Ab Initio Investigations of the Electric Field Dependence of the Geometric and Electronic Structures of Molecular Wires

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Theoretical investigations on the typical molecular wire, polyacetylene, which bridges two chemically inert electrodes, have been carried out at the Hartree−Fock level by incorporating the external electric field into the calculations. The results demonstrate that both the geometric and the electronic structures of the conjugated molecular wires are sensitive to the electric field. When the electric field increases, the carbon−carbon single bonds become shorter and the double bonds become longer, leading to a higher conjugation. The electric field reduces the HOMO−LUMO gap and increases the dipole moment. The spatial distributions of the molecular orbitals are used to analyze the electrical properties of the molecular wire. All of these features are more pronounced with increasing conjugation chain length. Quantitative correlations between most of these features and the electric field have been discussed as well.

Introduction

Since the first theoretical demonstration by Ratner and Aviram[1] that an organic molecule could function as a molecular diode, the idea of using organic molecules as functional units in electronic devices has received great attention. Tremendous efforts have been focused on the molecular wires,[2] diodes,[3] resonant tunneling diodes (RTD),[4] switches,[5] and storage devices[6] at real molecular level. Most of these devices consist of the conjugated molecules, which contain alternating single and double (or triple) bonds and facilitate the electron transport. All-trans polyacetylene (PA) is a prototype of the conjugated structure, and many other conjugated molecules can, in principle, be derived by the structure modification. Therefore, it has been studied intensively both experimentally[7] and theoretically.[8]

One of the requirements to use a functionalized molecule in molecular electronics is the ability to integrate it into the device architecture. To connect the functionalized molecules to one another or to the electrodes, molecular scale wires are essentially necessary. Experimental investigations on molecular wires have been carried out by using mechanically controllable break junctions,[9] nano-junctions,[10] and scanning probe microscopy (SPM).[11] Together with the experiments, a large number of theoretical studies have also been reported. Theoretical work can be broadly classified into two categories: one focuses on the geometric and electronic structures,[12] and the other on the electron transport properties based on the nonequilibrium Green's function (NEGF) formulism.[13] However, most of the previous theoretical studies seem to be less concerned with the surroundings, where the electronic device works. The NEGF method obtains a self-consistent solution in the presence of a finite applied bias, in which the effect due to the applied electric field (EF) is implicitly included along with the self-consistent effects due to the charge rearrangement and, therefore, is used widely recently for calculating the electronic transportation properties.[13] In these publications, molecules were optimized without considering the EF effect, and then all of the geometric parameters were kept frozen followed by the current−voltage calculation. It should be noted that any component in the electronic device must be subjected to a considerable external EF. Under this particular condition, the molecular geometric structure as well as the electronic structure, which plays a crucial role in determining the conductance of the molecular wire, is doubted to be the same as in the zero EF.[14] Because previous theoretical studies on the molecular wires did not take the EF effect into account, they rather look ex-situ.[12,15]

Application of external EF is feasible in calculations. For example, a number of EF-dependent molecular properties, such as nonlinear optical (NLO) properties,[16] polarizability,[17] and stability,[18] have been reported for polyacetylene in the previous publications. However, the molecular wire is essentially different from the "free" molecules. In particular, the molecular wire is usually covalently tethered onto the electrodes; it cannot be extended in the direction of the molecular axis. Therefore, a detailed study of the EF effect on the electronic and geometric structures of molecular wire is highly desired for precisely understanding the molecular electrical properties. Unfortunately, there is no systematic investigation on these characters yet. The purpose of this paper is to focus on a more likely in-situ theoretical approach to the design of molecular electronic devices, and further reveal the EF-dependence of the molecular geometry, electronic structure, SCF energy, dipole moment, and the spatial distribution of the frontier orbitals of the molecular wire. Because the conjugation length is an important factor determining the molecular wire conductance,[19] the chain length dependence of these properties has been studied as well.

