

## Hybrid material as a potential colorimetric sensor for heterocyclic aromatic amines

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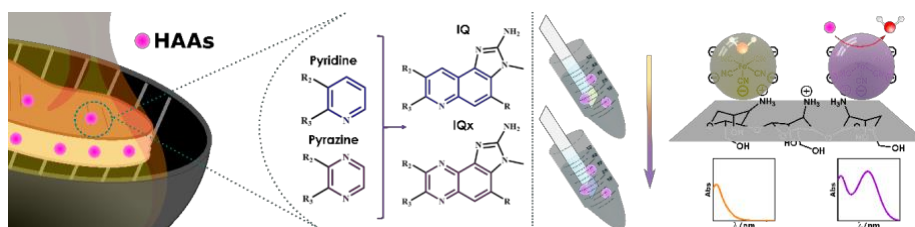
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**Thematic Area:** Materials Chemistry

**Keywords:** hybrid materials; heterocyclic aromatic amines; chitosan films.

Hybrid materials made up of organic and inorganic substances have aroused the interest of the academic community in the proposition of analytical sensors for presenting properties that expand their application possibilities. This work deals with the production of a hybrid material consisting of a chitosan film (organic portion) and the complex ion  $[\text{Fe}(\text{CN})_5(\text{OH}_2)]^{3-}$  (inorganic portion) because of the possibility of using this hybrid material to the detection of heterocyclic aromatic amines (HAAs) produced during the processing of meat of animal origin. The prospects of this work are using modified chitosan films coupled with prototype portable instrument. The immobilization of the complex ion on the film was carried out through adsorption processes, being confirmed by electronic absorption spectroscopy in the UV-Vis regions through the observation of bands associated with charge transfer ( $\sim 230$  nm) and ligand field transitions (438 nm). The amount of  $[\text{Fe}(\text{CN})_5(\text{OH}_2)]^{3-}$  adsorbed was quantified ( $57.43 \pm 0.86 \mu\text{mol g}^{-1}$ ) at 25 °C by atomic absorption spectroscopy. The use of these hybrid matrices in the detection of HAAs is based on the reaction of replacing the  $\text{H}_2\text{O}$  ligand by quinoxaline (IQx), the prove molecule used to mimic the interactions and interactions in real samples. The immersion of the hybrid matrix in aqueous solutions containing IQx showed a color change from yellow to purple as a result of the absorption at 536 nm, indicating the feasibility of using it as a colorimetric sensor.



**Acknowledgments:** CAPES, Funcap, CNPq.

### References

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## Impedimetric biosensor based on $\text{CoFe}_2\text{O}_4$ nanoparticles coated with Concanavalin A lectin for detecting *E. coli*

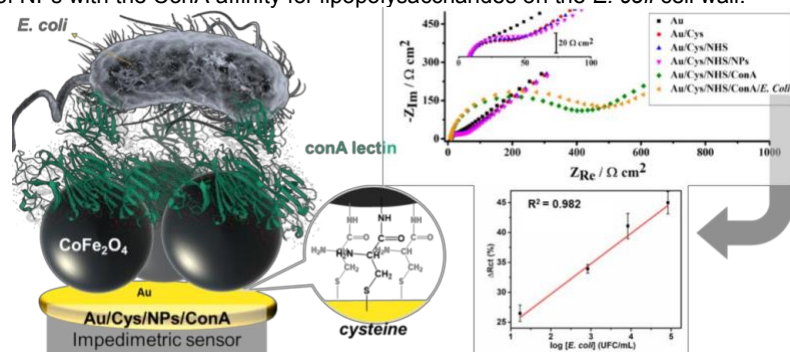
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**Thematic Area:** Materials Chemistry

**Keywords:** Impedimetric sensor, Lectin, *Escherichia coli*

Analytical biosensor for detecting bacteria such as *Escherichia coli* (*E. coli*) have found significant technological advancements in recent years, but they still lack meeting critical requirements as limit of detection (LOD), fast time of response, and ultra-sensitivity with high reproducibility. Impedimetric biosensors are powerful tools due to their low-cost, detection limits and sensitivity, where nanoparticles (NPs) can be used to modify electrodes to increase the surface area improving sensitivity. This work describes the results of an impedimetric biosensor based on a monolayer of cysteine (cys) on gold containing  $\text{CoFe}_2\text{O}_4$  NPs and the lectin concanavalin A (ConA) for detecting *E. coli*. Prior to the modification steps, the  $\text{CoFe}_2\text{O}_4$  NPs were synthesized and functionalized with (3-aminopropyl)triethoxysilane to provide  $\text{CoFe}_2\text{O}_4@\text{NH}_2$  NPs. The molecules of cys on gold were activated with N-hydroxysuccinimide (NHS) and N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide hydrochloride resulting in Au/Cys/NHS, which was then immersed in an aqueous solution of  $\text{CoFe}_2\text{O}_4@\text{NH}_2$  to produce Au/Cys/NPs. This electrode was then immersed in a ConA solution producing Au/Cys/NPs/ConA. Each modification step was monitored by impedance using  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  as probe species. The values of charge transfer resistance ( $R_{CT}$ ) increased from 50.4 to 532.5  $\Omega \text{ cm}^2$  for the Au/Cys/NPs and Au/Cys/NPs/ConA electrodes, respectively, showing the surface blockage with respect to probe after the lectin immobilization. The blockage effect was even stronger in solutions containing *E. coli* and showed a concentration dependence that allowed the use of Au/Cys/NPs/ConA for detecting *E. coli* within a linear range from  $1.7 \times 10^1$  to  $8.3 \times 10^4$  CFU/mL with an estimated LOD of  $0.2 \times 10^{-3}$  CFU/mL after 15 min of exposure. This low LOD value is ascribed to the association of the electrical conductivity and high surface area of NPs with the ConA affinity for lipopolysaccharides on the *E. coli* cell wall.



