YULIANA PÉREZ SÁNCHEZ

# Organic thin transistor based on graphene and push-pull $\pi$-conjugated heteroaromatic systems for biosensing applications and quantum rate theory for study electrochemical interfaces

*Relatório de Pós-doutorado realizado na Universidade Estadual Paulista (UNESP), Departamento de Engenharia, Física e Matemática , Instituto de Química, Araraquara*

*Supervisor:* Prof. Dr. Paulo Roberto Bueno

Fundação de Amparo à Pesquisa do Estado de São Paulo - N°2023/15384-0
Conselho Nacional de Desenvolvimento Científico e Tecnológico

Araraquara
2025

# 1 Summary of the initial proposal

Our research group has proposed a theory to enhance our understanding of electron transfer and transport phenomena at the nanoscale level. This theory has proven valuable in interpreting quantum properties and assessing the electronic structure (density-of-states, DOS) of electrochemical interfaces (e.g., redox monolayers) and donor-$\pi$-acceptor compounds (e.g., push-pull heterocyclic sites)–immobilized onto single layer graphene via $\pi$-$\pi$ stacking– through impedance-derived capacitive spectroscopy (ECS). For the later, single layer graphene (SLGO) as two-dimensional material composed of carbon atoms arranged in a hexagonal lattice can be utilized as suitable working electrode to immobilize heterocyclic compounds, standing out as one of the most promising materials for nanotechnology applications due to its unique properties, such as high electrical conductivity, large surface area, and mechanical flexibility. For both kind of interfaces, one can determine the associated DOS by measuring the quantum capacitance $C_q$ ($C_q \propto$ DOS), as function of $V$ at the characteristic frequency (e.g., equilibrium frequency $f_e$). This DOS represents the donor and acceptor states of the redox molecule tethered at the surface. At formal potential the total states are half reduced and half oxidized, exhibiting a gaussian-like shape for a redox-monolayer and a typical V-shape for SLG.

The main propose of this project was to develop field effect transistor (FET) devices based on graphene (GFET) as platform to immobilize D-$\pi$-A compounds and to access their electronic properties and structure using both of conventional DC and AC measurement modes. A set of two graphene-based interfaces purchased from Graphenea such as SLG and GFET were evaluated as potential surface to immobilize D-$\pi$-A compounds, synthesized by Prof. Dr. Maria Manuela M. Raposo's group, features cyanoacetic acid-derived groups (acceptor), and ether-based and ternary amine groups (donor), connected by a thiophene-based bridge ($\pi$ bridge). The obtained architecture was aimed to explore new sensing device for the detection and/or quantification of target the protein or DNA as proof of concept.

In parallel to the main research topic, we investigated the effects of frequency perturbation on the occupation of the electronic structure (DOS) of electroactive monolayers fabricated using redox peptides. The obtained results demonstrated that the accessibility of the DOS not only depends on potential or energy but also on frequency. Longer perturbation times allow for the occupation of a greater number of states by charge carriers. Conversely, shorter perturbation times split the single sharp peak into two broader and shorter peaks.

# 2 List of activities

## Published Articles

- Y. P. Sanchez, A. Santos, and P. R. Bueno (2025) *Potential Gradient Effects on Electron Transfer Reactions Mediated by Quantum Capacitive States.* ACS Electrochemistry. doi.org/10.1021/acselectrochem.4c0011.

## Submitted manuscripts

- E. V. G. Alarcón, Y. P. Sanchez, and P. R. Bueno. *Beyond the Dielectric Continuum Model: The Effect of the Electrolyte on the Rate of Electron Transfer Reactions from a Quantum Electrodynamics Perspective.* Electrochimica Acta (Attachment 6.3).

## Manuscripts in elaboration and revision

- Y. P. Sanchez, and P. R. Bueno. *Temporally Accessing to Density-of-States of Redox-active Self-Assembled Monolayer.* **Brief:** In this study, we studied the DOS distribution as a function of frequency for redox peptides self assembled over gold electrode, the obtained DOS profiles changed in function of frequency, implying that the occupation of the $C_q$ states is not only influenced by energy (Attachment 6.4.2).

- Y. P. Sanchez, E. F. Pinzon, and P. R. Bueno. *Electron Transfer Efficiency of Nanoparticle-Modified Interfaces Studied by Quantum Rate Model.* **Brief:** In this study, we employ the quantum rate theory to address such electron transfer constant efficiency conferred to the presence of gold NPs, which act as nano-scale electrodes, facilitating more efficient electron transfer by providing additional conduction pathways (Attachment 6.4.1).

- Y. P. Sanchez, and P. R. Bueno. *Quantum Rate Model for the Study of Electron Transfer and Transport Phenomena in Molecular Electronics.* **Brief:** In this study, we examine in more detail the rate-conductance relationship established by the quantum rate expression applied to dry configuration, for which the charge carries were calculated. The temperature - dependent measurements implies that the charge transport follows a non-resonant tunneling mechanism (Attachment 6.4.3).

## Supporting research group members

- *Collaboration with PhD Student*
  **Brief:** Participation in the analysis, interpretation and manuscript preparation (Attachment 6.3) of results obtained for the electron transfer reaction of redox monolayer in three different water-acetronitrile mixtures, as part of the PhD candidate Erika Viviana Godoy Alarcon's research. Additionally, collaboration in the electrochemical analysis of D-$\pi$-A compounds in solution, as part of the PhD candidate Nicolás Moreno Santos de Siqueira's research.

- *Assistance to undergraduate Student*

  **Brief:** I provided Training in laboratory activities to undergraduate student Natan Ribeiro. As continuation of the gold nanoparticle study using the quantum rate theory described in the manuscript (Attachment 6.4.1), a study of nanoparticle size influence on the electronic communication of hybrid structure was proposed as the student's scientific initiation project. During the initial stage of his research, I provided full-time guidance to help him acquire expertise in laboratory equipment, experimental protocols, as well as develop autonomy for his research activities. Additionally, I trained him in the use of the software for data analysis. Finally, I conducted preliminary studies to establish the initial steps (Section 3.3) for the second stage of his scientific initiation, which aims the study of long-range electron transfer using redox peptide multilayers.

# 3 Summary research results

## 3.1 Push-pull compounds and single layer graphene

Figure 3.1 illustrates the push-pull molecules aimed to be attached to the single layer graphene surface using $\pi$-$\pi$ stacking strategy [1]. The $\pi$-conjugate system, composed of the phenyl and thiophene moieties of the compound, provides a suitable structure for immobilization. The influence of the donor structure on the quantum properties, such as $C_q$ and $R_q$, and electronic structure of the D-$\pi$-A/SLG junction could be studied through ECS.

