



Rectifying behavior of [60]fullerene charge transfer complexes: A theoretical study

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ABSTRACT

New type of molecular diodes based on charge transfer complexes of fullerene[60] with organic donors has been proposed and studied theoretically. Current–voltage curves and the rectification ratios (RR) for three different molecular diodes were calculated using direct *ab initio* method at M06/LACVP(d) level of theory in the range from -2 to $+2$ V. The highest RR of 73.6 was determined for the complex of C60 with cyclic oligothiophene at 0.3 V (C60–CT8–Au). Other molecular diodes show lower RR, however, all complexes show RR higher than 1 at all voltages. The asymmetric evolutions and alignment of the molecular orbitals with the applied bias were found to be essential in generating the molecular diode rectification behavior. It seems that large donor–acceptor distance in C60–CT8 complex is crucial for the high RR in C60–CT8–Au compared to other complexes.

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1. Introduction

In recent years molecular electronics have been considered as one of the most promising alternatives for the future nanoscaled electronic devices [1]. Nowadays a great variety of potentially useful molecular electronic devices, such as molecular rectifiers, resonant tunneling diodes, wires and storage devices, have been designed and studied at both experimental and theoretical levels [2]. The first design of molecular rectifier is dated by year 1974, when Aviram and Ratner proposed a prototype of the donor–insulator–acceptor (D–B–A) molecular diode [3], with the functionality similar to *p–n* junctions. In D–B–A molecular diodes, D and A are the π donor and π acceptor, respectively, separated by an insulating sigma bridge (B).

The rectifying effect in molecular junctions of the form metal|molecule|metal, is defined in terms of the absence of inversion symmetry, $I(V) \neq -I(-V)$, where I and V are the current and the applied voltage, respectively. The dominant factors inducing rectification are geometric asymmetry in the molecular junction and the spatial profile of the electrostatic potential [4].

Many different molecules exhibiting rectifying effect have been designed, synthesized and studied in recent years [5]. The rectifying behavior of D–B–A diodes in Langmuir–Blodgett (LB) layers and in dyad chromophores aligned by self-assembly has been investigated too [6–8]. Recently, molecular diodes have been obtained

by the assembly of ionic acceptors and donors, yielding an rectification ratio (RR) of 100 at 1 V [9]. Rectification behavior has also been observed in derivatives of fullerene[60] [10] acting as a super-rectifier when operated between $+2$ and -2 V with a $RR=20\,000$ at 1.5 V. Electrical rectification from a fullerene[60]-dyad based metal–organic–metal junction of a monolayer LB film of fullerene C60-didodecyloxybenzene dyad sandwiched between two gold electrodes was found to be as high as 158 at 3 V [11].

This paper describes a new approach to the design of a molecular rectifier based on fullerene[60] molecule, which can be extrapolated to other acceptor molecules. According to the classical scheme of a molecular rectifier, fullerene[60], as acceptor moiety, is connected to a donor unit, through an insulator aliphatic chain. Since the modification of fullerene molecule, to introduce aliphatic chain is a very tedious process due to existence of multiple reactive sites, other method of creation of insulation barrier between donor and acceptor fullerene moiety is highly desirable. Fortunately, fullerene[60] is able to form stable charge transfer complexes with π -donor molecules [12]. They are easily to form and have relatively high binding energies [13]. Those complexes formally meet the requirements for a classical molecular rectifier of Aviram and Ratner, considering a space between fullerene and a donor molecule as equivalent to a sigma spacer in a classical model. Therefore, the goal of present manuscript is to study theoretically rectifying properties of fullerene charge transfer complexes.

1.1. Computational details

Three different charge transfer complexes (CTC) have been selected for the calculations; complexes of C60 formed with

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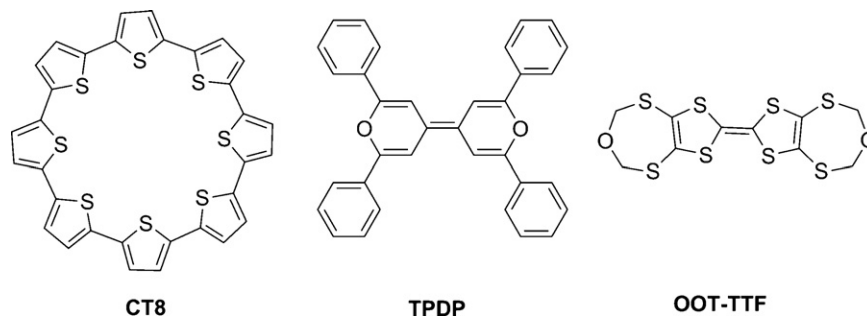


Fig. 1. Organic donors used in present study.

