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Controlling the torsional stochastic switching in phenylene ethynylene oligomer molecules by external electrostatic fields

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First-principles molecular-orbital theory was used to predict the possibilities to control the single-molecule conductance switching by external electrostatic fields in the case of nondipolar phenylene ethynylene oligomer molecule. External field directed perpendicularly to the molecular plane was shown to induce conductance switching, while field directed along axis lying within the molecular plane and being perpendicular to the principal molecular axis was shown to be capable of controlling the stochastic conductance by a strong modulation of the corresponding classical transition probability. The possibility for tuning the molecular switching properties could be attributed to the changes in the polarizability tensor components induced upon intramolecular torsion. The outlined possibilities are of fundamental importance in molecular engineering and design of single-molecule switches.

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I. INTRODUCTION

The success in miniaturization of the electronic components to nanoscale is strongly determined by the development of fundamental theoretical knowledge on all the aspects of function and control of single-molecule devices. Within the framework of the molecular electronic properties–related research a remarkable attention has been paid to the single-molecule switches. So far, the switching properties of various molecules have been investigated, among which the phenylene ethynylene oligomers (OPE) are of particular importance. In a recent study, scanning tunneling microscopy (STM) was used to examine impedance changing in single-molecule systems based on OPE.[1] In general, the molecular switching properties are either explained by the relative motion of molecule's internal structure or by the molecular charge state changes.[2–4] It seems that the intramolecular central phenylene ring (CPR) torsional motion may be a good model for cases when both sides of the molecule are chemically attached to electrodes, i.e., when intermolecular (molecule-electrode) conformational flexibility is reduced. The main problem that one faces in developing a molecule-based electronic device is the control of the stochastic behavior of the torsional oscillations. In our previous work we investigated the effects of halogenation of the CPR on the torsional dynamics and we found that halogenation can contribute to control the CPR torsions and also to fine tune the molecular impedance.[5] In this paper, we predict that external electrostatic fields may be used to control the single-molecule switching behavior in the basic OPE by controlling the dynamics of the CPR torsional motion. In comparison to previous works in the field, which have been focused on external field effects on molecular rectifiers and switches which posses a permanent dipole moment,[6–8] the present study is an extension to the case of nondipolar molecular switches.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

For the purpose of the present study, we employ a hybrid Hartree-Fock (HF) density-functional theory (DFT) methodology. Within the implemented hybrid HF-DFT approach, a combination of the Becke's three parameter adiabatic connection exchange functional (B3) (Ref. 9) with the Lee-Yang-Parr (LYP) (Ref. 10) (B3LYP) correlation one was used. The LANL2DZ basis set (Los Alamos ECP plus DZ on Na-Bi) was employed for orbital expansion, solving the Kohn-Sham self-consistent field (SCF) equations iteratively[11] for each particular case of this study, with an "ultrafine" (99, 590) grid for numerical integration (99 radial and 590 angular integration points). The appropriateness of the B3LYP/LANL2DZ methodology for the current problem was discussed in some more details in our previous study.[5] The minimum on the potential-energy surface (PES) of the free basic OPE (Fig. 1) at the employed theoretical level was located by Schlegel's gradient optimization algorithm.[12] Subsequently, electrostatic fields with strengths ranging from 0.001 to 0.050 a.u. were applied along x, y, and z axes and the changes in electron-density distributions and other molecular parameters relevant to switching phenomena were monitored. This was done by explicit inclusion of the electrostatic field $\mathbf{E}$ in the many-particle Hamiltonian, i.e., by iteratively solving the Schrödinger equation,

$$[\hat{H} - \mathbf{E} \cdot \mathbf{d}]\psi = \varepsilon\psi \qquad (1)$$

in an SCF manner. In Eq. (1), the operator $\hat{H}$ stands for the molecular Hamiltonian that includes the kinetic energy of the

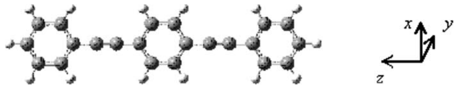

FIG. 1. The global minimum on the B3LYP/LANL2DZ PES of the basic OPE molecule, together with the definition of Cartesian axes.

