Modification of the electric properties of molecular devices via gradual increase of number of nitrogen atoms: A computational study

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ABSTRACT

This paper introduces a new means to manipulate electronic structures and, consequently, the electrical properties of molecular devices via gradual increase of number of nitrogen atoms in the backbone of conjugated organic molecular systems. Diblock molecules were selected for this purpose. Density functional theory (DFT) was used to investigate geometrical and electronic structures in the absence and presence of external electric field. Furthermore, the tendency of the anchor sulfur atoms toward electrodes in a simulated closed circuit was estimated from the relative condensed Fukui function. The obtained results indicated that HOMO–LUMO gap decreases steadily with increasing the number of nitrogen atoms, which would be used as a means for modifying the electrical properties in a regular mode.

1. Introduction

Due to physical limitations in silicon technology, much attention has been paid to the molecular electronics as a post-silicon technology. The development of this field began after the demonstration of how an organic molecule could function as a molecular device by Aviram and Ratner [1]. The principle idea behind the development of a molecular device is to mimic the electronic function of silicon-based devices using certain molecular systems as alternatives. The prime example was the Aviram–Ratner (AR) molecular rectifier [1].

The most important step in selecting of a molecular device is the control of its functionality as conductor, rectifier, etc. For example, one needs to control the electron flow through the rectifier diode to obtain the desired electronic properties. In this context, chemistry plays a key role in manipulating the electrical property of molecular device because of its ability to tune the electronic structures of molecules. Many structural factors were used for designing

particular molecular devices [2–13]. The most common factors are substitution [2–4], conformation [5,6], anchoring group [7–10], and molecular length [11]. There are also some other factors of minor importance such as the annulations [12] and isomeric [13] effects. All of these factors are able to modify the HOMO–LUMO gap (E_g), which is considered as the key for controlling electron transport in the molecular device. This paper introduces, for the first time, a new factor of increasing number of nitrogen atoms in the conjugated backbone of a molecular system to control regularly its electrical properties. This way could be be used for tailoring molecular electronic devices. We selected a series of diblock molecular systems, as shown in Fig. 1.

The electronic structure of a rectifying diode adopts itself to allow the current to flow preferably in one direction. Two important models of molecular rectifiers have been studied extensively in literatures; the first one consists of π-conjugated donor and accepter moieties insulated with a σ-insulator (D-σ-A) [1]. The second model contains the π-bridge instead of σ (D-π-A) [14]. Recently, a new class of molecular diodes has been synthesized and investigated based on diblock oligomers [15–20]. In

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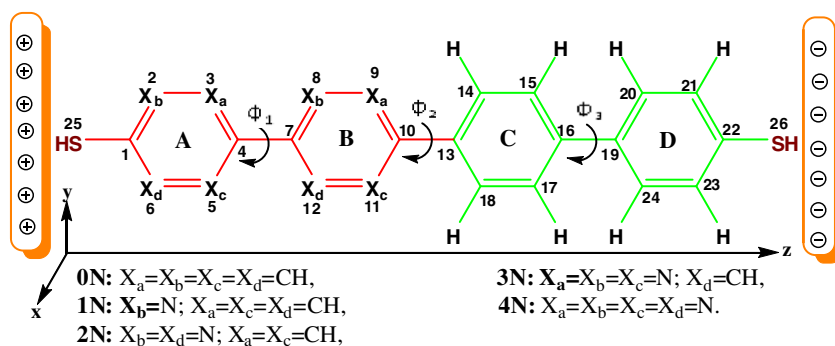 E-mail address: amelnahas@hotmail.com (A.M. El-Nahas).

Fig. 1. The general chemical structure of the investigated molecular systems under the effect of external uniform electrical field, and their abbreviated names are shown below the structure. Numbering scheme for atoms are shown on the structure. *A, B, C* and *D* symbols are labels for the four rings. The presented symbols Φ_1, Φ_2 and Φ_3 in the figure are the torsion angles between each two adjacent rings. The uniform external electrical field aligned along the two terminal sulfur atoms in positive *z*-axis direction is presented. All labels are unified for all studied molecules.

these oligomers, an electron rich unit is covalently bonded to an electron deficient unit without bridge where the forward current flows from the acceptor to the donor.

