Effects of Conformational Transformations on Electronic Transport Properties of Optical Molecular Switches: An *ab initio* Study

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1 Salicylidene Schiff Bases and Phenanthrenequinones

1.1 HOMO, LUMO and Energy Gap between HOMO and LUMO

The energy levels of the molecular orbits, especially HOMO and LUMO, are excellent indicators of many molecular properties, such as chemical activity and electronic transport. Fig. S1 shows the HOMO and LUMO levels, as well as their gaps (HLG), for the molecular switches of salicylidene schiff bases (SSBs) and phenanthrenequinones (PQs). In the entire bias window, the HOMO and LUMO levels are out of the region of bias window, which indicates that the total currents of SSBs with different junctions are not contributed by the HOMO and LUMO resonance, thus the current and conductance difference between OH-SSB and O-SSB can not be explained by the MPSH and HLG curves with the bias. However, in the PQs system, the HOMO level of m-PQ begins to enter the bias window at the bias of 0.5 V, which means that the HOMO resonance provides a channel for the electron transport of m-PQ. This tendency is in coincidence with the sharp current and conductance increasing rate of m-PQ. In such an open system, the Fermi level EF of the gold electrode aligns between HOMO and LUMO, therefore, the barrier for the electron transport is intensively relevant to HLG. In first approximation, it is proportional to HLG, when other factors are kept the same. As HLG of m-PQ is less than that of r-PQ, which results in a high conductance of m-PQ that is 2 ~ 3 orders of magnitude larger than that of r-PQ.