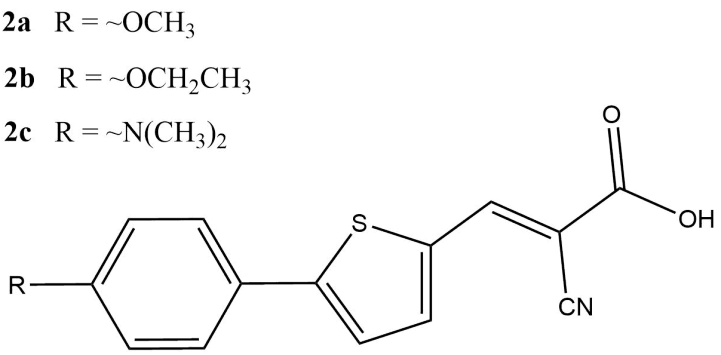


Figura 3.1: Chemical structure of the push-pull compounds. The R-substituents are $\sim OCH_3$ (**2a**), $\sim OCH_2CH_3$ (**2b**) and $\sim N(CH_3)_2$ (**2c**) and act as the electron donor groups, while the cyanoacetic acid-derived group acts as the electron acceptor group.

Given ECS's sensitivity to surface (or structural)[2] and interface changes (or environmental changes)[3], the graphene surface must maintain a stable and unmodified electronic density in order to accommodate the push-pull molecules. Figure 3.2 depicts the capacitive response and DOS distributed for a flawless SLG (violet dots) measured in PB

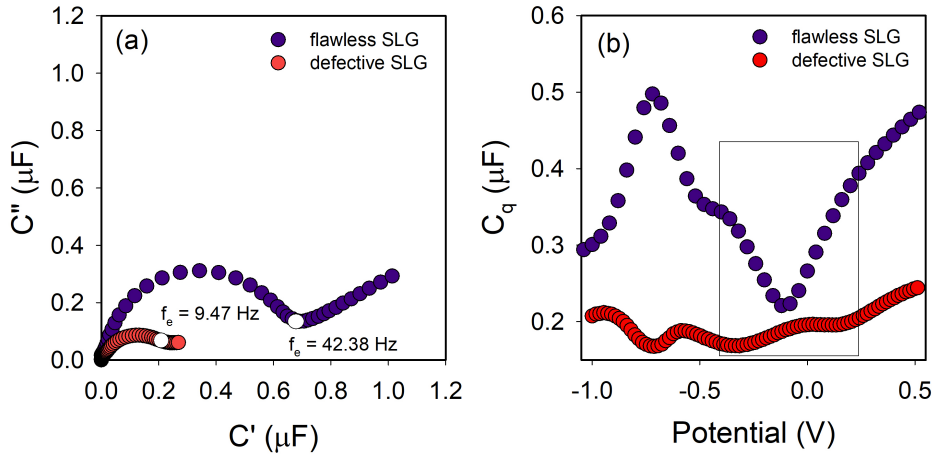


Figura 3.2: Evaluation of quality of the SLG by comparing the electrochemical response measured at OCP in PB (12 mM, pH 7.4). (a) Capacitive Nyquist plots for flawless SLG (OCP = 0.102 V) and defective SLG (OCP = -0.196 V). (b) Quantum capacitance of graphene exhibiting the expected V-shape of the DOS for the flawless SLG (violet circles), while for the defective SLG different DOS distribution.

[4]. Any imperfections lead to decreased capacitive values and altered DOS distribution, characterized by a significant reduction (or loss) in the V-shape as shown in Figure 3.2 by the red dots, indicating that the graphene surface is not suitable for modification. To address this challenge an anti-doping treatment using solvent cleaning was performed. Briefly, the SLG were cleaned by immersion in acetone for 12 hours. Subsequently, the samples were rinsed with isopropyl alcohol and dried with nitrogen or argon.

However, the electrochemical characterization shown in Figure 3.3*a* indicates that the SLG samples are not pristine, two semi-circles are obtained in the Nyquist plots instead of a single well-formed one as shown Figure 3.2*a* (violet dots). Additionally, the DOS distribution (Figure 3.3*b*) highlights imperfections in the SLG samples, revealing a shoulder at 0.25 V that is absent in a pristine SLG sample (see Figure 3.2*b*, violet dots). These imperfections may result from alterations in the electronic structure, which could be hinder the $\pi$-$\pi$ stacking between the push-pull compounds and the graphene. Therefore, the response observed in Figure 3.3 for the SLG samples modified with the compounds (red dots) may be attributed to signal drift.

Following the identification of quality concerns related to the SLG samples, the Nanobionics group initiated discussions with Graphenea to address the issue. As a result of the meeting, both parties agreed to explore alternative products that may better meet the technical and functional requirements, such as the Graphene Field-Effect Transistor Chip: S-20 (Figure 3.4). This graphene-based device provides 12 GFETs per chip: six graphene sheets (source 1 to 6) are connected to a common drain electrode, while the remaining six sheets (source 7 to 12) are connected to a second drain electrode.

However, electrochemical characterization of the GFET-S20 devices in phosphate buf-

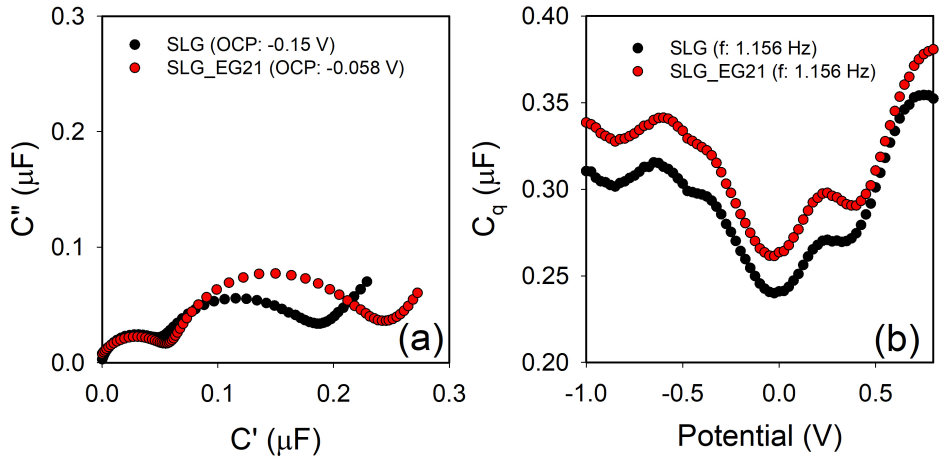


Figura 3.3: Evaluation of quality of the SLG and immobilization of push-pull compound measured at OCP in PB (12 mM, pH 7.4). (a) Capacitive Nyquist plots for SLG (OCP = - 0.15 V) and modified SLG with push-pull compound (OCP = -0.058 V). (b) Quantum capacitance of graphene exhibiting irregular V-shape of the DOS for both samples.

