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Qualitative and Quantitative Analysis of Electron Transport in Donor/Acceptor-Heterocycles Connected to Cumulenic Bridge

J. Laxmikanth Rao*

Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, Andhra Pradesh, India

** Corresponding author: E-mail: lkjoshiji@yahoo.com*
Telephone: +91-040-27191430. Fax: +91-040-27160921

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Abstract

Electron transport abilities for a series of donor/acceptor-heterocycles connected to the cumulenic bridge are qualitatively analyzed by using the *ab initio* Frontier Molecular Orbital (FMO) calculations. It can be seen from FMO analysis that the molecules having one *sp*-carbon atom in the cumulenic bridge act as rectifiers and can be treated as ideal alternatives to the traditional D-σ-A type of molecular rectifiers whereas the other molecules with the two *sp*-carbon atom behave as conductors and can be used as alternatives to the molecular wires in molecular devices. Furthermore to support the FMO analysis for the conductance behaviour of the latter molecules, analysis has been carried out using the semi empirical Extended Hückel Theory and Non-Equilibrium Green Function (EHT-NEGF) formalism, which confirms the FMO results of the proposed molecular conductors.

Keywords: Cumulenes, *I–V* characteristics, rectifier, conductors, potential drop.

1. Introduction

In recent times the field of molecular electronics is gaining importance experimentally as well as theoretically.[1–18] The era of molecular electronics began with the theoretical prediction of single D-σ-A molecular rectifier by Aviram and Ratner,[19] which mimics the junction diode in nature. In an electronic circuit the most commonly used electronic component is the rectifier. One way to make a molecular rectifier is to introduce asymmetry in the wire so that under an external field the molecule allows the current to flow in one direction while preventing flow in the other. In the D-σ-A molecule rectifier, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are localized on the donor and acceptor parts of the molecule respectively and at the same time the intervening σ-bond acts as a barrier and obstructs the charge transfer from the donor part to acceptor part, thereby preventing the spreading of the molecular orbitals from one part of the molecule to the other part. When such a D-σ-A molecule is subjected to the suitable bias voltage in the forward direction, tunneling of an electron from the acceptor side to the donor side occurs (provided the acceptor should be connected to the cathode and the donor to the anode), which results in the asymmetric *I–V* characteristic similar to that of the junction diode. In case of the reverse applied bias voltage, rectification occurs at higher applied voltage when compared to the forward voltage, which is not practicable. Till to date based on this approach of break in conjugation between the donor and acceptor, a lot of theoretical as well as experimental reports have been published.[20–26] Different types of mechanisms can be found in the literature,[2,27–31] for this rectification property associated with the single molecular systems. As per the mechanism proposed by Ellenbogen and Love,[32] the resonant transport of electron occurs from the LUMO (as soon as it is loaded from the cathode) to the next unoccupied level LUMO + k (k = 0, 1, 2…), which is localized on the donor part of the molecule. In case of the junction diode, the pn-junction part controls the flow of electrons, whereas in the D-σ-A molecular rectifier, the bridging unit controls the electron flow. In a molecular electronic device the simplest electronic component for the conduction of current is the molecule wire. The con-

struction of a molecular wire requires an elongated molecule through which electrons can flow easily from one end of the molecule to the other end. Normally, conjugated π-systems provide a path where electron clouds overlap between molecular components so that electrons can hop from one end of the molecule to other end.[25] Many theoretical efforts have been devoted to understanding the mechanism of electron transport through molecular wires. So far, the mechanism proposed from electronic structure calculations suggests that the peak current across the molecular wire is associated with complete delocalization of the lowest unoccupied molecular orbitals.[17] It has been demonstrated experimentally that small conjugated molecules can act as a conducting wire[33–36] and the molecules with asymmetric chemical structures are often observed for rectifying behaviors.[17,37,38]

In our previous study,[39] we have shown that the D-bridge-A type of systems can be treated as useful alternatives for the traditional D-σ-A type of molecular rectifiers/wires depending on the number of *sp*-carbon atoms present in the cumulenic bridge. The main aim of the present study is to analyze qualitatively and quantitatively the electron transport properties of some of these D-bridge-A molecules. To do so, we have chosen a set of D/A-heterocyclic cumulenes possessing high PD values from our previous study[39] and the thiol (SH) groups are substituted on the D/A-heterocycles at both ends of the molecule as shown in Fig. 1. All these molecules are thiolated because in a device, the thiol group acts as an alligator clip between the molecule and electrode surface.[34,35] In the present study the electron transport behaviour of these thiolated molecules has been analyzed using the ab initio FMO analysis. To support the FMO analysis of the molecules which behave like conductors, the electron transport characteristics i.e., the current-voltage (*I–V*) characteristics and conductance (*G-V*) spectrum have been analyzed using EHT-NEGF formalism.[40]