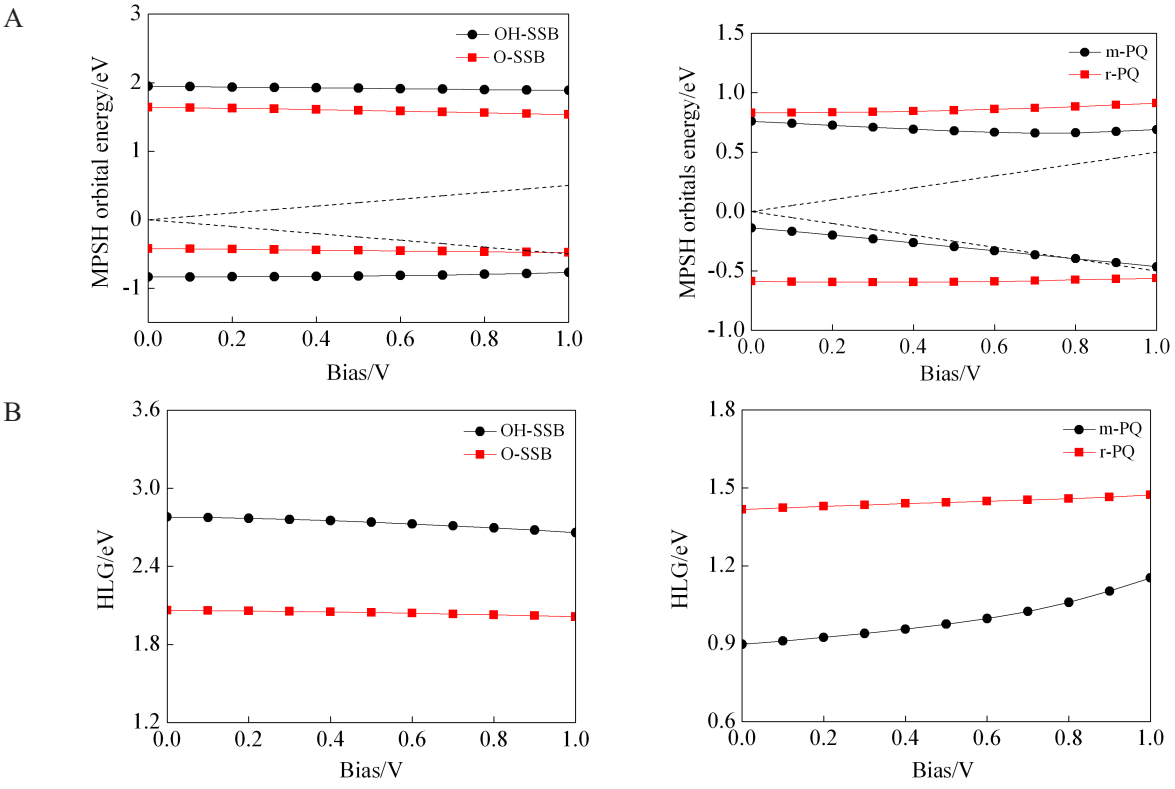

Fig. S1 A. The HOMO and LUMO levels of SSBs and PQs with all junctions (the region between the dashed lines stands for the bias window); B. The HLG dependence on external bias of SSBs and PQs with all junctions

1.2 Transmission and PDOS Spectra

The switching characteristics of these molecules can be understood from the energy dependence of transmission spectra, which are shown in Fig. S2. The transmission spectra of two forms of SSB and PQs display extraordinarily different characteristics. The systems with OH-SSB and O-SSB both have a wide and low transmission peak below the Fermi level. In a common sense, the transmission peaks height in bias window is mainly determined by the orbital delocalization. The similar HOMO and LUMO delocalization of OH-SSB and O-SSB makes these two similar HOMO peaks. As current is the integral of the transmission coefficient in bias window, the current of OH-SSB is still a little larger than that of O-SSB, thus the molecular switch with OH-SSB is in on state when the bias is 1.0 V.

When PQ is applied as a molecular switch, the transmission spectra show a different shape despite the same chemical transformations with SSBs upon photoexcitation. In the transmission spectra, only the LUMO resonance peak of m-PQ is in the bias window around the Fermi level, which verifies more contribution of this frontier molecular orbit to the electron transport. This is in coincidence with the high current and conductance of m-PQ. However, the peak location of HOMO and LUMO resonances for r-PQ is too far from the Fermi level, making it contribute less to the conductance at 1.0 V. Thus, it results in a low current and conductance of r-PQ.

The right panels in Fig. S2 show the PDOS which is projected density of states of the molecular part in the whole device system. For these two molecular switches, the peaks in PDOS spectra correspond to the peaks at the same position in transmission spectra. Especially the sharp LUMO resonance peak of m-PQ at 0.5 eV in PDOS corresponds to the strong transmission channel being opened in $T(E)$. The similarity of PDOS plot and transmission spectra for PQ results in a similar electron transport characteristic.

2 Azobenzenes and Dihydrodibenzodiazocines

2.1 HOMO, LUMO and Energy Gap between HOMO and LUMO

We focus on the effects of *E*/*Z* structures and connections on electronic structures by analyzing the static properties of azobenzenes (ABs) and dihydrodibenzodiazocines (AB-C2s). Fig. S3A plots the corresponding molecular orbital energy levels projected onto ABs and AB-C2s to the bias voltage. HOMO energy levels of *E*-isomers of AB and AB-C2 are both close to Fermi level. The electron emission from HOMO to LUMO can easily take place in the *E*-isomer switching unit. Meanwhile, only HOMO level of *E*-isomer of AB is in the bias

