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Electrochemical Grafting of Aryl Diazonium Salts in Deep Eutectic Solvents.

Quentin Lenne, Vivien Andrieux, Gaël Levanen, Jean-Francois Bergamini, Pauline Nicolas, Ludovic Paquin, Corinne Lagrost, Yann R. Leroux**

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ABSTRACT:

Deep eutectic solvents are seen as a new class of green and cheap solvents in electrochemical processes. Many electrochemical deposition techniques have been reported in the literature mainly focusing on metal electrodeposition and electro-polymerization. Here, we report for the first time the efficient electro-grafting of aryl diazonium salts on carbon surfaces using ethaline as an example of a natural and biodegradable deep eutectic solvent. Three different aryl diazonium salts have been tested, namely the 4-iodophenyldiazonium ion, 4-carboxymethylphenyl diazonium ion and 4-ethynylphenyldiazonium ion. Effect of concentration, deposition time and potential have been studied in relation to electrode blocking behavior toward redox probes in solution and deposited organic films thickness. Post-functionalization with redox active moieties is demonstrated on such electro-grafted organic layer to show their potential usefulness.

KEYWORDS: Deep Eutectic Solvent (DES), Aryl Diazonium, Surface Functionalization, Electro-grafting.

1. Introduction

Deep eutectic solvents (DES) are a new class of solvents that are gaining increasing attention as sustainable and safe solvents. [1,2] DES are mixture of two or three components whose melting temperature is considerably lower than that of each of the individual component because the components are strongly interacting with each other thanks to hydrogen bonds. [1,2] DES are often compared to room temperature ionic liquids (RTILs) as they are both designable and share many physico-chemical properties with them. However, DES are regarded as greener and cheaper alternative to RTILs that suffer from high cost and possible toxicity. [3] In contrast, DES are much easier to prepare by employing a range of inexpensive, widely available, biosourced and/or biodegradable components such as fatty acids, sugars and glycols. [1,2,4] The most widely studied DES are based on a combination of choline chloride and hydrogen bond donors such as urea, ethylene glycol or glycerol, belonging to the DES class III. Like RTILs, DES can be tailored for a dedicated application. They are currently used in organic synthesis, [5] in the preparation of nanomaterials (nanoparticles, nanocomposites, nanoassemblies), [6] in extraction processes, [4,7] CO_2 capture, [4] etc. Electrochemistry constitutes a major research area for DES, notably for metal electrodeposition. [1] More specifically, ethaline, mixing choline chloride and ethylene glycol in a 1:2 molar ratio, has a quite low viscosity (with respect to other DES) and a good conductivity which make it appealing for electrochemical applications. [8] As an example, ethaline was used as a solvent for electrodeposition of various metal as zinc, [9] copper [10] or silver [11] to name a few. Moreover, recently, electron transfer kinetic rate constants of redox probes in ethaline were shown to be just slightly lower than in classical solvent, hence much larger than in RTILs while the diffusion coefficients of charged redox probes are considerably less affected than in RTILs. [12,13] All these aspects point out the great potential of DES as

media for electrochemical applications. Considering electrochemical deposition techniques, since its discovery in 1992 by Pinson and coworkers, [14] the (electro-) reduction of aryl diazonium salts became a more and more popular technique that is nowadays commonly used to functionalize many surfaces, from conductors or semiconductors [15] to insulators. [16] Upon reduction, aryl diazonium ions lead to the formation of aryl radicals as intermediates, by the loss of nitrogen, which are highly reactive species than can add to the substrate. Due to the high reactivity of these intermediates, it generally leads to the deposition of multilayer films with various thicknesses, depending on both the nature of the aryl diazonium ion and the experimental conditions. In classical solvents, it has been shown that the blocking behavior of the modified electrode and the thickness of the deposited organic layer can be tuned by the concentration of the diazonium ion, the applied potential, the electrodeposition time and the medium. [17] Considering carbon materials, the bonding between the deposited organic layers and the substrates is a covalent C-C bond, making them very robust. Surprisingly, there is no example to date concerning the electrografting from aryl diazonium salts in DES whereas the reduction of aryl diazonium salts has been strongly investigated in RTILs, notably for the functionalization of carbon materials including single walled carbon nanotubes (SWNTs), [18] glassy carbon, [19,20] diamonds electrodes [21] and graphene materials. [22]

Herein, we report for the first time the electrografting of aryl diazonium salts in ethaline which is chosen as an archetypal example of DES on carbon materials. This type of solvents is nowadays prefer in industrial processes as they are sustainable (biodegradable), safer and cheaper than many classical organic solvents or ionic liquids. The electrodeposition of organic films is evaluated on both glassy carbon surfaces and pyrolyzed photoresist films (PPF) substrates. Three different aryl diazonium salts have been studied, namely the 4-

iodophenyldiazonium tetrafluoroborate (I-Ar-$N_2^+BF_4^-$), 4-carboxymethylphenyldiazonium tetrafluoroborate ($COOHCH_2$-Ar-$N_2^+BF_4^-$) and 4-ethynylphenyldiazonium tetrafluoroborate (Eth-Ar-$N_2^+BF_4^-$). I-Ar-$N_2^+BF_4^-$, $COOHCH_2$-Ar-$N_2^+BF_4^-$ and Eth-Ar-$N_2^+BF_4^-$ were chosen as they can be considered as useful platform for post-functionalization using Sonogashira cross-coupling reactions, [23,24] amide coupling [25] or click-chemistry [26] (Huisgen 1,3-dipolar cycloaddition). [27] The effect of aryl diazonium concentration in ethaline, electrodeposition time or applied potential have been studied on the blocking properties of the modified carbon materials and the thickness of the deposited organic layer. Finally, post-functionalization of the electro-grafted organic layers with electroactive species is demonstrated to prove their potential usefulness for many applications.

2. Experimental section.

2.1.Chemicals and reagents.