2. Computational Methods

The density functional theory (DFT) methods are quite suitable for the prediction of the electron transport behaviour of a single organic molecule, which are in good agreement with the experiment.[23–27] Hence for the electron transport properties, the geometries of the thiolated D/A-heterocyclic substituted cumulenic molecules **M1**–**M6** (Fig. 1) are optimized using DFT/B3LYP (Becke's three parameter Hybrid function in combination with Lee–Yang–Parr correlation function) method with 6-31G(d,p) basis set implemented in the G03W Program.[41] As frontier molecular orbitals play an important role in the electron transport process, the orbital population analyses have been carried out using the same level of theory. The spatial orientations and spatial locations of these FMOs are visualized using Gauss View 3.0 (a graphical interface for Gaussian program), which gives a visual presentation of the shapes of molecular orbitals.[42] In order to support the FMO analysis regarding the conductance behaviour of **M2**, **M4** and **M6** molecules, calculations have been carried out with EHT-NEGF formalism implemented in the interactive Huckel-IV 2.0 software available at

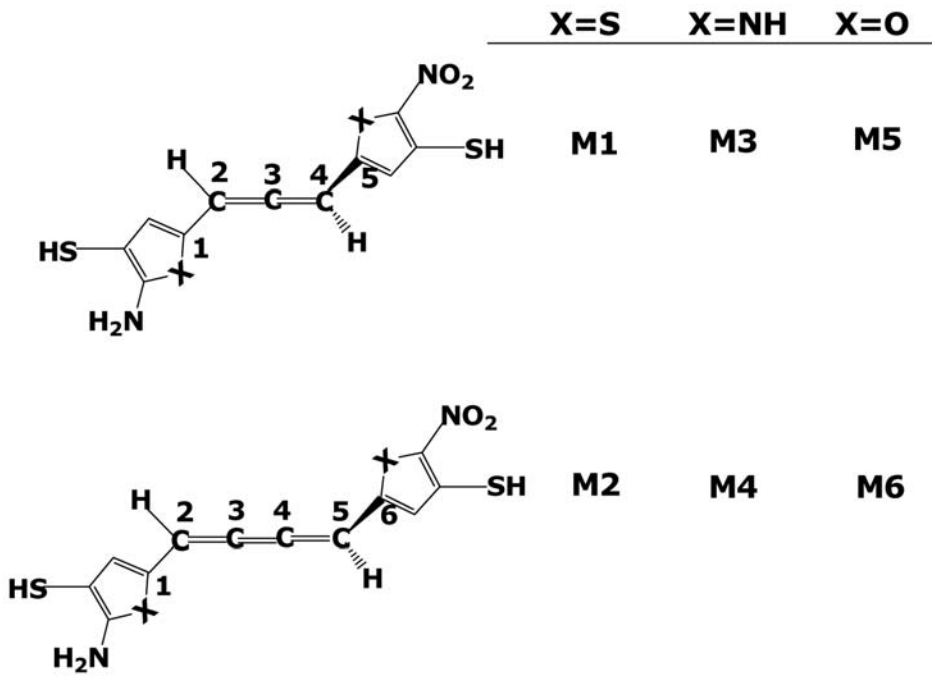

Figure 1. Molecular structures with thiol (SH) groups considered in this study with different heterocyclic moieties (namely **M1** and **M2** with D/A-thiophene, **M3** and **M4** with D/A-pyrrole and **M5** and **M6** with D/A-furan).

NANOHUB[40] which calculates *I–V* characteristics and molecular conductance (*G-V)* spectrum of a molecule sandwiched between two metallic contacts. The detailed theoretical considerations of these calculation implemented in this interactive software program can be found in the literature.[43] Previously this model has been successfully applied for quantitative analysis of experimentally observed *I–V* characteristics and *G-V* spectrum of benzene dithiol (BDT) molecule.[43] The molecular conductance and the influence of charging effect on the transport characteristics has been studied for 1,4-bis((2'-*para*-mercaptophenyl)-ethinyl)-2-acetylamino-5-nitrobenzene molecule[4] and also the electron transport through the DNA base pair.[44] Hence, in the present study the electron transport abilities for the molecules **M2**, **M4** and **M6** are analyzed from their *I–V* characteristics and *G-V* spectra using the above mentioned model.