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## Redox potential determination of Hell's gate globin I: a hemeprotein of an extremophile microorganism

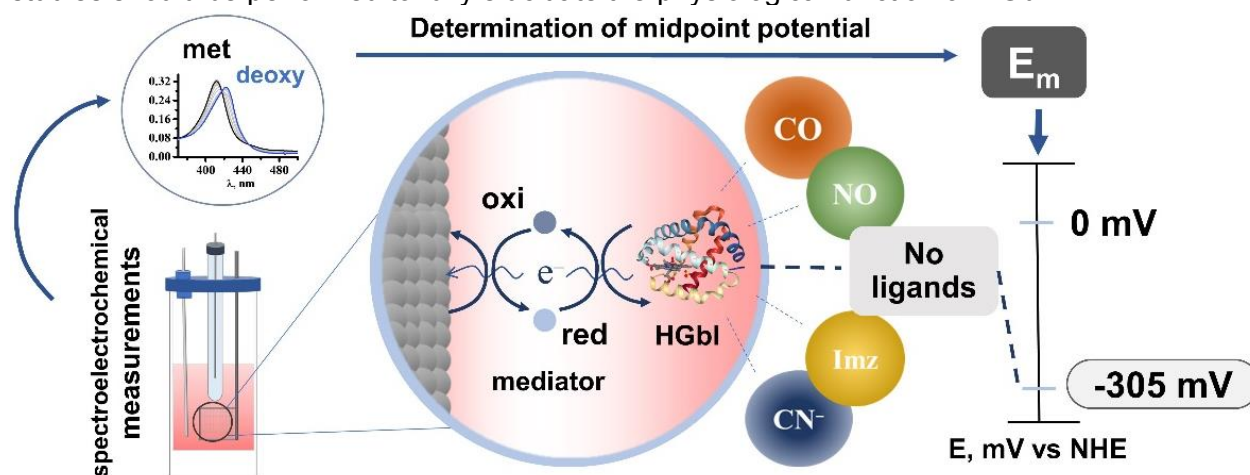
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**Thematic Area:** Biological Inorganic Chemistry

**Keywords:** hemeprotein, spectroelectrochemistry, Hell's Gate globin.

Hell's Gate Globin I (HGbl) is a hemeprotein found in *Methylophilum inferorum* which is a methanotroph bacteria that survives under extreme temperature and pH conditions. Indeed, in comparison to other globins, HGbl presents peculiar characteristics such as stability at pH 2.8 and very high oxygen affinity. Although the biological function of HGbl is still unsolved, the Fe<sup>III/II</sup> redox process seems to be intimately associated with it. Having assuming that, this work shows the spectroelectrochemical data obtained for HGbl in solution with and without relevant heme-binding molecules (CN<sup>-</sup>, imidazole, CO, and NO) aiming to shed light on its physiological function. The spectroelectrochemical measurements gave midpoint redox potential ( $E_m$ ) values of -305, -338, and -442 mV vs NHE for the HGbl unbounded protein and bounded to imidazole and CN<sup>-</sup>, respectively. Surprisingly, it was noticed an unusual high affinity to imidazole and CN<sup>-</sup> for ferrous HGbl. In the presence of CO and NO, the spectroelectrochemical curves showed hysteresis due to the complete dissociation of the ligands in the oxidized state. This behavior allowed the evaluation of only the oxidation potentials, which were at +385 and +130 mV vs NHE for CO-HGbl(Fe<sup>II</sup>) and NO-HGbl(Fe<sup>II</sup>), respectively. These results suggest HGbl protein is not involved in the storage or in the transport of oxygen in the *Methylophilum inferorum* microorganism. Nevertheless, further studies should be performed to fully elucidate the physiological function of HGbl.