Commercially available reagents were used as received. 4-iodophenyldiazonium tetrafluoroborate (I-Ar-$N_2^+BF_4^-$), [23] 4-carboxymethylphenyldiazonium tetrafluoroborate ($COOHCH_2$-Ar-$N_2^+BF_4^-$) [28] and 4-ethynylphenyldiazonium tetrafluoroborate (Eth-Ar-$N_2^+BF_4^-$) [29] were synthesized according to published procedures. All aqueous solutions were made employing ultrapure water (18.2 MΩ cm) and organic solvents were of reagent grade. The choline chloride/ethylene glycol DES mixture (ethaline) was prepared with a molar ratio 1:2. The constituents were mixed under stirring at 80°C for 2 h until a stable clear homogeneous liquid was obtained, then allowed to cool at RT. Water content was measure by Karl-Fisher and was always < 1.0 %.

2.2.Pyrolytic Photoresist Films (PPFs).

The fabrication of PPFs consists of a thermal processing of a standard positive photoresist. They were synthesized as previously described. [30] The PPFs were typically 15 x 15 mm² and were cleaned in an ultrasonic bath in acetone, methanol and 2-propanol, and dried under Argon before use.

2.3. Preparation of modified substrates.

All carbon electrodes were modified according to the conditions described in each section, as aryl diazonium concentrations, electrochemical techniques, deposition times and applied potentials are varied. Prior to modification, commercially available glassy carbon electrodes (IJ Cambria) were polished successively with 2400 and 4000 silicon carbide abrasive papers

(Struers) and thoroughly rinsed with ultrapure water and acetone. For PPFs, no pre-polishing step is necessary.

2.4. Electrochemical instrumentation.

All surface modifications were performed using a standard three-electrode setup using a potentiostat Autolab PGSTAT 302N (Metrohm). The set of electrodes consisted of glassy carbon (GC) disk electrodes (IJ Cambria, surface area 0.03 cm^2) or small squares (15x15 mm^2) of PPFs as working electrodes, a platinum mesh as the auxiliary electrode, and a saturated calomel electrode or a platinum (Pt) wire as reference in aqueous media and ethaline, respectively. In ethaline, the potential drift of Pt has been measured to be less than 4 mV during a 1 hour experiment with Pt = +0.357 V vs SCE. When necessary, a conventional gas inlet was used for bubbling argon inside the electrochemical cell to displace oxygen.

2.5. Atomic Force Microscopy.

Atomic force microscopy (AFM) experiments were acquired on a NT-MDT Ntegra microscope using silicon nitride tips (resonance frequency c.a 200 kHz). Scratching technique, as described by McCreery and co-workers, [31] was used to estimate the thickness of the organic layer grafted on the PPF samples. On each sample a topographic image (3 µm x 3 µm) was first carried out in semi-contact mode, then the organic layer was scratched by scanning a 0.5 µm x 0.5 µm square in contact mode with a force set-point voltage of 1 V. Finally, square-shaped scratch was imaged in semi-contact mode and the thickness of the organic layer was extracted from depth-profiles measured on the scratched region. In order to take into account the possible scratch of the PPF substrates, scratching experiments were also carried out on bare PPF for each

set of samples and the scratch thickness was subtracted to correct the thicknesses obtained on grafted samples. All images were treated using Gwyddion software. [32]

2.6. X-ray Photoelectron Spectroscopy.

X-ray photoelectron spectra were collected using a Kratos Axis Nova spectrometer using the Al-Ka X-ray source at 1486.6 eV with a spot size of 700 x 300 μm2. Survey spectra (0-1000 eV) were acquired with an analyzer pass energy equal to 160 eV (0.5 eV/step) while high resolution spectra were obtained with a pass energy of 40 eV (0.1 eV/step). Spectral calibration was determined by setting C1s at 285 eV. The atomic concentration for surface composition was estimated using the integrated peaks areas. The peaks areas were normalized by the manufacturer-supplied sensitivity factor (S_{C1s} = 0.278, S_{O1s} = 0.78, S_{N1s} = 0.477, S_{I3d} = 10.3, S_{Si2p} = 0.38, S_{Cl2p} = 0.891). The core level spectra were peak fitted using the CasaXPS software, LtD., version 2.3.18.

2.7 Post-functionalization.

Carbon electrode functionalized with $COOHCH_2$-Ar-$N_2^+BF_4^-$ were chemically modified through a carbodiimide coupling. [25] The diazonium modified GC electrodes were immersed in a 0.25 mol.L^{-1} aqueous solution of EDC (0.2mL) under stirring for one hour. A 0.5 mol.L^{-1} aqueous solution of NHS (0.4mL) was then added to the mixture and stirred for another hour. 20 mg of (5-aminopentyl)ferrocene [33] was dissolved in 1mL of THF before being added to the solution. The reaction mixture was stirred overnight. To perform Sonogashira cross coupling reaction [23,24] with I-Ar-$N_2^+BF_4^-$ modified electrode, an aqueous solution containing $PdCl_2$ (1 mg) and pyrrolidine (1 mL) was first prepared. After immersion of the GC electrode, solution

was heated at 50°C for 5 min. 35 mg of (12-bromododecyl)ferrocene [34] was then added and the reaction mixture was heated at 50°C for 24h. Carbon electrode modified with Eth-Ar-$N_2^+BF_4^-$ were post-functionalized using click chemistry. [26] First, the modified electrode is immersed in a stirring THF solution (5 mL) containing 5 mg of 11-azidoundecylferrocene. [35] 2.5 mL of a 10^{-2} mol.L^{-1} $CuSO_4$ solution is added before the solution was degassed with Argon for 15 min. Finally, 2.5 mL of a 2.10^{-2} mol.L^{-1} solution of sodium ascorbate is added dropwise and the solution is stirred 1 hour under Argon.

All post-functionalized carbon electrodes were then thoroughly rinsed with acetone and ultrapure water then dried under argon flow prior to electrochemical characterization.

