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Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-03-2022-000938.R1
Article Type:	Paper
Date Submitted by the Author:	01-May-2022
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## ARTICLE

## Electron transport through a (terpyridine)ruthenium metallo-surfactant containing a redox-active aminocatechol derivative

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Aiming to develop a new class of metallosurfactants with unidirectional electron transfer properties, a (terpyridine) ruthenium complex containing a semiquinone derivative L<sup>2</sup>, namely [Ru<sup>III</sup>(L<sup>terpy</sup>)(L<sup>2</sup>)Cl]PF<sub>6</sub> (**1**), was synthesized and structurally characterized as a solid and in solution. The electronic and redox behaviour of **1** was studied experimentally as well as by means of DFT methods, and is indicative of significant orbital mixing and overlap between metal and ligands. The complex forms stable Pockels-Langmuir films at the air-water interface and allows for the formation of thin films onto gold electrodes to prepare nanoscale Au|LB **1**|Au junctions for current-voltage (I/V) analysis. Complex **1** shows asymmetric electron transfer with a maximum rectification ratio of 32 based on tunnelling through MOs of the aminocatechol derivative.

### Introduction

Electron transport in E<sub>1</sub>|molecule|E<sub>2</sub> junctions is measured by the changes in current (I) associated with varying the potential (V) in I/V curves, and is described in terms of conduction, rectification, or insulation. Frequently used metal complexes in electron transport include modified ferrocenes, phthalocyanins, porphyrins, and polypyridines.<sup>1</sup> Metal-terpyridines are often used in both single-molecule or thin film junctions. The pioneer work of Park *et al.*<sup>2</sup> observed the conducting behavior of <sup>55</sup>Co<sup>II</sup> [Co<sup>II</sup>(S-terpy)<sub>2</sub>] species where electron transport was observed as a sigmoidal I/V curve attributed to the <sup>55</sup>Co<sup>II</sup>/<sup>55</sup>Co<sup>III</sup> redox couple. Coupling between the metal center and the gold electrodes was controlled by the length of alkyl chain spacers between the terpyridine and a self-assembling thiol; while a complex with pentacyl spacers showed an increased resistance that prevented current flow associated with small bias voltages (Coulomb blockade), another Co-complex with a thiol directly installed on the terpy showed a sudden temperature-dependent increase in current (Kondo effect). Interestingly, when a <sup>55</sup>Co<sup>II</sup> [Mn<sup>II</sup>(S-terpy)<sub>2</sub>] species was studied by van der Zant *et al.*<sup>3</sup> ligand reduction triggered a transition to low spin configuration, t<sub>2g</sub><sup>3</sup>e<sub>g</sub><sup>2</sup> + e<sup>-</sup> → t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>0</sup>, resulting in spin blockade. In these quasi-octahedral 3d species, the filling of t<sub>2g</sub> HOMOs led to current blockades even if the LUMO e<sub>g</sub>-manifold was empty. The HOMO/LUMO gap in 4d metal complexes is wider than that in 3d

systems,<sup>4</sup> and when Lee *et al.*<sup>5</sup> used a <sup>45</sup>Ru<sup>II</sup> [Ru<sup>II</sup>(terpy)<sub>2</sub>] system, negative bias switching enabled electron transport by bringing a ligand-based LUMO closer to the Fermi level of the Au substrate.<sup>6</sup> In these cases, the metal-terpy species acted as wires or transistors with electrons flowing back and forth between electrodes, but not as rectifiers. Rectification or unidirectional tunneling of electrons is characterized by asymmetric I/V curves that differ from the sigmoidal I/V response seen for the above examples. In order to attain such rectifying behavior with terpy units, Lacroix *et al.*<sup>7</sup> coupled a naphthalenediimine acceptor (A) through a phenyl bridge to Ru(terpy)<sub>2</sub>, which acts as a donor (D). In doing so they built a classic Aviram/Ratner/Metzger E<sub>1</sub>|D-π-A|E<sub>2</sub> design, in which the preferred electron flow is donor → acceptor.<sup>8</sup> Although the mechanism of rectification was not pursued, these systems usually rely on e<sub>g</sub>-like LUMO tunneling.<sup>5</sup> We addressed the issue of 3d<sup>6</sup>-induced blockades in quasi-O<sub>h</sub> species by building Au|LB|Au junctions based on Langmuir Blodgett films of metallosurfactants containing five-coordinate <sup>55</sup>Fe<sup>III</sup> (3d<sup>5</sup>, S = 5/2) ions.<sup>1</sup> Electron transport takes place through the SOMOs (d<sub>xz</sub>+d<sub>yz</sub>) when within 1 eV from the Fermi level of the electrodes.<sup>9</sup> The semi-occupied nature of these orbitals limits the amplitude of the current response due to Pauli's exclusion, but precludes the limiting <sup>55</sup>Fe<sup>II</sup> (t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>0</sup>) configuration when the metal center is momentarily reduced to 3d<sup>6</sup> Fe<sup>II</sup> during electron transport. The rectification process has been verified independently,<sup>10</sup> and other SOMO based rectifiers have been identified.<sup>11</sup>

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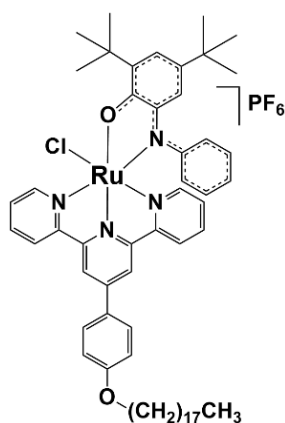
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



**Scheme 1:** Schematic representation of Complex **1**

This observation led us to consider that tunneling in terpy systems depends on the energies of LUMO,<sup>12</sup> and HOMO<sup>13</sup> as determined by the quasi- $O_h$  environment, as well as on terpy reduction. Therefore, we hypothesize that species in which  $O_h$  symmetry is further lifted by the presence of distinct donors and bond lengths will promote significant orbital mixing between metal- and ligand-based molecular orbitals, and may lead to affordable pathways for tunneling.

In order to investigate this possibility, we identified the terpy-based complex  $[Ru^{III}(L^{terpy})(L^2)Cl]PF_6$  (**1**) shown in **Scheme 1**, in which  $L^{terpy}$  is an amphiphilic terpyridine ligand, and the  $4d^5 Ru^{III}$  ion is bound to a deprotonated and redox-active aminocatechol derivative  $L^2$ . Here, we report on the electronic, electrochemical, and rectifying properties of this species, and discuss possible mechanisms.

## Results and discussion

### Rationale for the molecular design

In our attempt to attain directional electron transport by modulating frontier molecular orbital energy, we propose that the use of redox-active species and asymmetries will lead to significant orbital mixing and overlap. This enables a better match between molecular orbitals and the Fermi level of the electrodes, to foster electron tunneling. The bidentate aminocatechol ligand employed in this study increases the asymmetry of the entire system, possibly aiding in unidirectional electron transport.

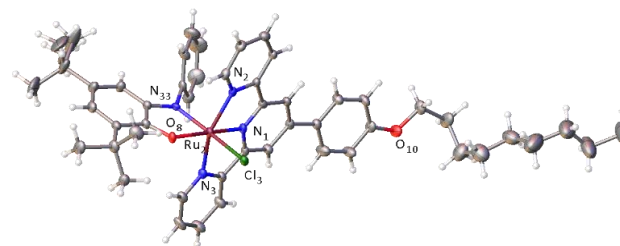
### Synthesis and Characterization

The tridentate 4'-(4-octadecyloxyphenyl)-2,2':6',2''-terpyridine ligand ( $L^{terpy}$ ) and the redox active 2,4-di-tert-butyl-6-(phenylamino)phenol ligand ( $H_2L^2$ ) were synthesized following procedures adapted from literature.<sup>14</sup> Complex **1**  $[Ru(L^{terpy})(L^2)Cl]PF_6$  was prepared by dropwise addition of one equivalent  $H_2L^2$  to a methanolic solution of  $Ru(L^{terpy})(DMSO)_4Cl_2$  using triethylamine as the base for phenol and (possibly amine) deprotonation. The synthesis was performed under anaerobic conditions and the

reaction system was treated with excess  $NH_4PF_6$  to precipitate the final product as a complex salt. Complex **1** was meticulously characterized by Fourier-transform infrared (FT-IR), 1D and 2D  $^1H$ -NMR and  $^{13}C$ -NMR, UV-visible, and HD-ESI mass spectroscopy analysis. The HD-ESI mass spectrum of **1** showed a signature peak cluster at 1009.47 corresponding to the monovalent  $[Ru(L^{terpy})(L^2)Cl]^+$  ion. A diagnostic isotopic envelope was observed, confirming the presence of all expected isotopes, including seven stable ruthenium and two chloride isotopes. The complex formation was further validated by the presence of distinct vibrational modes in the FT-IR spectrum, particularly, strong bands observed at 2924- 2853, 1584-1516 and 846  $cm^{-1}$  respectfully attributed to C-H, C=C, and P-F stretches.