fer (PB, 12 mM, pH 7.4), performed in collaboration with Prof. Dr. Raphael Nascimento and PhD candidate Nicolás Siqueira, revealed technical issues not only with the chip but also with the Graphenea Cartridge—a device that provides the electrical interface between the chip and the potentiostat. The similarity between the Nyquist plots of each

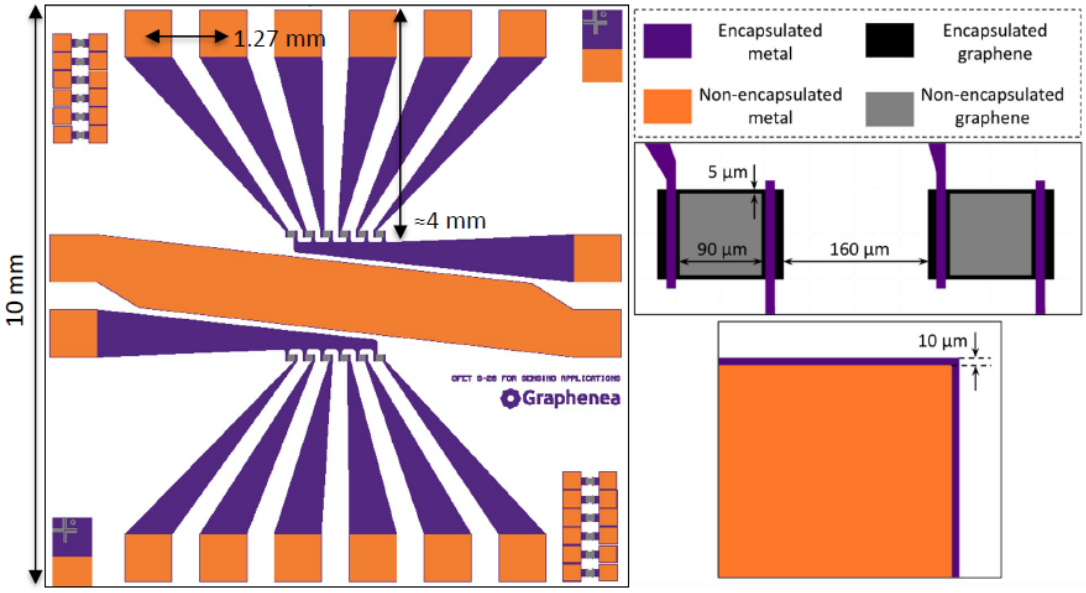


Figura 3.4: Layout of the GFET-S20 device from Graphenea. The twelve graphene sheets are divided into upper and lower regions, each comprising six graphene channels.

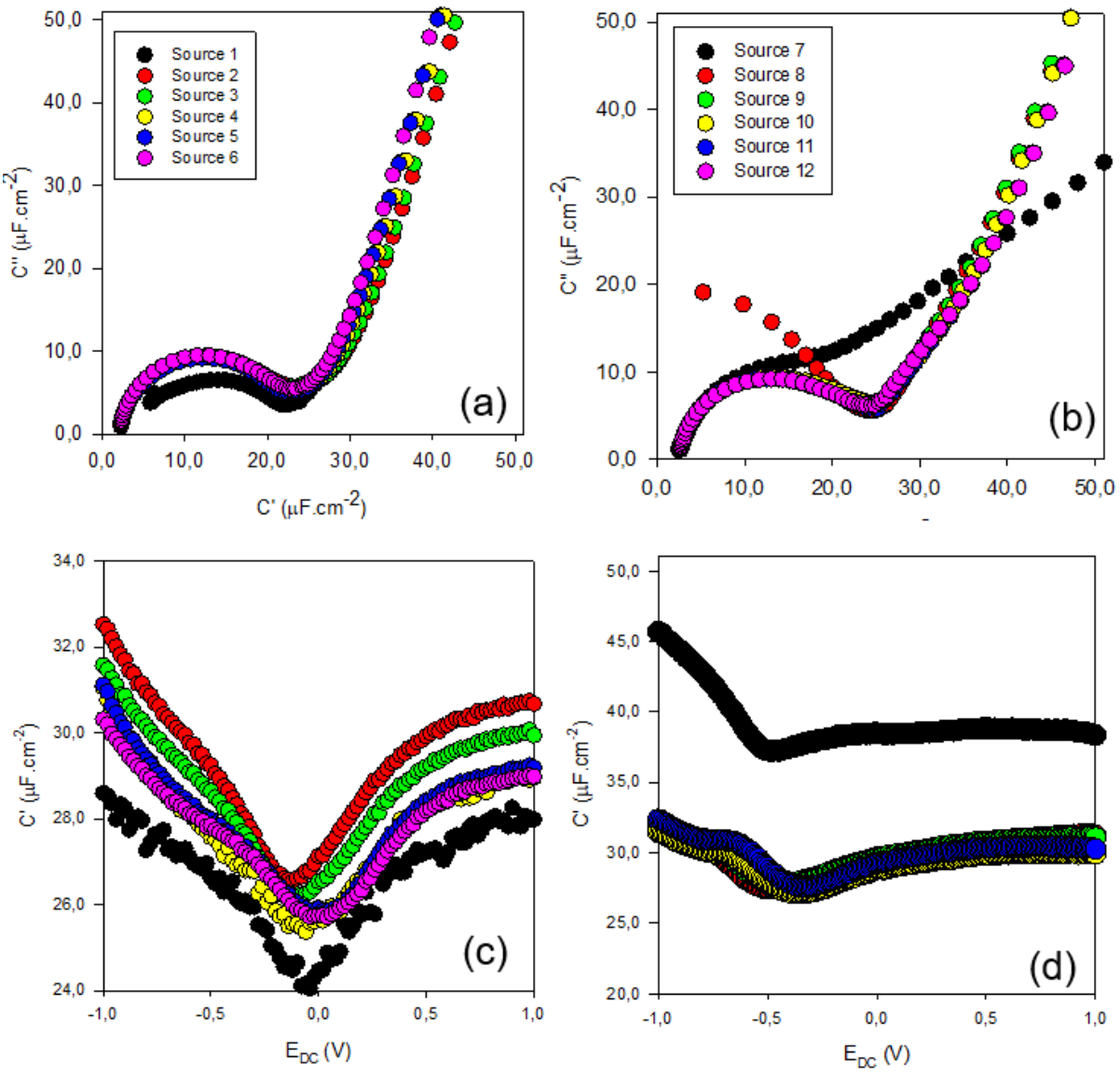


Figura 3.5: Electrochemical characterization of GFET-S20 devices in PB (12 mM, pH 7.4) across all 12 graphene sheets. Nyquist plots for (a) the upper and (b) the lower graphene regions as defined in Figure 3.4, and the corresponding DOS profiles shown in (c) and (d), respectively.

