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Thuan-Nguyen Pham-Truong, Hyacinthe Randriamahazaka, Jalal Ghilane. Electrochemistry of bi-redox ionic liquid from solution to bi-functional carbon surface. *Electrochimica Acta*, 2020, 354, pp.136689. 10.1016/j.electacta.2020.136689 . hal-02999629

HAL Id: hal-02999629

<https://hal.science/hal-02999629>

Submitted on 12 Nov 2020

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Electrochemistry of bi-redox ionic liquid from solution to bi-functional carbon surface

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Abstract

In this work, bi-redox molecule based ionic liquid was synthesized. Ferrocene donor group and anthraquinone acceptor group were linked to imidazolium cation. Next, the electrochemistry of the as synthesized molecule was investigated demonstrating the presence of two reversible redox systems. Furthermore, the diffusion coefficient and electron transfer rate constant were measured using the ferrocene oxidation and the anthraquinone reduction. Besides that, the bi-redox molecule was immobilized onto carbon electrode using two steps procedure based on the oxidative grafting of primary layer bearing diazonium head group followed by Gomberg-Bachmann coupling surface reaction. The surface characterization confirms the attachment of the imidazolium bi-redox molecule as well as the presence of the labile anion within the layer. Interestingly, the electrochemical investigations confirm the bi-redox grafting with an equi-distribution of the electron donor and acceptor within the attached layer. Finally, the attached layer exhibits an enhancement of double-layer capacitance which is correlated to the increase of the charge density and ionic property of the layer.

Keywords: Bi-redox ionic liquid; Electrochemistry; Surface functionalization; Double layer capacitance; Bi-redox grafting.

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1. Introduction

Tuning the materials properties through an external action leads to extend their potential applications. Surface modification has been proposed as an efficient strategy acquiring new functionalities to the surface and facilitating their integration in various applications such as molecular electronics, smart surface and energy storage [1-3]. Several approaches have been reported in the literature for the immobilization of ultrathin organic layers onto the material surface [4,5]. Within this expanding field, electrochemical assisted grafting methods have been proposed as powerful tool for decorating the electrode materials with different functional groups [6-8]. Therefore, depending on the selected anchoring group, reductive or oxidative grafting could alternatively used for performing covalent immobilization of large spectrum of functional groups [9-11]. The electrochemical process has been successfully achieved on various electrodes materials, including carbon based materials, noble metals and semiconductors [6,12]. The most studied electrochemical grafting process is based on the electro-reductive grafting of diazonium salts. Compared to others methods, the later has several advantages such as low reduction potential (from 0 to -0.5 V/SCE) and formation of covalent bond between the molecule and the surface [6,13]. However, this method frequently requires the synthesis of molecules bearing the diazonium function and the desired functional group. In order to overcome this limitation, different strategies have been proposed including the in situ diazonium generation in the electrochemical cell, leading to extend the grafting to aminophenyl derivatives and avoid the synthesis and isolation of the diazonium (caution: the diazonium is unstable and care should be taken during the synthesis) [14,15]. Besides, coupling diazonium grafting and surface chemistry leads to extend the range of molecules that could be attached onto the electrode surface [16,17]. Thus, the electrochemically attached layers could be used as a platform for post-functionalization using click chemistry, peptide coupling reactions and Gomberg-Bachmann reaction [18,19]. The advanced researches in the electrochemical grafting make possible the attachment of almost any desired functional groups including redox active molecules.

Besides that, tasks specific ionic liquids have been emerged as new compounds with interesting properties. The versatility of tuning the ionic liquid cation and/or anion leads to generate a large amount of ionic liquids with different properties. For example, several redox ionic liquids have been synthesized and found applications in supercapacitors and redox flow batteries [20,21]. The use of redox ionic liquid in redox flow batteries enhances the concentration of the redox molecule in the tank and as consequence the energy density of the device increases. Furthermore, bi-redox ionic liquid has been developed, where the ionic

liquid anion and/or cation are redox active, and were successfully used in energy conversion and storage devices [22,23]. Recently, the ionic liquids moved from their classical use as solvent to an advanced materials thanks to their immobilization onto different supports and open new potential applications in electrocatalysis, energy and smart material [24-26]. The immobilizations of thin organic layers, bearing the ionic liquid framework, using the diazonium grafting have been demonstrated [27-29]. As a result, the attached ionic layer contains immobilized cation and labile anion. In addition, molecules based redox ionic liquids have been successfully immobilized onto carbon electrode [29]. However, most of the reported works focus on the immobilization of either donor or acceptor redox group and a little attention have been devoted to the immobilization of bi-redox molecules based ionic liquid.