3. Results and Discussion.

3.1. Electrochemical reduction of aryl diazonium salts in ethaline.

The reduction of three different aryl diazonium salts were first studied by cyclic voltammetry (CV) in ethaline on glassy carbon (GC) electrodes. It is important to remember that no additional supporting electrolyte is added to the solution. We thus performed five consecutive cyclic voltammograms between +0.6 V and -0.9 V vs Pt, at a scan rate of 50 $mV.s^{-1}$ with a 10^{-2} $mol.L^{-1}$ concentration of aryl diazonium salt. The aryl diazonium ions show similar behavior as can be seen on Figure 1. On the first scan, an irreversible and broad reduction peak is observed at a potential comprised between 0 V and -0.5 V vs Pt, depending on the studied aryl diazonium salt. There is no oxidation peak associated with the reduction one, corresponding to the cleavage of N_2 groups coupled to the formation of aryl radicals. On the other scans, a strong inhibition of the electrochemical signal is observed. Depending on the aryl diazonium salt studied, the inhibition can be progressive or total even at the second scan. This is the characteristic behavior of an electrode blocked by the deposition of an insulating organic film. Also, one can notice that two reduction processes can be observed on the first scan. These two peaks have been clearly associated to a surface-catalyzed reduction step followed by an uncatalyzed reduction at a more negative potential. [36]

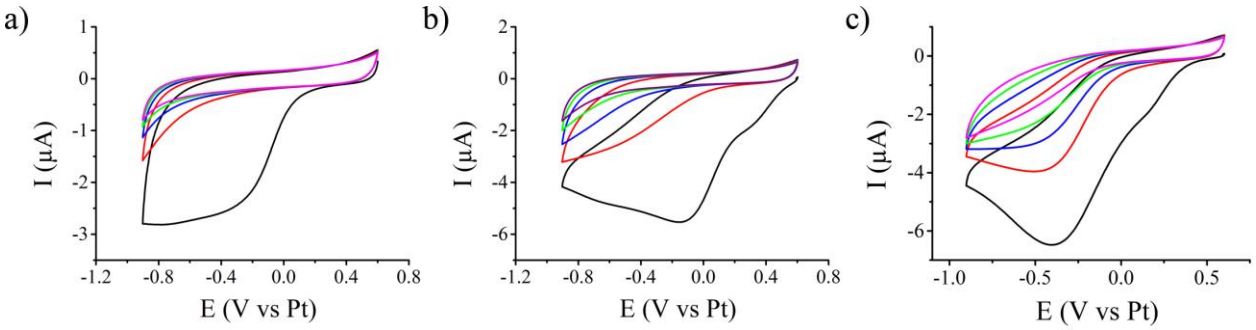


Figure 1. Electro-reduction in ethaline of 10^{-2} mol.L^{-1} a) Eth-Ar-$N_2^+BF_4^-$ b) I-Ar-$N_2^+BF_4^-$ and c) $COOHCH_2$-Ar-$N_2^+BF_4^-$ on a glassy carbon surface during 5 successive scans between + 0.6 V and - 0.9 V vs Pt at 50 mV.s^{-1}.

The blocking properties of the resulting electrodeposited organic films were examined through the oxidation of ferrocyanide as redox probe in an aqueous solution. As shown in Figure 2, ferrocyanide oxidation is totally inhibited in all cases after electro-grafting. This shows that the deposited organic films are homogeneous, without defects, and efficiently block the electron transfer between the carbon surface and the redox probe in solution. Concerning $COOHCH_2$-Ar-$N_2^+BF_4^-$, a small irreversible oxidation peak is observed at higher potential (> 0.4 V, Figure 2c) but is also visible in the absence of the redox probe (see figure S1). This electrochemical activity is attributed to the grafted organic film. Indeed, $COOHCH_2$-Ar-$N_2^+BF_4^-$ can form hydrogen bond with ethaline (vide infra) that can be trapped in the film. CVs in aqueous electrolytic solution of the grafted film (Figure S1) show irreversible oxidation signal at similar potential than in Figure 2c, which decreases upon cycling due to the removal of choline chloride trapped in the organic film.

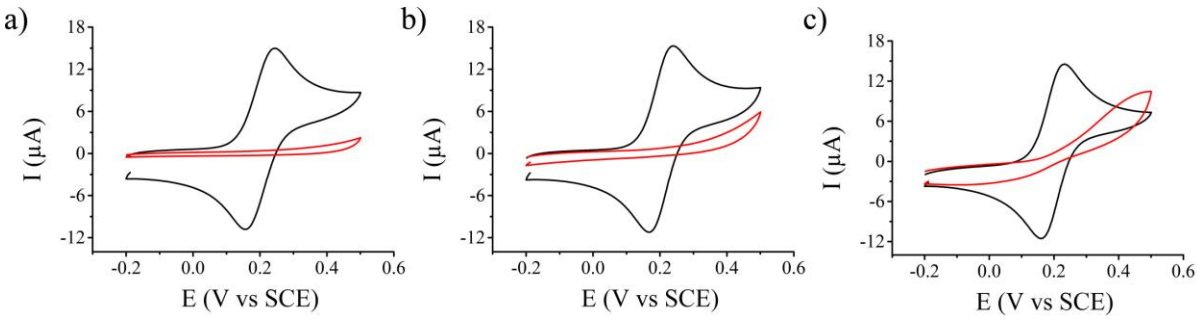


Figure 2. Cyclic voltammetry of 10^{-3} mol.L^{-1} ferrocyanide aqueous solution (+ 0.1 mol.L^{-1} KCl) on a bare GC surface (black curves) and after modifications with a) Eth-Ar-$N_2^+BF_4^-$ b) I-Ar-$N_2^+BF_4^-$ and c) $COOHCH_2$-Ar-$N_2^+BF_4^-$ (red curves). Scan rate = 0.1 V.s^{-1}.

