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Article

Dithienylpyrrole Electrografting on a Surface through the Electroreduction of Diazonium Salts

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Abstract: The control of the interface and the adhesion process are key issues for the development of new application based on electrochromic materials. In this work the functionalization of an electrode's surface through electroreduction of diazonium generated in situ from 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine (SNS-An) has been proposed. The synthesis of the aniline derivative SNS-An was performed and the electrografting was investigated by cyclic voltammetry on various electrodes. Then the organic thin film was fully characterized by several techniques and XPS analysis confirms the presence of an organic film based on the chemical composition of the starting monomer and allows an estimation of its thickness confirmed by AFM scratching measurements. Depending on the number of electrodeposition cycles, the thickness varies from 2 nm to 10 nm, which corresponds to a few grafted oligomers. In addition, the grafted film showed a good electrochemical stability depending on the scan rates up to 400 V/s and the electrochemical response of the modified electrode towards several redox probes showed that the attached layer acts as a conductive switch. Therefore, the electrode behaves as a barrier to electron transfer when the standard redox potential of the probe is below the layer switching potential, whereas the layer can be considered as transparent towards the electron transfer for redox probes with a redox potential above it.

Keywords: diazonium electroreduction; surface grafting; conducting polymer; dithienylpyrrole

1. Introduction

Conducting polymers (CPs) continue to be the center of intensive scientific research due to their unique properties (tunable band gap, redox properties, protection against corrosion and low cost) [1,2]. These characteristics have allowed the development of many technological applications [3], from organic and molecular electronic [4,5] to sensors [6–8] or smart surfaces [9–13]. Among many types of CPs, poly(thienyl-pyrrole-thienyl) derivatives have received great interest [14–18] especially for their electrochromic properties [19–23]. The structure of derivatives is generated from a central pyrrole units bearing two thiophene moieties attached on the C2 and C5 carbon atoms of the pyrrole and can be named SNS or Poly(SNS). As the starting monomer presents three aromatic units, their oxidation potentials are low (around 0.2 V/SCE) and as the pyrrole unit can be easily substituted on the nitrogen, new functions can be easily added on the conductive backbone. Moreover, many synthesis pathways have been developed to couple the SNS moieties and other monomers. Recently,

Guven et al. reported the synthesis of several SNS derivatives by click chemistry opening the way for new materials in electrochromic applications [20–22]. This approach allows one to achieve an effective post-polymerization functionalization of azide containing SNS monomer. Usually the deposition of CPs is performed either from the vapor phase or from solution (dip coating, self-assembly) or by electrochemical oxidation of a monomer. In such cases, the interface is often not well defined due to the weak interaction between the substrate and the polymer. This drawback can be overcome using surface pretreatment, such as adhesion primer grafting. It allows the modification of the surface by grafting the appropriate monomer chain. The adhesion layer can be introduced through two different ways: the cathodic polymerization [24,25] and the diazonium electroreduction [26,27]. The first pathway is generally restricted to acrylic derivatives whereas the latter is used to modify the surface with an aromatic based compound. For the latter the electrochemical reduction of a phenyldiazonium salt produces phenyl radicals in the vicinity of the electrode and these phenyl radicals react with the electrode surface leading to a covalent bond at the interface [26]. This reaction has been studied in different media [28,29] with several electrode materials such as metallic [30–33] and semi-conducting surfaces [34–37]. Moreover, this method is very versatile due to the wide variety of substituted phenyl diazoniums based on various amino derivatives [38,39]. Depending on the surface materials the strong adhesion of the organic film was established or was indirectly evidenced by the resistance to sonication that cannot be explained by weak interaction [40–42].

Many studies have been reported quite recently using diazonium electroreduction to graft conductive oligomers on surfaces [38,43–47]. Ultrathin layers can be generated since the growth is limited by the conductivity of the organic layer in the potential range required for the electroreduction of the diazonium salt. However, the structure of such films is not well defined compared to single monolayer as the growth generates multilayer films [40,48–50] but monolayers have also been reported considering the steric hindrance or solvent viscosity [51–54]. Despite the lack of layer organization, the reversible switching properties of conductive oligomers are retained and these properties are combined using a strongest metal/oligomer interaction compared to that obtained with vapor phase and dip coating, or by electrochemical oxidation.

In this present work, we investigate the electroreduction of a new derivative of SNS monomer to fabricate a stable adhesion layer on various electrode from 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine, as depicted in Figure 1a. The electrochemical reduction of the amino-phenyl moiety bearing an SNS group is investigated at glassy carbon (GC) and gold electrodes. Next, the morphology and the thickness of such layers are investigated using various techniques, such as X-ray photoelectron spectroscopy (XPS), cyclic voltammetry, and atomic force microscopy (AFM). More interestingly, using electrochemical techniques we demonstrated that the conductivity of the organic layer could change demonstrating a switching behavior towards a redox probe. This study paves the way for improving the adhesion of organic layer on electrode but also for exploring modulation or control behavior for electrochromic material.

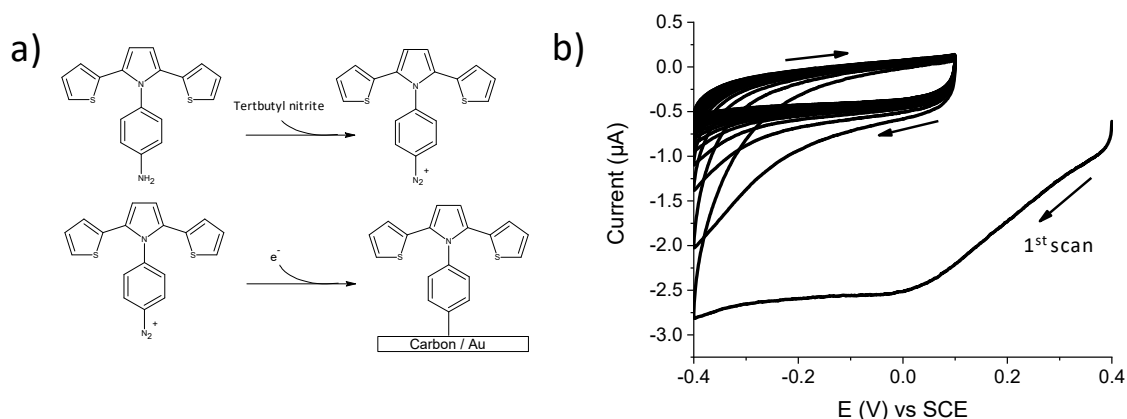


Figure 1. (a) schematic illustration of in situ synthesis of 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl diazonium cation and its electro-reduction onto metallic electrode. (b) Cyclic voltammogram of 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl diazonium cation electro-reduction (5×10^{-4} mol/L) in acetonitrile solution (20 cycles at 0.1 V/s) on carbon electrode.