set of graphene sheets, upper and lower region, shown in Figure 3.5*a* and *b* suggest that the shared drains may sensitize multiple sheets simultaneously and the slightly difference may be attributed to signal drift. This hypothesis is supported by the low DC resistance ($\sim$750 $\Omega$) between the sources.

Additionally, the DOS profiles shown in Figure 3.5*c* and *d* indicate that the electronic structure of the graphene in both the upper and lower regions is suboptimal when compared to the pristine SLG sample shown in Figure 3.2*b* (violet dots). Furthermore,

the calculated quantum resistance $R_q$ of $\approx$ 222.6 k$\Omega$ [1], which is approximately seven times higher than the von Klitzing constant ($R_K$= 25.8 k$\Omega$), reinforces the hypothesis of a defective graphene structure.

Based on these findings—and taking into account the functionality and usability issues observed with the provided cartridge—the working group has prepared a report for Prof. Paulo Roberto Bueno. As my postdoctoral appointment has ended, further research activities will be carried out under the responsibility of the remaining team members.

## 3.2 Electronic structure study in function of frequency

Electron transfer process in diffusion-less configuration involves the occupation of quantum capacitive $C_q$ states by the charge carriers, such as electrons and holes. The occupation of these $C_q$ follows the Fermi–Dirac distribution function $f = [1 + \exp(eV/k_BT)]^{-1}$, where the potential energy of electrons in the electrode is modeled as $-eV = \mu - E_F = E$, with $E_F$ stating for the Fermi level of the redox moieties chemically attached to the electrode [5, 6]. Incorporating the Fermi–Dirac distribution into the capacitance definition allows to consider the influence of temperature in real electrochemical systems, as described by the following equation,

$$C_q = \frac{e^2 N}{k_B T} f(1 - f), \tag{3.1}$$

This equation defines the number of available states $dn$ to be occupied per interval of energy $d\mu$. For electroactive monolayers fabricated using redox peptides, the occupation distribution reveals the DOS, which is measured at equilibrium frequency typically taking low values (ca. $f_e < 0.1$ s$^{-1}$) [7], exhibiting a Gaussian-like shape with a maximum $C_q$ value (or maximum states to be occupied).

Figure3.6 shows the measurements of DOS distribution as a function of frequency for redox peptides self assembled over gold electrode and measured in 20 mM Tetrabutylammonium perchlorate (TBAClO$_4$) in ACN/H$_2$O (1:4, v/v). The changes in the DOS shapes following the frequency increments, such as the split of the single peak to two peaks, indicate that the occupation of the $C_q$ states is not only influenced by energy (i.e, -eV = $\mu - E_F$) as noted by Eq.3.1 but also time-dependent. Peak deconvolution analysis evidences two distinct DOS shapes, as shown in Figure 3.6*b* and *c*, which suitable fitted using the modified version of Eq. 3.1:

$$C_q = C_{q_a} + C_{q_b} = \frac{e^2 N_a}{k_B T} f_a(1 - f_a) + \frac{e^2 N_b}{k_B T} f_b(1 - f_b) \tag{3.2}$$

In this equation, $C_q$ results from the addition of two functions, $C_{q_a}$ and $C_{q_b}$, where $f_a$ and $f_b$ are the Fermi–Dirac functions that describes the occupation of two populations

[1] Calculated as $R_q = 1/C_q f_r$, where $f_r$ is the frequency at the peak of the capacitive Bode diagram (not shown).

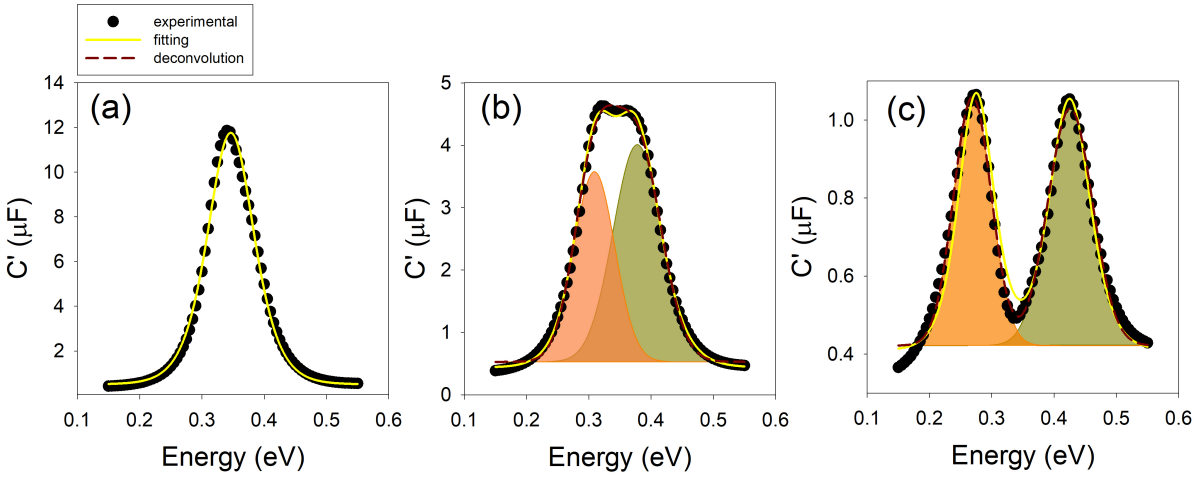


Figura 3.6: DOS distribution analysis for the same redox monolayer performed at (a) 0.1692, (b) 8.373 and (c) 36.16 Hz. In yellow solid line the fitting using Eq. 3.1 and Eq. 3.2, and in dashed line the accumulative deconvolution.

of states centered at $E_{F_a}$ and $E_{F_b}$, respectively. At $E_F \sim 0.36$ V, the $C'$ values of each DOS curve match with that of the bode diagram from the electrochemical impedance spectroscopy (EIS) data measured at $E_F \sim 0.35$ V, as depicted by Figure 3.7. Similar behavior is observed for EIS data measured at different potentials, emphasizing that the access to the capacitive states is temporally influenced. Moreover, the determination of quantum resistance $R_q$, as $R_q = 1/C'_{sc} f_r$) where $C'_{sc}$ is the capacitance value in he semicircle, suggests that the ET process, independently of frequency and energy, follows the quantized limit ($R_q = 12.9$ kΩ) with changing the amount of accessible $C_q$ states (see Table 3.1). The equivalent circuit analysis is detailed in the manuscript in preparation (Attachment 6.4.2) as well as the discussion of this results.