The chemical composition of each electro-grafted organic films was investigated by X-ray Photoelectron Spectroscopy (XPS) analyses. Figure 3 presents the survey spectra of a bare PPF substrate and of PPF substrates modified by the electroreduction of the three different aryl diazonium salts in ethaline. For all the modified PPF substrates, there is no signal located at ~404 eV, indicating the absence of any remaining diazonium functions within the modified layer. As expected, the chemical composition of the organic film formed from Eth-Ar-$N_2^+BF_4^-$ reduction (Figure 3b and S3) is closely similar to the one of the bare PPF (Figure 3a and S2), with photoelectrons peaks corresponding to C and O elemental species. The oxygenated species are commonly observed due to contamination of surfaces exposed to air. The spectrum corresponding to PPF substrate modified by the reduction of I-Ar-$N_2^+BF_4^-$ (Figure 3c and S4) also displays photoelectrons peaks due to carbon and oxygen but with additional peaks at binding energies corresponding to iodine. Specifically, the peak attributed to $I3d_{5/2}$ at 620.6 eV (Figure S4c) is characteristic of an iodoaryl unit, unambiguously demonstrating the grafting of the iodophenyl units. [37,38] Surprisingly, XPS survey spectrum of PPF modified by $COOHCH_2$-Ar-$N_2^+BF_4^-$ reduction shows peaks at binding energies corresponding to nitrogen (~ 400 eV). The peak-fitted high-resolution core level spectrum of N1s (Figure S5c) shows a main peak centered at 403.1 eV which cannot be attributed to diazonium function or azo linkage. [39] Decomposition of C1s core level spectrum (Figure S5a) shows a higher contribution of oxygenated carbon (C-O at 286.9 eV and OC=O at 288.6 eV) than for the ethynyl and iodo-based aryl diazonium modified surfaces. The component at 288.6 eV can be attributed to

carboxylic functions, while the component at 286.9 eV can also reflect a contribution of carbon atoms involved in a C-N bonds. Both observations suggest the presence of choline cation within the electro-grafted film.

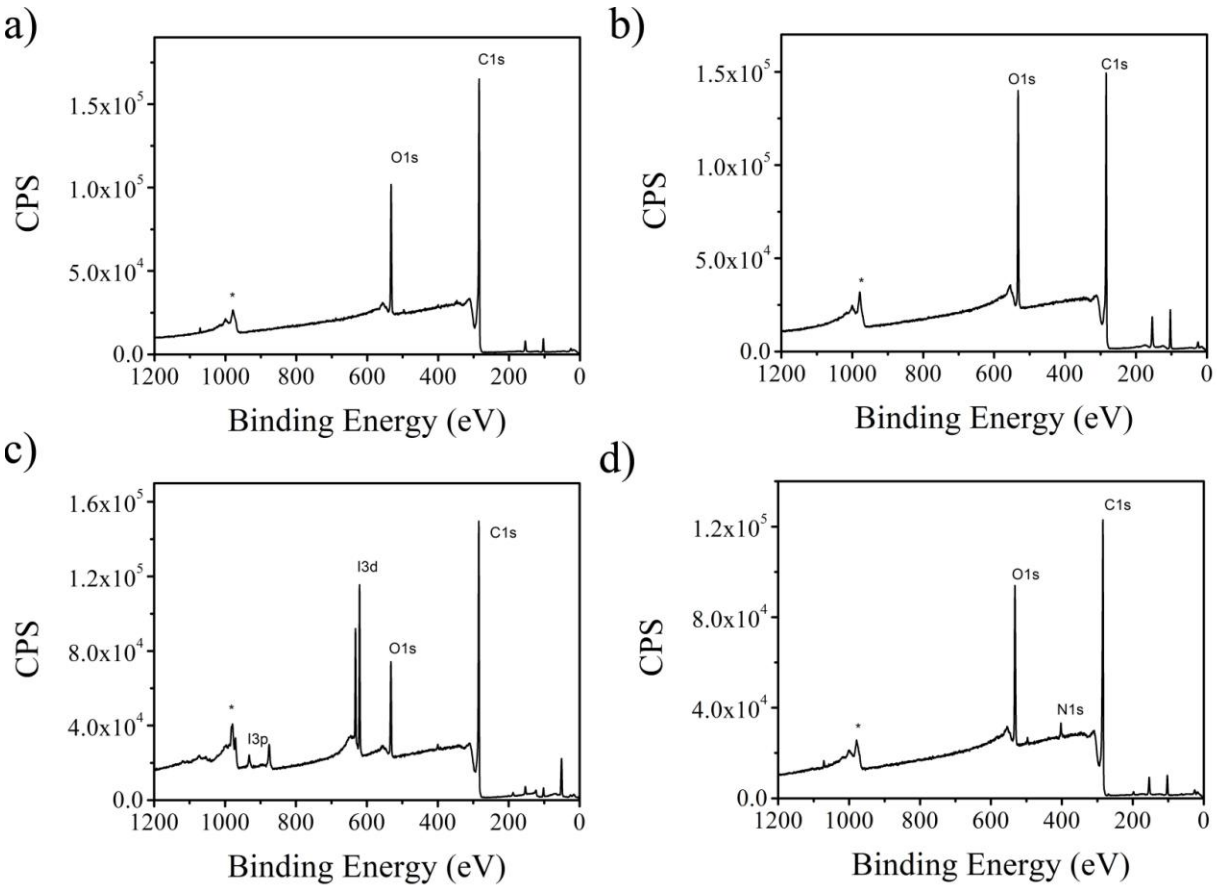


Figure 3. XPS survey spectra of a) bare PPF and PPF modified by the electroreduction of b) Eth-Ar-$N_2^+BF_4^-$ c) I-Ar-$N_2^+BF_4^-$ and d) $COOHCH_2$-Ar-$N_2^+BF_4^-$ in ethaline.

While ethaline have a neutral pH, [40] the pKa of a multilayered benzoic acid films is in the range of 2.8-3.3. [41] Hence, the electro-grafted organic film in ethaline will be deprotonated (negatively charged). We thus assume that choline, which is positively charged, is trapped in the organic film during electrografting. XPS analyses of choline-based nanocomposite were also

reported recently with binding energy for N1s core level spectrum at 402.9 eV. [42] The binding energy of the peak corresponding to the nitrogen in choline in our experiment is 0.2 eV higher and seems to be highly dependent of its environment.

Table 1. Surface Composition (% atom) of pyrolyzed pyrolytic films (PPF) grafted by the electroreduction of Eth-Ar-$N_2^+BF_4^-$, I-Ar- $N_2^+BF_4^-$ and $COOHCH_2$-Ar- $N_2^+BF_4^-$ in ethaline.

