Molecular diodes usually exhibit fixed current values at a specific bias and achieve sizable rectification ratio (RR) at voltages of ~1.0 V. Here, a series of custom-designed molecular films of ferrocenyl/ruthenocenyl-substituted biphenylthiolates and fluorenethiolates on Au (111) is presented, which exhibit a distinctly different behavior. When embedded into two-terminal junctions, they show two different conduction states, with a high conductivity state at a negative bias and a low conductivity state upon applying a sufficiently high positive bias. Comparing the current values for these two states, an effective RR of more than 1000 is obtained, a value comparable to the best performing molecular diodes but attained already at particularly low voltages. Significantly, the switching between the conduction states is reversible and the initial, high conductivity state can be recovered by the application of a negative bias. The proposed explanation for these observations is the bias-induced switching of the junction to a metastable state comprising oxidized ferrocenyl/ruthenocenyl entities, which are characterized by less delocalized frontier orbitals and cause the formation of a significant potential barrier within the junction. It is hypothesized that this state can be stabilized by structural changes in the monolayers, affecting also their coupling to the top electrode.

1. Introduction

The continuous demand for a miniaturization of electronic devices requires new approaches for their design and fabrication. A promising strategy in this context is provided by molecular electronics, employing individual molecules and their assemblies as functional units of circuitry, which perform specific electronic and sensing functions. Molecular rectifiers represent an important element for such a strategy, being potentially capable of becoming an alternative to current Si-based devices, carrying out a variety of functions in electronic circuits, such as signal processing, logical operations, and data storage. Generally, the design of molecular rectifier requires some sort of asymmetry in the junction, realized either by distinctly different couplings of the molecules or molecular films to the two connecting electrodes and/or by an asymmetric molecular structure. A promising strategy for realizing such a situation, which is also particularly relevant in the context of the present paper, is based on combining ferrocenes with aliphatic or hybrid aliphatic-aromatic backbones. This resulted in a family of molecular rectifiers with high rectification ratios (RRs). The first example of a ferrocene-based rectifier relied on self-assembled monolayers (SAMs) of 11-(ferrocenyl)-1-undecanethiol on Ag, embedded into a two-terminal junction with a eutectic GaIn (EGaIn) tip as top electrode. This allowed RRs of 90–180. This rectification was explained by negative biases modifying the electronic level alignment such that beyond a certain voltage the highest occupied molecular orbital (HOMO) of the ferrocenyl (Fc) enters into the conduction window. As a consequence, one observes distinctly higher currents for applied negative compared to positive bias voltages. Further studies revealed a strong dependence of the rectification behavior on the substrate type, on the character of the top electrode, on the structure of the molecular backbone, on the exact position of Fc in the backbone, on the orientation of the Fc unit, and on the SAM quality. Further improvements could be realized by enhancing the molecular asymmetry when combining two Fc units. For an Fc-based SAM on Ag at 1 V bias in these studies, a RR of 1.1 × 10^3 was recorded, which is comparable to the best molecular rectifiers relying on alternative designs and functional groups. Even RRs exceeding 10^5 were reported for Fc-based monolayers on Pt, but these extremely high values were observed only at...
a comparably high bias voltage of 3V.\textsuperscript{[9]} In contrast, the junctions comprising Fc-decorated molecules on Au yielded noticeably lower RRs, varying between 0.5 and 89 for a bias voltage of 1 eV, with the exact RR value depending on the details of the molecular structure and the quality of the SAM. These observations were explained by variations of the orientation of the terminal Fc moiety relative to the top EGaIn electrode as a function of the length of the aliphatic linker and by leakage currents flowing across defective parts in the monolayers.\textsuperscript{[8,11,12]}

The above results were obtained for SAMs consisting of molecules in which the Fc’s were either combined with an aliphatic backbone or in which the aromatic part of the backbone was decoupled from the Fc by an aliphatic linker.\textsuperscript{[12,13]} Notably, fully conjugated backbones directly linked to ferrocenes have, to the best of our knowledge, not yet been studied as molecular rectifiers, even though other π-conjugated oligomers incorporating redox-active groups have been reported.\textsuperscript{[17–20]}