2. Experimental Section

All chemicals were purchased from Sigma-Aldrich[®], Merck Chemical[®] as analytical grade. Tetrabutylammonium tetrafluoroborate (TBABF₄) was electroanalytical grade and thiophene, succinyl chloride, *p*-diaminophenylene were used as received. 1,4-di(2-thienyl)-1,4-butanedione and 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine (SNS-An) were synthesized according to literature [55]. NMR ¹H (CDCl₃): 3.87 (2H, s, NH₂); 6.53 (2H, dd, 3.60 and 1.15 Hz, 4-thienyl); 6.56 (2H, s); 6.64 (2H, dd, 3.65 and 5.10 Hz, 3-thienyl), 7.05 (2H, dd, 1.15 and 5.10 Hz, 2-thienyl); 6.72 (2H, dd, 6.58 and 2.15 Hz, phenyl); 7.10 (2H, dd, 6.58 and 2.15 Hz, phenyl).

2.1. Electrochemical Experiment

A conventional three-electrode cell was used with a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) (3 M KCl) as reference. The potentials were checked versus the ferrocene/ferrocenium couple, and all potentials were scaled against SCE. Two types of working electrode were used, namely glassy carbon (GC, 3 mm diameter) and gold (1 cm²) for XPS analysis. Prior to use the carbon electrodes were polished using decreasing sizes of diamond paste. Before any measurements the solutions were deoxygenated by bubbling argon for 30 min; during the experiment the electrochemical cell remained under argon. Electrochemical data were collected using a CHI 660C potentiostat (CH Instruments, Austin, TX, USA).

2.2. X-ray Photoelectron Spectroscopy

XPS analyses were performed on a modified gold substrate using a VG Scientific ESCALAB 250 system equipped with a microfocused, monochromatic Al KR X-ray source (1486.6 eV) and a magnetic lens which increases the electron acceptance angle and hence the sensitivity. A 650 μm X-ray beam was used at 20 mA × 15 kV. The spectra were acquired in the constant analyzer energy mode with pass energies of 150 and 40 eV for the survey and the narrow regions, respectively. Charge compensation was achieved with an electron flood gun combined with an argon ion gun. The argon partial pressure in the analysis chamber was 2×10^{-8} mbar. Advantage software (Thermo Electron) was used for digital acquisition and data processing. Spectra were calibrated by setting the main C_{1s} signal to 285 eV. Surface compositions (in at%) were determined from the integrated peak areas and the corresponding sensitivity factors corrected for the analyzer transmission.

2.3. Ellipsometry

A Horiba Jobin Yvon ellipsometer was used, with a He–Ne laser $\lambda = 6328 \text{ \AA}$, angle = 70.00° . The values for n_s and k_s were measured on a clean gold wafer from 300 to 800 nm and used to determine the thickness of the grafted layer (organic layer: $n_o = 1.46$, $k_o = 0.0$; substrate: $n_s = 0.230$, $k_s = 3.341$). The thickness was evaluated directly from these data by the ellipsometer software using a standard procedure of fitting.

3. Results and Discussion

We have synthesized 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine using previously described procedure [55]. As shown in Figure 1a, the diazonium salt was then generated in situ from the amino derivate by adding tertbutyl nitrite and the electrochemical grafting was carried out by cyclic voltammetry. Figure 1b shows the cyclic voltammograms (CV) of the reduction on a GC electrode of the 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenyl diazonium (SNS-P-N_2^+) generated in acetonitrile containing $0.5 \text{ mmol}\cdot\text{L}^{-1}$ of SNS-An in presence of tertbutyl nitrite (2 eq.) and 0.1 M of tetra-*n*-butylammonium tetrafluoroborate. The electrografting of the diazonium salt was optimized in order to obtain a thin and compact organic film onto the electrode. The recorded CV displays one irreversible reduction waves at 0 V/SCE and a high reduction current from 0.4 to -0.4 V . This behavior is associated to the reduction of SNS-P diazonium cation. During subsequent cycles, it shows significant decrease in the intensity of the reduction current and it disappears completely after 10 cycles. Similar behavior has been observed in the reduction of in situ-generated aryldiazonium cations. [26,49,56–58] It is attributed to the progressive modification of the electrode by the formation of an insulating organic film, which blocks the electron transfer in the observed potential range.

After the deposition, the electroactivity and the stability of the modified carbon electrode are investigated by cyclic voltammetry in an electrolyte solution (0.1 M LiClO_4 in ACN). The characteristic CV responses of these electrodes at various potential scan rates (v from 10 to 400 V/s) are shown in Figure 2a.

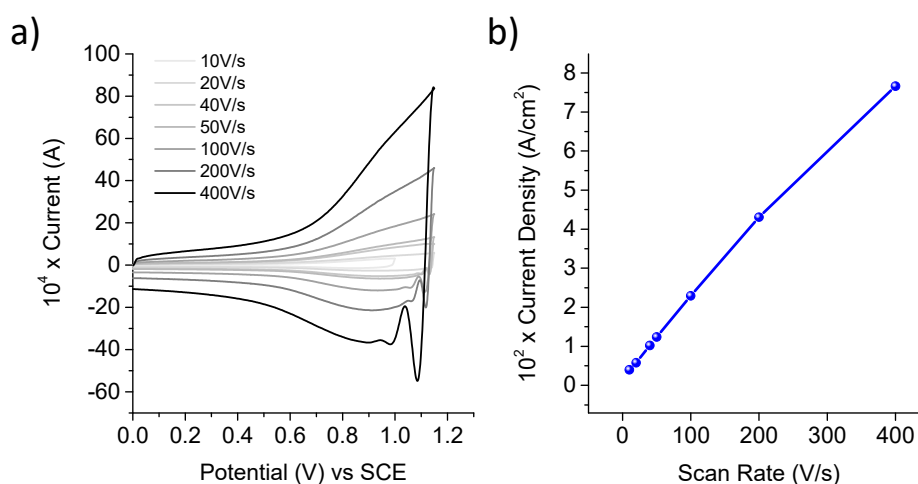


Figure 2. (a) Cyclic voltammograms of the modified electrode in 0.1 M LiClO_4 solution at various scan rates (from 10 to 400 V/s) with ohmic drop compensation. (b) Plot of anodic peak current density (at 0.9 V) versus scan rate of the grafted layer.

