Influence of the donor unit on the rectification ratio in tunnel junctions based on donor-acceptor SAMs

Manuel Souto,^{a,†} Valentin Díez-Cabanes,^b Li Yuan,^{c,‡} Adriana Kyvik,^a Imma Ratera,^a Christian A. Nijhuis,^{*cde} Jerome Cornil^{*b} and Jaume Veciana^{*a}

Dyads formed by an electron donor unit (D) covalently linked to an electron acceptor (A) by an organic bridge are promising materials as molecular rectifiers. Very recently, we have reported the charge transport measurements across self-assembled monolayers (SAMs) of two D-A systems consisting of the ferrocene (Fc) electron-donor linked to a polychlorotriphenylmethane (PTM) electron-acceptor in its non-radical (SAM **1**) and radical (SAM **2**) forms. Interestingly, we observed that the non-radical SAM **1** showed rectification behavior of 2 orders of magnitude higher than its radical analogue dyad **2**. In order to study the influence of the donor unit on the transport properties, we report herein the synthesis and characterization of two new D-A SAMs in which the electron-donor Fc unit is replaced by a tetrathiafulvalene (TTF) moiety linked to the PTM unit in its non-radical (SAM **3**) and radical (SAM **4**) forms. The observed decrease in the rectification ratio and increased current density for TTF-PTM based SAMs **3** and **4** in comparison to Fc-PTM based SAMs **1** and **2** are explained, supported by theoretical calculations, by significant changes in the electronic and supramolecular structures.

Introduction

Functional organic molecules anchored onto solid supports are of high interest for advanced molecular-controlled electronic devices with complementary features in areas including flexible electronics, memory devices, sensors, field-effect transistors or diodes.^{1–3} One of the advantages of molecular-based devices is the possibility to tune the device functionality via chemical modification of molecules inside these devices.^{4,5} It is still challenging, however, to optimize device performance of molecular junctions, such as, the value of R (defined as the ratio between the current in forward bias and the current in reverse bias) of molecular diodes.^{6,7}

The first theoretical proposal of a molecular rectifier by Aviram and Ratner in 1974 was based on a donor-acceptor (D-A) dyad formed by the electron-donor tetrathiafulvalene (TTF) unit linked to the electron-acceptor tetracyanoquinodimethane (TCNQ) through an insulating bridge.⁸ The idea to achieve molecular rectification was based on the asymmetrically positioning of energetically accessible molecular orbitals: the highest occupied molecular orbital (HOMO) localized on the donor and the lowest unoccupied molecular orbital (LUMO) localized on the acceptor. Charge transport is expected to occur at forward bias from one electrode to the LUMO, then to the HOMO, and finally to the second electrode. At reverse bias, the charge is transferred in the opposite direction but a larger potential is required to align the energy levels of the HOMO and LUMO with respect to the Fermi level of the electrodes to facilitate charge transport.⁹ Since the first experimental observations of rectification (see for an overview refs. ^{10,11}), values of R are often found to be low (below 100), but recently highly efficient molecular diodes have been reported with values of 10^3 to 10^5 .^{7,12–14}

During the last years, some of us have reported the detailed rectifying properties of SAM-based on alkanethiolates with ferrocene (Fc) head groups, observing that it is possible to obtain

large values of rectification ratio (R) with the presence of only one energetically accessible molecular orbital (the HOMO of the Fc).^{6,14–18} At positive bias, the HOMO of the molecules (centered on the Fc unit), which is slightly lower in energy than the Fermi levels of the electrodes, cannot participate in charge transport and the mechanism of charge transport is dominated by temperature-independent coherent tunneling. At negative bias, the HOMO can participate in the mechanism of charge transport and the mechanism switches to a temperature-dependent incoherent tunneling (hopping).^{6,14,17,18} Similar diodes with other redox-active groups have been reported since then.^{19,20}

Good control over the energy-level alignment of the molecular frontier orbitals with respect to the Fermi (E_F) level of the electrodes will therefore be mandatory in the design of new molecular diodes. The performance of a molecular diode also depends on the degree of asymmetry of the molecular component which is measured as the difference in the coupling parameter Γ_i (i indicates top (t) or bottom (b) electrode) of the molecular orbitals with the Fermi level of the electrodes, which, in turn, is directly related to the potential drop over the junctions. The asymmetry is parametrized with the dimensionless parameter $\eta_V = \Gamma_t / (\Gamma_b + \Gamma_t)$ and a junction rectifies when η_V is close to 0 or 1.^{17,21}

Besides the electronic structure of the molecule, it is also important to understand how the supramolecular structure of molecular junctions based on SAMs could affect the performance of the devices.^{22,23} In general, it is challenging to isolate electronic and supramolecular effects on the junction performance from one and the other since both are intertwined. Although most studies have focused in optimizing the energy level alignment of molecular junctions, we have found that defects in the SAM structure result in leakage currents that reduce the values of R considerably, despite good electronic configuration of the junctions.⁶

