

# The Mechanisms of Rectification in Au | Molecule | Au Devices Based on Langmuir–Blodgett Monolayers of Iron(III) and Copper(II) Surfactants\*\*

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Dedicated to Professor Robert Metzger on the occasion of his 75th birthday

**Abstract:** Langmuir–Blodgett films of metallocosurfactants were used in Au | molecule | Au devices to investigate the mechanisms of current rectification.

In electronic circuitry, solid-state diodes enable current to flow in a given direction and prevent reversibility. This directional flow is defined as current rectification and is fundamental to the conversion of alternating into direct current necessary for information management. Molecular rectification—originally proposed by Aviram and Ratner<sup>[1]</sup> as a gedanken experiment—anticipates the feasibility of directional current flow in a molecule with well-defined donor and acceptor moieties. It was evaluated experimentally<sup>[2,3]</sup> in the early 1990s using an electrode–monolayer–electrode, E | LB | E, junction containing hexadecylquinolinium-tricyanoquinodimethane. The use of physisorbed Langmuir–Blodgett (LB) monolayers<sup>[4]</sup> prevents the formation of interfacial dipoles known as Schottky barriers typical of self-assembled systems, so that molecular rectification takes place either by asymmetric or unimolecular mechanisms that involve the frontier

molecular orbitals (MOs) of the molecule. In asymmetric rectification, the lowest unoccupied LUMO of the acceptor in the molecule is energetically compatible with the Fermi levels of the electrodes, while the highest occupied HOMO is much lower in energy and does not participate in electron transfer (ET). On the other hand, in the unimolecular mechanism, the HOMO of the donor is equivalent in energy to the Fermi levels of an electrode, while the energy of the LUMO in the acceptor is equivalent to the second electrode.

Unimolecular rectification by organic systems has been reviewed in detail by Metzger et al.,<sup>[5–10]</sup> while the use of metal complexes has been considered to a lesser extent and predominantly on nickel and copper phthalocyanines.<sup>[11–14]</sup> The Yu group<sup>[15]</sup> studied a complex in which ruthenium(II) is coordinated to a thiophene-functionalized bipyridine and two fluorinated acetylacetonate (acac) groups. The rectification effect was explained by the presence of a permanent dipole moment perpendicular to the thiophene-functionalized bipyridine and along both acac ligands, being mediated through the HOMO, HOMO-3, and HOMO-4 orbitals associated with the  $t_{2g}$  set ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) of the ruthenium(II) ion. We recently reported on the redox and electronic behavior of five-coordinate complexes where the iron(III) ion is bound to low-symmetry, phenolate-rich,  $[N_2O_3]$  environments, and have shown that the molecular orbitals adapt their energies while the phenolate groups get oxidized.<sup>[16]</sup> These results served as base for another account<sup>[17]</sup> where an Au | LB | Au junction based on the alkoxyated iron(III) metallocosurfactant  $[Fe^{III}(L^{N_2O_3})]$  acts as a molecular rectifier, with rectification ratios ( $RR = [I \text{ at } -V_0 / I \text{ at } +V_0]$ ) varying from 4.52 to 12 between  $-2$  to  $+2$  V and from 2.95 to 36.7 between  $-4$  to  $+4$  V.

In this report we evaluate the rectification response in two redox-responsive metallocosurfactants aiming to correlate electronic structure and redox behavior with the mechanisms that determine molecular rectification in coordination complexes. These species are based on the new ligand  $[H_2L^{N_2O_2}]$  and are the high-spin  $3d^5$   $[Fe^{III}(L^{N_2O_2})Cl]$  (**1**) with an  $S = 5/2$ , sextet structure, and the  $3d^9$   $[Cu^{II}(L^{N_2O_2})]$  (**2**), ( $S = 1/2$ , doublet) shown in Scheme 1.

