Molecular Rectification Enhancement Based On Conformational and Chemical Modifications

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Supporting Information

ABSTRACT: Design principles for molecules with intrinsic directional charge transport will likely prove crucial for breakthroughs in nanotechnology and other emerging fields like biosensors and advanced photovoltaics. Here, we perform a systematic computational study to characterize the electronic rectification induced by conformational and chemical modifications at low bias potentials and elucidate design principles for intrinsic molecular rectifiers. We study donor-bridge-acceptor (D-B-A) systems that consist of phenylene units with geometrical rotation of the rings and representative



electron-donating and -withdrawing substituent groups at the donor and acceptor sites. We calculate transport properties using the non-equilibrium Green's function technique and density functional theory (DFT-NEGF) and obtain I-V characteristics and rectification ratios. Our results indicate that efficient intrinsic rectification at low bias voltages can only be obtained by combining dihedral angles of 60° between phenyl rings and asymmetric chemical substitution. Together, these structural features cause rectification enhancement by localizing the molecular orbital closer to the Fermi level of the electrode in one end of the molecular device. Our designed systems present rectification ratios up to 20.08 at 0.3 V in their minimum-energy geometry and are predicted to be stable under thermal fluctuations.

INTRODUCTION

The field of molecular electronics is devoted to the fabrication of electronic devices at the molecular scale. There is a tremendous interest for these devices due to their capability to perform similar tasks than current silicon-based solid state electronics and their potential to obtain functionalities that are not achievable with state—of—the—art materials.^{1—6} Additionally, at the molecular scale, optical, magnetic, and electronic properties can be tuned by several strategies, including the introduction of chemical functional groups, geometry modifications, or controlling the local environment.^{7—16} Such sensitivity makes molecular devices promising candidates for game-changing advancements in environmental science, diagnosis and treatment of diseases, digital logic technology, and energy science.^{17–22} Developments in such fields will require advanced design principles at the molecular level.

An essential component of current and future nanoscale devices are molecular rectifiers, which were the first kind of molecular devices proposed in 1974 by Aviram and Ratner.²³ These devices favor the electron current in one direction and disfavor it in the reverse direction, causing an asymmetry in the current–voltage characteristics (I-V curves). The performance of rectifier devices is characterized by the rectification ratio (RR) at a given voltage.²⁴ The RR is defined as the magnitude of the ratio between the current at a positive voltage, I(V), and

the current at a negative voltage with same magnitude, I(-V), as indicated in eq 1. A high RR can be understood as efficient rectification and in asymmetric molecular systems this ratio generally increases when voltage increases, except in cases where negative differential resistance (NDR) is present.²⁵

$$RR = \left| \frac{I(V)}{I(-V)} \right| \tag{1}$$

High rectification has been obtained in Langmuir–Blodgett films^{26–29} and self-assembled monolayers^{30–43} when voltage exceeds a certain threshold. In single molecules different strategies need to be used to induce rectification since at high bias potentials the chemical stability would be compromised.⁴⁴ The identification of specific chemical features that could induce high rectification in single molecules at low bias voltages has been subject of substantial interest.⁴⁵ One of the main motives to chemically characterize molecular rectification at low bias voltages is the potential application of molecular rectifiers in photovoltaic and photochemical cells, where chemical potential differences are usually small⁴⁶ and charge recombination decreases the efficiency.^{47,48} A rectifier linker arranged in

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Figure 1. (a) Model, tailored, and validation systems in the orientation considered for the molecular junctions. (b) Torsion angle definition. (c) Molecular junction architecture.

the correct orientation could enhance the directionality of the charge transfer and reduce the recombination process, increasing the overall efficiency of the cell.

