

# Switching mechanism of photochromic diarylethene derivatives molecular junctions

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(Dated: February 19, 2013)

## Abstract

The electronic transport properties and switching mechanism of single photochromic diarylethene derivatives sandwiched between two gold surfaces with closed and open configurations are investigated by a fully self-consistent nonequilibrium Green's function method combined with density functional theory. The calculated transmission spectra of two configurations are strikingly distinctive. The open form lacks any significant transmission peak within a wide energy window, while the closed structure has two significant transmission peaks on the both sides of the Fermi level. The electronic transport properties of the molecular junction with closed structure under a small bias voltage are mainly determined by the tail of the transmission peak contributed unusually by the perturbed lowest perturbed unoccupied molecular orbital. The calculated on-off ratio of currents between the closed and open configurations is about two orders of magnitude, which reproduces the essential features of the experimental measured results. Moreover, we find that the switching behavior within a wide bias voltage window is extremely robust to both substituting F or S for H or O and varying end anchoring atoms from S to Se and Te.

PACS numbers: 73.63.-b, 85.65.+h, 82.37.Vb

## I. INTRODUCTION

A critical mission of the molecular electronics is to develop innovative devices at single molecular scale. The representative molecular wires, rectifiers, switches, and transistors have been intensively studied in the past years.<sup>1,2</sup> Obviously, a single molecular switch holds great promise since the switch is a crucial element of any modern design of memory and logic applications. Now various schemes have been proposed to realize molecular switching process including relative motion of molecule internal structure,<sup>3,4,5,6,7</sup> change of molecule charge states,<sup>8,9</sup> and bond fluctuation between the molecule and their electrical contacts.<sup>10</sup> Recently, an alternative routine has been suggested to design switches based on single stably existing molecule which can reversibly transform between two conductive states in response to external triggers.<sup>11,12,13,14</sup> Among various triggers, light is a very attractive external stimulus because of the ease of addressability, fast response times, and compatibility with a wide range of condensed phases.

The switching properties through the so-called photochromic molecules have been carried out by several experimental and theoretical groups.<sup>15,16,17,18,19,20,21,22</sup> In particular, the dithienylcyclopentene (DTC) derivatives (as the central switching unit) hold great promise as artificial photoelectronic switching molecules because of their reversible photo-induced transformations that modulate electrical conductivity and their exceptional thermal stability and fatigue resistance.<sup>15,16,17,18,19</sup> Using the mechanically controllable break-junction technique, Dulić *et al.*<sup>16</sup> designed molecular switches based on DTC molecules (1,2-bis[5'-(5''-acetylsulfanyltien-2''-yl)-2''-methylthien-3'-yl] cyclopentene) with two thiophene linkers, however, which operates only one-way, i.e. from conducting to the insulating state under visible light with  $\lambda=546$  nm with resistance change at 2-3 orders of magnitude. Interestingly, He *et al.*<sup>17</sup> found that the transition can be optical two-way for DTC molecules where H atoms in cyclopentene are substituted by six F atoms (fluorinated-DTC). The single-molecule resistance in the open form is about 130 times larger than that of in the closed structure measured by using scanning tunneling microscopy with a gold tip. In a parallel study, Katsonis *et al.*<sup>18</sup> used aromatic (meta-phenyl) linkers and observed that the light-controlled switching of single DTC molecules connected to gold nanoparticles was reversible. Very recently, to improve the poor stability of such kind of conjugated molecules with thiols on both ends, Taniguchi *et al.*<sup>23</sup> developed an interconnect method in solution for diarylethene

photochromic molecular switches that can ameliorate electrode-molecule binding, molecular orientation, and device functions. In their experiment, one light-controlled switching molecule consists of a central fluorinated-DTC molecule, diaryls on two sides and two thiol groups at both ends. The corresponding closed and open forms are shown Figure 1(a). Consequently, the current through the molecular junction with closed structure is about 20 times larger than that of the open form measured by STM.<sup>23</sup>