As 2,5-dithienylpyrrole is a conjugated oligomer, the grafted layer is electroactive with one reversible electrochemical signal adding to the capacitive current of the bare electrode. This electrochemical signal has an onset at 0.7V/SCE and oxidative and reductive peaks close to 0.9V/SCE. It can be attributed to chemisorbed monomer or short oligo-monomer [55]. The scan rate dependence of the peak current was also analyzed. As expected for a surface electron-transfer process, the peak currents for modified electrodes are linearly dependent on v . The faradic charge measured between

0.7 V and 1.1 V and is 9.5×10^{-6} C which gives a surface concentration of 7×10^{-10} molecules/cm², a value close to that of a monolayer. Note also that this charge is independent of the scan rate and can, thus, be injected very fast in such layers as CV at scan rate as high as 400 V·s⁻¹ are still reversible.

Furthermore, to study the electrochemical properties of the modified electrode cyclic voltammetry (CV) was used to investigate the electrochemical behavior of the electrode towards several redox probes (Figure 3); Fe(CN)₆^{3-/4-}, ferrocene, decamethylferrocene (DmFc), or thianthrene. The used scan rate is set to 0.1 V·s⁻¹ so that electron transfer from the film to the electrode is not limiting the electrochemical signal of the probes. The CV curves of the modified electrode SNS-An/GCE in 1 mM K₃Fe(CN)₆ under Ar are presented in Figure 3a. On the bare electrode we observed the redox peaks centered to 0.2 V/ECS (black curve). In the case of the modified electrode no peaks appeared in the range of 0.6 to −0.4 V (red curve), indicating a strong blocking effect of these SNS-An films on the Fe(CN)₆³⁻ charge transfer process in this potential region. As Fe(CN)₆³⁻ is very sensitive to surface adsorption effects, this result underlines the strong homogeneity of the layer with no significant defect.

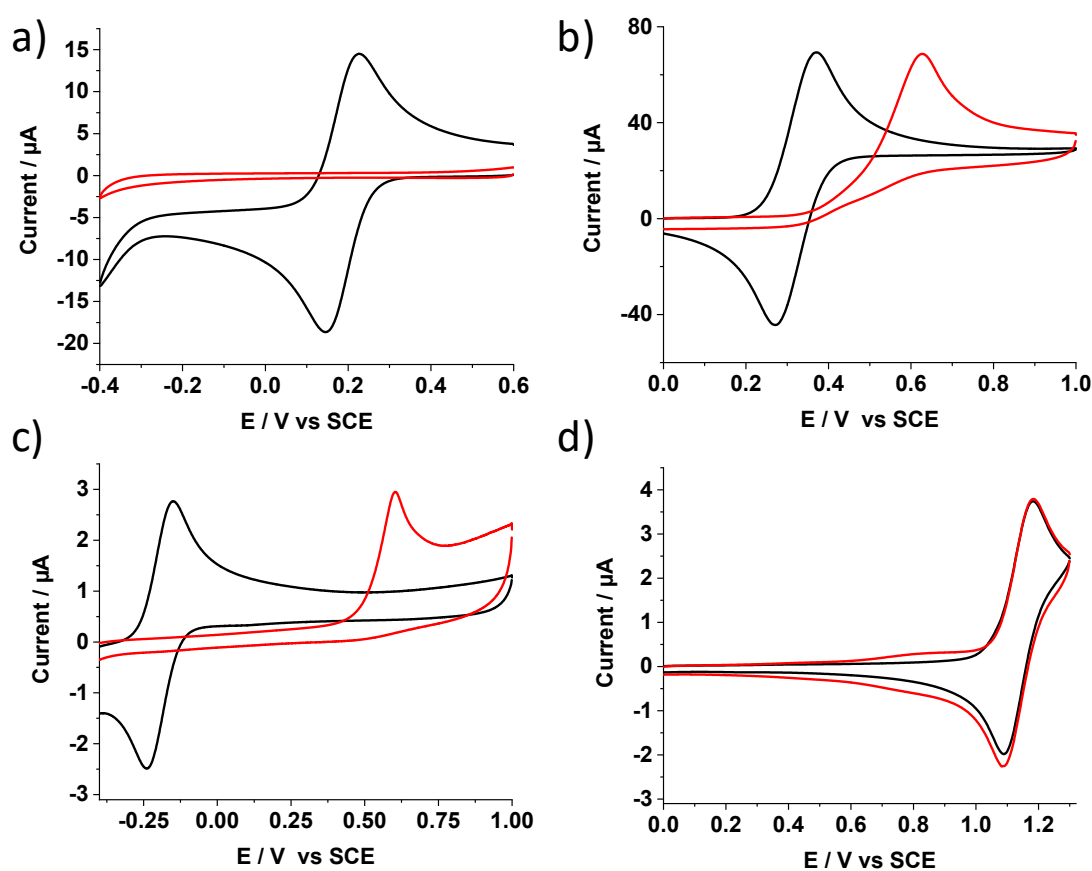


Figure 3. Electrochemical response of bare (black) and modified (red) electrodes in various redox probe solutions: (a) K₃Fe(CN)₆ 1 mM; (b) ferrocene 1 mM; (c) decamethylferrocene 1 mM; (d) thianthrene 1 mM with 0.1 M LiClO₄ in ACN solution.

In the case of Ferrocene probe, the SNS-An/GC electrode exhibits a typical diode-like behavior toward Fc (red curve) similar to that reported with a uniform modified GCE surface (Figure 3b) [57,59]. Briefly, no Fc electroactivity is observed at the expected potential but scanning at more positive potential exhibits an irreversible oxidation wave related to the oxidation of the ferrocene. Compared to the bare electrode Fc oxidation is shifted by at least 0.2 V/SCE due to the grafted layer. It seems that the layer acts as a barrier against the electron transfer for potential higher than a blocking potential around 0.4 V/SCE. The peak shape is also identical on both the bare and modified GC electrodes, suggesting that the heterogeneous rate constant for Fc oxidation is similar on both substrates. This shift can be

ascribed to the electrochemical properties of the organic layer. Indeed the layer becomes insulating for potential less negative than 0.4 V/SCE and conducting for highest potentials. Therefore, Fc^+ reduction is not observed on the reverse scan as it occurs at a more negative potential below the switching potential of the organic layer. Indeed this behavior is reversible as we can do many cycles in this potential range without decrease of current or change in the electrochemical behavior. However, if the organic layer is not well organized (presence of pinholes or defects in the layer) the layer is not completely insulating and the current of the shifted oxidation peak is lower than that on bare electrode and pinholes appear as ultra-micro electrodes and sigmoidal wave was observed at the standard potential of Fc (0.3 V/SCE). This experiment is a good proof of the homogeneity of the grafted layer and was confirmed by AFM analysis (see below).

