Negative Differential Resistance of Oligo (Phenylene Ethynylene) Self-Assembled Monolayer Systems: The Electric Field Induced Conformational Change Mechanism – Supporting Information

Hyungjun Kim[a,b], *Seung Soon Jang*[c], *Richard A. Kiehl*[d], *and William A. Goddard*[a,b,*]

[a]Graduate School of EEWS, Korea Advanced Institute of Science and Technology (WCU), Daejeon 305-701, Republic of Korea

[b]Materials and Process Simulation Center, Beckman Institute, California Institute of Technology, Pasadena, CA 91125,

[c]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245

[d]Department of Electrical and Computer Engineering, University of California, Davis, CA 95616

[*]To whom correspondence should be addressed. E-mail: wag@wag.caltech.edu.

Appendix S1.

The electric field (F) between two electrodes is proportional to the bias voltage, V. If we consider the distance between two electrodes, d, the proportional coefficient is around 0.1 $Å^{-1}$ ~ 0.05 $Å^{-1}$ because d is around 10 Å ~ 20 Å. As we mentioned in the manuscript, however, our limitations in the simulation (e.g. small size of periodic cell) requires a large external electric field to induce the phase transitions within a finite simulation time scale. Thus, we chose around one order larger value of conversion factor which is 0.93 $Å^{-1}$. We note that this converts the critical field strength, F_c = 0.56 V/Å into the critical bias voltage V_c of 0.6 V.

Appendix S2.

We calculated that the SAM of 5´-nitro monosubstituted OPE system (N-OPE) on Au (111) surface. We figured out that N-OPE also can have two conformations of P and T on the SAM by forming weak HB networks along $[11\bar{2}0]$ direction and $[10\bar{1}0]$ direction, respectively. The lack of amino group makes NO_2 form a weak HB with the positive aromatic H atoms of the adjacent molecules (Figure 10 of the manuscript).

The twist angles are χ = 4º and χ = 163º for P and T, respectively. These are almost identical to the values in AN-OPE case. Therefore, we expect the conductance ratio for N-OPE to be very similar to AN-OPE.

From PBE DFT calculations, P is more stable than T by 6.57 kcal/mol when no external field is applied. The dipole moment component in the $[0001]$ direction are 3.83 (2.01) debye for P and 6.61 (3.86) debye for T from the analysis of Mulliken charges, while the parenthetical values are from quantum mechanical wave-function. Thus, the favorable state is changed from P to T as the external field is applied (Figure S3). This suggests that the N-OPE also undergo conformational change from P

to T as the bias voltage increases. The critical field F_c is calculated as 0.49 V/Å using dipole moments from Mulliken charge. Since this is similar to the F_c in AN-OPE system (0.56 V/Å), the critical bias voltage where NDR occurs to be similar to the critical bias voltage of AN-OPE system of ~ 0.6 V, in agreement with the experimental results.