To gain better understanding of these experimental observations, several theoretical work have been carried out.<sup>20,21,22</sup> Li *et al.*<sup>20</sup> performed quantum molecular dynamics and density functional theory (DFT) calculations on the electronic structures and transport properties through several photochromic molecules with several different spacers sandwiched between gold contacts. They chose dithienylethene (DTE) derivatives to model the experimental measured molecules and predicted an about 30 times conduction enhancement when converting the open form into a closed one by optical technique. Subsequently, two research groups independently investigated the switching properties of DTC molecular junctions, and found that the transmission peak originates from the highest occupied molecular orbital (HOMO) of the closed form lying near the electrode Fermi level.<sup>21,22</sup> In their calculations, the electrodes are simulated with cluster models and the effects on the transport properties coming from six H hydrogen atoms substituted by F atom are not considered. Till now, to our best knowledge, there is no theoretical study about the switching mechanism through exactly the same measured molecules (fluorinated-DTC with two diaryls on two sides, named diarylethene in Taniguchi *et al.*'s experiment). In this paper, we employ the non-equilibrium green's function technique (NEGF) combined with DFT method to address electronic transport and switching behavior of diarylethene based molecular junction. Moreover, we examine the robustness of this type of switching device against various chemical substitution (where six F atoms in the peripheral of cyclopentene and S atoms in thienyl are substituted by H and O atoms, respectively) and alternations of anchoring atoms.

## II. COMPUTATIONAL MODEL AND METHOD

The computational model system is schematically illustrated in Fig. 1(b). The molecules with open and closed configurations are sandwiched between two gold electrodes through S-Au bonds. The Au (111) surface is represented by a (4×4) cell with periodic boundary con-

ditions. Since the hollow site configuration is energetically preferable by 0.2 and 0.6 eV than the bridge and atop sites, respectively,<sup>24</sup> the diarylethene molecule connects to sulfur atoms which are located at hollow sites of two Au (111) surfaces. Both electrodes are repeated by three layers (A, B, and C). The whole system is arranged as (BCA)-(BC-molecule-CBA)-(CBA), which can be divided into three regions including the left lead (BCA), the scattering region, and the right lead (CBA). The scattering regions include a diarylethene molecule, two surface layers of the left (BC), and three surface layers of the right lead (CBA), where all the screening effects are included into the contact region, within which the charge-density matrix is solved self-consistently with the NEGF method.

The electronic transport properties are studied by the NEGF combined with DFT calculations, which are implemented in ATK package.<sup>25</sup> This methodology has been adopted to explain various experimental results successfully.<sup>26,27</sup> In our calculations, Ceperley-Alder local-density approximation is used.<sup>28</sup> Core electrons are modeled with Troullier-Matris nonlocal pseudopotential, and valence electrons are expanded in a SIESTA localized basis set.<sup>29,30</sup> A energy cutoff of 150 Ry for the grid integration is set to present the accurate charge density. The optimized electrode-electrode distance is 39.5 Å for the closed configuration which is 0.7 Å longer than that of the open one. All atomic positions are relaxed and the corresponding gold-sulfur distance is 2.5 Å, which is close to the typical theoretical values.<sup>31</sup> In addition, we find that the geometric changes of two diarylethene molecule sandwiched between two Au(111) surfaces are negligible comparing to the corresponding free molecules.