Methodology

It is well known that the performance of a molecular wire (Figure 1a) is predominated by many factors, such as the nature

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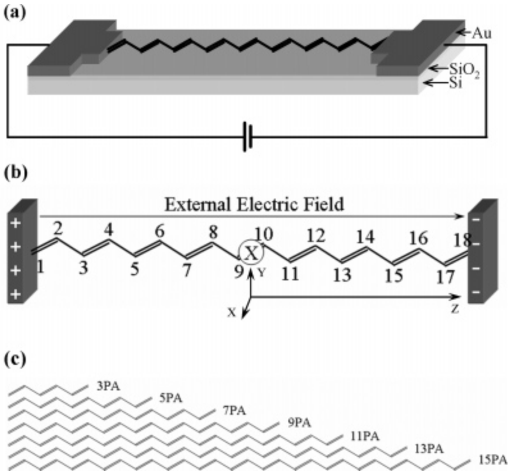


Figure 1. (a) Architecture of a typical molecular wire. (b) The simplified model of the molecular wire studied in the present work. The external EF is aligned along the two terminal carbon−carbon interatomic vector C1→C18. The dummy atom X is located in the center of bond C9−C10. (c) Sketches of the series of PAs studied in this work.

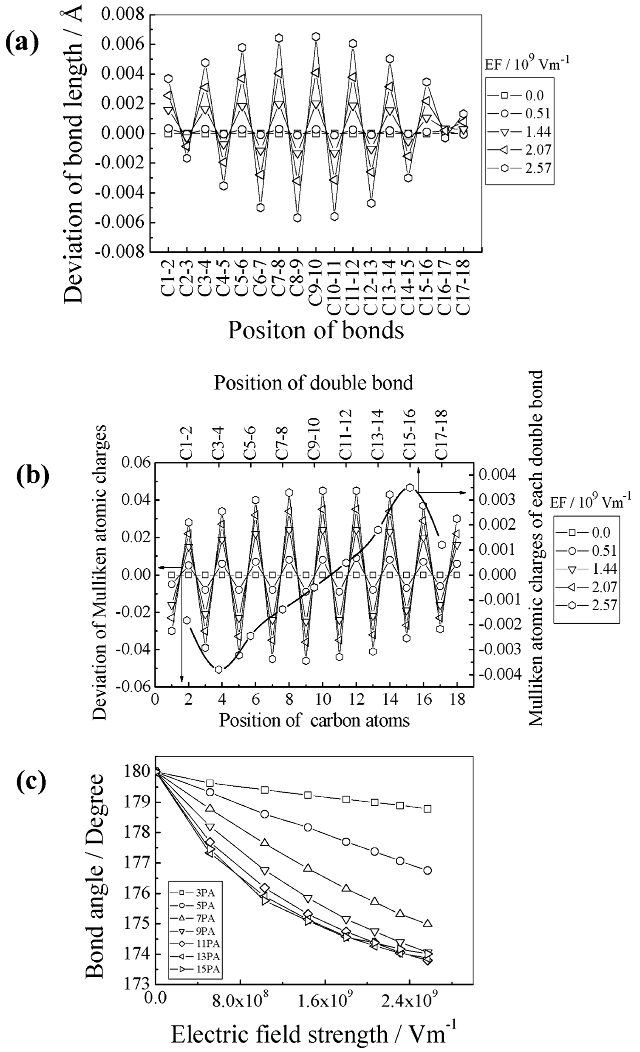


Figure 2. (a) Geometric deviation of the bond lengths of 9PA under various external EF (see chemical structures in Figure 1b for bond codes). The bond lengths under zero EF are referred to as zero. (b) Deviation of the Mulliken atomic charge of 9PA under various external EF (see chemical structures in Figure 1b for atom codes and bond codes). The Mulliken atomic charges of the PA under zero EF are referred to as zero. (c) EF effect on the selected bond angles (−C1−X−C2n), which are used to characterize the bend amplitude of PAs.