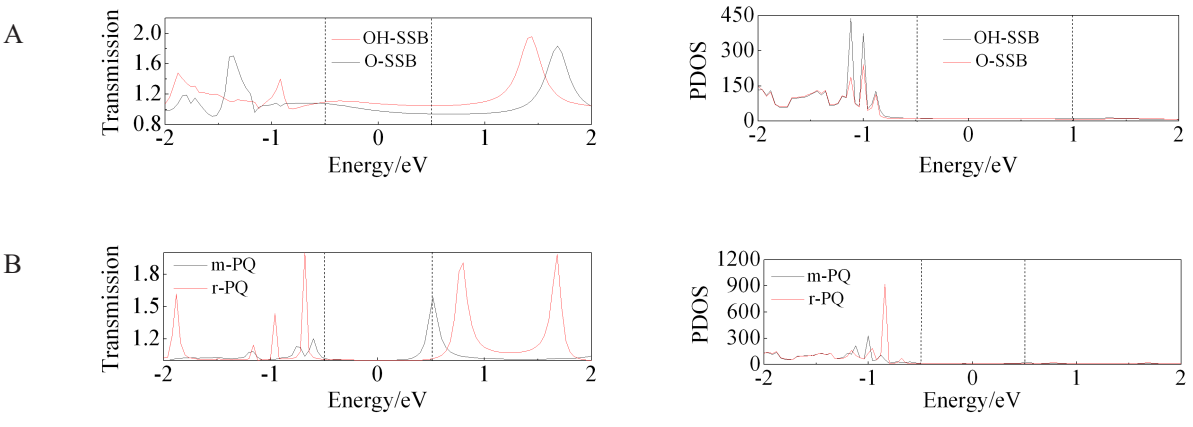

Fig. S2 Transmission and PDOS spectra for SSBs and PQs at 1.0 V (the region between the dashed lines stands for the bias window)

window since the bias is larger than 0.1 V, which results in the large conductance gap between *E*/*Z* isomers of AB. However, HOMO levels of *E*/*Z* isomers of AB-C2 are both in the bias window that leads to their conductance not formed the large difference that ABs have.

The energy offset between LUMO and HOMO, in other words HLG, is an indicator of the height of energy barrier that electrons have to cross over in the tunneling models. It is commonly thought that lower energy barrier height brings about a higher electronic conductance. Fig. S3B shows the HLG for *E*/*Z* isomers of AB and AB-C2. The HLG of *E*-AB is apparently smaller than that of *Z*-AB in the entire bias range, although it increases with the rise of voltage but that of Z-AB decreases. As a result, the electron of *E*-AB can inject into LUMO from electrode or hop into electrode from HOMO more easily than that of *Z*-AB. Therefore, the conductance of *E*-AB is larger than that of *Z*-AB. The similar conclusion can also be obtained from the HLG-*V* curves for *E*/*Z* isomers of AB-C2.

2.2 Transmission and PDOS Spectra

The switching characteristics of the ABs and AB-C2s systems can be understood from the transmission spectra. The calculated energy dependence of transmission spectra for *E*/*Z* isomers of AB and AB-C2 at 1.0 V are plotted in Fig. S4. As shown in the transmission spectra, the bias window is wide enough to include at least part of the main transmission waves. It is clearly shown that the transmission peaks of *E*-AB are wider and higher than that of *Z*-AB. Since a high peak corresponds to a large transmission probability, the conductance of *E*-AB is larger than that of *Z*-AB. In the case of AB-C2, the first peak around the Fermi level is mainly