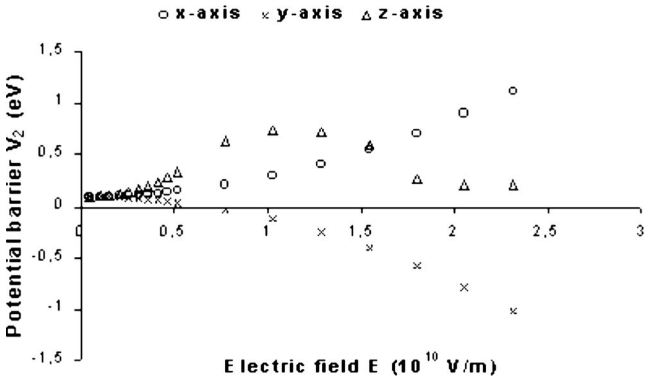

FIG. 2. Barrier heights to CPR torsion (V_2 in eV) versus electric field (E in V/m).

electrons and nuclei and the potential energy due to electrostatic interactions between the electrons as well as the electrons and nuclei. The term $\mathbf{E}\cdot\mathbf{d}$ represents the energy of interaction between a molecule of dipole momentum $\mathbf{d}$ and an external electric field $\mathbf{E}$. We carried out two types of calculations: (i) those in which the external fields were applied keeping the rigid geometry of the OPE molecule (i.e., considering only the electronic polarization) and (ii) flexible approach, in which actually the minimum on the (in-field) PES was located, i.e., considering both the electronic and geometry polarization effects. We have found that the most relevant effects arise from electronic polarization solely, and thus in this paper we focus on these results only. All quantum chemical calculations were carried out with the GAUSSIAN03 series of computer codes,[13] while for the other purposes described below, our own FORTRAN codes were developed.

III. RESULTS AND DISCUSSION

First, we consider the external field effects on the barrier to CPR intramolecular torsional motion, which is presumed to be of crucial importance for the switching. The planar structure (as depicted in Fig. 1) was found to correspond to global minimum on the studied PES, while the stationary point in which the CPR plane is perpendicular to the molecular plane is a second-order saddle point. The planar conformation is a conductive one, while the perpendicular is a nonconductive, as full electronic delocalizations in the frontier molecular orbitals (MOs) are impossible in the latter case. Neglecting the Coriolis coupling with the overall molecule's rotation (which is a correct assumption for an OPE molecule bound between two metal electrodes), the CPR torsional Hamiltonian has the form

$$\hat{H}_{\text{torsion}} = -\frac{\hbar^2}{2I_\varphi}\frac{\partial^2}{\partial\varphi^2} + \frac{V_2}{2}[1-\cos(2\varphi)], \qquad (2)$$

where φ denotes the torsional coordinate, defined as the dihedral angle describing the orientation of the CPR plane relative to the main molecular plane ($\varphi=0°$ for the planar conformation, $\varphi=90°$ for the perpendicular one), while I_φ is the corresponding moment of inertia. From the computed barrier heights (the V_2 values) at various external field strengths and orientations (Fig. 2), it can be seen that while fields applied along x axis monotonically increase the barrier height, an opposite trend is detected for fields applied along y. The case when field is applied along z axis appears to generate a more complex $V_2(E)$ dependence. These trends may be rationalized using the Buckingham expression for the energy of a molecule embedded in a homogeneous electrostatic field,[14]

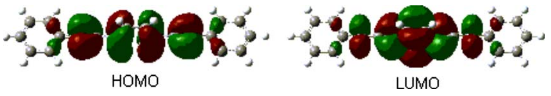

FIG. 3. (Color online) The frontier MOs for the perpendicular conformation of the basic OPE molecule.

$$\varepsilon(E) = \varepsilon(0) - \mu_\alpha E_\alpha - \frac{1}{2!}\alpha_{\alpha\beta}E_\alpha E_\beta - \frac{1}{3!}\beta_{\alpha\beta\gamma}E_\alpha E_\beta E_\gamma - \cdots, \qquad (3)$$

