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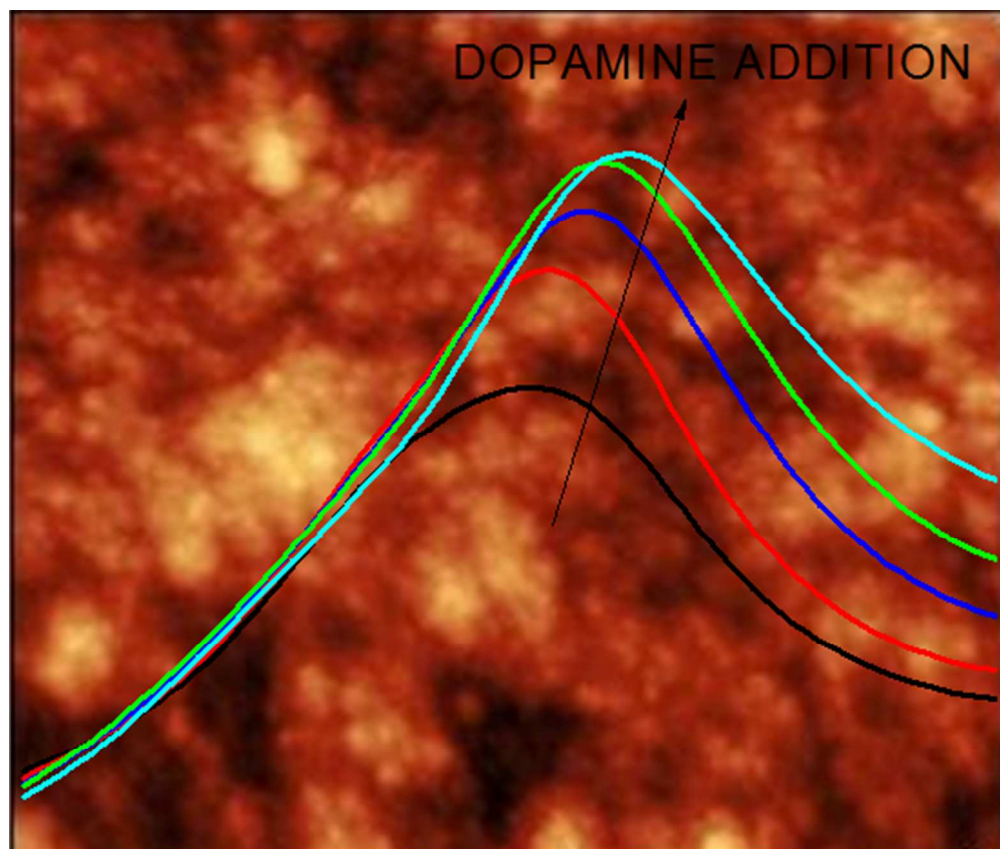


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An amperometric sensor based on an ITO electrode coated with a ferrocene clicked PEDOT:PSS is described and the electrocatalytic performance of the device toward dopamine is assessed.

## ARTICLE

## Dopamine amperometric detection at a PEDOT:PSS clicked ferrocene coated electrode

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Chemically modified electrodes are widely employed in electroanalytical chemistry and an important goal is to strongly anchor redox mediators on the electrode surface. In this work, Indium Tin Oxide (ITO) electrodes have been coated with a PEDOT:PSS that has been ferrocene-functionalized, by a two-step procedure consisting in the electrodeposition of PEDOT-N<sub>3</sub> followed by copper-catalyzed azide-alkyne cycloaddition of ethynylferrocene.

The coated electrodes have been characterized by XPS, showing the ferrocene successful immobilization, by AFM and by cyclic voltammetry (CV) which is dominated by the stable and highly reversible response of ferrocene. The electrocatalytical performance of the device is assessed by analyzing 3,4-Dihydroxyphenyl ethylamine, also commonly known as dopamine (DA). The sensor presents a linear range between 0.01 and 0.9 mM, a mean sensitivity of 196 mA M<sup>-1</sup> cm<sup>-2</sup> and a limit of detection (LoD) of 1 μM.

### 1. Introduction

Ferrocene (Fc) and its derivatives are well known as electron mediators<sup>1-7</sup> due to their good electrochemical reversibility, regeneration at low potential, and generation of stable redox forms. Ferrocene can catalyze the oxidation or reduction of many small molecules, such as peroxides<sup>8</sup> DNA<sup>9</sup>, glucose and AA<sup>10</sup>.

However, ferrocene is insoluble in aqueous solutions and it is difficult to strongly adsorb it and its derivatives to the electrode surface<sup>11</sup>, thus hindering a stable modification of electrodes by ferrocene compounds. To improve the attachment to electrode surface, many immobilization methods, including cross-linking, gels or polymer have been developed<sup>12,13</sup>.