In the present study, we investigate transport through monolayers of a family of metallocene-substituted biphenyl and fluorene ethynyl thiols (Figure 1a). In the past, such monolayers were studied in the context of self-assembly and electrochemical properties,\textsuperscript{[21–23]} but, to the best of our knowledge, their charge transport properties are unknown. In view of the extensive literature on ferrocene-containing junctions, we focused on Fc-based SAMs, but also studied analogous ruthenocenyl (Rc)-based systems, as also ruthenium complexes have been reported to have promising molecular rectification properties.\textsuperscript{[24–26]}

Monolayers built from the molecules shown in Figure 1a display a number of exceptional properties: First, they exhibit two pronounced conduction states, viz. a high conductivity state at negative bias and a low conductivity state triggered by applying a sufficiently large positive bias. Second, this switching is reversible and the initial, high conductivity state can be recovered by applying a negative bias voltage. Third, comparing the current density values for both conduction states, one gets effective RRs exceeding 1000 at very low bias voltages starting around 0.05 V. Note that the term “effective RR” reflects the specific character of our systems, where the conductivity for positive biases switches as a consequence of the exposure to sufficiently large positive bias values, as will be detailed below.

2. Results
2.1. Currents for Applying Either Positive or Negative Biases
For the following investigations, the molecules were assembled as SAMs on Au(111) substrates, which also served as bottom electrodes (see Experimental Section). The top electrodes were formed by EGaIn tips, stabilized by a ~0.7 nm thick Ga2O3 overlayer\textsuperscript{[27]} (Figure 1b). The bias was varied from 0 to either ~1.05 V or to +1.05 V. The log |J| versus V plots for the Fc-BPT and Rc-FluT SAMs (J is the current density in the junction) are shown in Figure 2a,b, together with the calculated effective rectification ratios defined as \(RR = |J(−V)|/|J(+V)|;\) the analogous data for the Rc-BPT and Fc-FluT monolayers are shown in Figure S1 (Supporting Information) and reveal a virtually identical behavior of these SAMs. At this stage it is important to stress that the values in the plots represent statistical averages over a large number of scans after the exclusion of curves showing a strongly deviating behavior (see Figures S2–S9 and Tables S1–S4, Supporting Information), which is the standard way to measure and to process \(I–V\) data for molecular junctions. As a consequence, the displayed averages represent the situation of a junction that has been repeatedly subjected to either positive (or negative) voltages of up to 1.05 V (~1.05 V), an aspect that will become relevant later, when discussing the conductivity switching. The detail of bias sweeping between negative and positive biases will be discussed in section 2.2.

For all studied SAMs, the log |J| versus V plots show significantly higher current density values at negative than at positive bias, which is also the case at very small bias values. The respective log RR values vary from ~2.3 at 0.05 V to a maximum value of ~3.3 at a bias of 0.2–0.25 V. The observation that the exceptional behavior regarding both J and RR values is essentially the same for all studied SAMs can be tentatively rationalized by the
similar structures of the SAM-forming molecules (Figure 1a) and similar charge transport properties of biphenyl and fluorene backbones.[28]

To ensure that the observed behavior stems from the presence of the Fc and Rc units, the charge transport characteristics of the Fc/Rc-substituted SAMs are directly compared to that of a biphenylthiolate (BPT) monolayer (Figure 2c), as the non-substituted analogue of the Fc-BPT and Rc-BPT SAMs. As expected,[29–31] the BPT monolayer, measured in the same fashion as the Fc/Rc-substituted SAMs, does not exhibit a noticeable rectification or a noticeable difference of the log |J| values at small negative versus positive voltages (Figure 2c).

Note that the analogous behavior is also displayed by F-, CH3-, and CF3-substituted BPT SAMs on Au(111),[30,31] once more underlining the decisive role of the redox-active Fc and Rc units for the observed, highly asymmetric I–V curves of the respective films.

