

Chapter 2

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

Abstract We investigate here a possible mechanism for the room temperature Negative Differential Resistance (NDR) in the Au/AN-OPE/RS/Hg self-assembled monolayer (SAM) system, where AN-OPE = 2'-amino, 5'-nitro oligo (phenylene ethynylene) and RS is a C14 alkyl thiolate. Kiehl and co-workers showed that this molecular system leads to NDR with hysteresis and sweep-rate-dependent position and amplitude in the NDR peak. To investigate a molecular basis for this interesting behavior, we combine first principles quantum mechanics (QM) and meso-scale lattice Monte Carlo (MC) methods to simulate the switching as a function of voltage and voltage rate, leading to results consistent with experimental observations. This simulation shows how the structural changes at the microscopic level lead to the NDR and sweep-rate dependent macroscopic I - V curve observed experimentally, suggesting a microscopic model that might aid in designing improved NDR systems.

2.1 Introduction

Esaki's discovery of the negative differential resistance (NDR) in Ge p - n diodes opened a new phase in semiconductor devices [1]. Since the NDR devices enable faster and more efficient circuits by reducing the number of transistors required, they have many applications such as high-speed integrated circuits and low-power memories. As the scale of electronic devices is reduced toward nano-scale sizes, it would be useful to demonstrate NDR in molecular electronic systems [2–13].

Derivatives of oligo (phenylene ethynylene) (OPE) have been identified as a good candidate for the molecular junctions due to its rigid and good conducting (fully conjugated) characteristics [9, 11–19]. Chen et al. reported that a SAM of amino-nitro substituted OPE (AN-OPE) between two Au electrodes exhibits NDR at 60 K with an applied voltage of ~ 2 V. The current-voltage (I - V) curve is fully reversible, but the NDR peak decays as the temperature increases. This NDR has been rationalized by the electrochemical oxidation/reduction or resonant-tunneling mechanism [15–17]. Support for this oxidation/reduction mechanism was the correspondence

between the threshold potential for the electrical conductance (2.09 V) and the electrochemical potential (1.67 V) [15, 19].

The device showing NDR at room temperature (RT) is important for many practical applications [20, 21]. However, the poor reproducibility in device construction and the limited device stability have hampered extensive study on NDR. Kiehl and co-workers showed that a SAM of AN-OPE deposited on an Au electrode coupled to a Hg electrode covered with a tetradecane-thiolate (RS) leads to a well-defined and stable NDR at RT [9]. In this system, a distinct sweeping-rate-dependency in the NDR hysteresis loop was observed for a bias voltage near ~ 0.6 V. The presence of hysteresis rules out the resonant tunneling mechanism [5–8, 10]. Based on the observed hysteresis and a variety of detailed features of the characteristics, they proposed a charge capture (QC) mechanism to explain the macroscopic I - V behavior. However, an atomistic level analysis of a charge capture process and other possible mechanisms has not yet been established.

Several studies suggest that the conformational change would be a plausible mechanism to explain hysteretic I - V curve [14, 22], and the external electric field can induce conformational change of the molecule in the junction [14, 23–26]. Especially, Donhauser et al. reported STM studies in which isolated AN-OPE molecules contained in a dodecane-thiolate SAM on the Au substrate show at least two states having different conductances [14]. They showed that the transition from the high-conductance state to the low-conductance state is switched by applying external electric field. However no detailed atomic level description of the mechanism was provided.

In this chapter, we use first principle theory to analyze the sweeping-rate-dependent hysteresis of NDR observed in Kiehl’s system, focusing on the possibility of electric field based conformational changes. We find that this system has two states:

- a high-conductance phase stable at low field (planar structure) and
- a low-conductance phase stable at high field (twisted structure).

The transition between the two phases is driven by the interaction between the external field and the molecular dipole moment of the middle phenylene ring in AN-OPE. This leads to consistent results with the charge capturing mechanism of Kiehl. Using coarse-grained Monte Carlo simulations, we investigated how such a molecular conformational change results in a sweep-rate-dependent hysteresis in the NDR as well as the detailed kinetics of transition.

2.2 Simulation Details

2.2.1 Computational Details of QM Calculations

To obtain the structures and energies of planar (P) and twisted (T) structures, we carried out QM calculations for a (1×1) periodic unit cell. We employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation exchange-correlation density-functional with a plane wave basis set (540 eV cutoff), using the Vienna

Ab initio Simulation Package (VASP) [27]. Only the gamma point is sampled in reciprocal space to reduce computational cost for this large system (67 atoms per periodic cell). For the electrodes, we used 3-layer of Au (111) surface with all gold atoms fixed at their bulk value ($a = 2.8838 \text{ \AA}$) during the geometry optimization steps. The OPE molecules were anchored on the 3×3 Au (111) surface through sulfur atoms with hexagonal packing.

To understand the local electronic structure and local interactions of the AN-OPE part, we performed non-periodic QM calculations of the isolated OPE with 3 connected Au atoms, using Jaguar package [28] with PBE exchange-correlation functional and LACVP** basis set. Using the geometries from VASP calculations, we carried out the single point calculations.

2.2.2 Conductivities of P and T Conformations (NEGF Calculations)

The I - V performance of each conformation is calculated by combining Green's function theory with the DFT Hamiltonian that are determined from the SeqQuest calculation with PBE functional [29, 30]. The current is calculated using following equation:

$$I(v) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E, V) [f_1(E, V) - f_2(E, V_2)] dE, \quad (2.1)$$

where $T(E, V)$ is the transmission function for the AN-OPE SAM part.

2.2.3 Coarse-Grained NN Interacting Hamiltonian

The NN interacting Hamiltonian which describes the AN-OPE SAM is

$$H = \sum_{i=1}^N (E_i^{\text{torsion}}(\chi) - D_i F) + \sum_{\text{NN}} U_{ij}, \quad (2.2)$$

where $E_i^{\text{torsion}}(\chi)$ is the internal torsional energy of the i -th AN-OPE molecule due to twisting the AN-OPE by an angle χ , D_i is the [0001] component of the dipole moment of the i -th AN-OPE, F is the [0001] component of the external electric field, U_{ij} is the intermolecular interaction energy between i -th and j -th AN-OPE, and summation over NN denotes that the summation is over nearest neighbors. There are two interactions each for three directions: $[10\bar{1}0]$, $[01\bar{1}0]$, and $[11\bar{2}0]$. To avoid double counting, however, we used just one interaction per direction.

