Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Theoretical estimation of size effects on the electronic transport in tailored graphene nanoribbons

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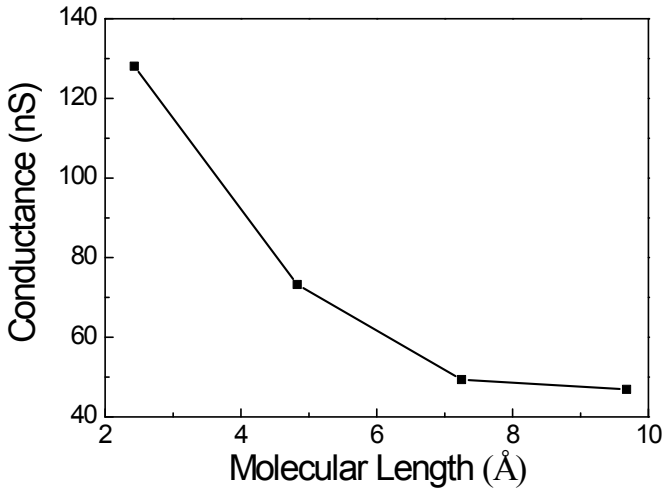

Figure S1. Differential conductance of graphene nanoribbons with different lengths.

Figure S1 gives differential conductance of graphene nanoribbons with different lengths. The conductance of L2-D2, L3-D2, and L4-D2 is 73.2, 49.4, and 46.9 nS, respectively, which decreases slightly. Because there is only one benzene unit in the junction in the model L1-D2, the electronic coupling between the two graphene sheets cannot be blocked effectively. Therefore, L1-D2 is 128.1 nS, about two/three times the conductivity of the others. The results indicate that the length along the electron transport direction has limited influence on the junction transport performance in these t-GNRs with the zigzag configuration. Therefore, we speculate that the uncertainty in the length as caused by manufacturing will not have a fatal impact on device

performance.

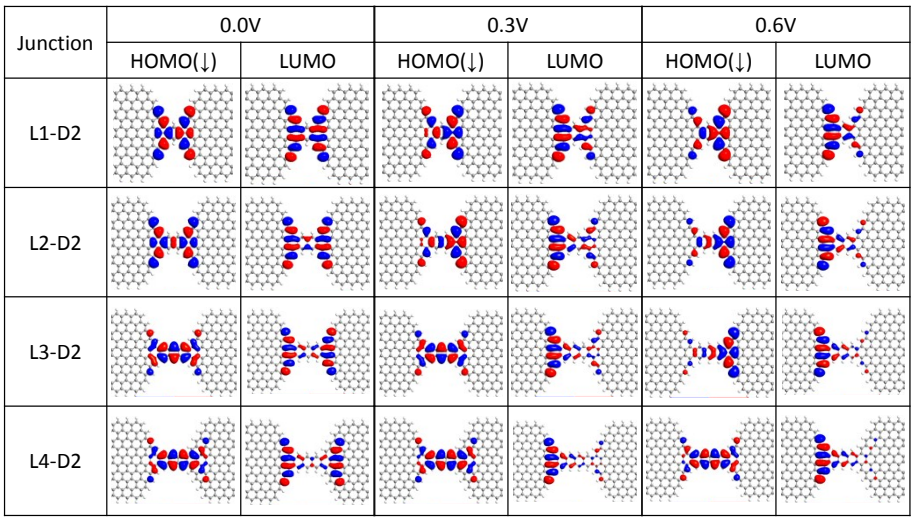

Figure S2. The spatial distributions of HOMO(spin down, ↓) and LUMO of the four systems at several representative biases. Isovalues are fixed at 0.03 for all isosurface plots.

Figure S2 shows the spatial distributions of HOMO and LUMO with spin down projected onto central part of the junction of the four systems at several representative biases. It can be seen that the HOMO and LUMO orbitals with spin down have the same feature as that of HOMO and LUMO with spin up. Both HOMO and LUMO in all four systems exhibit a good vertical symmetry at zero bias. Without the application of a bias, HOMO tends to be distributed on the fused benzene chain. It is most prominent in the longer system, such as L4-D2, indicating that short connecting chain, i.e. L1-D2, cannot block the coupling between two graphene nanosheets effectively. On the other hand, LUMO is mainly populated on the two extension regions. With increasing the chain length, the separation of LUMO becomes more significant.

