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Charge Transport and Rectification in Donor–Acceptor Dyads

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Supporting Information

ABSTRACT: Organic, conjugated donor-acceptor (D-A) systems are essential components of photovoltaic devices. Design and optimization of D-A systems is typically based on trial-and-error experimentation methods that would benefit from fundamental physical insights on structure-function relationships at the molecular level. Here, we implement a nonequilibrium Green's function methodology at the density functional theory (DFT) level and examine charge-transport and rectification properties of a series of conjugated D-A systems. We investigate 42 molecular junctions formed by D-A dyads bridging model gold electrodes, showing clearly how transport properties are determined by chemical composition, symmetry of frontier orbitals, and molecular conformation.



Key properties are compared to experimental data. Notably, an inverse correlation between conductance and rectification is found, with relatively large rectification ratios caused by the asymmetry of frontier orbitals near the Fermi level. We discuss design principles that should be valuable for the rational design of molecular D–A systems with appropriate transport properties.

INTRODUCTION

Multicomponent molecular assemblies that combine electronrich donor groups and electron-poor acceptor moieties are essential in organic materials for solar energy conversion¹⁻¹⁰ and molecular electronics.¹¹⁻¹⁴ The π -conjugated donor– acceptor (D-A) dyads, or push-pull systems, are valued for their intrisically narrow band gaps which stem from the high energy of the donor HOMO and the low energy of the acceptor LUMO. In turn, the HOMO-LUMO gap determines the optical band gap which can be tuned to permit absorption over a wide region of photon energies. Important applications include organic photovoltaics (OPVs) where D-A pairs in the form of either small molecules, oligomers, or polymers are typically employed for light-absorption.^{3,2,15-19} The D–A strategy also allows for the tuning of charge-separation rates and thermodynamic driving forces for charge transport. For example, establishing a gradient of LUMO energies along an electron transport path can facilitate directionality of charge separation, as often implemented in dye-sensitized solar cells and photoelectrochemical cells.^{5,8,20-22} In most applications of D-A systems, the overall charge-transport efficiency is critical for functionality. For example, the efficiency of polymer solar cells is crucially dependent on the conductivity of the holetransporting D–A copolymer.²³⁻²⁵ For this reason, organic films have been thoroughly investigated by experimental studies. Despite this, a fundamental description of the charge separation and the suppression of recombination via directional transport properties have yet to be established at the molecular level of OPV components.²⁶

D-A systems were theoretically proposed as molecular rectifiers¹² due to their predicted asymmetric response to a

forward vs reverse applied bias potential V. The rectification ratio (RR), an important measure of how effectively a species induces directional charge transport, is defined in terms of the ratio of forward and reverse currents, I(V) and I(-V) as follows:

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

Directional charge transport is potentially valuable in solarenergy conversion applications when applied to linkers between an antenna dye and a catalytic center, or in organic photovoltaic devices where the charges should move as efficiently as possible to their respective electrodes to minimize nongeminate recombination. Since such devices typically operate under low applied bias potentials, rectification is most useful if present even at low biases to minimize the need for overpotentials. The rectifying motifs here studied, while not directly applicable in such devices, are thus studied at modest biases of about 200 mV.

To model electron transport through molecules under small bias potentials, we assume that the molecule defines a tunneling barrier that affects the transmission probability of electrons undergoing elastic scattering. The overall conductance, G(E), is described by the Landauer formula as a function of the electron energy E, where the total transmission function, T(E), is a sum over all transmissive channels:²⁷

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The unitless T(E) approaches a maximum value of 2 for perfect transmission with two degenerate spins. The current is then obtained by integrating the transmission function over the bias drop V, as follows:²⁸

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E) (f(E - \mu_{\rm L}) - f(E - \mu_{\rm R})) \, dE \approx \frac{2e}{h}$$
$$\int_{E_{\rm F} - V/2}^{E_{\rm F} + V/2} T(E) \, dE \tag{3}$$

Here $\mu_{\rm L}$ and $\mu_{\rm R}$ are the potentials of the left and right electrodes, respectively, f is the Fermi–Dirac distribution function, and $E_{\rm F}$ is the Fermi level.