where $\varepsilon(0)$ is the energy of the unperturbed system, μ is the permanent dipole moment vector, α, β, and γ are the second-, third-, and fourth-rank tensors corresponding to static dipole polarizability and the first and second hyperpolarizabilities, respectively. The Greek indices imply summation over the Cartesian axes by the Einstein's convention. Due to the high symmetry of both conformations of the OPE molecule, the permanent dipole momentum is zero. For the planar conformation, the flexible π electrons contribute to the dipole polarizability tensor components α_{zz} and α_{xx} (α_{yy} is negligibly small). Upon CPR torsion into the perpendicular conformation, α_{xx} decreases (the flexibility of π electrons in the CPR decreases in this field orientation), while α_{yy} increases (due to the enhanced flexibility of the CPR π electrons). In other words, the changes in the polarizability tensor components due to intramolecular torsion enable tuning of the CPR torsional barrier height with external fields. As can be seen from Fig. 2, for field strengths over $\cong 10^{10}$ V/m (along y), the perpendicular conformation becomes the most stable one. As this conformation is a nonconductive one[5] due to the less delocalized character of the frontier MOs (Fig. 3), external field applied along y axis could enable conductance switching in OPE molecule. On the other hand, as discussed in more details below, external field applied along x axis could enable control of the stochastic conductance switching due to the thermally induced intramolecular torsional motion. Note that the V_2 values presented in Fig. 2 do not include the zero-point energy correction, as it is negligibly small compared to the overall barrier height (see Ref. 5). Regarding the $V_2(E)$ dependence when the field is directed along the z axis, for small field strengths it increases due to the somewhat smaller α_{zz} value for perpendicular than for planar configuration (the overall delocalization flexibility of the π electrons which could be achieved over the whole molecule is reduced in the perpendicular conformation). At higher field strengths, however, the first- and higher-order hyperpolarizabilities could predominate and cause a reversed trend in the $V_2(E)$ dependence. As the external field has been included in the many-particle Hamiltonian [Eq. (1)], the quantum chemical calculations which have been performed

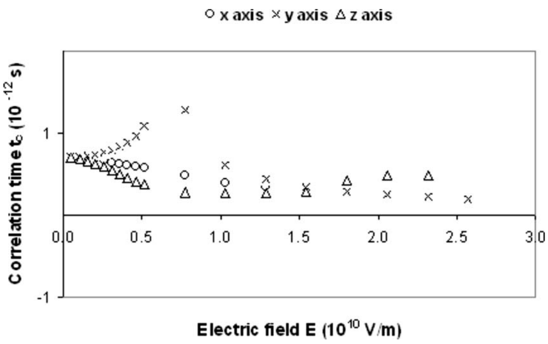

FIG. 4. Classical correlation time (t_c in s) versus electric field (E in V/m).

in the present study include in an explicit manner the external electrostatic field influence on the whole OPE molecule. In other words, the polarization of all rings has been accounted for in each step and the obtained results are of general importance for the considered molecular switch.

A change in the state of intramolecular torsional motion involving the CPR may be caused by three possible types of transitions: (i) transition from one torsional quantum state to another within one well of the CPR torsional potential; (ii) the intramolecular rotator may tunnel from one to an adjacent well of the potential; and (iii) it may be excited to a torsional state placed "over" the barrier which would lead to classical rotation before falling to a torsional state of the adjacent well. For a state at the top of barrier with energy practically equal to V_2, the time for classical rotation from one well to adjacent one (rotation by an angle π) can be found by the condition the rotational kinetic energy to be equal to the barrier height $I_\varphi \omega^2/2 = V_2$. Considering that the angular velocity $\omega = \pi/t_c$, where t_c stands for the classical correlation time, it follows $t_c = \pi(I_\varphi/2V_2)^{1/2}$. The dependence of the classical correlation time on the magnitude of the external electric field is given in Fig. 4.

Accounting for the probability that the intramolecular rotator may be found in energetic state above the barrier (assuming Boltzmann distribution in the population of torsional states), the classical transition probability from one well to the adjacent one is given by

$$W_{\text{class}} = \frac{1}{\pi}\left(\frac{2V_2}{I_\varphi}\right)^{1/2} \exp\left(-\frac{V_2}{kT}\right). \tag{4}$$

To account for the quantum contributions to the classical transition probabilities, we have solved the stationary Schrödinger equation for the CPR torsional Hamiltonian (2) by the Fourier grid Hamiltonian method (FGHM).[15] Following the time-dependent perturbation-theory treatment used in the approach by Bloembergen-Purcell-Pound (BPP), we have further computed the contribution to the transition probability due to quantum mechanical (QM) tunneling processes for twofold hindering potentials by the expression[16]