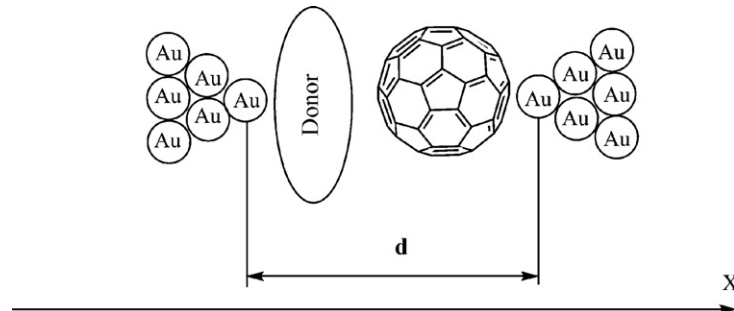


Fig. 2. Computational setup of molecular rectifier based on a C60 CT complex.

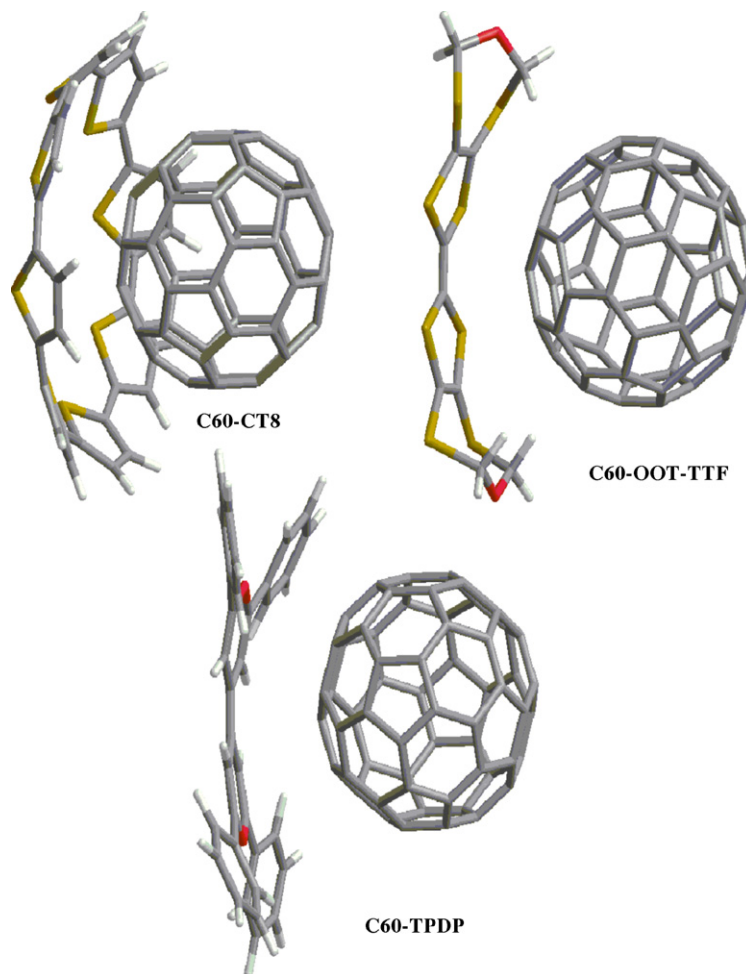


Fig. 3. M06/6-31G(d) optimized geometries of CT complexes.

