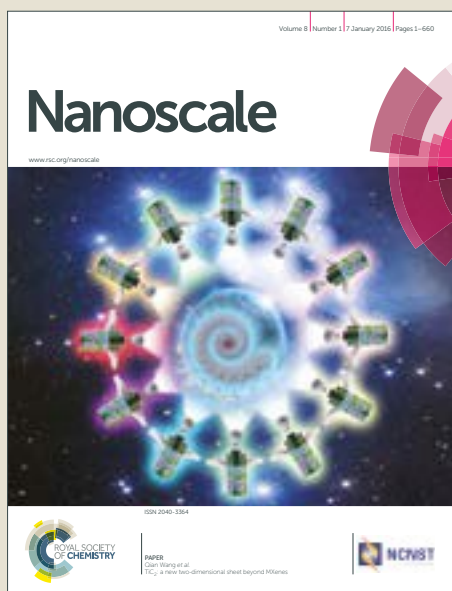


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HOMO-LUMO coupling: the fourth rule for highly effective molecular rectifiers[†]

Aaron Zhenghui Thong,^{*a} Milo S. P. Shaffer,^{b‡} and Andrew P. Horsfield^a

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Three rules for creating highly effective unimolecular rectifiers that utilize asymmetric anchoring groups have been proposed by Van Dyck and Ratner [Ratner *et al.*, *Nano letters*, 2015, 15, 1577–1584]. This study investigates their proposed rectification mechanism in a functionalised azafullerene system (4TPA-C₆₀) and identifies a fourth rule. NEGF-DFT shows that 4TPA-C₆₀ fulfills the three design rules, and finds that a saturated bridge is not required to fulfil the third rule, contrary to previous belief. Instead a twisted- π bridge decouples the donor and acceptor states whilst still providing a high conductance pathway. The molecular junction has a calculated rectification ratio of 145 at a bias of ± 1 V and the *U*-type rectification mechanism is driven by the pinning of the HOMO to the LUMO when the device is forward biased, but not when reverse biased. The switching behaviour is a result of a charge dipole forming at different interfaces for different bias directions. An additional design rule is thus proposed: charge transport should allow bias dependent coupling of filled to unfilled states. The findings in this work not only help in understanding charge transport in molecular rectifiers, but has wider implications for the design of molecular resonant tunneling devices.

In the continuing trend of miniaturizing devices, attention has turned to bottom-up approaches to produce molecular scale devices that aim to replicate the function of conventional semiconductor electronic devices, while achieving a higher spatial density. Molecular rectifiers, which allow unidirectional flow of current, are of interest as fundamental nanoelectric building blocks for more complex systems, such as molecular electronic computers^{1–3}.

Various transport mechanisms can contribute to rectification, and understanding these processes is crucial to the design of effective molecular rectifiers. These mechanisms can be broadly classified into 3 categories:⁴

1. *S* (Schottky)-type: asymmetric Schottky barriers at the left and right electrodes interfaces.
2. *A* (Asymmetric)-type: asymmetric placement of an electroactive group within the junction (*i.e.* conductive states localized closer to one electrode)
3. *U* (Unimolecular)-type: asymmetric distribution of the molecular orbitals which are accessed during the charge transport process

The three processes are not mutually exclusive; within a single system, all three processes can contribute to rectification. *U*-type rectification is considered to be the mechanism for true molecular rectification, as originally envisioned by Aviram and Ratner. *U*-type rectification is an inherent property of the molecule itself, and does not include any effects that arise at the metal-molecule interface.⁴

The performance of a rectifier is quantified by its rectification ratio (RR), defined as the absolute current through the device at bias *V* versus the current at $-V$. Most unimolecular rectifiers have reported rectification ratios in the low single digits^{5–8}. Capozzi and co-workers reported achieving a rectification ratio greater than 200 for thiophene derivatives in a scanning tunneling microscope based break junction.⁹ Their system relied strongly on an *S*-type mechanism, where a polar solvent was used to generate an electric double layer at the metal electrodes. Since rectification arose from asymmetry between the geometry of the two electrodes (sharp tip versus flat surface), it is difficult to scale up this mechanism for use in parallel device architectures. It is therefore advantageous to identify *U*-type systems which have rectifying properties inherent in their asymmetric molecular structure.