of the molecule itself,[20] the interface between the molecule and the electrode,[21] the electrode material,[22] and the electrode shape.[23] Because considering all of these factors looks impossible, here, we give a simplified model (Figure 1b) that a PA molecule bridges two chemically inert electrodes (applied here with the positive pole on the left side), meaning the effect of the electrode materials has been neglected. Theoretical modeling has been achieved as follows. Prior to the introduction of EF, all PAs were fully optimized at the HF/6-31G* level of theory.[24] The two terminal carbon atoms were then fixed in space to simulate the connection to the electrodes as shown in Figure 1b. All of the other geometric parameters were then optimized at the same level of theory in the application of uniform external EF. A uniform EF ranging from zero to 2.57 × 10^9 V/m and aligned along the two terminal carbon−carbon interatomic vector was applied to the model molecules, which may reasonably represent the working condition of the molecular electronic device.[25] To investigate the chain length effect, a series PA ($H-(CH{=}CH)_n-H$, referred to as nPA, $n = 3, 5, 7, 9, 11, 13$, and 15 as shown in Figure 1c) are considered in this work. In addition, free PA molecules optimized without restriction in the direction of the molecular axis were also investigated under the same conditions for comparison. All calculations were performed using the Gaussian 03 program.[26]

In our previous work,[27] comprehensive tests have been performed at the HF and DFT/B3LYP levels with a wide variety of basis sets, showing that HF/6-31G* is the relatively "good" one, which can be used with sufficient accuracy and sustainable computing time.

Results and Discussion

EF Effect on the Geometric Structure. The equilibrium geometry of all-trans PA without EF (zero EF) shows a coplanar conformation with C_{2h} symmetry as expected. After the application of EF, the molecular symmetry is destroyed, although the coplanar conformation remains for all of the model molecules. Figure 2a shows the evolution of the bond length with respect to that of zero EF for a representative example, 9PA, under various EF. When EF increases, the carbon−carbon single bonds become shorter and the double bonds become longer, resulting in a decreased bond length alternation (BLA, the average of the difference in the length between the adjacent carbon−carbon bonds in the polyacetylene). However, the EF-dependence of the bond length is not identical for all of the bonds as shown in Figure 2a. The maximum deviation occurs in the central part for both the single and the double bonds due to the better conjugation as compared to those toward the end of the molecule. Brédas et al.[16] presented a detailed theoretical analysis of the influence of an external EF applied along a donor−acceptor polyene using the semiempirical intermediate neglect of differential overlap (INDO) method. The system was fully optimized under the EF ranging from zero to 1.0 × 10^{10} V/m applied in such a way as to favor the charge transfer from the donor to the acceptor end. They showed that the increase of EF in a moderate amplitude from zero to 6.5 × 10^9 V/m induced a continuous decrease in bond length alternation for a set of linear π-electron chromophores. This trend agrees well with our ab initio calculations as shown in Figure 2a. However, after 6.5 × 10^9 V/m, a switch between single and double bonds resumed, and finally resulted in a complete reversal of bond length alternation (at EF equal to 1.0 × 10^{10} V/m). It should be noted, to keep the 6.5 × 10^9 V/m electric field, over 13 V bias is required for 9PA that is about 21 Å in length. Obviously, such high voltage can hardly be obtained for the molecular electronic devices.[25] In the present work, we use a comparatively moderate EF ranging from zero to 2.57×10^9 V/m, which is comparable to the realistic laboratory field.[4a,9a,11] Therefore, we did not observe the switch between the single and double bonds.

Because the molecular reconfiguration is directly related to the redistribution of the charges on each atom, it is important to know this behavior in the presence of the EF perturbation. As can be seen from Figure 2b, the Mulliken atomic charges on each carbon atom vary with the increase of EF, showing that those on the carbon atoms with odd number decrease and with even number increase due to the easier polarization of the double bond than the single bond. Here, the Mulliken atomic charges of the zero EF are referred to as zero. These observations are consistent with that reported by Brédas et al.[16] using INDO calculations for the donor−acceptor polyenes. Further quantitative analyses show that the Mulliken atomic charges on all of the carbon atoms evolve linearly with the EF. Similar to the bond length case, the maximum variation of the Mulliken atomic charges also occurs in the central part due to the easy polarization of the π-conjugation in the molecular center as discussed before. To determine the significance of the electron migration along the conjugation chain, the net charge of each double bond is analyzed in this work as shown in Figure 2b. After the introduction of EF, the double bonds toward the positive end are negatively charged, and, therefore, a charge separation can be observed in the molecule. As expected, this feature also shows great EF-dependence; that is, the higher is the external EF, the greater is the electron migration. However, the electron migration along the conjugation chain is almost 1 order of magnitude lower than that on each double bond (see the *y*-axis). One can conclude, under the EF interaction, the charge redistribution mainly occurs on each double bond. Similar trends have been also found in all of the other model molecules.

