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Designing Efficient Donor-Bridge-Acceptor Type of Molecules for nanowire and Molecular Electronics through Computational Methods

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ABSTRACT

Present developments in the field of nanomaterials chemistry show that, though inorganic nanomaterials are still the choices for many devices, interest in organic nanomaterials are growing day-by-day in view of their adaptability to various kinds of applications. Our studies deals with the molecular wires studies of some D-B-A type of molecules where the bridge is an allenic bridge. These bridges have some interesting features like, break in conjugation due to the presence of mutually orthogonal orbitals. So, in this chapter, a detailed structure property correlation study has been carried out with the above mentioned molecule in considering various D/A effects, increase in conjugation (inside and outside the allenic bridge) effects. Theoretical investigation has been carried out on electron transport properties of gold surface. In order to study the role of linkage in the conduction properties of molecular wire, different linkers such as nitrogen, oxygen, NO_2 and NH_2 have been considered. The electronic conduction has been analyzed from the change in the shape of molecular orbitals and the evolution of the HOMO–LUMO gap of molecule-gold complexes under the influence of the electric filed.

Keywords: Donor-Bridge-Acceptor, Allenic bridge, Molecular wire, Linkage, HOMO–LUMO gap, Gold cluster.

INTRODUCTION

The field of organic molecular materials has transformed the use of materials in the modern world in the last 20 years, and it can be seen that organic molecules provide wonderful opportunities to materials researchers to design custom-tailored materials whose properties at the macroscopic/microscopic level reflect closely to the modeled or actual behavior of individual molecules. In other words, development of novel functional organic materials is a rapidly growing area of science, which probably can replace the traditionally used materials with

cheaper and better-performing new ones in the near future, and also bring out some new applications[1]. In the introduction section to the Molecular Electronics, the detailed history, present trend and future activities are discussed. A light is thrown to describe the organic molecules, which can mimic the traditional semiconductor electronic components. As in the basic operation principle of these molecular electronic components is the Electron Transfer process, hence a brief description to this theory is also discussed. Again as the materials are to be used at molecular scale in the devices, hence in the view of the prominent quantum effect at molecular level, the role of frontier molecular orbitals (FMOs) and their energy levels in the electron transfer processes are described. Over thirty years ago, Aviram and Ratner proposed theoretically that molecular wire should have the ability to rectify electronic current [2]. Comprehension of chemical interaction between electrode metals and molecular wires is very fundamental and important to the basic design of single-electron devices. A molecular wire is an organic molecule that forms a conducting bridge between electronic contacts. A single organic molecule is likely to be the smallest entity to conduct electricity and thus molecular wires present many interesting challenges to fundamental science as well as enormous potential for technological applications, such as organic switching devices [3-6] and nanoscale memories [7,8]. One of the most important goals in the engineering of electronic devices is the miniaturization. The present technologies of micro-structuring semiconductor material are expected to reach their limits in the next decade. Construction of a molecular wire requires an elongated molecule consists of conjugated molecular units, which contain alternating single and double (or triplet) bonds through which electron can flow easily from one end to other. Recently, many experimental [9-11] and theoretical studies [12-16] have elucidated the transport properties through molecule/metal heterostructures. A particular challenge stems from the realization that the properties of molecular wires are strongly influenced by (i) characteristics of the molecule, (ii) the nature of linkage and thus metal-molecule interaction [17]. In the molecular level, the quantum effects play an important role. a theoretical analysis of the frontier molecular orbital's of these molecules will give a clear picture of the structure-property relationship and ultimately the synthetic strategy and molecular engineering techniques and energy difference between HOMO and LUMO known as HOMO-LUMO gap (HLG) can be utilized to reach the reality [18-20]. Here, HOMO denotes the highest occupied molecular orbital while LUMO shows the lowest unoccupied molecular orbital [21-22]. the energy gap has been estimated from two ways, namely, HOMO-LUMO gaps and the lowest excited energies [23]. Moreover, since the electronic devices must work under a large external electric field, it is important to understand how the molecular structure and HLG respond to the external electric field [24-25]. Molecule 1-7, one of the smallest conjugated oligomers, provides a good theoretical model for exploring the structural and electronic properties that control the electron transport [26]. Molecule 1-7 oligomers possess not only conductivity [27] but also ideal rigidity [28] and are promising materials for a wide variety of applications in molecular electronic devices. Molecule 1-7, seven of the smallest conjugated oligomers, provides a good theoretical model for exploring the structural and electronic properties that control the electron transport [29]. In this paper, a detailed theoretical investigation has been performed on electron transport properties of 1-7 molecules sandwiched between one gold cluster. In our investigated systems, the Para hydrogen's of two phenyl rings have been replaced by different linkers that are classified into atomic linkers such as, nitrogen and oxygen group linkers in which the mentioned atoms joined to the ring through nitrogen connector. Thus the group linkers are NH₂ and NO₂. The geometries and electronic structures of linker-terminated Molecule 1-7 interacting with gold

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(111) cluster have been investigated. Based on the binding energies and the shape of the electronic channels in the Molecule 1-7, based molecules we provide insights on the contribution of molecular orbital's and highlight the importance of the tuning parameters such as electric filed and type of linkage for the operation of molecular wire in the electronic devices.