The ligand  $[H_2L^{N_2O_2}]$  was synthesized by reacting one equivalent of 4,5-bis(2-methoxyethoxy)benzene-1,2-diamine with two equivalents of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde under an inert atmosphere and reflux for 18 h and

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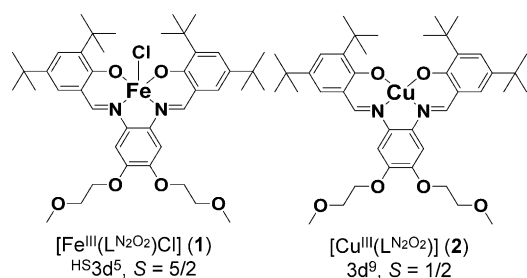
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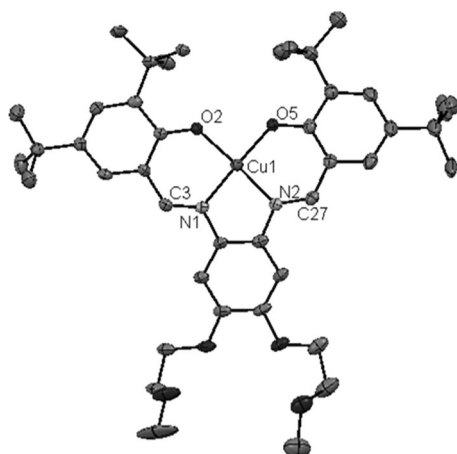


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**Scheme 1.** The metallosurfactants.

includes electron donating *tert*-butyl groups and methoxyethoxy groups that modulate the redox, electronic, and amphiphilic properties of the resulting complexes. After recrystallization,  $[\text{H}_2\text{L}^{\text{N}_2\text{O}_2}]$  was treated with one equivalent of the appropriate metal salt to yield complexes **1** and **2**. Synthetic schemes are shown in Scheme S1 in the Supporting Information. The IR spectroscopic data for **1** and **2** showed symmetric and asymmetric C–H stretching vibrations in the regions of  $2820\text{--}2960\text{ cm}^{-1}$  and a prominent peak at  $1585\text{ cm}^{-1}$  belonging to the C=N stretching vibrations. The high-resolution ESI-MS data showed  $[\text{M}^+]$  at  $m/z = 742.3641$  for **1** and  $[\text{M}+\text{H}^+]$  at  $m/z = 750.3661$  for **2** with isotopic patterns in good agreement with experimental and simulated data. The molecular structure of **2** was confirmed using X-ray crystal structure analysis (Figure 1, Table S2). It revealed the cop-

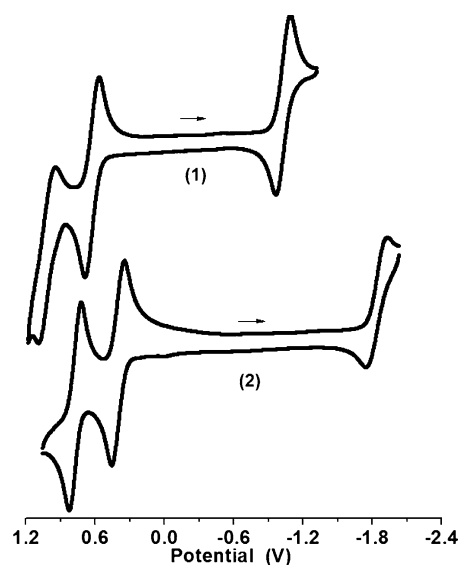


**Figure 1.** ORTEP representation at 50% probability for  $[\text{Cu}^{\text{III}}(\text{L}^{\text{N}_2\text{O}_2})]$  (**2**). H atoms omitted for clarity.<sup>[54]</sup>

per(II) complex in a square-planar geometry with an  $[\text{N}_2\text{O}_2]$  environment where the nitrogen and oxygen atoms are trans to each other. The Cu–O and Cu–N distances are in agreement with reported values.<sup>[18,19]</sup>