3. Results and Discussion

3. 1. Geometries

The molecular structures of all the thiolated Donor-Cumulenic Bridge-Acceptor (D-CB-A) molecules **M1**–**M6**, considered for this study are shown in their lowest energy conformation in Fig. 1. Some of the molecules, namely **M1**, **M3** and **M5** (containing one *sp*-carbon atom in the CB) contain the thiolated D/A-thiophene, D/A-pyrrole and D/A-furan heterocycles, respectively, which are connected to the two ends of the CB whereas the other molecules, namely **M2**, **M4** and **M6** contain similar thiolated D/A-heterocycles with two *sp*-carbon atoms in the CB (Fig. 1). The corresponding optimized bond lengths are shown in Table 1, along with the bond angles and twist angles for each molecule with reference to the central CB. It can be seen from the Table 1, that in the molecules **M1**, **M3** and **M5**, in which the CB contains one *sp*-carbon atom, the attached thiolated D/A-heterocycles are mutually perpendicular to each other having a dihedral angle of ~90°, similar to the unthiolated D/A counterparts.[39] In case of the other molecules (**M2**, **M4** and **M6**) in which the CB contains two *sp*-carbon atoms, the attached thiolated D/A-heterocycles are in plane with the CB having a dihedral angle of ~180°, similar to the unthiolated D/A counterparts[39] and show planar characteristics similar to stilbene-like system. Thus the positions of these thiolated D/A-substituents are in accordance with the rules governing the spatial orientations of the substituents in cumulenic systems.[45] It is observed that the S–H bond lengths at donor side and acceptor side of all these molecules remains 1.354 and 1.352 Å respectively, irrespective of the D/A-heterocycles present in the molecule. In all these molecules the CB remains almost linear with lesser deviations from the linearity (Table 1). The rigid linear structure of the CB present in these molecules may be attributed to the involvement of the *sp*-carbon atoms in the bonding, which is one of the essential criteria for device applications.

3. 2. Molecular Orbital Energy Levels

To understand the structure-property relationship of these molecules **M1**–**M6**, the population analysis has been carried out using the B3LYP/6-31G(d,p) optimized geometries along with the individual thiolated D/A-heterocycles (i.e., Thp(SH)(NH_2), Thp(SH)(NO_2), Pyl(SH)(NH_2), Pyl(SH)(NO_2), Fun(SH)(NH_2) and Fun(SH)(NO_2); where Thp, Pyl and Fun represent the thiophene, pyrrole and furan moieties, respectively) using the same methodology. The orbital energies of HOMO, LUMO, LUMO+1 and HOMO – LUMO gap (HLG) for **M1**–**M6**, with their unsubstituted thiolated counterpart molecules, along with their individual thiolated D/A heterocycles are presented in Table 2.

From the Table 2, it can be seen that in the case of the acceptor-substituted thiolated heterocycles (i.e., Thp(SH)(NO_2), Pyl(SH)(NO_2) and Fun(SH)(NO_2)), both the HOMO and LUMO are stabilized when compared to donor-substituted heterocycles (i.e., Thp(SH)(NH_2), Pyl(SH)(NH_2) and Fun(SH)(NH_2)) and the HLG of these molecules differ by ~1 eV. The donor-substituted thiolated heterocycles are susceptible for oxidation as the HOMO of these are less stabilized when compared to the HOMO of the acceptor-substituted thiolated ones (Table 2), hence the removal of one electron from the HOMO will be less

Table 1 Bond lengths (in Å), bond angles (in deg) and dihedral angles (DA) (in deg) for **M1**-**M6** molecules.

Molecules	R_{12}	R_{23}	R_{34}	R_{45}	R_{56}	A_{234}	A_{345}	DA (D12XY)
M1	1.449	1.316	1.317	1.458		179.0		90.7 (D1245)
M2	1.427	1.341	1.256	1.341	1.437	177.9	179.8	179.9 (D1256)
M3	1.445	1.319	1.317	1.457		179.4		90.3 (D1245)
M4	1.423	1.345	1.257	1.342	1.437	178.7	178.0	179.9 (D1256)
M5	1.441	1.315	1.316	1.449		179.0		89.9 (D1245)
M6	1.418	1.342	1.254	1.341	1.430	177.9	179.8	179.9 (D1256)

Table 2 Orbital Energies of HOMO (**H**), LUMO (**L**), LUMO+1 (**L+1**) and HLG (in eV), for D–CB–A molecules **M1**–**M6,** with their unsubstituted thiolated counter part molecules, along with their individual D/A–heterocycles. The potential drops (*PD*) and bias voltage (E_v) (in eV) are also shown for **M1**, **M3**, **M5** and **M2**, **M4**, **M6**, respectively.