Interestingly, the absolute values of log |J| for the Au/Fc-BPT/Ga2O3/EGaIn and Au/BPT/Ga2O3/EGaIn junctions in the negative bias range are very close to each other, despite the much longer molecular backbones of the Fc-BPT molecules. We tentatively explain this behavior by a better coupling of the Fc tail groups of the Fc-BPT SAM to the EGaIn electrode compared to the BPT case (it is well known that the identity of the tail group can affect currents in molecular junctions considerably, independent of the molecular length).[29–31] In particular, the curves for the Fc-BPT and BPT monolayers have nearly identical shapes between 0 and −0.5 V. For further increasing negative biases, the current in the Fc-BPT SAM rises more steeply, resulting in even higher log |J| values compared to the BPT case. Here, the value of −0.5 V corresponds coarsely to the transition voltage of the Fc-BPT SAM (for its determination see Figure S11 and Table S5, Supporting Information). In the present case, this value is most likely indicative of the involvement of the Fc HOMO in the charge transport process, similar to the model explaining the rectification behavior of Fc-substituted alkanethiolate (AT) SAMs (hopping transport between the EGaIn electrode and Fc HOMO at a sufficiently high negative bias).[5,6] This similarity is, however, only observed for negative biases, while the distinct drop in conductance in Fc/Rc-substituted SAMs at positive biases does not occur in the Fc-substituted alkanethiolate SAMs.[5,6]

2.2. Bias Dependence and Reversibility of the Switching

A further in-depth analysis reveals that the low log |J| values at positive biases for the Fc and Rc containing SAMs represent the averages over a large number of scans (vide supra), but do not reflect the initial states of the junctions. This is illustrated in Figure 3a,b for the example of a series of subsequent J versus V scans for the Fc-FluT and Rc-FluT SAMs (see Figure S12,
Supporting Information for the analogous data for the BPT-based monolayers. At very low positive biases, the first scan starts with the same log $|J|$ values as for very low negative biases but, with increasing positive bias, the current first saturates and then even decreases. The second scan then already starts from much lower $J$ values than the first one and is already rather similar to the averaged log $|J|$ versus $V$ curves in Figure 2 and Figure S1 (Supporting Information). This means that the major change in the conduction state of the monolayer occurs already during the first scan. For the next few scans, the current values further drop slightly, until they fully stabilize after 6–7 scans.

To understand, which positive bias is necessary to trigger the switching, we varied the bias only within a limited range and monitored the $J$ versus $V$ behavior, applying, similar to the data in Figure 2, a statistical analysis of a large number of scans. The bias range was then increased in several steps. The respective data for the Fc-FluT and Rc-FluT SAMs are presented in Figure 4a,b and Figures S13 and S14 (Supporting Information). According to these data, for the Fc-FluT SAM the bias variation up to +0.55 V (and up to a slightly lower value for the Rc-FluT monolayer) does not result in any bias-mediated switching of the electrical conductance. In fact, in the Rc-FluT case some of the +0.55 V curves show the original behavior while others already show lower current values, which indicates that this is exactly the bias at which the switching occurs such that depending on minute variations in different junctions applying a voltage of +0.55 V either already triggers the switching or not. To further illustrate that, an example of the respective bimodal distribution is shown in Figure S14 (Supporting Information). An increase of the bias beyond these ranges leads to a decrease of the current values. This decrease occurs in a successive fashion: the higher the maximum applied bias, the lower the current values become, until the final values similar to those in Figure 2a,b and Figure S1 (Supporting Information) are reached.

Notably, in accordance with the data in Figure 4, sweeping between moderate negative and positive bias values, such as between −0.5 and +0.5 V, does not result in the appearance of the low conductance state (see Figure S15, Supporting Information), thus, resulting in nearly symmetric $I$–$V$ characteristics.

To understand, whether the bias-induced switching is the consequence of some irreversible change in the junction, we studied to what extent the low conductance state can be converted back to the initial high conductance state by (several successive) scans at negative bias. The respective data for the Fc-FluT and Rc-FluT SAMs (as representative examples for the entire series) are presented in Figure 3c,d (see also Figure S16, Supporting Information). For these experiments, the samples were first brought into the low conductance state by scanning at positive biases. Then they were scanned at negative bias from 0 to −1.05 V, with the data for successive individual scans displayed in the plot. The current remained low during...
the first few scans (i.e., initially the SAM is in a low conductance state also for negative biases with currents roughly similar to the positive bias case). Upon further scanning the bias, the current sometimes exhibited a discontinuity, changing its value abruptly (see, e.g., the green and yellow curves in Figure 3d). However, after several subsequent scans at negative bias, the high conductance state was restored nearly completely. In contrast, when no scanning in the negative bias range was performed, the SAMs remained in the low-conductance state, as verified by measurements on the Au/Rc-FluT//Ga$_2$O$_3$/EGaIn junction (see Figure S17, Supporting Information).