To confirm the electrochemical behavior two redox probes with higher and lower redox potential than 0.4 V/SCE were used. The Figure 3c shows the CV of the modified electrode in an ACN solution containing 1 mM decamethyl Ferrocene and 0.1 M LiClO_4 . In the range of -0.3 to 0.4 V no current was observed for the modified electrode in comparison with the bare electrode. Then for higher potential an oxidation peak is observed corresponding to the oxidation of decamethyl ferrocene. As the standard potential of DmFc is -0.15 V, no reduction peak was observed due to the insulating properties of the grafted film below 0.4 V. In the opposite case when a redox probe with higher standard potential was used (thianthrene for example) the behavior was different. The Figure 3d presents the CV of modified electrode in an ACN solution containing 1 mM thianthrene and 0.1 M LiClO_4 . As expected the CV curves for bare and modified electrode are similar which confirm the conducting state of the layer for potential above 0.4 V.

One can note that as the structure of the molecule SNS-An is similar to the bithiophene phenyl amine (BTB) the value of the switching potential is closed to the potential found for the oligo(BTB) modified electrode [57].

The modified electrode was characterized by atomic force microscopy (AFM). It is a convenient way to investigate the morphology and the thickness of such surface. SNS-An was deposited on both carbon and gold electrodes in order to compare the surface morphology. The electroreduction of the diazonium salt was done as shown before using several cycles between 0.4 V and -0.4 V. Figure 4 shows the topography and the cross-section of SNS-An modified electrode with 10 cycles of grafting. The topography image revealed that the film appears homogeneous with very few defects, whereas the roughness was around 1 nm. The thickness of the layer was obtained by using the scratch method [60]. To do so the AFM tip was used to get a hole inside the organic layer by scratching the tip into the layer. After analysis the cross-section revealed a thickness of at least 2 nm which correspond to few layers of the SNS compound (of length). For less cycles of grafting the AFM analysis did not allow the thickness measurement but it is possible to obtain an organic layer of around 10 nm thickness by increasing the number of cycles (30 cycles). As it is already known the thickness of diazonium film depends on the bias range and the number of cycles [61]. It can be noted that even for very thin film the electrochemical behavior in redox probes solutions shows the good organization and homogeneity of the SNS layer.

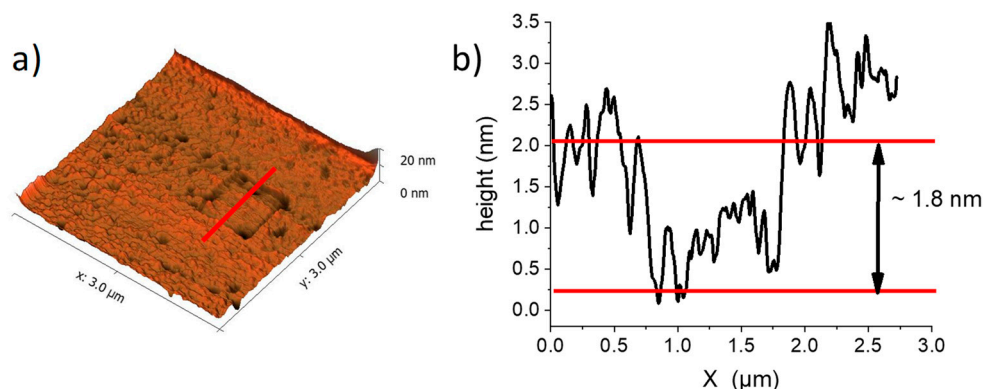


Figure 4. (a) AFM image of the modified electrode in tapping mode $3 \times 3 \mu\text{m}$. (b) Cross-section along the red line in Figure 4a performed by the scratch method [60].

Following that, the modified electrodes were characterized by XPS experiment to determine the chemical composition. XPS analysis leads to the surface composition of an organic layer and also the thickness. The electroreduction on gold was performed as for the carbon electrode and the signal of gold was used to estimate the thickness of the organic film. Figure 5 displays the wide-scale energy spectrum of a SNS-An sample and the high-resolution XPS spectrum for $\text{C}_{1\text{s}}$ (Figure 5b), $\text{S}_{2\text{p}}$ (Figure 5c), and $\text{N}_{1\text{s}}$ (Figure 5d) obtained for the SNS-An sample.