Molecules	Substituted						Unsubstituted		
	H	L	L+1	HLG[a]	PD[b]	E_v[c]	H	L	HLG[a]
M1	–5.527	–2.597	–1.305	2.930	**1.292**		–6.046	–1.350	4.696
M2	–5.326	–2.866	–1.668	2.460		**1.230**	–5.389	–2.439	2.950
Thp(SH)(NH$_2$)	–4.832	0.197		5.029					
Thp(SH)(NO$_2$)	–6.734	–2.613		4.121					
M3	–5.271	–2.257	–0.851	3.014	**1.406**		–5.627	–0.703	4.924
M4	–5.017	–2.508	–1.405	2.509		**1.254**	–4.949	–1.972	2.977
Pyl(SH)(NH$_2$)	–4.241	0.767		5.008					
Pyl(SH)(NO$_2$)	–6.335	–2.187		4.148					
M5	–5.346	–2.395	–0.934	2.951	**1.461**		–5.889	–0.926	4.963
M6	–5.204	–2.674	–1.536	2.530		**1.265**	–5.249	–2.225	3.024
Fun(SH)(NH$_2$)	–4.626	0.617		5.243					
Fun(SH)(NO$_2$)	–6.828	–2.459		4.369					

[a] HLG = |HOMO – LUMO|; [b] Potential Drop (*PD*) = $\Delta E_{LUMO} = E_{LUMO+1}$(*donor side*) – E_{LUMO}(*acceptor side*); [c] Bias voltage (E_v) = (½) HLG – *q*

energetic process. On the other hand, the acceptor substituted thiolated heterocycles are amenable for the reduction due to the fact that the LUMO of these are stabilized when compared to the LUMO of the donor-substituted thiolated ones (Table 2), hence the electron injection to the LUMO will be a lower energy process. When this type of redox couple is connected through a suitable bridge (here CB) and a suitable bias voltage is applied, the electron transfer takes place in the molecule from one end to other end, and the whole system can act like a rectifier or conductor depending on the number of *sp*-carbon atoms present in the CB.

It can be seen from the Table 2, that the HOMO and LUMOs of **M1**–**M6** molecules are stabilized and possess lower HLGs when compared to the HOMO, LUMO and HLGs of their unsubstituted thiolated counterparts. It can also be observed that the LUMOs of **M1**–**M6** molecules are more stabilized when compared to the LUMOs of the individual unsubstituted thiolated heterocycles, whereas the HOMOs are destabilized when compared to the HOMOs of the individual unsubstituted thiolated heterocycles (Table 2). This type of stabilizing and destabilizing of molecular orbitals may be attributed to the chemical perturbation arising from D/A substitution, which results in a drastic decrease in the HLGs of **M1**–**M6** molecules, when compared to the HLGs of individual unsubstituted thiolated heterocycles. From the Table 2, it can be seen that the HLG gap is very high for both the individual Thp(SH)(NH$_2$) and Thp(SH)(NO$_2$) with the values 5.029 and 4.121 eV, respectively, in contrast with the case when these two are connected through a CB as shown in Fig. 1 resulting in **M1** and **M2**, where the decrease in the HLG is less drastic, varying from 2.930 to 2.460 eV, when compared to the individual thiolated D/A-thiophene (*vide supra*). This decrease in the HLG plays a crucial role when these molecules **M1** and **M2** are connected to the two electrodes, as it is assumed that the Fermi level of the contact lies in between the HLG of the molecule[32] and can lead to a more favourable path for electron injection process to the system, when a suitable bias voltage is applied. Similar trend is observed with the other molecules, i.e. for **M3** and **M4** where the HLG varies from 3.014 to 2.509 eV, when compared to the individual Pyl(SH)(NH$_2$) and Pyl(SH)(NO$_2$) with the values 5.008 and 4.148 eV, respectively. For **M5** and **M6** the HLG varies from 2.951 to 2.530, when compared to the individual Fun(SH)(NH$_2$) and Fun(SH)(NO$_2$) with the values 5.243 and 4.369 eV, respectively.

3. 3. Electron Transport Analysis Based on FMO Analysis

To understand the electron transport through the molecule, it is useful to analyze the spatial extent of the frontier molecular orbitals (HOMO, LUMO and LUMO+1), which provides a strategy for understanding the rectifying or conducting properties of the molecular system. Hence the population analyses have been carried out. The spatial location and orientations of frontier molecular orbitals are shown in Fig. 2 for **M1**–**M6** molecules, in which the two ends of the cumulenic bridge (having one and two *sp*-carbon atoms in the bridge) are substituted with the thiolated D/A-heterocycles.