3. Discussion

The data in Figures 3 and 4 are also insofar relevant, as they show that the asymmetry of the curves in Figure 2a,b and the reported effective $RR$ are not due to a pronounced intrinsic current anisotropy of the SAMs. Consequently, Figure 2a,b rather represent the characteristics of the junction for stable positive and stable negative bias operation, i.e., the reported data are in particular representative of a high conductivity state at negative bias and a metastable low conductivity state that occurs in the junction for positive bias. In that sense, the bias-triggered switching and effective rectification observed here differ from the behavior reported for the analogous aliphatic and hybrid Fc-substituted monolayers, where the measured rectification has not been associated with any type of switching such that for the reported experimental conditions fixed current values for specific biases were observed.$^{[5–12,14]}$ Moreover, in contrast to the data in Figure 2a,b, for traditional Fc-substituted monolayer junctions no hugely different currents at small negative versus positive voltages were reported. The observation of such a difference in the present junctions shows that here the switching-induced effective rectification is apparently operative already at very small biases.

This leaves the question, which mechanisms cause the peculiar behavior of the SAMs studied here. The standard mechanisms of molecular rectification involve donor-accepter assemblies,$^{[32]}$ asymmetric level shifting by the electric field and through the charging energy,$^{[33,34]}$ and a combination of both these effects.$^{[35]}$ For ferrocene-substituted SAMs, the most accepted model is a shift of the HOMO into the conduction window at a sufficiently high negative bias.$^{[5,6]}$ In our opinion, all these models are hardly applicable here, since they all deal with “static” systems in which rectification occurs instantaneously. In contrast, our SAMs show a dynamic behavior and can also be seen as switches with the bias serving as an external stimulus (see ref.[36] for an example of bias-induced switching in stretched metal nanowires). We do not expect that stimulus to be related to chemical processes, such as protonation,$^{[37,38]}$ also significant changes in the molecular conformation, like in azobenzene-based SAMs,$^{[39,40]}$ are not possible because of the rigid molecular backbones. We can also rule out environmental effects, such as a change in humidity,$^{[26]}$ since the temperature and humidity did not change noticeably during the experiments.

Figure 4. a) Semilogarithmic $I$–$V$ plots for Au/Fc-FluT//Ga$_2$O$_3$/EGaIn (top panel) and Au/Rc-FluT//Ga$_2$O$_3$/EGaIn (bottom panel) junctions. For each curve (representing an average over a large number of scans) the bias was varied from +0.01 to the value indicated in the plot. b) log$_{10}$ |$J$| at V = +0.01 V for the entire dataset shown in panel (a). The +0.55 V data for Rc-FluT in panel (a) are presented by two curves (see text for details). The horizontal lines within the dark cyan boxes represent the medians of the distributions; the boxes denote interquartile ranges (IQRs); the error bars correspond to the values furthest from the boxes, up to a distance of 1.5 times the IQR; the points lying beyond these intervals are considered as outliers.
The above considerations and the comparison of the Fc/Rc-BPT and Fc/Rc-FluT SAMs with the non-substituted (Figure 2c) and F-/CH3-/CF3-substituted[30,31] BPT monolayers (in which no switching occurs) imply that the unusual charge transport behavior of the Fc/Rc-BPT and Fc/Rc-FluT systems is mediated by the Fc and Rc units. Notably, the measured structural and electronic parameters of the Fc/Rc-BPT and Fc/Rc-FluT SAMs are typical of densely packed molecular assemblies like the BPT and R-BPT monolayers (R = F, CH3, and CF3).[30,31] This has been reported in previous spectroscopic and electrochemical studies[22,23,41] and was additionally verified here by cyclic voltammetry (CV) and work function measurements (see Supporting Information). In particular, the packing density of the Fc/Rc-BPT and Fc/Rc-FluT SAMs, calculated on the basis of the CV data, is estimated at 3.4–4.0 × 10¹⁴ molecules cm⁻², with the lower values for the bulkier fluorene backbone. The molecular tilt angle, reported previously for the Fc-BPT and Rc-BPT SAMs,[22,41] is ~35–37°, which gives a similar orientation of the Fc/Rc moieties with respect to the top EGaIn electrode as in the Fc-substituted alkanethiolate SAMs on Au and Ag.[8] Finally, the electronic properties of the as prepared SAMs are inconspicuous: the position of HOMO, calculated on the basis of the CV data, varies only slightly from system to system between ~5.21 and ~5.29 V (see Tables S7 and S8, Supporting Information), which is very close to the analogous parameter of ferrocene (~5.1 eV).[6,10] Also the work function of the SAMs is determined to be 4.4 eV (see Figure S20 and Table S9, Supporting Information), which is identical to that of BPT/Au (also 4.4 eV), emphasizing a nonpolar character of the Fc and Rc moieties.