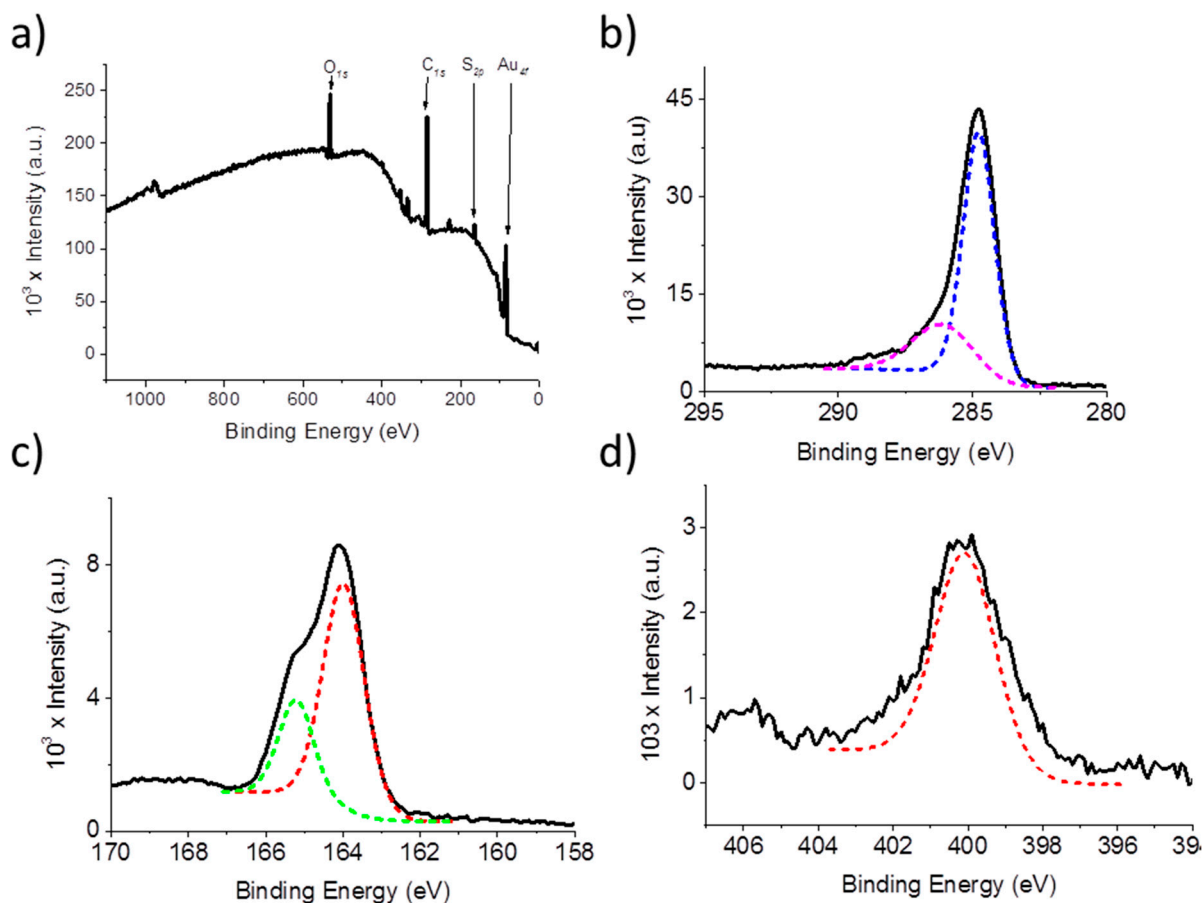


Figure 5. High-resolution XPS spectra of SNS-An modified gold surface. (a) XPS survey spectra of gold modified electrode. (b) $\text{C}_{1\text{s}}$ spectra. (c) $\text{S}_{2\text{p}}$ spectra. (d) $\text{N}_{1\text{s}}$ spectra.

A comparison of the XPS spectra before and after electrochemical grafting reveals several major changes. First, it is interesting to note that the spectrum exhibits intense inelastic backgrounds beyond

the Au 4f peaks (not shown), whereas it remains constant beyond the C and S signals. This clearly indicates that the C and S atoms are located at the extreme surface of the organic layer and an organic layer covers the Au surface.

Through the Au_{4f7/2} attenuation signal the thickness of the layer can be estimated. Using the Seah and Dench formalism [62] we have found a thickness between 2 and 3 nm in agreement with ellipsometry and AFM analysis (Figure 4).

Following the carbon, sulfur and nitrogen signals increase after the electroreduction of diazonium in comparison with the bare electrode which indicates the formation of an organic layer (the carbon on the bare surface before grafting is attributed to surface contamination). The high-resolution carbon signal can be deconvoluted in two contributions at 285 eV with a small shoulder at 286.1 eV. The highest signal correspond to the carbon of benzene, thiophene, and pyrrole units while the second peak can be referred to C-N or C-S bonds. Figure 5c displays the S_{2p} signals as a doublet with a relative ratio of 2:1 at 164–165.1 eV relative to the S_{2p3/2} and S_{2p1/2} which is in a good agreement with literature reports [63]. This doublet can be considered as the signature of thiophene sulfur on the grafted layer on the surface and is not seen on the bare electrode. The atomic ratio S_{2p}/N_{1s} is close to 2, which is the theoretical value for S/N ratio and suggests that the surface species is derived from SNS moieties. The C_{1s}/S_{2p} ratio is close to 11, whereas such ratio cannot be defined on the bare gold substrate. This ratio reaches a value compatible with the expected value of 9 for SNS-An oligomer grafted layers and the contribution from contaminants that are initially adsorbed on the gold surface and explain the large amount of carbon atoms measured, is now small. The N_{1s} peak at 400 eV reveals nitrogen atoms most likely due to the pyrrole moieties even though this signal can also be attributed to amino group or reduced nitrogen (the atomic ratio C_{1s}/N_{1s} below 23 for a theoretical value of 18). One also has to note that no peak corresponding to the nitrogen of the diazonium cation at 403 eV or corresponding to –N=N– (indicative of an undesired coupling reaction) was observed [64]. Overall, this analysis confirms that a thin layer of SNS oligomer has been successfully grafted onto the gold electrode.

4. Conclusions

As a conclusion the electrografting of the diazonium based on 4-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-phenylamine (SNS moieties) onto various electrodes has been demonstrated. XPS and AFM have shown that the organic layer grafted onto the electrode can be thin (2–3 nm of thickness) and the composition of the film correspond to what we expect for SNS moieties. The organic layer is electroactive and was tested at different scan rates to show the stability and the electron transfer rate. The electrochemical behavior of the modified electrodes was investigated in redox probes solutions (various standard potentials). We observed that the organic layer acts as a barrier against the electron transfer from the redox probe to the electrode when the E° of the redox probe is below the switching potential (0.4 V/SCE). However the layer becomes transparent for redox probe with a potential E° above 0.4 V/SCE. Such layer covalently coupling to the surface of the electrode can be used as adhesion primer layers for electropolymerization of conducting polymer based on thiophene or SNS units. The structure of the monomer is also an important point as the two rings (pyrrole and phenyl) are not planar and the molecular conductance could be strongly affected by the angle between the molecule and the surface. However, further investigations are needed to better understand the role of this specific structure in the electrochemical behavior.