2.2.4 Extracting NN Model Parameters from QM/FF Energies

The U_{ij} terms when $\{i, j\} \subset \text{P}$ or $\{i, j\} \subset \text{T}$ were determined from the Jaguar calculations (*vide infra*). In order to extract U_{ij} when $\{i \in \text{P}, j \in \text{T}\}$ or $\{i \in \text{T}, j \in \text{P}\}$,

we need to investigate inter-OPE interaction in the packed system from a larger simulation cell containing more than one OPE. Since this is too expensive for QM calculations (268 atoms), we used a simple DREIDING Force Field [31] (FF) in which the charges are based on QM. We considered six possible packings within a (2×2) unit cell:

- AP: all P's,
- AT: all T's,
- P3T1: 3 P's and 1 T,
- P2T2_{10 $\bar{1}$ 0}: 2 P's and 2 T's aligned along $[10\bar{1}0]$,
- P2T2_{01 $\bar{1}$ 0}: 2 P's and 2 T's aligned along $[01\bar{1}0]$,
- P2T2_{11 $\bar{2}$ 0}: 2 P's and 2 T's aligned along $[11\bar{2}0]$,
- P1T3: 1 P and 3 T's.

The FF energies are shown at Fig. 2.1a, b for when no external electric field and 1.2 V/Å external electric field is applied, respectively. Using FF energies under

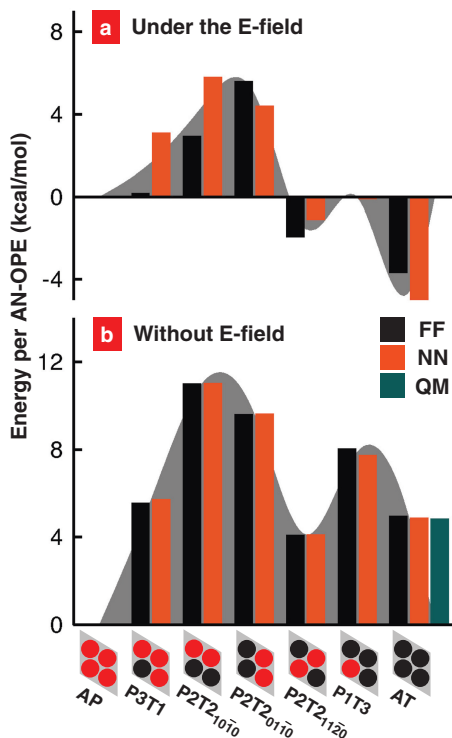


Fig. 2.1 (a) Energies of various conformations of AN-OPE relative to the AP conformation computed with a 1.2 V/Å external field from FF calculations (black histograms) and NN model calculations (orange histograms). (b) Energies of various conformations of AN-OPE relative to the AP conformation computed with no external field from FF calculations (black histograms), NN model calculations (orange histograms), and QM calculations (green histograms)

Table 2.1 AN-OPE interaction energies, U_{ij} , for Monte Carlo (MC) calculations

	$[10\bar{1}0]$ Pair	$[01\bar{1}0]$ Pair	$[11\bar{2}0]$ Pair
$\{i, j\} \subset P$	-3.95	-5.00	-7.19
$\{i, j\} \subset T$	-7.66	-3.12	-0.61
$\{i \in P, j \in T\}$ or $\{i \in T, j \in P\}$	-5.70	-2.56	3.13

All energy values are in kcal/mol.

zero external field, the U_{ij} terms when $\{i \in P, j \in T\}$ or $\{i \in T, j \in P\}$ were fitted. Values are in Table 2.1.

The torsional energy, $E_i^{torsion}$ is estimated from the energy versus twisting angle χ curve (Fig. 2.2), leading the 0.01 kcal/mol per AN-OPE when $i \in P$, and 0.23 kcal/mol when $i \in T$. The D_i values were optimized to fit the energies from Hamiltonian in Eq. 2.2 to FF energies under 1.2 V/Å external field. The fitted values are $D_i = 5.48$ debye per AN-OPE for P and 7.30 Debye for T, which are quite comparable to the dipoles from Mulliken charge analysis, $D_i = 5.74$ Debye per AN-OPE for P and 7.03 debye for T.

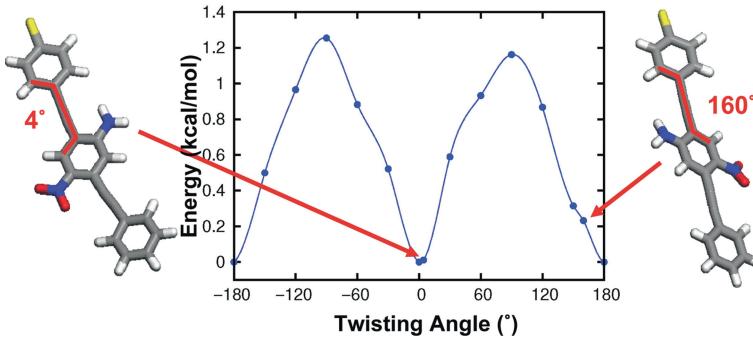


Fig. 2.2 Torsional strain energy $E_i^{torsion}$ as a function of twisting angle χ from QM (PBE) on the isolated molecule. The energy at $\chi = 4^\circ$ (corresponding to P) is 0.01 kcal/mol higher than the ground state energy at $\chi = 0^\circ$. The energy at $\chi = 160^\circ$ (which corresponds to T) is 0.23 kcal/mol higher than the energy at $\chi = 0^\circ$, leading the 0.22 kcal/mol higher $E_i^{torsion}$ of T compared to $E_i^{torsion}$ of P

All MD simulations with DREIDING FF were performed using LAMMPS (large-scale atomic/molecular massively parallel simulator) MD code from Plimpton at Sandia [32, 33]. The equations of motion were integrated using the velocity-Verlet algorithm [34], with a time step of 1.0 fs.

2.2.5 Coarse-Grained MC Simulations

The 2-dimensional rhombic MC simulation cell containing (50×50) lattice points with periodic boundary conditions. The MC simulations used the Metropolis

algorithm (our own code). Each Monte Carlo Step (MCS) is defined as 2,500 MC trials with a fixed external field applied in the z -direction. Our MC simulations are similar to the study of an Ising model in a time-dependent magnetic field [35].