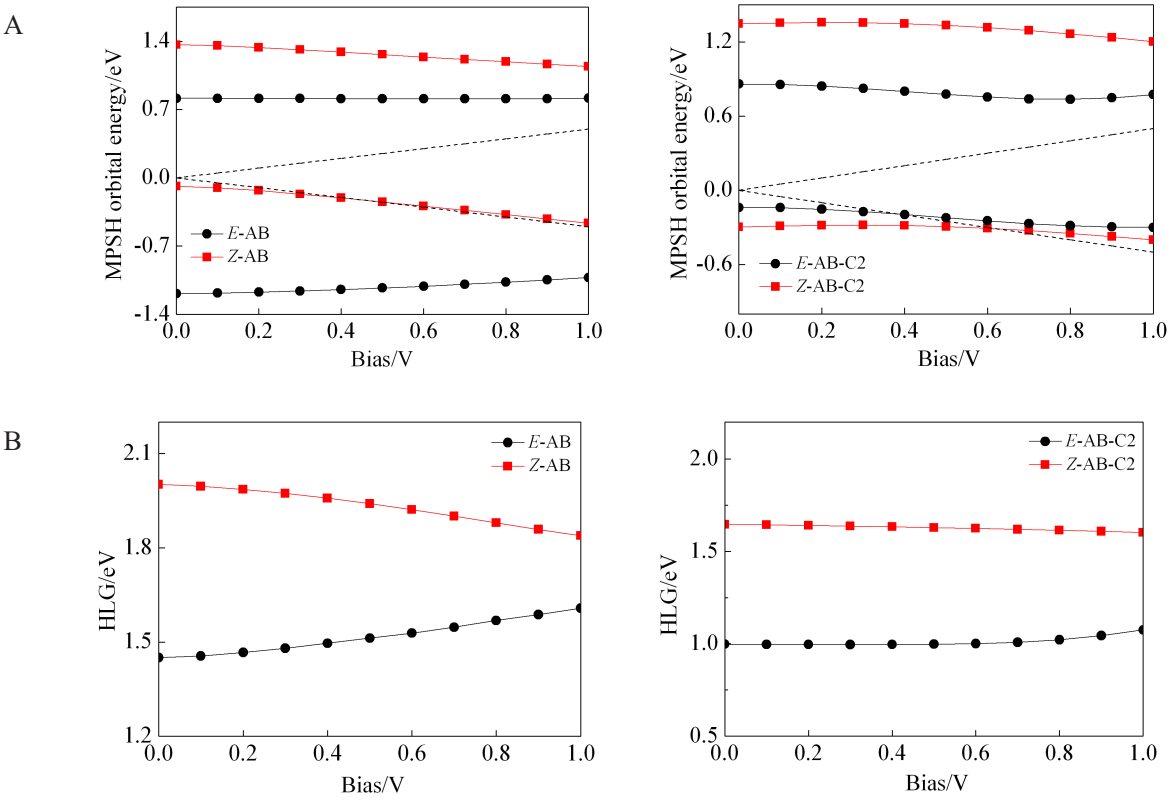

Fig. S3　A. The HOMO and LUMO levels for *E*/*Z* isomers of ABs and AB-C2s　(the region between the dashed lines stands for the bias window); B. The HLG dependence on external bias of *E*/*Z* isomers of ABs and AB-C2s

composed of the HOMO of the molecule. The integral area under the HOMO peak of *E*-AB-C2 is greatly larger than that of *Z*-AB-C2 in the bias window. Therefore, the current through *E*-AB-C2 is larger than that of *Z*-AB-C2 according to the expression of current above.

To understand the origin of the electron transport properties, we present the projected densities of states (PDOS) for *E*/*Z* isomers of AB and AB-C2 at 1.0 V in Fig. S4. The PDOS provides the information about the lineup of the molecular levels relative to the electrode Fermi energy level, and it determines and controls the electron transport across the molecule. From Fig. S4A, we find that in the bias window there is only a weak peak which originates from the HOMO level of *E*-AB (the peak height is about 13.78). This peak just corresponds to a transmission channel being opened in *T*(*E*). The similarity of PDOS plot and transmission spectra for ABs results in a similar electron transport characteristic. As shown in Fig. S4B, the HOMO peaks for *E*/*Z*-isomer of AB-C2 are both in the bias window, though they are very weak. The peak height of *E*-AB-C2 is closer to Fermi level than that of *Z*-AB-C2, which is also similar to the transmission spectra. The results below give an excellent explanation to the electron transport in *E*/*Z* isomers of AB and AB-C2 and their different photoswitching performance.