Author Contributions: Conceptualization, P.M. and J.-C.L.; methodology, T.H.L. and G.T.-A.; investigation, T.H.L. and V.Q.N.; writing—original draft preparation, P.M.; writing—review and editing, P.M. and J.-C.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Skotheim, T.A.; Lelsenbaumer, R.; Reynolds, J.R. *Handbook of Conducting Polymers, Conjugated Polymers: Processing and Applications*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2006; ISBN 9781574446654.
2. Demir, G.E.; Yıldırım, M.; Cengiz, U.; Kaya, İ. Multilayer electrochromic surfaces derived from conventional conducting polymers: Optical and surface properties. *React. Funct. Polym.* **2015**, *97*, 63–68. [[CrossRef](#)]
3. Ibanez, J.G.; Rincón, M.E.; Gutierrez-Granados, S.; Chahma, M.; Jaramillo-Quintero, O.A.; Frontana-Uribe, B.A. Conducting Polymers in the Fields of Energy, Environmental Remediation, and Chemical-Chiral Sensors. *Chem. Rev.* **2018**, *118*, 4731–4816. [[CrossRef](#)] [[PubMed](#)]
4. Oh, J.Y.; Kim, S.; Baik, H.-K.; Jeong, U. Conducting Polymer Dough for Deformable Electronics. *Adv. Mater.* **2016**, *28*, 4455–4461. [[CrossRef](#)] [[PubMed](#)]
5. van de Burgt, Y.; Melianas, A.; Keene, S.T.; Malliaras, G.; Salleo, A. Organic electronics for neuromorphic computing. *Nat. Electron.* **2018**, *1*, 386–397. [[CrossRef](#)]
6. Descamps, E.; Leïchlé, T.; Corso, B.; Laurent, S.; Mailley, P.; Nicu, L.; Livache, T.; Bergaud, C. Fabrication of Oligonucleotide Chips by Using Parallel Cantilever-Based Electrochemical Deposition in Picoliter Volumes. *Adv. Mater.* **2007**, *19*, 1816–1821. [[CrossRef](#)]
7. Duboriz, I.; Pud, A. Polyaniline/poly(ethylene terephthalate) film as a new optical sensing material. *Sens. Actuators B Chem.* **2014**, *190*, 398–407. [[CrossRef](#)]
8. Nair, S.S.; Mishra, S.K.; Kumar, D. Recent progress in conductive polymeric materials for biomedical applications. *Polym. Adv. Technol.* **2019**, *30*, 2932–2953. [[CrossRef](#)]
9. Semple, J.; Rossbauer, S.; Burgess, C.H.; Zhao, K.; Jagadamma, L.K.; Amassian, A.; McLachlan, M.A.; Anthopoulos, T.D. Radio Frequency Coplanar ZnO Schottky Nanodiodes Processed from Solution on Plastic Substrates. *Small* **2016**, *12*, 1993–2000. [[CrossRef](#)]
10. Zheng, G.; Wang, C.; Pei, A.; Lopez, J.; Shi, F.; Chen, Z.; Sendek, A.D.; Lee, H.-W.; Lu, Z.; Schneider, H.; et al. High-Performance Lithium Metal Negative Electrode with a Soft and Flowable Polymer Coating. *ACS Energy Lett.* **2016**, *1*, 1247–1255. [[CrossRef](#)]
11. Makhlof, A.S.H.; Abu-Thabit, N.Y. *Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications*; Elsevier: Amsterdam, The Netherlands, 2019; ISBN 9780128498705.
12. Nautiyal, A.; Qiao, M.; Cook, J.E.; Zhang, X.; Huang, T.-S. High performance polypyrrole coating for corrosion protection and biocidal applications. *Appl. Surf. Sci.* **2018**, *427*, 922–930. [[CrossRef](#)]
13. Camurlu, P. Polypyrrole derivatives for electrochromic applications. *RSC Adv.* **2014**, *4*, 55832–55845. [[CrossRef](#)]
14. Tuncagil, S.; Kiralp, S.; Varis, S.; Toppare, L. Immobilization of invertase on a conducting polymer of 1-(4-nitrophenyl)-2,5-di(2-thienyl)-1H-pyrrole. *React. Funct. Polym.* **2008**, *68*, 710–717. [[CrossRef](#)]
15. Söyleyici, H.C.; Ak, M.; Şahin, Y.; Demikol, D.O.; Timur, S. New class of 2,5-di(2-thienyl)pyrrole compounds and novel optical properties of its conducting polymer. *Mater. Chem. Phys.* **2013**, *142*, 303–310. [[CrossRef](#)]
16. Guven, N.; Camurlu, P.; Desde, M.; Yucel, B. Post Polymerization Functionalization of a Soluble Poly(2,5-dithienylpyrrole) Derivative via Click Chemistry. *J. Electrochem. Soc.* **2017**, *164*, H430–H436. [[CrossRef](#)]
17. Yiğit, D.; Hacıoğlu, Ş.O.; Güllü, M.; Toppare, L. Novel poly(2,5-dithienylpyrrole) (PSNS) derivatives functionalized with azobenzene, coumarin and fluorescein chromophore units: Spectroelectrochemical properties and electrochromic device applications. *New J. Chem.* **2015**, *39*, 3371–3379. [[CrossRef](#)]
18. Wu, T.-Y.; Li, J.-L. Electrochemical synthesis, optical, electrochemical and electrochromic characterizations of indene and 1,2,5-thiadiazole-based poly(2,5-dithienylpyrrole) derivatives. *RSC Adv.* **2016**, *6*, 15988–15998. [[CrossRef](#)]
19. Zhao, W.K.; Cui, B.; Fang, C.F.; Ji, G.M.; Zhao, J.F.; Kong, X.R.; Zou, D.Q.; Jiang, X.H.; Li, D.M.; Liu, D.S. Rectification inversion in oxygen substituted graphyne-graphene-based heterojunctions. *Phys. Chem. Chem. Phys.* **2015**, *17*, 3115–3122. [[CrossRef](#)]

