

Charge transfer complexes of fullerene[60] with porphyrins as molecular rectifiers. A theoretical study

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Abstract Molecular diodes based on charge transfer complexes of fullerene[60] with different metalloporphyrins have been modeled. Their current–voltage characteristics and the rectification ratios (RR) were calculated using direct ab initio method at PBE/def2-SVP level of theory with D3 dispersion correction, for voltages ranging from -2 to $+2$ V. The highest RR of 32.5 was determined for the complex of fullerene[60] with zinc tetraphenylporphyrin at 0.8 V. Other molecular diodes possessed lower RR, however, all complexes showed RR higher than 1 at all bias voltages. The asymmetric evolutions and alignment of the molecular orbitals with the applied bias were found to be essential for generating the molecular diode rectification behavior. Metal nature of metalloporphyrins and the interaction porphyrin–electrode significantly affect RR of molecular diode. Large metal ions like Cd^{2+} and Ag^{2+} in metalloporphyrins disfavor rectification creating conducting channels in two directions, while smaller ions Zn^{2+} and Cu^{2+} favor rectification increasing the interaction between gold electrode and porphyrin macrocycle.

Keywords DFT · Fullerene · Molecular diode · Porphyrin · Rectification

Introduction

In recent years molecular electronics have been considered as one of the most promising approaches for the future nanoscaled electronic devices [1–4]. 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 [5–10]. 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 rectifier [11], 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. [12, 13]

Many different molecules exhibiting rectifying effect have been designed, synthesized, and studied in recent years [14–16]. 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 [14, 17–26]. Recently, molecular diodes have been obtained by the assembly of ionic acceptors and donors, yielding a rectification ratio (RR) of 100 at 1 V [27]. The rectification behavior has also been observed in derivatives of fullerene[60] acting as a super-rectifier when operated between $+2$ to -2 V with a RR=20,000 at 1.5 V [28–30]. Electrical rectification from a fullerene[60]-dyad based metal–organic–metal junction of a monolayer LB film of fullerene C_{60} -didodecyloxybenzene dyad sandwiched between two gold electrodes was found to be as high as 158 at 3 V [31].

Recently, a new approach to the design of a molecular rectifier has been proposed by the authors [32, 33] consisting in using of charge transfer (CT) complexes as molecular rectifier. Thus, for complexes of fullerene[60] with various

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organic donors the rectification ratio up to 74 at 0.3 V has been estimated. It has been shown that the asymmetric evolutions and alignment of the molecular orbitals with the applied bias is essential in generating the molecular diode rectification behavior.

Porphyrins are organic donors where electronic properties can easily be modulated by the nature of the central metal ion such as ionization potential, electron affinity and the ability to form coordination bonds with other ligands. On the other hand, the most promising organic acceptor used as a part of molecular rectifier is C₆₀ molecule. From this point of view it seems very interesting to explore the rectification characteristics of CT complexes of fullerene [60] with metalloporphyrins. Unlike the classical molecular diodes proposed by Aviram and Ratner where donor fragment D and acceptor part A are linked by insulating aliphatic chain, in this particular case intermolecular interactions play a role of aliphatic spacer reducing the diode synthesis step to self-assembling. Therefore, this manuscript describes the rectification behavior of metalloporphyrins/C₆₀ CT complexes.

Computational details

All calculations except for B3PW91 [34, 35] single points calculations were carried out using Turbomole 6.5 suit of programs [36] with dispersion corrected (D3) PBE [37, 38] functional and def2-SVP basis set. This basis set uses pseudopotential to describe the core electrons starting from Rb. The resolution of identity method was used for the calculations [39]. It has been demonstrated that this model reproduces fairly well geometry and binding energy of C₆₀/tetraphenylporphyrin complexes [40]. The initial geometries of C₆₀/tetraphenylporphyrin complexes were taken from experimental data [41]. Additional calculations using B3PW91 functional using def2-SVP basis set were performed with Gaussian 09 suite of programs [42]. The bond lengths in Cu₂, Ag₂, and Au₂ dimers as well as ionization potentials (IPs) for Cu, Ag, Au, Cd, and Zn atoms were calculated and compared with experimental data [43] to validate PBE-D3/def2-SVP computational model. The difference between calculated and experimentally determined bond lengths differs from 0.01 Å for Cu₂ to 0.05 Å for Au₂ (singlet states). The IPs are reproduced within 0.4 eV. The largest error is for Ag (0.39 eV), while the smallest is for Cd (0.09 eV). Overall, PBE-D3/def2-SVP model delivers reasonable accuracy and, thus it has been adopted for all calculations.