The above considerations leave us with the well-known redox character of the Fc and Rc moieties as the most likely explanation for the unusual charge transport behavior of the Fc/Rc-substituted biphenyl/fluorene ethynyl thiol SAMs. Typically, redox processes in metallocenes occur in a reversible fashion, but an irreversible or only partly reversible behavior has also been reported.[23,42] Accordingly, we hypothesize that, upon applying a large enough positive bias, at least part of the molecules in the SAMs could be quasi-irreversibly oxidized. Quasi-irreversibly in this context means that the cations are in a metastable state, which is effectively reduced only upon applying a negative bias voltage. Counter-charges, e.g., trapped in the GaO₃ or as mirror charges in the electrodes could stabilize these oxidized species (see Figure S23, Supporting Information). Another factor stabilizing a metastable ionization of part of the metallocenes would be entropy. Moreover, the anodic oxidation of the metallocenes measured by cyclic voltammetry (see Figure S19 and Section 4.6, Supporting Information) shows a certain degree of irreversibility, providing an additional support of our hypothesis.

This raises the question, how cation formation would modify charge transport through our SAMs. First, it impacts the nature of the frontier orbitals: of particular relevance in this context is the highest occupied molecular orbital (the HOMO), which for thiol-bonded SAMs is typically responsible of charge transport.[6,43] In the neutral state, our simulations show that the HOMO is fully delocalized between the conjugated backbone and the ferroceny, as shown for Fc-BPT in Figure 5a. This situation changes fundamentally when the molecule becomes positively charged: Then the HOMOs of both spin channels become largely localized on the biphenyl part of the molecule (see Figure 5a and Figure S21, Supporting Information for a more detailed discussion). For the lowest unoccupied orbital (LUMO) a similar situation is observed, with the main difference that in the cation the LUMO becomes largely localized on the ferroceny (see Figure S21, Supporting Information). The localization of the frontier orbitals in the cation is accompanied by a localization of the excess charge, which for the cation...
is primarily found on the ferrocenyl: A natural bond orbital analysis suggests that 78% of the additional positive charge of the cation resides on the ferrocenyl both for the relaxed cation and the neutral geometries. This assessment is confirmed by the charge rearrangement upon ionization shown in Figure 5b (see also Figure S22, Supporting Information).

Such a charging-induced localization of the frontier orbitals (partly) interrupts the transport channel through the SAM between the two electrodes, but to be effective, the localization (and, thus, cation formation) would have to affect the majority of the molecules in the junction, which does not appear as a realistic scenario.

The presence of metastable molecular cations in the junction would, however, also have a second consequence, which should impact charge transport already at significantly reduced cation concentrations: A positive space charge layer within the junction would give rise to the formation of a sizable potential barrier for holes passing the junction. In this context it is worthwhile noting that the holes are expected to remain the dominant charge carriers even in the switched and partly oxidized junction, considering that thiolate SAMs typically are in a Fermi/HOMO-level pinning situation (as can be inferred from the data shown in refs. [44,45] and as has been explicitly discussed, for example, by Rodriguez-Gonzalez et al.[86]). For a semi-quantitative estimate of the barrier, we developed a simple electrostatic model that is described in detail in the Supporting Information. First, we assumed a homogeneous space charge layer (the ionized metallocenyls) separated from the two metal electrodes by the conjugated backbones and the GaOx. Setting the dielectric constant of both of these dielectric layers to 2 and assuming a distance of 10 Å between the space charge layer and each electrode, one obtains a potential barrier height of 2 eV, when 11% of the metallocenyl entities are ionized. When considering discrete nature of the charges the barrier is reduced in certain regions, as illustrated in Figure 5c. Still even then, the estimated minimum barrier for the above-described junction parameters remains higher than 1.2 eV. The actual height of that minimum barrier, of course, depends on the choice of the various parameters of the simple electrostatic model (see Supporting Information), but these considerations suggest that, if a fraction of the metallocenyls remained in a metastable cationic state, this would pose a sizable obstruction to hole transport through the junction.