Herein, a bi-redox ionic liquid was successfully synthesized, in which the ferrocene and anthraquinone redox molecules were linked to the imidazolium. Next, the bi-redox ionic liquid electrochemical behavior was investigated in organic solvent and in ionic liquid. The electrochemical investigations display almost similar diffusion coefficient and electron-transfer rate constant for the electron donor and acceptor groups. Then, the bi-redox molecule immobilization onto glassy carbon electrode was performed using a two steps procedure. The electrochemical as well as the chemical surface characterizations confirm the occurrence of the bi-redox grafting and resulting to a functional surface with multi-redox states. Finally, the double layer capacitance of the bi-redox ionic layer has been evaluated.

2. Experimental section

2.1. Synthesis of bi-redox ionic liquid

First, the chloroethyleneamidoanthraquinone was synthesized using the previously published procedure [30]. Briefly, 2-aminoanthraquinone ($4.5 \times 10^{-3} \text{ mol.L}^{-1}$) and pyridine ($6.2 \times 10^{-3} \text{ mol.L}^{-1}$) were dissolved in 60 ml of dichloromethane under vigorous stirring at 0 °C. Next, a solution containing the chloroacetylchloride ($5.4 \times 10^{-3} \text{ mol.L}^{-1}$) in 20 ml of dichloromethane was then added dropwisely. After stirring during 4 h, the solution was filtered and extracted with 20 ml HCl at 3 mol.L^{-1} . The organic layer was washed with 20 ml of saturated NaCl and recovered by decantation. A large amount of MgSO_4 was added to the organic phase to eliminate the traces of water. The solvent was evaporated and a brown residue was obtained. The crude product was further dissolved in 100 ml of dichloromethane and 100 ml of hexane was slowly added into the solution. The purified product was recrystallized in the mixture and then was filtered and dried under vacuum. $^1\text{H NMR } \delta$ (ppm), (Fig. S1a): 4.27 (s, 2H), 7.82 (m, 2H), 8.23 (s, 1H), 8.32 (m, 4H), 8.6 (s, 1H).

After that, chloroethyleneamidoanthraquinone ($0.33 \times 10^{-3} \text{ mol.L}^{-1}$) was mixed with N-ferrocenylmethylimidazole ($0.35 \times 10^{-3} \text{ mol.L}^{-1}$), the later was synthesized using the previously published procedure [31], and a catalytic amount of sodium iodide in 20 ml of acetone/dichloromethane (50:50 v/v). The reaction was performed under vigorous stirring at room temperature for 60 hrs. Then the product was recovered by filtration and washed with distilled water. The brown powder was obtained and dried under vacuum for 1 day.

The final product 1-ethyleneamidoanthraquinone-3-ferrocenemethylimidazolium bis(trifluoromethylsulfonyl)imide ([FcImAQ][TFSI]) was obtained by anion exchange reaction. Thus, 1-ethyleneamidoanthraquinone-3-ferrocenemethylimidazolium iodide ($2.5 \times 10^{-4} \text{ mol.L}^{-1}$) was added into a solution containing 20 ml of distilled water and lithium bis(trifluoromethylsulfonyl)imide ($7.5 \times 10^{-4} \text{ mol.L}^{-1}$). The solution was then heated at $70 \text{ }^\circ\text{C}$ for 24 hours to obtain a brown powder. The product was washed thoroughly with distilled water and dried under vacuum for 1 day. $^1\text{H NMR } \delta$ (ppm), (Fig. S1b): 4.27 (m, 7H), 4.45 (t, 2H), 5.26 (s, 2H), 5.28 (s, 2H), 7.81 (s, 1H), 7.92 (s, 1H), 8.04 (m, 2H), 8.18 (m, 1H), 8.24 (m, 3H), 8.47 (m, 1H), 9.15 (s, 1H), 11.18 (s, 1H). $^{19}\text{F NMR (CDCl}_3) \delta$ (ppm): -78.88 (s, 6F).