Recently, Van Dyck *et al.* proposed a new design for unimolecular devices capable of attaining high rectification ratios (RR =

^a Department of Materials and Thomas Young Centre, Imperial College London, London SW7 2AZ, UK; E-mail: a.horsfield@imperial.ac.uk

^b Department of Chemistry, Imperial College London, London SW7 2AZ, UK

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160) utilizing both the U and S mechanisms.^{10,11} Simulations showed that the HOMO and LUMO of their proposed molecule was asymmetrically coupled to opposing electrodes. The HOMO-LUMO gap (HLG) could thus be tuned by application of a potential difference across the molecule. A peculiar feature of their proposed system is the asymmetric response of the HLG to the direction of the applied bias: decreasing the HLG is much less efficient than increasing the HLG. Interestingly, this asymmetric response has not been previously observed in simulations of other systems involving two transmissive states. For example, the energy gap between the two transmissive states (HOMO and HOMO-1) in 1,2-bis(4-(phenylethynyl) phenyl)ethane has been reported to be linear with the applied bias, giving rise to a negative differential resistance (NDR) feature in the calculated $I(V)$ profile.¹² The presence of the NDR feature requires the two states to enter into and then move out of resonance again (*i.e.* the two states have to cross at some point). It is thus apparent that the restriction of level crossing is unique to certain Donor-Acceptor systems. This study aims to shed some light on the rectification mechanism proposed by Van Dyck *et al.*

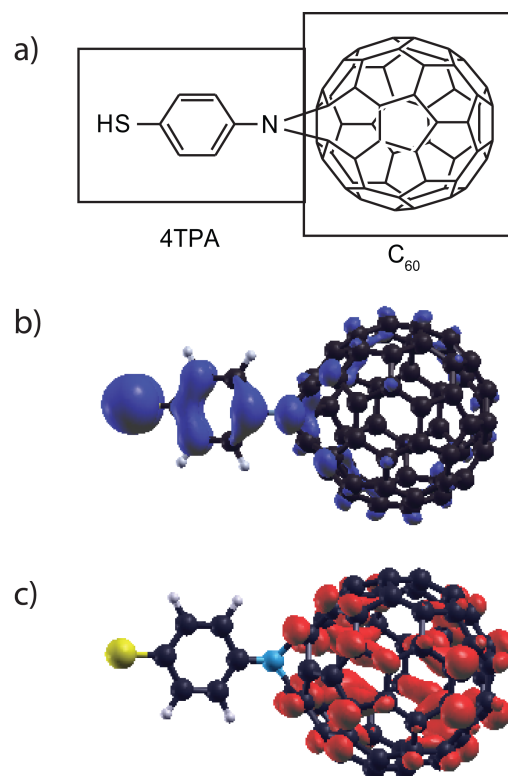
Three design rules were laid out by Van Dyck and Ratner for utilizing the proposed rectification mechanism¹⁰:

1. Asymmetric anchoring groups are chemically bound to the electrodes with an electron acceptor on one end and an electron donor on the other.
2. The anchoring groups must promote pinning of the frontier molecular orbitals near the Fermi energy levels of the electrodes
3. The π systems of the donor and acceptor fragments must be effectively decoupled to prevent delocalization of charge

In this work, a functionalized azafulleroid system, 4-thiophenylaza- C_{60} -fullerene (4TPA- C_{60} , as shown in Figure 1a) was investigated using density functional theory and the non-equilibrium Green's function formalism (NEGF-DFT)^{13,14}. Azafulleroids have been shown to be stable in the solution phase at liquid/liquid interfaces, and Langmuir-Blodgett monolayers of a similar azafulleroid have previously displayed highly asymmetric current-voltage profiles.¹⁵ It is further possible to attach these molecules between metallic contacts, as the protocols for grafting fullerenes to gold surfaces have been well documented in the literature.^{16,17}

We note that 4TPA- C_{60} fulfills all three rules laid out above. The system consists of an electron donor (4TPA) fused to an electron acceptor (C_{60}) via an open aziridine ring. The asymmetric anchoring groups, consisting of a thiolate donor on one end and a C_{60} acceptor on the other, both display strong coupling with Au surfaces, fulfilling the first rule.^{18–20} The pinning of the highest occupied molecular orbitals (HOMO) to the Fermi level of the electrode through the S–Au bond is well documented in the literature and has been attributed to surface dipoles formed due to charge redistribution at the interface.^{21,22} In the case of C_{60} , it has been shown in both experimental and theoretical work that the lowest unoccupied molecular orbital (LUMO) of C_{60} is pinned

Fig. 1 (a) Chemical structure of 4TPA- C_{60} . The donor is represented by the 4TPA fragment while the acceptor is represented by the C_{60} fragment. (b) HOMO and (c) LUMO isosurfaces as calculated at the DFT/PBE level of theory. The HOMO (LUMO) is primarily localized on the 4TPA (C_{60}) fragment as expected.