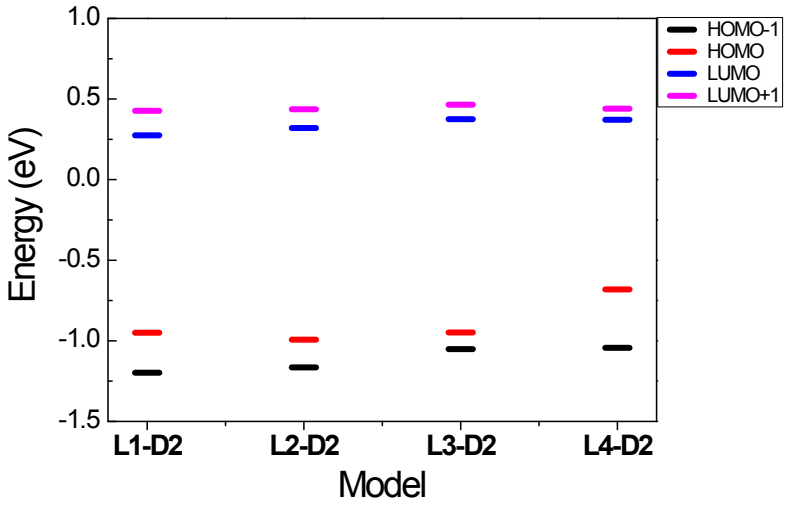

Figure S3. Energy levels of frontier molecular orbits of junctions with different lengths at zero bias.

The highest occupied molecular orbital (HOMO(↑)) and the lowest unoccupied molecular orbital (LUMO) are often used to predict the electron transport of molecular junctions. **Figure** S2 displays the energy levels of molecular orbitals around the Fermi level at zero bias. As we can be seen, the HOMO of all models has the similar energy, same as with the LUMO. The HLG of L1-D2, L2-D2, L3-D2, and L4-D2 is 0.74, 1.31, 1.30, and 1.07 eV, respectively. Except for L1-D2, the rest of the models almost have same energy, which agrees with the results in the *I-V* curve. L1-D2 is about twice the conductivity of the others, and others almost have same values.

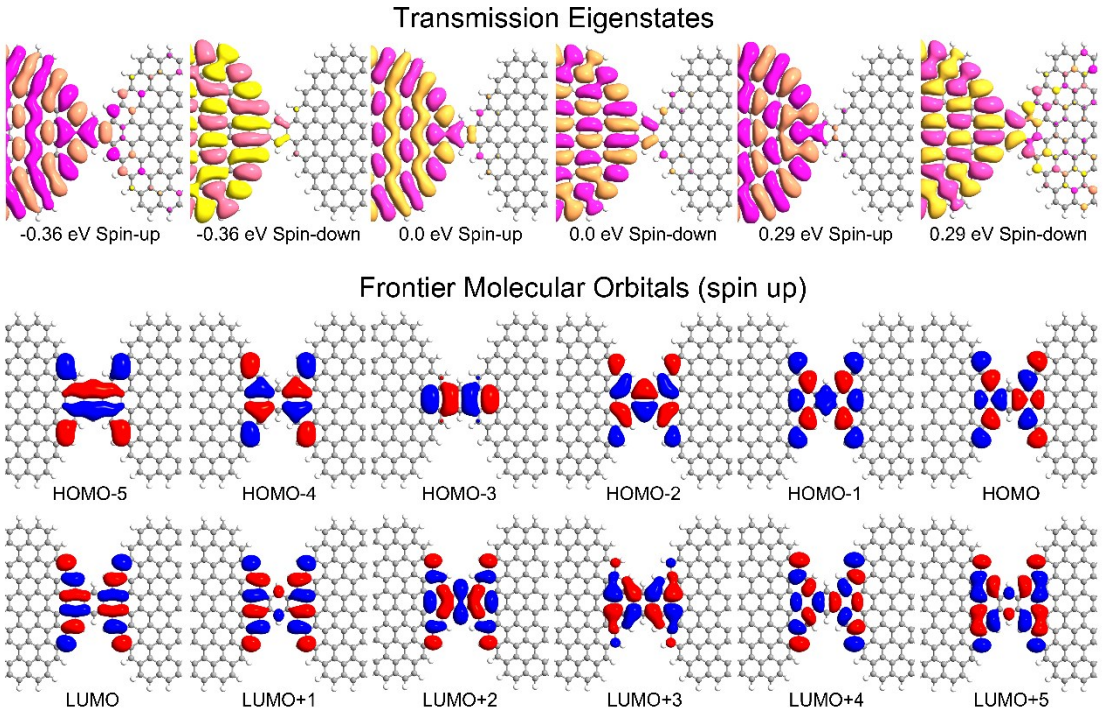

Figure S4. Transmission eigenstates and frontier molecular orbitals of L1-D2 junction at zero bias. Isovalues are fixed at 0.03 for all isosurface plots.

