Theoretical study on the rectification mechanisms of molecular *pn* diodes

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Molecular electronics aims at a utilization of single molecules as electronic device components such as wires, memories, and diodes. As an example, Aviram and Ratner (AR) proposed a molecular diode consisting of donor (D) and acceptor (A) molecular fragments separated by a spacer as shown in Fig. 1[1]. The proposed forward direction of the AR diode is the same as that of the bulk pn diode. However, the forward direction of the most D-A complexes, even including the AR diode [2], has been found to be opposite to the *pn* mechanism. This is because the positive bias voltage of the A⟶D (reverse bias) direction narrows the gap between the highest occupied molecular orbital (HOMO) of D and the lowest unoccupied MO (LUMO) of A.

Recently, we found two molecular diodes that show the same rectification direction to that of *pn* junctions. The molecular structures are given in Fig. 2. To investigate the relationship between molecular junction structures and the rectification mechanism, the non-equilibrium green's function method combined with density functional theory (NEGF-DFT) [3] was used. The molecular projected self-consistent Hamiltonian (MPSH) scheme was employed to analyze the response of MOs to applied bias. Electron transport in the carbazole oligomer is dominated by HOMO. The bias voltage affects its couplings to the left/right electrodes through the deformation of HOMO, which is the origin of the rectification. On the other hand, in the case of the Zn-porphyrin-imide complex, MOs are localized on either of porphyrin (L), imide (M), or benzene (R). The applied bias volatage modulates the energy level alignment of MOs and the resonance between those localized MOs causes the rectification behavior.

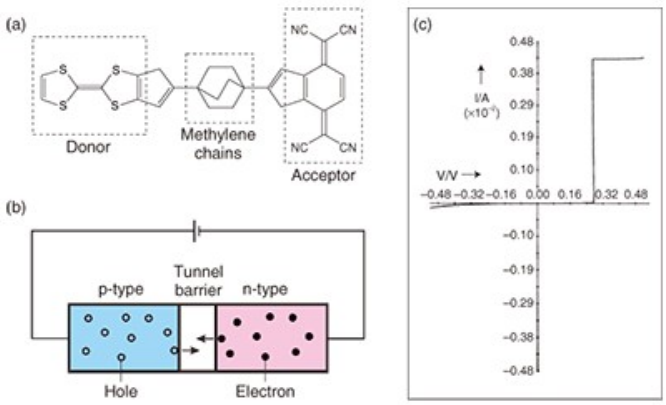

Figure 1: Aviram-Ratner diode. [1]

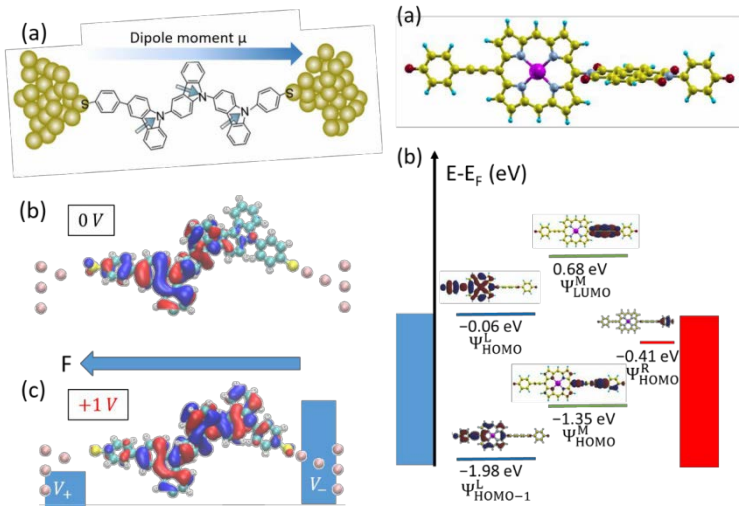

Figure 2: (Left) Carbazole oligomer diode. (a) Molecular structure and the distribution of HOMO under (b) 0 V and (c) 1 V. (Right) Zn-porphyrin-imide complex. (a) Molecular structure and (b) MO energy alignment.

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