In passing we note that we also considered the impact of charge transfer complexes between ionized ferrocenyls and counter charges trapped in the oxide. The resulting dipole layer would, however, cause a significant difference between the expected currents for positive and negative biases in the switched state, which would be at variance with the data in Figures 2 and 3, as already discussed above.

There are, however, two complications with the above model: First, the localization of charges in the molecules requires a weak coupling between the terminal Fc/Rc units and the EGaIn electrode in the oxidized state, in contrast to the proposed strong coupling in the neutral state (see discussion of Figure 2). Moreover, one might expect the change of the charge state of the molecules under positive and negative bias to occur rather quickly, e.g., in one bias scan. This is approximately the case for the oxidation process at positive bias (Figure 3a,b), while the restoration of the neutral state at negative bias requires multiple negative bias sweeps (Figure 3c,d).

A possible solution to the above problems could be that the initial (maybe only temporary) oxidation of the Fc/Rc units triggers a partial reorganization of parts of the SAMs (as proposed for some SAMs in Refs. [11, 47]), stabilizing the oxidized state in certain molecules and modifying the coupling to the EGaIn electrode. The dense molecular packing (see above) and the rigid character of the molecular framework prevent a significant bias-induced change of the molecular conformation. Thus, such a reorganization can only involve a minor change in the molecular tilt and a rotation of the terminal ferrocenyl and ruthenocenyl groups around the molecular axis. As shown in dedicated studies of odd–even effects in molecular diodes [8,11] even a slight change in the molecular tilt of the terminal Fc units can result in changes of the current density in the EGaIn junction by an order of magnitude or even higher, indicative of a significant change in the coupling. A rotation of the ferrocenyl and ruthenocenyl groups, affecting the exact orientation of these groups at the SAM/EGaIn interface, could even have a stronger impact on the coupling strength.

Interestingly, the above considerations of a bias/oxidation induced modification of the electronic coupling at the SAM/EGaIn interface suggest yet another mechanism for the switching: in line with the proposed strong coupling between the ferrocene and the EGaIn contact in the high conductivity state, one might encounter a situation in which the EGaIn Fermi level and the HOMO of the Fc-BPT are in resonance already prior to applying a bias due to interfacial dipoles in the oxide layer and/or interfacial charge transfer. This would, in fact, explain, why the presence of the ferrocene does not massively decrease the current compared to the BPT SAM (see discussion of Figure 2). This strong coupling and the high-conductivity situation could then be destroyed at large positive biases by processes like the ones discussed in the previous paragraph, resulting in a switching of the junction to a state in which the ferrocene units pose an additional tunneling barrier massively reducing the currents. Considering that we do not have any direct (transport-independent) information on the electronic structure of the buried Fc-BPT/EGaIn interface, this alternative model, unfortunately, has to remain at a rather speculative level.

4. Conclusions

We have experimentally studied charge transport properties of a series of fully conjugated metallocenyl (Fc and Rc) substituted biphenyl- and fluorenethiols, assembling the molecules on Au(111) and placing the respective monolayers within Au/SAM/Ga2O3/EGaIn junctions. In contrast to the observations in previous reports on Fc-substituted aliphatic and hybrid SAMs, we find two distinctly different conduction states for the systems described in the present study. At (small) negative bias voltages, current densities similar to those measured for related aromatic thiolate-SAMs (in particular for BPT) are observed. The situation changes fundamentally for positive biases, for which the observed current densities are by orders of magnitude smaller. This results in an effective rectification ratio of
10⁻³ to 10⁻⁵ at a bias voltage of ~0.25 V and of 10⁻³ to 10⁻⁵ at bias voltages close to 0 V. Especially at low biases these parameters are superior to most molecular rectifiers reported so far, making the present systems interesting for application. Notably, the appearance of the low-conductivity state is triggered by sufficiently high positive bias voltages and the switching of the junction can be reversed through a negative bias.