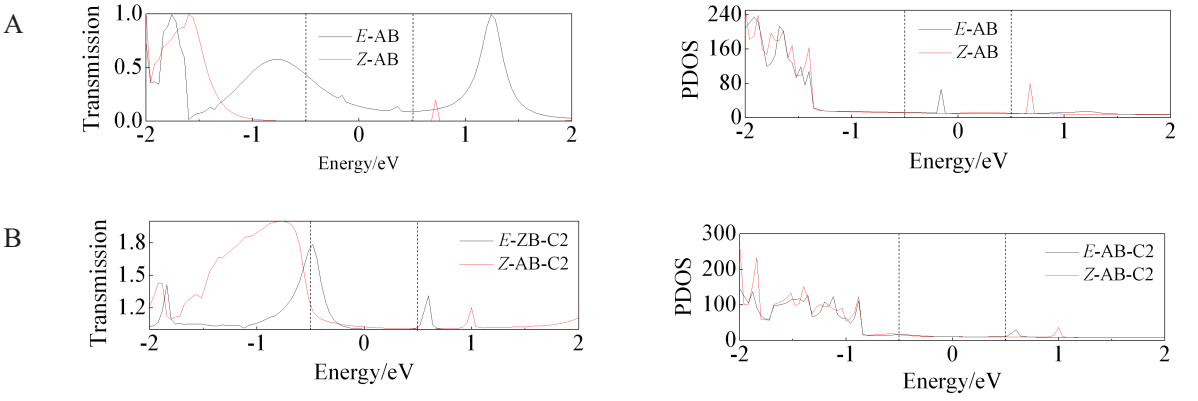

Fig. S4 Transmission and PDOS spectra for *E/Z* isomers of ABs and AB-C2s at 1.0 V (the region between the dashed line means for the bias window)

3 Fulgimides and Diarylethenes

3.1 HOMO, LUMO and Energy Gap between HOMO and LUMO

Several static features, including HOMO, LUMO energy levels and HLG have been well-characterized. Fig. S5A plots the HOMO and LUMO of fulgimides (FMs) and diarylethenes (DTs) with different junctions at 1.0 V. For FMs system, the HOMO and LUMO levels of closed ring forms are closer to Fermi level and the HOMO level is in the bias window when the bias is up to 0.2 V. The excellent conjugation of closed-FM narrows the energy gap. Although they both rise up after the application of bias, HLG keeps constant and lower than that of opened-FM. Thus, the on/off states of FMs have not been changed in the entire bias range.

In the case of DTs photochrome, the HOMO and LUMO levels of closed-DT are in the bias window at high bias and close to Fermi level, indicating both the HOMO and LUMO contribute to the conductance of closed-DT. However, in the DT switch with opened ring form, only the LUMO level is in the bias window. But as the LUMO level of closed-DT is closer to Fermi level than that of opened-DT, it provides a channel for electron transport of closed-DT more efficiently. As a result, the conductance and current of closed-DT are a little higher than those of opened-DT.

3.2 Transmission and PDOS Spectra

To explore the origin of the photoswitchable characteristics of these two systems, we further analyze the transmission and PDOS spectra. Fig. S6 plots the transmission spectra as function of the electronic energy at 1.0