### III. RESULTS AND DISCUSSION

#### A. Electronic structures of free diarylethene molecules with closed and open structures

Atomic positions of two free diarylethene molecules with closed and open structures are optimized by Gaussian03 package at general gradient approximation level.<sup>32</sup> In the ground electronic states, both optimized configurations are featured by out-of-plane distortions. The central dihedral angle is 60 degrees for the open form, while only about 8 degrees for the closed one. This distortion leads the distance between carbon and carbon bond (the bond can be broken by photon) close to 4.0 Å in the open case compared to 1.5 Å for the closed

configuration. These important geometric parameters are consistent with the previous DFT predictions for bisbenzothienylethene molecules.<sup>33</sup> Experimental studies have demonstrated that the molecule can transform reversibly between the closed and open forms by shining ultraviolet and visible lights, respectively.<sup>23</sup>

Drawing from the chemical intuition, one would expect that the electronic structures have distinctive characteristics due to the significant geometric difference between closed and open structures. For example, it is clear that both single and double bonds appearing in the central switching unit get almost swapped within the closed and open configurations as shown in Fig. 1(a). The number of double bonds is 9 in the open form in contrast to 8 in the closed one. Thus, the energy of HOMO in the open form is expected to be lower than that in the closed one.<sup>21</sup> In deed, the energies of the HOMO and lowest unoccupied molecular orbital (LUMO) of the closed form are -4.6 and -3.3 eV, respectively, whereas the HOMO and LUMO energies of the open one are -4.9 and -2.7 eV. The frontier orbital localizes primarily on each conjugated unit of the molecule or on the central switching unit for the diarylethene molecule with open configuration. The molecule in the closed form belongs to a conjugated system, whose HOMO and LUMO orbitals are essentially delocalized  $\pi$  orbitals extending over the entire molecule. More interesting, when six F atoms in the peripheral of cyclopentene are substituted by H atoms, we find that the HOMO and LUMO energies of this modified molecule shift dramatically to -4.2 and -2.5 eV for the closed form, and to -4.7 and -1.6 eV for the open one respectively. These remarkable differences of the geometries and electronic structures are expected to affect significantly transport properties.

### **B. Transport properties of diarylethene molecular junctions**

The currents through the molecular junction with closed and open configurations in the bias voltage range [-1.0, 1.0V] are calculated by the Landauer-Bütiker formalism.<sup>34</sup> It should be pointed out that at each bias voltage, the current is determined self-consistently under the nonequilibrium condition. The calculated I-V curves are presented in Figure 2. The triangles linking with black solid lines are for the diarylethene molecular junction, while the circles linking with short red dotted lines stand for the junction where six F atoms in the peripheral of cyclopentene are substituted by H atoms. The filled (empty) symbols correspond to the closed (open) structures. Our calculations capture the key features of the

experimental results.<sup>23</sup> The current through the closed form is remarkably higher than that of the open one. When the diarylethene molecule in the junction changes from a closed configuration to the open one, the molecular wire is predicted to switch from the *on* (low resistance) state to the *off* (high resistance) state. The current enhancement is quantified by the on-off ratio of current defined as  $R(V) = I_{closed}(V)/I_{open}(V)$ . For example, the current of the closed form at 1.0 V is about 4.5  $\mu\text{A}$ , which is about 500 times larger than that of the open case. Such a large on-off ratio in this given range of bias voltage can be readily measured and is desirable for the real application. Note that the predicted on-off ratio at 1.0 V is larger by about one order of magnitude compared to experiment.<sup>23</sup> We think one possible reason for this discrepancy is the limitation of the computational method. It is well known that the calculated value of the current through molecular junction using NEGF combined with DFT is larger about 1-2 orders of magnitude than that of these experimental measured result.<sup>26,31</sup> Other two possible reasons are environment effect and geometry difference. Firstly, solvent effect is not considered in presented calculations. Secondly, in our computational model, diarylethene molecules are directly bound to gold electrodes through Au-S bonds in vacuum. In the experimental setup, the central switching molecules bind to the long orientation control molecules (polyrotaxane), which connect to the interface control molecules (4-iodobenzenethiol) anchored with gold nanoelectrodes in solution (the distance between two electrodes is about 30 nm).<sup>23</sup> Note that the slight geometric distortion due to the molecule-electrode interaction can result in a slight asymmetry in the calculated I-V curves at small bias voltage range as shown in the inset below right of Fig. 2 in small scale for clarity.