To construct a molecular rectifier, the molecular orbitals are to be disturbed by twisting (i.e., by introducing an asymmetry in the molecule) or by introducing the electron-withdrawing and electron-donating groups in the molecule, which cause the molecular orbitals to localize on the different parts of the molecule, thereby blocking the electron flow. Thus the molecular rectifier adopts electronic structures that allow the current to flow in one direction only while preventing the flow in the other.[25,26] The construction of a molecular wire requires an elongated mole-

cule through which electrons can flow easily from one end to the other, i.e. the molecular orbitals are to be delocalized entirely all over the molecule. Normally conjugated systems provide a path where the π-electron clouds overlap between molecular orbital components so that electrons can hop from one to the other.[25,26,32] From Fig. 2 can be seen that in the case of **M1**, **M3** and **M5** (having one *sp*-carbon atom in the CB), the frontier molecular orbitals, i.e. HOMO and LUMOs are disturbed and are localized on the different parts of the molecule, hence one can expect the blockage of electron flow and these molecules can therefore behave as molecular rectifiers (*vide supra*). In the case of the **M2**, **M4** and **M6** (having two *sp*-carbon atoms in the CB), the frontier molecular orbitals, i.e. HOMO and LUMO are delocalized entirely all over the molecule, which facilitates the electron transport (*vide supra*) and hence these molecules can behave as molecular conductors.

3. 3. 1. Cumulenic Bridge With One *sp*-Carbon Atom

It can be seen from the Fig. 2 that for all the molecules containing one *sp*-carbon atom in the CB (**M1**, **M3** and **M5**) the HOMOs are localized on the donor side of the molecule and the LUMOs are localized on the acceptor side of the molecule and in both these molecular orbitals,