**Acknowledgments:** FUNCAP, CAPES, (23038.000509/2020-82), CNPq, FINEP (CV. 01.22.0174.00)

## A Redox-Driven Fluorescence “On-Off” molecular switch based on an azaacene dye

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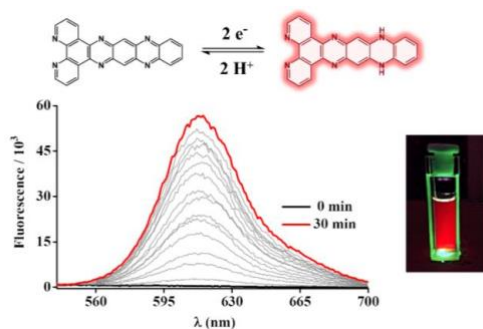
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**Thematic Area:** Photochemistry

**Keywords:** Azaacene, Fluorescence, Photoreduction

Azaacene derivatives have ultimately emerged as highly suitable for molecular electronic and optoelectronic devices due to their intrinsic electrical transport properties and redox behavior.<sup>1</sup> The presence of nitrogen atoms along the structure is responsible for increasing the electron affinity of these structures in comparison with acenes congeners.<sup>2</sup> In this work we synthesized a novel phenazine-based dye by condensing a modified phenanthroline with 2,3-diaminophenazine. The product, dipyridoquinoxalinophenazine (dpqpz) displays a photoreduction reaction by accepting two electrons and two protons in a coupled mechanism, giving dihydro-dpqpz. This last structure can also be obtained by redox mediators such as ascorbic acid or sodium dithionite ( $E = -0.39$  and  $-0.66$  V vs NHE, respectively). Dpqpz itself does not display fluorescence because its  $S_1 \rightarrow S_0$  transition is prohibited (oscillator strength  $f = 0.03$ ) and the excited state undergoes intersystem crossing, giving rise to a reactive state responsible for the photoreduction. However, the reduction product has a  $S_1 \rightarrow S_0$  transition allowed ( $f = 0.87$ ) and exhibits an emission band around the red region, which the exact wavelength and efficiency are very sensitive to the medium. This result suggests dpqpz can act as a fluorescent “on-off” switch, where the fluorescence is turned on in mild reducing conditions.



**Acknowledgments:** FUNCAP, CNPq, (PROEX 23038.000509/2020-82) and CENAPAD-UFC

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## Synthesis and characterization of a copper complex containing intercalative phenanthroline-based ligands

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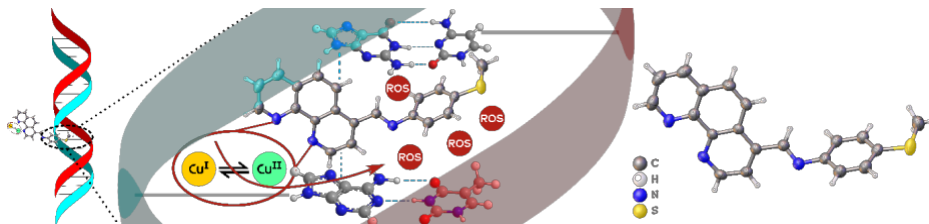
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**Thematic Area:** Biological Inorganic Chemistry

**Keywords:** copper complex, phenanthroline, reactive oxygen species

Copper complexes containing phenanthroline-based ligands have emerged as a real alternative towards cancer treatment due to the synergy between the redox properties of the metal center and the intercalation ability of the ligands. The redox changes of copper ( $\text{Cu}^{\text{III}}$ ) in aerated aqueous medium produce reactive oxygen species (ROS) that may lead to oxidative damage of biomolecules, including DNA. Regarding the intercalative ability, it has been widely shown that rigid delocalized systems such as phenanthroline (phen) derivatives intercalate into DNA through  $\pi$ -stacking interactions, as cartooned below (left image).



This work shows the results obtained for (*E*)-*N*-(4-(methylthio)phenyl)-1-(1,10-phenanthroline-5-yl)metanimine (phen-Bz-SMe) and its copper complex,  $[\text{Cu}(\text{phen})(\text{phen-Bz-SMe})](\text{NO}_3)$ . The Schiff base phen-Bz-SMe was produced by reacting 1,10-phenanthroline-4-carbaldehyde with 4-(methylthio)aniline giving yellow crystals which were characterized by <sup>1</sup>H NMR, X-ray diffraction (XRD, right image above), and electronic (UV-Vis) and vibrational (IR) spectroscopies. For the production of  $[\text{Cu}(\text{phen})(\text{phen-Bz-SMe})](\text{NO}_3)$ , the precursor compound  $[\text{Cu}(\text{PPh}_3)_2(\text{phen})](\text{NO}_3)$ , where  $\text{PPh}_3$  = triphenylphosphine, was firstly generated and fully characterized by means of NMR, XRD, UV-Vis, and IR. Spectroscopic (UV-Vis and IR) and electrochemical data supported by DFT calculations indicated the  $[\text{Cu}(\text{phen})(\text{phen-Bz-SMe})](\text{NO}_3)$  complex was successfully isolated. Studies on ROS generation and nuclease activity of  $[\text{Cu}(\text{phen})(\text{phen-Bz-SMe})](\text{NO}_3)$  are currently under investigation.

**Acknowledgments:** CNPq; FUNCAP; CAPES (PROEX 23038.000509/2020-82), FINEP (CV.

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