2.2. Surface and electrochemical characterizations.

X-ray photoelectron spectroscopy (XPS) analysis were performed using a Thermo VG Scientific ESCALAB 250 system, fitted with a micro focused, monochromatic Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$). The electrochemical measurements were performed on a CHI 900 electrochemical workstation (CH Instruments, Austin, TX). The counter electrode was a Pt wire, and a saturated calomel electrode (SCE) was used as reference electrode. For the electrochemical measurement in ionic liquid, polypyrrole covered Pt wire was used as a quasi-reference electrode [32]. The used working electrode was a glassy carbon (3 mm diameter). The glassy carbon electrodes were carefully polished using different alumina pastes (grain size ranging from $2 \text{ }\mu\text{m}$ to $0.3 \text{ }\mu\text{m}$). Before the electrochemical and surface analysis, the samples were systematically rinsed and then sonicated during 10 min to remove the weakly adsorbed molecules.

3. Results and discussion

3.1 Electrochemistry of [FcImAQ] [TFSI] in solution

The synthesized molecule based ionic liquid contains two redox centers, namely the ferrocene and the anthraquinone. The electrochemical behavior of [FcImAQ] [TFSI] in acetonitrile electrolytic solution was investigated Fig. 1.

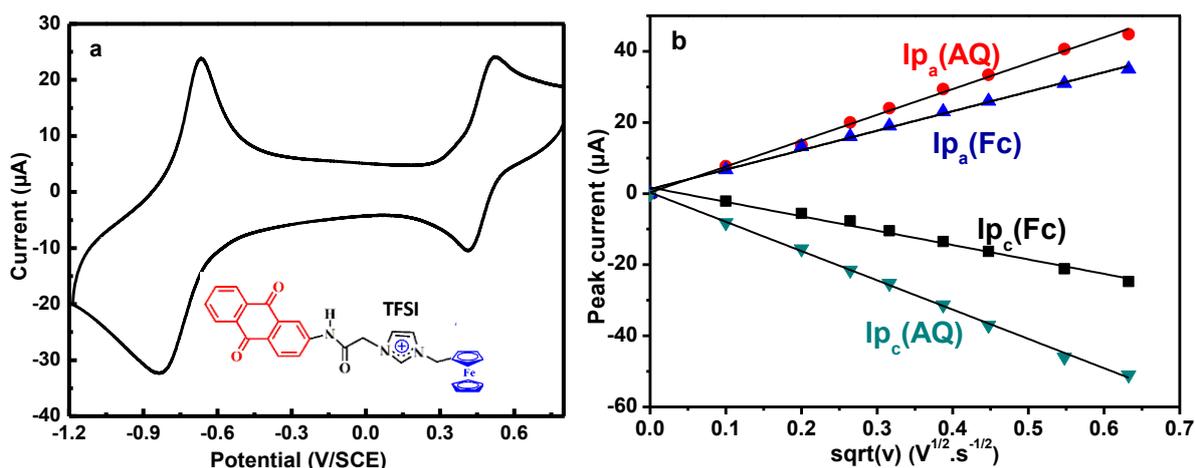


Fig. 1. (a) CV recorded in MeCN solution containing $1 \times 10^{-3} \text{ mol.L}^{-1}$ of [FcImAQ] [TFSI] and 0.1 M [EMIm][TFSI] at 0.1 V.s^{-1} . (b) Variation of the peak current in function of the square root of the scan rate.

The CV shows the electrochemical response of [FcImAQ] [TFSI] where two redox reversible systems are observed. Their half-wave potentials are observed at 0.55 V and -0.7 V/SCE and were attributed to the redox reaction of Fc and AQ moieties, respectively. The Fc and the AQ redox response, in non-protic solution, follow a one electron pathway with the generation of Fc^+ and the radical anion $\text{AQ}^{\cdot-}$ [33,34]. Next, several CV's were performed at different scan rates, from 0.01 to 100 V.s^{-1} (Fig. S2), and the variation of the peaks current were plotted as a function of the scan rate (Fig. 1b). For all the investigated peaks, a linear relationship between the peak current and the $v^{1/2}$ is observed indicating that the bi-redox electrochemical reaction is governed by the diffusion process. The bi-redox molecule diffusion coefficient could be estimated using Randle – Sevcik equation:

$$i_p = 0.446 nFCA \left(\frac{nFDv}{RT} \right)^{1/2}$$

Where n represents the number of transferred electrons, F the Faraday constant, A the electrode area, R the gas constant, T the absolute temperature, C the concentration, D the diffusion coefficient, and v the scan rate. The values of the Fc and AQ peaks current were corrected by subtracting the non-faradic current. The diffusion coefficient of [FcImAQ] was found to be $2.1 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$ when using the slope of the Fc oxidation. However, the AQ redox signal is not fully reversible as attested by a higher ΔE_p (160 mV) even for scan rate below 100 mV.s^{-1} . Thus, the diffusion coefficient using the AQ redox signal was estimated using the equations described for irreversible processes [35,36]. In this case, the $D(\text{FcImAQ})$ was found to be around $2 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$ and similar value was measured for using the ferrocene redox signal. Furthermore, the CV of the bi-redox molecule was recorded on Pt ultramicroelectrode

(5 μm radius Fig. S3) displays a sigmoid CV shape with a two distinct plateau corresponding to the oxidation and the reduction of Fc and the AQ within the bi-redox molecule. The value of the steady state current is around 4 and -4.2 nA for the Fc oxidation and AQ reduction, respectively. The steady current value leads to determine the diffusion coefficient of the redox species using the formula

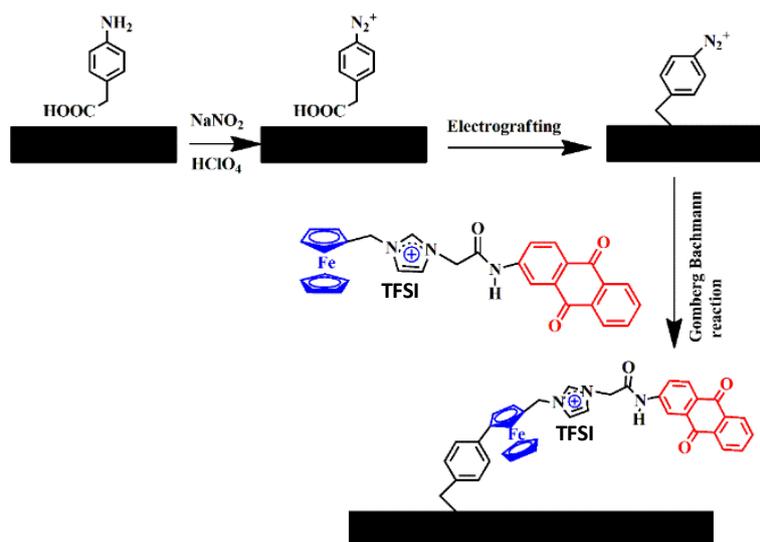
$$i = 4nFDCa$$

Where n is the number of electrons involved in the redox process, F the Faraday constant, D represents the diffusion coefficient of the mediator, C concentration of the native state mediator and a the radius of the tip. In this case, the average value of $D(\text{FcImAQ})$ is $2.2 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ which is consistent with the values measured using Randle–Sevcik and irreversible processes equations.

Next, the electron transfer rate constant was measured using Nicholson method, yielding to a value of $6 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$ and $3.5 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$ for the ferrocene and anthraquinone within the bi-redox molecule, respectively. These values are lower than that reported for mono-redox couple ferrocene and anthraquinone, but are similar to those measured for a bi-redox molecule based on quaternary ammonium 1-(4-ferrocenyl-n-butyl)-1'-[3-(trimethylammonio)propyl]-4,4'-bipyridinium cation [23].

3.2 Immobilization of [FcImAQ][TFSI]

The bi-redox molecule [FcImAQ][TFSI] was immobilized onto electrode surface using a two steps process as illustrated in Scheme 1.