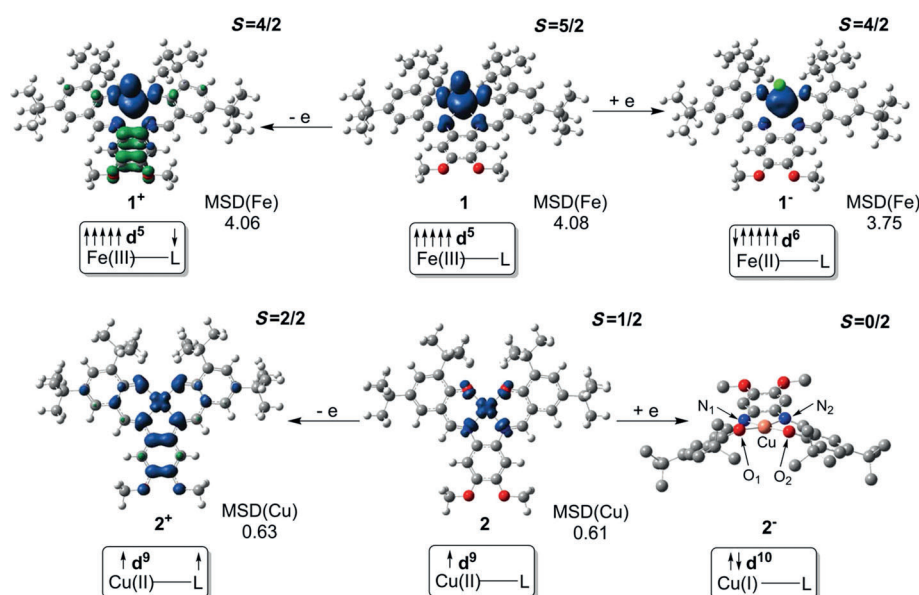
In order to access the nature of the frontier orbitals in **1** and **2**, electronic spectra were measured in  $1.0 \times 10^{-5}\text{ mol L}^{-1}$  dichloromethane solutions (Figure S1, Table S3). Ligand-based  $\pi \rightarrow \pi^*$  charge transitions were observed for  $[\text{H}_2\text{L}^{\text{N}_2\text{O}_2}]$  between  $280\text{--}360\text{ nm}$ . Species **1** showed bands at  $310, 351, 395,$  and  $447\text{ nm}$  with  $\epsilon$  values ranging from  $19200\text{--}49920\text{ L mol}^{-1}\text{ cm}^{-1}$ . According to literature<sup>[20–22]</sup> and con-

firmed by time-dependent DFT (TD-DFT)<sup>[23–25]</sup> calculations along with the natural transition orbital (NTO) method,<sup>[26]</sup> bands at  $310\text{--}400\text{ nm}$  are assigned as ligand-to-metal charge-transfer transitions (LMCT) from phenylenediamine- and phenolate-based  $p_\pi$  orbitals to  $d_{\sigma^*}$  and  $d_{\pi^*}$  iron(III)-based orbitals. The  $447\text{ nm}$  band belong to intraligand  $\pi \rightarrow \pi^*$  charge-transfer (ILCT) transitions<sup>[27]</sup> (Figure S2). Species **2** showed intense ILCT absorptions at  $320, 349, 372, 419, 446,$  and a low intensity d-d band at  $550\text{ nm}$  (Figure S1b). Four absorptions of reasonable oscillator strength have been found by TD-DFT calculations in the region of  $318\text{--}462\text{ nm}$  (Figure S3). Therefore, the metal-based singly occupied SOMO is energetically and symmetry-wise more available in **1** than in **2**. The cyclic voltammograms of **1** and **2** ( $1.0 \times 10^{-3}\text{ mol L}^{-1}$ ) were recorded versus the  $\text{Fc}^+/\text{Fc}$  couple and are shown in Figure 2.



**Figure 2.** Cyclic voltammograms for **1** and **2**; DCM, vitreous C, Pt, Ag/AgCl, TBAPF<sub>6</sub>. Potentials vs. the  $\text{Fc}^+/\text{Fc}$  couple.