Previous studies have obtained rectification in single molecules by different approaches, and their mechanism can be classified in two main categories: extrinsic and intrinsic. Extrinsic rectification is obtained mainly by modifying the coupling between the molecule and electrodes.^{49–56} Intrinsic rectification, which is the focus of this work, results mainly as a consequence of the electronic structure of the molecule and the response of the energy levels to an applied bias potential. For this reason, this behavior is considered as true unimolecular rectification.^{14,57,58} Intrinsic rectification is desirable because it does not depend on the nature of the contacts between the molecule and electrodes but merely on the molecular electronic structure.⁵⁹

The design of intrinsic unimolecular rectifiers has been challenging, both theoretically and experimentally. Single molecules that have shown intrinsic rectification include in their structures cross conjugation, aromatic fragments with electron-donating or -withdrawing groups, or amide linkages to break the conjugation and localize the electron density of a frontier orbital in one side of the molecule. Solomon and coworkers performed a theoretical study of cross-conjugated molecules to favor electron transport in one direction using quantum interference.^{60,61} Elbing et al.⁶² measured I-Vcharacteristics of molecular rods consisting of two separated π -systems fused by a biphenylic C–C bond. RRs averaged 4.5 at 1.5 V, when only one of the π -systems was substituted with fluoro groups. A rectifier based on dipyrimidinyl-diphenyl diblock molecule was reported by Tao and co-workers. They used an a.c.-assisted scanning tunneling microscope break-junction (STM-BJ) method.⁴⁴ This study was supported by theoretical predictions based on density functional theory (DFT) obtaining a RR of the same order of magnitude at such voltage. More recently, Batista and co-workers have shown that derivatives of N-phenylbenzamide exhibit RRs up to 1.8. at 0.8 V.^{59,63} This theoretical approach based on non-equilibrium Green's function technique and density functional theory (DFT-NEGF) was in good agreement with STM-BJ measurements. In the last three cases, the asymmetrical electron density distribution of the frontier orbital that dominates charge transport has been identified as the main factor that induces rectification.

Recent theoretical studies have highlighted relevant molecular characteristics to consider in the design of single molecular rectifiers. Conjugated molecules can present high values of conductance but favor electron transport in both directions. Therefore, weakly coupled conjugated fragments have emerged as preferred systems to function as rectifiers with predicted RRs up to 2 orders of magnitude at bias potentials of 1 V.^{64,65} The rectification due to the weakly coupled conjugated fragments was assisted by connecting the molecule with different anchoring groups to the left and right electrodes. The systems studied presented an asymmetry at the molecule-electrode contact sites, resulting in a combination of extrinsic and intrinsic rectification mechanisms. Aiming to elucidate structural design principles for low-bias intrinsic molecular rectifiers, two recent works using DFT-NEGF technique have been reported. The first study is a computational screening of nine different series of synthetically plausible molecular motifs.⁶⁶ It was shown that high rectification at 0.2 V can be obtained by a framework consisting of strong electron-donating substituent groups and amide linkages. RRs as high as 16.67 were reported. The second report is a computational search of donoracceptor (D-A) dyads which motifs have been used for organic photovoltaics.⁶⁷ It was found that the asymmetry and energy of the highest occupied molecular orbital (HOMO) lead to RRs up to 7.07 at 0.2 V. Despite these major breakthroughs, we find that important questions for the optimal design of intrinsic molecular rectifiers remain unanswered: Would a break in the conjugation be enough to induce rectification? Is there an optimal torsion angle that maximizes the RR? Would including electron donating and/or electron-withdrawing groups be sufficient to have asymmetric I-V characteristics? Would the combination of features enhance or cancel out rectification behavior? In this work, we aim to answer these questions.

Herein, we report a systematic computational study that analyses rectification induced at low bias voltages (e.g., ≤ 0.3 V) by conformational changes and chemical substituents in D– B–A systems based on polyphenylenes. We studied the effect of each parameter individually and collectively and rationalized the structure–property relationships of our results. Our calculations indicate that a combination of torsion angles and donor and acceptor groups are required to induce high rectification at low bias potentials. The best configuration for rectification is to form D–B–A systems with torsion angles of 60° between units. By using the obtained design principles, we



Figure 2. I-V curves of model systems under (a) conformational and (b) substituent modifications. Insets show their corresponding RR values.

designed two new molecular rectifiers at low bias voltages that can be used as linkers in molecular assemblies of dye-sensitized solar cells and water-splitting dye cells. We also used different substituents and bridge structure to show that our results are robust to structural modifications and that the rectification behavior is observed with different moieties.