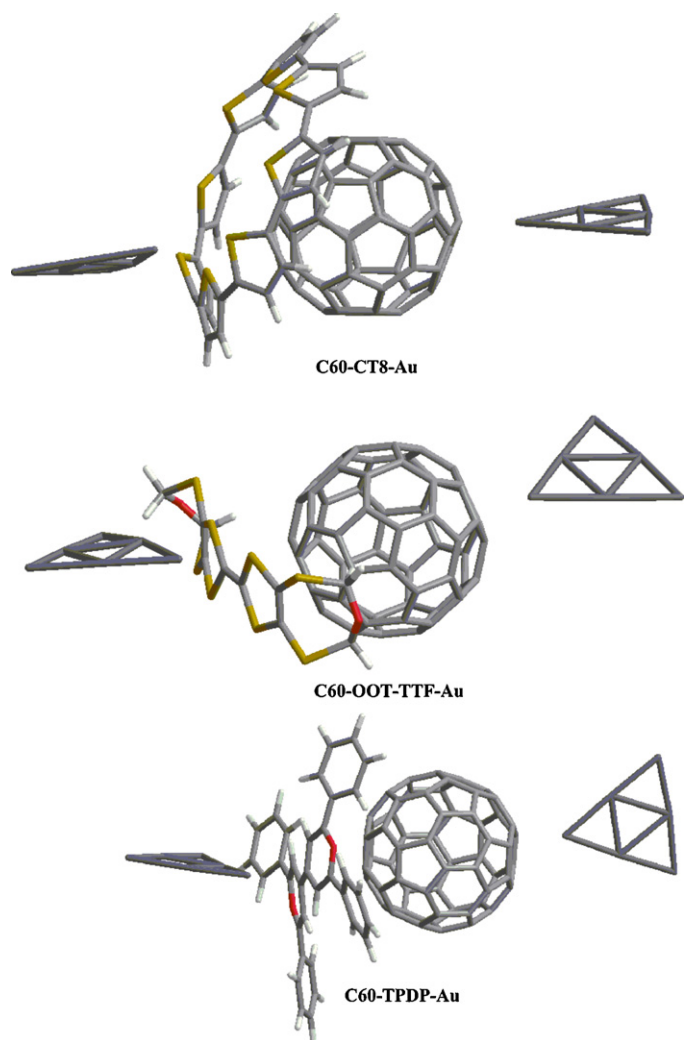


Fig. 4. M06/LACVP(d) optimized structures of the molecular rectifiers at 0 V.

bis(oxydimethylenedithio)tetrathiafulvalene (OOT-TTF), 3,3',5,5'-tetraphenyldipyranlydene (TPDP) and cyclo[8]thiophene (CT8). The chemical structures of donor moieties are shown in Fig. 1.

All calculations were carried out using Gaussian 09 suit of programs [14] with M06 [15] functional and 6-31G(d) basis set for all except gold atoms. LANL2DZ pseudopotential basis set was used to model gold atoms of the electrodes. This basis set is denominated as LACVP(d). M06 functional was shown to produce excellent results for weakly bounded complexes and transition metal complexes.

The selection of donor component has been motivated by the intention to explore the effect of electron donating ability of the donor fragment on the rectifying properties of charge transfer complexes. The electron donating ability of molecules TPDP, CT8 and OOT-TTF decreases from left to right, according to their HOMO energies (−0.15747, −0.18803 and −0.19029 a.u., respectively). The experimental data support this finding. Thus, the redox potentials determined vs. Ag/AgCl in acetonitrile were found to be of 0.15 and 0.66 V for TPDP and OOT-TTF, respectively [16]. To calculate I - V curves for CTC, the following computational setup was used (Fig. 2).

Electrodes are represented by a fragment of Au(1 1 1) surface. First, the complete system is fully optimized without any symmetry constraints. Then the distance d is frozen and optimization is repeated in the presence of electric field applied along x axis. The calculation of I - V curves was carried out using direct fully *ab initio* method described in the literature [17]. This method reproduces well the experimental finding at low bias voltage