Scheme 1. Immobilization strategy of [FcImAQ][TFSI] onto electrode surface via Gomberg-Bachmann reaction

The immobilization is performed through an electrochemical grafting reaction followed by a surface chemical reaction. First, the 4-aminophenylacetic acid is grafted onto the electrode

surface in a solution containing the diazotization agents (HClO_4 and NaNO_2 20 equiv/10 equiv, respectively). The addition of these reactants ensures a total conversion of the amine group onto the diazonium group. This transformation prevents the attachment of the molecule via amine oxidation. The electrochemical grafting occurs through the carboxylic group oxidation yielding to the attachment of organic layers bearing a diazonium as terminal group [37]. The electrochemical grafting of the primary layer was performed using the previously published procedure [27]. Briefly, 10 successive CV's cycles were performed from 0.5 to 1.8 V/SCE. During the first CV an anodic process observed at 1.4 V attributed to the oxidation of carboxylic group and the formation of the corresponding radicals, which are rapidly attached to the electrode surface [18]. For the following cycles, the current decreases suggesting the attachment of organic layer onto the electrode surface (Fig. S4). The absence of the characteristic oxidation peak of amine at 1.25 V/SCE confirms the occurrence of the diazotization reaction. Next, the modified electrodes were immersed in MeCN solution containing 5 mM [FcImAQ][TFSI] where it undergoes Gomberg-Bachmann reaction between the ferrocene group in the bi-redox molecule and the attached diazonium head group. After 2 hrs reaction at room temperature, the electrodes were removed from the solution, rinsed thoroughly with MeCN and dried under Ar stream.

The chemical surface composition was investigated by XPS and the results are presented in Fig. 2.