In the last years, poly(3,4 ethylenedioxythiophene) (PEDOT) is receiving great attention in the development of modified electrodes, due to its low-energy band gap<sup>14</sup> which makes it suitable for electro-optical applications. Moreover, bearing the ethylenedioxy substituent in the 3 and 4 position of the polythiophenic ring, it is regiochemically better defined than unsubstituted polythiophene.

PEDOT can be prepared by several chemical or electrochemical routes, both in aqueous or organic media; electrochemical polymerization methods allow obtaining PEDOT coated electrodes employing small amount of monomer and short polymerization times<sup>15</sup>.

The EDOT electropolymerization in aqueous media can be achieved using suitable water-soluble polyelectrolytes as emulsifier. In particular, good results have been obtained when the polymerization is carried out in the presence of the polyelectrolyte poly(styrene-4-sulfonate) ((PSS)<sup>1-</sup>). In this way, a film of PEDOT:PSS can be synthesized, in which the (PSS)<sup>1-</sup> polyanion is incorporated into the polymer to compensate the positively charged PEDOT. The PEDOT:PSS system has proven to produce films and micro-structured systems with facile electrochemistry, high-ionic conductivities, good electrochemical stability and a capacitance suitable for practical use in electrochemical supercapacitors<sup>16-20</sup>. Moreover, thanks to its good features, PEDOT:PSS has been recently employed for the fabrication of all-plastic electrochemical transistors (OECT)<sup>21-23</sup>.

We have chosen PEDOT:PSS as polymeric matrix to covalently bond ferrocene, in order to develop an amperometric sensor, that exploits the ferrocene redox mediator properties and the high conductivity of PEDOT:PSS.

In this work we have prepared ferrocene-functionalized PEDOT:PSS through copper-catalyzed azide-alkyne cycloaddition reaction. Copper-catalyzed azide-alkyne cycloaddition is one of those typical click reactions that have attracted interest for their high reaction yield, mild reaction condition, and stability of the products<sup>24,25</sup>. Due to their excellent performance, click reactions have become a suitable method for organic synthesis<sup>26</sup>, surface modification<sup>27</sup>,

macromolecular architecture tailor and optimization<sup>28</sup>. Recently, click reactions have also been applied as a versatile strategy for conducting polymer functionalization<sup>29–32</sup>.

The PEDOT based films have been prepared on ITO transparent glass electrodes, which enable also a spectroelectrochemical characterization of the polymer. The resulting conducting polymer films show a stable response and have been characterized by several techniques, all demonstrating the successful functionalization.

To probe the ability of the device to work as amperometric sensor, it has been tested for 3,4-Dihydroxyphenyl ethylamine, also commonly known as dopamine (DA), detection. DA is an important neurotransmitter in the mammalian central nervous system, and a loss of DA-containing neurons may result in some serious disease such as Parkinson's disease; thus, the determination of the concentration of DA is an important problem in analytical biochemistry that is stimulating the need for developing rapid and simple methods of detection<sup>33,34</sup>.

## 2. Experimental

### 2.1 Chemicals

Solvents were dried and distilled under nitrogen prior to use. The chemicals 3,4-dimethoxythiophene, 3-chloro-1,2-propandiol, 2,6-di-tert-butyl-4-methylphenol, sodium azide, ethynylferrocene, sodium ascorbate, copper(II) sulfate pentahydrate, sodium sulfate, sodium carbonate, dihydroxyphenyl ethylamine, polystyrene sulfonate, 3,4-ethylenedioxythiophene and lithium perchlorate have been purchased from Aldrich and employed without further purification. Column chromatography have been performed on silica gel, Merck, grade 9385, 230-400 M (Aldrich). NMR spectra were recorded using Varian Inova 300 (<sup>1</sup>H, 300.1; <sup>13</sup>C, 75.5 MHz), Varian Mercury 400 (<sup>1</sup>H, 399.9; <sup>13</sup>C, 100.6 MHz) spectrometers; chemical shifts were referenced internally to residual solvent peaks for <sup>1</sup>H (CDCl<sub>3</sub>: 7.26 ppm) and <sup>13</sup>C NMR (CDCl<sub>3</sub>: 77.00 ppm) spectra.

All the electrochemical experiments were carried out in a single compartment, three-electrode cell. Electrode potentials were measured with respect to an aqueous saturated calomel electrode (SCE). A Pt wire was used as the counter electrode and ITO glasses purchased from Optical Filters Ltd., England (surface resistivity = 12 Ω cm<sup>-2</sup>) as working electrodes. An Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer was used in all the electrochemical and spectroelectrochemical tests. UV–Vis measurements were obtained using a Hewlett-Packard 8453 diode array spectrophotometer with an in situ electrochemical cell (home-made).