METHODS

Geometry Optimizations. Geometry optimizations were performed using the B3LYP density functional with the 6-311 G(d,p) basis set as implemented in Gaussian 09.^{68,69,70} B3LYP functional has been widely used and is very reliable for organic molecules; thus, optimized structures and energies are simulated successfully with low computational effort.^{71–73}

We used phenylene-based systems as a framework to elucidate the design principles that maximize intrinsic rectification in organic molecules (Figure 1a) since they have been relevant structural units to fabricate functional materials at different scales.^{74,75} Derivatives of 1,4-bis(phenylethynyl)benzene (BPEB) were chosen as model systems to perform our systematic study. The photophysical properties of BPEB have been studied in detail and the presence of several conformations thermally accessible at room temperature have been reported.⁷⁶⁻⁷⁸ This backbone received great interest for their application as molecular resonant tunneling diodes, given its NDR at high voltage when the central ring is substituted.⁷⁹⁻⁸⁴ The chemical substituents considered for this study were amino $(-NH_2)$ and nitro $(-NO_2)$ groups. Amino groups are strong electron-donating groups, and nitro substituents have high electron-withdrawing ability.⁸⁵ These substituents were located in the ortho- positions in relation to the triple bond to prevent any substituent-electrode interaction. Torsion angles of 0, 30, 60, and 90° between subsequent rings were considered to evaluate the conformational effect on rectification (Figure 1b). In our model systems, the most stable conformers are planar. Therefore, we performed constrained optimization of geometries to generate structures with torsion angles. In a subsequent step, we studied derivatives of para-terphenyl, denoted tailored systems, to test our findings from our systematic study. Similar to BPEB derivatives, these systems consist of three aromatic rings, but no acetylene linkages are present. Their optimized structures

include torsion angles and constrained geometry optimizations are not necessary^{86,87} thanks to steric effects. We corroborated our findings by studying the optimized structures of two additional systems with different substituents and different bridge unit, labeled as validation systems. Our tailored and validation systems are suitable to be used as linkers for dyesensitized nanoparticles, the essential elements of Grätzel solar cells and photocatalytic solar cells for water splitting.⁸⁸

Transport Calculations. To evaluate the transport properties, the molecules were connected to electrodes to form molecular junctions (Figure 1c). We modeled the molecular junctions by following a setup that has been used successfully in previous works.^{89–91} We used Au (111)^{92,93} nanowires as electrodes. The molecules were connected to the electrodes via thiolate anchoring groups. Anchoring moieties consisting of sulfur atoms have been reported to provide a stable binding to gold electrodes^{94,95} and cause charge transport to be controlled by the HOMO of the molecular devices.⁹⁶ A detailed description of the molecular junctions and an accompanying scheme can be found in the Supporting Information. We used the DFT-NEGF method^{97–99} as implemented in

TranSIESTA¹⁰⁰ to obtain the transport properties. This method uses DFT to calculate the electronic structure and NEGF formalism^{101,102} for quantum transport (see Supporting Information for a detailed description of the method). DFT-NEGF has proved to be reliable to predict transport properties at a reasonable computational time.^{103,104} A double- ζ basis set was used for all transport calculations, which is sufficient to describe the dominant energy levels involved in electron transport.¹⁰⁵ The generalized gradient approximation (GGA) functional PBE¹⁰⁶ was used as the exchange correlation functional. To sample the Brillouin zone, 107 we used a 1 \times 1 x 50 Monkhorst type k-grid for the leads and only the gamma point for the device region. Finally, 200 Ry was used as the energy cutoff for the real space grid. The RR values were obtained from currents calculated at ± 0.2 V and ± 0.3 V, being the forward bias direction from left to right. A TranSIESTA input example can be found in the Supporting Information.

