Bipyridinium Molecular Switch: Ab-initio Electronic Structure Calculation

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Density functional study has been carried out using B3PW91/6-311G(d,p) method for bipyridinium molecule connected with poly-methylene chains (upto n = 9), reported experimentally to behave like molecular switch. Fully optimized geometries, electronic structures, HOMO-LUMO gaps, Mulliken point charge distribution and orbital orientation have been analyzed to understand the electronic behavior in this molecule. The electronic transport across the molecule has been explained assuming that the incoming electron passes through the lowest unoccupied molecular orbitals. The conduction barrier is determined from the energy levels of HOMO and LUMO energy states. From the results it is predicted that a bias voltage of 1.66 V is required to transfer one electron from metal electrode to the LUMO energy state, quite good in agreement with the experimentally reported results.

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1. Introduction

The use of single molecules as a “quantum dot” or “quantum wire” in charge transport has attracted considerable attention due to its exciting potential in future electronic devices. In the drive towards smaller electronic devices, many nanotechnologists are trying to exert chemical control over their components. Integrating molecular functions into this technology could lead to new types of electronic devices. Present developments in theoretical and experimental techniques have triggered enormous possibilities of using organic chemistry as a fundamental complement to silicon in semiconductors.\(^1\),\(^2\) This may allow the fabrication of logical circuits at the level of single molecules. Further advances in this area require precise knowledge of the electron transport across the organic molecule. The organic molecules are terminated using thiol groups, which has a greater affinity towards metal electrodes to accept electrons. Conjugated oligomers terminated with thiol group have long been used to synthesize molecular wire and their conductivity is measured by scanning tunneling microscopy.\(^3\),\(^4\) Apart from wires the molecular devices can be used to control the current based on their geometrical configuration as well as their redox properties. In a recent experimental demonstration Schiffrin and coworkers has shown that bipyridine molecule terminated by alkane thiol groups can behave like molecular switch when sandwiched between two metal electrodes.\(^5\) The conductivity through this molecule can switch between on and off by changing the oxidation state. The molecule under consideration consists of a bipyridinium moiety located at the center of a chain of 18 methylene units as shown in Fig. 1. The electron transport through this molecule was measured scanning tunneling microscope. It is observed that current flowing through this molecule is controlled by its oxidation state. The redox process corresponds to the formation of bipyridinium radical ion as

\[
\text{bipy}^{2+} + e^{-} \rightarrow \text{bipy}^{*+}
\]

Where bipy\(^{2+}\) corresponds to the bipyridinium group and bipy\(^{*+}\) represents bipyridinium radical cation.

This phenomenon has been explained in terms of resonant tunneling behavior of the electronic energy levels of the molecules. Resonant tunneling occurs through a molecule when one of the unoccupied energy level of the molecule resonates with the Fermi level of the attached metal electrode. Thus a precise knowledge of the electronic energy state is necessary to understand the resonant tunneling electron transport through this molecule. We report here the electronic and geometrical structure of bipyridine molecules and the corresponding bipyridinium moiety terminated with thiol groups.

2. Computation Details

Density functional theory (DFT) techniques\(^6\)–\(^10\) were used for total energy calculations. The functionals used are Perdew-Wang 91 for correlation and Becke-3 for exchange.\(^11\)–\(^14\) The notation B3 indicates a three-parameter Becke exchange functional where a portion of the exchange contribution has been calculated in the same fashion as in the Hartree-Fock (HF) procedure but using the Kohn-Sham non-interactive wave function instead of the HF wave function. The use of hybrid functionals is fully justified as many successful applications have been reported with a broad variety of systems. The basis set used was triply split-valence with
Table 1 Optimized bond lengths for neutral and anion bipyridine molecule. The optimization was done using B3PW91/6-311G(d,p) method.

<table>
<thead>
<tr>
<th>R(C-N)</th>
<th>Neutral planar</th>
<th>Neutral non planar</th>
<th>Anion planar</th>
<th>Molecule of figure 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2, 1-6, 8-9, 9-10</td>
<td>1.347</td>
<td>1.348</td>
<td>1.367</td>
<td>1.395</td>
</tr>
<tr>
<td>R(C-C)</td>
<td>2-3, 5-6, 7-8, 10-11</td>
<td>1.390</td>
<td>1.391</td>
<td>1.378</td>
</tr>
<tr>
<td>R(C-C)</td>
<td>3-4, 4-11-12, 7-12</td>
<td>1.405</td>
<td>1.402</td>
<td>1.437</td>
</tr>
<tr>
<td>R(C-C)</td>
<td>4-12</td>
<td>1.48</td>
<td>1.479</td>
<td>1.43</td>
</tr>
</tbody>
</table>

polarization functions. All calculations have been performed using Gaussian-98 programme.