### Molecular structure in the solid state

In spite of several attempts, the crystal structure for complex  $[Ru(L^{terpy})(L^2)Cl]PF_6$  **1** was not obtained. However, we solved the structure of an analogue displaying a shorter  $-OC_9H_{19}$  alkoxy chain, as illustrated in **Figure 1**, with selected data reported in **Table T1**. The complex shows pseudo-octahedral geometry around the ruthenium center, with  $L^{terpy}$  occupying the meridional plane. Two geometrical isomers are possible for this complex depending on the position of the  $-N$ -phenyl portion and O atoms of  $L^2$  in regard to the Cl group.<sup>15</sup> However, the crystal structure of this analogue indicates that the  $-N$ -phenyl group is preferentially oriented trans to the Cl atom in its favored thermodynamic product. Bond length between ruthenium and the central nitrogen atom, N1, of the terpyridine ligand is shorter (1.972 Å) than the other two Ru- $N_{terpyridine}$  bonds at 2.073 Å, 2.068 Å due to steric effects.<sup>16</sup> The observed Ru- $N_{terpy}$  bond lengths are in excellent agreement with literature reported values of similar compounds.<sup>14a, 17</sup> Moreover, the bond lengths between ruthenium and the O- and N-atoms of the aminocatechol ligand reach Ru-O8 = 2.0365 Å and Ru-N33 = 1.971 Å. The Ru-Cl bond distance of 2.3875 Å is comparable to the values reported by Lahiri et al.<sup>18</sup>, further

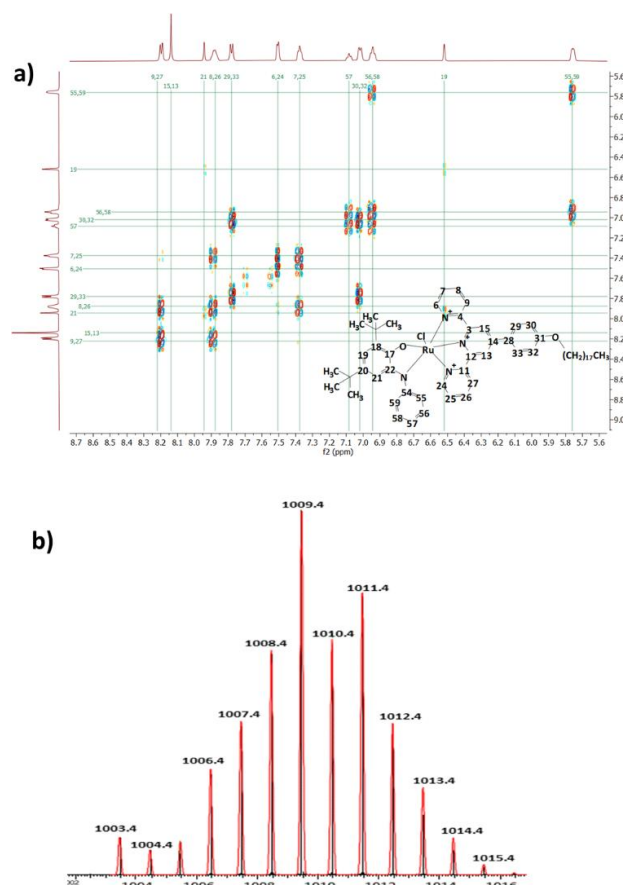


**Figure 1:** X-ray crystal structure of the  $[Ru(L^{terpy})(L^2)Cl]PF_6$  (CCDC 2156733) analogue displaying a shorter  $-OC_9H_{19}$  alkoxy chain at 50% probability; the  $PF_6$  counter ion is omitted for clarity. Selected bond lengths: Ru-N1 = 1.972(2), Ru-N2 = 2.073(3), Ru-N3 = 2.068(3), Ru-O8 = 2.0365(19), Ru-N33 = 1.971(2), Ru-Cl = 2.3875(7), C-N<sub>average</sub> = 1.394, C41-O8 = 1.281, C-C<sub>average</sub> = 1.4310 Å

implying that the  $-N$ -phenyl group is trans to  $Cl^-$ . The average C-C bond values reach 1.431 Å, while the specific distances of relevance are 1.281 and 1.347 Å for bond lengths of C41-O8 and C40-N33, respectively. When compared with literature reported bond lengths of similar species the structure of this analogue for complex **1** has bond length characteristics between those of structures for [Ru<sup>III</sup>-semiquinone] and [Ru<sup>II</sup>-quinone],<sup>15, 19</sup> and the assignment of the nature of L<sup>2</sup> in **1** on the basis of the solid structure of its derivative is not straightforward. However, lack of a proton in N33, allied to a careful analysis of bond lengths in other systems<sup>14b, c, 20</sup> strongly suggests the presence of a [Ru<sup>III</sup>-semiquinone].

## Molecular structure in solution

Ligands and complex **1** were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR nuclear magnetic resonance in deuterated dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>). The well-resolved peaks in the <sup>1</sup>H-NMR spectrum reinforces the description of species **1** as containing a 4d<sup>5</sup> Ru<sup>III</sup> metal center magnetically or electronically coupled to a semiquinonoid L<sup>2</sup> in a distorted octahedral field. The <sup>1</sup>H-NMR of H<sub>2</sub>L<sup>2</sup> shows two broad singlets with an intensity of 1 proton, which are assigned to OH and NH groups. These peaks are absent in the NMR spectrum of the metal complex indicating that the ligand is bound to the metal through these deprotonated functional groups. The aromatic region of the <sup>1</sup>H-NMR of **1** displays 12 signals corresponding to 21 protons. These signals are fully assigned based on coupling patterns exhibited in correlation spectroscopy (COSY) and heteronuclear single-quantum correlation spectroscopy (HSQC) data. COSY data indicate the interactions between nearby protons in the structure while HSQC experiment is used to determine the direct correlation between <sup>1</sup>H and <sup>13</sup>C atoms. **Figures 2(a)** and **S5** show aromatic region of COSY and HSQC for complex **1** respectively. Although there are two possible geometrical isomers for **1** associated with the relative position of the aminocatechol and chlorido ligands<sup>15</sup>, <sup>1</sup>H-NMR revealed the presence of only one species as the favoured thermodynamic product. This further validates the exclusive observation of the trans-species of derivative of **1** in the X-ray crystal structure. Upon coordination to the metal center, most of the protons of terpyridine ligand L<sup>terpy</sup> show a slight upfield effect, yet protons # 6 and 24 indicate a significant upfield shift compared to the free ligand. This is explained by considering the configuration of the molecule where the terpyridine is perpendicular to L<sup>2</sup> causing protons # 6 and 24 of L<sup>terpy</sup> to be above the aromatic plane of the amino-catechol ligand which increase the shielding effect. Similarly, protons # 55 and 59 of L<sup>2</sup> also exhibited a characteristic shielding effect in the metal complex relative to the uncoordinated ligand.<sup>21</sup> This upfield peak positions of protons # 6, 24, 55, and 59 in **1** suggest a preferential trans arrangement of the  $-N$ -phenyl portion of L<sup>2</sup> with respect to the Cl group.<sup>22</sup> As available in the experimental section, the peak distribution for <sup>1</sup>H-NMR compares well with the expected peak pattern and the COSY spectrum also exhibit the predicted correlations. In the aromatic region of the COSY spectrum, peaks at 6.51 ppm (# 19) and 8.14 ppm (# 15,13) do not show any correlation to other peaks. The aromatic protons # 30,32 and 29,33 of the phenyl



**Figure 2:** Analyses for complex **1**, (a) COSY NMR spectrum of the aromatic region in CD<sub>2</sub>Cl<sub>2</sub> (b) High resolution ESI-mass spectrum, the black bars show the experimental spectrum and the red continuous trace indicate the simulated spectrum.