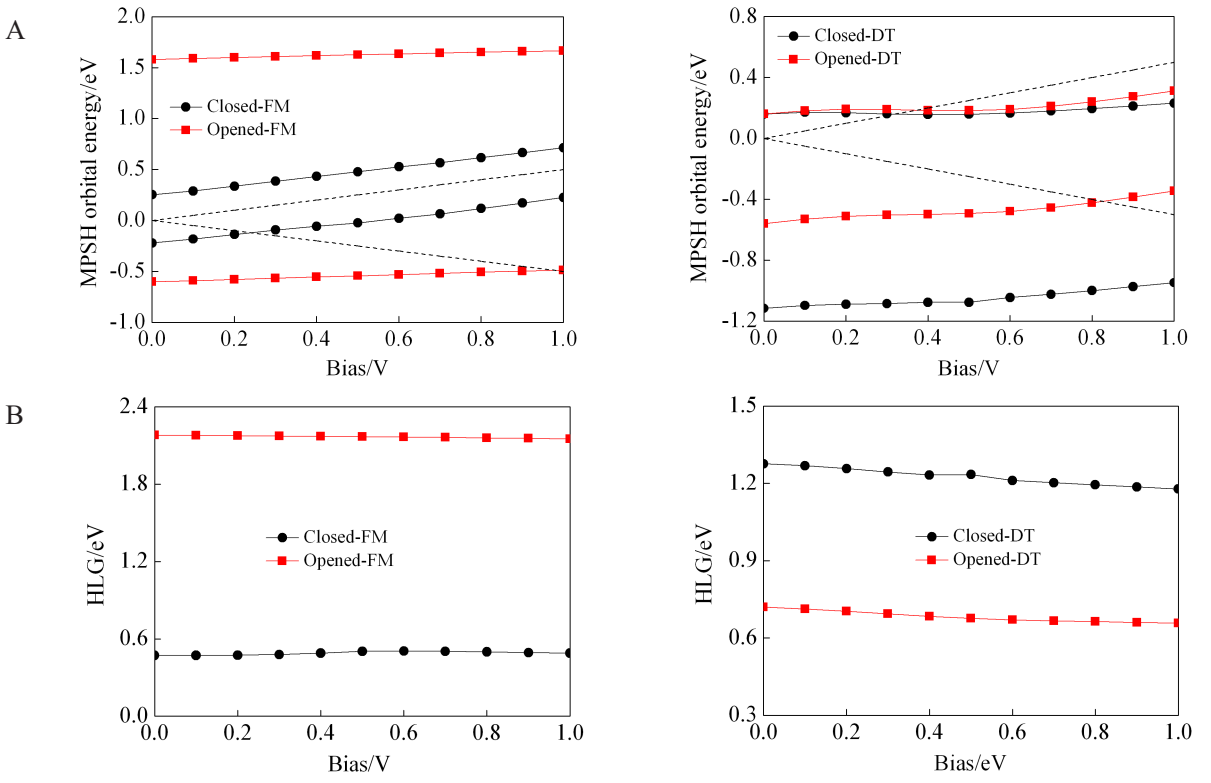

Fig. S5　A. The HOMO and LUMO levels of FMs and DTs with closed and opened-ring junctions　(the region between the dashed lines stands for the bias window); B. The HLG dependence on external bias of FMs and DTs with closed and opened-ring junctions

V. For FMs system, since there is only a peak in the bias window that is mainly contributed by the LUMO resonance of closed-FM, the conductance of closed-FM at 1.0 V is mostly caused by the LUMO resonance wave. The LUMO resonance peaks of closed-FM also can be observed at 0.4 eV. Combining with the sharp of LUMO peaks of closed-FM in the transmission and PDOS spectra, we can conclude that the LUMO state mainly contributes to the current of closed-FM. However, there are no apparent peaks in the bias window for opened-FM resulting in the low conductance of opened-FM.

In the transmission spectra of DTs, the most notable feature is the sharp and wide peaks with large transmission probability closer to the Fermi level for closed and opened ring forms despite the peak height for opened ring form is lower than that for closed form. These peaks are mainly contributed by the HOMO resonance. As the integral of the transmission coefficient of closed-DT is larger than that of opened-DT, the current of closed-DT is larger that that of opened-DT. Thus, the on/off state of DTs is determined.

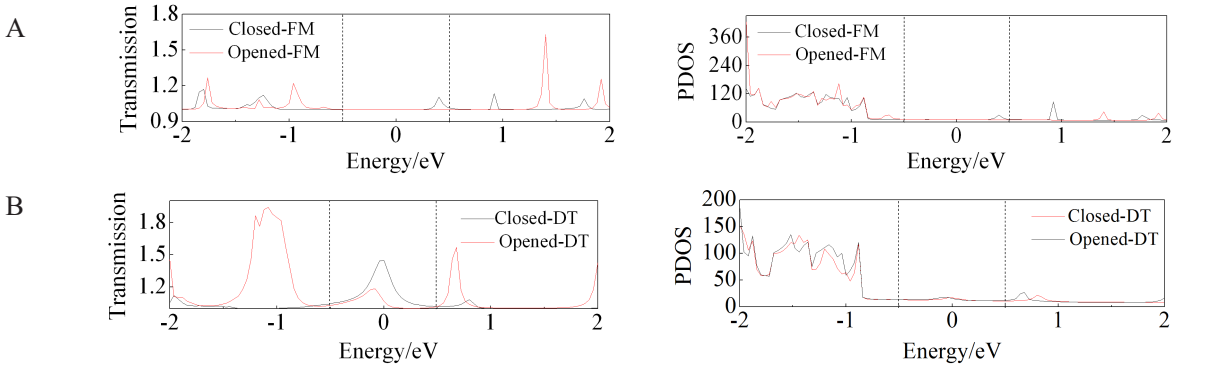

Fig. S6　Transmission and PDOS spectra for FMs and DTs with closed and opened-ring junctions　(the region between the dash lines stands for the bias window)