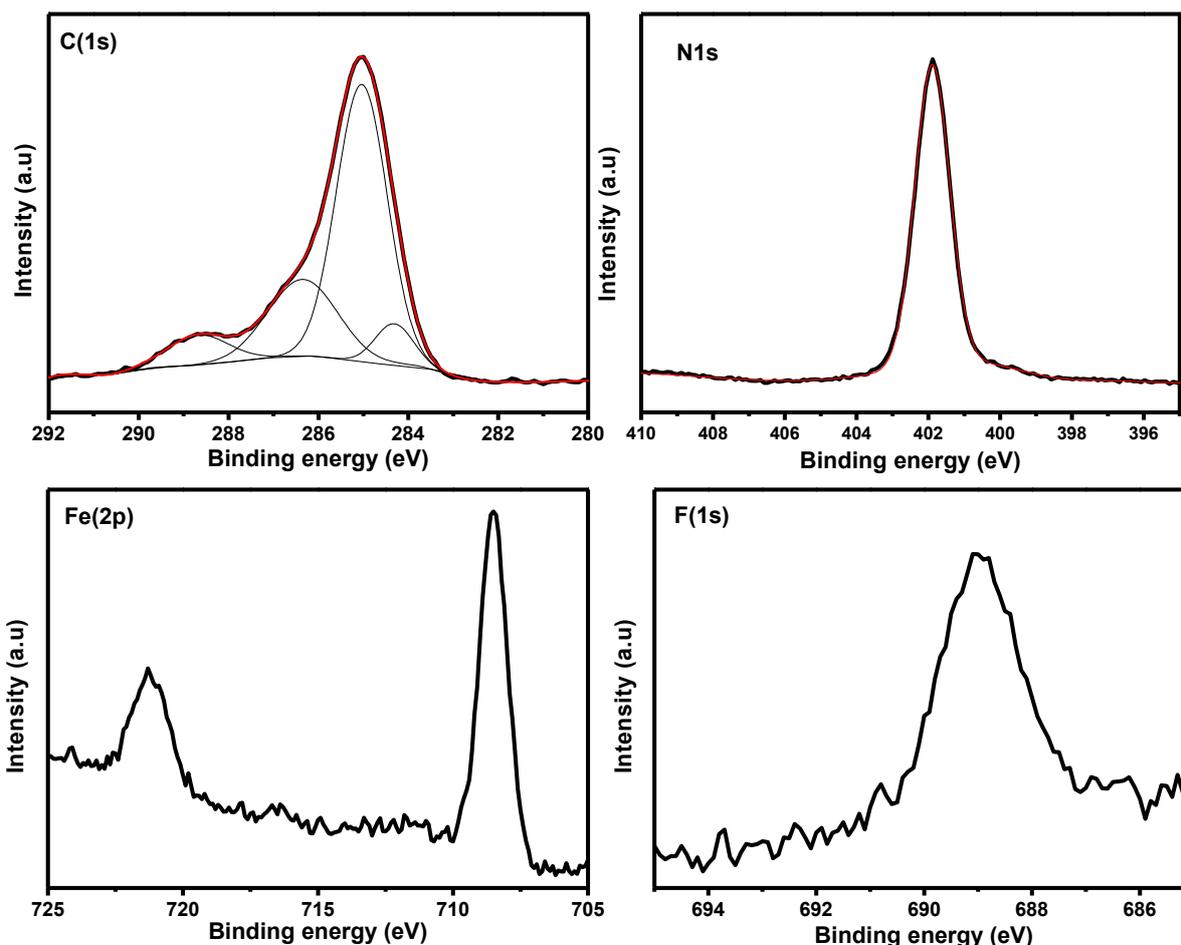


Fig. 2. High XPS resolution spectra of C(1s), N(1s), Fe(2p) and F(1s) .

The C1s spectrum of the modified electrode displays a major peak at 285 eV attributed to C–C bond and a minor peak located at higher binding energy 288.6 eV corresponding to C=O bond in the anthraquinone. Besides that, the main peak could be deconvoluted into three contributions located at binding energy 284, 286 and 287 eV which are attributed to C=C bond (aryl group), amide (C–N), –C=N group from imidazolium ring, respectively. The N(1s) XPS spectrum displays the presence of a component at 401.8 eV assigned to C–N in the imidazolium [29]. Furthermore, the absence of peak at 403.8 and 405.1 eV, corresponding to diazonium contribution, highlight the success of the coupling surface reaction between the ferrocene group, in the bi-redox molecule, and the attached diazonium head group [38]. The Fe(2p) spectrum shows a spin orbital doublets at 708 and 722 eV highlighting the presence of ferrocene moieties onto the modified surface. In addition, the XPS analysis displays the presence of peak at 689 eV attributed to F(1s) originated from the ionic liquid anion. Overall, the XPS investigations confirm the attachment of the bi-redox molecule [FcImAQ] as well as the presence of the [TFSI] anion.

3.3 Electrochemical investigations

The grafted bi-redox molecules were further investigated by recording their electrochemical responses in electrolytic solution. In this part, aqueous solution containing 0.1 mol.L⁻¹ HTFSI as supporting electrolyte was used for the electrochemical characterization. Under the acidic condition, the ferrocene moiety undergoes one electron oxidation process (donor-group), while anthraquinone involve a 2-electron and 2-proton reduction process (acceptor-group) [33].



The HTFSI electrolyte was selected because it has the same anion as in the attached layer, which avoids the anion exchange during the electrochemical measurements. In addition, the use of acidic electrolyte changes the anthraquinone electroreduction pathway to 2 electrons process and shift the reduction of AQ to less negative potential and thus minimizing the interference with the oxygen reduction. Fig 3a displays the CV recorded on modified electrode.

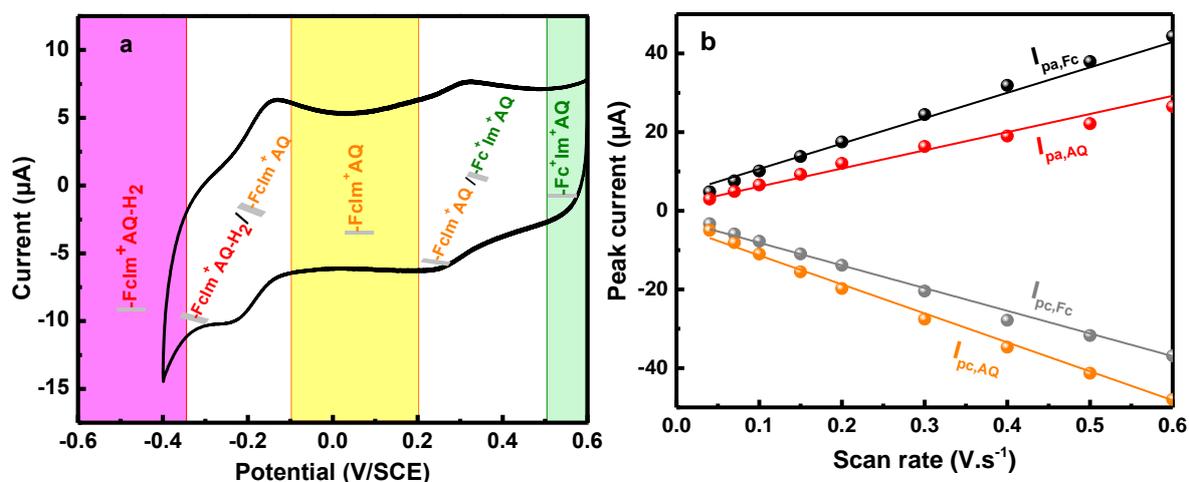


Fig. 3. (a) Cyclic voltammograms of immobilized [FcIm⁺AQ][TFSI] in aqueous solution containing 0.1 M of HTFSI, at $\nu = 0.1 \text{ V.s}^{-1}$, (b) Variation of the peak current as a function of the scan rate.