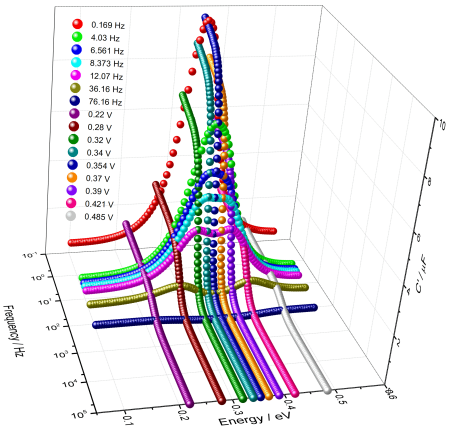


Figura 3.7: 3D plot of DOS distribution in function of frequency and energy and bode diagrams obtained at different potentials.

Tabela 3.1: Obtained values of $f_r$ and $C'_{sc}$ and the determined $R_q$ reported as a mean value $\bar{x}$ with the standard error ($\bar{x} \pm \sigma$), for at least three independently fabricated interfaces.

| Potential (V) | $f_r$ (Hz) | $C'_{sc}$ ($\mu$F) | $R_q$ ($\Omega$) |
|---|---|---|---|
| 0.212 ± 0.007 | 115 ± 45 | 0.6 ± 0.3 | 16001 ± 569 |
| 0.278 ± 0.008 | 30 ± 2 | 2.2 ± 0.3 | 14644 ± 1646 |
| 0.317 ± 0.006 | 10.68 ± 0.00 | 6.2 ± 0.6 | 15085 ± 1499 |
| 0.335 ± 0.005 | 7.7 ± 0.6 | 8.9 ± 0.9 | 14632 ± 1259 |
| 0.36 ± 0.01 | 7.411 ± 0.001 | 9.2 ± 0.7 | 14692 ± 1154 |
| 0.388 ± 0.008 | 11.1 ± 0.8 | 6.0 ± 0.6 | 14991 ± 650 |
| 0.43 ± 0.01 | 30 ± 2 | 2.1 ± 2 | 15163 ± 1084 |
| 0.50 ± 0.01 | 113 ± 15 | 0.6 ± 0.9 | 15361 ± 687 |

## 3.3 Electron transfer process in peptide bilayer structure

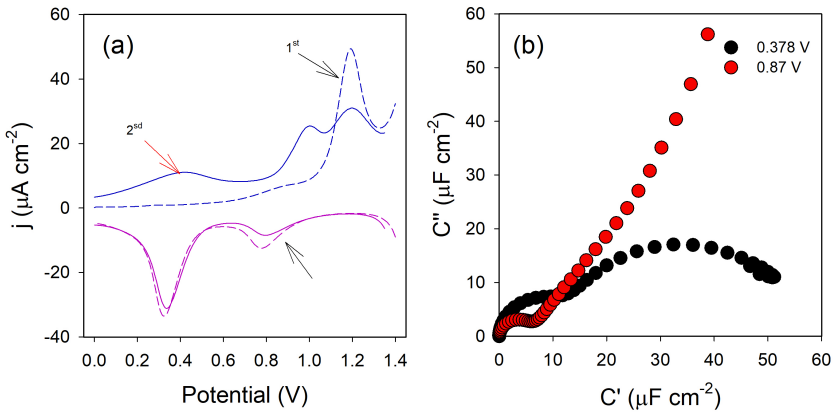


Figura 3.8: (a) DPV and (b) capacitive Nyquist for the redox peptide bilayer obtained in the electrochemical characterization performed in 20 mM TBA in ACN/$H_2O$ (1:4, v/v).

Since a variety of molecules can be self-assembled to metallic electrodes, this strategy has opened up new possibilities for studying the electronic coupling and evaluating the influence of the distance between the electrode and electroactive redox-centers [8]. This approach constitutes a key strategy for studying long-range electron transfer reactions as a particularly experimental method of scrutinizing electron transfer reactions. For instance, this approach has been useful for understanding electron transfer process in biological structures such as that operating in the photosynthesis and cellular systems.

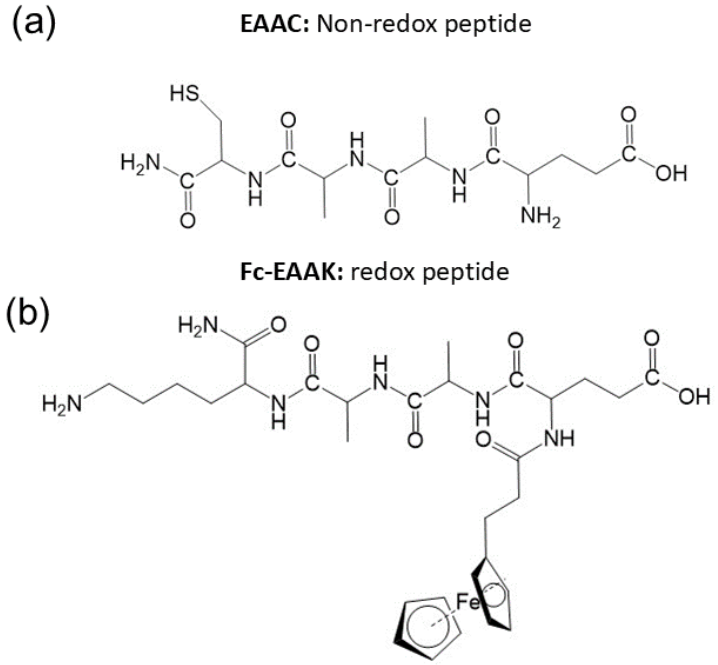


Figura 3.9: Chemical structure of non-redox (a) and redox (b) peptide for fabricating the electroactive bilayer.