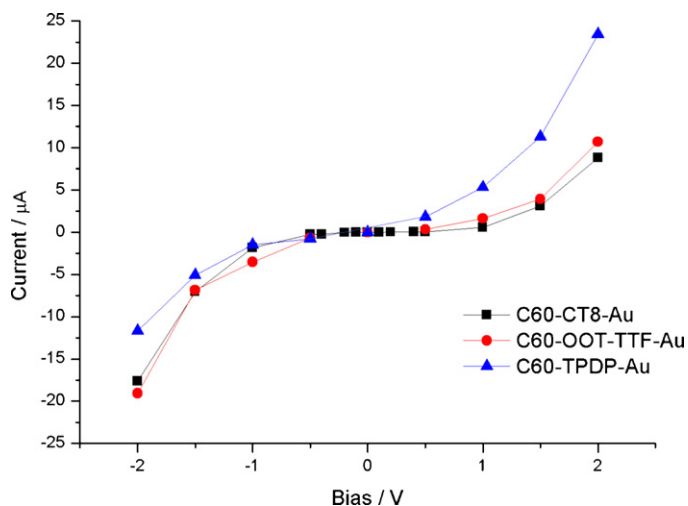


Fig. 5. Calculated I - V curves for studied molecular rectifiers.

(0–2 V). The current (I) is calculated according to the following equation:

$$I = \frac{2\Delta Q\Delta E}{\hbar}$$

where ΔQ is the charge difference at the electrode, before and after applied voltage, and ΔE is the energy difference with and without applied voltage. Mulliken population for individual atoms at right electrode has been used to calculate ΔQ .

2. Results and discussion

C60 molecule forms stable complexes with selected donor molecules. Their optimized geometries are shown in Fig. 3. The binding energies for studied complexes calculated with the basis set 6-311G(d,p), using 6-31G(d) optimized geometries, and taking into account the basis set superposition error as implemented in Gaussian 09 suit of programs, are of 21.7, 12.3 and 10.2 kcal/mol for C60-CT8, C60-OOT-TTF and C60-TPDP, respectively. It is noteworthy that the binding energies do not correlate with electron donating properties of donor molecules but rather depends on the donor molecule shape. Thus, the highest binding energy is found for C60-CT8 where C60 molecule fits into the molecular cavity of cyclic molecule. All CT complexes have small negative charge at

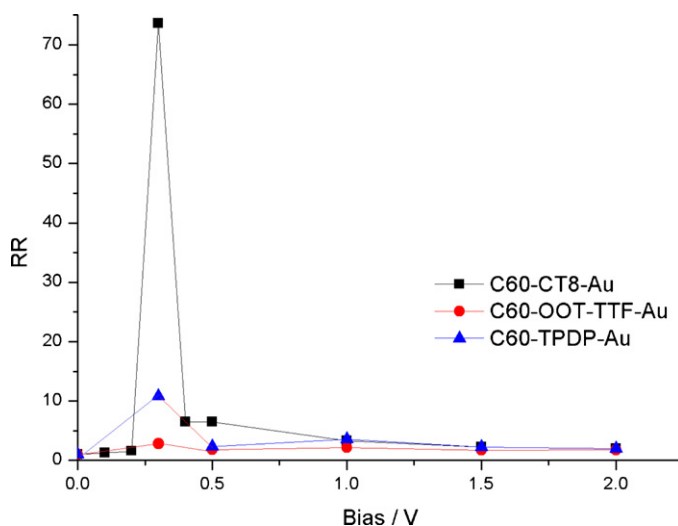


Fig. 6. Calculated rectification ratio for studied molecular rectifiers.