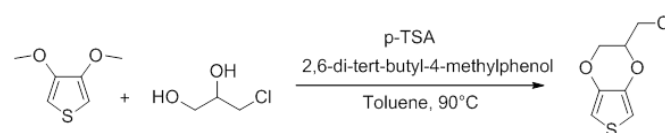
A PHI 5000 Versaprobe II Scanning X-ray Photoelectron Spectrometer, equipped with a monochromatic Al K-alpha X-ray source (1486.6 eV energy, 15 kV voltage and 1 mA anode current), was used to investigate surface chemical composition. A spot size of 100 micron was used in order to collect the photoelectron signal for both the high resolution (HR) and the

survey spectra. Different pass energy values were exploited: 187.85 eV for survey spectra and 23.5 eV for HR peaks. The core level spectra were deconvoluted with a nonlinear iterative least squares Gaussian fitting procedure.

An NT-MDT Solver P-47H Pro Atomic Force Microscope (AFM), operating in semi-contact mode, was used to measure PEDOT:PSS and PEDOT-N<sub>3</sub>:PSS film thickness and surface morphology through the acquisition of topographical images. The cantilevers (spring constant 14 N/m, resonance frequency 315 kHz) were obtained from MikroMasch (Tallinn, Estonia).

### 2.2 Synthesis of azidomethyl functionalized 3,4-ethylenedioxythiophene (EDOT-N<sub>3</sub>)

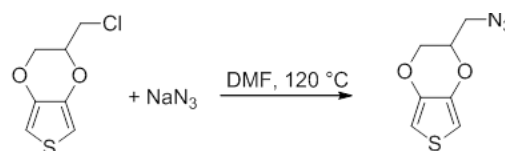
I step: Synthesis of chloromethyl functionalized 3,4-ethylenedioxythiophene (EDOT-Cl)



Scheme 1

Chloromethyl functionalized EDOT has been obtained by reacting, under nitrogen using standard Schlenk techniques, 0.50 g (3.47 mmol) of 3,4-dimethoxythiophene dissolved in anhydrous toluene (12 mL) with 0.87 mL (10.4 mmol) of 3-chloro-1,2-propandiol, in the presence of 0.762 mg (3.47 mmol) of 2,6-di-tert-butyl-4-methylphenol and 0.060 g (0.347 mmol) of p-toluenesulfonic acid (p-TSA) at 90°C. After 24h, 0.87 mL of 3-chloro-1,2-propandiol were added to the reaction mixture which was stirred at 90°C for further 3h. The solvent was removed under vacuum. Then 40 mL of a solution of Na<sub>2</sub>CO<sub>3</sub> (10% in water) were added to the crude and the product extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic phases were combined, washed with water (40 mL) and dried on Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the product 2-chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine obtained with a 72% yield by flash column chromatography on silica gel (eluent: 1:1 CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether).

II step: Synthesis of azidomethyl functionalized 3,4-ethylenedioxythiophene (EDOT-N<sub>3</sub>)



Scheme 2

Azidomethyl functionalized EDOT 2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4]dioxine was prepared by reacting 1 eq. of EDOT-Cl with 2 eq. of sodium azide in dimethylformamide at 120 °C for 3 h under nitrogen atmosphere<sup>35,36</sup>. EDOT-Cl and EDOT-N<sub>3</sub> have been characterized by means of NMR experiments whose results are

comparable with those reported in the literature (further details are available in the supporting information section).

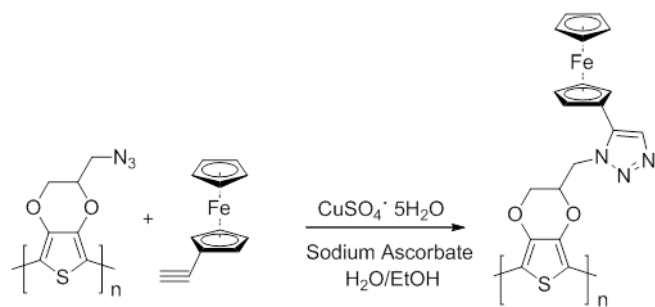
### 2.3 Electrochemical polymerization of EDOT-N<sub>3</sub>

The electrochemical polymerization was carried out on a ITO-coated rectangular glass slide (0.9 x 2.7 cm). Before use, ITO electrodes were cleaned by keeping them in an ultrasonic bath for 10 min in each of the following solvents: soapy water, water, acetone, ethanol. Then, the electrodes were rinsed with distilled water and dried with a stream of nitrogen. The electrode area was limited to 1.35 cm<sup>2</sup> with Teflon tape.