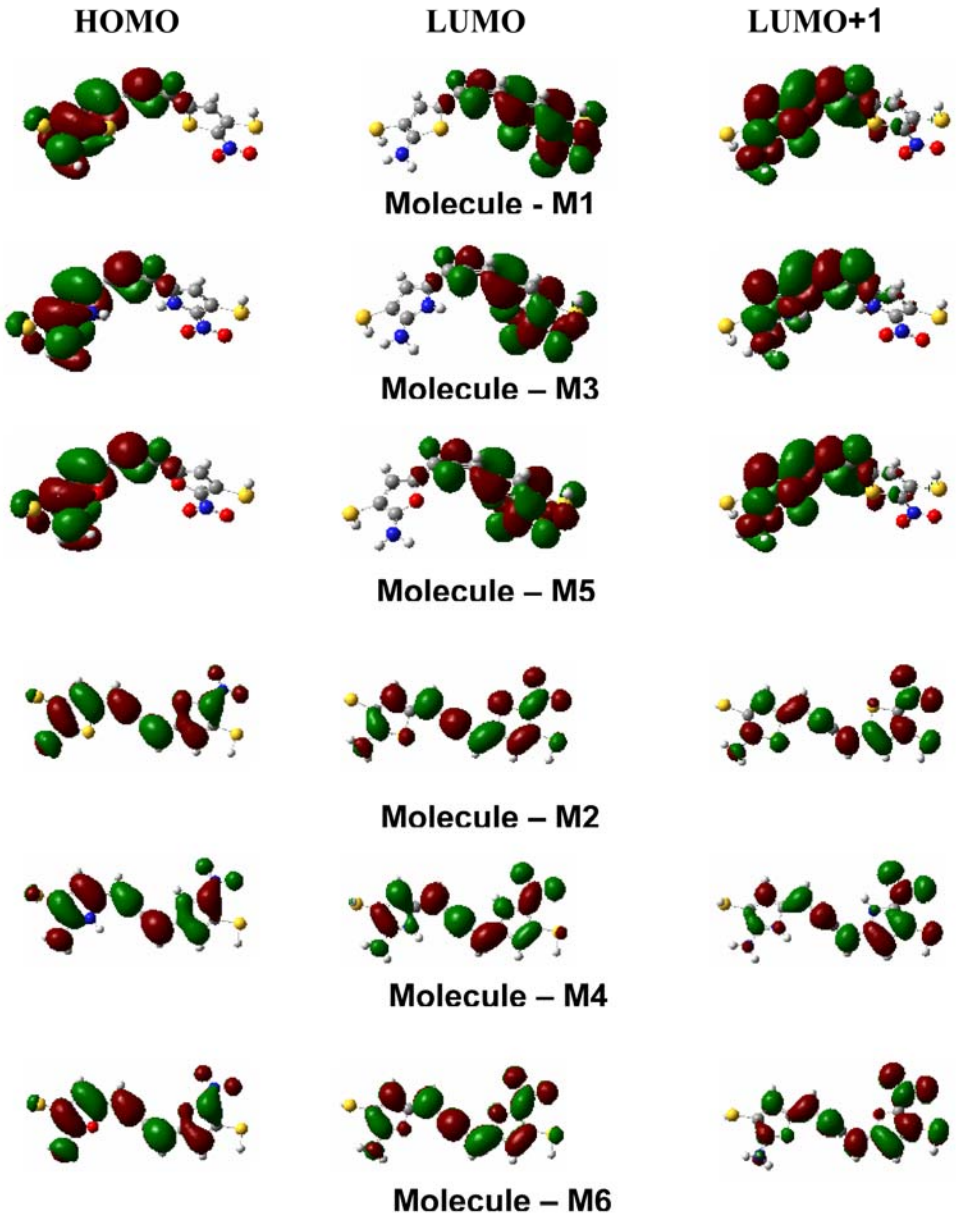

Figure 2. Frontier molecular orbital pictures of HOMO, LUMO and LUMO+1 (in the order from upper left to right) for **M1** and **M2** (with D/A-thiophene), **M3** and **M4** (with D/A-pyrrole) and **M5** and **M6** (with D/A-furan).

the elongation of orbital population onto the CB is also observed. This elongation of the orbital population along with the CB can be attributed to the π-electron cloud associated with the CB. It can be seen from the molecular orbitals of these molecules, the unoccupied orbital LUMO+1 which is the next unoccupied orbital, is localized on the donor side of the molecule (Fig. 2). The trend is the same irrespective of the thiolated D/A-heterocycles associated with the molecule. Generally when this type of D-CB-A molecule is connected through the electrodes, i.e. the acceptor is connected to the cathode and the donor to the anode and a suitable bias voltage is applied in the forward direction, then one electron will be injected to the molecule from the cathode. The incoming electron inside the system will be loaded to the LUMO of the molecule localized on the acceptor side and tunnels through the bridge to the next unoccupied orbital, i.e. LUMO+1, which is localized on the donor side of the molecule and from there to the anode. In the reverse direction, a similar process does not occur until a much higher voltage is applied, which is not feasible. Thus the molecule behaves as a rectifier molecule. This tunneling process in a molecular system is largely controlled by the unoccupied molecular orbitals (which are responsible for the electrical conduction inside the molecule) and is based on the energy mismatch between the two conducting unoccupied levels localized on different parts of the molecule.[32] From the molecular orbital energy values the potential drop (*PD*) across the molecule, which gives the idea of the effectiveness of the system to behave as a rectifier, when a suitable bias voltage is applied to the molecule is calculated using the following Equation 1,[32] and tabulated in Table 2.

$$\text{Potential Drop } (PD) = \Delta E_{\text{LUMO}} = E_{\text{LUMO}+k} - E_{\text{LUMO}};$$
$$k = 0, 1, 2 \qquad (1)$$

where E_{LUMO} is the orbital energy localized on the acceptor side and $E_{\text{LUMO}+k}$ is the orbital energy of the next unoccupied orbital (here it is LUMO+1), which is localized on the donor side of the molecule. From Table 2 it can be seen that the *PD* values for **M1**, **M3** and **M5** are 1.292, 1.406 and 1.461 eV, respectively. Therefore in all these molecules, when a suitable bias voltage is applied, the incoming electron is loaded in the LUMO from the cathode and tunnels to the unoccupied LUMO+1 orbital, which is localized on the donor side and from there to the anode. Because the frontier molecular orbitals are disturbed by twisting and are localized on the different parts, i.e. donor and acceptor parts of the molecule, these molecules cannot behave as molecular wires (*vide supra*). When one electron is loaded from the cathode to the LUMO level, which is localized on the acceptor side of the molecule, it is assumed that instantaneously it will be negatively charged until the total escape of the electron to the anode from the donor side takes place. To see the excess charge localization in this instantaneously negatively charged state, single point calculations have been carried out for the anions of these rectifier molecules by considering the B3LYP/6-31G(d,p) optimized neutral geometries, at the same level of theory and the charge accumulation data on donor and acceptor parts are shown in Table 3. It can be seen from this table that the excess charge is on the acceptor part of molecule only.