2.3 Results and Discussion

2.3.1 Two Conformations of AN-OPE

Figure 2.3a shows the minimized conformation of AN-OPE determined from the periodic DFT calculation. The three phenylene rings are coplanar, forming a well-conjugated structure, which we label as P (for planar). Here the lowest ring is connected to the Au electrode via a thiolate group. The middle ring (containing the functional groups) has a twist angle of $\chi = 4^\circ$ with respect to the bottom ring ($\chi = 0^\circ$ for the isolated OPE). This structure packs on the Au surface as (3×3) , with the axis of the molecule along the $[1\bar{1}00]$ direction, and a tilt angle $\theta = 66^\circ$ from the z -axis. The adjacent amino and nitro groups form hydrogen bonding (HB) networks along the $[11\bar{2}0]$ direction.

To understand the local electronic structure and local interactions of the organic molecular part, we performed a single point non-periodic QM calculation of an isolated OPE. The polar amino and nitro groups lead to a large dipole moment of 9.24 (7.22) debye with the z -axis component ($[0001]$) of 5.74 (3.55) debye, the component along $[1\bar{1}00]$ (tilt direction) of 4.44 (3.35) debye, and the component along $[11\bar{2}0]$ (HB direction) of 5.72 (5.32) debye. These dipole moments were determined from the analysis of Mulliken charges, while the values in parenthesis are from quantum mechanical wave-functions.

The inter AN-OPE interaction energies on the SAM, U_{ij} are determined from the difference between dimer energy and doubled monomer energy:

$$U_{ij} = E_{2 \times (AN-OPE \text{ w/ } 3Au)} - 2 \times E_{AN-OPE \text{ w/ } 3Au}, \quad (2.3)$$

where we included three Au atoms connected to the sulfur atom.

The value of U_{ij} between two P's are shown at Table 2.1, especially, U_{ij} along $[11\bar{2}0]$ direction shows the largest stabilization energy of -7.19 kcal/mol, due to the HB interaction.

Figure 2.3b shows the T (for twisted) conformation, which is 4.85 kcal/mol less stable than P. The middle and terminal phenyl rings are rotated from the bottom one by $\chi = 160^\circ$. Although we note that this twist angle is not stable for the isolated AN-OPE, it becomes meta-stable in the packed system (Fig. 2.2). The rotation of the middle ring changes the direction of amino/nitro groups along $[10\bar{1}0]$ from $[11\bar{2}0]$, leading the hydrogen bond network to be aligned along $[10\bar{1}0]$. The axis of the molecule is at $\theta = 71^\circ$ from the z -axis, which makes the T lies more down than the P. The height of the terminal phenyl ring of T is 7.60 Å while that of P is 8.73 Å from the Au surface. The lower height of T is comparable to the Don-

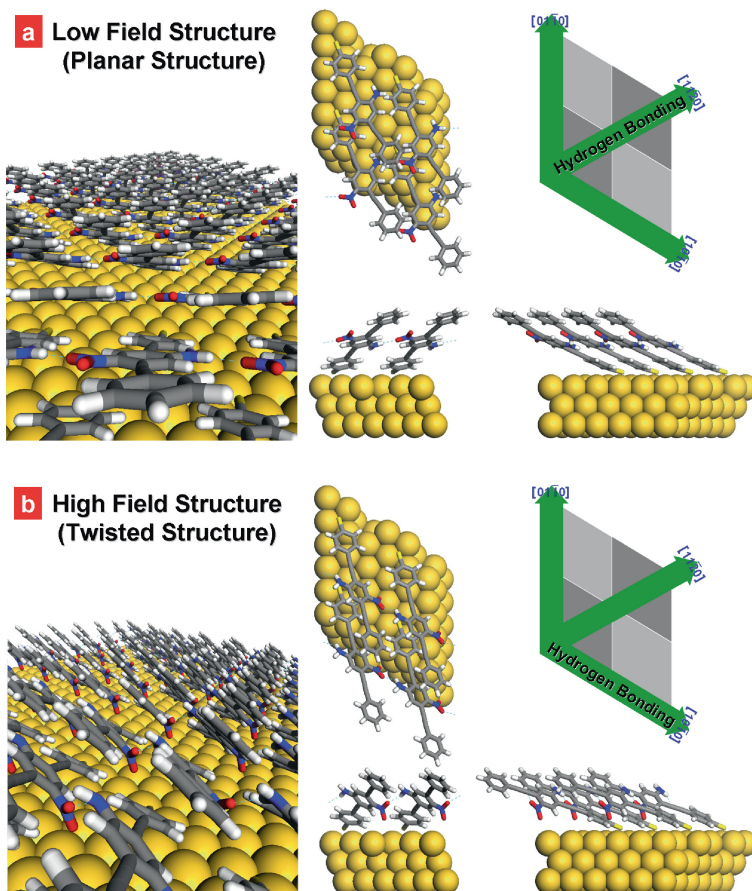


Fig. 2.3 (a) Optimized geometry for the low field structure (P) of AN-OPE SAM. Here [0001] is the surface normal and the views are along z-axis (*upper middle*), y-axis (*lower middle*), and x-axis (*lower right*). The left picture is a perspective along the axis of one plane of molecules. The hydrogen bonding network is aligned along the $[11\bar{2}0]$ direction. (b) Optimized geometry for the high field structure (T) of AN-OPE SAM. Here [0001] is the surface normal and the views are along z-axis (*upper middle*), y-axis (*lower middle*), and x-axis (*lower right*). The left picture is a perspective along the axis of one plane of molecules. The hydrogen bonding network is aligned along the $[10\bar{1}0]$ direction

hauser's observations from the STM experiment that exhibits ~ 3 Å lower height of low conductance phase to higher conductance phase [14].

The dipole moment of T is 8.71 (6.88) debye with the component along [0001] of 7.04 (4.62) debye, a component along $[1\bar{1}00]$ (tilt direction) of -3.32 (-3.40) debye and a component along $[\bar{1}010]$ (HB direction) of 5.12 (5.10) debye.

The value of U_{ij} between two T's shown at Table 2.1. For T conformation, U_{ij} along the $[10\bar{1}0]$ direction (HB network direction) is the most stable with the value of -7.66 kcal/mol.