Recently, we reported the mechanism of charge transport across SAMs based on D-A systems consisting of a polychlorotriphenylmethyl radical (PTM), an electron-acceptor, linked to an electron-donor Fc unit. These junctions made it possible to study how the mechanism of charge transport was affected by the electron-acceptor in the open-shell or closed-shell electronic structure. Interestingly, the rectification ratio can be tuned depending if the PTM unit is in its non-radical (**1**) or radical (**2**) forms (Fig. 1). This has been inferred to the participation of the single-unoccupied molecular orbital (SUMO), lying close to the Fermi level of the electrodes, on the charge transport mechanisms, turning rectification off in the radical dyad **2**.²⁴

In order to gain a deeper understanding about the possible electronic and supramolecular effects of the donor unit on the rectifying properties, it is interesting to replace the Fc electron-donor by a TTF moiety in view of the more accessible redox states, conducting properties and lower oxidation potential values²⁵ which should yield a HOMO energy value closer to the Fermi level of the electrodes. During the past years, some of us have synthesized several D-A systems consisting in a PTM radical unit linked to a TTF moiety which exhibits bistability in solution,^{26–28} as well as nonlinear optical (NLO) properties²⁹ and conductivity in the solid state.^{30–33} However, in spite of such promising properties these compounds have never been anchored on solid substrates. Herein, we report for the first time the synthesis and preparation of SAMs based on two different TTF-PTM dyads, which can be in the non-radical (**3**) and radical (**4**) forms (Schemes 1 and 2), supported by ultra-flat template-stripped Au and contacted by an eutectic alloy of gallium and indium top contacts (EGaln; Fig. 1). The rectification ratio (*R*) decreases whereas the current density increases for both TTF-PTM SAMs **3** and **4** in comparison to SAMs based on Fc-PTM dyads **1** and **2**. Rationalizing why the rectification ratio decreases when substituting Fc by a TTF donor unit in dyads **3** and **4** is highly desirable to understand how the electronic and supramolecular structures influence the performance of the devices; these insights will help establish “failure modes” of molecular junctions⁶ and to design new molecular rectifiers.

Fig. 1. Schematic representations of the junctions based on Au bottom electrodes, SAMs **1–4** and Ga₂O₃/EGaln top electrodes.

Results and discussion

Preparation of dyads **3** and **4** and their SAMs

Non-radical dyad **3** was prepared as outlined in Scheme 1 and the syntheses of precursors **5** and **6** are described in the Supporting Information. First, the alcohol derivative **7** was obtained through a Wittig-Horner-Emmons reaction between the formyl-hydroxymethyl-TTF (**5**)³⁴ and the phosphonated PTM derivative (**6**)³² in 33% yield. The high stereoselectivity of this reaction gave the *trans* isomer of the vinylene bridge (Fig. S1), as observed for similar TTF-PTM dyads.^{26,30} The esterification reaction between the methyl alcohol **7** and the (±)- α -lipoic acid then gave compound **3** in a 65% yield, isolated as a reddish powder which was characterized by NMR (Fig. S2). Dyad **3** was obtained as a mixture of isomers *E/Z* which cannot be separated, as also reported for other similar TTF derivatives.³⁶

Scheme 1. Synthetic route for the preparation of non-radical dyad **3**.

Radical dyad **4** was synthesized as shown in Scheme 2 (see also SI). First, the subsequent deprotonation of **7** with tetrabutylammonium hydroxide (TBAOH) and the *in-situ* oxidation of the generated carbanion with silver nitrate gives **8** in 76 % yield. The radical dyad **4** is then obtained, as a mixture of *E/Z* isomers, through an esterification reaction between the methyl alcohol **8** and the ($\pm$)- α -lipoic acid in a 55 % yield and was fully characterized (See Fig. S3-S5).

Scheme 2. Synthetic route for the preparation of radical dyad **4**.

SAMs of dyads **3** and **4** were prepared following a previously reported procedure^{24,37} by immersion of template-stripped Au substrates in a 1.0 mM solution of **3** or **4** in toluene under nitrogen atmosphere, in the absence of light to avoid PTM radical decomposition. The SAMs were formed at 40 °C for one hour, after which the solutions were allowed to cool down and left at room

temperature for an additional 24-48 h. The functionalized gold substrates were rinsed thoroughly with anhydrous toluene to remove any physisorbed material and were dried under a nitrogen stream.

Characterization of supramolecular structure and electronic properties of SAMs

We characterized the SAMs of **3** and **4** by means of ion mass spectrometry (ToF-SIMS) (Fig. S6), electron spin resonance (ESR) (Fig. S7), cyclic voltammetry, X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption (NEXAFS).