As conventional models for rectification in molecular junctions do not account for the switching behavior observed here, we propose several possible alternative explanations (motivated by theoretical modelling and the electrochemistry data): assuming that a fraction of the molecules was switched into a metastable cation state by a sufficiently high positive bias (in line with the electrochemistry data), the asymmetry in the I–V characteristics could be the consequence of a localization of the frontier electronic states in the Fe/Rc-substituted molecules. The formation of metastable cations would also give rise to a significant potential barrier for hole transport. The charging of the Fe/Rc groups would require a significantly reduced coupling between these groups and the top electrode, which could be related to structural changes in the monolayers. Alternatively, in the strong coupling regime one might be in a high conductivity situation with states on the Fe/Rc groups in resonance with the EGaIn Fermi level (i.e., a Fermi-level pinning situation). This favorable situation would then be destroyed by the significant weakening of the coupling to the electrode at high positive biases. In the future, such mechanisms could be specifically targeted in advanced, custom-designed systems, in this way opening new perspectives for molecular electronics.

5. Experimental Section

Materials and SAM Preparation: Fe-BPT, Rc-BPT, Fe-FluT, and Rc-FluT compounds were synthesized according to literature procedures.[20–23] Reference BPT compound was purchased from Sigma–Aldrich as well as all other reagents. Au substrates were purchased from Georg Albert PVD-Beschichtungen. They were prepared by thermal evaporation of 30 nm of gold (99.99% purity) onto polished single-crystal silicon (100) wafers (Silicon Sense) that had been precoated with a 9 nm Ti adhesion layer. The Au films were polycrystalline, exposing predominantly (111) oriented surfaces of individual crystallites, as verified by the angular distributions of the Au 4f photoelectrons[49] and by the characteristic binding energy shift of the Au 4f photoemission.[64] The RMS value of the Au surface was estimated at ~0.8 nm as average over the 0.5 × 0.5 µm² and 5 × 5 µm² scans (according to the specification of the manufacturer). This roughness is sufficiently low to avoid a negative effect on the quality of the charge tunneling rate measurements.[50] In particular, the respective current density values measured for several test systems reproduce well the values reported for the ultimately flat template-stripped substrates,[50] which was additionally verified by the dedicated experiments for the reference BPT SAM (not shown). It was also questionable to what extent the latter substrates are compatible with the dimethylformamide (DMF), selected as the solvent for the SAM preparation,[50] which was one more reason to proceed with the evaporated substrates.

Short before the SAM preparation, the Au substrates were cleaned by ultraviolet light and subsequently ultrasonicated in ethanol. The SAMs were formed by immersion of the substrates into 1 × 10⁻² M solutions of the SAM precursors in DMF for 24 h, under ambient conditions and at room temperature, following the established procedures.[20–23] After immersion, the samples were ultrasonicated in DMF (to remove possible physisorbed material), rinsed with DMF, and blown dry with a stream of nitrogen or Ar. Multiple sets of the samples were prepared for the repeated measurements (for the sake of statistic) and different experiments, with good reproducibility and consistency of the results. The reference BPT SAM was prepared according to the literature procedure, using the immersion procedure with ethanol as the solvent.[50]

Charge Transport Measurements: Charge transport experiments were carried out at ambient conditions; the temperature and humidity did not vary noticeably during the measurements. The measurements were performed with a custom-made two-terminal molecular junction setup, based on the Keithley 2635A source meter.[51] The reliability of the setup has been confirmed by previous experiments.[20,23] The gold substrate and a sharp tip of eutectic GaIn (EGaIn), covered by a ultrathin GaO film (~0.7 nm thick),[54,55] served as the bottom and top electrodes, respectively. Tunneling junctions were formed by contacting grounded SAM/Au samples with the EGaIn tips and applying a potential (bias). The voltage was varied either between ~0.01 and ~1.05 V or between ~0.01 and ~1.05 V in 0.01 V steps; the measurement of one curve took ca. 5 min. More than 200 I–V curves, measured at several different places (spots) for several different samples, were recorded for each sample type, with a yield of reliable data of 39–98%; the exact data (i.e., provided in Tables S1 and S2 [Supporting Information]). Average values of the current density were calculated with either Gaussian mean or median with confidential interval 95% (CI 95%) for expressing the precision of the statistical estimation.[55] Both procedures resulted in nearly identical values of the current density but somewhat different error bars. For the sake of clarity, the data calculated with Gaussian mean was presented.