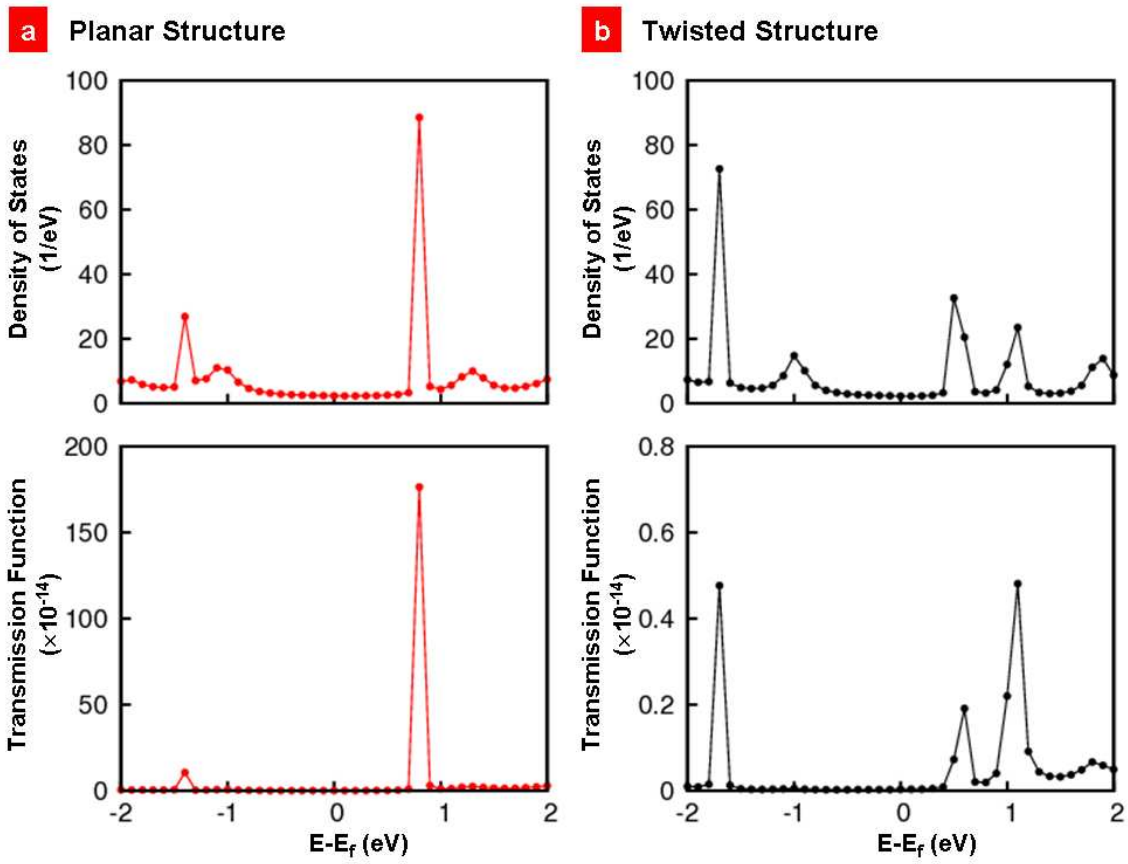

Figure S1. Density of state (DOS) and transmission function T(E) of (a) P structure and (b) T structure. The top electrode is located 20 Å above from the bottom electrode.