So far two well-known examples of diblock diodes have been studied; dipyrimidinyl-diphenyl diblock [15,18–20] and dithiophenyl-dithiazolyl diblock [16,17] molecular diodes. Both diodes showed a pronounced rectifying ability due to a built-in chemical asymmetry. However, it was demonstrated experimentally that the rectification is an intrinsic property of a molecule and not due to the asymmetry of the electrodes and/or molecule-electrode interfaces [16,17,21]. For this reason, many authors used to apply electric field (EF) on isolated molecules without taking into account effect of electrodes. They considered electrical properties of a given molecular device as intrinsic characters of the molecule itself [22–31].

The prominent problem that makes the molecular electronics hard to apply is the difficulty of finding an efficient way to attach the molecule reproducibly to the electrode [32]. The non-reliability and non-reproducibility in the experimental measurements for the function of molecular device were considered as the obstacle behind that [32]. In experiment, the diblock molecular system adsorbs on the metal substrate via anchors. The thiol groups are placed at the terminuses of the molecule to function as clips for linking it to the electrode surface. It is important to predict the local reactivity of sulfur anchoring sites toward the interaction with the metal electrodes.

Our objective herein is to investigate the effect of gradual increase of the number of nitrogen atoms on geometrical and electronic structures of the diblock molecular systems as well as on the condensed Fukui function (CFF) [33] in the absence and presence of EF. To the best of our knowledge, this is the first time to use CFF as a descriptor to predict the strength of interaction between anchors the electrodes under the action of electric field. This study includes five molecules whose abbreviated names 0N, 1N, 2N, 3N and 4N as depicted in Fig. 1. The right number of letter N refers to the number of nitrogen atoms in each heterocyclic ring. Except 0N, the molecules are diblock consisting two segments; donor (diphenyl) and acceptor (heterocyclic) segments.

The density functional theory (DFT) is a very useful framework for calculating local reactivity descriptors such as condensed Fukui function $f(r)$ of the molecular system [33]. It is defined as the sensitivity of the electron density $\rho(r)$ at various points in a species to a change in the number of electrons (N) in the molecular system at constant external potential $\upsilon(r)$ [33]. Thus, it was used to predict the variation in reactivity of different sites in a given molecule.

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{\upsilon(r)} \tag{1}$$

Because of the discontinuity in the derivative at the *N*-value of Eq. (1), two definitions for Fukui function were introduced [34]:

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{\upsilon(r)} \text{ for a nucleophilic attack, and} \tag{2}$$

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{\upsilon(r)} \text{ for an electrophilic attack} \tag{3}$$

Using the finite difference approximation, the above indices could be written as [35]:

$$f^+(r) = \rho^{N_0+1}(r) - \rho^{N_0}(r) \tag{4}$$

$$f^-(r) = \rho^{N_0}(r) - \rho^{N_0-1}(r) \tag{5}$$

where $\rho^{N_0}(r)$, $\rho^{N_0-1}(r)$ and $\rho^{N_0+1}(r)$ represent the electronic density function of neutral, cationic and anionic species, respectively, calculated at the same optimized geometry of the neutral species. The approximate integration of the Fukui function over atomic regions gives more informative function called condensed Fukui functions [35]. Consequently, the condensed Fukui functions are denoted as:

$$f_k^+ = q_k^{N_0+1} - q_k^{N_0} \tag{6}$$

$$f_k^- = q_k^{N_0} - q_k^{N_0-1} \tag{7}$$

where $q_k^{N_0}$, $q_k^{N_0-1}$ and $q_k^{N_0+1}$ are the atomic electron populations at atom k for neutral, cationic and anionic species, respectively.