2.3.2 Electrical Conductivities of P and T

The electrical conductivity, σ , was predicted using non-equilibrium Green's function (NEGF) theory for P and T structures with QM on the (1×1) unit cell. These calculations partition the tunneling Hamiltonian using the Gaussian basis function representation. The semi-infinite electrode is calculated interactively using 3 explicit layers of Au [29].

The experiments use a top Hg electrode covered with a tetradecane-thiolate (RS), the atomic structure of which is not certain due to the amorphous character of the Hg electrode and the fluctuations in the alkyl thiol at room temperature. Instead, our calculations use a second 3-layer of Au (111) surface $12 \text{ \AA}$ above the bottom electrode. We also tested placing the top electrode in contact with the OPE, which $20 \text{ \AA}$ above the bottom electrode.

The density of states (DOS) with the transmission function $T(E)$ were computed (Figs. 2.4 and 2.6), and these are used to obtain the I - V curve and the σ - V curve (Figs. 2.5 and 2.7). Over the range of 0–1.5 V, we see that the average ratio of σ_P to σ_T is 10 for the thickness of $12 \text{ \AA}$, and 163 for the thickness of $20 \text{ \AA}$. Since the experimental value is ~ 13 fold larger σ_P than σ_T , we adopted the case of $12 \text{ \AA}$.

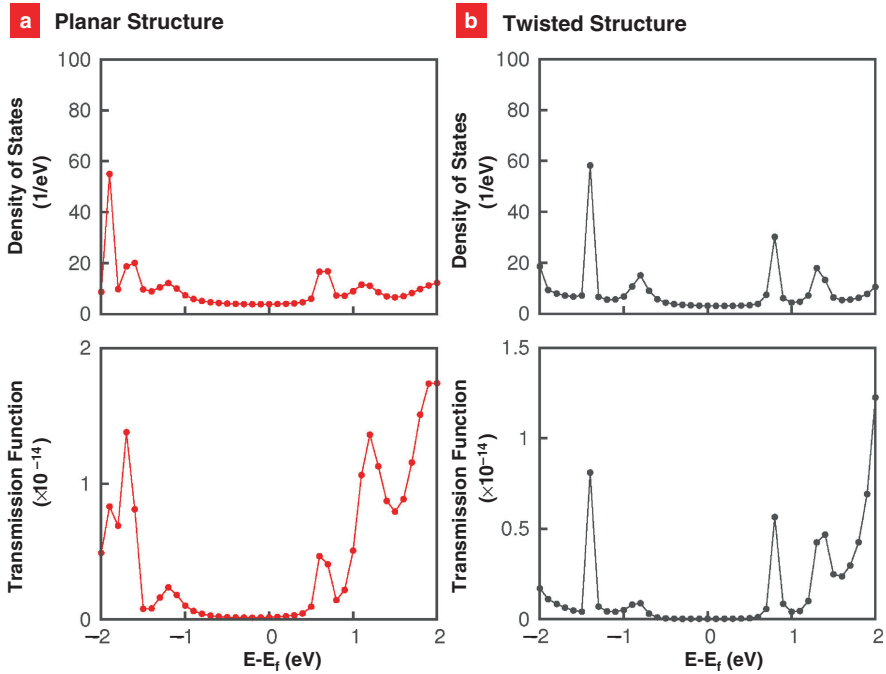


Fig. 2.4 Density of state (DOS) and transmission function $T(E)$ of P structure (a) and T structure (b). The *top* electrode is located $12 \text{ \AA}$ above from the *bottom* electrode

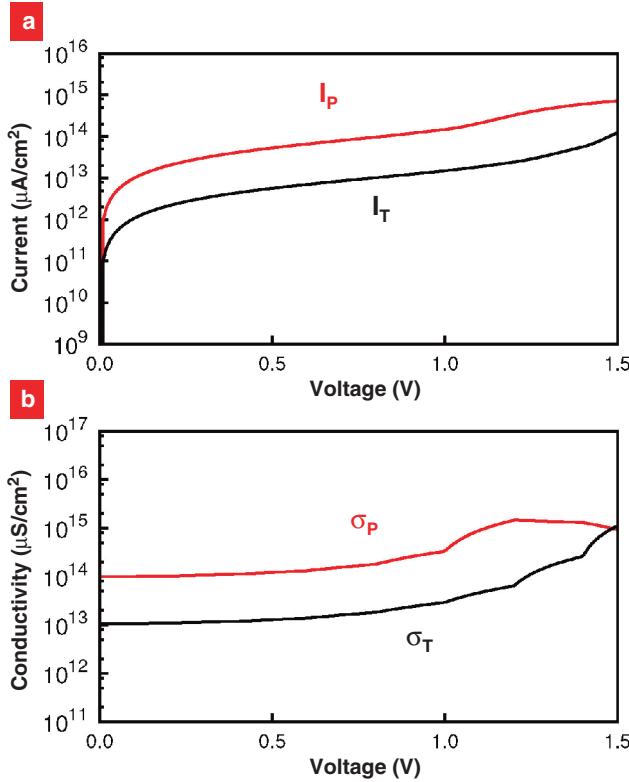


Fig. 2.5 (a) Current through P conformation, I_P and current through T conformation, I_T versus the bias voltage V determined from the NEGF calculations using the DOS and $T(E)$ of Fig. 2.4. (b) Conductivity of P conformation, σ_P and conductivity of T conformation, σ_T versus the bias voltage V determined. The *top* electrode is located 12 Å above from the *bottom* electrode. σ_P is ~ 10 times larger than σ_T

The calculated I - V curves lead correctly to a smaller σ for the high field stable phase. The difference in σ is explained by two factors:

1. the loss of π - π orbital overlap due to the rotation of the middle phenyl ring (which contributes to the conductivity through the molecules) and
2. the increase of vacuum distance due to the lower height of T phase.

Previous studies showed that the rotation of the ring by χ reduces the conductivity by factor of $\cos^4 \chi$ (Fig. 2.8) [36]. Thus, using the QM minimized structures, which are twisted by 4° and 160° , yield an average ratio of σ_P to σ_T by ~ 1.3 times. However, considering the distribution of angles from the MD, we find an average ratio of σ_P to σ_T of ~ 3.5 times. (Details are discussed in Section 8.2.)