Fig. 2 and Table 1 show the cyclic voltammetry data of SAMs derived from **3** and **4** on Au. The experiments were carried out with the functionalized substrate as the working electrode, and silver and platinum wires as the quasi-reference and counter electrodes, respectively. The cyclic voltammogram (CV) of SAM **3** shows two reversible redox peaks with formal redox potentials of $E_{1/2}^{\text{ox1}} = 0.48$ V and $E_{1/2}^{\text{ox2}} = 0.78$ V assigned to the oxidation process of the TTF moiety to $\text{TTF}^{\cdot+}$ and TTF^{2+} , respectively. In the case of SAM **4**, the two formal oxidation potentials related to the TTF moiety lie at $E_{1/2}^{\text{ox1}} = 0.45$ V and $E_{1/2}^{\text{ox2}} = 0.75$, and a reduction process with $E_{1/2}^{\text{red}} = -0.18$ is assigned to the reduction of the PTM radical unit to the corresponding carbanion. A schematic representation of the four different redox states of SAM **4** is shown in Scheme 3. In both SAMs **3** and **4**, the peak current (i_{pa}) increases nearly linearly with different scan rates (Fig. S8), which is characteristic of surface-confined electroactive species. The peak-to-peak separations ($\Delta E_p = E_{\text{anodic}} - E_{\text{cathodic}}$) are on the order of 60-70 mV at low scan rates for the different redox processes. The full width at half maximum (fwhm) for an imaginary system without any lateral interaction between the redox active molecules should be 90 mV and the ratio of the peak currents ($i_{\text{pox1}}/i_{\text{pox2}}$) the unity.³⁸ The deviations from the latter fwhm value thus gives information about the redox centers, especially related to their intermolecular interactions. In our case, the fwhm values of the first oxidation peak of dyads **3** and **4** are 142 and 177 mV, respectively, whereas these values are lower for the second oxidation peak (96 and 120 mV, respectively) (Fig. S9). This kind of CV shape has been observed in other TTF-based SAMs.³⁹⁻⁴¹ Indeed, Levillain and coworkers reported a detailed study on the deviation of both fwhm and ratio of the peak currents ($i_{\text{pox1}}/i_{\text{pox2}}$) from an ideal system as a function of the surface coverage for TTF SAMs on the basis of Laviron's model.³⁹

Table 1. CV data of SAMs **3** and **4**.

SAM	$E_{1/2}^{\text{red}}$		$E_{1/2}^{\text{ox1}}$			$E_{1/2}^{\text{ox2}}$			
	$E_{1/2}^{\text{red}}$ (V)	ΔE_p (mV)	$E_{1/2}^{\text{ox1}}$ (V)	ΔE_p (mV)	E_{FWHM} (mV)	$E_{1/2}^{\text{ox2}}$ (V)	ΔE_p (mV)	E_{fwhm} (mV)	$i_{\text{pox1}}/i_{\text{pox2}}$
3	N.A.	N.A.	0.48	70	142	0.78	58	96	0.6-0.7
4	-0.18	67	0.45	66	177	0.75	60	116	0.5-0.6

Integration of the oxidation wave gives the total charge from which the surface coverage of (1.2 ± 0.4) and $(1.1 \pm 0.4) \times 10^{-10}$ mol/cm² for SAMs **3** and **4**, respectively, was determined. These values are lower than the corresponding values for the related unsubstituted TTF SAM (2.2×10^{-10} mol/cm²)³⁸ and for Fc-PTM SAMs **1** and **2** (Table 2). This lower surface coverage could promote higher degrees of freedom for the molecules and hence the formation of more loosely packed SAMs in the case of dyads **3** and **4** than for **1** and **3**, likely because the SAMs were derived from a mixture of *E/Z* isomers of the disubstituted TTF units.

Fig. 2. CVs of a) SAM **3** and b) SAM **4** on Au recorded at different scan rates (100, 300, 500 and 700 mV/s) with 0.1 M LiClO₄ solution in acetonitrile as electrolyte. **Scheme 3.** Schematic representation of the four different electronic states of SAM **4**.