RESULTS AND DISCUSSION

Model Systems. First, we present the results for our model systems, starting with the individual effects of conformational



Figure 3. I-V curves of the model systems while rotating the right ring (a) when substituted by an electron-donating group and (b) when substituted by an electron-withdrawing group. Insets show their corresponding RR values.

modification and chemical substitutions in the electron transport mechanism (Figure 2). The I-V curves when rotating one terminal ring are highly symmetric (Figure 2a), implying that conformational changes alone do not induce high rectification, even at higher voltages. This is because the HOMO, the energy level which dominates the transport, remains with a degree of delocalization across the molecule. Additionally, increasing the torsion angle decreases the current under bias potentials, this result was expected since the conjugation decreases.

When only one type of substituent is present $(-NH_2 \text{ or } -NO_2)$, small rectification ratios are obtained when molecules are in a planar conformation. The I-V curves that present this effect are shown in Figure 2b. These curves are slightly asymmetric, and it is observed that when amino substituents are used higher currents are obtained at negative bias. Thus, donor groups favor the reverse direction (i.e., right to left or current response under a negative bias) when they are located at the ring connected to the right electrode. This result suggests that amino groups should be placed in the left ring to favor the forward transport direction (current response under a positive voltage).

Next, we analyzed the effect of conformations when only donors or acceptors are present, as shown in Figure 3. The asymmetry of the curves moderately increases with the torsion angle. This agrees with the results reported for pyrimidinylphenyl derivatives.¹⁰⁸ For the systems substituted with amino groups (Figure 3a), NDR is observed at voltage values higher than 0.2 V. This behavior was also present in previously reported single molecular rectifiers based on amide linkages.¹ We attribute this feature to a misalignment between the molecular energy levels and the Fermi level of the electrodes as a result of the energy shifts induced by the bias voltage.^{110,111} In systems where only nitro groups are present (Figure 3b), no NDR is observed at 0.3 V. I-V curves resulted from rotating the terminal ring that is not substituted (i.e., left ring) can be found in Figure S2. When amino substituents are used, we found that the transport properties are independent of the terminal ring that is rotated. In contrast, when nitro groups are present, rotating the substituted ring resulted in higher RR.

In a subsequent step, we introduced both types of substituents, donors and acceptors, to our model system, placing the amino groups in the left terminal ring and the nitro groups in the right terminal ring, forming D-B-A systems. The results obtained are shown in Figure 4. To evaluate the conformational effect on rectification we considered the rotation of both terminal rings in the same direction and in the opposite. The setup D-B-A favors transport in the forward direction, which can be observed in the I-V curves for these model systems (Figure 4a). Also, it is important to note that all I-V curves show asymmetry. We attribute this asymmetry to a complete localization of the HOMOs (Figure 4c,d) in the left terminal ring, or donor site. This can only be achieved by combining conformational changes and chemical modifications. (See HOMOs of model systems in Figures S38-S43.) NDR can be observed when the molecule is planar, but this behavior is not observed for the other systems shown in Figure 4a. The I-V curves for molecules with torsion angles of 60° are shown in Figure 4b to show the degree of rectification obtained with a combination of this dihedral angle and asymmetric chemical substitution. An important characteristic of these I-V curves, in addition to their asymmetry, is that when a negative bias is applied, the current in the reverse direction is essentially suppressed, an ideal feature of intrinsic rectifiers.

To determine the origin of the asymmetric I-V curves of the systems with torsion angles of 60° , we analyzed the dependence of the transmission function with respect the voltage. Transmission distributions offer a more detailed insight of the energy levels of the device region at zero bias and their changes once a bias is applied. The transmission functions of the substituted model systems when the terminal rings are rotated 60° are shown in Figure 4c,d. For simplicity, the Fermi levels, $E_{\rm F}$, of the electrodes have been shifted to zero. The main peak of each transmission function corresponds to the molecular energy level that participates in the charge transport. In this particular case, this peak corresponds to the HOMO, and it is clearly seen from the isosurfaces that the electron density is localized in the left ring of the molecule. When this localization is achieved, increasing the bias to positive values displaces the main peak toward the Fermi level, and the