2. Computational details

All calculations were performed using the Gaussian 03W program [36]. The investigated molecular systems were fully optimized using the hybrid B3LYP functional [37–39] with the 6-31+G(d,p) basis set. To simulate the connection of the selected molecules with the electrodes, the two anchoring sulfur atoms of the fully optimized structure were fixed in space then allowed them to be optimized again under the effect of a uniform electric field [24] ranges from *zero* to 2.00×10^{-3} a.u. This corresponds to a range of bias voltage from *zero* to 2 volt (V). The field was aligned with and against the molecular axis, Fig. 1. Single point calculations have been performed using BLYP/DNP [40] method as implemented in DMOL3 [41] package to calculate the condensed Fukui function of the sulfur atoms.

3. Results and discussion

3.1. Effect of gradual increase of nitrogen atoms on the geometrical and electronic structures

Previously [24], we have studied the influence of electric field on the geometrical structure of 0N and 2N mole-

Table 1
Torsional angles (°), Φ_1, Φ_2 and Φ_3, between adjacent rings in the molecular systems of the investigated molecules. The angles are assigned in Fig. 1.

Species	#N[a]	Φ_1	Φ_2	Φ_3
0N	0	−38.99	−38.66	38.26
1N	2	18.03	−37.94	38.18
2N	4	−0.67	−37.96	38.31
3N	6	−19.25	−18.78	37.28
4N	8	38.41	−0.17	37.34

[a] #N refers to number of nitrogen atom in acceptor subunit.

cules. Therefore, in this paper we will consider only the effect of gradual increment of nitrogen atoms on the geometrical structures of the investigated molecules in the absence of electric field as they have similar results to those of 0N and 2N molecules. As reported in Table 1, all molecules optimized to twisted structures. The replacement of a CH group(s) in rings *A* and *B* by nitrogen atom(s) perturbs the electronic structure and, thereby, the geometry of the molecule. Two factors are responsible for such perturbation: steric hindrance and π-electron conjugation. If the latter dominates, the *A* and *B* rings tend to be coplanar as emerged from the values of dihedral angles, Φ_1 and Φ_2, in 2N and 4N, respectively; otherwise they twist significantly as in the other cases. In the case of 4N, the steric hindrance is completely reduced and the π-electron conjugation reaches its maximum producing coplanar *B* and *C* rings. In other word, the change in torsion angles Φ_1 and Φ_2 depends on the position of nitrogen atom(s) in the heterocyclic ring. However, the torsion angle between the two phenyl groups, Φ_3, is almost unaffected with increasing number of nitrogen atoms in the heterocyclic block.