SAMs of **3** and **4** were also fully characterized by X-ray photoelectron spectroscopy (XPS). The C 1s spectra (Fig. S10a) are dominated by four peaks for both SAMs at 284.8, 285.8, 286.8 and 288.7 eV. These peaks are assigned to the aliphatic/aromatic, C-S, chlorinated and carbonyl carbon atoms, respectively. The S 2p spectra show two doublets characteristic of the S 2p_{3/2} and S 2p_{1/2} signals centered at 162.1 and 164.1 which are attributed to the S-Au bond and the sulfur atoms present in the TTF moiety, respectively (Fig. S10b).⁴² The intensity ratio between these two doublets is 1.8/4.2 and 1.7/4.4 for SAM **3** and SAM **4**, respectively, in agreement with the theoretical value of 2S(Au-S)/4S(TTF) (errors are ~4% as estimated from the fits of the peak of S2p spectra).^{37,43} The Cl 2p spectra of both SAMs (Fig. S10c) show a doublet with Cl 2p_{3/2} binding energy at 200.8 eV (C-Cl) which is typical for PTM-based SAMs.^{24,44} Au_{4f} high resolution spectra of both monolayers (Fig. S8d) show the expected doublet at 84 eV (Au 4f_{7/2}) and 87.7 eV (Au 4f_{5/2}) and gave us information about the thickness of both SAMs (~2.1 nm) (see Table 2 and Supporting Information).

Fig. S11 and S12 show the valence band spectra of SAMs **3** and **4** and the cut-off of the HOMO peak near the Fermi Edge (see Supporting Information for experimental details). The peak that appears near the Fermi edge (0.6 eV) is attributed to the HOMO orbital mainly localized on the TTF moiety since it appears at similar energies compared to other TTF-based monolayers.⁴³ The intensity of the HOMO peak in TTF-PTM SAMs **3** and **4** is lower in comparison to Fc-PTM SAMs **1** and **2** (Fig. S12), as has been previously observed for other SAMs based on TTF derivatives.⁴³ The bands of TTF-PTM SAMs at higher energies, which are related to the occupied orbitals from the PTM moiety, appear at similar binding energies as those of Fc-PTM SAMs **1** and **2** (see Fig. S12).²⁴

Table 2. Electronic and supramolecular properties of SAMs **1-4**. Molecular orbital energies defined with respect to vacuum.

	CV ^a		UPS ^b		NEXAFS ^c		XPS ^d	CV
SAM	E_{HOMO} (eV)	E_{SUMO} (eV)	WF (eV)	E_{HOMO} (eV) ^a	E_{SUMO} (eV)	E_{LUMO} (eV)	d (nm)	Γ_{SAM} ($\times 10^{-10}$ mol/cm ²) ^e
1	-5.19 ± 0.01	N.A.	4.40	-5.15	N.A.	-2.75	2.2 ± 0.2	1.50 ± 0.2
2	-5.15 ± 0.01	-4.36 ± 0.01	4.45	-5.10	-3.75	-2.85	2.3 ± 0.2	1.50 ± 0.2
3	-4.89 ± 0.02	N.A.	4.34	-5.02	N.A.	-2.75	2.0 ± 0.2	1.21 ± 0.4
4	-4.86 ± 0.02	-4.23 ± 0.02	4.30	-5.05	-3.75	-2.85	2.1 ± 0.2	1.10 ± 0.4

^a HOMO energies extracted from CV. The error bar represents the standard deviation from three independent measurements. ^b HOMO energies extracted from UPS with respect to vacuum. The error is ± 0.05 eV, which is the resolution of the UPS. ^c SUMO and LUMO energies are extracted from NEXAFS data. ^d Thickness of SAMs calculated from XPS data. The error is ± 0.2 nm, calculated from three independent experiments. ^e Surface coverage calculated from CV data.

The near edge X-ray adsorption fine structure (NEXAFS) spectra recorded around the C *K*-edge at normal and grazing incidences for SAMs **3** and **4** (Fig. S13) show an intense peak at 286.4 eV that has been assigned as C(Ph) $\rightarrow \pi^*$ resonance in the perchlorinated benzene rings.⁴⁵ The main difference between NEXAFS spectra of SAM **3** and SAM **4** is the small peak at 282.6 eV observed in the open-shell monolayer which is absent in the closed-shell monolayer. This peak has been assigned to the single unoccupied molecular orbital (SUMO) of the PTM radical units.^{24,45,46} At higher energies, the peaks around 289 eV and 288.4 eV can be attributed to C1s transitions into the π^* orbital of the carboxyl group. NEXAFS data were also used to extract the SUMO/LUMO energy levels for SAMs **3** and **4** (Table 2).

According to the UPS and CV data (see Supporting Information for experimental details), the HOMO energy levels for SAMs **3** and **4** are higher in energy (0.1-0.2 eV) than those for SAMs **1** and **2** (Table 1) whereas the SUMO/LUMO energy levels extracted from NEXAFS spectroscopy remain similar among the four systems. The peak related to the SOMO orbital localized on the PTM moiety in SAM **4** should appear at higher energies than the HOMO and overlap with the HOMO and HOMO-1 peaks, as supported by theoretical calculations (Table 3) and reported in previous studies.²⁴