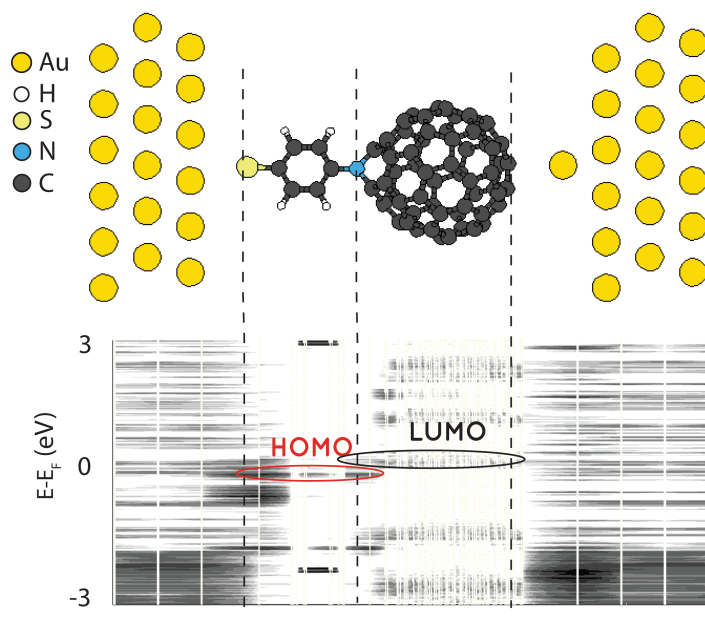
closely to the Fermi energy (E_F) of Au electrodes, thus fulfilling the second rule.^{23,24}

Instead of a conventional σ bridge found in most molecular rectifier designs^{2,3,6,8,25}, the decoupling moiety between Donor and Acceptor in the 4TPA- C_{60} system is closer to that of a twisted π structure.²⁶ The geometric constraint enforced by the rigid ring structure between phenyl ring and C_{60} prevents effective overlap between the π system in the donor and acceptor halves. Using density functional methods, the calculated HOMO and LUMO of the molecule are shown to be localized to the 4TPA and C_{60} halves of the molecule respectively (Figure 1b,c), fulfilling the third rule.

The calculated density of states of the metal-molecule-metal junction was projected along the molecular axis in the junction (Figure 2). At zero bias, the HOMO is shown to be localized on the 4TPA portion of the molecule, with the N lone pair acting as a good electron donor. On the other hand, the LUMO is localized on the C_{60} half of the molecule. The HLG of adsorbed 4TPA- C_{60} is reduced to 0.23 eV as compared to the calculated gap of 1.32 eV in the isolated gas phase molecule (see Supporting Information). While DFT simulated band gaps tend to be underestimated, the relative qualitative trends are generally accepted to be sound.²⁷

HLG reduction of organic molecules in metallic junctions has

Fig. 2 (top) Simulation cell used for ground state calculations showing the molecule adsorbed at an Au junction. (bottom) Projected density of states across one dimension of the junction. Dotted lines correspond to the position of the atom in the schematic.