To understand the dramatic difference in conductivities of the closed and open configurations, we compute the energy dependence of total zero-bias voltage transmission spectra shown in Figure 3, where the Fermi level ( $E_F$ ) is set to be zero for clarity. Generally speaking, the conductance of the molecular junction is determined by the number of the eigenchannel, the properties of the perturbed frontier orbitals of the molecule due to the presence of the gold electrodes and the alignment of the metal Fermi level within the perturbed HOMO-LUMO gap.<sup>25</sup> Applying an effective scheme named molecular projected self-consistent Hamiltonian (MPSH) method,<sup>25</sup> the orbital energies and eigenstates (referred as perturbed MOs) of the MPSH are obtained and plotted in Fig. 3. The energy positions of these perturbed MOs relative to the  $E_F$  are denoted in Figs. 3(a) and 3(b) with red short

vertical lines, which match nicely with the transmission peaks. The spatial distributions of the perturbed-HOMOs and -LUMOs are presented in Fig. 3 locating on the right and left sides of the  $E_F$ , respectively. Both calculated conductances are very small at zero bias. It is  $4.2 \times 10^{-2} G_0$  ( $G_0 = 2e^2/h$ ) for the closed configuration at the  $E_F$ , and only  $5.4 \times 10^{-5} G_0$  for the open one which is about 800 times smaller than the former one. The diarylethene molecule with a closed structure has two broad and strong transmission peaks locating at -0.8 and 0.5 eV, respectively. For the open form, note that the lack of any significant peaks in between -1.5 and 1.7 eV clearly elucidates its lower conductivity.

More importantly, the transmission spectra display extraordinarily discrepant characteristics. It is clear that for the diarylethene molecular junction with closed structure, the significant transmission peaks locating below and above the  $E_F$  (about -0.8 and 0.5 eV) are mainly contributed by the perturbed-HOMO and -LUMO, respectively. Notably, the perturbed HOMOs and LUMOs of the closed configuration in Fig. 3(a) are delocalized  $\pi$ -conjugated orbitals, which provide good channels for electron tunneling through the molecular junction and lead to two significant transmission peaks. Very interestingly, the transport properties are predominated by the tail of the perturbed LUMO contributed transmission peak at small bias voltage (for example, less than 1.0 V), since the transmission coming from the perturbed LUMO is just 0.5 eV away from  $E_F$ , which is 0.3 eV closer than that of the perturbed HOMO. Note that this finding is different from the microscopic pictures of other existing molecular junctions based on photochromic DTE and DTC switching molecules,<sup>21,22</sup> azobenzene,<sup>20</sup> and quintuple bond [PhCrCrPh] molecules,<sup>14</sup> whose transport properties are prevailed by the transmission peak contributed by the perturbed HOMO.

Yet contradictorily, the spatial profiles shown in Fig.3 (b) of the perturbed LUMO strongly localizes at the central switching unit with open configuration. This leads to no appreciable transmission peaks in the wide bias window (i.e. from -1.5 to 1.7 eV). The significant transmission peak at -1.7 eV originates from the perturbed HOMO and HOMO-1 (both are  $\pi$  orbitals) for the open structure, however, it is located too far away from the  $E_F$ . Here, comparing to the closed case, we note that the position of the perturbed HOMO for the open configuration is buried deeply below the  $E_F$ , which is consistent with the previous theoretical results of DTC molecules.<sup>21,22</sup> These theoretical findings ensure us to conclude that the sharp contrast of the alignment of the perturbed orbital energies with respect to the electrode Fermi level and the shape of these perturbed frontier molecular orbitals are

the essential causes for the striking contrast in transport properties through diarylethene molecular junctions with closed and open configurations.