The electron transport characteristics of a single molecular device can be evaluated from the extent of the spatial distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and their energy gap [42]. Fig. 2 displays good correlations between the reduction in HOMO, LUMO energies and their energy gap with the number of nitrogen atoms per heterocyclic ring. Evidently, the energies of both HOMO and LUMO decrease gradually with nitrogen atoms. However, the degree of stabilization of the LUMO is larger than that of the HOMO. Consequently, the HOMO–LUMO gap decreases regularly too. Gradual addition of nitrogen atoms increases the electron deficiency at the heterocyclic moiety (acceptor) and enhances its electrophilicity and
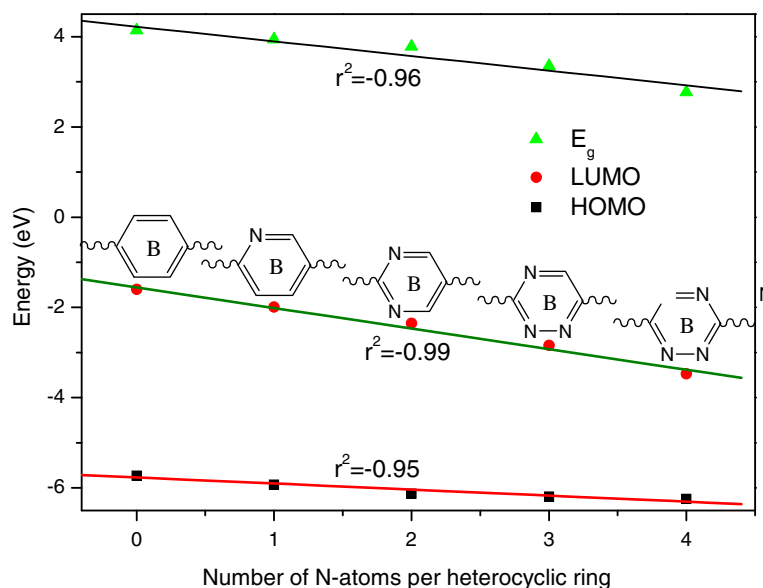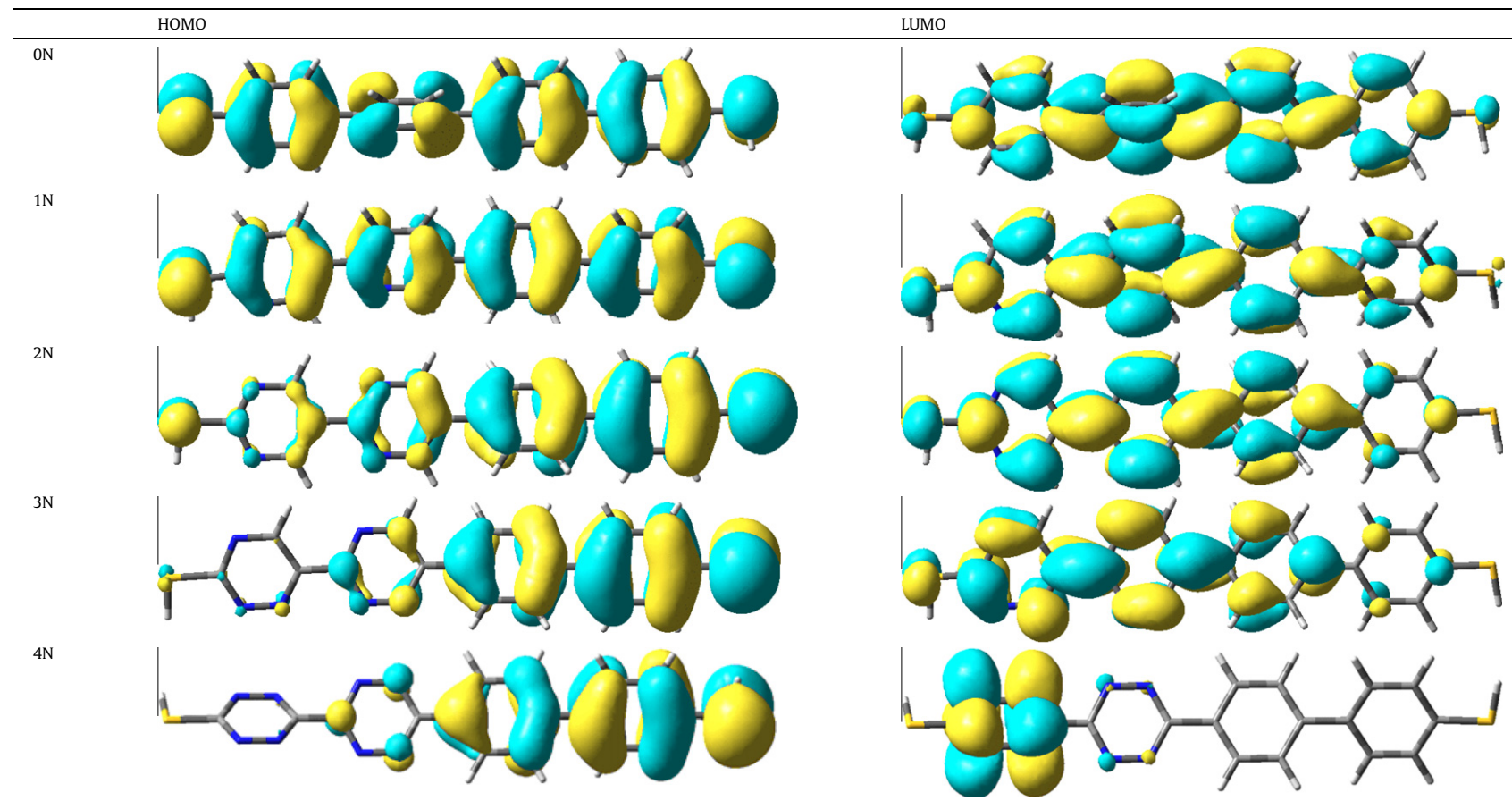

Fig. 2. Plots of HOMO, LUMO energies and their energy gab (E_g) versus number of nitrogen atoms per heterocyclic ring. The symbol r^2 is the correlation coefficient.