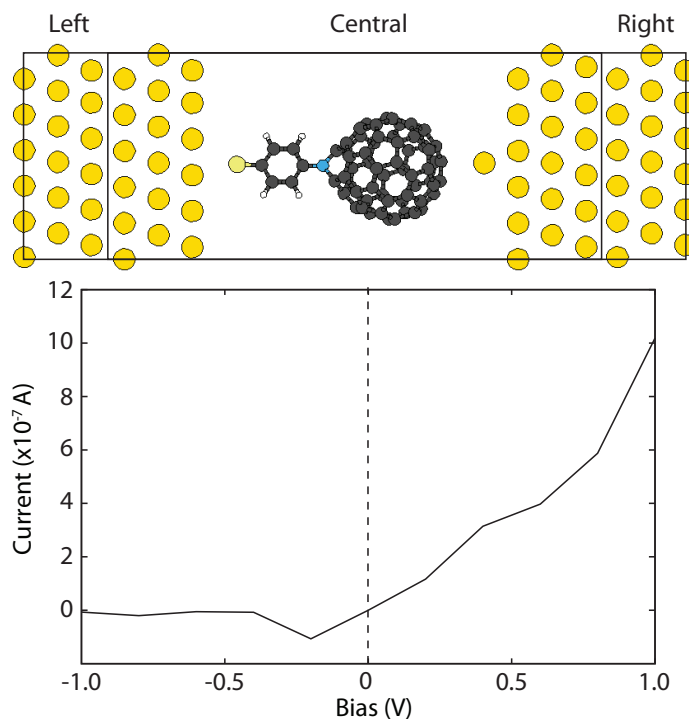


been previously attributed to Fermi level pinning of the molecular states when attached to metal electrodes.^{10,22} Likewise, the HLG reduction of 4TPA-C₆₀ is attributed to Fermi level pinning of the HOMO and LUMO at the Au/thiolate and C₆₀/Au interfaces respectively, which aligns the HOMO and LUMO independently of the isolated gas phase energy gap.

The electronic response of the molecule to finite biases was then calculated within the NEGF-DFT framework (see Methodology for details). Several gold electrode layers were included into the calculation of the central scattering region so as to account for interface effects (Figure 3). With an equilibrium HLG of 0.23 eV, one should expect that the current should peak at roughly the same applied bias, assuming perfect pinning of HOMO/LUMO to their respective electrode Fermi energies. However, from the calculated IV profile, it is evident that this is not the case (Figure 3). Instead, the current climbs steadily with increasing bias in the forward (positive) direction, but remains almost totally flat in the reverse (negative) direction (here defined as $V_{\text{right}} - V_{\text{left}}$), resulting in a high rectification ratio of 145 at ± 1 V. A rectification ratio of 2 orders of magnitude is extremely good for single-molecule rectifiers in comparison to both calculated and experimental values found in the existing literature.^{5,7}

The results prove that a high rectification ratio can be obtained using twisted π Donor-Acceptor systems despite suggestions that a saturated bridge is required to fulfil the third rule.¹⁰ The twisted π geometry also allows 4TPA-C₆₀ to achieve a high zero-bias conductance of $0.021 G_0$ due to the absence of an insulating bridge. Conductance through similar geometries have been shown to be higher by an order of magnitude as compared to σ -linked bridges.²⁸ Simultaneous access to high rectification and high conductances in single-molecule devices has seldom been

Fig. 3 (top) Simulation cell used for the transport junction. Boxed regions indicate left and right leads as well as the central scattering region. (bottom) Calculated current-voltage (IV) profile of the single-molecule junction from -1 V to 1 V. Rectification ratio at ± 1 V is calculated to be 145.



shown in the literature, making the 4TPA-C₆₀ system all the more appealing as a single-molecule rectifier.

The asymmetric response of the HLG to the direction of applied bias can be seen in the projected density of states (PDOS) of the 4TPA-C₆₀ system (Figure 4). From the PDOS, it is clear that the HOMO and LUMO quickly enter into resonance in the forward bias. This resonant state is maintained even at higher biases. The LUMO becomes pinned to the HOMO, while the HOMO itself continues to be pinned almost perfectly to the left electrode ($\epsilon_{\text{HOMO}} - E_{F,\text{left}} \approx -0.06$ eV in the bias range investigated). The HOMO-LUMO pinning effect restricts the crossing of the HOMO and LUMO, and results in them merging into one conductive manifold which forms a highly conductive channel over a wide bias window.

On the other hand, in the reverse bias regime, the HOMO and LUMO almost perfectly track the Fermi energies of the left and right electrodes respectively. The HLG increases from 0.23 eV to 1.02 eV as the voltage bias placed across it increases from 0 V to -1.0 V. As the HOMO and LUMO are pulled out of resonance, the transmission pathways across the junction decrease and the device becomes more insulating. The asymmetric response of the LUMO to the direction of the applied bias is thus responsible for the effective rectification of the system, classifying 4TPA-C₆₀ as a *U* type rectifier.

Why does the LUMO have this asymmetric bias dependence? Mulliken charge analysis of the on-site population of the donor and acceptor sheds some light on the behavior (Figure 5). The

Fig. 4 Density of states projected along the transport axis of the molecule (shown above) and their corresponding transmission spectra (in red) at varying junction biases in the forward (0.2 to 1.0 V) and reverse (-0.2 to -1.0 V) directions. The transmission spectra are shown in log scale from 10^{-5} to $10^0 G_0$ and share the same energy axis ($E - E_F$) as the DOS plots. Horizontal green (blue) lines indicate E_F at the left (right) leads. Transmission features found within the transmission window between the green and blue lines contribute to the calculated current.