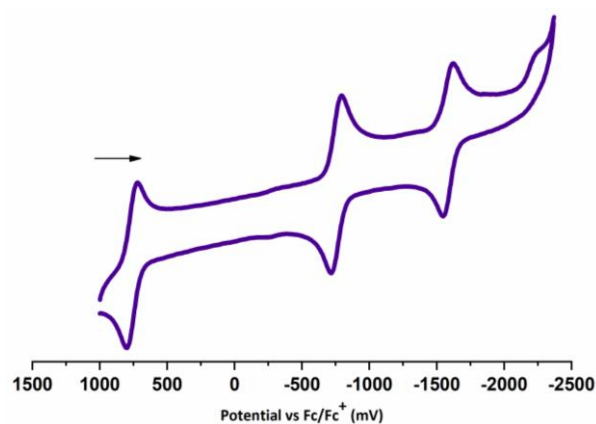
ring attached to terpyridine show correlation to each other, as expected. Additionally, the protons # 8 and 26 of the terpyridine exhibit coupling to both the protons # 7, 25 and # 9, 27 in the COSY spectrum, whereas the protons # 7 and 25 also show correlation peaks with protons # 6 and 24. The hydrogen atoms # 56 and 58 in the phenyl ring attached to the aminocatechol demonstrates interactions with protons # 55, 59 and 57. Significant coupling between protons can be observed in the aliphatic region of the COSY spectrum due to the presence of 17 -CH<sub>2</sub> groups. Hence, the 1D and 2D NMR spectroscopy data confirm the expected structure for complex **1**.

## Electronic structure

The UV-visible spectroscopy data for complex **1** was recorded in dichloromethane using a 10<sup>-4</sup> M solution (**Figure S7**) in an attempt to determine the electronic structure of **1** and the nature of the aminocatechol derivative. Complex **1** shows intense absorption bands in the UV region around 230, 284 and 320 nm corresponding to  $\pi \rightarrow \pi^*$  intraligand (IL) transitions.<sup>15, 23</sup> The strong absorption band observed in the visible region at 577 nm ( $\epsilon \approx 24,500 \text{ M}^{-1}\text{cm}^{-1}$ ) can be attributed to a metal to ligand charge transfer (MLCT) transition,<sup>24</sup>

whereas the broad band at around 1070 nm ( $\epsilon \approx 410 \text{ M}^{-1}\text{cm}^{-1}$ ) is tentatively identified as either a d-d transition or a low intense MLCT transition. Final assignment will rely on TD-DFT calculations. The MLCT electronic transitions are governed by interactions between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the complex,<sup>24c, 25</sup> and their attribution have been the topic of intense debate because both the metal and the L<sup>2</sup> derivative can attain several redox states. Ruthenium can either be <sup>15</sup>4d<sup>6</sup> Ru<sup>II</sup> or <sup>15</sup>4d<sup>5</sup> Ru<sup>III</sup>, whereas L<sup>2</sup> can exist in its protonated and reduced aminocatecholoid (AC), oxidized and deprotonated semiquinonoid (SQ) or fully oxidized and deprotonated quinonoid (Q) form. On the one hand, Fujita *et al.*<sup>19a</sup> and Lahiri *et al.*<sup>15</sup> did extensive studies on similar [Ru(terpy)(iminobutylQ)Cl]<sup>+</sup> and Ru(terpy)(iminobenzoQ)Cl]<sup>+</sup> complexes, respectively. Their contributions suggest considerable mixing of Ru (d $\pi$ ) and amino catechol derivative ( $\pi^*$ ) orbitals with significant contributions from both Ru<sup>II</sup>-quinone (Q) and Ru<sup>III</sup>-semiquinone (SQ) resonance forms. Mixing of orbitals yields a highly delocalized molecular structure.<sup>19a, b, 26</sup> The peak in the visible region which dominates the UV-visible spectrum of these complexes was assigned as a transition from a molecular orbital with metal character to an aminocatechol-based MO, namely  $t_{2g}(d_{yz}) \rightarrow \pi^*$ , by Fujita and co-workers<sup>19a</sup>. Even though this absorption band is presented as a MLCT transition, this is a simplification as contributions from distinct metal- and ligand-based MOs make it a ML-to-LM transition. Furthermore, they suggest that frontier molecular orbitals are comprised of destabilized Ru  $t_{2g}(d_{xy}$  and  $d_{x^2-y^2})$  orbitals and  $\pi/\pi^*$  orbitals of the aminocatechol derivative, with only minor contributions from Cl ligand. We have observed similar orbital mixing in other metallosurfactants with bipyridine-ruthenium(II) and redox-active ligands<sup>27</sup>. On the other hand, Lahiri and co-workers<sup>15</sup> interpret these electronic transitions differently. According to experimental data and complementary theoretical calculations, the most intense transition in the visible region was assigned as an electron transfer  $\text{Ru}(d\pi) + \text{Cl}(\pi) \rightarrow \pi^*(\text{terpy})$ .<sup>28</sup> With the  $d\pi$  MO necessarily belonging to the  $t_{2g}$  manifold in an O<sub>h</sub> point group, the authors refrain from a more specific attribution. Nonetheless, this attribution assumes that the ground state of the [Ru(terpy)(iminobenzoQ)Cl]<sup>+</sup> complex entails a trivalent and spin-coupled singlet 4d<sup>5</sup> Ru<sup>III</sup>-SQ form with minor contributions from the Ru<sup>II</sup>-Q state. Finally, to increase complexity, the characteristic broad band that appear in the near IR region has been identified as a transition  $\text{Ru}(d\pi) \rightarrow \pi^*(\text{SQ})$  by a classic treatment of orbital mixing in ruthenium/quinone ligands by Lever and coworkers,<sup>24c</sup> ergo within the  $t_{2g}$  manifold again. However, the molar extinction coefficient of the observed band in **1** is significantly less intense than the value observed for the  $\text{Ru}^{\text{II}} \rightarrow \pi^*(\text{SQ})$  transition; hence, it can be described as a d-d band. While the peak positions and intensities of electronic spectrum for **1** correlates well with Fujita's observations, we thought prudent to conduct our own DFT calculations, in correlation with the redox properties of complex **1**, as recorded in dichloromethane using TBAPF<sub>6</sub> as the supporting electrolyte and illustrated in **Figure 3**. The cyclic voltammogram of **1** revealed a rich electrochemical response attributed to four redox processes within the experimental potential