A study of electron transfer processes between redox sites strategically localized between layers of a peptide multilayer architecture was study. The use of non-redox peptide (EAAC, Figure 3.9*a*) allowed for the formation of the first monolayer. Subsequently, redox peptide (Fc-EAAK, Figure 3.9*b*) with chemical groups in both extremes that enable chemical attachment to the modified gold surface, was employed. In the initial stage, the C-terminal groups of the peptide chain in the non-redox monolayer were activated using the EDC/NHS carbodiimide reaction [9] to facilitate the bonding of amine groups of the redox peptide,forming the bilayer structure.

Figure 3.8 shows the preliminary electrochemical characterization using differential pulse voltammetry (DPV) and ECS for the obtained bilayer. For the potential range explored in the DPV, no redox peaks are observed, and the instability of the surface is evident due to the differences between the first and second anodic and cathodic DP curves. The capacitance profile performed at 0.378 V and 0.87 V indicates the absence of quantum-related capacitive process.

Measurements in different pH values, comparing unmodified and modified electrodes, were performed to investigate possible electron transfer reaction coupled to proton transfer reaction with the solvent due to the ionizable protons of the peptide. Figure 3.10 exhibits indistinguishable profiles for unmodified and modified electrodes, implying that the bilayer structure was unsuccessfully obtained. The use of activators such as N,N-diisopropylethylamine (DIEA) and Hydroxybenzotriazole (HOBt) is suggested to immo-

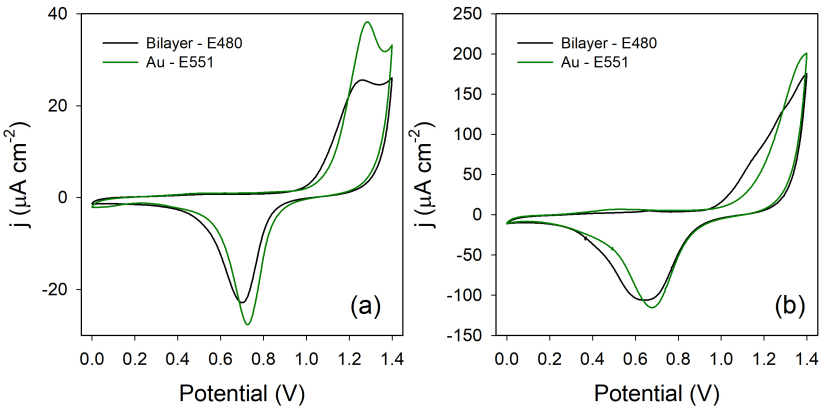


Figura 3.10: Cyclic voltammetry of unmmodified and modified electrode performed in 20 mM TBA in ACN/$H_2O$ (1:4, v/v) with ajusted pH of 3.71 (a) and 6.53 (b).

bilize the redox peptide. This work was assigned to an undergraduate student for the second stage of his/her scientific initiation activities.

# 4 Data management plan

All research results, including data analysis and graphical plotting, were prepared using the NOVA 2.0, Origin Graphics, Sigma Plot 12.5, and Excel software. Generated files and data treatment are storage using the research group's hardware devices.

Manuscripts were stored using LaTeX.

# 5 Complementary Activities

## Evaluation of institutional support received in the period

The support provided by São Paulo State University "Júlio de Mesquita Filho"and the São Paulo State Research Support Foundation has been crucial for the successful execution of this project. The assistance in terms of professionals, physical space, and infrastructure for maintaining research laboratories, generously provided by Unesp and the Chemistry Institute (IQ-Araraquara), has played a pivotal role in advancing the project. Additionally, IQ-Araraquara has graciously granted access to its multi-user laboratories, which are equipped with a Raman spectrometer and other essential resources.

Financial support from the São Paulo Research Foundation, including the provision of a postdoctoral scholarship and technical reserve, has been instrumental in creating favorable conditions for carrying out the activities outlined in the projects funded by FAPESP. This combined support has been essential in ensuring the successful implementation and progress of our research endeavors.

### Participation in scientific event

- XXXVI Congresso de Iniciação Científica da Unesp-IQ/Araraquara. September 24th, 2024. (Attachment 6.1)

### Participation as evaluation committee member

- Concurso público para Professor Adjunto A, area de Engenheria Química, EDITAL PROGEPE nº 60/2024 - UFLA, São Sebastião do Paraíso (Attachment 6.2)

# Bibliografia


[1] LIU, J.; TANG, J.; GOODING, J. J. Strategies for chemical modification of graphene and applications of chemically modified graphene. *Journal of materials chemistry*, Royal Society of Chemistry, v. 22, n. 25, p. 12435–12452, 2012.

[2] GARROTE, B. L. et al. Reagentless quantum-rate-based electrochemical signal of graphene for detecting sars-cov-2 infection using nasal swab specimens. *ACS Sensors*, v. 7, n. 9, p. 2645–2653, SEP 23 2022.

[3] GARROTE, B. L.; SANTOS, A.; BUENO, P. R. Perspectives on and precautions for the uses of electric spectroscopic methods in label-free biosensing applications. *ACS sensors*, ACS Publications, v. 4, n. 9, p. 2216–2227, 2019.

[4] LOPES, L. C.; BUENO, P. R. Sensing the quantized reactivity of graphene. *Analytica Chimica Acta*, v. 1177, SEP 8 2021.

[5] BUENO, P. R. Book. *The Nanoscale Electrochemistry of Molecular Contacts*. [S.l.]: Springer, 2018. (SpringerBriefs in Applied Sciences and Technology). ISBN 978-3-319-90486-3.

[6] MIRANDA, D. A.; BUENO, P. R. Chemical hardness of mesoscopic electrochemical systems directly analyzed from experimental data. *Journal of Physical Chemistry C*, v. 123, n. 34, SI, p. 21213–21223, AUG 29 2019.

[7] SANCHEZ, Y. P.; SANTOS, A.; BUENO, P. R. Quantum rate efficiency of the charge transfer mediated by quantum capacitive states. *Electrochimica Acta*, v. 434, DEC 1 2022.

[8] SHAH, A. et al. Electron transfer in peptides. *Chemical Society Reviews*, Royal Society of Chemistry, v. 44, n. 4, p. 1015–1027, 2015.

[9] HERMANSON, G. Book. *Bioconjugate Techniques*. 2nd. ed. [S.l.]: Academic Press Maryland Heights, 2008. 214-233 p.