Calculations herein are based on the nonequilibrium Green's function (NEGF) methodology, as implemented in the TransSIESTA software package, which has been used for studies of charge transport and rectification in molecular junctions.²⁹⁻³³ Calculations describing the electronic structures at the density functional theory (DFT) $level^{29-31,34,35}$ have shown that spatially asymmetric frontier orbitals close to the Fermi level often cause molecular rectification.^{36,37} Since the electronic coupling between orbitals depends on both their spatial distance and their energy difference, an orbital that is spatially asymmetric (e.g., more localized on the left side of the molecule) is generally more strongly coupled to the spatially local left electrode regardless of bias voltage, since electronic coupling decays rapidly as distance increases. The energy of that orbital will follow the $E_{\rm F}$ of the left electrode both for positive and negative biases. At positive biases (here defined as the left electrode having a higher Fermi level than the right), this orbital's transmission peak moves up in energy, i.e., toward $E_{\rm F}$ for an occupied orbital, into the transmission integration window (as defined in eq 3), whereas for negative biases the orbital moves down in energy and correspondingly out of the integration window. It is via this mechanism that molecular rectification is observed. The closer the unbiased orbital is to the Fermi level, the smaller the bias magnitude required to observe rectification. An orbital that is spatially symmetric with respect to the two electrodes is equally coupled to those electrodes in a junction at zero bias, and no rectification is observed.

Here, we build upon earlier work^{36,38} to investigate the rectification capabilities of π -conjugated D–A systems exhibiting asymmetric frontier orbitals and high conductance. We study a series of donor and acceptor motifs, previously employed in D–A copolymers for OPV applications, to understand and quantify their electron-transport properties. We analyze 42 D–A dyads that result from the combination of the 7 donors and 6 acceptors shown in Chart 1. After DFT geometry optimization, their charge transport properties are analyzed as connected by thiolate groups to gold electrodes.³⁹ We first discuss the electronic and conformational properties of the dyads, essential to subsequent rationalization of their nonequilibrium conductivity and rectification as quantified by their voltage-dependent transmission functions.

COMPUTATIONAL DETAILS

The 42 dyads composed of electron donor (Chart 1A) and electron acceptor moieties (Chart 1B) were optimized at the DFT level using the $PBE0^{40}$ and PBE^{41} functionals, the 6-

Chart 1. Schematic Representation of the 7 Electron Donor (A) and 6 Electron Acceptor (B) Moieties Investigated^{*a*}



 ${}^{\prime\prime}R$ = alkyl chains in experiments for solubility; R = methyl in our calculations for computational expediency.

31G(d,p) basis set, and default convergence criteria in Gaussian 09.⁴² Co-dimers of the 42 pairs were optimized at the same levels of theory. Infinite copolymer HOMO energies ($E_{\rm HOMO}$) were estimated by plotting $E_{\rm HOMO}$ of the mono- and dimer vs the reciprocal number of units, 1/n, and fitting to a Hückel equation. Extrapolating the fitted function to $1/n \rightarrow 0$ according to a previously reported approach then gives the infinite copolymer $E_{\rm HOMO}$.^{2,43-45} The potential energy surface (PES) for rotation around the single bond connecting the donor and acceptor moieties were computed with a relaxed scan of the dihedral angle using the PBE0 and PBE⁴¹ functionals for two representative dyads, CDTBT and SeII. The orbital populations of the electron donor and acceptor fragments were quantified using GaussSum3.⁴⁶ Orbital isosurfaces were generated with the Chimera software.⁴⁷

Atomistic models for transport calculations were based on two semi-infinite hexagonal close packing (hcp) Au gold nanowire electrodes with alternating planes of 3 and 7 gold atoms⁴⁸ attached via their Au₇ hcp (0001) surface to the optimized dyads, using thiolate anchors as described in previous studies.^{36,38} The dyads were oriented parallel to the gold nanowires and the anchoring bond lengths were obtained from a semioptimized Au₂₈–S–phenyl system where the Au atoms were kept frozen and the organic molecule was relaxed at the PBE0/Def2SVP⁴⁹ level of theory.