Electrodes are represented by a fragment of Au crystal containing two layers, 25 atoms each (50 atoms in total), located parallel to each other, with CT complex sandwiched between the electrodes. First, CT complex and the electrodes were optimized separately without any symmetry constraints. Then the electrodes and CT complexes were placed together

and the system was optimized again. The calculation of *I-V* characteristics was carried out using direct fully ab initio method described in detail elsewhere [44, 45]. This method reproduces well the experimental finding at low bias voltage (0–2 V). The current (*I*) is calculated according to the following equation:

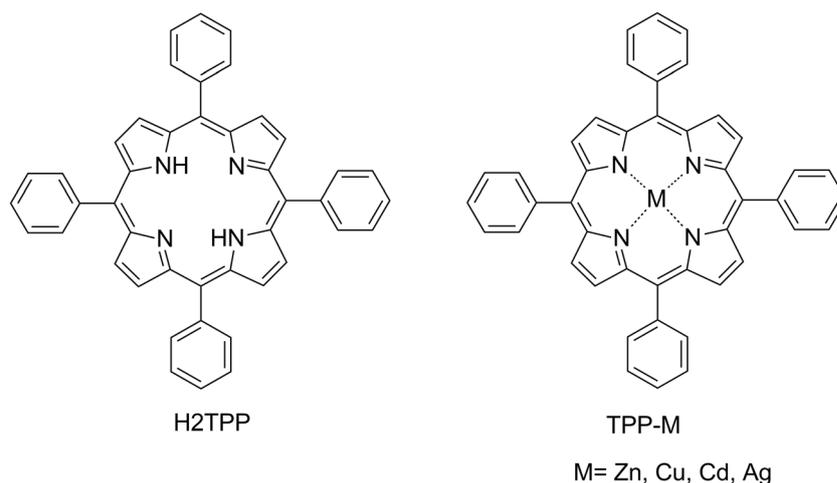
$$I = \frac{2\Delta Q\Delta E}{h}$$

where ΔQ is the charge difference at the electrode, before and after applied voltage, and $\Delta E = E_0 - E_v$, where E_0 is the total electronic energy of the system under the study without applied electric field while E_v is the total electronic energy with applied electric field. Natural (NBO) charges for individual atoms were used to calculate ΔQ . The rectification ratio (RR) reflects the efficiency of a diode. The higher the better. It represents a ratio between direct and inverse current at a given bias voltage (*V* and $-V$, respectively). RR was calculated as $I(-V)/I(V)$, where $I(-V)$ is the electric current under the voltage $-V$ and $I(V)$ is electric current under the voltage *V*, respectively. Pristine tetraphenylporphyrin and the corresponding tetraphenylporphyrins containing Zn²⁺, Cu²⁺, Cd²⁺, and Ag²⁺ ions have been explored as the donors for CT complexes (Fig. 1). The computational setup of the molecular rectifier is shown in Fig. 2. A set of seven inner Au atoms, which represents best electrode surface was used for ΔQ calculations.

The studied CT complexes are denoted as follows: **X-Y/C60** where **X** refers to a tetraphenylporphyrin macrocycle, (H2 for metal free porphyrin) and **Y** for a metal dication of metalloporphyrin. Molecular diodes are referred to as **Au-X-Y/C60** where Au stands for gold electrodes.