3. 3. 2. Cumulenic Bridge with Two *sp*-Carbon Atoms

In electronic circuits, the molecular conductors serve the purpose of molecular wires. The molecules in which the molecular orbitals are fully delocalized all over the molecule behaves as molecular wires. The presence of delocalized unoccupied orbital levels is responsible for

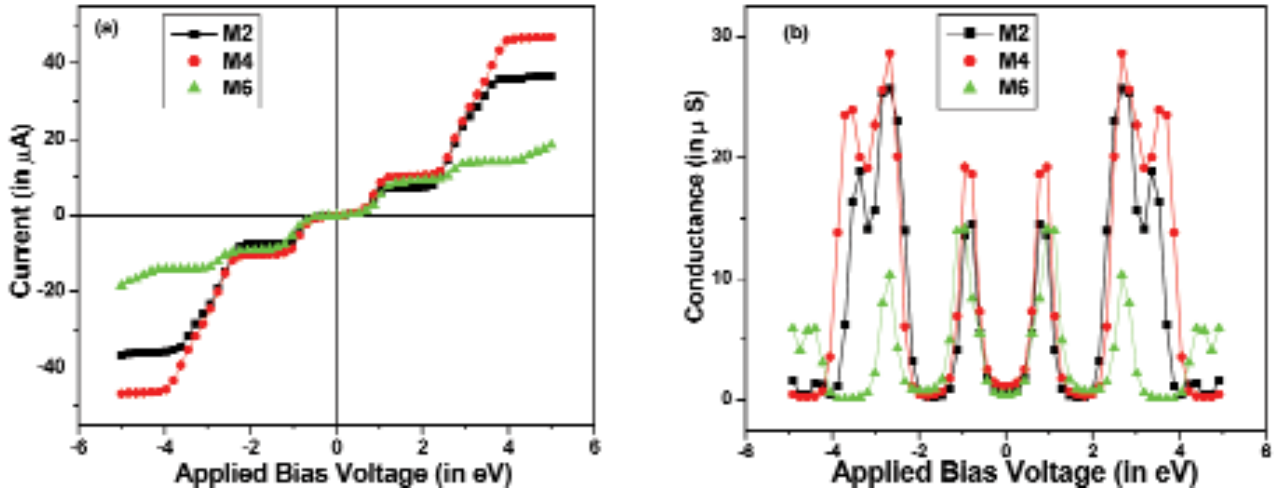

Figure 3. (a) Current (*I*)-voltage (*V*) dependence and **(b)** conductance (*G*)-voltage (*V*) spectrum for molecules **M2** (with D/A-thiophene), **M4** (with D/A-pyrrole) and **M6** (with D/A furan).

the molecular conduction in these molecules. It can be seen from the Fig. 2 that in the molecules containing two *sp*-carbon atoms in the CB (**M2**, **M4** and **M6**) the HOMO and LUMOs are delocalized entirely all over the molecule including the cumulenic bridge. This may be due to the planarity possessed by the molecule. When such type of a molecule is connected through the electrical contacts and a suitable bias voltage is applied, the loaded electron in the LUMO from the cathode can directly pass to the donor side through the CB and shows the conductance. Thus the LUMO will itself serve as a conduction channel for electron transport. Thus these molecules can be served as the molecular wires in the electronic circuits. To determine the bias voltage (E_v) required for electron transport across the molecule, we have assumed that the Fermi energy of the metal electrode is aligned in the middle of the HLG of a molecule.[32] The bias voltage (E_v) can be estimated using the following Equation 2,[25,46] and tabulated in Table 2.

$$\text{Bias voltage } (E_v) = (½)\ \text{HLG} - q \qquad (2)$$

where $q = 0$, when the conduction channel is LUMO and $q = (E_{LUMO} - E_{LUMO+k})$, when the conduction channel is other than LUMO (i.e., if LUMO is not fully delocalized, the conduction channel will be the next higher unoccupied orbital (LUMO+*k*) which is fully delocalized all over the molecule). Here in case of **M2**, **M4** and **M6** molecules, the LUMO is fully delocalized all over the molecule, hence $q = 0$. From Table 2, it can be seen that the bias voltage required for molecular wire of **M2**, **M4** and **M6** are 1.230, 1.254 and 1.265 eV, respectively. Accordingly the electron injection process will be easier in **M2** when compared to the others. Hence the increasing trend in molecular conductance among the D/A-heterocycles connected to the cumulenic bridge is as follows: furan < pyrrole < thiophene and the molecule **M2** can be considerably more efficient conductor than molecules **M4** and **M6**. To see the excess charge localization in the instantaneously negatively charged state, when one electron will be loaded from the cathode to the LUMO level which is localized on the acceptor side of the molecule, single point calculation for the anions of all the suggested molecular conductors have been carried out by considering the B3LYP/6-31G(d,p) optimized neutral geometry at same level of theory, and the charge accumulation data of donor and acceptor parts are shown in Table 3. It can be seen from this data that the excess charge is on the acceptor side of the molecule only.