range of  $\pm 1.80 \text{ V}_{\text{Ag}/\text{AgCl}}$  (at an equivalent  $+1.30$  and  $-2.30 \text{ V}_{\text{Fc}/\text{Fc}^+}$ ). The first reversible process occurred at  $+1.26 \text{ V}_{\text{Ag}/\text{AgCl}}$  ( $+0.76 \text{ V}_{\text{Fc}/\text{Fc}^+}$ ,  $\Delta E = 0.09 \text{ V}$ ,  $|i_{\text{pa}}/i_{\text{pc}}| = 1.18$ ), while the other processes were observed respectively at  $-0.25 \text{ V}_{\text{Ag}/\text{AgCl}}$  ( $-0.76 \text{ V}_{\text{Fc}/\text{Fc}^+}$ ,  $\Delta E = 0.07 \text{ V}$ ,  $|i_{\text{pa}}/i_{\text{pc}}| = 0.95$ ),  $-1.10 \text{ V}_{\text{Ag}/\text{AgCl}}$  ( $-1.60 \text{ V}_{\text{Fc}/\text{Fc}^+}$ ,  $\Delta E = 0.07 \text{ V}$ ,  $|i_{\text{pa}}/i_{\text{pc}}| = 1.11$ ) and  $-1.74 \text{ V}_{\text{Ag}/\text{AgCl}}$  ( $-2.22 \text{ V}_{\text{Fc}/\text{Fc}^+}$ ). Even though this redox behavior is typical for ruthenium polypyridine complexes with similar redox-active ligands, relating these redox states with electronic forms of the molecule is challenging. Hence, similar to the previous section, distinct groups have interpreted these processes differently.<sup>29</sup> Fujita and co-workers<sup>19a, 26</sup> suggest that the ground state of [Ru(terpy)(iminobutylQ)Cl]<sup>+</sup> favors Ru<sup>II</sup>-Q form, based on theoretical calculations, experimental UV-visible and spectro-electrochemical studies. Consequently, the first process observed for their system at  $1.17 \text{ V}_{\text{Ag}/\text{AgCl}}$  was assigned to the Ru<sup>II</sup>/Ru<sup>III</sup> couple and the process at  $-0.21 \text{ V}_{\text{Ag}/\text{AgCl}}$  as Q/SQ couple. However, based on EPR and DFT calculations, Lahiri *et al.*<sup>15</sup> proposes an alternative assignment in which these processes are all metal-based. The electrochemical potentials observed for our complex **1** are comparable to the values reported by Lahiri *et al.*,<sup>15</sup> and together with <sup>1</sup>H-NMR, mass spectroscopic and UV-visible spectroscopic analysis, this suggests that [Ru(L<sup>terpy</sup>)(L<sup>2</sup>)Cl]PF<sub>6</sub> (**1**) has similar Ru<sup>III</sup>-SQ characteristics. This is also supported by the X-ray structure of the derivative of **1**. Thus, the first positive process at  $+1.26 \text{ V}_{\text{Ag}/\text{AgCl}}$  can be assigned to the Ru<sup>III</sup>/Ru<sup>IV</sup> redox couple, whereas the next two processes are attributed to reduction of the L<sup>2</sup> ligand from aminosemiquinone to aminocatechol and to the Ru<sup>III</sup>/Ru<sup>II</sup> couple, respectively. The most reduced peak is



**Figure 3:** Cyclic voltammogram of complex **1** in  $1 \times 10^{-3} \text{ M}$  DCM. Glassy carbon as working electrode, Ag/AgCl as reference electrode, Pt wire as auxiliary electrode, and 0.1 M TBAPF<sub>6</sub> supporting electrolyte

ascribed to a terpyridine-based process.

### DFT calculated structure

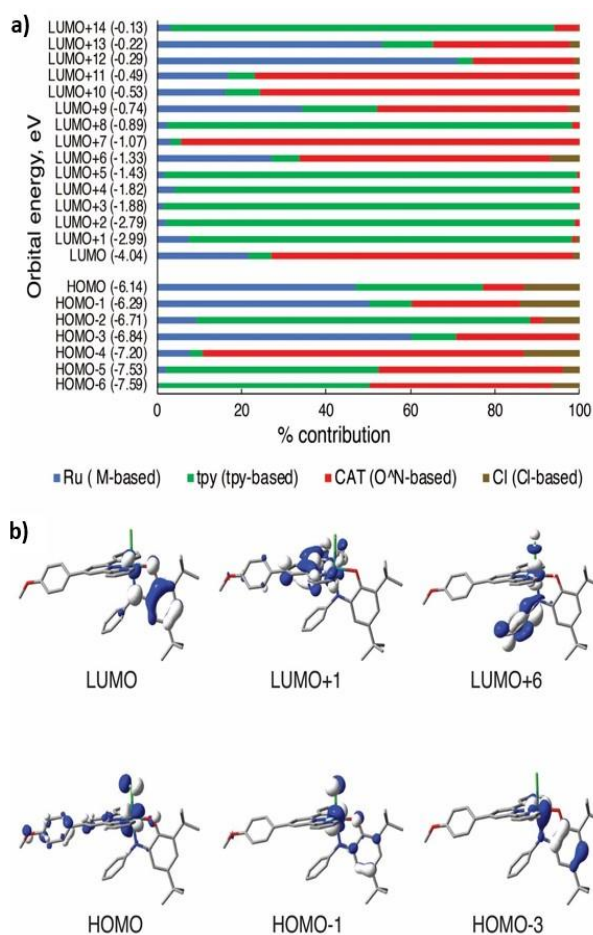
DFT calculations at the B3LYP-D3/SDD,6-311G\* level were used to evaluate the nature and energies of the frontier molecular orbitals in compound **1** to provide insight into the observed electronic and electrochemical results, and to serve as basis to discuss electron

transfer. The  $-(\text{CH}_2)_{17}\text{CH}_3$  alkoxy group in **1** was replaced with a  $-\text{OCH}_3$  group for the simplicity of calculation. Removal of this group is not expected to affect the electronic properties of the calculated molecules. Two different models were considered, namely a singlet and a triplet ground state configuration. Our calculations identify the most stable ground state for complex **1** as the singlet state ( $^1\text{L}^2\text{d}^5 \text{Ru}^{\text{III}}\text{SQ}(\uparrow\downarrow)$ ), being favourable by 10.60 Kcal/mol over the triplet spin state  $\text{Ru}^{\text{III}}\text{SQ}(\uparrow\uparrow)$ . Furthermore, an excellent correlation was attained between the metal-ligand bond lengths and angles in the crystal structure of **1** and that of the calculated singlet ground state, suggesting the presence of a  $^1\text{L}^2\text{d}^5 \text{Ru}(\text{III})$  metal center coupled with the unpaired electron of SQ ligand. The calculated Ru-O8 and Ru-N33 bond lengths reach 2.07 and 1.98 Å and therefore are slightly longer than the observed experimental values by 0.03 and 0.01 Å, whereas the Ru-Cl bond is calculated at 2.42 Å, thus 0.03 Å longer. A detailed analysis of theoretical and experimental bond lengths is provided in Table T3 (See Supplementary Information). Interestingly, in spite of multiple attempts, a purely antiferromagnetically coupled  $\text{Ru}^{\text{III}}\text{-SQ}$  state did not converge to a minimum using B3LYP-D3. This is similar to the calculations performed by Fujita *et al.*<sup>19a</sup> This observation implies that the  $\text{Ru}^{\text{III}}\text{-SQ}$  species is electronically coupled; a simplified scheme can be drawn in which the singly-occupied SQ  $\pi$  orbital

strongly interacts with a singly-occupied  $\text{Ru}^{\text{III}} t_{2g}$  orbital, generating a bonding and an antibonding combination (see HOMO-3 and LUMO in Figure 4). The resulting bonding MO is doubly-occupied, while the antibonding MO is unoccupied. In fact the picture is more complex with contributions of terpy and Cl orbitals. Fragment orbital analysis was performed to quantify the frontier molecular orbital localization on the metal and different ligands in the singlet state of **1**. There are four fragments used in this study namely, Ru, terpyridine, catechol and chloride. As expected for a standard polypyridine complex, the main contribution for occupied molecular orbitals in **1** comes from the  $\text{Ru}_{d\pi}$  orbitals, or the  $t_{2g} (d_{xy}^2, d_{xz}^2, d_{yz}^2)$  subset of a quasi- $O_h$  symmetry.<sup>27</sup> Specifically, the HOMO, HOMO-1 and HOMO-3 orbitals show about 47-60% localization on the metal ion with minor contributions from the orbitals in the chloride and terpyridine ligands. While the HOMO and HOMO-1 show  $\pi$ -donor interactions between the Cl and Ru, HOMO-3 displays a  $\pi$ -bonding interaction between the Ru and the aminocatechol derivative, suggesting that  $L^2$  acts as a  $\pi$ -acceptor in this system. Interestingly, the HOMO-2 orbital in **1** consists mainly of a terpy-based molecular orbital, emphasizing the extension of orbital mixing in this system. The LUMO is predominately located on the aminocatechol derivative with a significant contribution ( $\sim 20\%$ ) from Ru, while LUMO+1 through LUMO+5 are predominantly terpy-based with 91-98% electronic contribution. The orbital diagram with percent composition of molecular orbitals shown in Figure 4. indicate that complex **1** exhibits significant overlap between  $\text{Ru}(d\pi)$ , terpy and  $L^2$  orbitals.