Regarding the supramolecular properties of SAMs **3** and **4**, the surface coverage calculated from CV and XPS data was found 27 % lower of that calculated for Fc-PTM SAMs **1** and **2** (Table 2) in agreement with the CV data. This suggests that the TTF-PTM molecules are more loosely packed than in SAMs **1** and **2**. In addition, the reduced thickness of SAMs **3** and **4** of ~10% with respect SAMs **1** and **2** (see Table 2 and Supporting Information) indicates a possible variation of the tilt angle as a consequence of looser packing. Indeed, the tilt angles of TTF units from SAMs **3** and **4** are $\sim 23^\circ$ with respect to the surface normal, calculated from the NEXAFS spectra (see spectra in Supporting Information). Such small

tilt angles suggest SAMs **3** and **4** are in standing-up phase, therefore these SAMs are not disordered albeit with a lower packing density than SAMs **1** and **2**.

Electronic calculations of SAMs

We focus here on the nature of the frontier molecular orbitals of the isolated molecules (computed for the isolated SAM at low coverage) with disulfide end groups and how they change upon interaction with the metallic electrode (see Fig. S16). The lowest coverage has been chosen at first stage in order to discard the effects of the intermolecular interactions. Determining at the theoretical level the alignment of the molecular electronic levels with respect to the Fermi level of gold is a complex issue since it depends on the HOMO-LUMO gap of the isolated molecule, the nature of the anchoring geometry and the resulting strength of the orbital hybridization at the interface (see Fig. S17 and S20), image charge effects induced by the polarization of the metallic electrodes, and electronic shifts due to intermolecular interactions at relatively high coverage (see Fig. S18). Accordingly, we rely here only on the relative changes in the electronic structure when comparing the two molecules or when comparing the molecules before and after adsorption on the surface rather than absolute values. Note, however, that the added value of GGA functionals (see Supporting Information) is that the typical underestimation of the HOMO-LUMO gap of isolated molecules partly compensates the neglect of the image charge effects (since there is no explicit charge in our calculations) so that the theoretical data are expected to be semi-quantitative. Secondly, the energy level alignment in the SAMs has been calculated by studying the evolution of the MOs energy with the degree of coverage, i.e., with one ($\theta=0.25$), two ($\theta=0.5$), three ($\theta=0.75$) and four ($\theta=1$) molecules per unit cell (see Fig. S19). Since the experimentally calculated surface coverages correspond to values of $\theta_{\text{SAM1}} = \theta_{\text{SAM2}} = 0.80$, $\theta_{\text{SAM3}} = 0.62$ and $\theta_{\text{SAM4}} = 0.68$, we report in Table 3 the level energies for these specific degrees of coverage.

Table 3. Calculated energies of the frontier molecular orbitals of the SAM-forming molecules with respect to vacuum.

SAM	SOMO (eV)	HOMO (eV)	SUMO (eV)	LUMO (eV)
1	N.A.	-5.12	N.A.	-2.96
2	-5.22	-4.99	-4.07	-2.87
3	N.A.	-4.30	N.A.	-2.98
4	-4.76	-4.29	-3.96	-2.93

Table 3 shows the frontier molecular orbitals of the SAM-forming molecules, as calculated by interpolation to the experimental surface coverage (see Fig. S19). Note that these energies have been corrected to be properly aligned with the experimental Au Fermi level (-4.2 eV) to ease the comparison with CV and UPS measurements. The SUMO level localized on the PTM radical in the open-shell form SAM **2** lies close to the experimental Au Fermi level (~ 0.13 eV above the Fermi level) whereas the HOMO of SAM **1** and SAM **2** molecules, localized on the Fc units, are located further away (~ 0.92 eV and ~ 0.79 eV below the Fermi level, respectively) (Fig. 3 and Fig. S18). This is consistent with the NEXAFS and UPS measurements (see Table 2) yielding the SUMO level closer ($\sim +0.45$ eV) to the Au Fermi level than the HOMO of SAM **1** (~ -0.95 eV).²⁴

In the case of SAMs **3** and **4**, both SUMO and LUMO levels display similar offsets as the Fc-PTM SAMs which are ~ 0.11 eV and ~ 0.04 eV above the Fermi level, respectively (Table 3). Moreover, the calculated energy difference between the SUMO and LUMO is also consistent with the NEXAFS data (1.03 eV (Table 2) versus 0.90 eV (Fig. S16), respectively). The HOMO energy levels for TTF-PTM SAMs **3** and **4** are found to be closer to the Fermi level than in the Fc-PTM SAMs **1** and **2** (by 0.7-0.8 eV, see Table 3), in agreement with the observed trends in the experimental values inferred from CV and UPS measurements and also with other values reported for Fc⁴⁴ and TTF⁴⁵ systems.