Species **1** showed a quasi-reversible reduction at  $-1.02\text{ V}$  ( $\Delta E_p = 0.12\text{ V}$ ,  $|I_{pa}/I_{pc}| = 0.93$ ) assigned to the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  redox couple, along with anodic processes at  $0.64\text{ V}$  ( $\Delta E_p = 0.12\text{ V}$ ,  $|I_{pa}/I_{pc}| = 1.08$ ) and at  $1.05\text{ V}$  ( $\Delta E_p = 0.11\text{ V}$ ) attributed to ligand oxidations. Species **2** displayed two well-defined oxidation processes at  $0.40\text{ V}$  ( $\Delta E = 0.114\text{ V}$ ,  $|I_{pa}/I_{pc}| = 1.1$ ) and  $0.78\text{ V}$  ( $\Delta E = 0.106\text{ V}$ ,  $|I_{pa}/I_{pc}| = 1.0$ ) along with a quasi-reversible process at  $-1.85\text{ V}$  ( $\Delta E = 0.192\text{ V}$ ,  $|I_{pa}/I_{pc}| = 1.9$ ) attributed to the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  reduction.<sup>[28]</sup> Spectroelectrochemical experiments (Figures S5 and S6) were revealing; the reduction of **1** into **1**<sup>−</sup> at  $-1.38\text{ V}_{\text{Fc}^+/\text{Fc}}$  was accompanied by a decrease in the bands between  $300\text{--}750\text{ nm}$  with a new band appearing at  $451\text{ nm}$ , whereas the spectrum obtained for the reduction **2** to **2**<sup>−</sup> at  $V_{\text{Fc}^+/\text{Fc}} = -2.07$  showed a decrease in all  $\pi \rightarrow \pi^*$  transitions associated with the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple. The first oxidation process for **1**<sup>+</sup> at  $0.88$  and for **2**<sup>+</sup> at  $V_{\text{Fc}^+/\text{Fc}} = 0.49$  showed an overall increase in intensity. Dominant features were observed at  $1400$  and  $1100\text{ nm}$  respectively for **1**<sup>+</sup> and **2**<sup>+</sup> and attributed to ILCT  $\pi \rightarrow \pi^*$  transitions. The electrochem-



**Figure 3.** DFT-calculated spin density plots (isodensity 0.004 a.u.) showing oxidation and reduction for **1** and **2**. Hs omitted in  $2^-$ .

ical events for **1** and **2** were further investigated using DFT methods.<sup>[29]</sup> Figure 3 shows spin densities for the relevant structures. The reduction of **1** was confirmed as an  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  event leading to the  $^{\text{HS}}3d^6$  ( $S=4/2$ ) iron(II) species **1**<sup>-</sup> and associated with the observed disappearance of the  $\text{PhO}^- \rightarrow \text{Fe}^{\text{III}}$  metal-to-ligand charge-transfer (MLCT) band.

The reduction of **2** is also confirmed as metal-centered and the resulting  $3d^{10}$  copper(I) complex, **2**<sup>-</sup>, is a closed shell singlet ( $S=0$ ) and severely distorted. The two phenoxy rings are no longer coplanar leading to significant disruption of the  $\pi$  conjugation in the ligand framework responsible for the decrease in the ILCT processes observed in the spectroelectrochemical experiment. Therefore, we conclude that the metal reduction potentials corroborate with the spectroscopic results and confirm that the iron(III) SOMOs display lower energy than the copper(II)  $d_{x^2-y^2}$  SOMO. On the other hand, the first oxidation to **1**<sup>+</sup> is ligand-based yielding a radical delocalized over the phenylenediamine moiety. This  $\pi$  radical can couple antiferromagnetically (AF) with an electron from the singly occupied  $d_{\pi}$  orbital of iron producing an  $S=4/2$  that is lower in energy than the counterpart ferromagnetically (F) coupled heptet ( $S=6/2$ ) state by 3.7 kcal mol<sup>-1</sup>. Oxidation of **2** is also found to be ligand-centered. In this case, the resulting phenylenediamine  $\pi$ -radical cannot couple with the copper-based singly occupied  $d_{x^2-y^2}$  orbital and the HS triplet ( $S=1$ ) state is found to be lower in energy than the AF coupled state ( $S=0$ ) by 1.5 kcal mol<sup>-1</sup>. The oxidation loci for **1**<sup>+</sup> and **2**<sup>+</sup> are different than the phenolate rings, as observed for the previously published rectifying  $[\text{N}_2\text{O}_3]$  iron(III) complex,<sup>[17]</sup> but consistent with results presented by Thomas and co-workers.<sup>[18,19]</sup> The second oxidation for both **1**<sup>++</sup> and **2**<sup>++</sup> involves a phenolate to phenoxy process, as illustrated in Figure S4.<sup>[30–32]</sup>