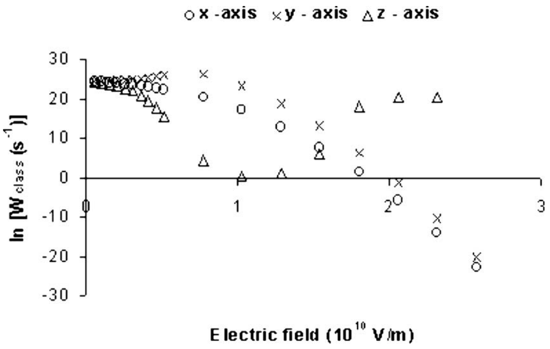

FIG. 5. Classical transition probabilities (W_{class} in s^{-1}) versus electric field (E in V/m).

$$W_{\text{tunn}} = \frac{2\pi}{4} \frac{\sum_m \Delta\omega_m \exp\left(-\frac{\langle \hbar\omega_m\rangle}{kT}\right)}{\sum_m \exp\left(-\frac{\langle \hbar\omega_m\rangle}{kT}\right)}. \tag{5}$$

In Eq. (5), $\hbar\Delta\omega_m$ is the energy of tunneling splitting of the mth torsional state, while $\langle \hbar\omega_m\rangle$ is the average energy of the mth level pairs split due to tunneling. We have found that the tunneling contributions to the total transition probabilities (classical+tunneling) are very small, except for the extremely low barrier heights in the case of fields applied along y axis near the point in which the sign of V_2 changes. This is in line with the results obtained in earlier studies.[2] A general conclusion may thus be derived that the incoherent classical jump-over-the-barrier motion will govern the torsional dynamics in the studied system (which is strongly temperature activated). We therefore first focus on these overall trends. In Fig. 5, the dependence of transition probability on the external field strength is shown for various field orientations. When field is applied along the x axis, the transition probability monotonically changes from the order of 10^{11}–10^{-10} s^{-1} (i.e., the stochastic conductance switching due to thermal motion is strongly modulated by this component of the external electrostatic field). For fields applied along the z axis, in the lower field strength region the switching is first turned off (W_{class} changes from 10^{11} to 10 s^{-1}), while for higher field strengths it rises again at values up to 10^9 s^{-1}.

The key quantitative parameter directly related to molecular admittance is the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap (HLG). A decrease in the HLG in a conductive molecular system implies an increase in the corresponding admittance. The computed HLG dependences on the external electrostatic field strength (for various field orientations) for the planar and perpendicular conformers of the basic OPE are given in Fig. 6. External field applied along the x and y axes exhibits only a moderate modulation effect on the HLG, the corresponding values for each field strength being higher for the perpendicular (nonconductive) conformer. Besides that, also the HOMO and LUMO are not fully delocalized over the whole molecule, implying a nonconductive molecular state (the delocalization of the wave function is a prerequisite