It should be pointed out that the number of transmission paths can not account for the dramatic difference in conductivities of the closed and open configurations since the eigenchannel analysis indicates that there is a single eigenchannel for both cases within a wide window (i.e.  $[-1.5, 1.5]$  eV). According to the features mentioned above of the calculated zero-bias transmission spectra (Fig. 3), One can speculate that this type of molecular switch can operate robustly in a pretty wide range of bias voltages with fairly large on-off ratio. Additional currents through the diarylethene molecular junctions with two different configurations at -2.0, -1.5, 1.5 and 2.0 V are also calculated. The on-off ratios of current are predicted to be about two orders of magnitude. This suggests that the bias voltage window of this kind of molecular switch (in Taniguchi *et al.*'s experiments<sup>23</sup>) with reasonably large on-off ratio is surprisingly wider than that of other photo-sensitive molecules.<sup>13,21</sup>

Experimentalist found that diarylethene molecular switch is reversible when the molecules are sandwiched through aromatic linkers.<sup>18,23</sup> Theoretical calculations argued that whether it can be switched reversibly or not depending on the molecule-electrode hybridization.<sup>21</sup> The weak interaction between molecule and electrode is required to facilitate the desired reversible transition. According to these findings, the reversible transition between the open and closed configurations in this diarylethene derivatives based molecular junction is highly possible, since the molecules are sandwiched with phenyl linkers and the molecule-electrode hybridization is weak.

### C. Substituting effect on diarylethene molecule

Previous theoretical calculations focus on the end linking groups,<sup>20</sup> no attempts so far have been made to examine the side substituting effect on transport properties through the diarylethene derivations. It is important to investigate the conductance of the molecular junction, where six F atoms in the peripheral of cyclopentene are substituted by H atoms. The calculated transmission spectra for the H-substituted molecular junction with the closed and open forms at zero bias voltage are shown by black solid lines in Figures. 4(a) and 4(b), and two corresponding I-V curves are presented in Fig. 2 with filled and empty circles (linked by red dotted lines), respectively. The current through the H-substituted



molecular junction with closed configuration is about half of that of the cyclopentene with six F atoms in the peripheral. The reasons are summarized in the following three points. (1) The replacement of H with F on the switching unit results in the variation of band gaps. The energy gap of the H-substituted diarylethene molecule is about 1.7 eV, while the gap of diarylethene (F) molecule is about 1.3 eV. (2) The alignment of the Fermi level is different for two systems. For the junction with the H-substituted molecule, the peak coming from the perturbed HOMO locates at -0.7 eV, which is closer to the Fermi level than the perturbed LUMO transmission peak (at 1.0 eV). This result is consistent with these previous theoretical studies on other DTC and DTE derivations.<sup>21,22</sup> However, the Fermi level lies close to the transmission contributed by the perturbed LUMO for the diarylethene (F) molecular junction, as shown in Fig. 3. (3) The transport properties under small bias voltage are mainly determined by the tail of the transmission peak coming from the perturbed LUMO for the closed diarylethene (F) molecular junction. However, the conductivity of the closed H-substituted one is controlled the tail of transmission peak contributed by the perturbed HOMO. Nonetheless, the light-controlled switching feature is undoubtedly retained.

Experimental and theoretical results revealed that the visible adsorption spectra changed when two S atoms of the switching unit were substituted by O atoms.<sup>35</sup> Thus, the transmission spectra of the molecular junction shown in Fig.1 (b) where two S atoms in central switching unit are replaced by O atoms are also calculated here, as shown in Fig. 4 with red dotted lines. Clearly, the switching behavior does not depend sensitively on the O-substituent. However, it should be pointed out that the positions of significant transmission peaks obviously shift when compared to Fig. 3. Particularly, the transmission peaks coming from the perturbed HOMO and LUMO locates at -0.7 and 0.8 eV, respectively. Again, the tail of perturbed HOMO transmission peak contributes largely to the low bias electronic conductance.