The CV displays two well defined redox reversible systems at 0.3 and -0.2 V/SCE assigned to the redox signal of the attached ferrocene and anthraquinone, respectively. The presence of two available redox-states confirms the successful bi-redox molecule grafting. In acidic condition, the oxidation state of the oxidized [FcImAQ] is (+2), while the [FcImAQ] and its reduced form have the same oxidation state (+1). The electrochemical switching window from the reduced state to oxidized state is about 0.5 V in acidic solution. The electrochemical

stability of the film was confirmed by performing 100 successive scans from -0.4 V to 0.6 V/SCE. The peaks current, for both redox systems, shows a small variation, less than 3%, when comparing the 1st and the 100th cycle. This result emphasizes the electrochemical stability of the attached layer which is suitable for further electrochemical investigations. Next, by performing CV's at different scan rate ranging from 0.01 V.s⁻¹ to 10 V.s⁻¹, a linear relationship between the peak current and the scan rate was obtained which is a typical characteristic of immobilized redox system onto the electrode surface (Fig. 3b). Furthermore, from the plot of the peak potential as a function of the scan rate, the electron transfer rate constant was calculated using Laviron's equation [39]. The obtained electron transfer rate constants values are 22 s⁻¹ and 25 s⁻¹ for Fc and AQ moieties, respectively (Fig. S5). These values are comparable to those reported for immobilized redox molecule [40], suggesting that the electron transfer rates constant is not altered by the presence of the bi-redox group.

Besides that, the integration of the ferrocene anodic peak and the AQ cathodic peak leads to electrochemically estimate the quantity of the charge and thus the surface concentration using the formula $\Gamma = Q/nFA$. The surface coverage of redox groups has been determined using the peak integration at low scan rate, 40 mV.s⁻¹. For Fc signal a value about 1.8×10^{-10} mol.cm⁻² is measured and a similar value was measured when using the AQ redox signal 1.9×10^{-10} mol.cm⁻². This similarity suggests that the same quantity of attached Fc and AQ are electrochemically detected despite their position within the film. The surface concentration value suggests the formation of a saturated monolayer of bi-redox molecule. In the literature, the surface concentration in a mixed redox layer, containing thiol-terminated ferrocene and anthraquinone, were found to be 2.8×10^{-10} mol.cm⁻² for anthraquinone and 4.0×10^{-10} mol.cm⁻² for Fc terminated layer [41-43]. In addition, the work shows that the ratio $\Gamma_{AQ} / \Gamma_{Fc}$ vary from 5 to 10 depending on the Fc and AQ based thiol concentration ratio. However, most of the reported works on mixed organic layers highlight the difficulty of controlling the layer composition due to the high and unselective reactivity of the attached molecule [44]. In our case, the ratio $\Gamma_{AQ} / \Gamma_{Fc}$ is equal to 1 providing an equi-distribution of the electron donor and acceptor within the attached layer.

Interestingly, the attached ionic layer contains immobilized imidazolium that is positively charged and a labile anion, TFSI. Recently, our group has demonstrated the capability of the ionic layer in acting as a self-double layer leading to record electrochemical measurement in the absence of supporting electrolyte [45]. The capacitive behavior of the layer was investigated by sweeping the potential in the capacitive region between -0.1 and 0.1 V in protic solution (Fig. 4a).