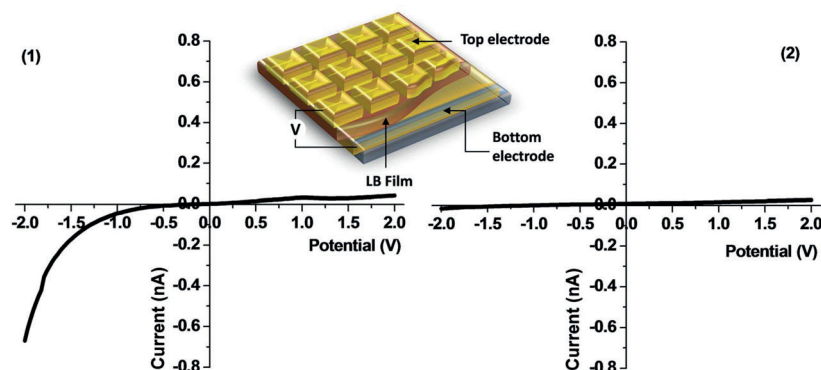
Metallosurfactants **1** and **2** form Langmuir (L) films, as measured by isothermal compression and Brewster angle

microscopy (BAM; Figure S7). The surface pressure ( $\pi$ ) vs. average molecular area ( $A$ ) isotherm obtained for **1** showed an area of interaction of  $74 \text{ \AA}^2 \text{ molecule}^{-1}$ , lacked acute phase transitions, and showed constant collapse pressure<sup>[33]</sup> around  $40 \text{ mN m}^{-1}$ , with a critical area of  $71 \text{ \AA}^2 \text{ molecule}^{-1}$ . The BAM obtained during compression confirmed the formation of a homogeneous film from  $9\text{--}38 \text{ mN m}^{-1}$ . At  $40 \text{ mN m}^{-1}$  Newton rings were detected and associated with the collapse of the L film at the air/water interface.<sup>[34]</sup> Species **2** also showed good L-film formation with an area of interaction of  $79 \text{ \AA}^2 \text{ molecule}^{-1}$  in spite of a lower collapse at  $30 \text{ mN m}^{-1}$ . BAM images reveal the formation of a homogenous film between  $7\text{--}28 \text{ mN m}^{-1}$ . Both films follow the Ries mechanism of collapse<sup>[35]</sup> discussed in other reported metallosurfactants.<sup>[36]</sup> Monolayers and multilayers were deposited onto glass, mica, and gold substrates at distinct surface pressures and analyzed by multiple methods. To probe the chemical integrity of the deposited molecules of **1** and **2**, the electronic spectra of 50-layer films on glass substrates were recorded. A comparison between film and solution spectra (Figure S8) shows that both species conserve the main original electronic processes, with minor decreased absorptions and red-shifting attributed to conformational changes associated with film packing<sup>[37]</sup> and J-type chromophore aggregation.<sup>[38,39]</sup> Infrared reflection absorption spectra (IRRAS) were also measured using  $p$ -polarized light at an angle of incidence of  $30^\circ$  for **1** and  $40^\circ$  for **2**,<sup>[40,41]</sup> and compared to the bulk IR spectra of **1** and **2** (Figure S9), showing equivalent peak patterning. Both species showed prominent bands belonging to  $\text{C}=\text{C}_{(\text{aromatic})}$  stretching and  $\text{CH}_n$  deformation vibration bands at  $1610\text{--}1300 \text{ cm}^{-1}$ , as well as pronounced  $\text{C}=\text{N}$  stretching at  $1581$  and  $1587 \text{ cm}^{-1}$  suggesting that the imine ligands remain intact after film deposition. Inference of film orientation by analysis of  $\text{CH}_2$  vibration intensities<sup>[40–45]</sup> is limited because of the dominant contributions given by fourteen  $\text{CH}_3$  groups present in both **1** and **2**. However, the  $\text{CH}_3$  peak position in bulk and in the film shift from  $2956$  to  $2964 \text{ cm}^{-1}$  for **1** and  $2954$  to  $2961 \text{ cm}^{-1}$  for **2**, as expected in a well-packed film. Similarly, determination of molecular alignment angles for complex surfactants is elusive. However, contact angle measurements on the monolayers of structurally related species<sup>[17]</sup> indicate hydrophobic nature with the methoxyethoxy substituents attached to the glass substrate by van der Waals interactions and the *tert*-butyl groups oriented outwards. AFM measurements were carried out on LB monolayers deposited onto mica substrates at  $15, 25, 30, 35, 37,$  and  $40 \text{ mN m}^{-1}$  for **1** and at  $5, 10, 20, 25, 30,$  and  $32 \text{ mN m}^{-1}$  for **2** (Figures S10 and S11), with transfer ratios nearing unity. Monolayers of **1** deposited at

lower surface pressures showed random film organization and pin hole defects, while ordered and defect-free films were obtained at 30–35 mN m<sup>-1</sup>. Homogeneous film formation for **2** was observed at 20–25 mN m<sup>-1</sup>.