#### D. Effect of varying end anchoring atoms

In general, the transport properties of molecular junctions depend nontrivially on the end linking atoms.<sup>36,37</sup> Now we turn to explore the effect of alternating end anchoring atoms. The calculated transmission spectra at zero bias voltage are shown in Figure 5. The black solid and red dotted lines stand for end Se- and Te-anchored cases, respectively. It is clear

that the main characteristics of the transmission spectra are maintained and the closed structure is undoubtedly more conductive. For the end Se-anchored case, the energies of perturbed MO are quite close to the data presented in Fig. 3 of the end S-anchored one. Interestingly, clearly observable changes have been shown for the end Te-anchored case. The transmission peaks originating from the perturbed HOMO and LUMO for the molecular junction connecting to gold electrodes through Te atoms locates at -1.0 (-0.8 for S-anchored one) and 0.3 eV (0.5 for S-anchored one), respectively. The very interesting finding of this study is that the switching behavior of diarylethene derivatives based molecular junctions is robust to vary end anchoring atoms from S to Se and Te.

To examine the sensitivity of results shown in Fig. 3 to small change of the electrode-electrode distance, we compute the zero-bias transmission spectra of diarylethene switches with the closed and open structures as elongating and shortening electrode-electrode separation up to 0.3 Å. We find that the transmission spectra experience little change, and transport properties of this kind of diarylethene molecular junction is not detectably sensitive to the electrode-electrode distance. It indicates that this kind of light-controlled switching based on diarylethene derivatives is stable as a molecular switching device. Note that the transport behavior is described by the electron elastic scattering theory in our calculations. The effect arising from the electronic vibration and the accompanying heat dissipation on the calculated on-off ratio can be neglected because of the remarkable difference of the I-V curves.<sup>38</sup>

#### IV. CONCLUSION

In summary, we investigate the transport properties of the diarylethene with closed and open structures using the NEGF combined the DFT method. The zero-bias transmission function of two different forms is strikingly distinctive. The open form lacks any significant transmission peak within a wide energy window, while the closed structure has two significant transmission peaks on the both sides of the Fermi level. The electronic transport properties of the molecular junction with closed structure under a small bias voltage are mainly determined by the tail of the transmission peak contributed unusually by the perturbed lowest perturbed unoccupied molecular orbital. The calculated on-off ratio of currents between the closed and open configurations is about two orders of magnitude, which

reproduces the essential features of the experimental measured results. Moreover, although the alignments of the perturbed molecular orbitals’s energies with respect to the electrode’s Fermi level are not exactly the same, we find that the switching behavior within a wide bias voltage window is extremely robust to both substituting F or S for H or O and varying end anchoring atoms from S to Se and Te.

## ACKNOWLEDGMENTS

This work was partially supported by the National Natural Science Foundation of China under Grants 10674121, 10574119, 50121202, and 20533030, by National Key Basic Research Program under Grant No. 2006CB922004, by the USTC-HP HPC project, and by the SCCAS and Shanghai Supercomputer Center. Work at NTU is supported in part by A\*STAR SERC grant (No. 0521170032).

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Figure 1: (Color online) (a) The diarylethene derivative in closed and open configurations. (b) A schematic of the switching junction. Diarylethene molecules are sandwiched between two Au (111) surfaces, and two S anchoring atoms are located at the hollow site. The vertical blue line denotes the interface between the scattering region and the left or right gold electrode.

Figure 2: (Color online) The calculated current-voltage characteristics of the diarylethene and its derivative molecular junctions with two different configurations. The triangles linking with black solid lines are for the diarylethene molecular junction, while the circles linking with short red dotted lines stand for the junction where six F atoms in the peripheral of cyclopentene are substituted by H atoms. The filled (empty) symbols correspond to the closed (open) structures. The inset below right is the I-V curve for the open structures (with F and H atoms in the peripheral, respectively) in small scale for clarity.