As a kind of soft material, PA is so flexible that it can be distorted by the introduction of environmental perturbation. The reconfiguration of the series of PA molecules has been evident from our theoretical calculations. While EF increases, the molecular wire bends down (negative direction for *y*-axis) in the π-conjugation plane from the original straight configuration (Figure 2c). A simple definition of the bend angle (−C1−X−C2n, the dummy atom X is located in the midpoint of the central C═C bond and the C2n is the terminal carbon atom) is used to characterize the bend amplitude of the molecular wire. It can be seen that the bend angle is decreased with increasing EF for all molecules. While the conjugation length increases, the sensitivity of molecular bending increases too. However, when the conjugation chain is 11PA or longer, the sensitivity tends to be identical. Because the molecular wires are not typically rigid, the EF-caused molecular bending is to be taken into account in the design of the molecular electronic device. The bending of the molecular wire is, possibly, originated from the interaction between the external EF and the induced dipole moment of each double bond, because there is an angle between them.

A quantitative correlation between the variation of the molecular property and the applied EF is of great importance for designing a novel molecular electronic device. Figure 3a shows the good linear relationship between the double bond length and the square of EF in the concerned EF range. This linear dependence varies depending on the location of the double bonds. The largest slope corresponds to that in the central part of the conjugation chain. Similar trends have been also observed for all of the other PAs. As expected, the largest slope shows obvious chain length dependence. Importantly, the slopes of the central bond yield a linear dependence of the chain length as shown in Figure 3b. Because the molecular geometry relaxation in EF follows an energy gradient, the change of the interaction energy could be an indicator of the EF-dependence of many molecular properties. As calculated by the method proposed in the present work, the induced dipole moment of a double bond is about 10 times the induced dipole moment of the whole molecule (Figure 2b). The interaction between EF and induced dipole moment of each double bond is the most important factor in the determination of molecular energy, which may consequently predominate the stable molecular geometry. It is well known that the induced dipole moment is proportioned to the EF. We can then expect that the interaction energy is proportional to the square of EF.

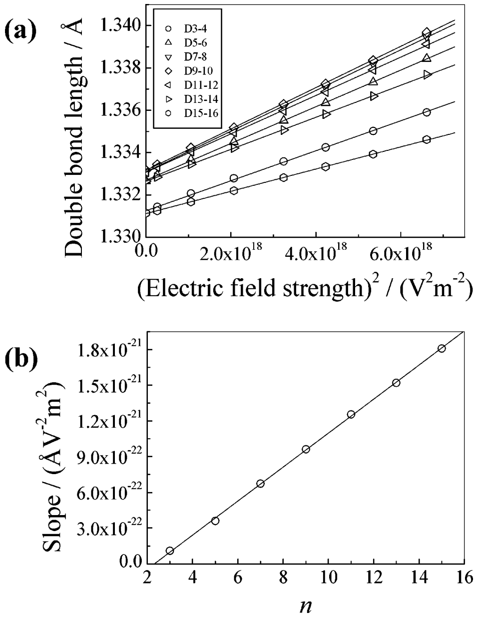


Figure 3. (a) Correlation between the double bond lengths and the square of EF for 9PA. (b) Linear relationship of the largest slopes and the number of double bonds (*n*).

Although a simple quantitative relationship between single bond lengths and the external EF has not been found, after analyses among the data, we found that single bond lengths evolve linearly with the EF to the power of α (α is noninteger). The value for α varies from 1.60 to 3.05 corresponding to the chain length from 3PA to 15PA. The nonlinearity between the variation of single bond and the square of EF also proves that the interaction between EF and induced dipole moment is predominant in the EF-induced molecular evolution.

EF Effect on the Dipole Moment and Self-Consistent-Field (SCF) Energy. Because of the delocalized π-electrons of conjugated organic molecules, when an external EF is applied, their charge distributions are easily modified and consequently lead to the changes of the dipole moment as well as the SCF energy. Figure 4a shows the EF-dependence of the dipole moment of the series of PA molecules. It can be seen that the induced dipole moment increases linearly with the external EF although 11PA or longer ones slightly deviate from the linear manner. As expected, the EF-dependence of the dipole moment varies with the chain length; that is, the longer is the chain length, the greater is the induced dipole moment of the molecule.