# 6 Attachments

## 6.1 Participation in scientific events

## 6.2 Participation as committee member

***MINISTÉRIO DA EDUCAÇÃO***
***UNIVERSIDADE FEDERAL DE LAVRAS***
***SESSÃO DE APLICAÇÃO DA PROVA DIDÁTICA***

Ata de reunião da sessão de aplicação da prova didática do concurso para Professor Adjunto A, nível 1, área Engenharia Química, Banca Examinadora designada pela Portaria ICTIN n° 26, de 13/03/2025. Às sete horas e cinquenta e nove minutos de 09/04/2025, na sala PAV1-103 do Instituto de Ciência, Tecnologia e Inovação (ICTIN) - Câmpus São Sebastião do Paraíso, reuniu-se a Banca retromencionada, sob a Presidência do Professor Leonilson Kiyoshi Sato de Herval (ICTIN/UFLA) e com a presença dos professores: Erivelton Antonio dos Santos (ICTIN/UFLA), Diego Bedin Marin (ICTIN/UFLA), Yuliana Perez Sanchez (UNESP) e Leandro Hostert (USP), com a finalidade de avaliar e julgar a prova didática do referido concurso que foi sobre o tema nº 05 (Estequiometria Industrial). A banca recebeu o material a ser utilizado pelos candidatos e procedeu ao sorteio da ordem de apresentação dos mesmos. Às oito horas e nove minutos foi iniciada a prova didática, que foi gravada, com a apresentação dos candidatos na seguinte ordem:

| Horário | Candidato |
|---|---|
| 08:09 | Bianca Paula de Sousa |
| 09:15 | Vinícius de Macedo |

Após a exposição, os membros realizaram o lançamento das notas e justificativa no sistema de gestão de concursos. Às onze horas e quarenta minutos o Presidente encerrou a reunião, da qual para constar, eu, Erivelton Antonio dos Santos, secretário desta banca, lavrei esta ata, que depois de lida e aprovada, será assinada pelo Presidente e demais membros da Banca.

São Sebastião do Paraíso, 09 de abril de 2025.

Leonilson Kiyoshi Sato de Herval gov.br Documento assinado digitalmente LEONILSON KIYOSHI SATO DE HERVAL Data: 09/04/2025 11:44:35-0300 Verifique em https://validar.iti.gov.br

Erivelton Antonio dos Santos gov.br Documento assinado digitalmente ERIVELTON ANTONIO DOS SANTOS Data: 09/04/2025 11:42:16-0300 Verifique em https://validar.iti.gov.br

Diego Bedin Marin gov.br Documento assinado digitalmente DIEGO BEDIN MARIN Data: 09/04/2025 11:46:24-0300 Verifique em https://validar.iti.gov.br

Yuliana Perez Sanchez gov.br Documento assinado digitalmente YULIANA PEREZ SANCHEZ Data: 09/04/2025 11:49:17-0300 Verifique em https://validar.iti.gov.br

Leandro Hostert gov.br Documento assinado digitalmente LEANDRO HOSTERT Data: 09/04/2025 11:47:42-0300 Verifique em https://validar.iti.gov.br

## 6.3 Submitted paper



unesp

Yuliana Perez Sanchez <yp.sanchez@unesp.br>

**Please verify your contribution to Beyond the Dielectric Continuum Model: The Effect of the Electrolyte on the Rate of Electron Transfer Reactions from a Quantum Electrodynamics Perspective**

1 mensagem

**Electrochimica Acta** <em@editorialmanager.com> 14 de abril de 2025 às 14:40
Responder a: Electrochimica Acta <support@elsevier.com>
Para: Yuliana Pérez Sánchez <yp.sanchez@unesp.br>

*This is an automated message.*

Journal: Electrochimica Acta
Title: Beyond the Dielectric Continuum Model: The Effect of the Electrolyte on the Rate of Electron Transfer Reactions from a Quantum Electrodynamics Perspective
Corresponding Author: Professor Paulo Roberto Bueno
Co-Authors: Erika Viviana Godoy Alarcón; Yuliana Pérez Sánchez
Manuscript Number:

Dear Yuliana Pérez Sánchez,

The corresponding author Professor Paulo Roberto Bueno has listed you as a contributing author of the following submission via Elsevier's online submission system for Electrochimica Acta.

Submission Title: Beyond the Dielectric Continuum Model: The Effect of the Electrolyte on the Rate of Electron Transfer Reactions from a Quantum Electrodynamics Perspective

Elsevier asks all authors to verify their co-authorship by confirming agreement to publish this article if it is accepted for publication.

Please read the following statement and confirm your agreement by clicking on this link: Yes, I am affiliated.

I irrevocably authorize and grant my full consent to the corresponding author of the manuscript to: (1) enter into an exclusive publishing agreement with Elsevier on my behalf (or, if the article is to be published under a CC BY license, a non-exclusive publishing agreement), in the relevant form set out at www.elsevier.com/copyright ; and (2) unless I am a US government employee, to transfer my copyright or grant an exclusive license of rights (or for CC BY articles a non-exclusive license of rights) to Elsevier as part of that publishing agreement , effective on acceptance of the article for publication. If the article is a work made for hire, I am authorized to confirm this on behalf of my employer. I agree that the copyright status selected by the corresponding author for the article if it is accepted for publication shall apply and that this agreement is subject to the governing law of the country in which the journal owner is located.

If you did not co-author this submission, please contact the corresponding author directly at paulo-roberto.bueno@unesp.br;prbueno.iq@gmail.com.

Thank you,
Electrochimica Acta

More information and support
FAQ: What is copyright co-author verification?
https://service.elsevier.com/app/answers/detail/a_id/28460/supporthub/publishing/
FAQ: How can I reset a forgotten password?
https://service.elsevier.com/app/answers/detail/a_id/28452/supporthub/publishing/
For further assistance, please visit our customer service site: https://service.elsevier.com/app/home/supporthub/publishing/
Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about Editorial Manager via interactive tutorials. You can also talk 24/7 to our customer support team by phone and 24/7 by live chat and email

## 6.4 Manuscript in preparation

### 6.4.1 Manuscript in final stage

# Electron Transfer Efficiency of Nanoparticle-Modified Interfaces Studied by Quantum Rate Model

Yuliana Pérez Sánchez[a], Edgar Fabian Nieto Pinzon[a] and Paulo Roberto Bueno[a,*]

[a]Institute of Chemistry, São Paulo State University, Araraquara, 14800-060, São Paulo, Brazil

ARTICLE INFO

*Keywords*:
Gold nanoparticle
Electron transfer efficiency
Quantum capacitive states
Density-of-States

ABSTRACT

Electron transfer (ET) in molecular monolayers is a critical process in many electrochemical systems, typically characterized by a distance-dependent tunneling mechanism. Modifying these monolayers with gold nanoparticles(NPs) alters ET dynamics, suppressing the distance-dependence. We employ the quantum rate theory to address such ET constant efficiency conferred to the presence of gold NPs, which act as nano-scale electrodes, facilitating more efficient ET by providing additional conduction pathways. Additionally, this theory quantum rate theory permits to study experimentally the constant rate $k$ in a suitable way since the conductance quantum and the quantum capacitance that defines $k$ are directly obtained experimentally via impedance methodologies. The direct measurement of $k$ is achieved by measuring the quantum capacitance $C_q$ of the interface. In agreement with the literature, our results reveal the potential of AuNP-modified interfaces to improve the performance of electrochemical devices by enhancing ET efficiency. This study contributes to the broader understanding of ET processes in nanoparticle-modified interfaces, providing insights into their application in biosensors, energy conversion, and other electrochemical technologies.