Results and discussion

Optimized geometries of nanoaggregates are shown in Fig. 3. The calculated center to center distances for **H2TPP/C60**, **TPP-Zn/C60**, **TPP-Cd/C60**, **TPP-Cu/C60**, and **TPP-Ag/C60** complexes were found to be 2.67, 2.65, 2.97, 2.64, and 2.79 Å, respectively. The calculated binding energies are of 27.0, 29.3, 23.3, 26.1, and 22.1 kcal mol⁻¹, correspondingly. As seen center to center distances for **TPP-Cd/C60** and **TPP-Ag/C60** are larger, compared to the rest of the complexes due to larger metal ion radii. As a consequence, the binding energies for **TPP-Cd/C60** and **TPP-Ag/C60** are lower compared to those of the rest of the complexes. The electron donating properties of different porphyrins can be compared examining their IPs. Thus, calculated adiabatic IPs for **H2TPP**, **TPP-Zn**, **TPP-Cd**, **TPP-Cu**, and **TPP-Ag** are of 6.07, 6.11, 6.00, 6.16, and 5.62 eV, respectively. As seen, IPs depend only moderately on the metal nature. This is because the atomic orbital of the

Fig. 1 Porphyrins used in this study

metal barely participates in HOMO of metalloporphyrins. As seen the lowest IPs have **TPP-Ag** and **TPP-Cd**, while the highest -**TPP-Zn** and **TPP-Cu**. Ag^{2+} and Cd^{2+} ions possess higher polarizability compared to Cu^{2+} and Zn^{2+} allowing better stabilization of the positive charges in **TPP-Ag** and **TPP-Cd**; isotropic polarizabilities of Zn, Cd, Cu, and Ag dications estimated at PBE/def2-SVP level of theory were found to be 1.13, 3.76, 1.76, and 4.12 bohr³, respectively.

There is no correlation whatsoever between the binding energies of the CT complexes and the electron donating properties of the porphyrins (IPs). The binding energy correlates, however, with center to center distances in CT complexes. As it has been stated, the nature of binding in C_{60} /porphyrin complexes is mostly dispersion. The dispersion is a short range interaction which is affected strongly by the distance.

Figure 3 depicts the optimized structures of the molecular diodes with the corresponding electrodes. The interactions between the electrodes and CT complexes affect the geometry of both, the electrode and CT complex. On the one

hand, center to center distances between C_{60} and porphyrin increases due to interactions of each fragment of the CT complex with the electrodes. The interaction involves metal ions of the porphyrin fragment as seen from Fig. 3. The metal ions are notably out of porphyrin plane due to the interaction with the electrode surface, especially in the case of Cd^{2+} and Zn^{2+} . The center to center distances in diodes increase to 2.89, 2.75, 3.13, and 2.88 Å for **Au-TPP-Zn/C60**, **Au-TPP-Cu/C60**, **Au-TPP-Cd/C60**, and **Au-TPP-Ag/C60**, respectively. In the case of **Au-H2TPP/C60** diode the center to center distance does not change at all.

The averaged interaction energy between CT complex and the electrode can be estimated as follows:

$$E_{\text{int}} = E_{\text{d}} - (E_{\text{CT}} + 2E_{\text{Au}})$$

where E_{d} is the total electronic energy of a diode, E_{CT} is the total electronic energy of a CT complex and E_{Au} is the total electronic energy of one electrode. The estimated interaction