The minimized structures for P and T lead semi-log plots of I - V curves (Fig. 2.5) to show similar slopes for both phases, in disagreement with experiment showing a slope ratio of ~ 3.2 . From previous study [36], we found that the slope of the

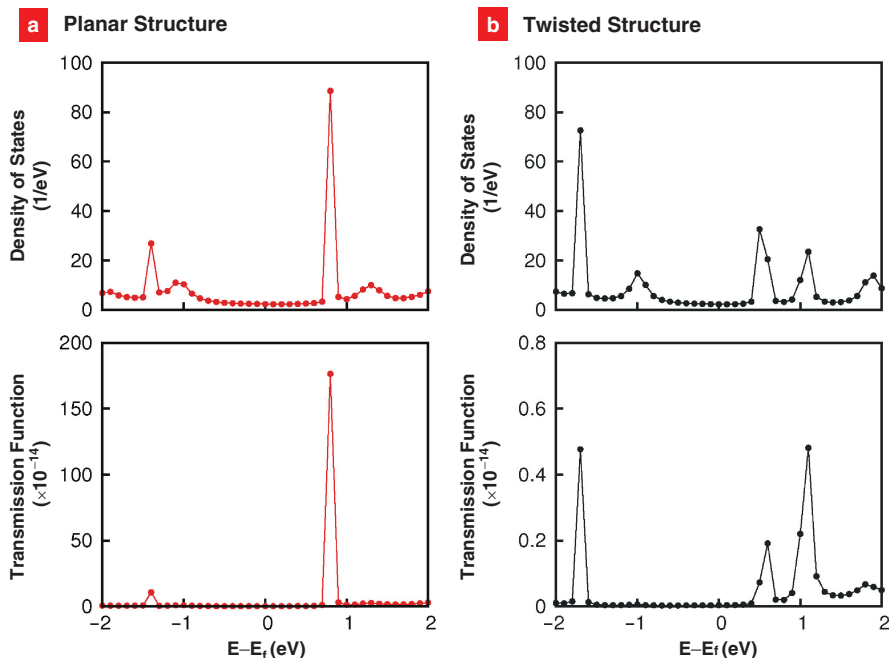


Fig. 2.6 Density of state (DOS) and transmission function $T(E)$ of P structure (a) and T structure (b). The *top* electrode is located 20 Å above from the *bottom* electrode

semi-log plot of I - V curve strongly depends on the χ , and it decreases until almost zero when the molecule twisted with $\chi = 90^\circ$ (Fig. 2.8a). This is a reasonable result since the slope of semi-log plot is related to the height of tunneling barrier, Φ_B which highly depends on the π - π orbital overlap. Therefore, consideration of the twisted structure from MD simulations, which has a significant population near 90° , well explains the distinct difference between the slopes of semi-log I - V plots for both structures observed in the experiment.

2.3.3 Response to Constant External Field

In order to describe the structural rearrangement process of the AN-OPE SAM, we use a (50×50) unit cell containing 2,500 AN-OPE molecules. To describe the dynamics of such a large simulation cell, we developed a simplified nearest neighbor (NN) interaction Hamiltonian with the model parameters extracted from QM and Force Field (FF) energies (Fig. 2.1). Important feature of the NN model is that the energetically favorable state changes from P to T as the external electric field increases, due to the higher dipole moment along [0001] of the T phase. In this model, the critical field for which the energies of both states are same is $F_c = 0.56 \text{ V/\AA}$.

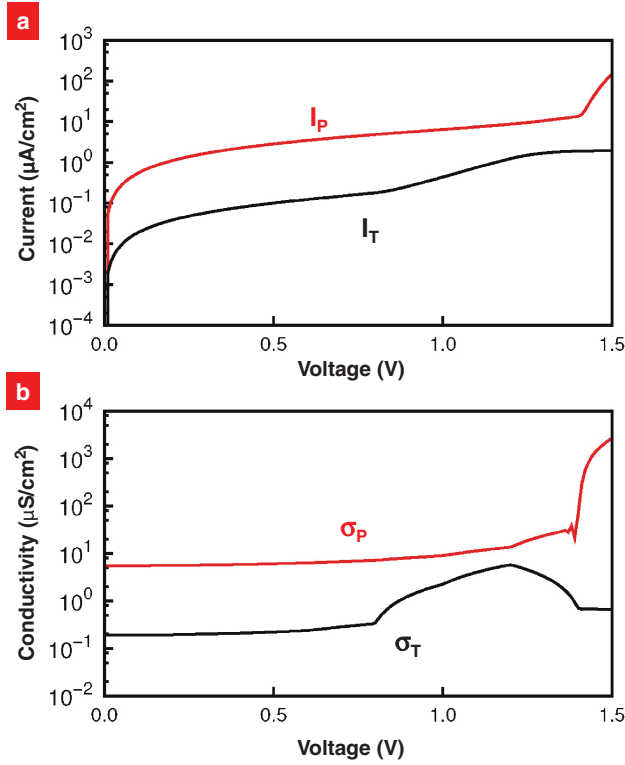


Fig. 2.7 (a) Current through P conformation, I_P and current through T conformation, I_T versus the bias voltage V determined from the NEGF calculations using the DOS and T(E) of Fig. 2.6. (b) Conductivity of P conformation, σ_P and conductivity of T conformation, σ_T versus the bias voltage V determined. The *top* electrode is located 20 Å above from the *bottom* electrode. σ_P is ~ 163 times larger than σ_T .

We simulated the response of the SAM of the P's to the $1.2 \text{ V}/\text{\AA}$ external field during 1.2×10^6 Monte Carlo steps (MCS) at $T = 300 \text{ K}$. Figure 2.9a, b show the time evolution of the system starting with all P's and ending with all T's and the population change with the electrical conductivity change during this P-to-T transition, respectively. There were no T states until just before 55,184 MCS, but within the next 15 steps, half of the neighbors along $[11\bar{2}0]$ have transformed, and after another 15 steps the entire $[11\bar{2}0]$ line is transformed to the T. Then, by 405,907 MCS, totally 19 $[11\bar{2}0]$ lines have transformed, which are all neighbors to the original one. Then, at 486,389 MCS, we see that a second $[11\bar{2}0]$ swath has nucleated. By 697,272 MCS, these two have grown to 28 and 7 adjacent lines but still just two swathes, and from 697,273 MCS, they are merged into one swath. Finally, by 1,008,706 MCS the full system is transformed to T. Along with the decrease of the P population, the total conductivity through the SAM also decreases.