3. 3. 3. Electron Transport Analysis Based on *I–V* Characteristics

A number of theoretical models have been developed for calculating the *I–V* characteristics for molecular wires using semi empirical[47–54] as well as *ab initio*[5,10,12,13,17,55–62] methods. The *ab initio* methods are computationally expensive and time consuming, while the semi empirical methods are simple, flexible and computationally inexpensive and are useful in describing the molecular conduction quantitatively. To support the FMO analysis of the molecules having two *sp*-carbon atoms in the CB namely **M2**, **M4** and **M6**, which act as molecular conductors, the electron transport abilities of these molecules are analyzed from their *I–V* characteristics and *G-V* spectrum using EHT-NEGF formalism implemented in the interactive Huckel-IV 2.0 software available at NANOHUB.[40] For these calculations we have followed the procedure cited in the NANOHUB. We have applied the similar Fermi level (E_f), to all the thiolated molecules (**M2**, **M4** and **M6**), which is approximated by HLG.[27,32] These calculations have been carried out under the symmetric coupling condition (coupling between the electrode and molecule at cathode and anode) and the bias voltage is applied across the molecule in forward as well as reverse directions. The observed *I–V* characteristics and *G-V* spectrum are shown for **M2**, **M4** and **M6** in Fig. 3. It can be seen from these results that these molecules have similar characteristic like a diode, with relatively high conductance at the low bias region, which coincides with the FMO results and are useful as molecular conductors in molecular devices.

4. Conclusions

Qualitative FMO analyses have been carried out by using DFT/B3LYP/6-31G(d,p) method for a series of thiolated D/A-heterocycles connected to the two ends of the cumulenic bridge (having one and two *sp*-carbon atoms in

Table 3 Mulliken Point Charge Analysis for Neutral as well as Anions (from single point calculation at B3LYP/6–31G(d,p) optimized neutral geometry) for **M1**–**M6** molecules.

Molecules	Excess charge localization on acceptor part (charges on A_{anion} – charges on $A_{neutral}$)	Excess charge localization on donor part (charges on D_{anion} – charges on $D_{neutral}$)
M1	–0.665	–0.138
M2	–0.421	–0.287
M3	–0.654	–0.145
M4	–0.423	–0.282
M5	–0.675	–0.153
M6	–0.447	–0.299

the bridge) for their electron transport abilities. Population analysis has been carried out at the same level of theory to know the exact nature of the orbital population/orientation, thereby the electron transport properties resulting in the rectifying/conducting behavior of these molecules. From FMO analysis it can be seen that the thiolated D/A-heterocycles connected to the CB having one *sp*-carbon atom in the bridge, both the HOMO and LUMOs are localized on the donor and acceptor part of the molecule respectively and the LUMO+1, which is the next unoccupied orbital responsible for electron tunneling is localized on the donor part of the molecule, irrespective of the hetero atom present in D/A heterocycles. Due to the presence of asymmetry in these molecules (i.e., the twisting between the donor and acceptor parts of the molecule) and also the molecular orbitals are localized on different parts of the molecule, behaves as molecular rectifiers and can be useful as alternatives to the conventional D-σ-A systems. In the case of the thiolated D/A-heterocycles connected to the CB having two *sp*-carbon atoms in the bridge, both the HOMO and LUMOs are fully delocalized all over the molecule. The delocalization of molecular orbitals indicates that these molecules can behave as good conductors and are useful as molecular wires in the electronic circuits. To support the FMO analysis of the molecular conductors, *I–V* characteristics and *G-V* spectrum analysis have been carried out using the semi empirical EHT-NEGF formalism and found to confirm these FMO observations.

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Povzetek

Z uporabo *ab initio* računskih metod mejnih molekulskih orbital (FMO) smo kvalitativno raziskali sposobnosti transporta elektronov v seriji donor/akceptor-heterociklov povezanih s kumulenskim mostom. Iz FMO analize je razvidno, da molekule, ki vsebujejo en *sp*-ogljikov atom v kumulenskem mostu delujejo kot usmerniki in jih zato lahko obravnavamo kot idealne alternative tradicionalnega D-σ-A tipa molekulskega usmernika; ostale molekule, ki vsebujejo dva *sp*-ogljikova atoma, pa se obnašajo kot prevodniki in jih lahko uporabljamo kot alternative molekulskim vodnikom v različnih molekulskih napravah. Da bi dodatno podprli rezultate FMO analize prevodniškega obnašanja molekul z dvema *sp*-ogljikoma, smo izvedli analize še z uporabo semi empiričnih metod razširjene Hücklove teorije in neravnotežne Greenove funkcije (EHT-NEGF), ki potrjujejo rezultate FMO izračunov za predlagane molekulske prevodnike.