#### Correlation of calculations to electronic and redox data

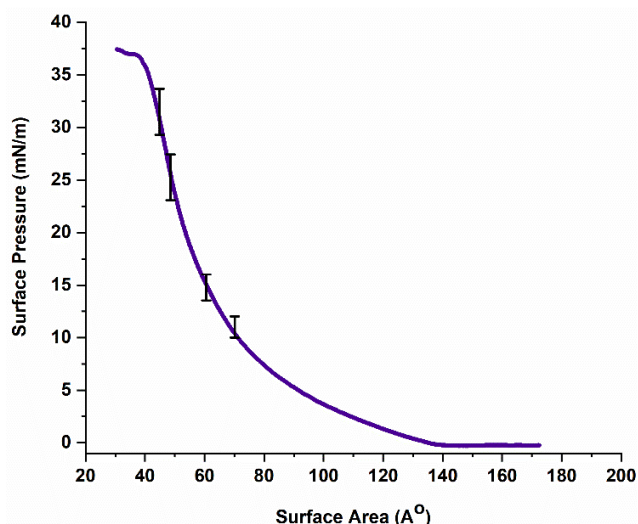
DFT methods were used to obtain the UV-visible and oxidation/reduction potentials of **1** in solution. The resulting electronic properties showed comparable features with the experimental data, with one intense absorption band in the visible region and one in the near-IR region (Figure S13). The calculated UV-visible spectrum exhibit a systematic hypsochromic shift of 0.1-0.2 eV relative to the experimental spectrum. The theoretical spectrum displays peaks at 527 and 981 nm, which correlate with experimental peaks at 577 and 1070 nm. The intense absorption band in the visible region includes a complex MLCT ( $\text{Ru}(d\pi) \rightarrow \text{terpyridine/aminocatechol ligand}$ ) and ligand to ligand (LL) charge transfer transition ( $\pi \rightarrow \pi^*$ ) localized on the amino catechol ligand. The peak in the near-IR region is composed of two main hole-particle pairs that display MLCT from  $\text{Ru}(d\pi) \rightarrow \pi^*$  of amino catechol-based ligand and LL charge transfer based on amino catechol ligand. The tentative experimental attribution to a d-d process was not observed. Theoretical analysis of redox properties suggests good correspondence between calculated and experimental potentials for the first cathodic and first anodic peak potentials with a difference of 0.05 and 0.15  $V_{\text{Fc}/\text{Fc}^+}$  respectively. Nonetheless the calculated second and third cathodic redox potentials show a respective difference of 0.60 and 0.80  $V_{\text{Fc}/\text{Fc}^+}$  from the experimental peaks. This is due to the fact that the calculated redox potentials did not account for the proton transfer that is expected to be coupled with the second and third cathodic potentials.



**Figure 4:** (a) Calculated molecular orbital energy diagram for Complex **1** (b) Frontier molecular orbitals for singlet state of **1**

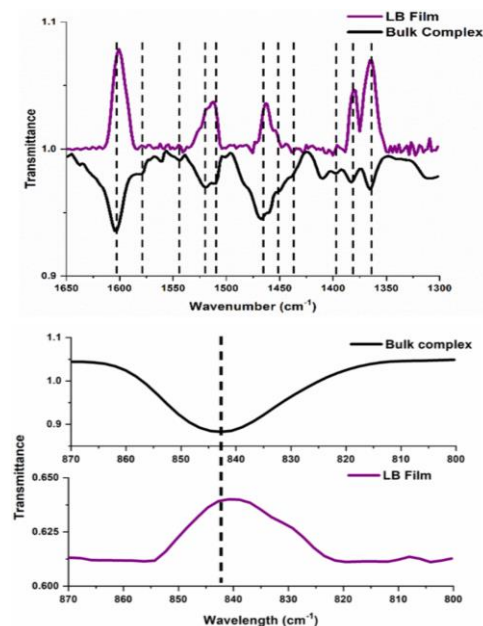
## Interfacial behavior and film formation

In order to build the Au|LB|Au junction that enables the study of electron transfer properties for complex **1**, it is necessary to study the behavior of molecular monolayer films at the air|water and air|solid interface. The presence of *tert-butyl* and alkyl groups give a hydrophobic nature to this complex. Yet, the polar and charged nature of the ruthenium lends hydrophilicity that makes **1** a practical redox-active surfactant to enable the deposition of Langmuir-Blodgett monolayers. The surface properties of [Ru(L<sup>terpy</sup>)(L<sup>2</sup>)Cl]PF<sub>6</sub> (**1**) were initially evaluated by compression isotherm and Brewster angle microscopy (BAM), as shown in **Figure 5**. and the complex forms a stable Pockles-Langmuir monolayer<sup>30</sup> at the air|water interface with a collapse pressure of 37 mN/m. An approximate critical area for **1** was calculated using the parameters provided by the X-ray crystal structure in **Figure 1**, and is estimated at about 80–85 Å<sup>2</sup>. This value is in good agreement with the experimentally observed critical area of 77 Å<sup>2</sup>, which is indicative of formation of a compact monolayer at the air-water interface. Furthermore, BAM images exhibit collapse as an array of Newton rings occurring due to multilayer formation after the collapse of the monolayer. The Langmuir-Blodgett films were structurally characterized by infrared reflection absorption spectroscopy (IRRAS), UV-visible spectrometry, and electrospray ionization mass spectrometry (ESI-MS) methods. Although the molecular devices are built with monolayers, spectroscopic analysis of a monolayer cannot be completed accurately due to the detection limit of instruments. Therefore, we used a sample with 57 monolayers of complex **1** for IRRAS and UV-visible measurements. Langmuir-Blodgett monolayers of [Ru(L<sup>terpy</sup>)(L<sup>2</sup>)Cl]PF<sub>6</sub> (**1**) were transferred onto glass, mica, or gold substrates Y-type dipping with a head-head and tail-tail configuration. A constant pressure of 27 mN/m was maintained during the deposition at 23 °C. The IRRAS method uses polarized light at a specific angle to obtain the vibrational peak patterns of the deposited thin film.<sup>31</sup> A comparison between IR spectrum of the bulk sample and the IRRAS spectrum of the film recorded at p-polarized light at an incident angle of 30° is shown in **Figure 6**. The IRRAS spectrum of the LB film shows good agreement with the bulk IR spectrum of the complex and exhibits equivalent peak positions. The symmetric and asymmetric stretching vibrations related to -CH<sub>2</sub> groups of the long alkyl chain appear at 2924, 2842 cm<sup>-1</sup> respectively. The shift of -CH<sub>2</sub> stretching frequencies suggest a condensed and well-ordered film formation with preferential *all-trans* confirmation in alkyl chain.<sup>31-32</sup> Stretching frequencies corresponding to -CH<sub>3</sub> groups in the bulk sample are observed at 2956 cm<sup>-1</sup>, and shift to 2965 cm<sup>-1</sup> in the LB film suggesting that the alkane chains are somewhat tilted with respect to the surface. Prominent peaks observed between at 1600 and 1300 cm<sup>-1</sup> are attributed to aromatic C=C, C=N stretching and CH<sub>3</sub>/CH<sub>2</sub> bending vibrations, and indicative that the aromatic ligand remains intact after deposition onto solid substrates. Furthermore, the vibration of the PF<sub>6</sub> counterion appears at 840 cm<sup>-1</sup> for the deposited thin film. The presence of positive



**Figure 5:** Compression isotherm for complex **1**. The vertical error bars display limits over three compression experiments.