The transmission function obtained at the DFT–NEGF level with the TranSIESTA software^{39,50} is based on a DFT Hamiltonian with the PBE functional and a double- ζ basis set,⁵¹ which permits efficient convergence while retaining good accuracy.^{36,38} The Brillouin zone was sampled with $1 \times 1 \times 80$ *k*-points for the leads and the gamma point for the scattering region, which consisted of the dyad and 27 adjacent Au atoms, as shown in Figure 1.

The transmission functions T(E) for all 42 junctions were calculated at -200, 0, and +200 mV. Currents were evaluated according to eq 3 and RRs as introduced by eq 1. The bias magnitude of 200 mV was selected because of its



Figure 1. Lead-anchor-D-A-anchor-lead junction setup used for the DFT-NEGF calculations, as exemplified with the T32TBT dyad. The respective leads extend semi-infinitely to either side in the calculations.

correspondence to a typical energy offset in solar energy applications, such as the driving force for injection of photoexcited electrons in dye-sensitized solar cells and photocatalytic cells,⁵² as well as the energy offset between the polymer and fullerene in bulk heterojunction OPVs.¹⁵ Representative example dyads SeBT, T32TQ, and T32TBTI were further investigated at several bias voltages between -300 and +300 mV.

Representative dyads, including CDTBTz, DTPyQ, OBDTBT, SeQ, T32TII, TBT, TII, and TBTz as well as all dyads with the TPD and BTI acceptors, were rotated in steps of 10° around the transport direction defined by the fixed gold leads. Transport calculations for all rotational conformations were then used to construct thermally Boltzmann-averaged rectification ratios, comparable to experimental room-temperature conditions.

RESULTS AND DISCUSSION

Equilibrium Properties. Structural and electronic properties of conjugated donor–acceptor systems are commonly studied computationally with DFT methods.^{2,43,53–56} Like OPV light-harvesters, the dyads investigated in this paper have donor and acceptor moieties connected by single bonds.^{17,57} Coplanarity between the moieties favors conjugation and thus transport. Strongly conjugated conformations are energetically favored although often partially compromised by steric repulsion between substituents in the D and A fragments. Figure 2 shows that a relatively small energy is required to



Figure 2. Potential energy surfaces (PES) associated with rotations about the single bond connecting the D and A moieties of CDTBT and SeII, corresponding to the most and least coplanar dyads, respectively.

induce out-of-plane distortion in CDTBT and SeII which show a high and low degree of coplanarity, respectively. We note that the choice of exchange—correlation functional is critical for proper geometry optimization; the inclusion of some exact exchange in the hybrid functional PBE0 yields a better description of delocalization and planarity. Table 1 reports the resulting minimum-energy out-of-plane dihedral angles for the complete set of 42 D—A dyads investigated.

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Table 1. Out-of-Plane Dihedral Angle [°] Between Donor and Acceptor in the 42 D–A Dyads^a

acceptor \rightarrow donor	↓ BT	BTI	BTz	z II	Q	TPD	mean			
CDT	0.0	8.5	0.6	20.7	10.0	0.0	6.6			
DTPy	0.7	12.7	0.8	21.8	18.9	0.5	9.2			
IDT	0.0	0.1	1.3	21.4	0.0	0.0	3.8			
OBDT	7.4	9.2	2.5	23.7	24.3	8.6	12.6			
Se	0.0	13.4	0.6	26.0	0.0	0.0	6.7			
Т	0.1	15.7	0.2	25.1	18.6	0.0	9.9			
T32T	0.1	14.4	0.4	24.9	11.7	0.0	8.6			
mean	1.2	10.6	0.9	23.4	11.9	1.3	8.2			
⁴ Mean values for each donor and acceptor are reported in the rightmost column and bottom row, respectively.										