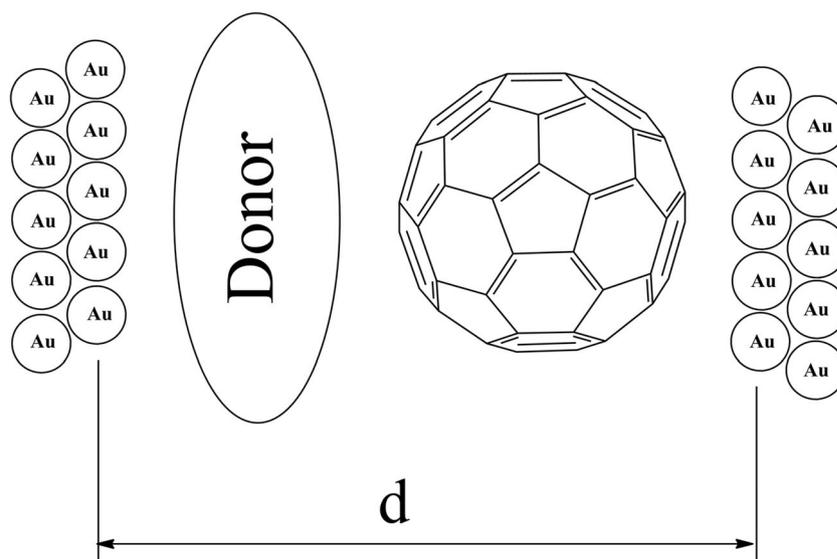
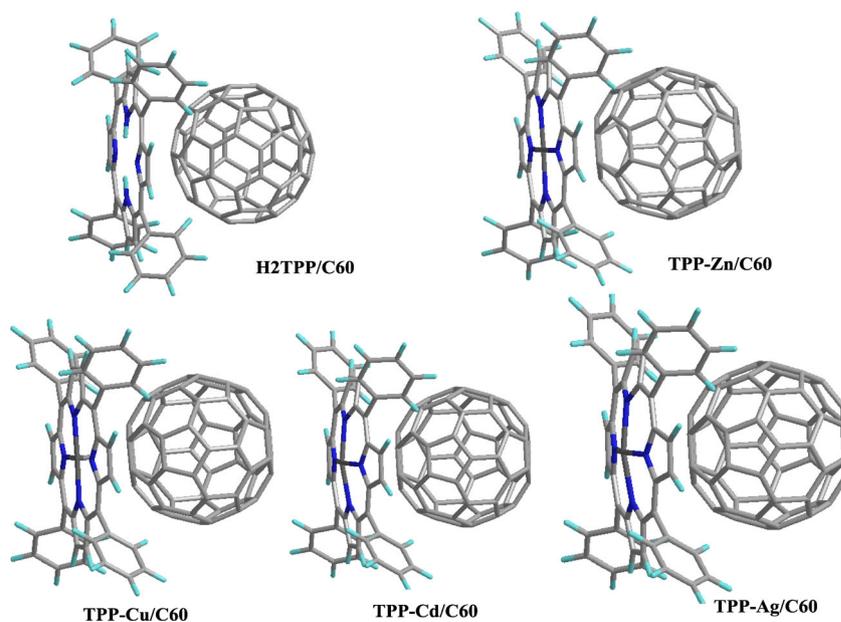
Fig. 2 Computational setup of molecular rectifier based on a C_{60} CT complex used in the current study

Fig. 3 Optimized geometries of CT complexes



energies (E_{int}) of electrode-CT complex are notably high being of 59.0, 65.6, 61.0, 66.0, and 61.3 kcal mol⁻¹, per electrode for **Au-H2TPP/C60**, **Au-TPP-Zn/C60**, **Au-TPP-Cu/C60**, **Au-TPP-Cd/C60**, and **Au-TPP-Ag/C60**, respectively. Since all

diodes differ only by the metal ion, the differences in the binding energy between the electrode and CT complexes are related to the nature of that ion. As seen, any metal ion increases binding energy compared to the metal free porphyrin