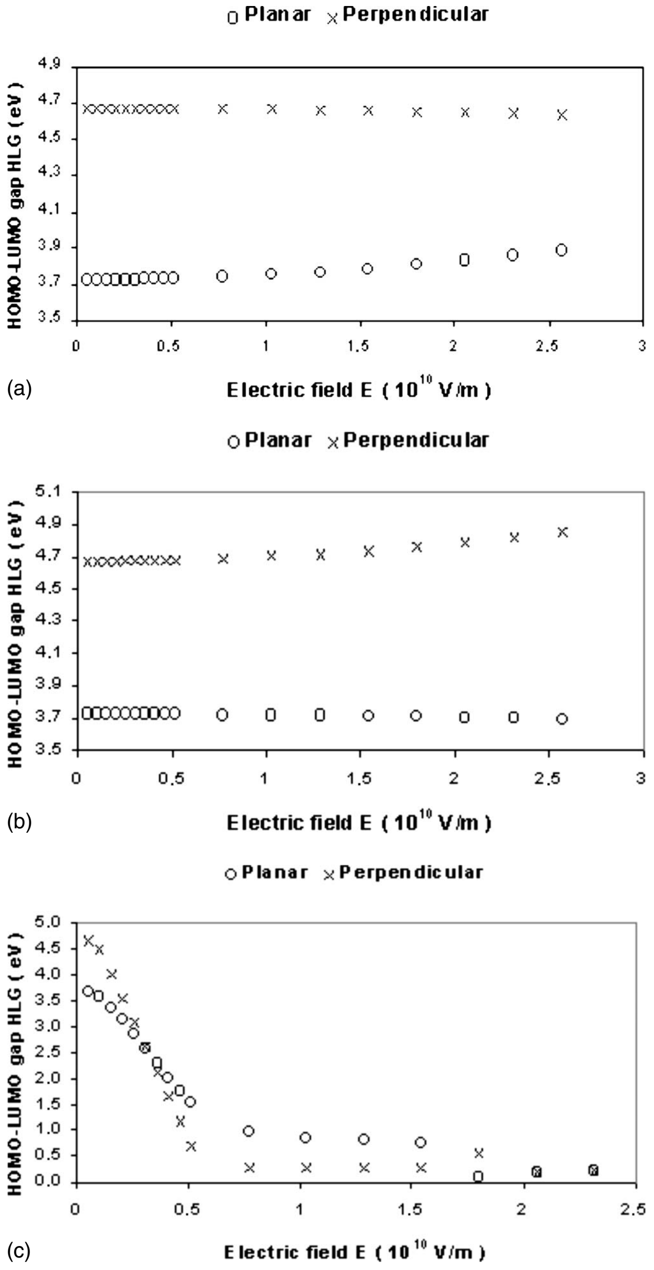

FIG. 6. Plots of the HOMO-LUMO energy differences (HLG in eV) for planar and perpendicular conformations of the OPE molecule versus external electrostatic field (*E* in V/m) oriented along (a) *x* axis, (b) *y* axis, and (c) *z* axis.

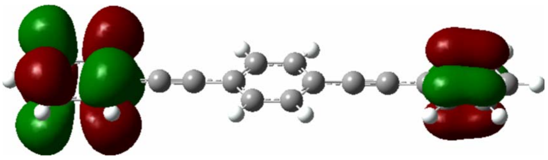

FIG. 7. (Color online) Electrostatic field effects on the localization of the frontier MOs and conductance switching (the magnitude of the applied field for the represented case is $E=2.057\times10^{10}$ V/m).

for a high transmission coefficient to the electron transport through the molecular wires). The opposite trends induced by the fields applied along the *x* and *y* axes on the HLGs for each particular conformer may be explained accounting for the contribution of the corresponding HOMO and LUMO states to the respective polarizability tensor component (i.e., the flexibility of electronic motions in these states). Field applied along the *z* axis, however, affects much more significantly the HLG in both conformers. As seen from Fig. 6(c), within a considerably wide interval of field strengths, the HLG of perpendicular conformer falls below the corresponding value for the planar one. This, however, does not mean that the perpendicular conformer becomes more conductive than the planar one, since the HOMO and LUMO in neither case allow for a full electronic delocalization over the whole molecular backbone. Moreover, at field strengths higher than about 3×10^{9} V/m, even for the conductive planar conformer, the delocalization of the wave functions corresponding to frontier MOs does not extend over the whole molecular wire, implying an abrupt conductivity decrease in such cases (Fig. 7). In other words, this is another channel (apart from the conformational one) of turning the molecular switch "off" at high voltages (after it has been turned "on" at some threshold potential). Regardless of the fact that very high voltages are not intended to be applied in molecular nanocircuit applications, the described behavior enables an electronic density driven safety switch off in a case of short circuit. These results obtained in our study are similar to those implied in the recent work of Sabzyan and Farmanzadeh.[17] In their paper, however, the conclusions regarding the safety switch off have been implied rather indirectly by analyzing the dihedral angle changes in external fields.

IV. CONCLUSIONS

To summarize, in the present paper we have demonstrated the possibilities to control and modulate the conductance of a nondipolar basic OPE molecule by external electrostatic fields. External field directed perpendicular to the molecular plane was shown to induce conductance switching in OPE molecule, while field directed along axis which lies within the molecular plane and is perpendicular to the principal molecular axis controls the stochastic conductance by a strong modulation of the corresponding classical transition probability. The predicted trends, enabling the possibility for tuning the molecular switching properties, could be attributed to the changes in the polarizability tensor components induced upon intramolecular torsion. We consider that the outlined possibilities may be of fundamental importance in molecular engineering and design of single-molecule switches.

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