Table 2
The effect of increment in number of nitrogen atoms involved in the investigated molecules on the shape of HOMO and LUMO surfaces under zero bias voltage.

	HOMO	LUMO
0N		
1N		
2N		
3N		
4N		

thereby the electron transfer from the biphenyl block, i.e. the coupling between two blocks will increase. This leads to a decrease in the LUMO energy compared to HOMO and, thereby, a reduction in the energy gap between HOMO and LUMO. Such reduction is important based on the assumption that the Fermi level of the metal contacts is aligned with the midpoint of the E_g [42]. Because of dependence of the rate of electron tunneling between metal and electrode on E_g, it is expected that the applied EF will cause different rates as a result of different E_g produced from gradual increase of nitrogen atoms. We can conclude that the strategy of increasing nitrogen atoms can be used as a means for tuning the electronic structures of molecular devices and consequently their electrical properties.

Table 2 presents the spatial distribution of the frontier molecular orbitals (FMOs) of the investigated molecules. It is apparent that the increase in the number of nitrogen atoms perturbs both HOMO and LUMO. This might change the electronic functionality and/or the efficiency of the molecular device. For instance, both HOMO and LUMO of the hydrocarbon moiety are delocalized entirely over the whole molecular skeleton especially at the anchoring atoms. The replacement of two CH groups with two nitrogen atoms, i.e. 1N, almost has no effect. Therefore, 0N and 1N could function as molecular wires. Adding extra two nitrogen atoms, 2N, slightly shifts the spatial distribution of the HOMO and LUMO toward biphenyl and heterocyclic blocks, respectively. Experimentally, this molecule shows a pronounced molecular rectification [15]. Increasing the number of nitrogen atoms increases the shift of FMOs. The most prominent effect appears in 4N, where the HOMO is highly localized on the biphenyl block and the LUMO is confined to the terminal heterocyclic ring. Therefore, 4N is similar to AR molecular rectifier in which the HOMO is entirely localized over the electron donating subunit while the LUMO is completely localized on the electron accepting subunit [43,44].

3.2. Effect of EF on the relative energy and dipole moment

Flexible conjugated molecules are expected to adopt new conformations under the action of an electric field due to the changes in their electronic structures. All produced conformers are more stable than the original one either under positive or negative voltages. This can be observed by plotting the relative energy of the produced conformers against the bias voltage as shown in Fig. 3. The influence of voltage on the relative energy has symmetrical feature reflecting the symmetrical electronic structure of the 0N molecule. On the other hand, the stability depends on the number of nitrogen atoms. Under the positive bias, the following order was found: 0N > 4N > 1N > 3N > 2N. This order is reversed under the negative voltage.