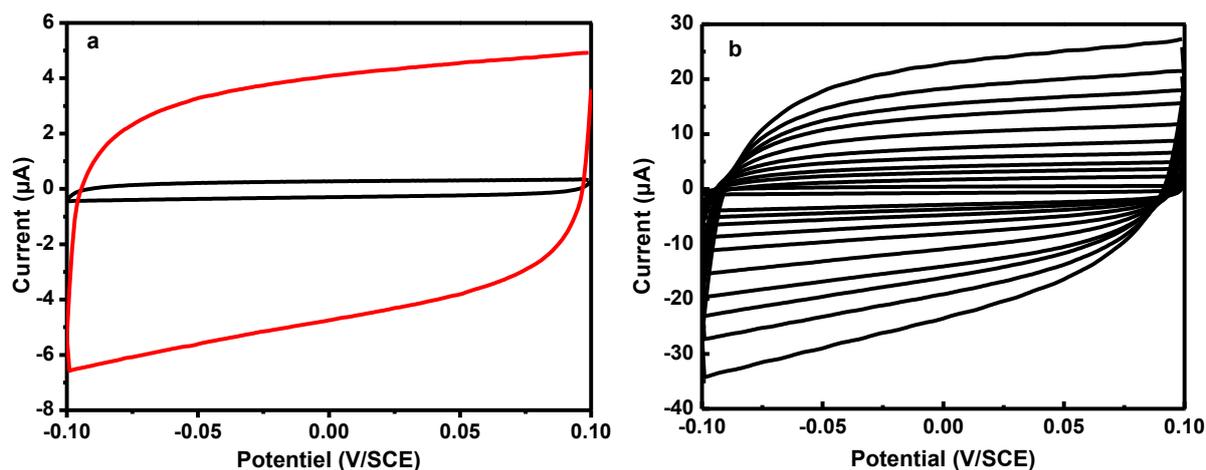


Fig. 4. (a) Cyclic voltammograms of immobilized [FcImAQ] (red line) and bare glassy carbon (black line) in aqueous solution containing 0.1 M of HTFSI, scan rate 0.1 V.s⁻¹. (b) CV's of immobilized [FcImAQ], in the same solution as (a), at different scan rate ranging from 0.005 to 0.8 V.s⁻¹.

The CV's of the modified electrode displays a quasi-rectangular shape characteristic of capacitive current and highlight the absence of faradic process within the explored potential window. Compared with the CV of bare GC electrode, the modified electrode displays a higher current as well as large CV area suggesting a higher capacitance. In addition, the effect of scan rates was investigated as shown in Fig. 4b. For the different scan rates, the quasi-rectangular shape is maintained confirming high ionic and electronic transport of the modified electrode. The variation of the capacity current during the negative and the positive scan, especially for higher scan rates, could be related to the ability of the electrolyte ions to penetrate the attached layer [46]. At different potential value, a linear relationship between the capacitive current and the scan rate is observed. The slope value represents the double layer capacitance, which is found to be around 500 $\mu\text{F}\cdot\text{cm}^{-2}$ for the attached bi-redox molecule, while a value of 20 $\mu\text{F}\cdot\text{cm}^{-2}$ has been measured for bare GC. The attachment of the ionic layer exhibits double layer capacitance increases by a factor of 25 when compared to bare glassy carbon. This variation is related to the ionic properties of the attached layer leading to an increase of the charge density.

4. Conclusions

In summary, a bi-redox based ionic liquid has been successfully synthesized, where both redox species are linked to the imidazolium cation. The electrochemical investigations of the bi-redox molecule, in electrolytic organic solution, were investigated and display two redox reversible system, donor and acceptor groups. Next, by using the appropriate functionalization method, the [FcImAQ] was successfully attached onto glassy carbon electrode. The XPS

investigations confirm the attachment of the imidazolium bearing the Fc and the AQ as well as the presence of the ionic liquid anion. The generated interface exhibits interesting electrochemical behaviors, including multi-redox state and a high double layer capacitance. These properties are linked to the high ionic density of the immobilized species and the formation of the double junction at the electrode surface. This approach opens a promising way for the immobilization of donor and acceptor moieties as well as the formation of ionic layer. We anticipate that the immobilization of molecule based ionic liquid could be extended to various carbon porous substrates for a potential use as a supercapacitor as well as pseudo-capacitor which include the redox activities of the bi-redox molecule.

ACKNOWLEDGMENT

The author's thank the support from the CNRS and doctoral school (ED388). The authors thank Dr. Philippe Decorse for performing the XPS measurements and for the valuable discussions.

Declaration of interest

The authors declare no competing financial interests.

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