Fig. 4 Optimized structures of the molecular rectifiers

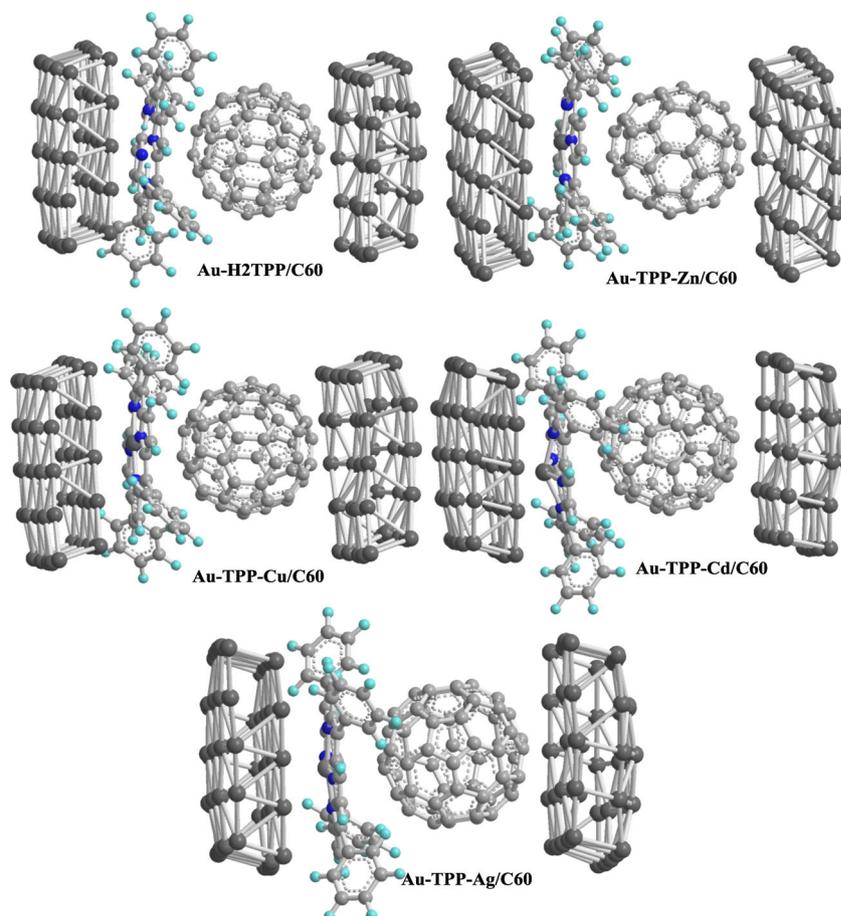
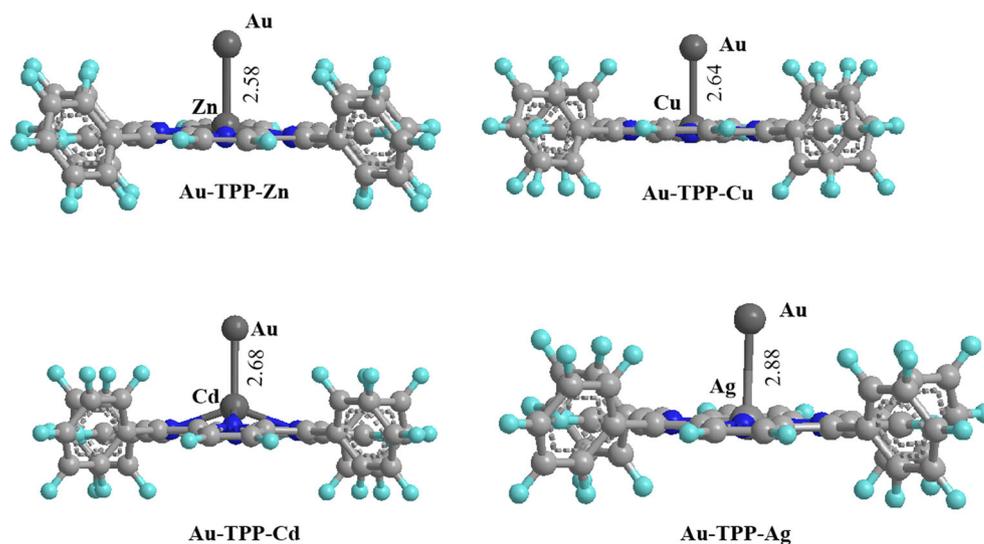


Fig. 5 Interaction of Au atom with metalloporphyrins. Optimized geometries



due to metal-electrode interactions. For Cu^{2+} and Ag^{2+} ions this increase is only marginal, while for Zn^{2+} and Cd^{2+} the increase is more notable being around 6 kcal mol^{-1} . The affinity of the metal ions to the gold surface can be quantified comparing N-M-N angles of the porphyrin unit in CT complexes and in diodes, where M is metal. The smaller the angle corresponds to the higher affinity of the metal ion M^{2+} to the electrode gold surface (Fig. 4). In all cases N-M-N angles are smaller in diodes compared to free CT complexes. Those differences are of 11.5 , 4.6 , 23.3 , and 5.3° for Zn^{2+} , Cu^{2+} , Cd^{2+} , and Ag^{2+} containing systems, respectively. As can be seen those values correlate with average interaction energies between electrodes and CT complexes of diodes, being the largest for **Au-TPP-Cd/C60** and the smallest for **Au-TPP-Cu/C60**.