As a result of changing electronic structures of the investigated molecules under external EF, their dipole moments are changed. Fig. 4 illustrates the relation between bias voltage and dipole moments of the molecules under investigation. It is evident that the produced conformers have higher dipole moments under negative bias voltage compared to positive one. However, the dipole moments of the molecules change to different extents under the effect of bias in either direction. For instance, applying EF shows a symmetrical change in the dipole moment around *zero* bias for 0N. Insertion of nitrogen atoms breaks this symmetry. Sweeping the voltage from −2 to 2 V decreases the dipole moments of 2N and 3N. For 1N and 4N, the dipole moments decrease monotonously until 1.5 and 1 V respectively, followed by gradual increase producing minima. It is worth mentioning that 2N also produces minima around 2 V as we reported in a previous study [24]. This behaviour is attributed to the built-in electric field that opposes the applied electric field in the positive direction and aligns with it in the negative direction [24]. We can conclude that the insertion of nitrogen atoms in 0N produces asymmetry in the dipole moments with opposite
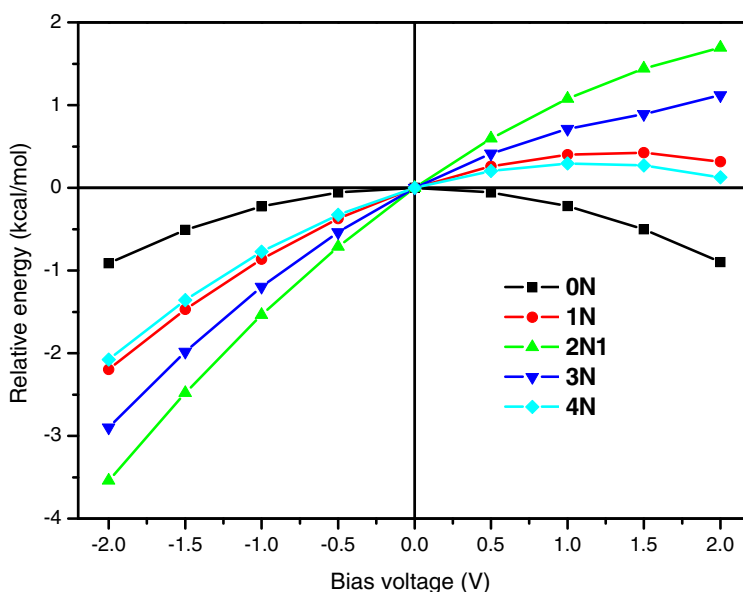

Fig. 3. External bias voltage dependence on the relative energy of the investigated molecules.
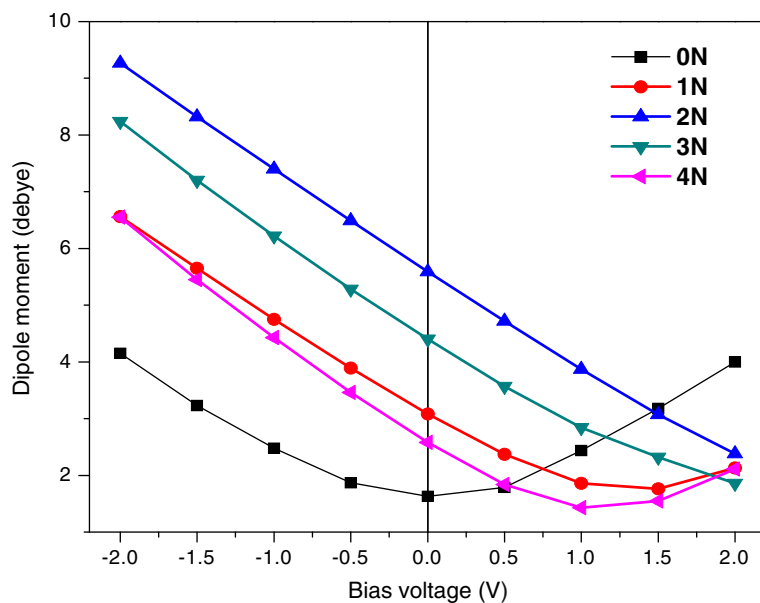
Fig. 4. External bias voltage dependence on the dipole moment of the investigated molecules.
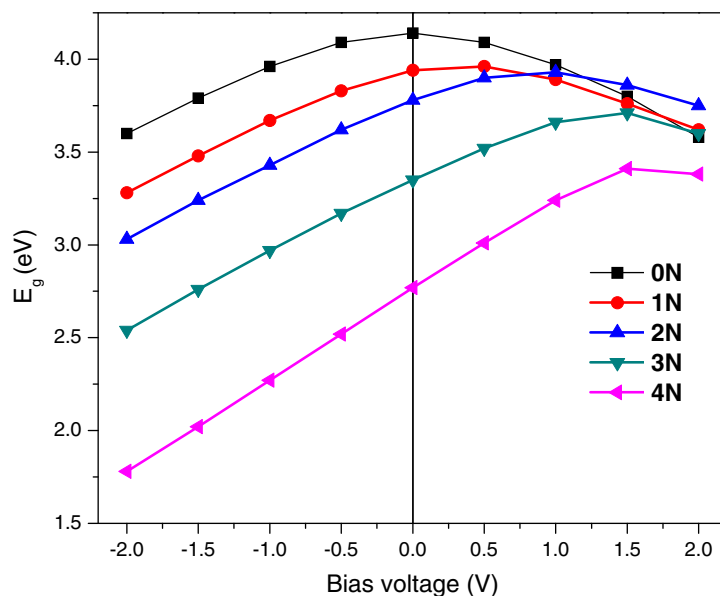