The transmission eigenstate is an analysis option for the intuitive electron transmission image[66-68]. The transmission eigenstates of L1-D2 at zero bias are also shown in **Figure** S4. The initial state of transmission eigenstate is contributed by the left electrode. Comparing the transmission eigenstates with the molecular orbitals at zero bias, the transmission eigenstates have a clear resemblance with the LUMO orbitals, respectively. It means that the main transmission channel of L1-D2 junction mainly originates from the LUMO orbitals.

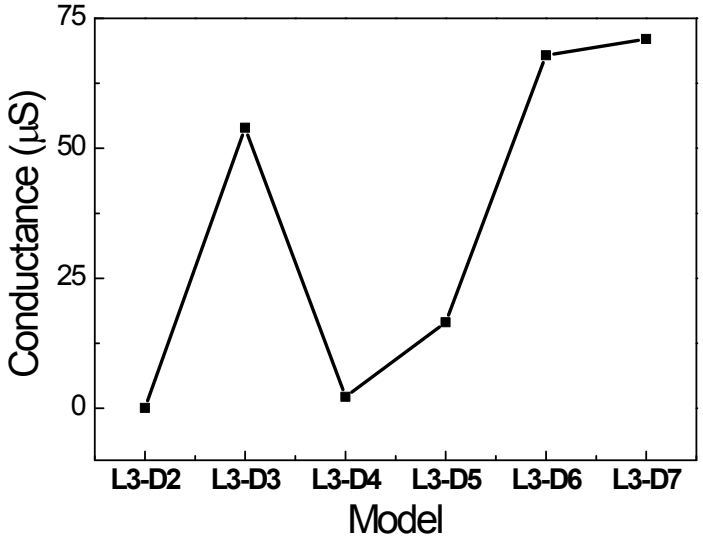

Figure S5. The zero-bias conductance of the series of junctions with different widths.

However, as shown in **Figure** S5, L3-D2 has a zero-bias conductance of 0.05 μS, much smaller than all others. Then, the junction conductance suddenly jumps to 53.93 μS for L3-D3. Further increase of the junction width leads to a decrease of the conductance, i.e., 2.19 μS for L3-D4 and 16.52 μS for L3-D5. However, there are only small difference among L3-D6 (67.90 μS), and L3-D7 (71.03 μS). From these results we may speculate that the minimum width should be wider than L3-D6 (1.35 nm) to minimize the influence from the manufacturing error, when the t-GNR is used as a junction in the electronic devices.