A few trends are identified in Table 1. The BT, BTz, and TPD acceptors have no atoms experiencing steric repulsion and therefore yield a small D–A dihedral angle. Larger conjugated systems show larger stabilization of planar structures, resulting in small dihedral angles for the large IDT donor, and vice versa with large angles in the thiophene (T) dyads. OBDT is a very weak donor (deep HOMO),⁴³ producing nonplanar dyads.

Generally, conjugated organic systems function as hole conductors since their HOMOs are closer than their LUMOs to the work function of most electrode materials, including gold for which the work function is -5.1 eV. For the same reason, the HOMO is typically the dominant transporting orbital in Au molecular junctions of small conjugated systems.^{29,31,36,38,58}

The energy and symmetry of the frontier orbital proximate to the Fermi level (HOMO in our dyads) are critical parameters for conductance and rectification. The applied bias potential typically shifts the position of the frontier orbital relative to $E_{\rm F}$ and changes the overall transmission as defined by eq 3. Table 2 reports the calculated HOMO energies of the 42 dyads, and a few trends are identified. IDT is the strongest donor as indicated by the high HOMO energies of its dyads.⁴³ For a given donor, the nature of the acceptor also modulates the dyad HOMO energy, although its effect is smaller than that of the donor. As shown in Table 2, the BTz and TPD acceptors induce the highest and lowest HOMO energies, respectively, in agreement with earlier work.⁴³ Smaller D-A pairs exhibit larger HOMO-LUMO gaps. Figure 3 compares the DFT HOMO energies to the corresponding experimental HOMO energies of 20 D-A copolymers, as reported in the literature (see the Supporting Information (SI) for details). Overall, the observed correlation provides partial validation of our computational approach.

The asymmetry of the HOMO electronic density determines the asymmetric response of the transport channel to forward vs reverse bias potentials. Here we introduce a simple quantification of such asymmetry in terms of the projection of the HOMO onto the donor moiety of the D–A molecule, and the results are tabulated in Table 3. The high percentages reported for most dyads in Table 3 confirm that the HOMO is predominately localized on the donor fragment.

Figure 4A shows the frontier orbitals of OBDTQ and TII, as representative examples of dyads with HOMOs localized on the donor or acceptor fragments, respectively. Dyads with the large acceptor II coupled to a small donor (Se, T, and T32T) are the only assemblies with a HOMO localized more on the acceptor than on the donor. Conversely, the HOMO donor localization is nearly complete for the larger donors OBDT and IDT, which in the case of OBDT is reinforced by the lack of coplanarity

Tabl	e 2.	DFT	номо	Energies	in eV	/ for	All	42	D–A	. Dyads"
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	acceptor \rightarrow donor \downarrow	BT	BTI	BTz	II	Q	TPD	mean
	CDT	-5.33	-5.40	-5.13	-5.24	-5.20	-5.53	-5.30
	DTPy	-5.26	-5.35	-5.07	-5.20	-5.20	-5.47	-5.26
	IDT	-5.20	-5.27	-5.04	-5.15	-5.09	-5.36	-5.18
	OBDT	-5.51	-5.62	-5.37	-5.44	-5.43	-5.61	-5.50
	Se	-6.00	-5.93	-5.71	-5.63	-5.86	-6.25	-5.90
	Т	-5.82	-5.83	-5.58	-5.57	-5.70	-6.04	-5.76
	T32T	-6.02	-5.96	-5.72	-5.63	-5.76	-6.31	-5.90
	mean	-5.59	-5.62	-5.37	-5.41	-5.46	-5.80	-5.54
a		_			_			

^aMean values for rows and columns are reported in the last column and row, respectively.