Fig. 5. External bias dependence on HOMO–LUMO energy gap (E_g) of the investigated molecules.

electronic demands in the molecule which is required for rectification [43].

3.3. Effect of EF on HOMO–LUMO gap

As an approximation, the Fermi level is defined as the midway between the HOMO and LUMO energy levels [45]. The values of E_g under EF are shown in Fig. 5. The EF has symmetrical feature around zero bias for 0N. The gradual insertion of nitrogen atoms breaks this symmetry. For

example, while the curve of 0N molecule (black) has maximum at 0 V, the maximum was shifted toward 0.5, 1 and 1.5 V by gradual insertion of nitrogen atoms in the conjugated backbone of 0N. However, it was observed that as the number of nitrogen atoms increases, E_g of the molecule significantly reduces under the effect of negative voltages compared to the situation that under the positive voltages. Hence, the gradual reduction in E_g of molecule with increasing number of nitrogen atoms can be used as a means for changing the electrical property of molecular devices.
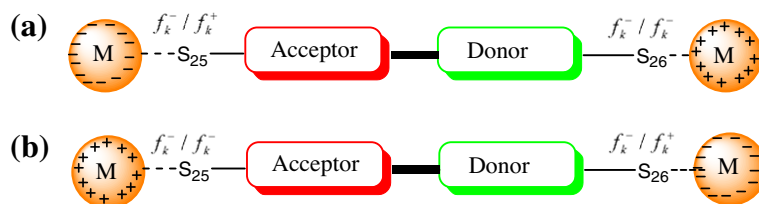
Fig. 6. A model for the interaction of sulfur anchor atoms with electrode metals under (a) negative and (b) positive bias voltages.

Table 3
The relative nucleophilicity (f_k^-/f_k^+) and relative electrophilicity (f_k^+/f_k^-) of sulfur atoms of 2N molecule under the action of various bias voltage.

Negative voltage			Positive voltage		
Voltage (V)	$(f_k^-/f_k^+)_{S25}$	$(f_k^+/f_k^-)_{S26}$	Voltage (V)	$(f_k^+/f_k^-)_{S25}$	$(f_k^-/f_k^+)_{S26}$
−2.00	0.73	0.23	2.00	1.49	4.70
−1.50	0.71	0.23	1.50	1.47	4.70
−1.00	0.71	0.22	1.00	1.45	4.70
−0.50	0.70	0.22	0.50	1.45	4.60
0.00	0.70	0.22	0.00	1.44	4.57

Table 4
The relative nucleophilicity (f_k^-/f_k^+) and relative electrophilicity (f_k^+/f_k^-) of sulfur atoms of the investigated molecule under the action of various bias voltage.