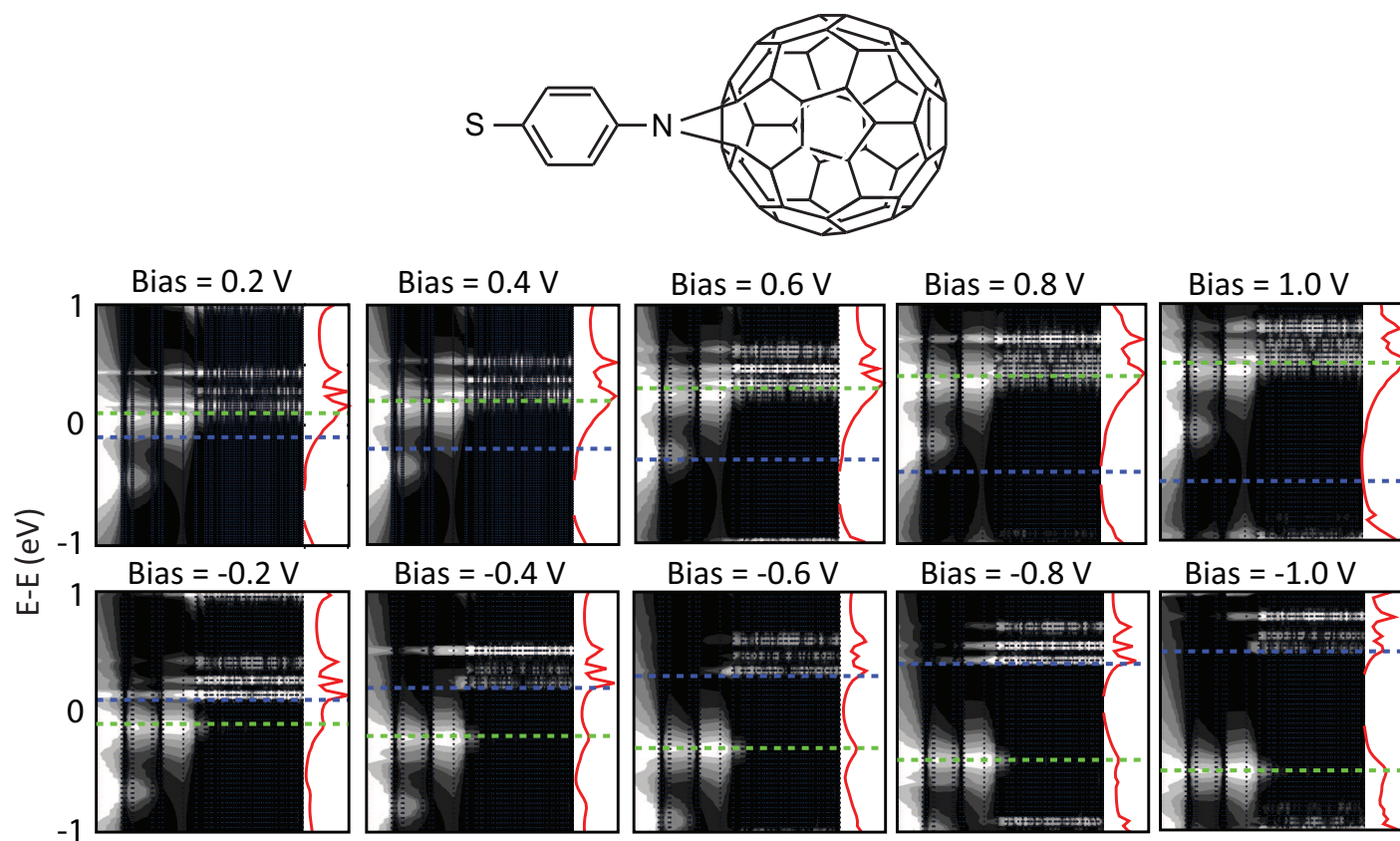
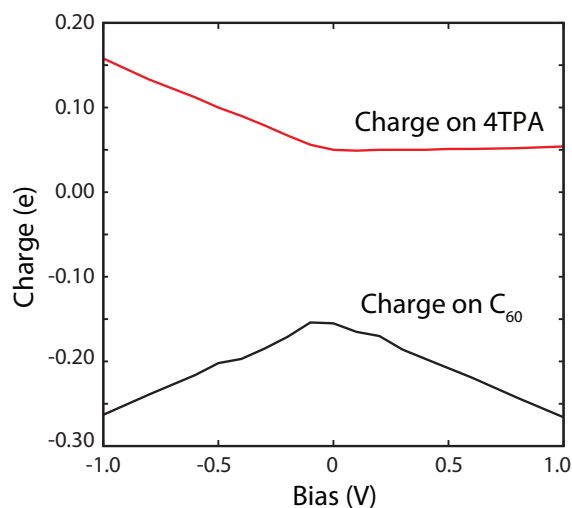