To get a deeper insight into the nature of the interaction of the porphyrin metal ion with gold electrode surface, the geometry of a system consisting of a metalloporphyrin and a single gold atom has been optimized and the electronic structure of the system has been explored (Fig. 5). The nature of the ground states for **Au-TPP-Cu** and **Au-TPP-Ag** was found to be the open shell singlets with $\langle S^2 \rangle$ expectation values around 1. The corresponding closed shell solutions for **Au-TPP-Cu** and **Au-TPP-Ag** are 7.6 and $2.6 \text{ kcal mol}^{-1}$ less stable. When comparing M-Au bond lengths of **Au-TPP-Zn** with **Au-TPP-Cu** and **Au-TPP-Cd** with **Au-TPP-Ag**, (the metal with similar ionic radii) it can be seen that the bonds are notably shorter for **Au-TPP-Zn** and **Au-TPP-Cd**. The natural charges calculated for Au atom of the complexes are of -0.17 for **Au-TPP-Zn** and **Au-TPP-Cd** and -0.11 for **Au-TPP-Cu** and **Au-TPP-Ag**. As follows from the natural population analysis in the case of **Au-TPP-Zn** and **Au-TPP-Cd** the extra electron density are transferred to 6S orbital of Au atoms resulting in an increase of the M-Au bonding energy due to electrostatic interactions.

Table 1 shows the calculated currents and the rectification ratios for studied diodes at different bias voltages. As seen

Table 1 Direct (+) and inverse (−) currents (I), μA in studied diodes

Diode	V	RR	I^+	I^-
Au-H2TPP/C60	0.4	2.12 (2.08)	0.11 (0.11)	0.050 (0.053)
	0.8	2.19 (2.27)	0.62 (0.61)	0.28 (0.27)
	1.2	1.50 (1.38)	1.38 (1.41)	0.922 (1.02)
	1.6	1.98 (1.95)	4.43 (4.44)	2.24 (2.27)
	2.0	1.91 (1.97)	9.67 (10.1)	5.05 (5.12)
Au-TPP-Zn/C60	0.4	1.71	0.04	0.02
	0.8	32.5	0.62	0.019
	1.2	17.0	2.45	0.14
	1.6	4.96	6.30	1.27
	2.0	3.90	13.0	3.33
Au-TPP-Cu/C60	0.4	1.11	0.02	0.02
	0.8	6.14	0.55	0.09
	1.2	13.5	2.34	0.17
	1.6	4.22	6.12	1.45
	2.0	3.52	12.60	3.57
Au-TPP-Cd/C60	0.4	11.5	0.02	0.00
	0.8	1.33	0.14	0.10
	1.2	2.41	0.70	0.29
	1.6	12.5	1.98	0.16
	2.0	5.97	4.37	0.73
Au-TPP-Ag/C60	0.4	1.53	0.04	0.03
	0.8	1.10	0.42	0.38
	1.2	2.04	2.21	1.08
	1.6	2.21	5.72	2.59
	2.0	2.18	12.2	5.59

Rectification ratios (RR) under different bias voltages (V), volts. Data obtained at B3PW91/def2-SVP level, using D3 dispersion corrected PBE/def2-SVP level are given in brackets