Figure 4. (a) I-V curves of the D–B–A model systems at different dihedral angles. (b) I-V curves of the D–B–A model systems with torsion angles of 60°. The insets of panels a and b show their corresponding RR values. Panels c and d show the transmission functions for the systems shown in panel b when both rings are rotated on the same and opposite directions respectively and the isosurface of their corresponding HOMOs. The insets show the transmission functions in the integration window from -V/2 to +V/2 used for the calculation of the currents at ± 0.2 V according to eq 14 of the Supporting Information.

opposite effect occurs for negative bias. This goes in line with the findings of Ding et al.¹⁰⁹ who stated that localization of the HOMO on one region of the molecule causes rectification behavior. This asymmetric response for an applied bias is not observed in the abscence of substituents even when the π conjugated system is decoupled (see Figures S3-S6). When molecules are planar and have only one type of substituent, the main peak of the transmission distribution is shifted by an applied bias voltage either closer or further from the Fermi energy depending on the voltage sign. Also, under positive voltage, the width of the main peak decreases. The opposite effect occurs when a negative bias is applied (see Figures S7 and S15). When twisting and chemical substituents are combined the displacement of the main peak of the transmission function is larger. For the cases where NDR were present, the main peak shifts against the Fermi level for a 0.3 V applied bias, resulting in a decrease in the RR value (see transmission functions in the Supporting Information). The insets of Figure 4c,d, which correspond to close-ups of the transmission functions clearly show why higher current is obtained at 0.2 V than at -0.2 V

because the current is proportional to the integral of the transmission function (see eq 14 from the Supporting Information).

The values of conductance at zero bias and RR for all model systems are summarized in Table 1. The zero bias conductance is proportional to the transmission probability at the Fermi level. Results in Table 1 show that zero-bias conductance decreases when the torsion angle increases. This is due to the break in the conjugation between aromatic rings. On the contrary, RR increases with torsion angle as previously reported.^{67,109} Therefore, conformational features show a trade-off between rectification efficiency and conductance values. Torsion angles of 90° enhance rectification but at the cost of decreasing considerably the conductance and are not considered for the discussion. Conductance and RR values for systems with torsion angles of 90° can be found in Table S1. The presence of donors increases the conductance due to the higher electron density and better alignment of the HOMO with the Fermi level; the inverse effect occurs under substitution with acceptors. Higher conductance is obtained

substituent	rotation direction	torsion (deg)	$G(G_0)$	$\frac{RR}{(0.2 V)^a}$	$\frac{RR}{(0.3 V)^a}$
none	left	0	1.80×10^{-2}	1.03	1.12
		30	1.34×10^{-2}	1.09	1.20
		60	4.51×10^{-3}	1.11	1.25
donors	left	0	3.34×10^{-2}	1.18	0.87
		30	2.53×10^{-2}	1.22	0.87
		60	7.99×10^{-3}	1.34	0.93
	right	0	3.34×10^{-2}	1.18	0.87
		30	2.43×10^{-2}	1.24	0.91
		60	8.23×10^{-3}	1.36	0.94
acceptors	left	0	7.00×10^{-3}	1.35	1.60
		30	5.29×10^{-3}	1.36	1.64
		60	1.82×10^{-3}	1.37	1.67
	right	0	7.00×10^{-3}	1.35	1.60
		30	5.80×10^{-3}	1.42	1.76
		60	1.84×10^{-3}	1.69	2.09
both	same	0	1.40×10^{-2}	1.74	1.64
		30	8.63×10^{-3}	1.98	2.40
		60	7.31×10^{-4}	2.58	7.08
	opposite	0	1.40×10^{-2}	1.74	1.64
		30	9.22×10^{-3}	1.89	2.04
		60	1.36×10^{-3}	2.64	6.86

 Table 1. Conductance and RR Values of Model Systems Due

 to Conformational and Chemical Modifications

 $^{a}\mathrm{RR}$ values given in the orientation that favors the forward bias direction.

when the terminal rings are rotated in opposite directions, but less rectification is obtained.