Figure 3: (Color online) The zero-bias voltage transmission spectra versus the energy  $E-E_F$  of diarylethene molecular junctions with the closed (a) and open (b) configurations. Here,  $E_F$  is the Fermi level of electrodes. The red short vertical lines stand for the positions of MPSH molecular energy levels. The spatial distributions of the perturbed HOMOs and LUMOs are inserted in the figure, and placed at the right and left sides of the  $E_F$ , respectively.

Figure 4: (Color online) The calculated transmission spectra versus the energy  $E-E_F$  at zero-bias voltage for diarylethene molecular junctions with closed (a) and open (b) forms, respectively. One case is that six F atoms in the peripheral of central cyclopentene are substituted by H atoms (with black solid lines); the other is that two S atoms are replaced by O atoms (with red dotted lines). The red short vertical lines stand for the positions of MPSH molecular energy levels.

Figure 5: (Color online) The calculated transmission spectra for diarylethene molecular junctions with closed (a) and open (b) structures. The black solid and red dotted lines stand for the end anchoring Se and Te atoms, respectively. Here, the red short vertical lines stand for the positions of MPSH molecular energy levels.

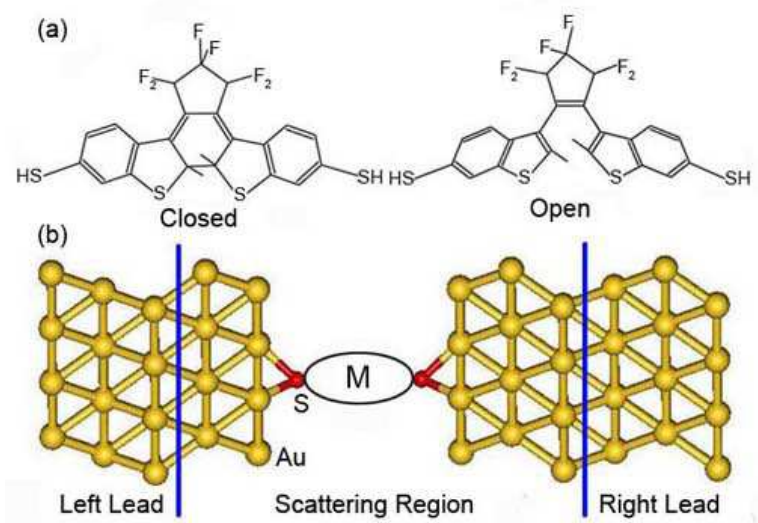


Fig.1 of Huang *et al.*



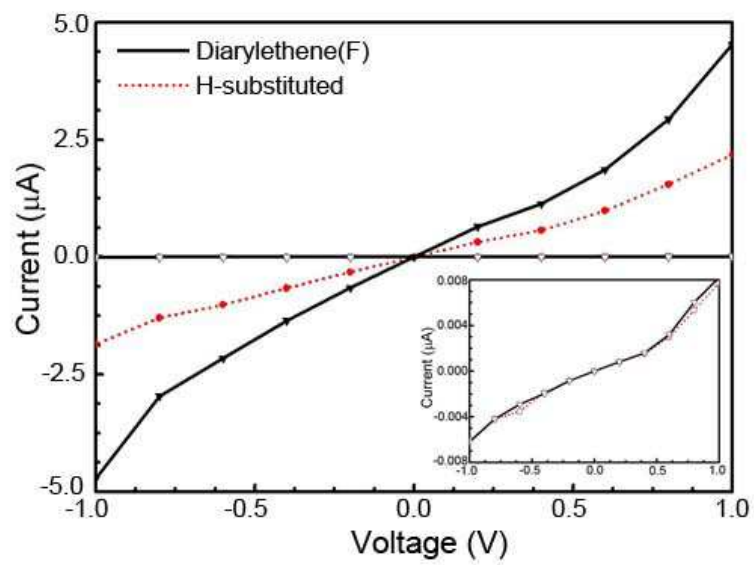


Fig.2 of Huang *et al.*

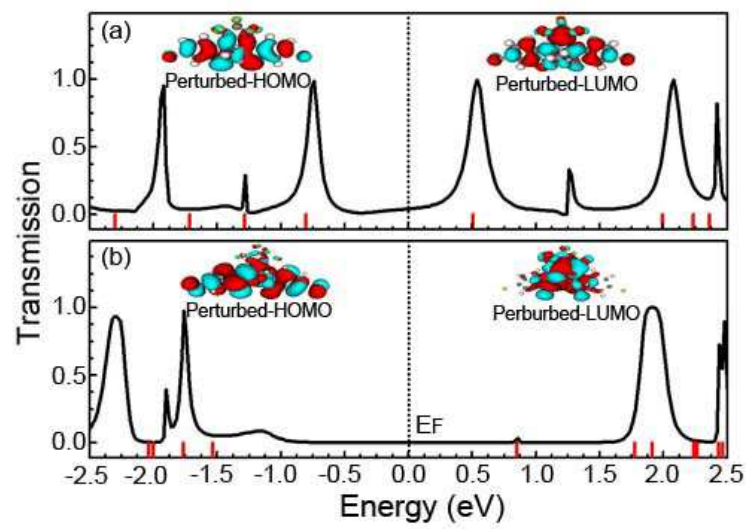


Fig.3 of Huang *et al.*

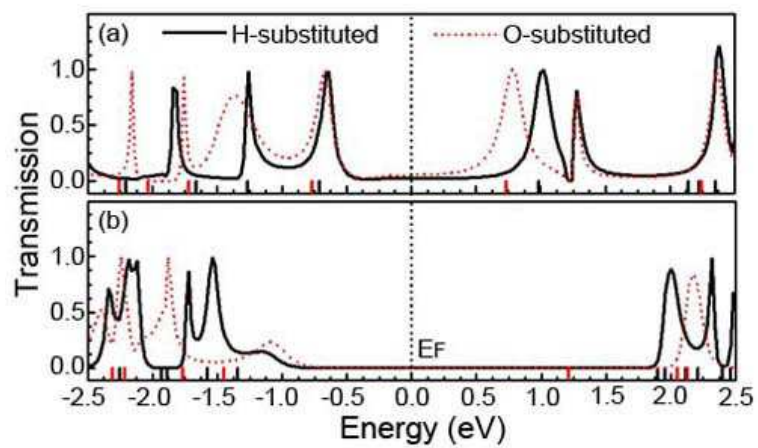


Fig.4 of Huang *et al.*

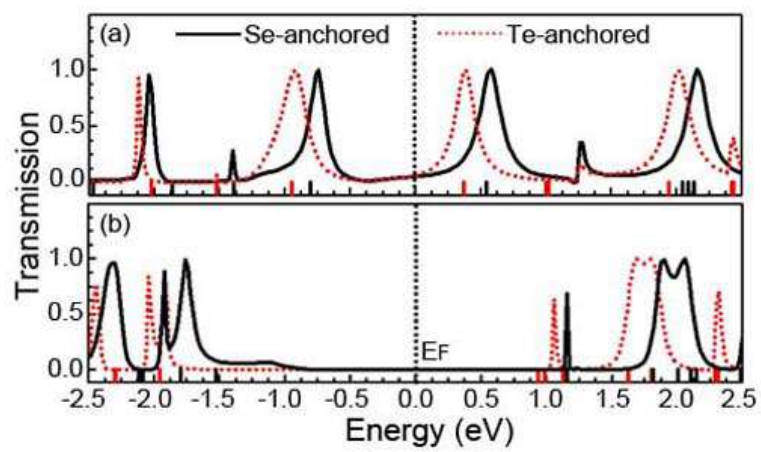


Fig.5 of Huang *et al.*