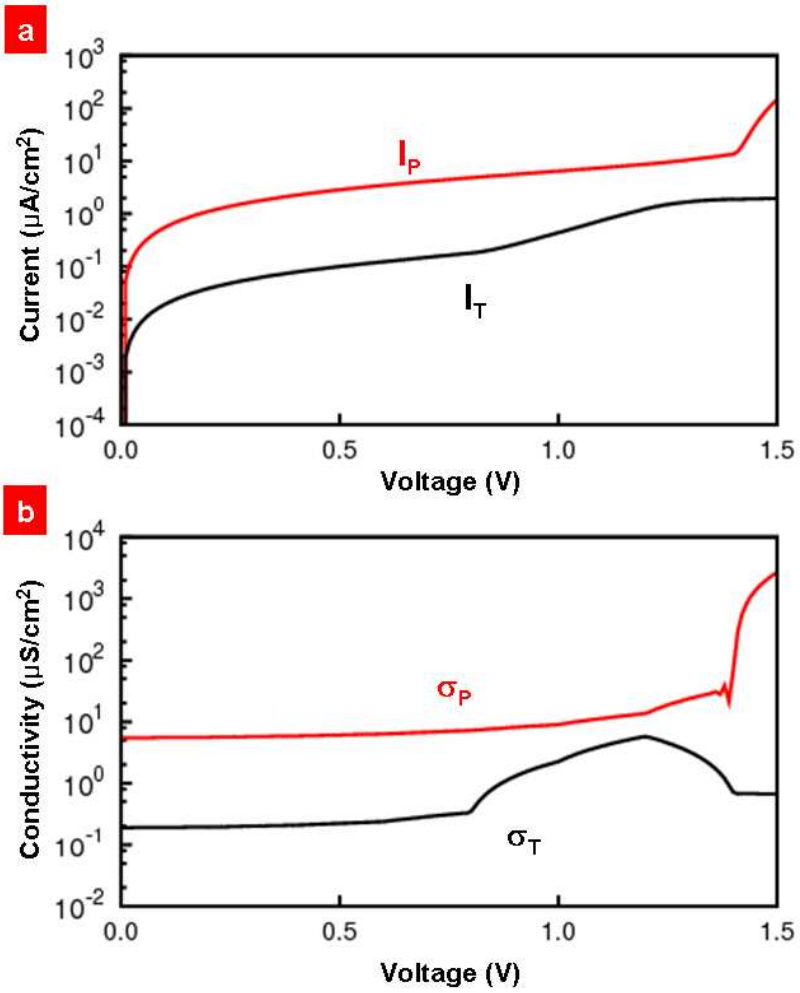

Figure S2. (a) Current through P conformation, I_P and current through T conformation, I_T versus the bias voltage V determined from the NEGF calculations using the DOS and T(E) of Figure S1. (b) Conductivity of P conformation, σ_P and conductivity of T conformation, σ_T versus the bias voltage V determined from (a). The top electrode is located 20 Å above from the bottom electrode. σ_P is ~ 163 times larger than σ_T.

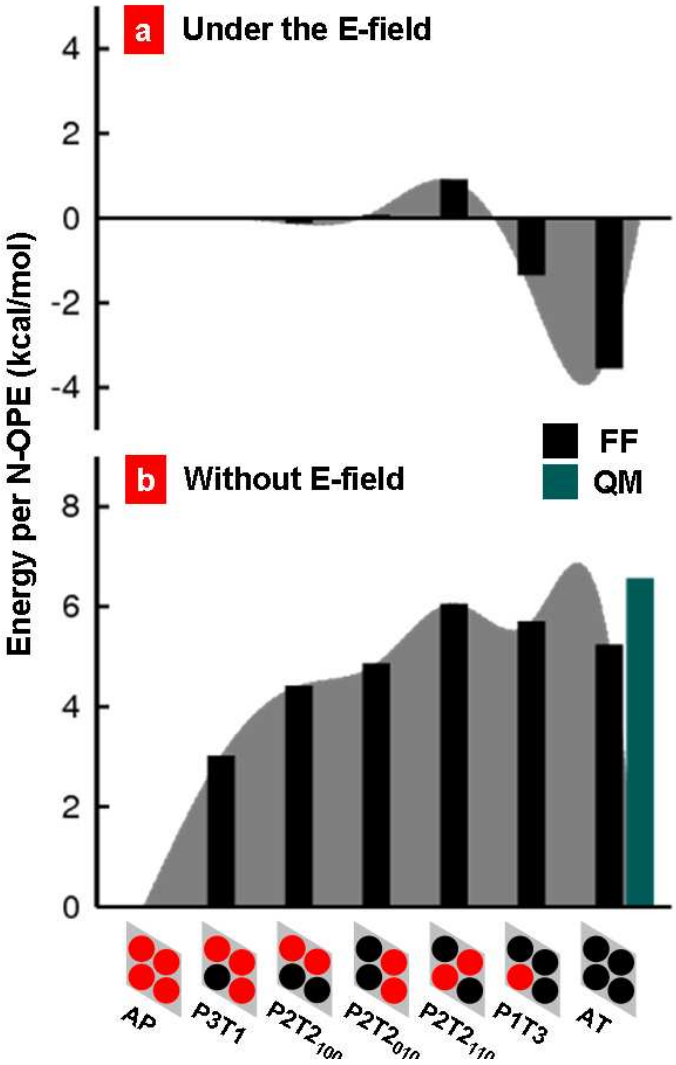

Figure S3. (a) Energies of various conformations of N-OPE relative to the AP conformation computed with a 0.6 V/Å external field from FF calculations (black histograms). (b) Energies of various conformations of AN-OPE relative to the AP conformation computed with no external field from FF calculations (black histograms) and QM calculations (green histograms).