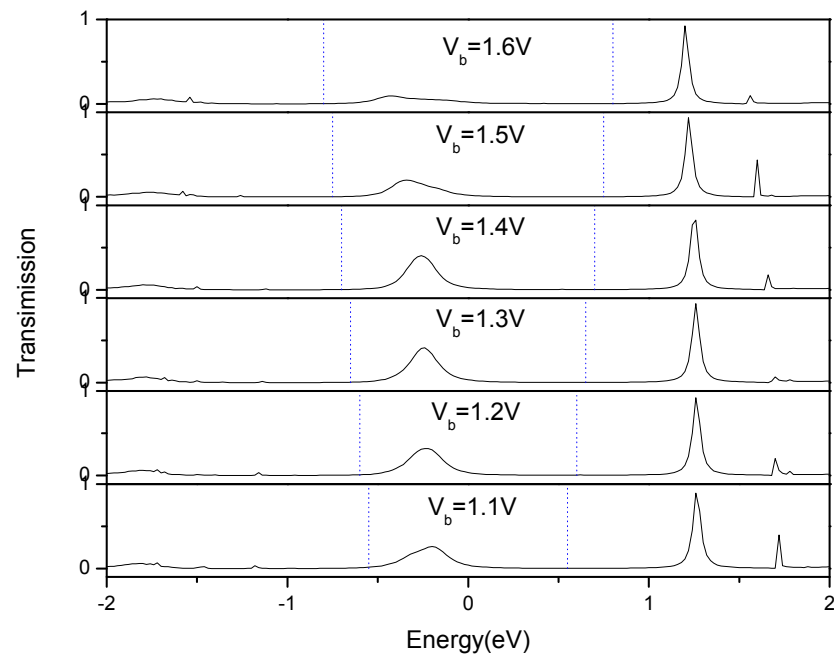


Figure 9.