2. Computational details

The molecules considered here (molecules 1-3) are constructed with an extended conjugation (vinyl substitution) in the D and/or A side and are shown in Figure 1.a. And for molecules 4-7, the effect of increasing the conjugation inside the allenic bridge by increasing the number of spcarbon atoms are accounted in the structure-property correlation of some molecules containing the even and odd number of cumulenic double bonds. All the molecules considered for the study i.e., molecules 4-7 are shown in Figure 1.b.

It is necessary to include the metal contact in any study of a molecular device, and in the present work, we choose a three atom gold nanocluster, Au (III). The calculations have been performed at the density functional theory level with the B3LYP functional. The basis set is split 6-31G* for H, N, O atoms and the Los Alamos National Laboratory effective core potentials with a double-zeta valence (LANL2DZ) for the gold atoms [30]. All calculations performed with three steps. In the first step a geometry optimization of molecule 1-7 joined to two different linkers was carried out. Then the interaction between molecules (after removal of the end H atoms of NH2) and gold (111) cluster has been studied. In this configuration, gold cluster consists of three atoms that are placed as equilateral triangle with side of 2.88 A° to simulate the gold (111) surface [31]. The relative positions of the gold atoms fixed in each triangle. Relevant geometrical parameters for all the metal-molecule complexes studied in this work. The position of linker (or any end atom of linker) in the molecule interfacial region, also one terminal gold clusters were fixed in the space and the others were optimized. To optimize (Au3 molecule1-3) and (Au3 molecule 4-7) complexes, the range distance between the linker atom and the gold plane has been adjusted between 2.13 and 3.93 A°. Step 3: Then, the one terminal gold cluster was fixed in space to simulate the connection to the electrode. All other geometric parameters were, then, optimized at the same level of theory in an external EF. The EF ranging from zero to 0.103 V/A° defined as uniform and aligned along the metal/molecules inter-atomic vector, applied to each complex that can reasonably represent the working condition of the molecular wire [32-34]. All calculations were carried out using GAUSSIAN 03 program [35].





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Fig.1[a,b]: molecular junctions so constructed and Different linkers Linker= O, N, NH₂, NO₂

MOLECULE	HOMO	LUMO	GAP
1	-5.217	-2.329	2.887
2	-5.575	-2.539	3.035
3	-5.205	-2.460	2.745

Table 1.a: HOMO, LUMO and HLG	levels (in eV) in free molecules
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Table1.b				
MOLECULE	HOMO	LUMO	GAP	
4	-5.343	-2.641	2.701	
5	-5.402	-2.525	2.363	
6	-5.219	-2.850	2.877	
7	-5.337	-2.759	2.578	

RESULTS AND DISCUSSION

3.1. Electronic structure of free molecules

The primary requirement for a molecule to behave as a molecular wire is that it should have a fully delocalized low lying vacant molecular orbital spreading all over the molecule which serves

a channel of conduction in the electron transfer process, i.e. the higher the delocalization, the faster the electron transfer [36,37]. Table1(a:molecule 1-3, b: molecule 4-7) gives a comparison of energy levels in HOMO and LUMO as well as their gap (HLG) for seven molecules.



Table .2.a :The shape of HOMOand LUMO orbitals in free molecules.

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The corresponding molecular orbital pictures for all molecules obtained from their optimized geometries visualized in Table 2 (a:molecule 1-3, b: molecule 4-7). Table 2a,b shows a comparison of energy levels in HOMO and LUMO. For two molecules (4,6), both HOMO and LUMO are fully delocalized along the whole molecular backbone, so they can serve the purpose of conduction channel in the electron transfer process.