According to the finite-field approach,[28] the energy (E) of the centrosymmetric molecule perturbed by a static uniform EF

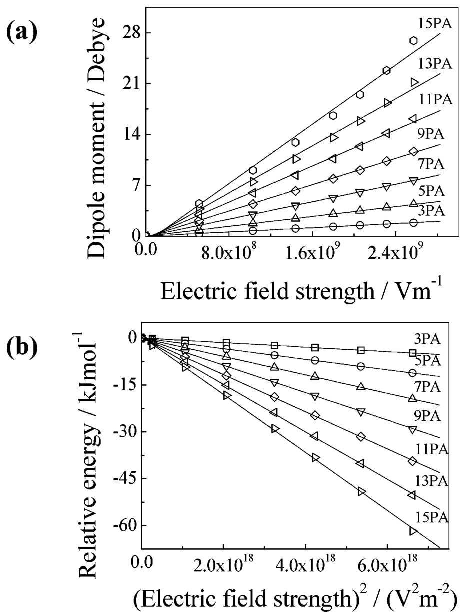


Figure 4. EF-dependence of (a) the dipole moments and (b) the relative SCF energies of PAs. The SCF energy of each PA under zero EF case is referred to as zero.

TABLE 1: Static Longitudinal Linear Polarizability Values (in au) of the PA with Terminal Carbon Atoms Fixed (Fixed PA) and the PA with Terminal Carbon Atoms Free (Free PA) Calculated by Using the HF/6-31G* Method

	fixed PA	free PA	PA*[a]
chains	HF/6-31G*	HF/6-31G*	HF/6-31G
3PA	146.5	146.5	141.9
5PA	341.5	341.2	332.0
7PA	594.3	596.5	575.4
9PA	883.3	892.4	853.2
11PA	1195.7	1216.4	853.2
13PA	1525.1	1560.7	1459.9
15PA	1868.8	1914.4	1777.5

[a] PA* values are taken from ref 29, obtained from the HF/6-31G method.

(F) in the longitudinal direction can be written as:

$$E(F) = E_0 - \frac{1}{2}\alpha_L F^2 - \frac{1}{4!}\gamma_L F^4 - ... \quad (1)$$

where E_0 is the energy of the molecule in the absence of the external EF; α_L is the longitudinal component of the dipole polarizability; and γ_L is the longitudinal component of the second dipole hyperpolarizability. For the series of PA molecules, the numerical values of α_L were obtained from a least-squares fit of the SCF energy as a function of the external EF using a second-order polynomial in EF because the effect of higher order polynomials is negligible (Figure 4b). The longitudinal linear polarizability of the series of PA molecular wires is given in Table 1. For comparison, the longitudinal linear polarizability for the free PA molecules (the two terminal carbon atoms are fixed in the x and y directions but freely optimized in the z direction) is also presented in Table 1. When the chain length is 3PA and 5PA, α_L values of the fixed molecular wires and the free molecules are the same. When the conjugated chain is 7PA or longer, the results for α_L of the fixed molecular wires are just slightly lower than those of the free molecules, which can partially be attributed to the pronounced bending of the conjugation chain in EF as mentioned before. All of the values are slightly higher than that published previously by ab initio HF calculation with the 6-31G basis set.[29]