Figure 3. Correlation plots of DFT HOMO energies of D–A pairs as molecular dyads (black circles) or D–A copolymers (red triangles) vs the experimental D–A copolymer HOMO energies.

between the donor and acceptor fragments (see Table 1). Figure 4B shows a rough correlation between high $E_{\rm HOMO}$ and large HOMO donor localization, both properties being promoted by strong donors.⁴³

Conductance. The current produced by an organic photovoltaic device is often limited by the conductivity of the light-harvesting material (often a polymer) and/or the recombination rate of photogenerated electron—hole pairs, depending on the morphology and molecular weight of the polymer.^{59–62} The properties of the D and A moieties composing the conducting polymer or molecule play an important role in determining these properties. Our NEGF calculations predict large electric currents through the junctions, which is largely due to the orientation of the dyads parallel to the transport vector and the strong coupling between electrode and dyad afforded by the thiolate anchors which also promote high E_{HOMO} . Previous studies have explored the effect of the orientation of the conducting molecule relative to the transport direction in more detail.⁶³ Here we focus on the strong coupling limit, descriptive of D–A pairs covalently



Figure 4. (A) Isodensity surfaces of the frontier orbitals of OBDTQ and TII, representing D–A dyads whose HOMOs are most or least localized on the donor moiety, respectively. (B) Correlation of the percentage of the HOMO localized on the donor moiety and the HOMO energy.

bound as in a conducting polymer. Table 4 lists the current through the junctions obtained according to eq 3 with transmission functions T(E) calculated with NEGF at an applied bias of -200 mV (see SI for +200 mV data).

Figure 5A shows the calculated transmission functions for IDTBTI, IDTQ, and DTPyBTz, representing the dyads with respectively the smallest, intermediate, and largest currents at -200 mV, i.e., I(-0.2 V). Figure 5B shows the corresponding density of states, projected onto the D–A molecular part of the

Table 3. Percentage of	the D-A Dyac	l HOMO Localized	on the	e Donor l	Moiety'
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acceptor \rightarrow donor \downarrow	BT	BTI	BTz	II	Q	TPD	mean
CDT	77%	67%	75%	61%	80%	77%	73%
DTPy	78%	68%	76%	63%	81%	77%	74%
IDT	84%	77%	82%	73%	86%	85%	81%
OBDT	92%	82%	89%	72%	94%	92%	87%
Se	54%	35%	48%	19%	61%	58%	46%
Т	47%	34%	48%	18%	55%	56%	43%
T32T	67%	49%	62%	33%	72%	69%	59%
mean	71%	59%	68%	48%	76%	73%	66%

^aMean values for rows and columns are reported in the last column and row, respectively.

Table 4. Current	I in μA ,	Calculated a	ıt −200 mV,	for All 4	42 Au—	-D-A-	-Au Junctions ^a	
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acceptor \rightarrow donor \downarrow	BT	BTI	BTX	II	Q	TPD	mean				
CDT	3.17	0.65	3.55	1.09	2.67	0.66	1.96				
DTPy	2.68	0.88	4.07	0.87	2.45	0.69	1.94				
IDT	1.73	0.47	2.54	0.67	1.70	0.54	1.27				
OBDT	1.42	0.48	1.23	0.74	1.28	0.60	0.96				
Se	3.29	1.11	3.94	1.22	3.03	1.44	2.34				
Т	2.80	1.10	3.88	1.21	2.89	0.89	2.13				
T32T	2.63	0.77	3.67	1.10	2.26	1.02	1.91				
mean	2.53	0.78	3.27	0.99	2.33	0.83	1.79				
^a Mean values for rows and columns are reported in the last column and row, respectively.											