The electrosynthesis of PEDOT-N<sub>3</sub> was carried out, under N<sub>2</sub> atmosphere, potentiodynamically, by cyclic voltammetry, cycling ten times the potential between 0.0 V and 1.5 V at 0.05 V s<sup>-1</sup>, in a 0.1 M PSS aqueous solution containing 10 mM EDOT-N<sub>3</sub> monomer. Prior to the application of the potential pulse, the aqueous suspension was vigorously stirred for 20 minute and the electrochemical polymerization was carried out under moderate stirring. After the electrodeposition, the film was repeatedly washed with deionized water to remove both the supporting electrolyte and the excess monomer and finally allowed to dry in air.

### 2.4 Post functionalization of PEDOT-N<sub>3</sub> coated ITO with Ferrocene by click reaction

Different conditions were explored changing the ethynylferrocene concentrations: 1 mM, 3 mM or 10 mM. 6.3 mg, 18.9 mg or 189.0 mg (0.030 mmol, 0.090 mmol or 0.90 mmol) of ethynylferrocene were dissolved in EtOH (15 mL), then 15 mL of water, containing 0.75 mg, 2.25 mg or 22.5 mg (0.0030 mmol, 0.0090 mmol or 0.090 mmol) of CuSO<sub>4</sub>·5H<sub>2</sub>O and 2.97 mg, 8.91 mg or 89.1 mg (0.015 mmol, 0.045 mmol or 0.45 mmol) of sodium ascorbate were added (in the case of 10 mM solution a partial precipitation of ethynylferrocene was observed while adding water). Then PEDOT-N<sub>3</sub> coated ITO slides were submerged in resulting mixture and maintained under stirring for 24h.



Scheme 3

## 3. Results and discussion

### 3.1 Electrochemical polymerization

EDOT-N<sub>3</sub> was electropolymerized by cyclic voltammetry (ten cycles between 0.0 and +1.5 V at a potential scan rate of 0.05 V s<sup>-1</sup>) from a 10 mM solution containing 0.1 mM PSS as the supporting electrolyte to enable the entrapment of PSS anion during the electropolymerization reaction. For comparison the EDOT monomer was electropolymerized in the same conditions. Figure 1 shows the CVs obtained during the growth of the PEDOT:PSS (panel A) and PEDOT-N<sub>3</sub>:PSS (panel B) polymers on ITO substrates. The polymer growth was also monitored by spectroelectrochemistry: Figure 1C shows the plot of the absorbance at λ= 650 nm (at this wavelength PEDOT is known to absorb light) as a function of time to get some information on the kinetics of the polymers growth.

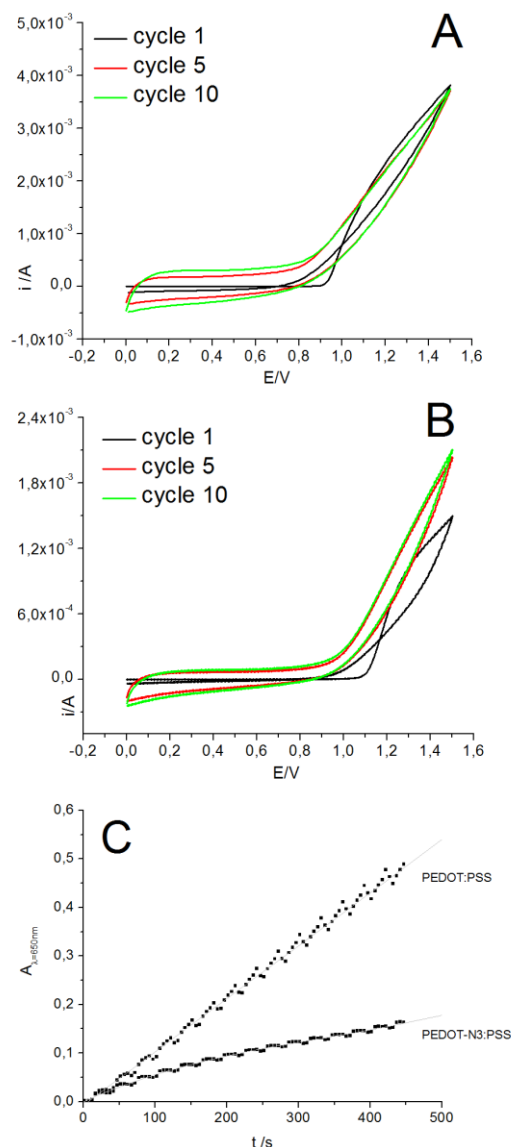


Figure 1. CV cycles obtained at an ITO electrode in 0.1 M PSS aqueous solution containing 10 mM EDOT (A) and 10 mM EDOT-N<sub>3</sub> (B). Scan rate: 0.05 V s<sup>-1</sup>. Panel C shows the plot of the Absorbance (at λ=650nm) recorded during the polymers growth.