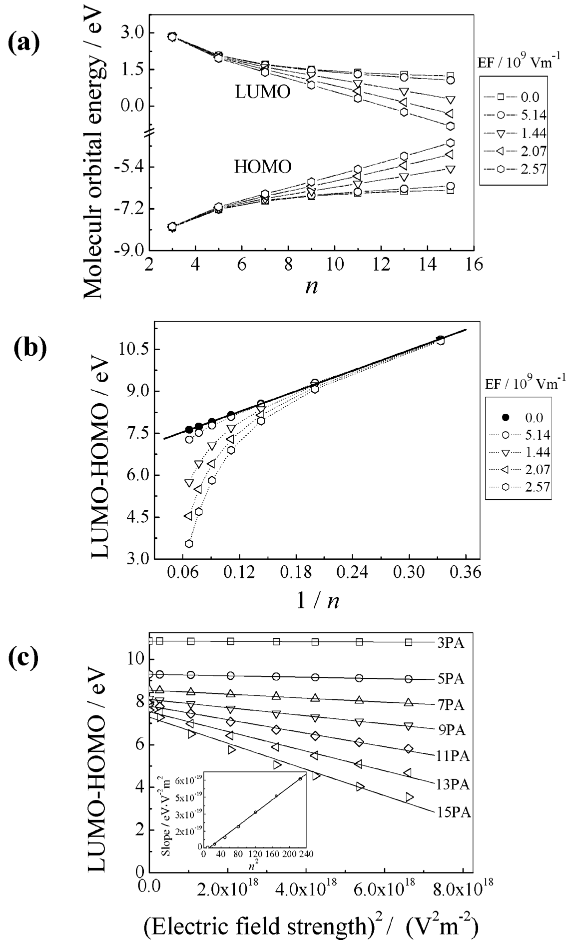
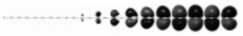
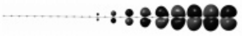


Figure 5. (a) LUMO and HOMO energies as functions of the chain length (n, number of double bonds) of PA at various EF. (b) HOMO−LUMO gaps as functions of the reciprocal of the number of the double bonds ($1/n$) at various EF. (c) HOMO−LUMO gaps as functions of square of EF for PAs. The inset shows the linear relationship of the slopes in Figure 5c and the square of the number of double bonds (n^2).

EF Effect on the Electronic Structure. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), known as the energy gap (HLG), is a crucial parameter in the determination of the conductance of molecular wire.[30] It is predominated not only by the nature of the molecule, but also the surroundings. Especially, when a considerable external EF is applied, the HLG of the molecular wire is expected to vary. To study and eventually to be able to modulate the electrical properties of the molecular wire, it is important to understand the details of how the HLG responds to the external EF. Figure 5a shows the evolutions of the energy levels of LUMO and HOMO as functions of the chain length n (n, the number of double bonds of the molecule) under various EF for the series of PAs. Increasing the chain length, LUMO and HOMO move toward each other almost symmetrically, resulting in a narrowed HLG. For short conjugated molecular wires, 3PA and 5PA for example, the EF-dependence of HOMO and LUMO is insensible. However, obvious EF-dependence is observed when the conjugation chain is 7PA or longer. Similar evolution of HOMO and LUMO for π-electron chromophore was found also by Brédas et al.[16] using semiempirical INDO calculations.

It is well known that many properties of the homologous compounds of straight molecules are the function of the reciprocal of the number of carbon atoms.[31] Figure 5b shows the chain length dependence of the HLG of the series of PA

TABLE 2: Orbital Spatial Orientations of LUMO+2, LUMO+1, LUMO, HOMO, HOMO−1, and HOMO−2 for 15PA under Different Magnitudes of EF

Orbitals	EF=0.0 V/m	EF=1.44×10^9 V/m	EF=2.57×10^9 V/m
LUMO+2			
LUMO+1			
LUMO			
HOMO			
HOMO-1			
HOMO-2			

molecules. At zero EF, the HLG evolves linearly with the reciprocal of the number of double bonds (1/*n*) as expected. By a simple extrapolation, the HLG of the infinite chain length ($(\mathrm{HLG})_\infty$) can be obtained. For the series of *n*PAs, a linear extrapolation to infinite chain length yields a HLG of approximately 6.81 eV. This result is slightly less than that predicted by the semiempirical Complete Neglect of Differential Overlap (CNDO) calculation (7.46 eV)[32] and the ab initio "exact exchange" LCAO calculation (7.24 eV).[33] Nevertheless, all of these values are much larger than the experimental measurement of 1.35 eV[34] and 1.8 eV[35] for all-trans polyacetylene.