3.2. Interaction with gold cluster

The electrical performance of a molecule sandwiched between one metal electrode is predominated by many factors, such as the nature of the molecule itself [38], the interface between the molecule and electrode [39], the electrode material [40], and the electrode shape [41]. The gold-molecule interface has been demonstrated to acquire particular importance in the transport properties of molecular wires. Investigation on nature of interaction between the molecule and the gold cluster has proven indispensable for reproducible results of electronic conductivity [42,43]. The ease of electron transfer within a molecule determines whether the complex acts as a metallic conductor, semiconductor or insulator; which of course is highly significant for molecular electronic applications. Giving the position of the terminated atoms in the hollow site of the gold cluster, the orientation and the structure of complexes were obtained. We are firstly looking for the energetically optimal distance between the gold cluster and the terminated atom in each complex. It can be found that molecule 1-7 remain planar and perpendicular to the gold surface in all complexes. We compared just the bond distance between terminal atom and Au, because the geometries of other atoms in molecules were barely affected. Table 3(a:molecule 1-3, b: molecule 4-7) presents the energetic and typical geometrical parameters for the optimal distance between the terminated atom (the bolded atoms) and the gold surface. In all complexes the distances between the gold cluster and the terminated atom are within 2.13–3.44 Å. The binding energy is defined as:

Binding energy =E (molecule/Au (111))-[E (molecule) +2E (Au (111))]

where E (molecule 1-7) is the total energy of molecule 1-7 when both end of the molecules are substituted by O, N, NH_2 or NO_2 groups. E (Au (111)) and E (molecule/Au (111)) are total energies of gold cluster and the complex of molecule on the gold cluster, respectively. We compare the connection of nitrogen and oxygen as linkage between metal and molecule interfaces. Two different sets of linkers have been investigated. In the first set (NO_2 , NH_2) the mentioned linkages are directly connected to gold cluster and molecule 1-7. In this case a lone pair of electron on N and O involves in the resonance leading to electron delocalization all over the molecular backbone. To summarize, among seven complexes studied in this work (molecule 1-7), five of them (1,3,4,6,7) are stabilized due to interaction with gold surfaces.

Fable 3.a: (Calculated distance between AU and the linker(Å),binding energies ,HOMO, LUMO .and	HLG
	(Ev)for the seven complexes. ^a	

MOLECULE	d _{Au-L}	Binding energy	E _{HOMO}	E _{LUMO}	HLG
1	2.110	-1.514	-5.650	-3.701	1.948
2	2.378	1.308	-5.676	-3.616	2.051
3	2.135	-1.440	-5.434	-3.508	1.926

MOLECULE	d _{Au-L}	Binding energy	E _{HOMO}	E _{LUMO}	HLG
4	2.254	-1.358	-5.662	-3.914	1.748
5	2.135	1.296	-5.516	-3.611	1.904
6	2.135	-1.515	-5.539	-3.763	1.776
7	2.135	-1.487	-5.542	-3.672	1.870

Table 3.b

MOLECULE	НОМО	LUMO
1	., 2, 2, 2, 2 2 2 2 2 2 2 2 2 2	••************************************
2	••••••••••••••••••••••••••••••••••••••	
3		, :-::: ::::::::::::::::::::::::::::::::

 Table.4a.: The shape of HOMO and LUMO orbitals for complexes 1-7

4.b:



Finally, it is interesting to describe changes in molecular levels after the interaction with gold cluster. The shift of HOMO and LUMO can be attributed to the variation of the electron density when the gold cluster and the molecule bond exist. The reported orbital energies in Table(1and

3) show that complexes of molecule 1-7 with gold cluster have lower HLG than the isolated molecule 1-7. Table 4 presents the frontier molecular orbital pictures for the molecule 1-7 after interaction with gold (111) cluster. For complexe 4, HOMO-1 and LUMO+2 and complex 6 LUMO and HOMO-2 remains fully delocalized along the whole complex. In these complexes where the coupling to gold cluster is through nitrogen, and hydrogen junction, the conduction of HOMO and LUMO are delocalized and remain the same as its free molecule. For complex 1,2,3,5,7 HOMO and LUMO are partially localized so that electron charge has gathered around the complex structure. However, the delocalized nature of frontier molecular orbitals which can be treated as conduction channel demonstrates that these complexes can be expected to behave as potential molecular wire.

CONCLUSION

Density functional theory studies have been carried out to explore the role of linkage in the interaction between molecule 1-7 and gold cluster. In the present study we focus on the geometrical and electronical structure of molecule 1-7 based molecular wire, however the electron transport properties can be also studied based on the non-equilibrium Green's function formalism [44-47]. Among seven different molecules studied in this paper, molecule 1-7 make the most stable complexes with 3,4,6,7. The charge transfer analysis shows that the gold can strongly couple with molecule 1-7 via NH₂ linkage, while the weak interaction of gold with molecule 1-7 through NO₂ linkage has non-covalent nature. These observations give us an insight how to modulate tunable parameters such as the nature of interfacial contact in the operation of molecular wire.

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