Fig. 5 Sum of Mulliken charges residing on 4TPA and C_{60} fragments after subtracting the nuclear charges. The partial positive charge ($\delta+$) residing on 4TPA becomes more positive at increasingly negative biases. In comparison, the partial negative charge ($\delta-$) residing on C_{60} becomes more negative as the magnitude of the applied bias increases in either direction.



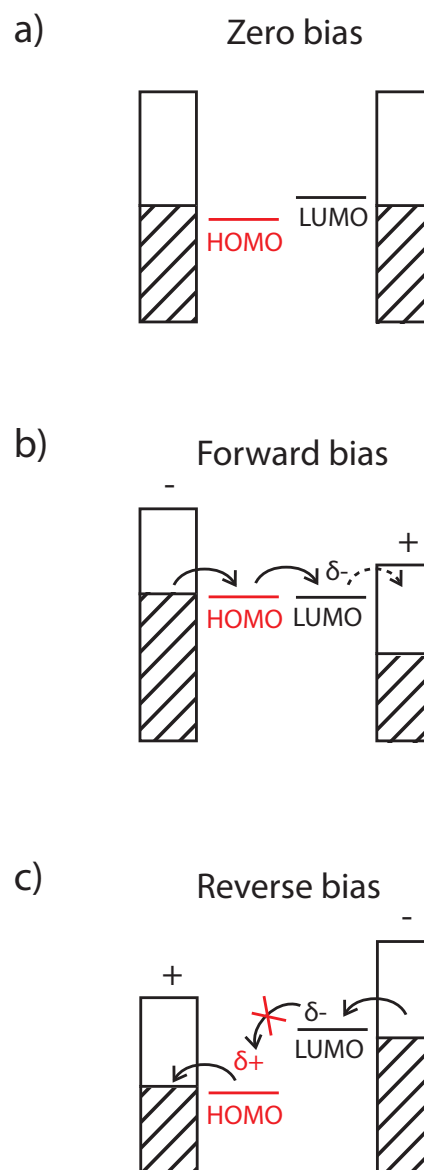
charge residing on each molecular fragment (Q_{4TPA} and $Q_{C_{60}}$) can be correlated as a function of the applied bias. The charge on the donor (Q_{4TPA}) remains almost constant in the forward bias, from $+0.050e$ at 0 V to $+0.054e$ at +1 V, but showed a large increase to $+0.158e$ at -1 V. In contrast, the partial negative charge residing on C_{60} ($Q_{C_{60}} = -0.155e$ at zero bias) has an almost symmetric response to the bias, reaching $-0.263e$ at -1 V and $-0.266e$ at +1 V.

From the calculated Mulliken charges and projected DOS, the asymmetric response of the HOMO-LUMO gap to the external bias is proposed to arise from unidirectional charge transfer from donor to acceptor within the 4TPA- C_{60} system (Figure 6). In the reverse bias regime, charge is extracted from the donor to the left electrode and injected from the right electrode to the acceptor. Poor charge transfer from C_{60} to 4TPA results in a $\delta+$ charge forming on 4TPA and a $\delta-$ charge forming on C_{60} . The charge buildup on the two fragments creates a large interface dipole between the 4TPA and C_{60} halves of the molecule, increasing the HOMO-LUMO gap and making the junction more insulating.

Conversely, under a forward bias, the rate of charge injection from the left electrode into the 4TPA fragment is approximately equal to the rate of charge transfer from 4TPA to C_{60} . As a result, Q_{4TPA} is not dependent on the magnitude of the applied voltage in the forward bias direction. However, transmission at the tip/ C_{60} interface is reduced due to the limited number of states on the monoatomic gold tip, and most of the electronic wavefunctions are reflected back into the fullerene cage.^{29,30} As a result, a $\delta-$ charge builds up on C_{60} , which raises the energy of the LUMO and prevents HOMO/LUMO level crossing. Preliminary simulations suggest that a stronger coupling between the gold contact and the C_{60} enables the HOMO and LUMO to cross more easily and a full analysis will be the subject of a future paper.