The curves of Figure 1 demonstrate that the electrochemical polymerization of EDOT- $N_3$  (panel B) occurs to a similar extent to that of EDOT (panel A). The anodic current density of EDOT- $N_3$  starts to grow rapidly around 1.15 V vs SCE; the monomer oxidation occurs at a higher potential than that of the EDOT (0.95 V)<sup>37</sup>, due to the presence on the monomer of the azide electron-attracting group. Comparing the slopes of the lines  $A_{\lambda=650}$  versus time (panel C), we can state that the presence of the  $N_3$  group slows down the growth of the polymer (about 4 times slower than for EDOT).

Figure 2 shows the AFM images of a  $5\mu\text{m} \times 5\mu\text{m}$  region of PEDOT:PSS (panel A) and PEDOT- $N_3$ :PSS (panel B) film. The morphology of the polymers appears to be similar with a mean RMS roughness of  $(29 \pm 6)$  nm. AFM allows also estimating the thickness of the coatings which was of  $(540 \pm 30)$  nm for PEDOT:PSS and  $(210 \pm 10)$  nm for PEDOT- $N_3$ :PSS, confirming the slower kinetic of the polymer growth in the latter case.

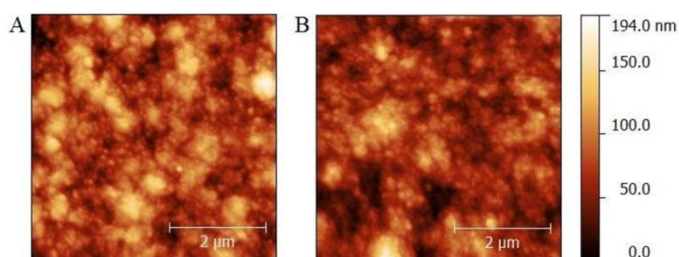


Figure 2: AFM maps of PEDOT:PSS (panel A) and PEDOT- $N_3$ :PSS (panel B).

The presence of the azide group on the polymer chain also affects the spectroelectrochemical features of the polymer. Figure 3 shows the UV-Vis spectra acquired during the CV experiments (the potential was scanned between -0.9 V and +0.8 V at a potential scan rate of  $0.02 \text{ V s}^{-1}$ ) of ITO electrodes coated by PEDOT:PSS (panel A) and PEDOT- $N_3$ :PSS (panel B) prepared as described in the Section 3.1. It's worth to note that the intensities of the recorded absorbances are higher when PEDOT:PSS is used since in such a case the thickness of the coating is higher.

Comparing the spectra of the most reduced form of the polymers, we can note that the presence of the azide group leads to a shift of about 20 nm of the absorbance maximum (from 600 nm to 580 nm). With PEDOT- $N_3$ , scanning the potential from -0.90 V to 0.80 V, the absorption peak at 580 nm decreases and the absorption peak at about 750 nm increases at the same time, with the appearance of an isobestic point at 690 nm. Compared with the spectrum of PEDOT:PSS, the azide containing polymer shows also an absorbance peak at about 350 nm whose intensity is independent of the status of the polymer.

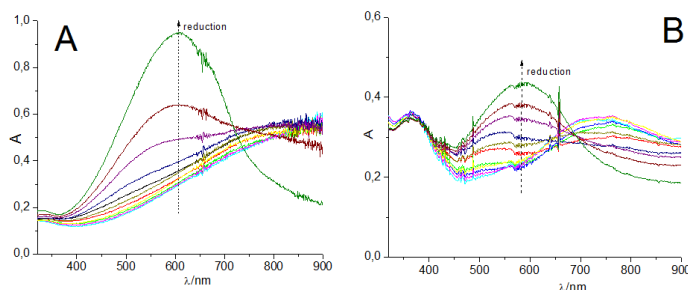


Figure 3. Spectra recorded during a CV experiment in 0.1 M  $\text{LiClO}_4$  solution (scan rate:  $0.02 \text{ V s}^{-1}$ ) at an ITO electrode coated with PEDOT:PSS (A) and PEDOT- $N_3$ :PSS (B). The potential was varied between -0.9 V and +0.8 V.

### 3.2 Characterization of PEDOT-Fc: PSS coated electrode

Figure 4 shows a comparison between the CV curves recorded at an ITO electrode coated by PEDOT-Fc:PSS prepared by click reaction with 1mM or 3 mM ethynylferrocene solution and PEDOT- $N_3$ :PSS coated electrodes in 0.1 M  $\text{LiClO}_4$  aqueous solution.