Fig. 3 sheds light on the shape of the frontier electronic levels of the different SAMs. Note that the levels localized around the anchoring group and strongly hybridized with the Au orbitals⁴⁶ are not discussed here since they generate gap states strongly localized at the metal/organic interface which will not contribute to the transmission properties.⁴⁷ Only the levels with a significant delocalization over the D-A units will give rise to a significant transmission, and hence will contribute to the transport across the junction.

In the studied D-A SAMs, the LUMO/SUMO/SOMO orbitals are mostly localized over the acceptor (PTM) unit and the HOMO over the donor Fc/TTF part, as expected from the D-A character although there is in each case enough delocalization over the whole D-A unit to guarantee a good electronic transmission. Interestingly, the HOMO level in SAM **1** is strongly localized on the Fc unit (92.8%) whereas the HOMO in SAM **2** is more delocalized over the PTM unit and the vinyl bridge (24.6%) due to the change of hybridization to sp^2 of the carbon atom, thus yielding in the case of the open-shell form two interesting results (*vide infra*): (i) a more symmetric I/V curve with respect to bias by avoiding a strong asymmetric

positioning of the HOMO orbital within the junction; and (ii) a higher current due to the extended delocalization of the transporting level. The HOMO levels in SAM **3** and SAM **4** are highly localized on the TTF unit (97.1% and 95.2% respectively), whereas the LUMO/SUMO levels show a high delocalization (52.3% and 62.1% respectively). In this case, there are no major differences in orbital delocalization when going from the closed to open-shell forms.

Fig. 3. Shape of the frontier orbitals for the SAMs **1** to **4** (from left to right) adsorbed on Au. The gap states are not reported here. The isovalue used was 0.02 a.u. The corresponding energy levels are reported in Fig. S16.

Charge transport measurements with molecular junctions

We fabricated stable and reproducible molecular junctions based on SAMs **3** and **4** on template-stripped gold (Au^{TS}) bottom electrodes and eutectic indium-gallium (EGaIn) top electrodes using previously reported methods. Here, the EGaIn is a non-Newtonian liquid metal that forms non-invasive contacts to SAMs. On EGaIn, a 1 nm highly conductive Ga_2O_3 forms spontaneously which provides mechanical stability and prevents the bulk EGaIn from alloying with the gold contact.^{9,51} Charge transport measurements across the junctions were measured in the bias window of ± 2.0 in steps of 0.05

mV (Fig. 4). We measured more than 450 of $J(V)$ curves for each type of junction (Table 4). All junctions were fabricated, and all data were recorded and analyzed, following previously reported procedures^{24,52} (see SI). In short, for each applied V , we plotted all measured $\log_{10}|J|$ in histograms to which we fitted Gaussian to obtain the Gaussian log-average values of J , $\langle \log_{10}|J| \rangle_G$, and the log-standard deviation. These values were used to construct the $\langle \log_{10}|J| \rangle_G$ vs V curves shown in Fig. 4. We determined the Gaussian log-average values of R at ± 2.0 V by and the log-standard deviation of R ($\delta_{\log}$), by fitting Gaussian to the histograms of R (Fig. 4C and D).

Fig. 4. *Top:* Semi-log plot of the absolute current densities, $|J|$ (A/cm²), plotted vs bias voltages (V) of a) the junctions Au^{TS}-SAM 3//Ga₂O₃/EGaIn and b) Au^{TS}-SAM 4//Ga₂O₃/EGaIn (B). *Bottom:* Histograms with a Gaussian fit of the rectification ratio (R) of c) the junctions based on SAM 3 and d) on SAM 4 at ± 2.0 V.

Table 3 shows that the value of R for junctions with SAM 3 is about 7 times lower than for junctions with SAM 1. In addition, the values of J (Table 3) from junctions with SAM 3 are 2 orders of magnitude higher than those for junctions with SAM 1 despite that both types of SAMs have very similar lengths. In a series of studies, we have shown that structural disorder in the SAMs can lower the value of R drastically due to an increase on the off-currents (here at positive bias). As discussed before, the CV and XPS data indicate that SAMs 3 and 4 have a lower surface coverage than SAMs 1 and 2, indicating that the former suffer from structural disorder probably due to the presence of the mixture of *E/Z* isomers of the disubstituted TTF units. We believe that this structural disorder lowers the value of R in junctions with SAM 3 relative to those with SAM 1. Junctions with SAM 3 have 2 orders of magnitude higher on currents than junctions with SAM 1. Our previous studies on Fc-based diodes indicated that structural disorder can account for about one order of magnitude change in the values of the currents at forward bias, but not two orders of magnitude. Junctions with SAM 4 (with the PTM in the radical form) have a factor of 10 smaller values of R than those junctions with SAM 3 (with the PTM in the non-radical form). Thus, as in the case of junctions with SAM 1 and SAM 2, the redox-state of the PTM can be used to switch