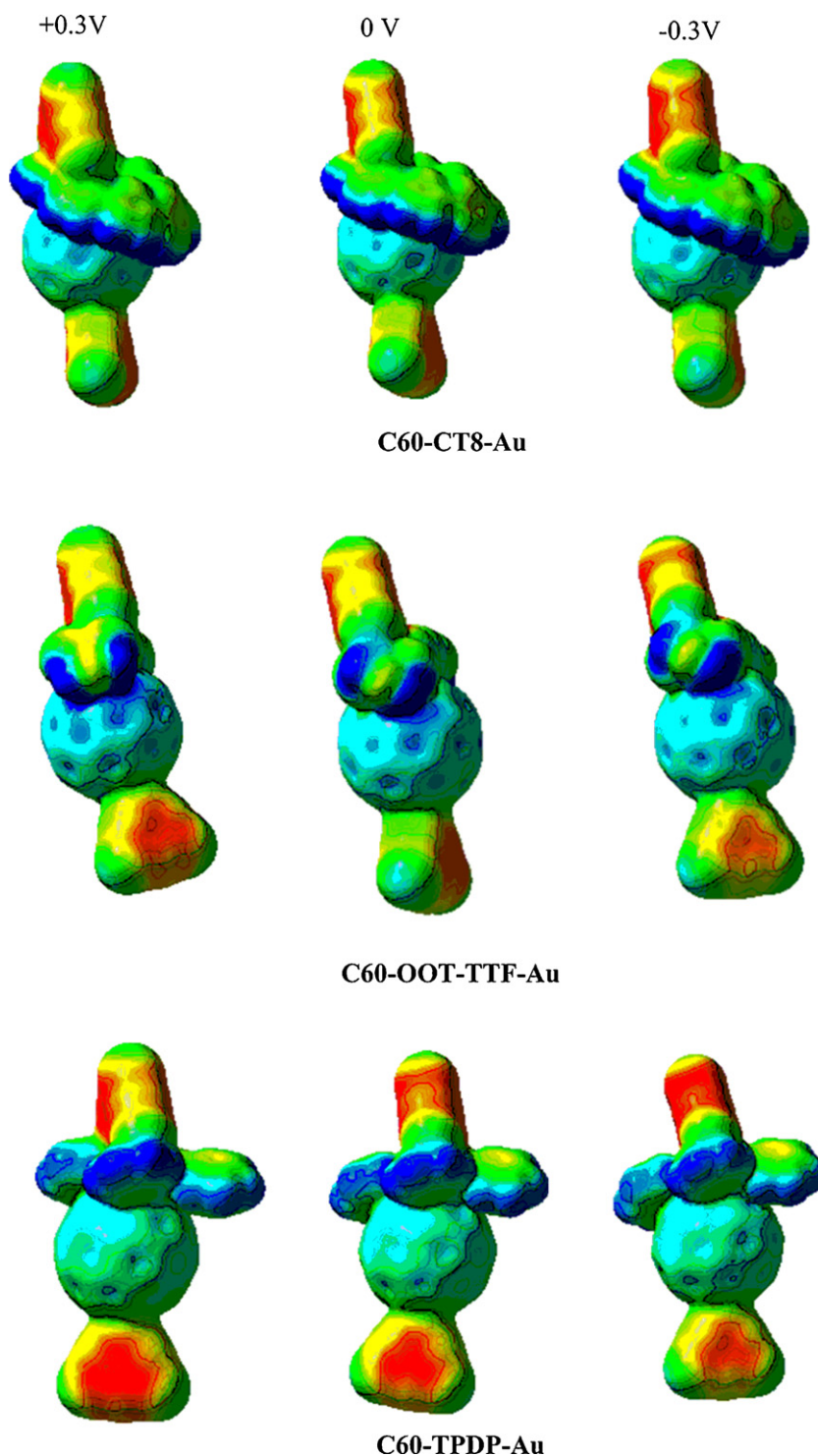


Fig. 7. Electrostatic potential mapped onto total electronic density of studied molecular rectifiers for different applied bias voltages. Red and blue colors correspond to negative and positive potentials, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

acceptor C60 moiety; -0.090 , -0.060 and $-0.084 e$ for C60-OOT-TTF, C60-CT8 and C60-TPDP, respectively.

The shortest distance between donor and acceptor units does not correlate either with electron donating properties of donor units or with the binding energies of CT complexes, depending only on geometrical parameters of the donor molecule. For C60-TPDP complex this distance is of 3.02 \AA , while for C60-CT8 and C60-OOT-TTF complexes the shortest distances are of 3.38 and 3.12 \AA , respectively, due to the presence of bulky sulphur atoms.

Fig. 4 shows optimized geometries of molecular rectifiers at 0 V . The geometry of the complexes is not altered significantly by the presence of the electrodes. Thus, the shortest acceptor–donor distances in the molecular rectifiers are of 3.40 , 3.03 and 3.03 \AA for C60-CT8-Au, C60-OOT-TTF-Au and C60-TPDP-Au, respectively.