(upward) and negative (downward) peaks in the IRRAS is explained by surface selection rules.<sup>33</sup> A positive peak is observed for a functional group that has a surface-perpendicular transitional dipole moment with respect to the dielectric substrate, whereas the surface-parallel component of a transition moment yields a negative band in the IRRAS spectrum.<sup>33-34</sup> The UV-visible spectrum of the LB film of complex **1** shows excellent agreement with the bulk UV-visible spectrum, as shown in **Figure S10** and the general spectral characteristics were preserved, including the MLCT band that occurs at 581 nm. The slight red shift observed is attributed to aggregate formation in the multilayer arrangement.<sup>35</sup> The LB films deposited on glass substrate were scraped off and further analysed via ESI-MS. The

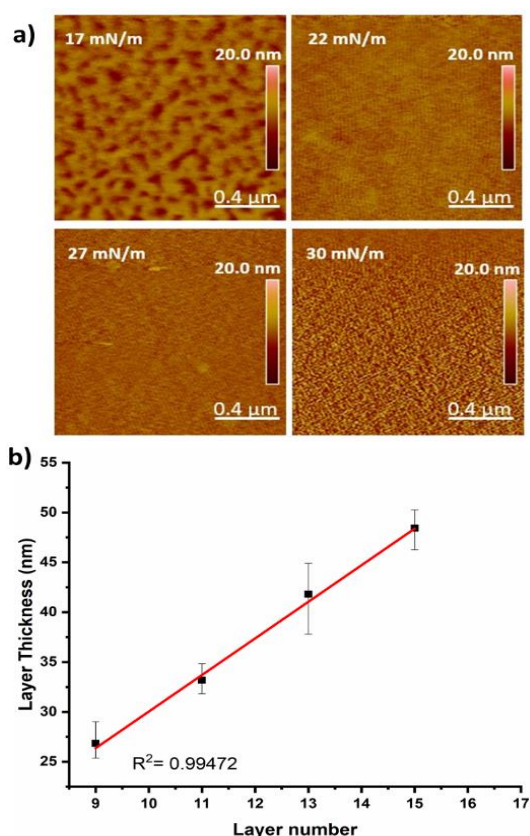


**Figure 6:** Comparison of IRRAS spectrum of 57 layers of LB film and IR spectrum of complex **1**

mass spectroscopy data confirmed that the bulk  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^2)\text{Cl}]\text{PF}_6$  (**1**) and multilayer LB films exhibit similar isotopic distribution and  $m/z$  value (Figure S10(b)).

## LB film deposition and morphological analysis

LB monolayers of the complex were deposited at different surface pressures and analysed by Atomic Force Microscopy (AFM) images. To ensure complete transfer of the film on the substrate, the transfer ratio was maintained near unity. As shown in Figure 7(a), the AFM analysis indicates that the films deposited at the low surface pressure of 17 mN/m have a higher number of pin hole defects, whereas films deposited above 30 mN/m pressure exhibit significantly rougher surfaces indicative of aggregate formation. Monolayers deposited between 22 and 27 mN/m display a smoother film surface and were further considered. The thickness of a monolayer film of **1** was determined by blade-scratching method using quartz substrates with nine to fifteen layers. These films were scratched, and the depth of the resulting trench was measured using AFM in the contact mode. The resulting values yield a linear relationship between the thickness and the number of layers, which indicates homogeneous film deposition. The plotting of layer thickness vs. layer number shown in Figure 7(b) indicates an average thickness of ca. 30-32 Å per monolayer. Using the parameters from the crystal structure for



**Figure 7:** (a) AFM images of monolayers of complex **1** deposited on mica substrates at different surface pressures (b) Graph of layer thickness versus number of layers of complex **1**

comparison, the approximate length of compound **1** can be estimated at  $\sim 43$  Å. However, due to the presence of hydrophobic and flexible groups at both ends of the molecule, we assume that the terpyridine moiety lies nearly flat on the surface. Rather than in a linear configuration, both t-Bu and alkyl groups bend out of the surface plane. The film thickness reflects this non-linear arrangement.

## Fabrication of Au|LB|Au junctions

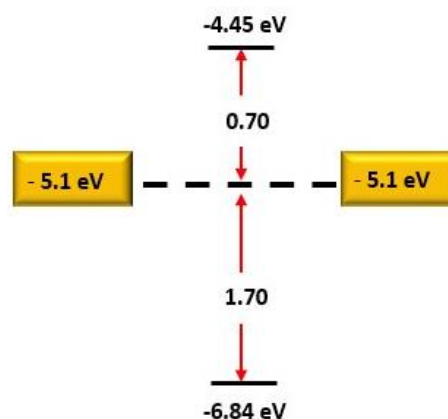
The monolayer of compound **1** was deposited on a pre-cleaned gold substrate ( $\text{Au}_1$ , bottom) at a surface pressure of 27  $\text{mNm}^{-1}$ , and dried in a desiccator for five days under reduced pressure. The top gold electrode ( $\text{Au}_2$ ) was deposited using shadow masking<sup>36</sup> with an Effa-Coater gold sputter. Four assemblies containing 16 individual  $\text{Au}_1|\text{LB}|\text{Au}_2$  junctions were prepared, yielding a total of 64 junctions to be analyzed for their current-voltage ( $I/V$ ) characteristics at room temperature using a Keithley 4200 semiconductor parameter analyzer connected to a Signatone S-1160 Probe Station.

## Feasibility and observation of electron transport

For electron transport to happen it is necessary that the energies of the electrodes and the molecule are compatible. Therefore, knowing that the gold electrode displays Fermi levels at -5.1 eV below the vacuum level,<sup>5, 9d, 37</sup> we convert the reduction and oxidation potentials of complex **1**, obtained via cyclic voltammetry, to assess the solid-state energies associated with the frontier molecular orbitals of the molecule. The experimental potentials measured vs. Ag/AgCl are transformed into saturated calomel electrode potentials ( $V_{\text{SCE}}$ ), and then converted into the first electron affinity ( $V_a$ ) and first ionization energy ( $V_i$ ) of the molecule as respectively given by the Hips and Armstrong models:<sup>5, 38</sup>

$$V_a = 4.7 \text{ eV} + E_{1/2}^{\text{red}}(\text{SCE}) \quad (\text{Eq.1})$$

$$V_i = 4.7 \text{ eV} + (1.7) E_{1/2}^{\text{ox}}(\text{SCE}) \quad (\text{Eq.2})$$



**Figure 8:** Frontier molecular orbital energy values (from CV data) for complex **1** compared with Fermi energy of gold electrodes



These energies are given in eV, and can be considered approximately similar to the respective LUMO and HOMO energies of complex **1**.<sup>9c, 38</sup> As such, the LUMO of the complex is at -4.45 eV or 0.7 eV above gold, whereas the HOMO energy level is about 1.7 eV below (**Figure 8**). The excellent match within 1 eV between LUMO and Fermi level suggests that electron transport based on tunnelling through the molecule is feasible.

In order to probe our hypothesis that distortions of the  $O_h$  symmetry will lead to significant orbital mixing between molecular orbitals ruthenium, terpy, aminocatechol and chlorido ligand, leading to affordable pathways for tunnelling, we tested electron transport experimentally. We probed the current-voltage characteristics of multiple  $Au_1|LB1|Au_2$  junctions in each assembly by applying a bias voltage to the top electrode while maintaining the bottom gold electrode at zero bias voltage (**Figure 9**). Although, due to monolayer defects, *ca.* 8-10 devices of each assembly were short circuited, an average of 35-40% of devices among four assemblies signify asymmetric electron transfer behaviour with higher current in the negative quadrant of the  $I/V$  curve compared to the negligible current response in the positive side. The amplitude of observed current response for **1** is comparable to similar studies reported in the literature, which employed LB films for molecular device preparation.<sup>9a, d, 39</sup> This unquestionable directional electron transport was further established by the rectification ratio (RR=  $|I$  at  $-V/|I$  at  $+V$ ), which varied from 4 to 18 between -2 V to +2 V and from 5 to 32 between -4 V to +4 V. Repetition of measurements on the same device leads to lower currents that tend to display a more sigmoidal  $I/V$  behavior. This has been tentatively explained as an effect of molecules to decrease their energy in high electric fields by reorganizing their dipole moments.<sup>8b, 9a, 38c</sup> Compared to similar asymmetric terpyridine-based metal complexes, the  $I/V$  characteristics of **1** are analogous to the Ru-based dyad electrografted on gold, studied by Lacroix *et al.*<sup>7</sup> using Ti/Au as the top electrode. This species showed a substantially large RR of 300 at  $\pm 2.5V$ . Even though the RR value of complex **1** is smaller, these

studies confirm the feasibility of directional electron transfer of **1**. Based on the reasonably low LUMO-Fermi energy gap of 0.7 eV and the asymmetric placement of **1** between the top and bottom electrodes, we suggest that directional electron transfer shown in this study likely entails an asymmetric rectification mechanism in which the electrons tunnel through the ligand-based LUMO without necessary involvement of the metal-based HOMOs. It has been shown that incorporation of alkyl chain in the molecule causes an asymmetric displacement of the redox active moiety from the top electrode and leads to a potential drop between alkyl chain and the electrode.<sup>40</sup> Consequently, this asymmetric placement is also regarded as a favorable factor for through-molecule directional charge transport. However, the incorporation of these insulating chains can result in limited transport and blockades,<sup>7, 40-41</sup> which may explain the moderate rectification ratios obtained for **1**, when compared with other systems.<sup>7, 40, 42</sup>