rectification on and off. Therefore, we believe that the high values of J for junctions with SAM 3 are caused by both electronic effects and supramolecular disorder resulting in leakage currents; the latter also lower the values of R . It is worth to note that the main electronic difference between SAMs 1-2 and 3-4 is that the HOMO localized on the TTF moiety is 0.3 eV (CV data in Table 3 and in agreement with the DFT calculations, Fig. S16) closer to the Fermi level in comparison to the Fc and this should lead, for a given bias, to a higher current density in the case of the TTF derivatives. Nevertheless, we cannot rule out that junctions based on dyads 3 and 4 can be dominated by leakage currents (i.e., currents flowing across the diode in the off state) which could also explain the increase in current density despite a decrease in surface coverage.^{22,23} All these findings are corroborated by DFT calculations discussed below.

Table 4. Statistics of the data for SAMs 1-4 junctions.

Parameter	SAM 1 ^a	SAM 2 ^a	SAM 3	SAM 4
Number of junctions	25	20	21	26
Number of shorts	3	1	2	4
Number of traces	528	456	504	624
Non-shorting junctions (%)	88	95	90.5	84.6
$J(-2V)/J(+2V)$ (A/cm ²)	$10^{-3}/10^{-5}$	$10^{-1}/10^{-1}$	$10^{-1}/10^{-1.5}$	$10^{-1}/10^{-1}$
Rectification ratio ($\delta_{\log}$)	99 (0.7)	5.6 (0.6)	13 (0.29)	1.2 (0.33)

^a Data from ref. 24

Calculations of transmission properties and $J(V)$ characteristics of junctions

To rationalize the experimentally observed current densities and rectification ratios, we performed further calculations adding a second electrode on top of the SAMs to investigate the voltage dependence of the transmission spectra as well as the $J(V)$ characteristics (see Supporting Information for more details). The calculations are limited here to single molecule junctions to assist the interpretation of the experimental data. Since the crystalline structure of the Ga₂O₃/EGaIn electrode is very difficult to be reproduced with Periodic Boundary Conditions (PBC), we have considered here a model system where the Ga₂O₃/EGaIn top electrode has been substituted by an Au electrode. Note however that measurements made with EGaIn junctions and conductive probe Atomic Force Microscopy (cp-AFM) using an Au tip have shown different absolute values in terms of current intensity due to difference in the effective contact areas, but similar trends charge transport behavior.⁵³ The top Au electrode was placed in a van der Waals contact with the top of the molecule (see section 4.2 of the SI for more details). The evolution of the transmission spectra of the studied SAMs 1-4 under bias is presented in Fig. 5.

Fig. 5. Evolution of the transmission spectra with bias (positive above and negative below zero) for SAM 1, SAM 2, SAM 3, and SAM 4 (from top to bottom). The continuous and dash lines of the SAM 2 and SAM 4 graphs represent the spin up (α) and spin down (β) contributions, respectively. The bias step used was 0.4V. Dashed

straight lines show the trend evolution of the HOMO at different bias.

In a first stage, we have compared the calculated transmission and $J(V)$ values (see Methodology in SI) through the Fc-PTM SAMs between the closed and open-shell forms (1 and 2, Fig. 5 and 6 top). In the case of the open-shell form (SAM 2), the transmission is divided into the spin up (α) and spin down (β) contributions. The main difference obtained for SAM 2 when compared to SAM 1 lies in the appearance of a single occupied (SOMO for spin up (α)) and unoccupied level (SUMO for spin down (β)). Focusing first on the spin down (β) contribution, the $J(V)$ curve of SAM 2 (SAM 2- β) shows a current increase when the SUMO enters the bias window around 0.5 eV whatever the polarity. As a consequence, the SUMO dominates transport for both bias and the $J(V)$ curve is highly symmetric $R_{\text{SAM2-}\beta}(2V) = 2.6$. On the other hand, for the spin up (α) contribution, since the SOMO lies below the HOMO, the charge transport is dominated by the HOMO level. This same level also dominates the transport in the closed-shell form SAM 1. However, as in SAM 2, the HOMO is more delocalized over the Fc-PTM dyad, there is an increase in current intensity and a more symmetric charge transport with respect to SAM 1, yielding a rectification ratio $R_{\text{SAM2-}\alpha}(2V) = 27.5$, one order of magnitude lower than the value obtained for SAM 1, $R_{\text{SAM1}}(2V) = 383.7$. This difference in the $J(V)$ curves symmetry between the two forms has been measured as the ratio between closed- and open-shell rectification degrees and is found to be very similar at both experimental and theoretical levels (17 vs 14 by considering only the α contribution giving rise to the largest rectification).