Figure 5. (A) Transmission functions T(E) at -200 mV for IDTBTI, IDTQ, and DTPyBTz junctions, exhibiting respectively small, medium, and large currents. (B) Density of states projected onto the D–A molecular part of the junction, showing that a molecular orbital coincides with, and is responsible for, the strong transmission peak near $E - E_{\rm F} = -0.1$ eV. (C) Isodensity plot of the conducting state that is responsible for the strong transmission peaks of IDTBTI, IDTQ, and DTPyBTz junctions as calculated with TranSIESTA, compared to isodensity plots of the HOMOs of the corresponding isolated D–A molecules calculated at a higher level of theory with Gaussian, demonstrating that HOMO is the dominant transmission channel.

junction (PDOS). Figure 5C compares the isodensity plot of the transmissive state to the equilibrium HOMOs of the three dyads in isolation, unambiguously showing that the D-A HOMO is the dominant transport channel. The strong transmission through the DTPyBTz junction is attributed to a very delocalized HOMO; Table 3 and Figure 5C show that its HOMO is evenly distributed between the D and A moieties.⁴³ The BTz acceptor contributes significantly to the HOMO of the DTPyBTz dyad, which exhibits the highest E_{HOMO} of the set (Table 2). This is a general trend for dyads with the BTz acceptor, showing delocalized HOMOs of high energy and largest average currents (Table 3). This observation is consistent with high hole mobilities (i.e., >0.54 cm² V⁻¹ s⁻¹) reported by space-charge limited current (SCLC) experiments on films based on BTz-containing copolymers,⁶⁴ suggesting efficient transport at both intramolecular and intermolecular levels.

IDT is a strong donor that determines the high energy of the IDTQ HOMO, a frontier orbital slightly less delocalized than the HOMO of DTPyBTz (see Figure 5C), resulting in a smaller current. The smallest current at -200 mV is observed for IDTBTI, a dyad with only modest delocalization of the HOMO and with a BTI acceptor⁶⁵ showing suboptimal alignment with the transport direction. Similar observations are common for the whole BTI series of dyads, explaining why these show smaller mean currents than dyads with other acceptors. Of the donors, OBDT forms dyads with the smallest average current; OBDTBTI has a calculated current of only 0.48 μ A, and its D–A copolymers have also been shown to be very poor hole conductors with experimental SCLC mobilities of 5.5 × 10⁻⁵–1.9 × 10⁻⁴ cm² V⁻¹ s⁻¹ depending on side chain branching.⁶⁶

Rectification Capabilities. Molecular rectification is determined by the response of the transmissive state(s) to the perturbational effect of forward and reverse bias potentials. The state closest in energy to the Fermi level is the main transmission channel since it dominates the contribution to the transmission amplitude within the integration range $[E_{\rm F}-V/2]$, $E_{\rm F}+V/2$ that determines the overall current, see eq 3. The opposite response of the frontier orbital to the influence of forward or reverse bias potenitals is determined by the asymmetric distribution of electronic density. The HOMO of our D-A dyads is the state proximate to the Fermi level and its asymmetric spatial distribution determines the level of rectification, which can be enhanced by a strong donor that localizes the dyad HOMO on the D side of the junction. When the donor is on the left side of the junction, a positive bias (i.e., a potential ramp decreasing from left to right) shifts the HOMO toward the Fermi level giving rise to super-Ohmic current, while a negative bias shifts the state away from the

Fermi level giving sub-Ohmic behavior. Consequently, D–A dyads with asymmetric HOMOs show rectification ratios RR = |I(0.2 V)/I(-0.2 V)| > 1.

Rotation of the dyad around the transport vector affects the calculated RR of dyads with the TPD and BTI acceptors, e.g., by up to a factor of 7 for CDTTPD, as illustrated in Figure 6.



Figure 6. (A) Rotation of the dyad around the transport vector, illustrated for CDTTPD as an example. (B) Relative energy and rectification ratio of the example CDTTPD junction as a function of the molecule–lead dihedral angle φ , demonstrating that a wide range of conformations are thermally accessible at 298 K and contributing to the average RR for this dyad.