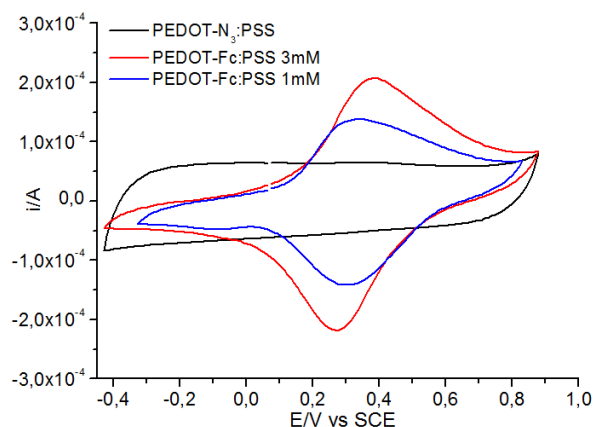


Figure 4. CV curves recorded at ITO electrodes coated with PEDOT- $N_3$ :PSS and PEDOT-Fc:PSS in 0.1 M  $\text{LiClO}_4$  solution. Scan rate:  $0.05 \text{ V s}^{-1}$ .

The signal of PEDOT- $N_3$ :PSS coated electrodes is characterized by a capacitive shape, typical of conducting polymers and very similar to that of PEDOT:PSS polymer; completely different is the shape of the curves of PEDOT-Fc:PSS polymers, which are dominated by the faradaic signal of ferrocene, whose intensity is higher when the click reaction is carried out using 3 mM ethynylferrocene; moreover, we can note that when ferrocene is bonded to the PEDOT chain, a very low capacitive current is recorded; the two redox peaks are located at a potential of 0.38 V and 0.27 V, values typical of ferrocene redox couple. The signal is highly reversible since  $i_{pa}/i_{pc}$  is 1.

The electrodes were also characterized by spectroelectrochemistry, making an experiment similar to that described above for PEDOT- $N_3$ , to ascertain if the presence of

ferrocene leads to a modification of the electrochromic properties of the polymer. The spectra recorded and their evolution with the potential are identical to those obtained for PEDOT-N<sub>3</sub> (Figure 3 B). It's worth to note that attempts were also made to increase the ferrocene signal, by modifying the click chemistry reaction conditions, and, in particular, by further increasing the ethynylferrocene concentration up to 10mM, but the best results, in terms of intensity of ferrocene peaks, stability of the CV and reproducibility of the procedure were achieved using 3 mM ethynylferrocene solution. The reproducibility of the procedure was tested over 5 electrodes, calculating the percentage standard deviation associated to the peak current intensities which resulted only of 3%.

The polymers obtained in the best conditions were also characterized by XPS to assess azide-functionalization and ferrocene covalent immobilization. Figure 5 shows the deconvoluted XPS spectra of PEDOT-N<sub>3</sub>:PSS coated ITO in the C 1s, O 1s, S 2p and N 1s regions. The components obtained through the deconvolution of each core level and their integrated peaks areas are reported in Table 1. In the C 1s core level spectrum, the peak is deconvoluted into three components assigned to C-C/C-H, C-S and C-O bonds of PEDOT<sup>38,39</sup>. In the O 1s core level spectrum, the component at lower eV is ascribed to oxygen of S=O bonds, whereas the other two at higher eV are associated to oxygen involved in C-O bonds of PEDOT. The main peaks of S 2p core-line spectrum have been deconvoluted in five components: neutral S of PEDOT (163.7-164.9 eV), cationic S<sup>+</sup> (165.3 eV) associated with the PEDOT backbone and highly oxidized SO<sub>3</sub><sup>-</sup> (167.8-169.0 eV)<sup>38,39</sup>. In the N 1s region, two components, at 404.4 and 400.7 eV, have been determined after curve-fitting, respectively, assigned to the central, electron-deficient N atom in the azide group, and to the two nearly equivalent azide N atoms<sup>40</sup>, providing evidence for functionalization of PEDOT polymer. After the “click” reaction with 3 mM ferrocene, the components and the integrated peaks area for C 1s, O 1s and S 2p core level spectra show negligible differences compared to those observed for PEDOT-N<sub>3</sub>:PSS-coated ITO, whereas the N 1s region for ferrocene-functionalized polymer shows differences in terms of integrated peaks area of deconvoluted components. The area ratio between high- and low-BE peaks of N 1s core level increases after ferrocene bonding (Table 2), indicating a partial transformation of the azide group into the 1,2,3-triazole unit bound to the terminal ferrocene head<sup>40</sup>. The Fe 2p region, reported in Figure 6, shows the peaks associated to Fe (II) species at *ca* 708 eV and to Fe (III) species, at 711 eV, which are consistent with binding energies values reported in the literature for surface-anchored ferrocene and ferrocenium salts, respectively<sup>40,41</sup>. The narrowness of Fe(II) component suggests an assignment to a well-defined surface species. To confirm the presence of covalently bonded ferrocene, also a film just kept in contact with ferrocene solution (in the same conditions employed for the synthesis but without copper catalyst) was analyzed: no signal ascribable to Fe 2p level core has been observed for this system.