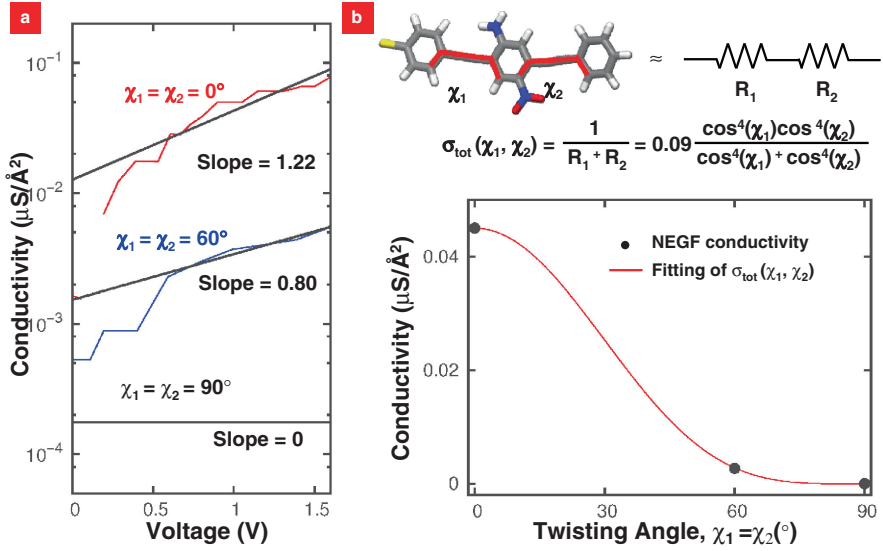


Fig. 2.8 Conductivities depending on the twisting angle are extracted from the previous study [36], which are the results from NEGF calculations. (a) Semi-log plots of I - V curves shows that the slope decrease as the twist angle approaches to 90° , which means that the tunneling barrier from the *bottom* electrode to *top* electrode, Φ_B increases as the π - π orbital overlap decreases. (b) Since the conductivity is dominated by the π - π orbital overlap, we assumed that the conductivity between two phenyl rings, $\sigma_i = 1/R_i$ is proportional to $\cos^4(\chi_i)$. From simple calculation leads the total conductivity σ_{tot} to be proportional to the $\cos^4(\chi_1)\cos^4(\chi_2)/(\cos^4(\chi_1) + \cos^4(\chi_i))$, which shows good agreement with the NEGF results

The analysis of the snapshots demonstrates that the time to complete the transformation of each line in $[11\bar{2}0]$ after initiation is 26.32 MCS, leading to the rate constant of propagation, $k_{[11\bar{2}0]} = 5.48 \text{ \AA}/\text{MCS}$. The $k_{[11\bar{2}0]}$ shows almost no dependence on the temperature (Fig. 2.10a, top), which infers that the energy barrier for the propagation is zero or quite negligible. Thus, once one AN-OPE is switched as a nucleation, the transformation propagates quickly along the $[11\bar{2}0]$ line, which is quite reasonable in terms of the energetic stability of $\text{P2T2}_{11\bar{2}0}$ (Fig. 2.1). Then, another nucleation occurs for subsequent transformation of another $[11\bar{2}0]$ line. Typically this subsequent transformation takes place right next to the precedent transformed line in the $[1\bar{1}00]$ direction.

Therefore, the nucleation is the key step governing the time scale of the transition. The middle panel of Fig. 2.10a shows the probability, $P(t)$ of exhibiting no nucleation until time t . To obtain the nucleation time (τ) when we have a transformed $[11\bar{2}0]$ line already, the nucleation events initiated next to $[11\bar{2}0]$ line are analyzed among the snapshots. The nucleation process is found to be a Poisson process, in which $P(t)$ decays exponentially with time. The value of τ was obtained as 5,583 MCS by fitting of $P(t)$.

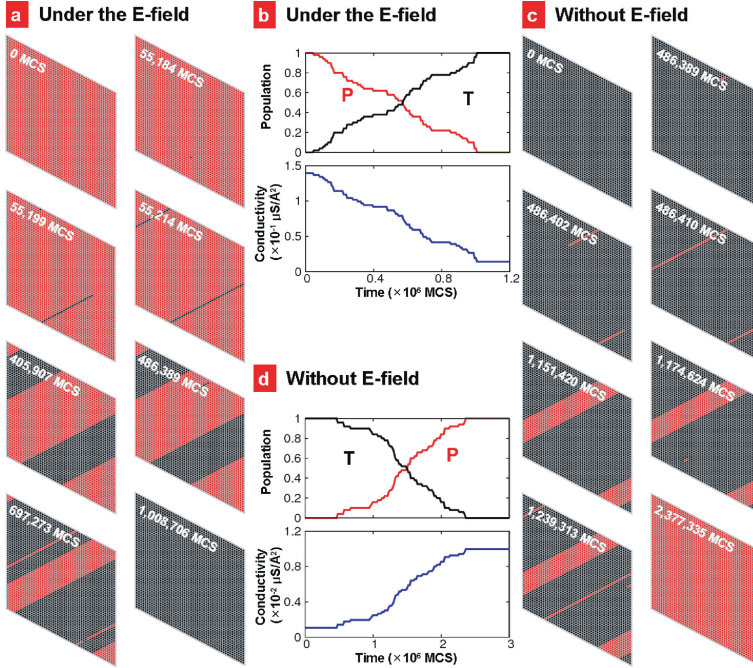


Fig. 2.9 (a) Snapshots during P-to-T transition from MC simulation with 1.2 V/Å external field. The first nucleation is occurred at 55,184 MCS, then, the $[11\bar{2}0]$ line propagates until 55,214 MCS. More nucleation and propagation along $[11\bar{2}0]$ are taken place, and finally, the full system is transformed by 1,008,706 MCS. We note that increased bias voltage yields a faster P-to-T transition. (b) Time dependence of P and T populations and electrical conductivity through the SAM during P-to-T transition. (c) Snapshots during T-to-P transition from MC simulation without an external field. The first nucleation is occurred at 486,389 MCS, then, the $[11\bar{2}0]$ line propagates until 486,410 MCS. More nucleation and propagation along $[11\bar{2}0]$ are taken place, and finally, the full system is transformed by 2,377,335 MCS. (d) Time dependence of P and T populations and electrical conductivity through the SAM during T-to-P transition

To obtain the nucleation time (τ_0) in the absence of $[11\bar{2}0]$ line, we carried out additional 50 simulations to find when the first P transforms to the T, showing that this process proceeds as a Poisson process with $\tau_0 = 274,193$ MCS that is ~ 50 time larger than τ (Fig. 2.10a, bottom panel).