The dependency of RR with the dihedral angle φ is due to the nonlinear geometry of the dyads. To account for thermal configurational sampling, we perform a Boltzmann average of RRs across different conformations as follows:

$$RR_{ave} = \frac{\int RR(\varphi) e^{-\Delta E(\varphi)\beta} d\varphi}{\int e^{-\Delta E(\varphi)\beta} d\varphi} \approx \frac{\sum_{\varphi=0^{\circ}}^{110^{\circ}} (RR(\varphi) e^{-\Delta E(\varphi)\beta})}{\sum_{\varphi=0^{\circ}}^{110^{\circ}} e^{-\Delta E(\varphi)\beta}}$$
(4)

where ΔE is the electronic energy relative to the minimumenergy, $\beta = (k_{\rm B}T)^{-1}$ with T = 298 K, and angles $0-110^{\circ}$ are sampled since the hcp leads are invariant to a 120° rotation. The dyads without TPD or BTI acceptors are more linear and therefore show much smaller sensitivity to φ : RR(φ)_{MAX} – RR(φ)_{MIN} < 0.6 in all tested cases. Table 5 reports the calculated RRs for all 42 junctions.

The analysis of transmission functions as a function of applied bias potentials can provide additional valuable details on the dyad charge-transport properties. The transmission functions T(E) under various applied bias potentials of three representative dyads SeBT, T32TQ, and IDTTPD whose junctions respectively show the smallest, median, and largest RRs, are plotted in Figure 7A–C, respectively. Figure 7D shows their PDOS in a wider energy window. SeBT exhibits a spatially symmetric HOMO, yielding negligible rectification. T32TQ shows a moderate rectification ratio, mostly due to the downshift of the transmission function peak (corresponding to the HOMO) under the influence of negative bias potentials. IDTTPD exhibits strong rectification due to the shift of the transmission function for both positive and negative biases (Figure 7C). The large RR for IDTTPD is attributed to the significant donor localization of its HOMO and the orientation of the TPD acceptor, misaligned with the transport vector. Other dyads with the BTI and TPD acceptors also exhibit similar behavior, with average rectification ratios of 4.57 for BTI and 3.28 for TPD.

Figure 7 demonstrates that, for the D–A dyads investigated, only the HOMO contributes significantly to the overall transmission at modest bias potentials; other frontier orbitals are energetically inaccessible, falling outside the integration window (eq 3). Therefore, design and optimization of D–A dyads for directional charge transport could be informed by analyzing the symmetry and energetics of their HOMO. For the specific model leads investigated, the transmission functions typically decrease at larger biases, a behavior due to the thinness of the model nanowire leads with a low density of states.

An important aspect that needs to be emphasized is the trade-off between the values of RR and conductance. Higher RR is obtained for systems with narrow bands in the transmission function near the Fermi level. Sharper T(E)peaks give larger RRs since they shift more distinctly in and out of the integration window by forward and reverse bias potentials, respectively. However, higher conductance is observed for systems that couple more effectively with the metallic leads and therefore show broadening of their energy levels and wider corresponding bands in the transmission function. As an example of this trade-off, systems with saturated spacer groups typically have highly asymmetric HOMOs and provide very high rectification ratios. However, the spacers interrupt the coupling between the molecular transport orbital and the contact leads, drastically reducing the level of conductance.⁶⁷⁻⁷⁰ Our study is focused on conjugated systems with symmetric anchors that couple strongly with both electrodes, so comparatively modest RRs should be expected. The use of different anchoring groups for the left and right electrodes is reported as a strategy to improve the overall

Tabl	e 5.	Calculated	Rectification	Ratios	RR :	= I((0.2	V)/	Ί (-0.2	V)	l f	for .	All	Dyada	s"
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acceptor \rightarrow donor \downarrow	BT	BTI	BTz	II	Q	TPD	mean
CDT	1.43	5.42	1.44	4.11	2.07	5.86	3.39
DTPy	1.86	5.38	1.08	5.12	1.77	5.26	3.41
IDT	2.91	6.25	1.89	4.94	3.08	7.07	4.36
OBDT	1.38	4.01	1.07	1.74	1.50	3.05	2.12
Se	0.84	2.60	1.27	1.74	1.27	1.99	1.62
Т	0.93	2.52	1.28	1.59	1.26	1.65	1.54
T32T	1.36	3.41	1.14	2.83	1.64	2.10	2.08
mean	1.60	4.23	1.31	3.15	1.80	3.85	2.65

"Values for TPD- and BTI-containing dyads are thermally averaged as described in the text. Mean values for rows and columns are reported in the last column and row, respectively.