From the above results, we conclude that conformational changes alone are not enough to enhance rectification at low bias potentials. However, under the presence of electron-donating and/or -withdrawing groups, torsion angles increase the RR. The effect is maximized at 60° . This ideal angle for an efficient rectification is in agreement with the one found by Batista and co-workers in D–A dyads.⁶⁷ From our model systems, we found that the highest RR values are obtained when electron-donating and -withdrawing groups are attached at the beginning and at the end of the forward transport

Article

direction, respectively. In addition, the rectification is slightly higher when the terminal rings are rotated in the same direction.

At this point, we would like to emphasize that our model systems were used to characterize the effect of torsion angles and substituent effect on rectification. As shown in the Supporting Information, where we present the potential energy surfaces of the torsion angles (Figure S46), the energy barriers are sufficiently low to allow the rotation of the rings at room temperature and have all possible conformations at different angles, decreasing the rectification efficiency.

Tailored Systems. Having found the optimal parameters for rectification from our model systems, we evaluated our results in four new systems based on para-terphenyl. These molecular structures are nonplanar in their minimum-energy geometry due to steric effects. Two systems correspond to conformations of unsubstituted para-terphenyl with terminal rings rotated to the same and opposite direction. In their optimized geometry, these systems have torsion angles around 40° . The other two systems are substituted *para*-terphenyl molecules with amino and nitro groups and torsion angles close to 60°. Figure 5 shows the I-V curves of our tailored systems. When no substituents are present no asymmetric curves are obtained (Figure 5a), consistent with our results from our unsubstituted model systems. The I-V curves when substituents are present are shown in Figure 5b. The asymmetry of the I-V curves indicates that the systems behave as rectifiers at low bias voltages. This rectification behavior is attributed to the incorporation of the design principles that we found are optimal to enhance rectification (i.e, the substituent groups on the positions that favor the forward transport direction and torsion angles close to 60°). Transmission functions for these systems can be found in Figures S33 and S34. The peaks that corresponds to the HOMOs in the transmission functions present the same response at forward and applied bias as those shown in Figure 4, and the electron density is completely localized in the left ring.

The conductance and RR values of tailored systems are found in Table 2. The torsion angles of the optimized structures are also indicated. Similar to our model systems, higher conductance is obtained when both terminal rings are



Figure 5. I-V curves of the (a) unsubstituted and (b) substituted tailored systems. Insets show their corresponding RR values.

Table 2. Conductance and RR Values of the Tailored Systems Studied in This Work

substituent	rotation direction	torsion (deg)	$G(G_0)$	RR (0.2 V)	RR (0.3 V)
none	same	39	1.53×10^{-2}	1.10	1.21
	opposite	40	1.69×10^{-2}	1.09	1.21
both	same	-63, 65 ^{<i>a</i>}	6.57×10^{-4}	2.59	20.08
	opposite	64, 68 ^a	1.60×10^{-3}	2.47	9.69
^{<i>a</i>} The two	torsion angl	les correspoi	nd to the left	and rig	ht ring,

respectively.

rotated to the opposite direction, but rectification is enhanced with rotations in the same direction. Under an applied positive bias, the main peak of the system rotated to the same side shifts closer to the Fermi level than the system rotated to the opposite side; in other words, the transmission function when the rings are rotated in the same direction is slightly more sensitive to the bias potential resulting in higher RR (see Figures S33 and S34). The unsubstituted tailored systems have low RR values at 0.2 and 0.3 V, but the substituted tailored systems show efficient rectification at 0.2 V and higher rectification at 0.3 V. Notably, a RR = 20.08 at 0.3 V is obtained by rotating the terminal rings in the same direction.