Figure 2.9c, d show the time evolution of the system with no external field starting with all T's and ending with all P's and the population change with the electrical conductivity change during this T-to-P transition, respectively. The overall process is quite similar to that of P-to-T transition except for the detailed numbers. The first nucleation occurred at 486,389 MCS, and then, the neighbors along $[11\bar{2}0]$ showed fast transition to P within 21 MCS. While this swath is growing along $[1\bar{1}00]$ direction, the second and the third nucleation without next transformed line occurred at 1,174,624 MCS and 1,239,313 MCS, respectively. Finally, the full system is

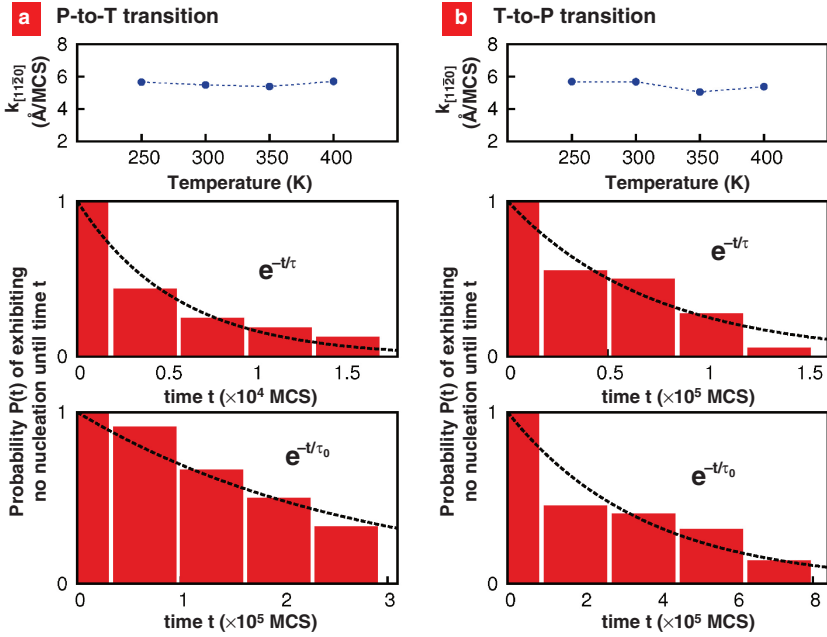


Fig. 2.10 (a) P-to-T transition; (b) T-to-P transition; *Top panels* show the temperature dependence of the propagation rate along $[11\bar{2}0]$, $k_{[11\bar{2}0]}$. *Middle panels* show the probability, $P(t)$ of exhibiting no nucleation by time, t for the case when the nucleation is initiated next to another $[11\bar{2}0]$ line. The *dotted lines* is an exponential fit of $P(t)$. This leads to a nucleation rate of $\tau = 5,583$ MCS for the T-to-P transition and $\tau = 72,926$ MCS for the P-to-T transition. *Bottom panels* show the probability, $P(t)$ of exhibiting no nucleation by time, t for the case when the nucleation is initiated in the absence of next $[11\bar{2}0]$ line. The exponential fit leads to a nucleation rate of $\tau_0 = 274,193$ MCS for the P-to-T transition and $\tau_0 = 357,135$ MCS for the T-to-P transition

transformed to P by 2,377,335 MCS. During the transition, the total conductivity through the SAM increases along with the decrease of the P population.

During T-to-P transition, the average time to complete each line of $[11\bar{2}0]$ growth is 25.38 MCS, leading to $k_{[11\bar{2}0]} = 5.68$ Å/MCS with no temperature dependency (Fig. 2.10b, top panel).

The nucleation times are studied in the same manner with the P-to-T transition. The nucleation process follows Poisson process with the $\tau = 72,926$ MCS and $\tau_0 = 357,135$ MCS in the presence and the absence of the next transformed $[11\bar{2}0]$ line, respectively (Fig. 2.10b, middle and bottom panels).

The interaction between P-T is smaller than the interaction between P-P or T-T by ~ 8.6 kcal/mol in average (Table 2.1), due to the loss of HB or less-favorable van der Waals interaction caused by the packing of two different conformations. This infers that the boundary of $[11\bar{2}0]$ line is energetically less stable, leading a fast transformation at the boundary. This well explains the smaller τ than τ_0 .

We also found τ during P-to-T transition is smaller than τ during T-to-P transition (which is responsible to that NDR is not shown during the backward sweep). This is because the formation of T-T HB network is accompanied with the expansion of $[11\bar{2}0]$ swath along $[1\bar{1}00]$ during the P-to-T transition, while the loss of T-T HB network is accompanied during the T-to-P transition.

2.3.4 NDR for Time Dependent Electric Field

Applying a time dependent external field, we calculated the response of the system to voltage sweeps at various sweep rates. For each sweep, the magnitude of the external field was increased linearly until $F = 1.4 \text{ V/\AA}$ (corresponding to 1.5 V bias voltage in forward sweep) and then it was decreased at the same rate until the field was $0 \text{ V/\AA}$ (corresponding to 0 V bias voltage in backward sweep). (Section 8.4 discusses the conversion factor between the external electric field and the bias voltage.) The sweep rates were 1×10^{-8} , 4×10^{-8} , and $2 \times 10^{-7} \text{ V/MCS}$. The resultant I - V curves are shown in Fig. 2.11a. Although the current drops dramatically at sufficiently high voltage, similar for all cases, we found that faster sweep let the systems stay in