% atom	Unmodified PPF	Eth-Ar-N_2^+BF4$^-$ modified PPF	I-Ar-N_2^+BF4$^-$ modified PPF	CH_2COOH-Ar-N_2^+BF4$^-$ modified PPF
% Si	2.3 %	6.6 %	1.8 %	3.3 %
% C	84.4 %	74.15 %	85.45 %	79.3 %
% O	13.3 %	19.25 %	10.9 %	15.1 %
% N	-	-	-	1.8 %
% I	-	-	1.25 %	-

Having demonstrated the efficient electrografting of aryl diazonium cations in a DES, variations of the experimental conditions including aryl diazonium concentration, applied potential and electrodeposition time are now examined in order to evaluate their influence on the films properties and organization in such unconventional media. For sake of comparisons, the electro-grafting of aryl diazonium ions is achieved by constant potential electrolysis in the following.

3.2. Effect of aryl diazonium concentration.

First, the influence of aryl diazonium concentration regarding the blocking properties of the deposited film was evaluated. For all aryl diazonium ions, we apply a fixed potential of -0.6 V vs Pt for 60 s. This value was chosen to allow a reasonable rate of surface modification without applying an excessive overpotential. [17] The concentrations of the aryl diazonium ions were chosen to be 5.10^{-4} mol.L^{-1}, 10^{-3} mol.L^{-1}, 2.10^{-3} mol.L^{-1}, 5.10^{-3} mol.L^{-1} and 10^{-2} mol.L^{-1}. As mentioned before, we use ferrocyanide as redox probe to assess the blocking properties of the modified electrode surfaces. Ferrocyanide is very sensitive to surface state and it can easily probe the deposition of monolayer films onto surfaces. [29,43] Figure 4 presents the results obtained for Eth-Ar-$N_2^+BF_4^-$ modified surfaces whereas the results obtained with the other aryl diazonium salts can be found in supporting information (Figure S6 and S7). For the first three concentrations, i.e. 5.10^{-4}, 10^{-3} and 2.10^{-3} mol.L^{-1}, small variations of the ferrocyanide oxidation behavior are observed. Peak to peak separations values (ΔE) are similar to that on bare GC but a small decrease in current peak intensity is observed as the concentration in aryl diazonium salts increases. This decrease in peak current intensity is no more than 20% compared to the value obtained on bare GC. The fact that the ΔE is similar on bare and modified GC electrodes means that ferrocyanide can easily reach the GC surface to transfer its charges, or in other words, that not all the GC surface is covered by an electrodeposited organic film. The small variation of the peak current intensity highlights a small decrease in the GC surface area, strengthening this first conclusion. On the other hand, when the concentration is 5.10^{-3} mol.L^{-1}, a clear change in the shape of the ferrocyanide oxidation voltammogram is observed. The observed S-shape curve is typical from an array of non-interacting ultramicroelectrodes (UMEs). [44] We can thus conclude that the GC surface is now mainly covered by an electrodeposited organic film that is

not compact and presents pinholes. Finally, when a 10^{-2} mol.L^{-1} concentration of Eth-Ar-$N_2^+BF_4^-$ is used, the ferrocyanide oxidation is totally inhibited which is a clear indication of the electrodeposition of a compact and dense insulating organic film onto the whole GC surface. Similar conclusions can be drawn concerning the two other aryl diazonium salts: a progressive covering of the electrode surface with increasing aryl diazonium concentration. However, small differences between aryl diazonium salts can be observed. The ferrocyanide oxidation is not totally inhibited when carbon substrates are modified with 10^{-2} mol.L^{-1} I-Ar-$N_2^+BF_4^-$ concentration (Figure S6f). Indeed, longer deposition time is needed (vide infra). Also, as previously described, an irreversible oxidation peak is observed at higher potential when $COOHCH_2$-Ar-$N_2^+BF_4^-$ is used (Figure S7f) which is attributed to the electrochemical activity of the grafted organic film due to the presence of trapped choline cations (vide supra).

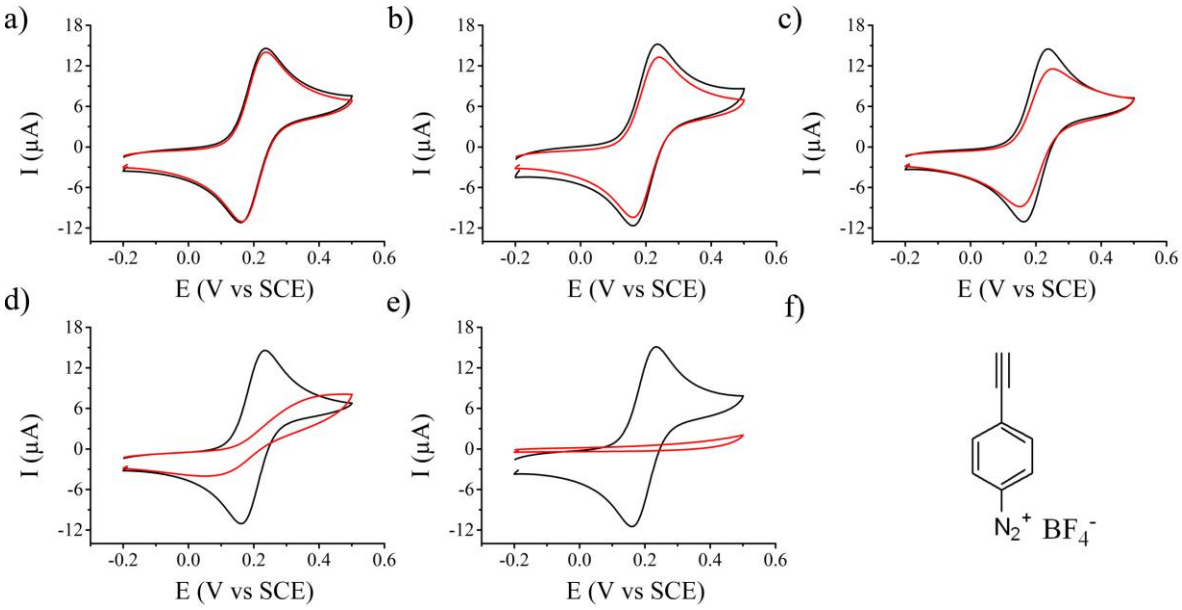


Figure 4. Cyclic voltammetry of 10^{-3} mol.L^{-1} ferrocyanide aqueous solution (+ 0.1 mol.L^{-1} KCl) on a bare GC surface (black curves) and after electro-reduction of a a) 5.10^{-4} mol.L^{-1}, b) 10^{-3} mol.L^{-1}, c) 2.10^{-3} mol.L^{-1}, d) 5.10^{-3} mol.L^{-1}, and e) 10^{-2} mol.L^{-1} Eth-Ar-$N_2^+BF_4^-$ solution by

constant potential electrolysis during 60 s at -0.6 V vs Pt (red curves). Scan rate of 0.1 $V.s^{-1}$ .f) Schematic representation of Eth-Ar-$N_2^+BF_4^-$.