The distance between right electrode and C60 molecule is of 2.31 – 2.33 \AA for all three complexes, while the distances between left electrode and donor units varies depending on the donor nature. Thus, for C60-TPDP-Au, Au–donor distance is of 2.77 \AA ,

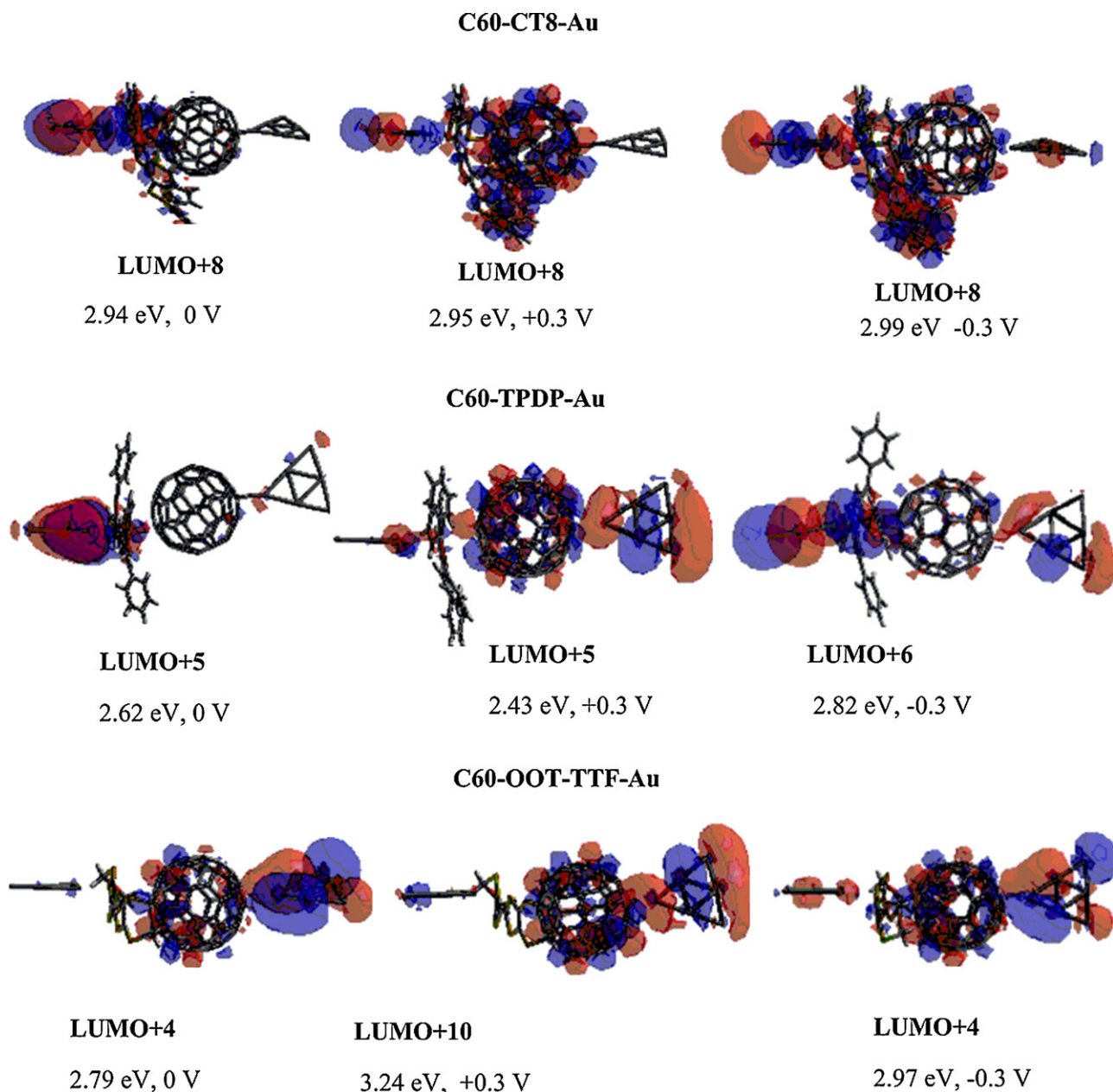


Fig. 8. Selected virtual orbitals of C60–CT8–Au, C60–TPDP–Au and C60–OOT–TTF–Au under positive and negative biases and their relative energies with respect to HOMO levels.

while for donors containing sulphur atoms this distance slightly increases to 2.80–2.90 Å due to larger valence radius of sulphur atoms compared to carbon and oxygen atoms of TPDP.