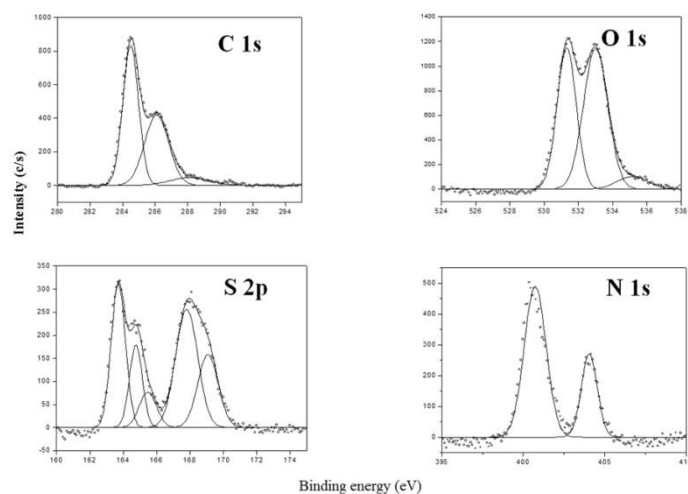


Figure 5: Core level spectra of C 1s, O 1s, S 2p and N 1s for PEDOT-N<sub>3</sub>:PSS coated ITO. Scattered lines represent the experimental data and solid lines the deconvoluted contributions.

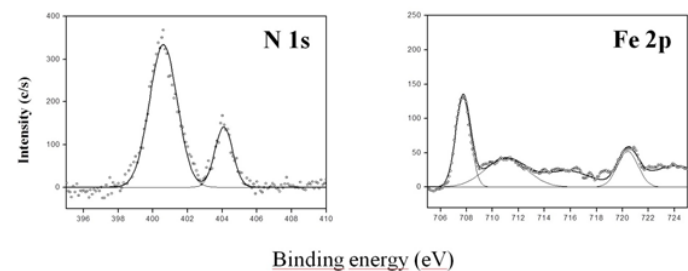


Figure 6: Core level spectra of N 1s and Fe 2p for PEDOT-Fc:PSS coated ITO. Scattered lines represent the experimental data and solid lines the deconvoluted contributions.

Table 1. Deconvoluted contributions of C 1s, O 1s, S 2p, N 1s core level spectra for PEDOT-N<sub>3</sub>:PSS coated ITO

C1s		O1s		S2p		N1s	
Peak position (eV)	Peak area (%)	Peak position (eV)	Peak area (%)	Peak position (eV)	Peak area (%)	Peak position (eV)	Peak area (%)
284.4	52.3	531.4	46.3	163.8	26.4	400.7	71.1
286	44.1	533.1	49.6	164.9	11.3	404.4	28.6
288.7	3.6	535.1	4.1	165.3	10.2		
				167.8	30.9		
				169.0	21.2		

Table 2. Deconvoluted contributions of N 1s and Fe 2p core level for PEDOT-Fc:PSS coated ITO

N1s		Fe2p	
Peak position (eV)	Peak area (%)	Peak position (eV)	Peak area (%)
400.7	78.7	707.8	26.0
404.1	21.3	711.0	23.1

### 3.3 Dopamine amperometric detection

To assess the electrocatalytic properties of the covalently bonded ferrocene, linear scan voltammeteries were recorded in 0.1 M LiClO<sub>4</sub> solution containing different DA amounts (Figure 7).

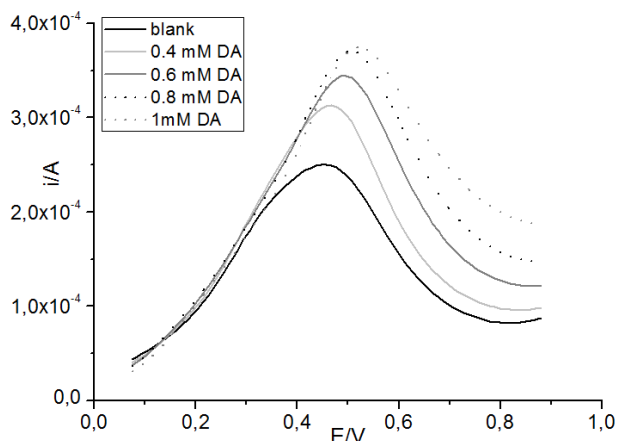
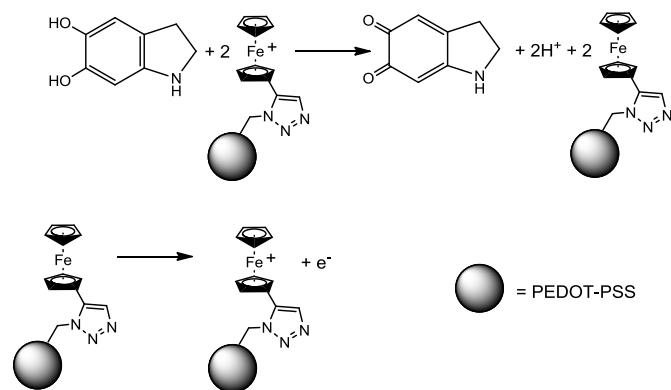


Figure 7. Linear scan voltammeteries recorded in 0.1 M LiClO<sub>4</sub> solution containing different DA amounts. Potential scan rate: 0.05 V s<sup>-1</sup>.