In order to understand the role of the HOMO localized on the Fc in a spatially asymmetric junction (as in SAM 1) over the rectification ratio, we have calculated the transmission spectra and $J(V)$ curve for the SAM including only the donor Fc unit without any PTM unit (see Fig. S21 and S22). This system gives rise to a high rectification ratio calculated theoretically equal to $R = 91.3$, which is about a factor 2 higher than the value of $R = 41$ measured experimentally in our previous work,²⁴ but very similar to values of R of 100 for $\text{S}(\text{CH}_2)_n\text{Fc}$ of similar length. We attribute this difference in R for junctions with Fc SAMs derived from alkanethiols (surface coverage = $4.8 \times 10^{-10} \text{ mol/cm}^2$) and disulfides (surface coverage of $4.2 \times 10^{-10} \text{ mol/cm}^2$) due to the difference in surface coverages between these two systems probably due to the steric hindrance of the ester group.^{22,23} In summary, the theoretical results rationalize the higher current across the junction and the lower rectification ratio in the open-shell form, SAM 2, with respect the close-shell form, SAM 1, observed at experimental level.

Next, we analyzed theoretically the TTF-PTM SAMs in the closed- vs. open-shell configurations (Fig. 5 and 6 bottom). As in the previous case, the open-shell form (SAM 4) yields two contributions for the current arising from the two spin α and β orientations. The $J(V)$ curve of spin down (β) SAM 4 (SAM4- β) shows a SUMO resonance around 0.15 eV for both bias while the HOMO resonance is located 0.1 eV below the Fermi level. Consequently, the charge

transport is dominated by these two levels in the entire applied bias range, resulting in flat $J(V)$ curves and a similar rectification ratio compared to SAM2- β equal to $R_{\text{SAM4-}\beta}(2V) = 3.5$. In contrast, the spin up (α) contribution follows the same behaviour as in SAM 3: the HOMO level is resonance with the Au Fermi level at any bias and the LUMO level enters inside the voltage window around 1.4 eV for both bias. The similar orbital patterns of the HOMO and LUMO in SAM 3 and 4 results into a low rectification ratio in both cases: $R_{\text{SAM3}}(2V) = 1.2$ and $R_{\text{SAM4-}\alpha}(2V) = 8.1$. Interestingly, the theoretical results yield a current much larger (10^{-1} - 10^{-2} A) for TTF derivatives for almost all biases, thus suggesting that experimental trends can be rationalized by the changes in the electronic structure of the SAMs without necessarily invoking leakage currents.

When comparing the closed-shell form (SAM 1 and 3) of Fc-PTM versus TTF-PTM SAMs (Fig. 5 and 6 left), the more asymmetric transport through SAM 1, the smaller offset of the HOMO level in SAM 3, and the participation of the LUMO level in SAM 3 concur to a higher current and lower rectification ratio of the TTF-PTM SAM with respect to Fc-PTM-based SAM. These results point to the huge influence of the nature of the donor substituent in the measured charge transport characteristics.

Fig. 6. Calculated $J(V)$ curves for a) SAM 1, b) SAM 2, c) SAM 3 and d) SAM 4. The continuous and dashed lines for SAM 2 and SAM 4 represent the spin up (α) and spin down (β) contributions, respectively

Conclusions

In summary, we have reported the preparation and characterization of new self-assembled monolayers SAMs 3 and 4 on gold of a D-A system based on the electron-acceptor PTM unit, in its open-shell and closed-shell forms, linked to the electron-donor TTF unit by a vinylene bridge. Moreover, an exhaustive characterization of the SAMs were performed in

order to determine the energy values of the HOMO and SUMO/LUMO orbitals localized on the donor and acceptor moieties, respectively. It was concluded that the HOMO energy levels of TTF-PTM dyads 3 and 4 were lower in energy in comparison to those of Fc-PTM dyads 1 and 2. In addition, EGaIn junctions with SAMs of 3 and 4 showed a lower rectification ratio and increased current density compared to SAMs 1 and 2 based on the Fc-PTM SAMs. The difference in the charge transport properties can be explained by taking both electronic and supramolecular effects present in these monolayers into consideration. On the one hand, the HOMO localized on the TTF moiety is aligned closer to the Fermi level in comparison to Fc and, thus, can be in resonance over the entire applied bias range. Thus our results strongly suggest that a change in the electronic structure is important. On the other hand, the supramolecular characterization of TTF-PTM SAMs points to a higher disorder than in the case of Fc-PTM SAMs that could cause leakage currents and reduction of values of R . Our results demonstrate that here supramolecular effects can only explain our observations partially and thus electronic effects are important for these D-A system. The energy level alignment in SAMs as well as $J(V)$ characteristics of the junctions were qualitatively rationalized by theoretical calculations. This work shows that the choice of the donor unit in D-A based SAMs as well as the optimization of both electronic and supramolecular structures have to be taken into account for the rational design of donor-acceptor molecular diodes.

Conflicts of interest

There are no conflicts to declare.

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