A simple comparison of the HLG evolutions among the series of PAs is very instructive for understanding the electric conductance of the molecular wire.[36] When EF increases from zero to 2.57×10^9 V/m, the HLG is decreased by 0.052, 0.231, 0.619, 1.253, 2.086, 3.046, and 4.077 eV for 3PA, 5PA, 7PA, 9PA, 11PA, 13PA, and 15PA, respectively. Nearly 80 times difference has been found between 3PA and 15PA, indicating that the HLG for longer conjugation is easier to modulate by the external EF.

Figure 5c illustrates the evolution of HLG for the series of PAs as functions of the $(\mathrm{EF})^2$. The HLG decays almost linearly with the $(\mathrm{EF})^2$ for all of the PAs, although the linearity is less pronounced for 13PA and 15PA. As mentioned before, this unideal feature is possibly caused by the chain bending under the EF interaction (see Figure 2c). The sensitivity of the EF-dependence of HLG can also be identified via the slopes of the lines in Figure 5c. The inset shows the linear relationship between the slopes and the square of the number of double bonds (n^2). Almost a linear relationship is observed between them.

As discussed above, the HLG is the function of both EF and chain length, *n*, and therefore a general expression of HLG is necessary. By detailed analysis, we can use the following formula to describe Figure 5b and c in the concerned EF range:

$$\mathrm{HLG} = k_1/n + (\mathrm{HLG})_\infty - k_2 \times n^2 \times (\mathrm{EF})^2 \qquad (2)$$

where k_1 and k_2 are constants, which can be obtained from the slopes in Figure 5b and the inset of Figure 5c, respectively. To the best of our knowledge, this is the first time that the chain length and electric field are used to determine the quantitative feature of HLG of the polyacetylene molecular wire. In most cases, the electron transport barrier is directly correlated to the HLG.[37] This general HLG expression may give insight into understanding many electron-transfer behaviors of the molecular wire, and further facilitate the design of the novel molecular electronic devices. In previous studies, the absolute value of the electron tunneling barrier height of single molecules and molecular layers has been treated as a constant for a wide variety of materials.[38] These can be true for the saturated alkyl molecules,[39] because the EF-dependence of HLG looks insensible for them. However, as proven in present study, this rule cannot be valid for the conjugated molecular wire. The longer is the chain length, the more pronounced is the HLG variation.

Changes in the spatial distribution of molecular orbitals (MO), especially those of the HOMO, LUMO, and a few in their neighborhood, are excellent indicators of many molecular properties. Table 2 shows the spatial distribution of HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 for 15PA under various magnitudes of external EF. At zero EF, the LUMO, HOMO, and their neighboring MOs (LUMO+2, LUMO+1, HOMO−1, and HOMO−2) are delocalized throughout the whole molecule symmetrically. However, with the increase of EF, HOMO and LUMO change oppositely from fully delocalized to a partially localized form. Meanwhile, HOMO−2, HOMO−1, and HOMO move to the negative potential side, whereas LUMO, LUMO+1, and LUMO+2 move to the positive one. We also find whose MOs closer to the HOMO and LUMO shift more significantly. This feature also shows great chain length dependence; that is, the longer is the chain length, the more obvious are the shifts of the spatial distribution of the MOs. Detailed analyses of these features are very instructive for understanding not only the conductance of the molecular wire, but also the photoemission that depends on the vertical electron transmission and the injections of either hole or electron in the light-emitting diodes (LEDs)[40] in the existence of the external EF.

Concluding Remarks

In this work, we have proposed a more likely in-situ theoretical approach to the modeling of molecular electronic devices. Typically, a series of the molecular wires, polyacetylene, have been systematically studied at the ab initio HF level. It proves both the geometric and the electronic structures of the molecular wires are sensitive to the external EF. In particular, the external EF makes the molecular BLA and HOMO−LUMO gap decrease and dipole moment increase. The spatial distributions of frontier molecular orbitals vary from the fully delocalized form to the partly localized with the increase of the external EF. Furthermore, all of these properties show great chain length dependence.

The evidence provided in the present studies reminds us that the interaction between the EF and the molecular materials may greatly influence the device performance. For example, some chemical bonds that are very robust in the neutral state, perhaps, become very weak under the interaction of EF. Therefore, a novel molecular electronic device designed without considering the EF effect should be questionable in practice. The results reported in this paper may give more insight into the design or rationalization of molecular electronic devices.

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