20. Guven, N.; Camurlu, P.; Yucel, B. Multichromic polymers based on pyrene clicked thienylpyrrole. *Polym. Int.* **2015**, *64*, 758–765. [\[CrossRef\]](#)
21. Guven, N.; Camurlu, P. Electrosyntheses of anthracene clicked poly(thienylpyrrole)s and investigation of their electrochromic properties. *Polymer* **2015**, *73*, 122–130. [\[CrossRef\]](#)
22. Guven, N.; Camurlu, P. Optoelectronic Properties of Poly(2,5-dithienylpyrrole)s with Fluorophore Groups. *J. Electrochem. Soc.* **2015**, *162*, H867–H876. [\[CrossRef\]](#)
23. Soganci, T.; Soyleyici, S.; Soyleyici, H.C.; Ak, M. High Contrast Electrochromic Polymer and Copolymer Materials Based on Amide-Substituted Poly(Dithienyl Pyrrole). *J. Electrochem. Soc.* **2017**, *164*, H11–H20. [\[CrossRef\]](#)
24. Defever, T.; Deniau, G.; Palacin, S.; Goux-capes, L.; Barrau, S.; Mayne-l'hermite, M.; Bourgoin, J.-P. Cathodic electropolymerization on the surface of carbon nanotubes. *J. Electroanal. Chem.* **2006**, *589*, 46–51. [\[CrossRef\]](#)
25. Shao, Y.; Jin, Y.; Sun, X.; Dong, S. A method for cathodic polymerization of aniline by in situ electrogenerated intermediate at gold surface. *Thin Solid Films* **2004**, *458*, 47–51. [\[CrossRef\]](#)
26. Mahouche-Chergui, S.; Gam-Derouich, S.; Mangeney, C.; Chehimi, M.M. Aryl diazonium salts: A new class of coupling agents for bonding polymers, biomacromolecules and nanoparticles to surfaces. *Chem. Soc. Rev.* **2011**, *40*, 4143–4166. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.M.; Saveant, J.M. Covalent modification of carbon surfaces by grafting of functionalized aryl radicals produced from electrochemical reduction of diazonium salts. *J. Am. Chem. Soc.* **1992**, *114*, 5883–5884. [\[CrossRef\]](#)
28. Brooksby, P.A.; Downard, A.J. Electrochemical and atomic force microscopy study of carbon surface modification via diazonium reduction in aqueous and acetonitrile solutions. *Langmuir* **2004**, *20*, 5038–5045. [\[CrossRef\]](#)
29. Ghilane, J.; Martin, P.; Fontaine, O.; Lacroix, J.C.; Randriamahazaka, H. Modification of carbon electrode in ionic liquid through the reduction of phenyl diazonium salt. Electrochemical evidence in ionic liquid. *Electrochem. Commun.* **2008**, *10*, 1060–1063. [\[CrossRef\]](#)
30. Bernard, M.-C.; Chaussé, A.; Cabet-Deliry, E.; Chehimi, M.M.; Pinson, J.; Podvorica, F.; Vautrin-UI, C. Organic Layers Bonded to Industrial, Coinage, and Noble Metals through Electrochemical Reduction of Aryldiazonium Salts. *Chem. Mater.* **2003**, *15*, 3450–3462. [\[CrossRef\]](#)
31. Martin, P.; Della Rocca, M.L.; Anthore, A.; Lafarge, P.; Lacroix, J.-C. Organic Electrodes Based on Grafted Oligothiophene Units in Ultrathin, Large-Area Molecular Junctions. *J. Am. Chem. Soc.* **2012**, *134*, 154–157. [\[CrossRef\]](#)
32. Adenier, A.; Bernard, M.-C.C.; Chehimi, M.M.; Cabet-Deliry, E.; Desbat, B.; Fagebaume, O.; Pinson, J.; Podvorica, F. Covalent modification of iron surfaces by electrochemical reduction of aryldiazonium salts. *J. Am. Chem. Soc.* **2001**, *123*, 4541–4549. [\[CrossRef\]](#)
33. Lebon, F.; Cornut, R.; Derycke, V.; Jousselme, B. Fine growth control of electrografted homogeneous thin films on patterned gold electrodes. *Electrochimica Acta* **2019**, *318*, 754–761. [\[CrossRef\]](#)
34. Ranganathan, S.; McCreery, R.L. Electroanalytical performance of carbon films with near-atomic flatness. *Anal. Chem.* **2001**, *73*, 893–900. [\[CrossRef\]](#)
35. Zhong, Y.L.; Loh, K.P.; Midya, A.; Chen, Z.-K. Suzuki Coupling of Aryl Organics on Diamond. *Chem. Mater.* **2008**, *20*, 3137–3144. [\[CrossRef\]](#)
36. Samanta, S.; Bakas, I.; Singh, A.; Aswal, D.K.; Chehimi, M.M. In Situ Diazonium-Modified Flexible ITO-Coated PEN Substrates for the Deposition of Adherent Silver–Polypyrrole Nanocomposite Films. *Langmuir* **2014**, *30*, 9397–9406. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Bui-Thi-Tuyet, V.; Cannizzo, C.; Legros, C.; Andrieux, M.; Chaussé, A. Modification of fluorine-doped tin oxide surface: Optimization of the electrochemical grafting of diazonium salt. *Surf. Interfaces* **2019**, *15*, 110–116. [\[CrossRef\]](#)
38. Stockhausen, V.; Ghilane, J.; Martin, P.; Trippe-Allard, G.; Randriamahazaka, H.; Lacroix, J.-C. Grafting Oligothiophenes on Surfaces by Diazonium Electroreduction: A Step toward Ultrathin Junction with Well-Defined Metal/Oligomer Interface. *J. Am. Chem. Soc.* **2009**, *131*, 14920–14927. [\[CrossRef\]](#)
39. Polsky, R.; Harper, J.C.; Wheeler, D.R.; Arango, D.C.; Brozik, S.M. Electrically Addressable Cell Immobilization Using Phenylboronic Acid Diazonium Salts. *Angew. Chem. Int. Ed.* **2008**, *47*, 2631–2634. [\[CrossRef\]](#)
40. Itoh, T.; McCreery, R.L. In situ raman spectroelectrochemistry of electron transfer between glassy carbon and a chemisorbed nitroazobenzene monolayer. *J. Am. Chem. Soc.* **2002**, *124*, 10894–10902. [\[CrossRef\]](#)