The LB monolayers transferred at surface pressures near collapse showed rougher surfaces with aggregate formation. Therefore, device fabrication used monolayers deposited onto gold-coated mica substrates at 35 and 25 mN m<sup>-1</sup> for **1** and **2**, respectively, to minimize defects. The films were topped with a gold layer deposited using shadow masking.<sup>[6]</sup>

The resulting assemblies contained 16 Au|LB1|Au and Au|LB2|Au devices (Figure 4 inset) and had their rectifica-



**Figure 4.** *I/V* characteristics observed for Au|LB1|Au and Au|LB2|Au. Inset: Representation of the assembly and individual devices.

tion behavior probed as current–voltage (*I/V*) curves measured at ambient conditions. The reproducibility of the *I/V* characteristics were probed by measuring multiple devices of a given assembly, as well as by measuring different assemblies. An average of 25–30% of devices showed rectification in three assemblies. The data obtained for **1** and **2** are shown in Figure 4 and Figure S12.

Devices of Au|LB1|Au showed asymmetric current response with elevated electrical current in the negative quadrant and negligible current response in the positive quadrant, as indicative of rectifying behavior (Figure S12 a–d). The observed rectification ratio (RR =  $|I$  at  $-V_0/I$  at  $+V_0$ )<sup>[46]</sup> ranges from 3.99 to 28.6 between  $-2$  to  $+2$  V and from 2.04 to 31 between  $-4$  to  $+4$  V. Reversing of the source and drain contacts reversed the *I/V* response, thus confirming the rectification behavior of **1** (Figures S12 e and S12 f). The amplitude of the forward current signal with reversed source and drain contacts is smaller, at around 0.3 nA, reflecting differences in molecular orientation of the film. Repeated measurement cycles led to a decrease in magnitude (Figure S12 b and S12 d) culminating in near-sigmoidal current responses (Figure S12 g). This behavior has been attributed to molecular reorientation to minimize the dipole moment and decrease the energy of a stable monolayer.<sup>[46]</sup> Remarkably, Au|LB2|Au yielded flat *I/V* curves characteristic of non-rectifying devices.

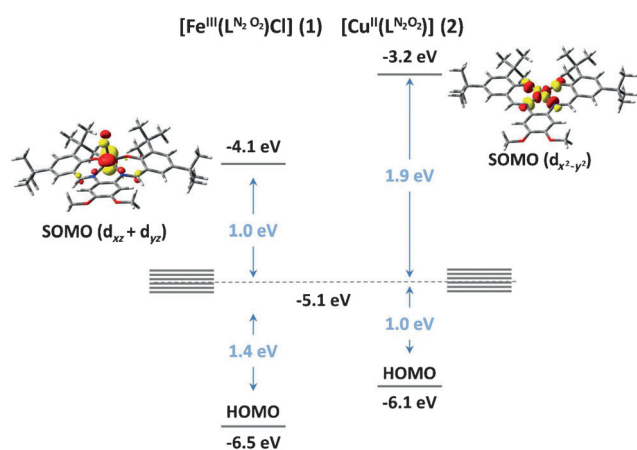
Considering the distinctive behavior of **1** and **2**, an evaluation of the possible rectification mechanisms must take into account plausible ET pathways. As discussed

previously, we reject a pure Schottky mechanism<sup>[6,8]</sup> because LB1 and LB2 are physisorbed by weak van der Waals interactions between two identical electrodes. However, we can suggest that the molecules are consistent with a [D–A] type structure, and that could support unimolecular mechanisms if the involved molecular orbitals display favorable energies. Nonetheless, these species lack an obvious HOMO/LUMO bridge to decrease electronic coupling, making this an unlikely mechanism of rectification.