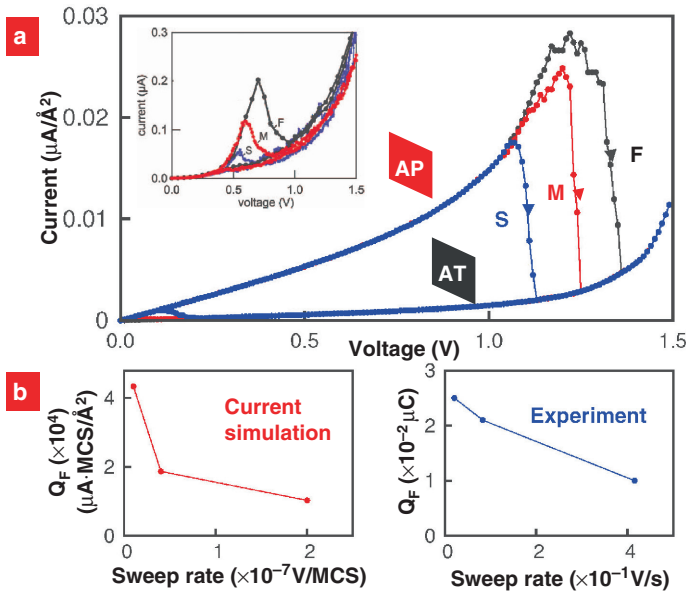


Fig. 2.11 (a) Current-voltage (I - V) curves calculated at 300 K from MC simulations combined with the I - V results of the Green's function calculations. Results for three sweeping rates are shown: S (blue line): $1 \times 10^{-8} \text{ V/MCS}$, M (red line): $4 \times 10^{-8} \text{ V/MCS}$, and F (black line): $2 \times 10^{-7} \text{ V/MCS}$. Inset is the experimental I - V curves from the reference [9] with 3 different sweeping rates: S (blue line): 21 mV/s, M (red line): 83 mV/s, and F (black line): 415 mV/s. (b) The sweep rate dependence of the integral of the current from the peak to the valley during NDR, Q_F from current simulation (left panel) and experiment [9] (right panel)

the P phase at higher voltage, which is in a good agreement with the experimental observation. Clearly, the simulations show both the NDR phenomena and hysteretic behavior with sweep rate dependence as observed experimentally.

We found that the P-to-T transition voltage is located at 1.1–1.4 V, depending on sweep rate. This can be compared to the experimental results in which the transition is completed by 0.6–1.0 V. During the backward sweep, the simulations found that the T state transforms back to P at ~ 0.2 V bias voltage with slower sweep rates.

To determine the total charge associated with the NDR region, we integrated the current from the peak to the valley in Fig. 2.11a. This amount of charge (Q_F) flowing through the junction during NDR, is an important physical quantity that characterizes the QC model [9]. The calculated Q_F values are

- $Q_F = 4.34 \times 10^4 \mu\text{A} \cdot \text{MCS}/\text{\AA}^2$ ($\sim 1.76 \times 10^6$ e/AN-OPE), for sweep rates of 1×10^{-8} V/MCS,
- $Q_F = 1.87 \times 10^4 \mu\text{A} \cdot \text{MCS}/\text{\AA}^2$ ($\sim 7.57 \times 10^5$ e/AN-OPE), for sweep rates of 4×10^{-8} V/MCS, and
- $Q_F = 1.03 \times 10^4 \mu\text{A} \cdot \text{MCS}/\text{\AA}^2$ ($\sim 4.17 \times 10^5$ e/AN-OPE), for sweep rates of 2×10^{-7} V/MCS.

Figure 2.11b shows the sweep rate versus Q_F plots from the simulation (left panel) and from the experiment (right panel). The simulations reproduce the experimental observation that Q_F decreases with increasing sweep rate. Additionally, we find that changing the sweep rate by 20 times only changes the Q_F by 4.2 times, which is comparable to the experimental observation that the Q_F varies 2.5 times while the sweep rate changes by ~ 20 times [9].

The NDR peak from the MC simulations leads to a voltage range of ~ 0.15 V while the experimental NDR range is ~ 0.25 V. One issue is the time scale. Our MC sweep frequency was $\sim 10^{-7}$ V/MCS whereas experimental sweep frequency is $\sim 10^{-1}$ V/s. To convert from MCS to second, we compared the initial nucleation rate expressed in MCS to that expected from the transition state theory using the predicted barrier in kcal/mol. The result is 1 MCS equals $\sim 10^{-13}$ s (see Section 8.1.), indicating the theoretical sweep frequency $\sim 10^6$ times the experimental sweep frequency. This faster sweep should decrease the NDR range. In addition, the small size of our periodic cell, $1,620 \text{ nm}^2$, compared to the experiment of $O(\text{cm}^2)$ would also tend to decrease the NDR range.

A limitation in our MC simulations is that we idealized the degrees of freedom for the molecules into two states, which consider as the perfectly crystallized phases where an infinite AN-OPEs are connected through the HB network. In order to investigate the effect of molecular fluctuations, we performed a series of MD simulations with a (10×10) unit cell (100 independent AN-OPE molecules). The MD simulations account for two aspects missing from the MC simulations:

1. The AN-OPE is allowed to have a distribution of conformations, accounting for the much lower current for χ near 90° while losing the HB network at high fields. This distribution in χ leads to decreased current at a given voltage, leading to a lower slope in the higher-field due to the larger $\Delta\Phi_B$.

2. The AN-OPE forms a partially disordered phase with some HB along $[10\bar{1}0]$ in the low field (Section 8.2). The loss of the HB network at high field decreases the hysteresis during the backward sweep since the loss of HB in the high field decreases the T-to-P transition barrier.

In addition, we found that once a disordered area is developed, it does not easily recover the P phase; hence, the development of a disordered part on the SAM yields less dramatic changes in conductivity. The experimental observation of slight current decrease with successive sweeps may result from the expansion of the disordered area during the sweep cycles.

In order to validate the suggested mechanism for NDR for AN-OPE, we investigated the possibility of NDR from the system N-OPE which contains no NH_2 group and the bare B-OPE containing no functional group. We found that the N-OPE system shows NDR behavior very similar to AN-OPE, in agreement with experiment [37]. However, we found no NDR behavior for B-OPE, also in agreement with experiment (Section 8.3).

2.4 Conclusions

Summarizing, we find that a coarse-grained model based on parameters from first principles calculations leads to a mechanism for room temperature hysteretic NDR that is in qualitative agreement with experiments on AN-OPE, N-OPE, and B-OPE. This provides a plausible mechanism for understanding this phenomena which maybe useful in developing new NDR systems.

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