The ferrocene anodic peak current increases as DA concentration increases, up to a 1 mM DA concentration, demonstrating that ferrocene can mediate the electrooxidation of dopamine according to the reaction reported in Scheme 4.



Scheme 4

DA determination was therefore realized under hydrodynamic conditions, by chronoamperometry under magnetic stirring, at  $E_{app} = 0.50$  V with successive additions of DA into the electrolyte solution. As an example, Figure 8 shows the response of the device under eight successive 4  $\mu$ M DA additions. The response is very stable and rapid being the average response time of only 10 s.

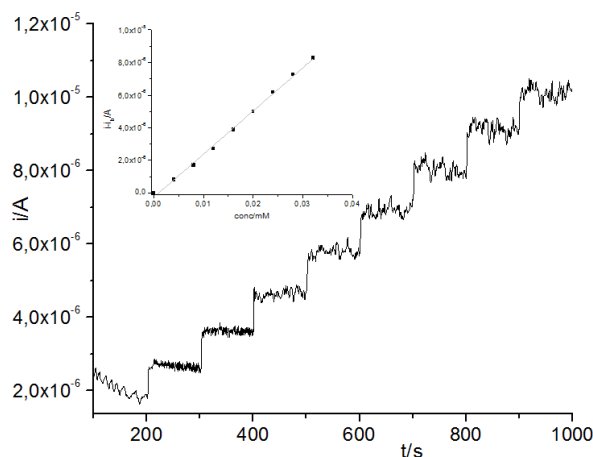


Figure 8. Chronoamperometric response at 0.50 V vs. SCE of an ITO electrode coated with a PEDOT-Fc:PSS film, in 0.1 M LiClO<sub>4</sub> solution to 4  $\mu$ M successive dopamine additions. The inset shows the relevant calibration curve.

Calibration curves were obtained by plotting the steady state current, measured after subtraction of the base line current, vs. substrate concentration (see the inset in Figure 8). Three different ITO electrodes were prepared and the reproducibility and repeatability of the sensors were examined. For a given electrode, the relative standard deviation (RSD) was 6 % for nine additions of 0.04 mM DA. These sensors presented a linear range between 0.01 and 0.9 mM and a mean sensitivity of 196 mA M<sup>-1</sup> cm<sup>-2</sup>. The limit of detection (LoD), determined at a signal-to-noise ratio of 3, was 1  $\mu$ M.

### Conclusions

We have coated ITO slides with PEDOT-Fc:PSS, by a two-step procedure consisting in the electrodeposition of PEDOT-N<sub>3</sub> followed by copper-catalyzed azide-alkyne cycloaddition of ethynylferrocene. The ITO coated electrodes have been characterized by CV before and after the ferrocene immobilization: the signal of PEDOT-N<sub>3</sub>:PSS is characterized by a capacitive shape, typical of conducting polymers, whereas completely different is the shape of the curve recorded at PEDOT-Fc:PSS coated ITO, which is dominated by the reversible faradaic signal of ferrocene with the presence of two redox peaks located at 0.38 V and 0.27 V, values typical of ferrocene redox couple. The coatings are stable, and the developed procedure is highly reproducible being the standard deviation associated to the ferrocene peak current of only 3%. To demonstrate the successful immobilization, and to make sure that ferrocene is covalently bonded to the polymer chain, the coated electrodes have been characterized by XPS, which highlights the partial transformation of the of the azide group into the 1,2,3-triazole unit bound to the terminal ferrocene head and the presence of Fe (II) and Fe(III) species.



The electrocatalytical performance of the device has been assessed by analyzing 3,4-dihydroxyphenyl ethylamine, also commonly known as dopamine (DA). The sensor presents a linear range between 0.01 and 0.9 mM, a mean sensitivity of 196 mA M<sup>-1</sup> cm<sup>-2</sup> and a limit of detection (LoD), 1 μM.

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## Notes and references

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Electronic Supplementary Information (ESI) available: [<sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> (400 MHz) of 2-Chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT-Cl) and of 2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4] dioxine (EDOT-N<sub>3</sub>). See DOI: 10.1039/b000000x/

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