From the present observations, 10^{-2} $mol.L^{-1}$ in aryl diazonium salt correspond to an optimal value of concentration for allowing the deposition of a compact and dense organic film onto the electrode surface. Hence, we will study the effect of the applied potential and deposition time with a concentration in aryl diazonium salt in ethaline of 10^{-2} $mol.L^{-1}$.

3.3. Effect of applied potential.

We choose to apply five different potentials of 0.6 V, 0.3 V, 0 V, -0.3 V and -0.6 V vs Pt in constant potential electrolysis experiments during 60 s to probe the effect of the applied potential on the blocking properties and film thickness of organic deposits generated through aryl diazonium salt electro-reduction in ethaline. Figure 5 shows the CV of ferrocyanide oxidation in aqueous solution on bare GC and GC electrode modified by the electro-reduction of Eth-Ar-$N_2^+BF_4^-$ at different applied potentials. As expected, the oxidation of ferrocyanide remains similar as the one obtained on bare GC electrode when the potential applied is higher than the onset potential (0.06 V vs Pt) of the reduction of Eth-Ar-$N_2^+BF_4^-$. However, small variation can still be observed as ferrocyanide is very sensitive to surface modification and aryl diazonium salt are known to spontaneously graft onto surfaces. [45] This effect is limited as the GC surfaces are in contact with the aryl diazonium salt solution for only 60 s. Once the onset potential of aryl diazonium ion is reached, the CV of ferrocyanide oxidation is altered. At low overpotential (until 0 V vs Pt), the ferrocyanide oxidation CV is partially inhibited with decreased peak intensities and increased peak-to-peak separation (ΔE), whereas at high overpotential (-0.6 V vs Pt), the signal is totally inhibited. Between these two behaviors, an intermediate behavior that is

characterized by an S shape CV curve (-0.3 V vs Pt) can be observed. Similar behaviors are observed for the other aryl diazonium salts and are presented in supplementary information (Figure S8 and S9). Same differences between aryl diazonium salts are observed as previously described. In general, the evolution of ferrocyanide oxidation behavior is progressive and follow the increase of the applied potential. The larger the overpotential, the more the blocking properties increase. A quantitative evaluation of the blocking properties of the modified GC electrodes was performed by following the increase in ΔE as shown in Table 2.

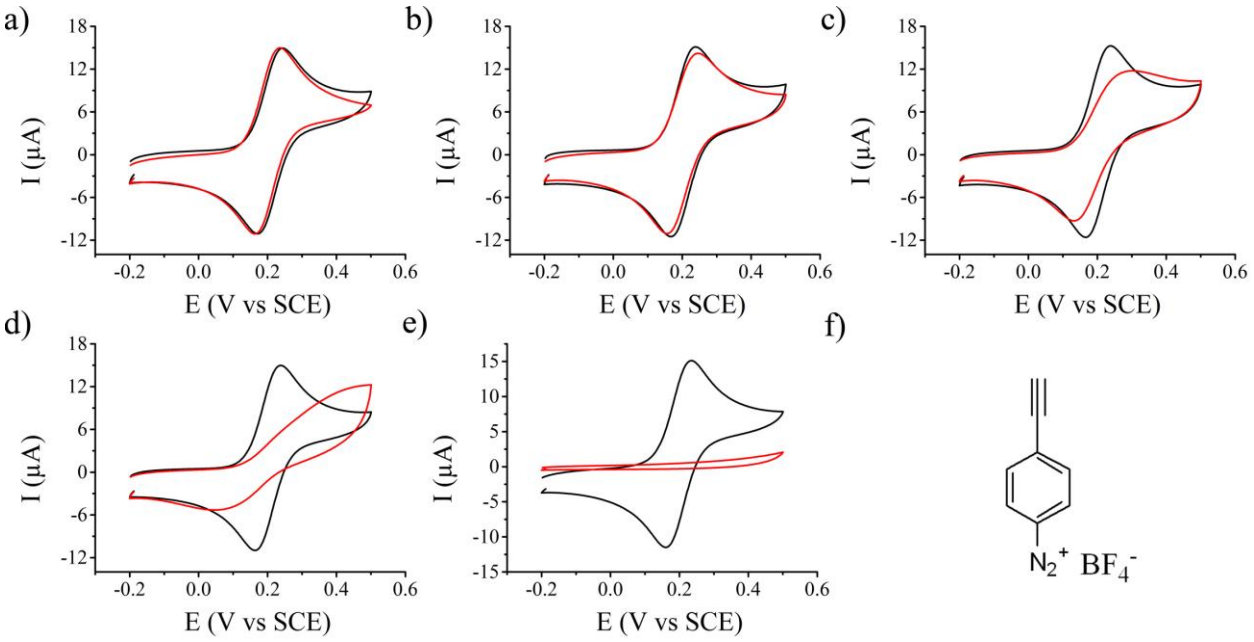


Figure 5. Cyclic voltammetry of 10^{-3} mol.L^{-1} ferrocyanide aqueous solution (+ 0.1 mol.L^{-1} KCl) on a bare GC surface (black curves) and after electro-reduction of Eth-Ar-$N_2^+BF_4^-$ by constant potential electrolysis during 60 s at a) 0.6 V, b) 0.3 V, c) 0V, d) -0.3 V and e) -0.6 V vs Pt (red curves) at a scan rate of 0.1 V.s^{-1}. f) Schematic representation of Eth-Ar-$N_2^+BF_4^-$.