	Bias voltage = −1		Bias voltage = +1	
	$(f_k^-/f_k^+)_{S25}$	$(f_k^+/f_k^-)_{S26}$	$(f_k^+/f_k^-)_{S25}$	$(f_k^-/f_k^+)_{S26}$
0N	1.95	0.52	0.51	1.91
1N	1.26	0.33	0.80	3.04
2N	0.71	0.22	1.45	4.70
3N	0.65	0.32	1.53	3.13
4N	0.54	0.26	1.86	3.92

3.4. The potential interactions between molecule and electrodes

Thiol group is the most popular anchoring group used to connect molecules with gold electrodes [3,32,45–48]. The formed molecular junction, even at small bias, has a finite lifetime after which a breakdown in the molecule-electrode contact takes places [32]. The speed of the breakdown process increases with increasing the strength of applied field [32]. This breakdown was ascribed to current-induced local heating of single-molecular junctions [49–54] or current-induced force (electro-migration) [207,208]. Studying local reactivity at alligator sulfur atoms may give some insight about such breakdown. Thus, the local reactivity of sulfur atoms toward the two gold electrodes under the effect of electric field has been calculated. Relative condensed Fukui function (f_k^-/f_k^+) for nucleophilicity and (f_k^+/f_k^-) for electrophilicity could be used for this purpose as it gives better results than separate CFF values [55].

Fig. 6 displays a model of interaction of sulfur anchors with the positive and negative electrodes under the effect of electric field. Upon applying negative EF, S25 and S26 attach to the negative and positive electrodes, respectively, as shown in Fig. 6a. Therefore, the interaction of S25 and S26 atoms with the negative and positive electrodes would have electrophilic and nucleophilic features. The relative nucleophilicity (f_k^-/f_k^+) and electrophilicity (f_k^+/f_k^-) of S25 and S26 atoms could be used for calculating their response toward electrophilic and nucleophilic attack from electrodes. Under positive bias voltage, the S25 and S26 atoms attach to the positive and negative electrodes, respectively, Fig. 6b. Consequently, the relative electrophilicity and nucleophilicity will figure out the interaction of S25 and S26 atoms, respectively, with electrodes. They define the reactivity of a given site to be attacked; the greater numerical value of relative Fukui function the more the interaction between the anchor and electrode.

Table 3 presents the relative electrophilicity and nucleophilicity of S25 and S26 atoms for 2N under negative and positive bias voltages, as a representative example. As shown, the influence of electric field is not significant on the relative electrophilicity or nucleophilicity. Similar situation has been observed for the other investigated molecular systems.

An important observation is the dependence of reactivity of anchor atoms on the number of nitrogen atoms. This can be seen from the values of relative local reactivity at bias voltages between −1 and +1 V, Table 4. For example under −1 V, the values of (f_k^-/f_k^+) and (f_k^+/f_k^-) for S25 and 26 atoms decrease steadily with the gradual increase of number of nitrogen atoms. Reversing the applied voltage at the same value (1 V) causes an increase in (f_k^-/f_k^+) and (f_k^+/f_k^-) for S26 and S25 atoms. For 2N, the values of relative electrophilicity and nucleophilicity of sulfur under positive bias are greater than unity indicating a stable molecule–metal contact at both sides. Upon reversing the electric field, these values become less than unity which predicts a breakdown in the molecular junction as observed experimentally [15]. A similar situation was observed for 3N and 4N. The low values of relative electrophilicity of S26 under the negative bias reflect its affinity toward the electrode producing a weak metal–molecule contact. Accordingly, we expect all of the investigated molecular systems to suffer breakdown in the molecule–metal contact under negative bias voltage. Based on the above results, it is concluded that relative CFF could be used to understand potential interactions between anchors and electrodes.

4. Conclusion

In this study, DFT method has been used to introduce a new structural means for rational design of molecular devices via increasing number of nitrogen atoms in the

conjugated backbone. To achieve this objective, we have investigated the effect of increasing nitrogen atoms on the changes of geometrical and electronic structures as well as on relative condensed Fukui function of diblock molecules in the absence and presence of electric field (EF). The results obtained can be summarized as follows:

(1) The gradual reduction in E_g of molecule with increasing number of electronegative hetero atoms can be used as a means for gradual changing in the electrical properties of molecular devices.
(2) This study sheds some light on the use of relative condensed Fukui function for determining the affinity of anchor groups to connect with electrodes during the working of molecular device.
(3) Reactivity of anchor atoms depends on the number of incorporated nitrogen atoms.

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