Charge redistribution has been used to rationalize a variety

Fig. 6 (a) HOMO and LUMO are pinned to the left and right electrode respectively (b) In the forward bias, the LUMO obtains a $\delta-$ charge due to charge redistribution from donor to acceptor. As a result, the LUMO becomes pinned to the HOMO energy, maintaining the conductive channel. (c) HOMO and LUMO remain pinned to the left and right electrode Fermi energies respectively under reverse bias. Charge redistribution from acceptor to donor cannot occur, hence a $\delta+$ and $\delta-$ charge is built up on the HOMO and LUMO respectively.



of physical effects observed in molecular electronic systems. At metal/organic interfaces, reorganisation of charge from filled to unfilled states results in alignment of the metal and organic energy levels.³¹ Charge redistribution can also give rise to rectification by exploiting the asymmetric response of the molecular dipole to an external electric field.³² However, it is important to understand the implication of charge transfer in the context of *U*-type devices, especially at the point where molecular states are driven into resonance. It is shown here that charge reorganisation is responsible for preventing HOMO/LUMO level crossing and, instead, gives rise to HOMO-LUMO pinning. Locking of the filled and unfilled states dramatically increases the efficiency of the rectifying device by maintaining the conductive channel over a wide bias window. Since the locking mechanism does not occur in the reverse direction, the current remains low, thus maximizing the rectification ratio. The mechanism proposed here further accounts for level crossing being observed in systems which involve only filled states (*e.g.* HOMO and HOMO-1),¹² as charge redistribution would not be effective when both states are already filled. Thus, to fully utilize the HOMO-LUMO pinning effect in the design of *U*-type molecular rectifiers, a new rule is added to the first three:

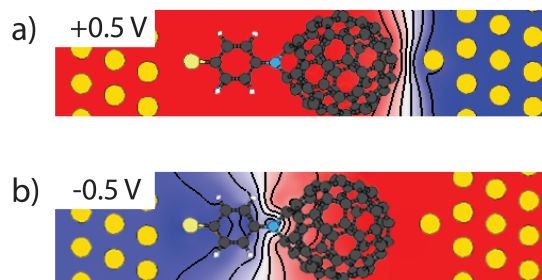
4. Charge transport should allow bias dependent coupling of filled to unfilled states.

Note that unlike pinning at the metal/organic interface, HOMO-LUMO pinning does not occur at zero-bias, but only when driven into resonance by an external potential. This difference arises due to the discrete energies of the molecular states compared to the wide bands at the metal interface. As a result, HOMO-LUMO pinning will only be observed when the energy gap is sufficiently decreased and the two states are driven into resonance.

Lastly, the new rectification mechanism is also studied by analyzing the electrostatic potential difference profiles of the molecular junction (Figure 7). The electrostatic potential difference is calculated as $V_H(B) - V_H(0)$, where V_H is the Hartree potential of the system at the applied bias, B . A voltage drop across the molecule is often regarded as a requirement for rectification, while a voltage drop at the molecule/electrode interface typically results in little to no rectification observed.³³ In the case of 4TPA- C_{60} , a unique switching behavior is seen in the location of the potential drop. Charge buildup on the LUMO of 4TPA- C_{60} in the forward bias regime results in a sharp potential drop at the C_{60} /right electrode interface. Under a reverse bias, the large potential drop is seen at the 4TPA/ C_{60} interface instead, due to the buildup of δ^+ and δ^- charges on the 4TPA and C_{60} , respectively. HOMO-LUMO pinning thus enhances rectification by switching the device between two regimes: a conductive regime where the voltage drop occurs at the molecule/metal interface and an insulating regime where the voltage drop occurs across the molecule itself.

Having fulfilled the three proposed design rules, 4TPA- C_{60} has been shown to behave as an effective single-molecule rectifier, with a large calculated rectification ratio of 145 obtained at ± 1 V.

Fig. 7 Electrostatic potential difference contour plots at +0.5 V (a) and -0.5 V (b). A large potential drop can be seen at the C_{60} /Au interface under a bias of +0.5 V. In contrast, the potential drop is seen between 4TPA and C_{60} when a bias of -0.5 V is applied.