AFM analyses and scratching experiments [31] were performed to evaluate the homogeneity of the deposited organic layers and to estimate their thickness on carbon surfaces. These experiments consist of scratching a rectangular area on the modified surfaces by exercising with the AFM tip in contact mode a force sufficient to remove the organic layer. Profiling depth measurements of the scratching area allow an estimation of the thickness difference between the bare substrate and the organic deposit. For these experiments, pyrolyzed photoresist films (PPFs) were chosen as carbon materials as they present similar reactivity than GC substrates but with low roughness allowing AFM experiments. The estimated thicknesses are listed in Table 2 and the images can be found in supporting information (Table S1). Only a sparse organic deposition is observed by AFM experiments at low overpotential (between 0.6 V and 0 V), in good agreement with the weak blocking properties against ferrocyanide as highlighted above. In contrast, thicker and more compact organic film can be observed at higher overpotential (between -0.3 V and -0.6 V). Moreover, the organic layer thickness increases with increasing overpotential, forming multilayered and disordered organic deposits as commonly observed with aryl diazonium electrografting in conventional solvents. No monolayer films are formed under these conditions in ethaline.

Table 2. Effect of the applied potential on the blocking properties and thicknesses of organic films deposited by the electro-reduction of aryl diazonium salts in ethaline during 60 s.

Applied potential (E vs Pt)	0.6 V	0.3 V	0 V	-0.3 V	-0.6 V
$\Delta E_{\text{Eth-Ar-N2+BF4-}}$ increase	103 %	121 %	232 %	S shape	inhibited
Thickness $_{\text{Eth-Ar-N2+BF4-}}$ (nm)	-	-	-	2.0 ± 0.1	3.1 ± 0.3
$\Delta E_{\text{I-Ar-N2+BF4-}}$ increase	108 %	100 %	100 %	167 %	S shape

Thickness $_{I\text{-}Ar\text{-}N2+BF4\text{-}}$ (nm)	-	-	-	0.8 ± 0.1	0.9 ± 0.1
ΔE $_{COOHCH2\text{-}Ar\text{-}N2+BF4\text{-}}$ increase	104 %	152 %	219 %	256 %	inhibited
Thickness $_{COOHCH2\text{-}Ar\text{-}N2+BF4\text{-}}$ (nm)	-	-	-	0.5 ± 0.1	0.9 ± 0.1

3.4. Effect of electrodeposition time.

In the same way as the experiments performed to assess the effect of the applied potential, we study the effect of the electrodeposition time onto the blocking properties and film thickness of the organic film grafted by the electroreduction of aryl diazonium ion in ethaline. In constant potential electrolysis, we used a 10^{-2} mol.L^{-1} aryl diazonium solution and applied a potential of -0.6 V vs Pt for 3 s, 10 s, 60 s, 120 s, 300 s and 600 s. Figure 6 shows the results obtained with Eth-Ar-$N_2^+BF_4^-$. As presented in Figure 6a, a rapid inhibition of the ferrocyanide oxidation signal is observed for electrodeposition time ≥ 10 s indicating the deposition of a compact and dense organic layer. Figure 6b presents the variation of film thicknesses estimated by AFM scratching experiments at different electrodeposition time. A rapid increase in film thickness is first observed until 60 s, then the increase in film thickness is slower until reaching a maximum value close to 2.5 nm. Similar behaviors are observed for the other aryl diazonium salts with thickness maximum value of 1.6 nm and 2.0 nm for I-Ar-$N_2^+BF_4^-$ (Figure S10) and CH_2COOH-Ar-$N_2^+BF_4^-$ (Figure S11) respectively. Such a behavior is also observed using classical organic and aqueous solvents. However, the maximum thickness values obtained are smaller than the one expected using these classical solvents. For example, the electroreduction of Eth-Ar-$N_2^+BF_4^-$ in acetonitrile leads to ethynylphenyl films with thickness of 6 to 7 nm [29,30] while I-Ar-$N_2^+BF_4^-$ electroreduction in acetonitrile leads to iodophenyl films of ~5 nm [24] which is 2.5 to 3 times thicker than in ethaline under similar electrochemical deposition conditions. Moreover, we observed that the thickness quickly reaches a plateau (after 120 s of electrolysis), suggesting a

self-limiting growth process in the DES. Similar behavior has been evidenced when using RTILs. [46,47,48] However, thinner layers were reported in RTILs (thickness < 1.5 nm) than the ones obtained herein with ethaline. [46,47,48] It is likely that specific solvation shell (ionic shell) and interface structuring of the ionic liquids compared to those of ethaline could explain such a difference. Even, if generally considered as an ionic liquids subclass, DES differ greatly from ionic liquids in that they are not composed entirely of ions but instead have a predominant molecular component. It is thus anticipated that solvation and interface structuring would be basically different in ethaline.

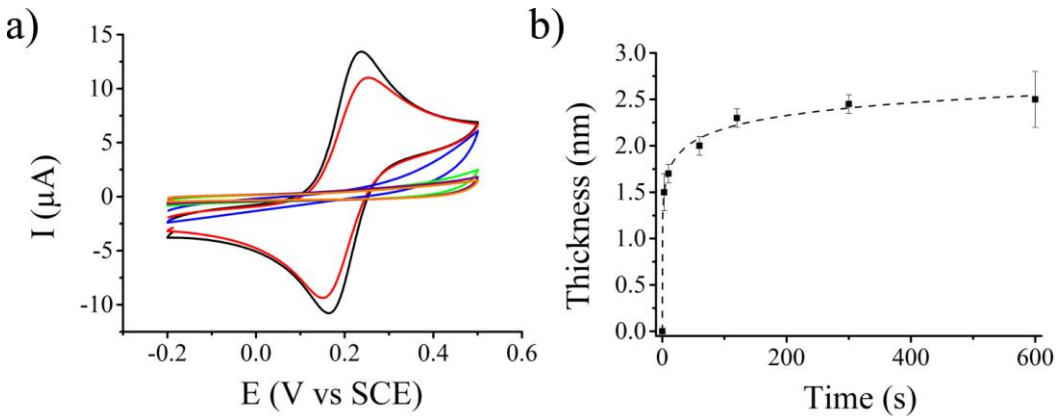


Figure 6. a) Cyclic voltammetry of 10^{-3} mol.L^{-1} ferrocyanide aqueous solution (+ 0.1 mol.L^{-1} KCl) on a bare GC surface (black curves) and after electro-reduction of Eth-Ar-$N_2^+BF_4^-$ by constant potential electrolysis at -0.6 V vs Pt during 3 s (red curve), 10 s (blue curve), 60 s (green curve), 120 s (magenta curve), 300 s (marine curve) and 600 s (orange curve) at a scan rate of 0.1 V.s^{-1}. b) Plot of film thickness versus deposition time for the electro-reduction Eth-Ar-$N_2^+BF_4^-$ at -0.6 V vs Pt, measured by AFM scratching experiments.