Fig. 6 HOMOs of molecular rectifiers under positive and negative biases

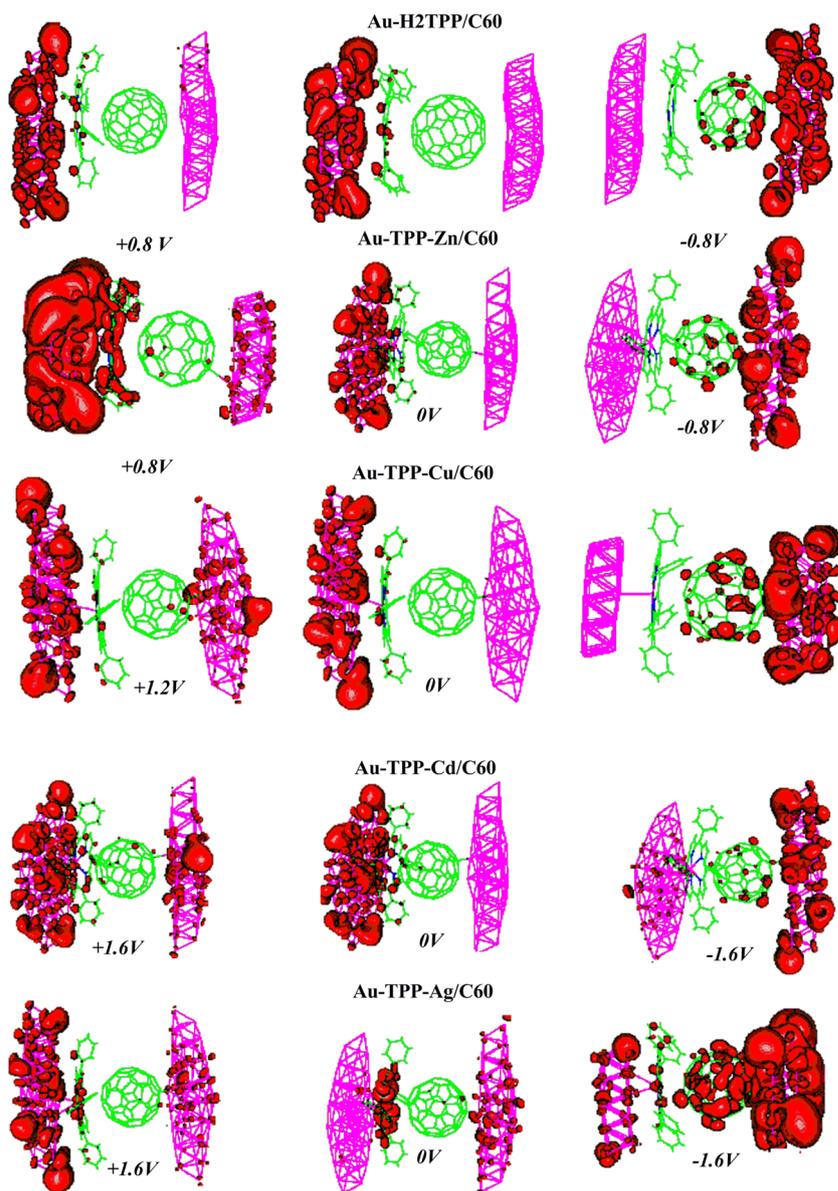
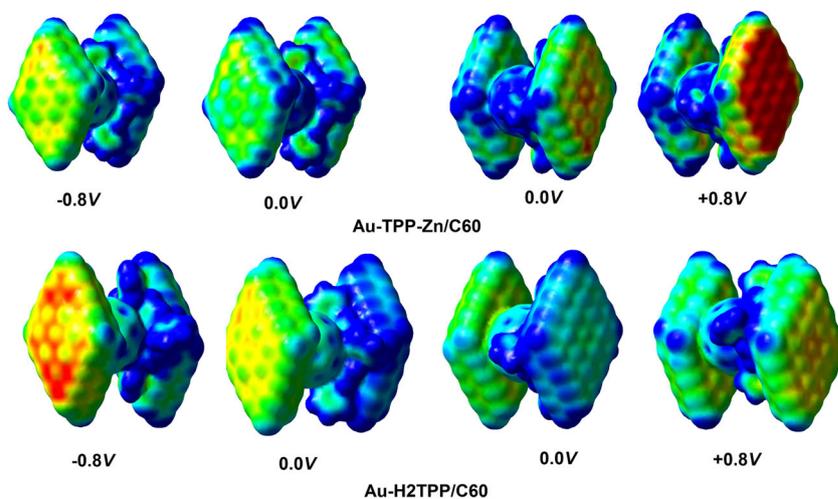


Fig. 7 Electrostatic potential mapped onto total electronic density of studied molecular rectifiers for different applied bias voltages. Red and blue colors correspond to negative and positive potential, respectively



from Table 1 RRs are higher than 1 in all cases, proving that all systems are molecular diodes. However, the rectification ratios differ greatly from one system to another and also RR is the function of the applied bias voltage. As a rule, maximal rectification ratios are calculated for bias voltages between 0.8 and 1.6 V. RR decreases below and above those values.

Since no experimental data are available for those systems additional single point calculations using B3PW91 functional have been carried out for comparison purpose. B3PW91 functional was used in original papers describing direct fully ab initio method [44, 45]. As seen from Table 1 the results of both models are rather similar for **Au-H2TPP/C60** system proving that the results do not depend significantly on the functional choice.