Investigation of the rectification mechanism reveals an asymmetric response of the HOMO and LUMO with respect to the direction of the applied bias. The results show that a saturated bridge is not required to obtain high rectification ratios *via* control of molecular orbitals, in contrast to previous suggestions in the literature.^{10,22}

The asymmetric response of the HOMO and LUMO is attributed to unidirectional charge transfer from donor to acceptor within the molecule, which prevents HOMO-LUMO crossing at higher forward biases. This HOMO-LUMO pinning effect results in the molecule being able to switch between a conductive state under forward bias and an insulating state under reverse bias. In light of this discovery, a fourth design rule is proposed in the design of effective *U*-type molecular rectifiers: charge transport should allow bias dependent coupling of filled to unfilled states.

This rule is also consistent with other observations reported in the literature. *U*-type single molecule devices which involve the HOMO and LUMO states do not undergo level crossing^{6,10,34}, whereas studies of systems which involve two filled¹² (HOMO and HOMO-1) or unfilled³⁵ (LUMO and LUMO+1) states report crossing of the levels resulting in a NDR feature. While this study has helped to shed light on the HOMO-LUMO pinning mechanism responsible for highly effective single-molecule rectifiers, it raises an interesting question about the system. At what point in the forward bias regime do the HOMO and LUMO decouple again to form a NDR feature?

A fully decoupled HOMO-LUMO system should not be expected to display any pinning since no charge redistribution can occur between the two decoupled states. Preliminary investigation of a donor/acceptor biphenyl system indicates a dependence of HOMO/LUMO pinning on the coupling between the donor and acceptor fragments as parameterized by the dihedral angle between the phenyl rings (see Supporting Information). It is expected that the fourth rule is a necessary but insufficient condition in observing HOMO-LUMO pinning. It is therefore desirable to develop a more complete understanding of the interplay between the coupling at the three interfaces (metal/donor, donor/acceptor and acceptor/metal) in order to develop a framework for designing effective molecular devices. The impact of this study is thus

not only limited to the design of molecular rectifiers, but has broad implications for research into the next generation of electronic molecular devices such as double-well resonant tunnelling devices.⁴

Methodology. A plane-wave based code QUANTUM ESPRESSO³⁶ was first used to relax the geometry of the molecule on a gold slab (3 layers $\times$ 12 atoms) at the DFT/PBE level of theory³⁷. This supercell arrangement corresponds to a $2\sqrt{2} \times 2\sqrt{2}R30^\circ$ overlayer of 4TPA-C₆₀ on the Au(111) surface, which is typically seen in C₆₀ assemblies on Au(111) surfaces.³⁸ The gold atoms were frozen in the bulk arrangement during the optimization process for computational simplicity, which is common practice in the literature.^{5,10,39,40}

Once the optimized geometry was found, a second gold slab with a gold adatom was fixed 3 Å from the C₆₀ moiety on the top slab (Figure 2). This distance was obtained by relaxing the C₆₀ at the Au(111) interface. In the above calculations, a kinetic energy cutoff of 30 Ry and 240 Ry was used for the wavefunctions and charge density respectively. The electron-core interactions were modelled using RRKJ ultrasoft pseudopotentials⁴¹. A vacuum spacing of 10 Å along the z -axis was also added to simulate the slab structure. Forces were converged to a threshold of 10^{-5} a.u. and a $4 \times 4 \times 1$ regular grid mesh is used to discretize k -space.

An alternative code, TranSIESTA⁴², was used to simulate transport properties under finite bias in the NEGF-DFT framework. The equivalent slab geometry from above was used as the central scattering region for the transport calculations. The entire junction consisted of 12 layers of Au atoms (3 layers were used to simulate the left and right electrodes each) with the molecule placed in between (see Figure 3 for geometry of simulation cell). To speed up calculations, the transmission function was only calculated at the gamma point. As above, exchange and correlation were modelled with the PBE functional. All atoms were modelled using double- ζ -polarised (DZP) basis sets except Au atoms which were modelled with a single- ζ -polarised (SZP) basis set. Norm-conserving GGA (PBE) pseudopotentials were used to treat the electron-core interactions.

Although PBE functionals are known to underestimate the band gap, no significant differences in the ordering of the levels were observed when compared with calculations performed using B3LYP functionals (see Supporting Information). Thus, we do not expect the findings to change significantly with respect to the chosen functionals for the simulations.

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