3.5.Post-functionalization.

In order to highlight the usefulness of the immobilization of such organic films by the electroreduction of aryl diazonium salts in ethaline, post-functionalization was investigated. As surface reaction, Click Chemistry (Huisgen 1,3-dipolar cycloaddition), [27] Sonogashira cross-coupling and Carbodiimide coupling reactions were employed for post-functionalizing ethynylphenyl-, iodophenyl- and phenylacetic acid films respectively with alkylferrocenyl derivatives. The resulting post-functionalized organic films were studied in dichloromethane solution containing 0.1 M $TBAPF_6$ (Figure 7). Well-defined ferrocene/ferrocenium system are observed between 0.3 V and 0.4 V vs SCE in all cases, with a linear variation of the peak current (Ip) versus scan rate (v) in agreement with an immobilized redox system. The surface concentrations of active ferrocene centers (Γ) were derived from these experiments according to $\Gamma = 4aRT/F^2S$ where F is the Faraday constant, a the slope of Ip vs v variation, R the universal gas constant, T the temperature and S the surface area of the sample. A surface concentration of $\Gamma = 2.71\ (\pm 0.06) \times 10^{-10}$ mol.cm^{-2} was derived for post-functionalized ethynylphenyl films which is in agreement with the literature. [29] Post-functionalization of iodophenyl films leads to $\Gamma = 1.80\ (\pm 0.05) \times 10^{-10}$ mol.cm^{-2} which is a little bit lower but of the same magnitude than what was reported previously. [24] Finally, post-functionalization of phenylacetic acid film leads to $\Gamma = 4.15\ (\pm 0.01) \times 10^{-10}$ mol.cm^{-2} which is really close to the maximum theoretical coverage of ferrocenyl moieties. [49] Click Chemistry and Carbodiimide coupling use mild and biocompatible synthetic conditions allowing the immobilization of biomolecules with no loss of their functions onto the ethynylphenyl and phenyl acetic organic layers. On the other hand, Sonogashira cross-coupling reaction performed on iodoaryl organic layer lead to the

immobilization of molecules through ethynylphenyl bridge, which is more adapted when electronic communication between the surface and the immobilized molecule is desired. Such results show that a wide range of functional groups and molecules can be immobilized on organic films grafted in ethaline.

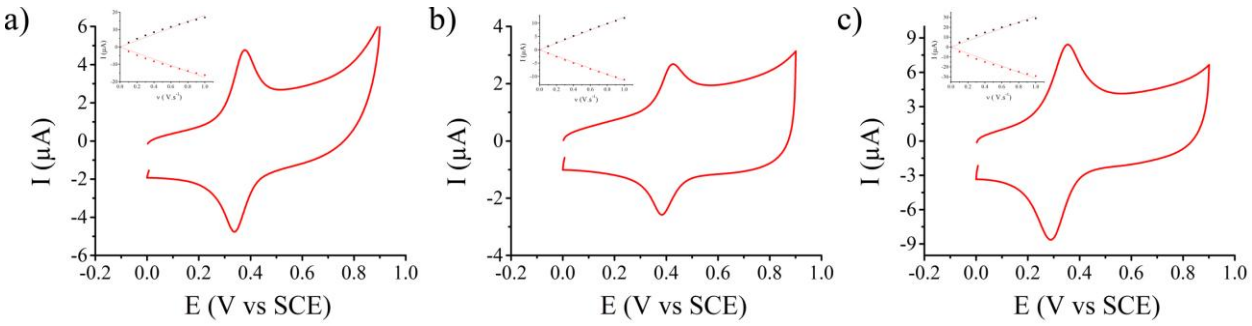


Figure 7. Cyclic voltammogram in dichloromethane + 0.1 mol.L^{-1} $TBAPF_6$ of modified-GC electrode after post-functionalization with ferrocenyl derivatives on modified-GC electrode with a) Eth-Ar-$N_2^+BF_4^-$, b) I-Ar-$N_2^+BF_4^-$, and c) $COOHCH_2$-Ar-$N_2^+BF_4^-$. Scan rate: 0.2 V.s^{-1}. Inset: Variation of the anodic and cathodic peak current with the scan rate.

4. Conclusions.

We have demonstrated in this study that aryl diazonium ions can be easily reduced electrochemically in Deep Eutectic solvents (DES) and specifically in ethaline, at potentials close to the ones observed in conventional solvents. The blocking properties and film thicknesses could be finely modulated through electrochemical (applied potential, electrodeposition time) and chemical (concentration) parameters until the formation of dense and compact films with no pinhole or defect. All the results point to the formation of thinner organic films than in classical solvents, yet less thin than those observed in RTILs, probably due to a different molecular organization of the DES. Post-functionalization of ethynylphenyl, iodophenyl and phenylacetic acid films formed in ethaline leads to the immobilization of high density of active redox molecules and shows that such strategy can be employed to immobilized a wide range of functional groups and/or (bio) molecules. However, due to the nature of the DES, strong interaction (hydrogen bonding) can occur with specific aryl diazonium ions which can alter the composition and structure of the electro-grafted organic films. Special attention has to be paid to the choice of the DES and the aryl diazonium combination to this regards.

ASSOCIATED CONTENT

Supporting Information. The following file is available free of charge.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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