Along with the above measurements, representing the major result of the present work, several specific I–V experiments were performed, targeting the evolution of the systems in the course of successive bias variation, dependence of the conduction state on the bias variation range, recovery of the high conductance state, and stability of the low conductance state. The number of I–V curves in each particular experiment varied depending on its character but, in most cases, statistically meaningful data could be derived. The bias voltage was varied in either 0.01 or 0.02 V steps.

Electrochemistry: A custom-built electrochemical cell having both solution and SAM measurement capabilities was used for the measurements. Ag/AgCl (non-aqueous) and Pt wire were used as the reference and counter electrodes, respectively (Osilla, UK). The cyclic voltammograms (CVs) of Fe-FluT and Rc-FluT in DMF solution (0.1 M tetrabutylammonium tetrafluoroborate electrolyte) and the Fe-BPT, Rc-BPT, Fe-FluT, and Rc-FluT SAMs prepared on Au working electrode surfaces (0.1 M HClO₄ electrolyte) were recorded using a Zahner potentiotstat (model IM6E). The Au working electrodes used for the SAM electrochemistry had the same structure as the gold substrates used for the charge transport measurements. The area of these electrodes exposed to the HClO₄ electrolyte was ~1 cm² at an electrochemical scan rate of 100 mV s⁻¹ in the range from 0 to +0.7 V. For the solution electrochemistry, Glassy carbon electrodes were used. Before consecutive measurements these electrodes were cleaned with DMF and ethanol and finally oven-dried at 80 °C. Before measuring each voltammogram, the electrochemical solvent was degassed for at least 10 min by purging Ar.

Work Function Measurements: Work function measurements were carried out using a UHV Kelvin Probe 2001 system (KP technology Ltd., UK). The work function values were referenced to that of a hexadecanethiolate SAM on Au(111), viz. 4.3 eV.[54] The latter value was additionally verified by comparison to the WF of freshly sputtered gold at 5.2 eV.[57]

Theoretical Simulations: For reasons described in the Supporting Information, the simulations were restricted to molecular systems. All simulations were performed employing Gaussian 16, Revision A.03.[58] Unless otherwise noted, the B3LYP functional was used (as implemented in the Gaussian code, i.e., using the nonlocal correlation from the LYP expression, and VWN functional III for local correlation instead of functional V). A 6–31G(d,p) basis set was employed for the light atoms and the Stuttgart/Dresden effective core potential (SDD) for Fe[59] (where, for the sake of comparison, most simulations

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were repeated employing the Los Alamos effective core potential plus DZ (LANL2DZ)[69]. Additionally, full potential studies were performed for selected cases employing the 6–311G(df,p)[60–63,66–68] basis set for all atoms (including Fe). All neutral molecules were calculated in the singlet spin configuration and all ions as doublets. For the sake of comparison, also tests employing the PBE[69] and the PBE0[70] functionals were performed. In this context it is worthwhile noting that especially when dealing with ionic species, it is not always straightforward to achieve convergence, and even worse, depending on the settings in the self-consistent field (SCF) procedure, convergence into different charge densities has been observed. Here it was consistently found that charge densities calculated employing the quadratically convergent SCF procedure (QC)[71] were lower in energy. Therefore, only results obtained with that procedure or data for calculations yielding identical total energies as QC test calculations were reported. When accounting for dielectric screening effects, (see the self-consistent reaction field method was used in the flavor of the polarizable continuum model)[72–74] as implemented in Gaussian.[58] The solvent was set to “Benzene” with a dielectric constant of ε = 2.228.

All plots of isodensity surfaces and molecular structures were prepared using OVITO.[75]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors thank Maximilian Schöner for the participation in some experiments in context of this project. A.A. acknowledges the financial support by the DAAD-ACEH Scholarship of Excellence. S.D. and M.Z. acknowledges the financial support by German Research Foundation (DFG; grant ZH 63/39-1). Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords
metallocenes, molecular diodes, molecular electronics, rectification ratio, self-assembled monolayers, two-terminal junctions

Received: March 17, 2022
Published online: May 17, 2022

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