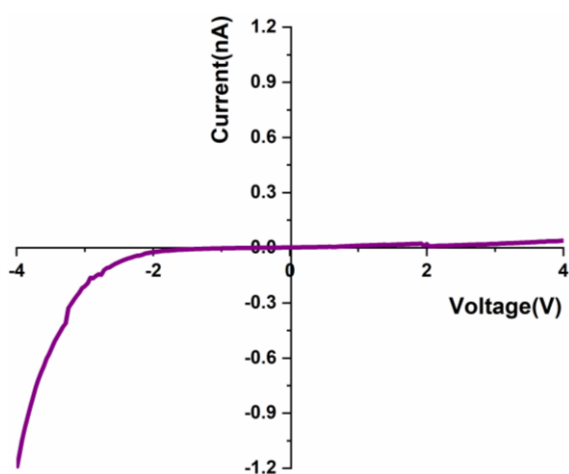
## Conclusions

We have successfully designed and studied a redox-active ruthenium metallosurfactant  $[Ru^{III}(L^{terpy})(L^2Cl)]PF_6$  (**1**) with extensive orbital mixing between the Ru center, the terpy and the semiquinone ligands. The electronic and redox properties suggest that **1** has a low lying LUMO primarily associated with the semiquinone ligand, which can partake in directional electron transport in  $Au|LB1|Au$  junctions. The asymmetric  $I/V$  profile of **1** is in distinct contrast with the symmetric response obtained by similar (terpy)M species discussed in this account, and validate our hypothesis that heavily distorted  $O_h$  species with distinct donors will enable tunnelling through empty and heavily mixed molecular orbitals. Further studies will examine the effect of temperature and magnetic fields on the observed current and rectification ratio of similar molecular species.

## Experimental Section

### Materials and Methods

Reagents and solvents were used as purchased from commercial sources. A Varian 500 MHz instrument was used for  $^1H$ -NMR,  $^{13}C$ -NMR, COSY and HMQC NMR spectra. The Fourier-transform Infrared spectrum of ligands and the complex were recorded as KBr pellets using a Tensor 27 spectrometer in the range of 4000-400  $cm^{-1}$ . Elemental analysis of complex **1** was performed by Midwest Microlab, Indianapolis, USA. ESI mass spectroscopy data in the positive mode for both the complex and its thin films was acquired using a Waters micromass ZQLC/MS instrument. A UV-3600 Shimadzu spectrophotometer was used to measure UV-visible spectra in the range of 190-1600  $cm^{-1}$ . Cyclic voltammetry experiments were performed using a BAS 50W potentiostat with a standard three-electrode cell consisting of a platinum wire auxiliary electrode, glassy carbon working electrode and Ag/AgCl reference electrode. Experiments were conducted under argon at room temperature using TBAPF<sub>6</sub> as the supporting electrolyte. All the



**Figure 9:**  $I/V$  curve for  $Au|LB1|Au$  molecular junction between  $\pm 4 V$

potentials were referenced according to the potential of ferrocene<sup>43</sup> used as the internal standard.

### Syntheses.

**4'-(4-octadecyloxyphenyl)-2,2':6',2''-terpyridine (L<sup>terpy</sup>).** The terpyridine ligand was synthesized according to the Kröhnke synthesis method.<sup>44</sup> Two equivalents of 2-acetyl pyridine (0.64 mL) was reacted with one equivalent of 4-octadecyloxy benzaldehyde (0.93 g) in the presence of two equivalents of KOH (0.30 g) and NH<sub>4</sub>OH (7.36 mL). The reaction mixture was refluxed for 4 h at 60 °C. The off-white product was recrystallized in absolute ethanol to obtain a white color precipitate. Yield (30%). ZQ-MS(m/z<sup>+</sup>) = 576.93 (100%) for [C<sub>39</sub>H<sub>51</sub>N<sub>3</sub>O] (calculated= 577.86). FT-IR (KBr cm<sup>-1</sup>) 2850-2920 (ν C-H), 1584-1516 (ν C=C, aromatic), 1469 (ν C=N, aromatic). <sup>1</sup>H-NMR, ppm (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ 8.74 (m,6H), δ 7.89 (m,4H), δ 7.38 (t,2H), δ 7.05 (d,2H), δ 4.06 (t,2H), δ 1.83 (t,2H), δ 1.28 (m,30H), δ 0.89 (t,3H).

**Ru(DMSO)<sub>4</sub>Cl<sub>2</sub>.** RuCl<sub>3</sub> · XH<sub>2</sub>O (2.00 g), dissolved in DMSO (25 mL) was refluxed at 80 °C until the deep red colour changed to orange. After cooling down to room temperature, acetone (40 mL) was added to the reaction mixture and the final solution was cooled in an ice bath to obtain a yellow precipitate. Yield (80 %)

**Ru(L<sup>terpy</sup>)(DMSO)Cl<sub>2</sub>.** One equivalent of Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (0.22 g) was reacted with one equivalent of L<sup>terpy</sup> (0.25 g) in ethanol (20 mL) under dark conditions. The solution was refluxed for 18 h under argon. The crude product was washed with cold ethanol and water and dried under vacuum. Yield (67 %). FT-IR (KBr, cm<sup>-1</sup>) 2922, 2852 (long chain C-H), 1603, 1519, 1467, 1402 (Pyridine rings), 1080 (S=O). <sup>1</sup>H-NMR, ppm (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ 9.27 (d, 2H), δ 8.19 (d, 4H), δ 7.96 (t, 2H), δ 7.78 (d, 2H), δ 7.63 (t, 2H), δ 7.06 (d, 2H), δ 4.06 (t, 2H), δ 2.75 (s, 6H), δ 1.85 (t, 2H), δ 1.28 (m, 30H), δ 0.89 (t, 3H).

**2,4-di-tert-butyl-6-(phenylamino)phenol (H<sub>2</sub>L<sup>2</sup>).** 2.00 g of 3,5-di-tert-butylcatechol was dissolved in n-heptane in the presence of triethylamine (0.12 mL). Then aniline (0.82 mL) was dissolved in n-heptane separately and was added to the 2,4-di-tert-butyl-6-(phenylamino)phenol solution. Final mixture was refluxed for 5 h and then stored at 4 °C to obtain needle-like crystals. Yield (89%). FT-IR (KBr, cm<sup>-1</sup>) 2961(tert-butyl group C-H), 1600, 1496, 1418, 1363 (Pyridine rings). <sup>1</sup>H-NMR, ppm (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz) δ 7.25 (d, 1H), δ 7.20 (t, 2H), δ 7.07 (d, 1H), δ 6.84 (t, 1H), δ 6.67 (d, 2H), δ 6.48(s, 1H), δ 1.45 (s, 9H), δ 1.28 (s, 9H).