Figs. 5 and 6 show calculated current–voltage and rectification ratio (RR) curves, respectively for studied molecular rectifiers. It is noteworthy that in all cases and at all voltages, there is a rectification effect. The maximum RR is observed for C60–CT8–Au system reaching 73.6 at 0.3 V. For all other systems maximum RR is also observed at 0.3 V although not as high as for C60–CT8–Au; 10.6 for C60–TPDP–Au and 2.8 for C60–OOT–TTF–Au.

Fig. 7 depicts the electrostatic potential mapped onto total electronic density of studied molecular rectifiers for 0, +0.3 and –0.3 applied bias voltages. As can be seen, the most notorious changes of electrostatic potential on applied bias voltage occur at electrodes. Thus, positive bias decreases electron density at the electrode

connected to the donor fragment and increases electron density on the opposite electrode. On the other hand, the negative bias increases the electron density at the electrode connected to donor fragment and decreases the electron density at the opposite electrode implying electron transfer between electrodes on applied bias voltage.

It can also be noted from Fig. 7 that the electron density at the electrode connected to the donor units increases with electron-donating properties of the fragment from C60–OOT–TTF–Au to C60–TPDP–Au.

To understand the nature of the rectification effect in molecular complexes, the molecular orbitals have been analyzed. Applied bias voltage allows the electron tunneling through the space between donor and acceptor fragments, which can be rationalized in terms of molecular orbitals as a formation of a virtual orbital involving both