The proposed model for ET through species in contact with metal electrodes requires that the Fermi levels ( $E_F$ ) of the electrodes be compatible with the energies of the molecular frontier orbitals, when resonant tunneling can occur by different redox states of that given species. In gold electrodes  $E_F$  is 5.1 eV below vacuum,<sup>[47–49]</sup> and ET will be favored by the systems with the best match between  $E_F$  and HOMO/LUMO or HOMO/SOMO (singly occupied) energies. Therefore, we need to consider the redox behavior of the metallosurfactants, knowing that the difference between the first oxidation potential ( $E_{pa1}$ ) and the first reduction potential ( $E_{pc1}$ ) is roughly equivalent to the energy of the HOMO–LUMO gap. The iron(III) species **1** displayed a smaller  $\Delta E$  ( $= E_{pa1} - E_{pc1}$ ) of 1.78 V when compared to that of the copper(II) species **2** given by  $\Delta E = 2.39$  V, suggesting a narrower HOMO–LUMO energy gap for **1**. The molecular redox

potentials measured from cyclic voltammetric experiments, can be converted to comparable solid-state potentials using the following equations,  $V_a = 4.7$  eV +  $E_{1/2}^{red}(SCE)$  and  $V_i = 4.7$  eV +  $(1.7)E_{1/2}^{ox}(SCE)$ , where  $V_a$  and  $V_i$  are very close to the first electron affinity and first ionization energy levels of the molecule supported on the electrodes, respectively.<sup>[50–53]</sup> The  $E_{1/2}^{red}(SCE)$  and  $E_{1/2}^{ox}(SCE)_{1/2}$  values are the measured half-wave first reduction and first oxidation potentials at  $-0.61$  and  $1.05$  V for complex **1**, respectively, and  $-1.46$  and  $0.79$  V for complex **2**, referenced versus the saturated calomel electrode (SCE).

Using these values, the  $V_a$  energy of the first metal-centered SOMO is calculated to be  $-4.1$  eV for **1** and  $-3.2$  eV for **2**, respectively. Similarly, the  $V_i$  energy equivalent to the first ligand-centered HOMOs are found to be  $-6.5$  and  $-6.1$  eV for **1** and **2**, respectively. Therefore, the model depicted in Figure 5, shows that the gold Fermi levels are approximately 1.0 eV below the lowest energy Fe-based SOMO of species **1**. Because of the asymmetry of the molecule, this SOMO is a linear combination described as  $d_{xz} + d_{yz}$ , when the molecular  $z$  axis is maintained along the Fe–Cl direction. Electrode-to-molecule ET is likely to occur when a bias is applied triggering the population of that orbital—which corresponds to the generation of an iron(II) center—and subsequent lowering of the energy of the resulting doubly occupied MO. On the other hand, the only available SOMO for **2** is the copper-based  $d_{x^2-y^2}$  orbital that lies approximately 2 eV above the electrode Fermi level. This MO is likely not attainable at the applied bias, and this



**Figure 5.** Electron transfer model involving the Fermi levels of the electrode into the metal-based SOMOs of **1** and **2**.

energetic mismatch accounts for the observed *I/V* non-rectifying behavior of the copper(II) complex. The gap of 1.4 eV between  $E_F$  and  $V_i$  for **1** suggests that the ligand-based HOMOs are not involved in the rectification process, whereas the difference between  $E_F$  and  $V_a$  for **1**. As no rectification has been observed for the copper(II) species, it indicates that the molecule-to-electrode ET cannot be the determining step. Thus, considering 1) the rectifying behavior for **1** along with the appropriate energy match between  $E_F$  and  $V_a$  and the possible mismatch between  $E_F$  and  $V_i$ , and 2) the non-rectifying behavior of **2** where the difference between  $E_F$  and  $V_a$  is large and  $E_F$  and  $V_i$  is small, an asymmetric current rectifying mechanism is tentatively proposed. Additionally, local orbital asymmetry might also play a role; while the  $d_{x^2-y^2}$ -based SOMO of the non-rectifying **2** is described as  $D_{2h}$ , the  $(d_{xz} + d_{yz})$ -based SOMO of the rectifying **1** displays an idealized  $C_s$  symmetry. This aspect is being explored in further detail.

In summary, we have successfully compared the behavior of new iron(III) and copper(II) surfactants **1** and **2** towards current rectification. The lowest metal-centered SOMO in **1** seems energetically affordable for electrode-to-molecule ET, and an asymmetric rectification mechanism is suggested. Thus, a generalization can be proposed that metallosurfactants in defect-free monolayers might exhibit rectification properties if available SOMOs display energies similar to those of the Fermi levels of gold electrodes. Molecular geometry, electronic configurations, and local symmetries will further determine which SOMO is energetically favorable.

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