**[Ru(L<sup>terpy</sup>)(L<sup>2</sup>Cl)]PF<sub>6</sub>(1).** A mixture of Ru(L<sup>terpy</sup>)(DMSO)Cl<sub>2</sub> (0.40 g) and H<sub>2</sub>L<sup>2</sup> (0.44 g) was refluxed in argon-degassed ethanol for 18 h. The volume of the resultant solution was reduced and NH<sub>4</sub>PF<sub>6</sub> (0.10 g) was added. The dark-purple product was isolated and further purification was done by column chromatography using neutral alumina with dichloromethane:acetonitrile (9:1). Yield (10%). ZQ-MS(m/z<sup>+</sup>) = 1009.4717(100%) for [C<sub>59</sub>H<sub>76</sub>ClRuN<sub>4</sub>O<sub>2</sub>]<sup>+</sup> (calculated= 1009.47). FT-IR (KBr, cm<sup>-1</sup>) 2924, 2853 (long chain C-H), 1603, 1519, 1467, 1383, 1365 (Pyridine rings C=C, C=N), 1243 (t-butyl), 1183 (C-O-C), 843 (PF<sub>6</sub>). <sup>1</sup>H-NMR, ppm (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz) δ 8.20 (d, 2H), δ 8.14 (s, 2H), δ 7.94 (s, 1H), δ 7.89 (t, 2H), δ 7.77 (d, 2H), δ 7.51 (d, 2H), δ 7.38 (t, 2H), δ 7.09 (t, 1H), δ 7.03 (d, 2H), δ 6.95 (t, 2H), δ 6.52 (s, 1H), δ 5.77 (d, 2H), δ 4.06 (t, 2H), δ 1.87 (s, 9H), δ 1.42 (t, 2H), δ 1.28 (s, 30H), δ 1.12 (s, 9H), δ 0.88 (t, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR, δ 187.40, δ 169.63, δ 161.73, δ 157.28, δ 153.26, δ 153.18, δ 149.05, δ 148.97, δ 147.16, δ 145.52, δ 139.68, δ 131.10, δ 129.14, δ 128.85, δ 128.13, δ

127.32, δ 126.18, δ 123.73, δ 120.58, δ 119.09, δ 115.28, δ 112.06, δ 102.20, δ 68.42, δ 35.96, δ 35.44, δ 31.89, δ 29.89, δ 29.68, δ 29.44, δ 29.32, δ 29.20, δ 28.87, δ 26.04, δ 22.65, δ 13.8. Elemental analysis calculated for [C<sub>59</sub>H<sub>76</sub>ClRuN<sub>4</sub>O<sub>2</sub>PF<sub>6</sub>]: C, 61.37; H, 6.63; N, 4.85. Found: C, 61.23; H, 6.59; N, 4.54.

### Other methods

#### DFT Calculation

Complex **1** was optimized in its singlet, triplet, quintet, and septet electronic states employing B3LYP functional<sup>45</sup> with Grimme's D3 dispersion correction.<sup>46</sup> The SDD effective core potential (ECP) and associated basis set for Ru atom<sup>47</sup> were used and the 6-311G\* basis set was used for all other atoms (Cl, O, N, C, and H).<sup>48</sup> Solvent effects, (dichloromethane), were included in the calculations through polarizable continuum model (PCM).<sup>49</sup> The ultrafine grid was used in the calculations. Vibrational frequency analysis was performed on optimized structures to confirm their convergence to the local minima at their respective potential energy surfaces. Natural orbital (NO) analysis was applied to determine the character of open-shell electronic states. AOMix program<sup>50</sup> was performed to determine the compositions of molecular orbitals and molecular fragments of the singlet ground state. Time-dependent density functional theory (TD-DFT)<sup>51</sup> was employed for excited-state analysis, using the same level of theory as the ground state calculations. The stick spectrum was broadened using Lorentzian functions with a half-width at half-maximum (HWHM) of 0.12 eV. Solvent effects (dichloromethane) were included via the polarizable continuum model (PCM).

Half-wave potentials (E<sub>1/2</sub>) were determined relative to the ferrocene/ferricenium (Fc/Fc<sup>+</sup>) redox couple through equation 3:

$$E^{\circ} (eV) = -\frac{\Delta G_{sol}}{nF} - 5.00 \quad (3)$$

Where ΔG<sub>sol</sub> is the change in solvated free energy upon reduction, *n* is the number of electrons (in this case, 1), and *F* is the Faraday constant. The specific reactions are the oxidation of Ru(III) complex (in singlet state) to Ru(IV) complex (in doublet state) and the reduction of Ru(III) complex (in singlet state) to Ru(0) complex (in doublet state). The calculated redox potentials are referenced to the Fc/Fc<sup>+</sup> by subtracting the estimated absolute reduction potential of Fc/Fc<sup>+</sup>, 5.00 eV.<sup>43, 52</sup> All calculations were carried out using the Gaussian 16 software package (Revision A.03).<sup>53</sup>

**Formation of Pockels-Langmuir and Langmuir-Blodgett** An automated KSV Minitrough (Biolin, Espoo, Finland) was used to obtain the pressure vs. area (Π-A) isotherms at the air/water interphase. All experiments were performed at 23 ± 0.3 °C using ultra-pure water from a Barnstead Nanopure system as the subphase. Before the experiment, the impurities present at the surface of the aqueous subphase were removed by vacuum. The complex was dissolved in highly volatile dichloromethane solvent to prepare spreading solutions with a concentration of 1 mg/mL. Approximately 30-40 μL of spreading solution was introduced over the subphase for each trial and about 20 minutes waiting time was maintained before monolayer compression. The barriers were compressed at a rate of 10 mm min<sup>-1</sup> during each measurement and a paper Wilhelmy plate (20 x 10 mm) was used to measure the surface pressure of the isotherm. At least three reproducible measurements were recorded for the complex.

**Brewster angle microscopy (BAM).** The BAM micrographs of the complex was recorded using a CCD detector of KSV-Optrel BAM 300 with a HeNe laser (10 mW, 632.8 nm). The monolayer compression rate was maintained at 10 mm min<sup>-1</sup>.

**AFM measurements.** Atomic force microscope images of the sample surfaces were taken using a Bruker Bioscope Catalyst AFM. A MicroMasch CSC 38 cantilever with a spring constant of 0.09 N/m was used to image the surface in contact mode imaging in air. The cantilevers were cleaned with ethanol, followed by DI water before doing an experiment. The cleaned cantilever was then mounted on a cantilever holder, and the sum signal was maximized using the easy align system of the AFM. The AFM head was then placed on top of the AFM base plate where the prepared sample was placed. The cantilever was manually lowered carefully to approach the surface of the sample before engaging it automatically. The AFM hood was closed to avoid noises and vibrations from external factors, and the system was allowed to settle for about 5 minutes before starting the scan. All scanning was done with a scan rate of 1 Hz (10 μm/s tip velocity). For the roughness measurements, nine images of size 5 μm x 5 μm at nine different locations for each sample were taken and then cropped 2 μm x 2 μm size images from the original 5 μm x 5 μm image for further analysis. The roughness analysis of the images was done using the NanoScope Analysis 1.5 software from Bruker. To measure the thickness of the coated layers, several scratches were made on the samples with a sharp blade. Scratches were then scanned in contact mode imaging in air and analyzed with the same software.

**Measurement of I/V curves.** Nano-scale devices were fabricated using gold-coated mica substrates covered with Langmuir-Blodgett monolayers of complex 1. The top Au-electrode was coated on an EffaCoater gold sputter using the shadow masking method. The current–voltage (I/V) characteristics of the devices were measured using a Keithley 4200 semiconductor parameter analyser coupled to a Signatone S-1160 Probe Station at ambient conditions.

## Author Contributions

Samudra Amunugama: Methodology and writing of original draft, syntheses, spectroscopic analysis, junction fabrication

Eyram Asempa: Formal analysis of theoretical calculations and writing of original draft for DFT calculations

Ramesh Chandra Tripathi: Formal analysis of morphological characterization of films, thickness measurements of films, writing of methodology for AFM

Habib Baydoun: Formal analysis and methodology for X-ray diffraction

Dakshika Wanniarachchi: Synthesis and characterization of complex for X-ray analysis

Peter Hoffmann: Supervision of AFM morphological characterization

Elena Jakubikova: Formal analysis, supervision and writing of DFT section

Cláudio Verani: Overall conceptualization, formal analysis, data curation, funding acquisition, project administration, supervision, and manuscript revising and writing

## Conflicts of interest

There are no conflicts to declare

## Acknowledgements

The authors thankfully acknowledge the support from the National Science Foundation through the grant NSF-CHE1904584 to CNV, including financial support to SA, and from the US Army Research Office under the contract W911NF-19-2-0194 to EJ including financial support to EAA. We also acknowledge the use of the NCSU High-Performance Computing Center. Prof. Héctor Abruña at Cornell University is thanked for a discussion on the attribution of the electrochemical processes in 1.

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