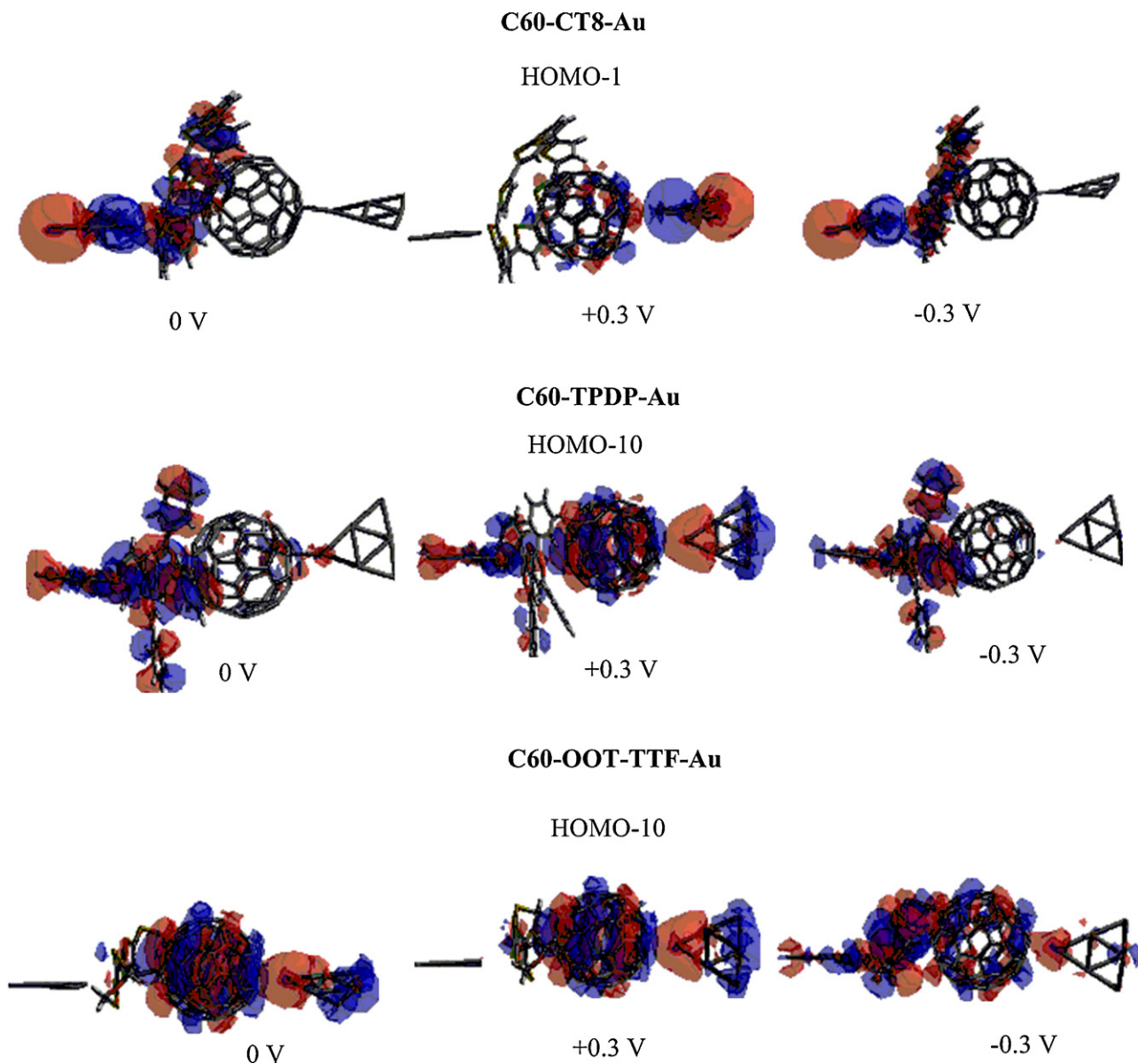


Fig. 9. Selected occupied orbitals of C60-CT8-Au, C60-TPDP-Au and C60-OOT-TTF-Au under positive and negative biases.

donor and acceptor fragments. The lower the energy difference between HOMO and this virtual orbital, the higher the probability of the electron transfer between those fragments. Since the strongest rectification effect has been observed for the bias of 0.3 V, the molecular orbitals at this voltage were analyzed to clarify the rectification mechanism of charge transfer complexes.

The selected molecular orbitals for all 3 complexes at biases +0.3 and -0.3 V are shown in Fig. 8. As seen, the applied bias voltage strongly modifies shape and energy of the molecular orbitals. At zero bias voltage LUMO+8 orbital of C60-CT8-Au is mostly located at the donor fragment and the left electrode, while the applied bias voltage modifies this orbital to involve both donor and acceptor fragments. Moreover, positive bias lower the energy of this orbital compared to negative one, thus promoting electric current for positive bias. This phenomenon can be rationalized analyzing occupied orbitals (HOMO-1) for C60-CT8-Au (Fig. 9). For zero and negative biases, HOMO-1 is localized at donor fragment and left electrode, while when positive bias is applied, the electron density moves to the acceptor fragment and the right electrode, thus reflecting the rectification phenomenon. Similar mechanism of the

rectification for the charge transfer complexes can be noted for other two complexes where applied bias asymmetrically modifies the energies of virtual molecular orbitals involving both donor and acceptor fragments (Fig. 8). This results in asymmetrical modification of occupied molecular orbitals (Fig. 9) for positive and negative biases, respectively. No correlation between RR and ionization potential of the donor moiety or the binding energy has been found. However, the higher RR ratio of C60-CT8-Au compared to other studied molecular diodes might be related with larger donor-acceptor distances in the former. As it has been mentioned above, the shortest acceptor-donor distances in the molecular rectifiers are of 3.40, 3.03 and 3.03 Å for C60-CT8-Au, C60-OOT-TTF-Au and C60-TPDP-Au, respectively. Significant overlap of π -orbitals in C60-OOT-TTF-Au and C60-TPDP-Au, due to short distances between donor and acceptor fragments, makes the electron tunneling between them very easy independently of applied bias, thus decreasing RR. On the other hand, relatively large distance between donor and acceptor fragments in C60-CT8-Au creates an adequate insulating barrier to promote asymmetric tunneling of the electrons between the fragments.

3. Conclusions

Calculations demonstrated that charge transfer complexes of C60 with donor molecules possess rectification behavior and can be considered as possible candidates for molecular rectifiers. Asymmetric current–voltage (I – V) characteristics were observed for all complexes with the maximum rectification ratio of 73.6 which has been found for the complexes of C60 with oligocyclothiophene (C60–CT8–Au) at 0.3 V. The maximum RRs for other complexes (C60–TPDP–Au and C60–OOT–TTF–Au) 10.8 and 2.8, respectively also corresponded to the bias voltage of 0.3 V. The asymmetric evolutions and alignment of the molecular orbitals of the molecular diode with the applied bias were found to be essential in generating this rectification behavior. It seems that large donor–acceptor distance in C60–CT8 complex is crucial for high RR in C60–CT8–Au compared to C60–TPDP–Au and C60–OOT–TTF–Au.

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