41. Chen, P.; McCreery, R.L. Control of Electron Transfer Kinetics at Glassy Carbon Electrodes by Specific Surface Modification. *Anal. Chem.* **1996**, *68*, 3958–3965. [\[CrossRef\]](#)
42. Liu, Y.-C.; McCreery, R.L. Reactions of Organic Monolayers on Carbon Surfaces Observed with Unenhanced Raman Spectroscopy. *J. Am. Chem. Soc.* **1995**, *117*, 11254–11259. [\[CrossRef\]](#)
43. Villemain, E.; Lemarque, B.; Vũ, T.T.; Nguyen, V.Q.; Trippé-Allard, G.; Martin, P.; Lacaze, P.-C.; Lacroix, J.-C. Improved adhesion of poly(3,4-ethylenedioxythiophene) (PEDOT) thin film to solid substrates using electrografted promoters and application to efficient nanoplasmonic devices. *Synth. Met.* **2019**, *248*, 45–52. [\[CrossRef\]](#)
44. van Nguyen, Q.; Martin, P.; Frath, D.; Della Rocca, M.L.; Lafolet, F.; Barraud, C.; Lafarge, P.; Mukundan, V.; James, D.; McCreery, R.L.; et al. Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature. *J. Am. Chem. Soc.* **2017**, *139*, 11913–11922. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Saxena, S.K.; Smith, S.R.; Supur, M.; McCreery, R.L. Light-Stimulated Charge Transport in Bilayer Molecular Junctions for Photodetection. *Adv. Opt. Mater.* **2019**, *7*, 1901053. [\[CrossRef\]](#)
46. Pichereau, L.; López, I.; Cesbron, M.; Dabos-Seignon, S.; Gautier, C.; Breton, T. Controlled diazonium electrografting driven by overpotential reduction: A general strategy to prepare ultrathin layers. *Chem. Commun.* **2019**, *55*, 455–457. [\[CrossRef\]](#)
47. Delaporte, N.; Belanger, R.L.; Lajoie, G.; Trudeau, M.; Zaghib, K. Multi-carbonyl molecules immobilized on high surface area carbon by diazonium chemistry for energy storage applications. *Electrochim. Acta* **2019**, *308*, 99–114. [\[CrossRef\]](#)
48. Kariuki, J.K.; McDermott, M.T. Formation of Multilayers on Glassy Carbon Electrodes via the Reduction of Diazonium Salts. *Langmuir* **2001**, *17*, 5947–5951. [\[CrossRef\]](#)
49. Saby, C.; Ortiz, B.; Champagne, G.Y.; Bélanger, D. Electrochemical modification of glassy carbon electrode using aromatic diazonium salts. 1. Blocking effect of 4-nitrophenyl and 4-carboxyphenyl groups. *Langmuir* **1997**, *13*, 6805–6813. [\[CrossRef\]](#)
50. Solak, A.O.; Eichorst, L.R.; Clark, W.J.; McCreery, R.L. Modified Carbon Surfaces as “Organic Electrodes” That Exhibit Conductance Switching. *Anal. Chem.* **2003**, *75*, 296–305. [\[CrossRef\]](#)
51. Leroux, Y.R.; Fei, H.; Noël, J.-M.; Roux, C.; Hapiot, P. Efficient covalent modification of a carbon surface: Use of a silyl protecting group to form an active monolayer. *J. Am. Chem. Soc.* **2010**, *132*, 14039–14041. [\[CrossRef\]](#)
52. Menanteau, T.; Dias, M.; Levillain, E.; Downard, A.J.; Breton, T. Electrografting via Diazonium Chemistry: The Key Role of the Aryl Substituent in the Layer Growth Mechanism. *J. Phys. Chem. C* **2016**, *120*, 4423–4429. [\[CrossRef\]](#)
53. Fontaine, O.; Ghilane, J.; Martin, P.; Lacroix, J.-C.; Randriamahazaka, H. Ionic Liquid Viscosity Effects on the Functionalization of Electrode Material through the Electroreduction of Diazonium. *Langmuir* **2010**, *26*, 18542–18549. [\[CrossRef\]](#)
54. Combellas, C.; Kanoufi, F.; Pinson, J.; Podvorica, F.I. Sterically Hindered Diazonium Salts for the Grafting of a Monolayer on Metals. *J. Am. Chem. Soc.* **2008**, *130*, 8576–8577. [\[CrossRef\]](#)
55. Camurlu, P.; Bicil, Z.; Gültekin, C.; Karagoren, N. Novel ferrocene derivatized poly(2,5-dithienylpyrrole)s: Optoelectronic properties, electrochemical copolymerization. *Electrochim. Acta* **2012**, *63*, 245–250. [\[CrossRef\]](#)
56. Santos, L.M.; Ghilane, J.; Fave, C.; Lacaze, P.-C.; Randriamahazaka, H.; Abrantes, L.M.; Lacroix, J.-C. Electrografting polyaniline on carbon through the electroreduction of diazonium salts and the electrochemical polymerization of aniline. *J. Phys. Chem. C* **2008**, *112*, 16103–16109. [\[CrossRef\]](#)
57. Fave, C.; Leroux, Y.; Trippé, G.; Randriamahazaka, H.; Noël, V.; Lacroix, J.-C. Tunable Electrochemical Switches Based on Ultrathin Organic Films. *J. Am. Chem. Soc.* **2007**, *129*, 1890–1891. [\[CrossRef\]](#)
58. Bélanger, D.; Pinson, J.; Belanger, D.; Pinson, J.; Bélanger, D.; Pinson, J. Electrografting: A powerful method for surface modification. *Chem. Soc. Rev.* **2011**, *40*, 3995. [\[CrossRef\]](#)
59. Fave, C.; Noël, V.; Ghilane, J.; Trippé-Allard, G.; Randriamahazaka, H.; Lacroix, J.-C. Electrochemical Switches Based on Ultrathin Organic Films: From Diode-like Behavior to Charge Transfer Transparency. *J. Phys. Chem. C* **2008**, *112*, 18638–18643. [\[CrossRef\]](#)
60. Anariba, F.; DuVall, S.H.; McCreery, R.L. Mono- and Multilayer Formation by Diazonium Reduction on Carbon Surfaces Monitored with Atomic Force Microscopy “Scratching”. *Anal. Chem.* **2003**, *75*, 3837–3844. [\[CrossRef\]](#)
61. Fluteau, T.; Bessis, C.; Barraud, C.; Della, M.L.; Martin, P.; Lacroix, J.-C.; Lafarge, P. Tuning the thickness of electrochemically grafted layers in large area molecular junctions. *J. Appl. Phys.* **2014**, *116*, 114509. [\[CrossRef\]](#)

62. Seah, M.P.; Dench, W.A. Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surf. Interface Anal.* **1979**, *1*, 2–11. [[CrossRef](#)]
63. Noh, J.; Ito, E.; Nakajima, K.; Kim, J.; Lee, H.; Hara, M. High-Resolution STM and XPS Studies of Thiophene Self-Assembled Monolayers on Au(111). *J. Phys. Chem. B* **2002**, *106*, 7139–7141. [[CrossRef](#)]
64. Breton, T.; Be, D.; Bélanger, D. Modification of Carbon Electrode with Aryl Groups Having an Aliphatic Amine by Electrochemical Reduction of In Situ Generated Diazonium Cations. *Langmuir* **2008**, *24*, 8711–8718. [[CrossRef](#)] [[PubMed](#)]



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