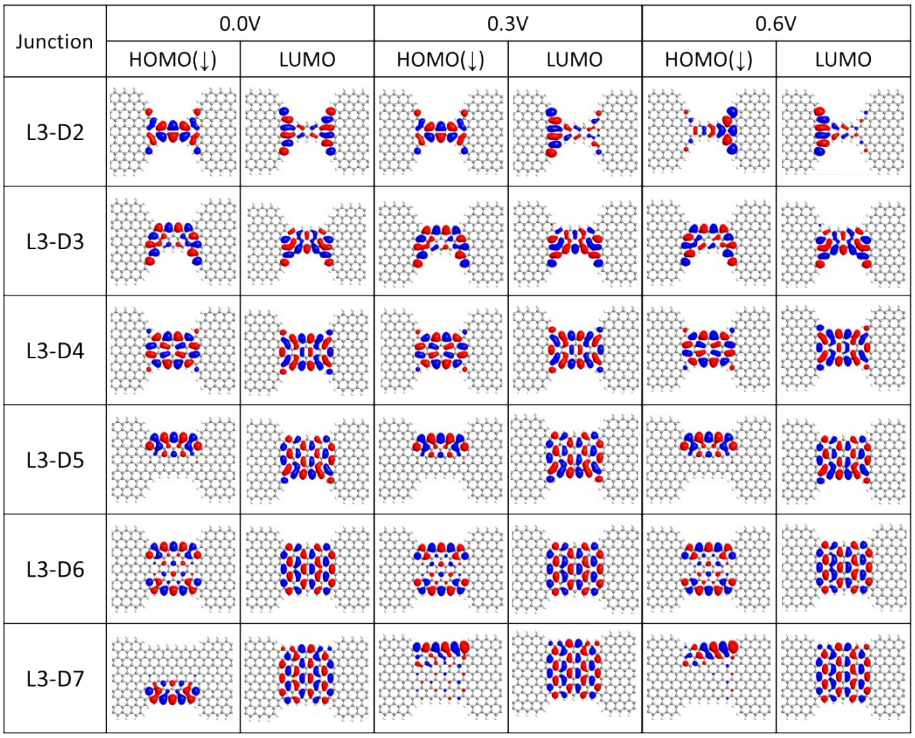

Figure S6. The spatial distributions of HOMO(spin down, ↓) and LUMO of the six systems at several representative biases. Isovalues are fixed at 0.03 for all isosurface plots.

Figure S6 shows the spatial distributions of HOMO with spin down and LUMO projected onto central part of the junction of the six systems at several representative biases. It can be seen that the HOMO with spin down and LUMO orbitals have the same feature as that of HOMO with spin up and LUMO. HOMO prefers to be located at the edges of the central nanoribbon all the time, which is especially prominent in the wide systems, such as L3-D6. On the other hand, the odd systems are all asymmetric relative to the electron transport direction, as also evidenced in spatial distribution. HOMO is spreading along only one side of the nanoribbon. LUMO shows the same feature, though it is not very prominent. According to the analysis of zero-bias spatial distribution, the electron transfer is considered to pass through the edges of the nanoribbon, which governs the odd-even variation of the junction conductivity. Besides, the spatial distributions of HOMO and LUMO are not sensitive to the applied bias, except for L2-D3 and L7-D3.

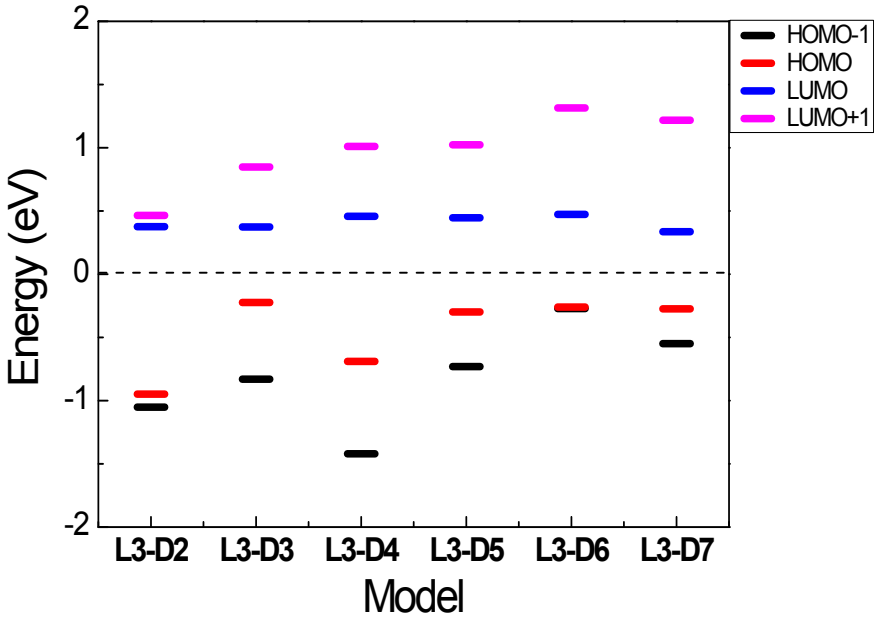

Figure S7. Energy levels of frontier molecular orbits of junctions with different widths at zero bias.

Figure S7 gives HOMO with spin up and LUMO energy levels of junctions with different widths at zero bias. Obviously, with the increasing of widths, the value of HLG shows a clear odd-even variation. The HLGs value of even models are higher than that of odd models, which is consistent with the result that odd models have greater conductivity than even models. However, while the size is wider than L3-D5 (1.14 nm), the amplitude of the variation decreases and the models have close HLG values. Taking L3-D5 and L3-D6 for example, their HLG values are 0.60 eV and 0.64 eV, respectively.