3. Results and Discussion

Total energy calculations have been performed for bipyridine molecules where in one case the two pyridine rings are coplanar and in the other case two pyridine rings are perpendicular to each other. It is found that the perpendicular geometry for bipyridine molecule is 30 meV more stable than the corresponding planar configuration. The gap between HOMO and LUMO energy levels is found to be 5.12 and 5.87 eV for planar and perpendicular geometries, respectively. However, when both configurations were optimized, the ground state structure for perpendicular configuration shows that the two benzene rings are at an angle of 140°. The bond lengths between C-N and C-C atoms remains almost similar for both planar and nonplanar configurations (shown in Table 1). To understand the behavior of charge localization in presence of one excess electron we have also optimized the geometry of bipyridine anion. The optimized geometrical parameters are listed in Table 1. It is seen that the bond lengths between C-C and C-N bonds of bipyridine molecules are significantly affected in the presence of excess electron. From the difference of total energy of neutral and negative ion molecule the electron affinity of the bipyridine molecule is calculated to be 0.68 eV, which can be used as a parameter to understand the electronic admittance in bipyridine molecule.

Experimentally to observe the electron transport behavior, bipyridinium moiety was placed at the center of a chain of 20 methylene units in an α, ω-poly(methyle nedithiol) compound as shown in Fig. 1. The long alkane chain was used to give stability to the bipyridine moiety so that gold cluster should not influence much on the bipyridine electronic structure. The geometry of these molecules have been optimized using B3PW91/6-311G(d,p) level of theory. Table 2 summarizes the results for bipyridinium molecules connected to alkane chains of different lengths up to n = 9, where n represents the number of carbon atoms in the polymethylene chain in one side. It has been noted that while the initial configuration has been taken as non-planer structure of bipyridine moiety however, the final geometry shows a planar configuration as the lowest energy structure. From the table it is found that the gap between HOMO and LUMO energy levels has significantly decreased as compared to the free bipyridine molecules. The reason may be due to charge transfer from thiol groups to the ring atoms. For example it has been noticed from Mulliken point charge analysis that while the charge on N atom for free bipyridine is -0.36 but for bipyridine moiety connected with thiol groups is -0.62. This fact has further been corroborated by the significant change in the bond lengths between C-N and C-C atoms as listed in Table 1. It is seen that C-N and C-C (away from C-N bonds) bond lengths increases in case of thiol terminated bipyridine moiety whereas C-C bonds adjacent to C-N bonds and the C-C bonds at the bridging between two pyridine rings decreases as compared to the free bipyridine molecule. Comparison of the energetics for the series of molecules corresponding to Fig. 1, it is seen that the HOMO-LUMO gaps of the bipyridine molecules increases with the increase in length of the alkane chains.

To understand the transport behavior in molecular systems it has been assumed that the metal electrodes inject the electrons on the LUMO state and therefore in a first approximation, the barrier for transport of electrons will be half of the HLG (HOMO-LUMO). From the current–voltage curve of the molecular switch (corresponding to Fig. 1) a very sharp resonance peak has been observed for the applied voltage in the range of 1.5 to 1.8 V. The electronic structure of this molecule shows a gap between HOMO and LUMO energy levels is 3.33 eV. Therefore, from the calculation results it is predicted that the required bias voltage for resonant tunneling through this molecule would be 1.66 V approximately which is in good agreement with the experimental results. It can be mentioned here that normally DFT calculations predict HOMO-LUMO gap smaller than the actual one. However, the present molecule could be a special case where it agrees very well.

4. Conclusion

The geometry and electronic structure of free bipyridine molecule and bipyridine moiety connected with alkane chains terminated by thiol groups have been calculated using density functional theory. Gaussian software package has been used for all the calculations. The potential barrier for electron con-
duction through these molecules have been calculated based on the assumption that the incoming electrons pass through the lowest unoccupied molecular orbitals connected across the molecules. The applied voltage required for resonant tunneling through this molecule has been calculated to be 1.66 V, in good agreement with the experimental results.

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REFERENCES