To evaluate the thermal stability of the tailored system, we performed relaxed potential energy surface scans corresponding to the rotation of the rings. At each step the geometry was optimized while maintaining the corresponding torsion angle constant. The results obtained are shown in Figure 6. The energy barriers for the substituted systems lay between 0.6 and 0.9 eV, and as mentioned before, the optimized geometries already have torsion angles close to 60°. Given that the energy necessary to change between conformers is considerably higher that the thermal energy at 298.15 K, our tailored systems could function as stable and robust devices at room temperature. The final rectification will be a contribution from the small range of conformations that are thermally accessible at room temperature, but the average RRs are expected to be closer to the calculated RR values. Therefore, the tailored systems represent promising single molecular rectifiers to operate at low voltage,

in contrast to our model systems and other D–A systems previously studied,⁶⁷ where the rotational barriers are low enough to allow free rotation at room temperature.

Validation Systems. To evaluate the robustness of our results, we incorporated different electron-donating and -withdrawing groups. As seen in Figure 7a, using -OH and -F substituents give similar qualitative results than our tailored systems. The torsion angles obtained for this structure were 62 and 46° for the left and right torsions, respectively. We also changed the bridge structure as seen in Figure 7b. The steric effect of the bulkier bridge unit increased the left torsion angle to 86° and the right torsion angle to 76° . Hence, less current was obtained, but RR values are similar. For both cases our results prevail, indicating that the proper placement of substituents combined with the correct conformation will enhance the rectification of molecular devices.

CONCLUSIONS

In this report, we present a systematic computational study on the effects of conformational and chemical modifications on intrinsic rectification in phenylene-based molecules at low voltages. We used model systems to study the individual and combined effects when the torsion angles between the phenyl groups are modified to break the conjugation and when chemical substitutions are introduced through electrondonating $(-NH_2)$ and electron-withdrawing $(-NO_2)$ groups. Using only one modification, either a conformational change or a chemical substitution is not sufficient to cause significant rectification and a combined effect is necessary to maximize it. Our findings indicate that a donor-bridge-acceptor (D-B-A)setup and torsion angles of 60° between each phenylene unit gives optimal rectification ratio values. Transmission functions and orbital distribution analysis indicate that these structural design principles enhance rectification because they cause the perfect localization of the HOMO in only one of the terminal rings. Under a positive voltage, this frontier orbital shifts toward the Fermi level and under negative voltage it shifts away from the Fermi level in an asymmetrical way.

By considering our design principles, we designed two new molecular rectifiers based on *para*-terphenyl molecules whose



Figure 6. Potential energy surfaces for tailored systems rotated to the (a) same and (b) opposite direction. The arrows indicate the angles of the optimized structures.



Figure 7. (a) I-V curve of validation system with different substituents and (b) I-V curve of validation system with different bridge unit. Insets show their corresponding RR values and zero-bias conductance.

optimized structures already have torsion angles close to 60° between phenyl rings, and we include chemical substitution for a D–B–A setup. Potential energy surface scans show that at room temperature these tailored systems would not fluctuate easily into other conformations that may decrease rectification. These systems present rectification ratios up to 20.08 at 0.3 V. Finally, we tested the robustness of our finding with a set of validation systems where we modified the bridge unit and used different electron-donating and -withdrawing groups to build a D–B–A systems. Similar rectification behaviors were obtained.

We think that the chemical features and molecular systems found and designed in this work can be applied in a variety of applications where directional electron transfer is a crucial mechanism. In particular, we consider that these results are relevant for the design of novel photovoltaic devices, such as dye-sensitized solar cells and water-splitting dye cells, since our rectifiers and design principles could improve electron injection and charge transport efficiency, suppressing charge recombination to build robust and highly efficient photovoltaic cells. Recently, molecular linkers similar to our unsubstituted tailored system were used in dye-sensitized photochemical cells,⁸⁸ and we expect that our results inspire the synthesis of substituted linkers to enhance electron injection efficiency.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b12780.

Scheme of extended molecule, detailed computational methods, accuracy considerations, additional results, Cartesian coordinates of individual optimized structures, prediction and validation systems in gold–electrode junctions and sample input files (PDF).

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Notes

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The Journal of Physical Chemistry C

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