## 1. Introduction

Electron transfer (ET) mechanisms in molecular monolayers are pivotal in a wide range of electrochemical applications, from biosensors [1] to molecular electronics devices [2]. In these systems, ET typically occurs via tunneling through the monolayer, where the efficiency of ET is highly dependent on the distance between the redox-active sites and the electrode surface [3]. This distance dependence is often quantified using the attenuation factor $\beta$, which describes the exponential decay of ET rate with increasing length of the molecular linker [4, 5]. However, when molecular monolayers are modified with nanoparticles (NPs), the ET dynamics can change dramatically [6, 7].

The incorporation of nanoparticles into molecular monolayers significantly alters the ET characteristics by providing additional conduction pathways. These NPs, often gold nanoparticles NPs, act as electron reservoirs or "nanoscale electrodes" that facilitate ET across the monolayer [8, 9]. This enhancement is attributed to the high density of states (DOS) of the metal NPs, which increases the ET rate constants by several orders of magnitude compared to ET involving redox species in solution [10]. Consequently, the distance dependence of ET in the presence of NPs is markedly reduced, leading to a nearly distance-independent ET rate, as indicated by a $\beta$ value approaching zero [11]. This phenomenon has been experimentally observed and theoretically supported by studies on the quantum mechanical reflection probability and resonant tunneling mechanisms [12, 11].

Experimentally, the ET properties of NP-modified monolayers are often assessed using techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) [8, 13, 14, 9]. These methods provide insights into parameters like charge transfer resistance ($R_{ct}$) and interfacial capacitance by fitting the impedance data with Randles circuit [9, 15, 12]. For instance, the presence of gold NPs has been shown to significantly decrease $R_{ct}$, indicating more efficient ET pathways [9]. Regarding the ET constant, common methodologies are primary based on controlled potential such as chronoamperometry [16] and voltammetry methods [17]. These methods have been frequently used, but the determination of $k$ is conducted an indirect way outside of the equilibrium electrochemical condition [15, 6, 7]. These potential-step experiments require to take the system out of the electrochemical equilibrium by means of a potential perturbation $V$ in order to access $k$ of the ET reaction. Nonetheless, conceptually, $k$ is a kinetic parameter that must be considered at a dynamical equilibrium condition of the reaction, which in the case of a redox monolayer reacting with an electrode is associated to a resonant faradaic current and the redox reaction occurs in the diffusionless regime, as discussed previously [18].

The unique properties of NPs, such as their large surface area, and ability to act as "tiny conduction centers," make them ideal for enhancing the performance of electroactive interfaces [8]. In heterogeneous structures, NPs not only improve ET but also enable the formation of well-defined electronic structures that support resonant tunneling, thereby suppressing the distance dependence of ET [10]. This behavior is particularly relevant in applications involving redox-active species immobilized on electrode surfaces, where efficient ET is critical for device performance [6].

The quantum rate theory (supplementary information, SI.1)has been applied to analyze the electrodynamics of electrochemical interfaces [19]. This theory addresses the diffusionless kinetics of ET at electroactive interfaces, aligning with Laviron's approach but also incorporating properties like quantum capacitance ($C_q$) and quantum resistance

*Corresponding author
paulo-roberto.bueno@unesp.br (P.R. Bueno)
ORCID(s):

### 6.4.2 Manuscript A in writing stage

# Temporally Accessing to Density-of-States of Redox-active Self-Assembled Monolayer

Yuliana Pérez Sánchez and Paulo Roberto Bueno*

*Institute of Chemistry, São Paulo State University (UNESP), 55 Prof. Francisco Degni St., Araraquara, São Paulo, 14800-060, Brazil*

E-mail: paulo-roberto.bueno@unesp.br

**Abstract**

Here goes the abstract.

## keywords

Density-of-states, quantum electrodynamics, quantum capacitance, conductance quantum, quantum electrochemistry.

## Introduction

Redox-active molecules self-assembled onto metallic electrodes (SAMs) constitute a class of electroactive interfaces in which redox-active molecules are chemisorbed onto electrode surfaces via strong anchoring groups such as thiols on gold,[1] as the case of peptides with cysteine residues.[2,3] SAMs obtained using Ferrocene-based peptides exhibit a reversible electrochemical behavior that arises from their well-defined spatial organization and the fixed distance between the incorporated ferrocene moieties and the electron,[4,5] and then the characteristic electron transfer (ET) kinetics is diffusionless[6] and follows quantum electrodynamics

### 6.4.3 Manuscript B in writing stage

# Quantum Rate Model for the Study of Electron Transfer and Transport Phenomena in Molecular Electronics

Yuliana Pérez Sánchez,[†] Adriano dos Santos,[†] Richard L. McCreery,[*,‡] and Paulo Roberto bueno[*,†]

†*Institute of Chemistry, São Paulo State University (UNESP), 55 Prof. Francisco Degni St., Araraquara, São Paulo, 14800-060, Brazil*

‡*Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada.*

E-mail: richard.mccreery@ualberta.ca; paulo-roberto.bueno@unesp.br

## Keywords

Electron transfer rate, molecular conductance, electrochemical capacitance, Density-of-states, quantum channels

**Abstract**

A decade ago, the correlation between molecular conductance and charge transfer rate has been proposed as a nonlinear rate–conductance relationship. The quantum rate theory proposes that the electron transfer (ET) constant rate $k$ is correlated with the molecular conductance $G$ by means of the electrochemical capacitance $C_\mu$, as $k = {}^{G}/_{C_\mu}$. This theoretical tool allows us not only to understand the charge transfer/transport phenomena but also to access to electric properties by means of impedance spectroscopy