When analyzing Table 1 it can be seen that the highest rectification ratio of 32.5 is found for **Au-TPP-Zn/C60** system, while the lowest rectification ratios were found for **Au-TPP-Ag/C60** and **Au-H2TPP/C60** diodes. Since the method used for current estimation is based on the electron density polarization under the electric field, the analysis of the molecular orbitals delocalization under different bias voltages can provide an important insight into the mechanism of the molecular rectification in porphyrin/C₆₀ complexes. Electrons of HOMO are the most polarizable ones, therefore, they contribute the most to the molecular currents. Figure 6 depicts HOMOs of molecular diodes under the bias voltages corresponding to the maximal RRs, and those without applied bias voltage, respectively.

As seen from Fig. 6 the RRs can be correlated with different delocalization of HOMOs for different diodes. Thus, in the case of **Au-TPP-Zn/C60**, having the highest rectification ratio, HOMO delocalization is very different for the direct and inverse bias voltage at 0.8 V. Under the direct bias HOMO is delocalized over the entire diode creating the conducting channel from one electrode to another resulting in high current. In the case of inverse bias HOMO is mostly localized at the right electrode, no conducting channel is created in this case, resulting in low current and high RR, correspondingly.

On the other hand, when we look at HOMOs of **Au-TPP-Ag/C60** at different bias voltages it can be noted that the conducting channel is formed for both positive and negative voltages, thus decreasing RR for this system.

In all cases the calculated direct current is higher than the inverse one. As seen from Table 1 the highest RRs show diodes with metals having the smallest ionic radii; Zn²⁺ and Cu²⁺. On the other hand, **Au-H2TPP/C60** with metal free porphyrin shows the lowest RR. It is noteworthy that the natural charges at porphyrin metal ions do not depend on the applied bias voltage, depending only on the electronegativity of the metal. Thus, charges drop with the electronegativity being of +1.65, +1.48, +1.35, and 1.17 for Zn²⁺, Cd²⁺, Cu²⁺, and Ag²⁺, respectively.

Lower RRs shown by **Au-TPP-Ag/C60** and **Au-TPP-Cd/C60** could be related with more diffuse orbital of Ag and Cd compared to Zn and Cu, creating conducting channel in both

directions. Low RR, observed for the metal free porphyrin system **Au-H2TPP/C60** may be related to the weaker interaction of metal free porphyrin with the surface of gold electrode as shown above. Weaker interactions decrease the orbital overlap between the porphyrin macrocycle and the electrode, which reduces the diode sensitivity to the voltage change.

Rectification in CT complexes can be visualized using electrostatic potentials maps. Figure 7 depicts the electrostatic potential mapped onto total electronic density for the best (**Au-TPP-Zn/C60**) and worst rectifier (**Au-H2TPP/C60**) at zero, +0.8 V and -0.8 V applied bias voltage. As can be seen, the most notorious changes of electrostatic potential at applied bias voltage occur at electrodes. The buildup of electron density at the right electrode of **Au-TPP-Zn/C60** at positive bias is much higher than the increase of the electron density at the left electrode at negative bias. This difference reflects high RR found for this system. On the other hand, the difference in electrostatic potentials between right and left electrodes at positive and negative bias voltages for **Au-H2TPP/C60** is much less as seen from Fig. 7 in agreement with low rectification ratio for this diode.

Conclusions

It has been found that all donor- acceptor CT complexes of porphyrins and fullerene[60] possess rectifying properties to one extent or another. Interestingly, the calculated RRs do not depend on the binding energies of the complexes and ionization potentials of the porphyrin moieties. The rectification occurs due to asymmetrical deformation of the molecular orbitals under direct and inverse voltages creating different currents in opposite directions. The metal nature in metalloporphyrins and the interaction porphyrin-electrode significantly affects RR of molecular diode. Large metal ions like Cd²⁺ and Ag²⁺ in metalloporphyrins disfavor rectification creating conducting channels in two directions, while smaller ions Zn²⁺ and Cu²⁺ favor rectification increasing interaction between gold electrode and porphyrin macrocycle.

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