Figure 7. Voltage-dependent transmission functions and isodensity plots of the transmissive states. (A) The SeBT junction exhibits the smallest RR of the set. The isodensity plot corresponds to the main transmission channel associated with the HOMO. (B) T32TQ exhibits an intermediate RR. (C) IDTTPD exhibits the largest RR of all D–A junctions. (D) Density of states projected onto the D–A molecule in junctions of SeBT, T32TQ, and IDTTPD (representative conformation).

rectification, 71,72 but this does not correspond to the intrinsic properties of the D–A core.

Figure 8A clearly illustrates the rectification-conductance trade-off. Strongly rectifying junctions show weaker currents while none of the strongly conducting junctions rectify significantly. Note, for example, that IDTBTI is the weakest conductor and the second strongest rectifier. Figure 8B,C shows the correlation of RRs with HOMO energies and HOMO asymmetries, computed as the amplitude of the projection of the HOMO onto the D moiety. The trends show that the RR is enhanced by a HOMO with high energy and large D localization. Both of these properties are readily computed in the absence of applied bias potentials, providing qualitative descriptors for efficient computational screening. Nevertheless, detailed characterization of transport behavior can only be obtained from more expensive nonequilibrium transport calculations.

CONCLUSIONS

We have investigated charge-transport and molecular rectification properties of π -conjugated D–A dyad systems, as determined by the molecular and electronic structure of the D and A components. Our systematic analysis of 42 D–A dyads based on DFT–NEGF calculations shows that the properties of the HOMO are critical for the efficiency of charge transport and rectification under low applied bias potentials. We find that equilibrium electronic-structure calculations thus could provide valuable insights for rapid screening and identification of promising candidates with desired transport properties. In particular, the proximity of the HOMO to the Fermi level and the asymmetric distribution of electronic density relative to the transport direction strongly correlate with conductance and rectification.

High conductance is observed with extended π -conjugation across the D–A system when thiolate anchoring groups establish strong electronic coupling to both electrodes. A trade-off between conductance and RRs applies to the series of D–A dyads since both delocalization of the frontier orbitals and strong dyad–lead electronic couplings enhance conductance but reduce rectification. Conversely, more localized frontier orbitals result in weaker coupling to one of the leads, giving lower conductance but higher RRs, particularly when the HOMO energies are close to the Fermi level. The reported analysis thus provides clear trends particularly relevant to the



Figure 8. (A) RRs($\pm 200 \text{ mV}$) vs the current at -200 mV showing a qualitative inverse correlation. (B) Correlation plot between RR($\pm 200 \text{ mV}$) and the HOMO energy of the isolated dyad. (C) Correlation plot between the RR($\pm 200 \text{ mV}$) and the amplitude of the projection of the HOMO onto the donor. The points corresponding to the largest and smallest values in each panel are given distinct color and shape to facilitate comparison across the three panels.

design of D–A dyads for charge separation. The DTPy donor forms dyads with high HOMOs close to the Fermi level that exhibit high RRs. The dyad combination of the TPD acceptor and the IDT donor exhibits RR > 7 while retaining a fully intact conjugation as necessary for high levels of conductance. The IDTTPD dyad is thus a promising assembly for directional charge transport.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b05749.

Calculated currents at +0.2 V for all 42 dyads; calculated transmission functions over a large range of energies and voltages for SeBT, T32TQ, and T32TBTI; sample input files; and coordinates of all optimized dyads in gold–electrode junctions. (PDF)

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