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► **To cite this version:**

Olivier Alévêque, Eric Levillain, Lionel Sanguinet. Spectroelectrochemistry on electroactive self-assembled monolayers: Cyclic voltammetry coupled to spectrophotometry. *Electrochemistry Communications*, 2015, 51, pp.108-112. 10.1016/j.elecom.2014.12.014 . hal-02063332

**HAL Id: hal-02063332**

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Submitted on 25 Oct 2019

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## Spectroelectrochemistry on electroactive self-assembled monolayers: cyclic voltammetry coupled to spectrophotometry

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ARTICLE INFO	ABSTRACT
<p><i>Keywords:</i></p> <p>Self-assembled monolayers Spectroelectrochemistry EC<sub>Dim</sub> mechanism Bithiophene</p>	<p>We present a spectroelectrochemical bench involving an electrochemical/spectrophotometric coupling dedicated to probe electroactive self-assembled monolayers (SAMs). This bench is validated by the study of the oxidation of a 5,5'-disubstituted-2,2'-bithiophene immobilized on Au substrate, producing a reversible dimerization of the radical cation (i.e. EC<sub>Dim</sub> process) leading to a dimer. A direct comparison between thin layer spectroelectrochemistry in solution and spectroelectrochemistry on SAMs shows that a SAM could be viewed as a highly concentrated solution.</p>

### 1. Introduction

The frantic race towards nanotechnologies has led to the development of modified electrodes having smaller and smaller thicknesses and the molecular scale has been reached by a simple and reproducible way: the self-assembled monolayers (SAMs) [1].

The nanometric dimensionality has never been a problem for the electrochemical characterization of SAMs with usual techniques (cyclic voltammetry, I-E measurements...) because the limiting factor is not the thickness of the layer, but the number of redox species immobilized on the electrode surface. Despite a global, and not local, response of the electrode, some investigations showed that the profile of the electrochemical responses could be a salient tool in order to describe the nanometric organization of the SAMs [2].

The nanometric scale of the electroactive layer limits the possibility to characterize SAMs via usual absorption and fluorescence spectroscopic methods because 1) their optical densities are very weak, 2) signal-to-noise ratio is very low according to classical spectroscopic instruments and 3) no turnkey system is available especially for these nanometric systems. However, some studies showed that it was possible to estimate the surface coverage and to set up molecular engineering rules. More specific techniques, such as near-field spectroscopy (AFM, STM...) [3, 4], ellipsometry [5], IRRAS [6], SERS [7], allowed to obtain some structural informations about the SAM, but generally the experimental conditions demand to operate on a "non-wet" surface.

How about spectroelectrochemistry on SAMs? A literature survey shows that this domain is not really studied. To the best of our knowledge, less than a dozen publications report experimental results involving an electrochemical/spectroscopic coupling dedicated to monolayers, essentially in potentiostatic conditions (i.e. fluorescence [8], PM-IRRAS [9], SERS [7], UV-visible absorption [10, 11], fluorescence microscopy [12] ...). This work clearly show that spectroelectrochemical coupling provides excellent tools to establish detailed structure–property relationships.

Here, we present a time-resolved spectroelectrochemical measurement bench which allows to finely follow the absorption spectrum evolution of a self-assembled monolayer as function of the applied redox potential. In order to demonstrate the ability of this new tool, we validated the bench with electroactive SAMs prepared on Au substrates from a disubstituted bithiophene derivative (compound **1**) and confronted the data on SAMs to those obtained on the parent compound in solution (*i.e.* thin layer conditions).

## 2. Experimental

### 2.1 Chemicals

The synthesis of the compound **1** was adapted from the parent thiol derivative described elsewhere [13] and is depicted on Figure 1A.

### 2.2 Au substrate and SAM preparation

Au substrates were prepared by deposition of ca. 5 nm of chromium followed by ca. 100 nm of gold onto a glass substrate through a shadow mask (MECACHIMIQUE / France) using physical vapor deposition system (PVD ME300 PLASSYS / France) and were made immediately before use. This protocol provides reproducible Au(111) surfaces with high crystallographic quality, low roughness (Ra less than 2 nm) and with a defined geometry. They do not undergo post-treatment after completion and that is an advantage.

SAMs were prepared on fresh Au substrates (0.2 cm<sup>2</sup>) by immersing for 15 min in 1 mM solution of **1** in methylene chloride at 293 K [13].

### 2.3 Spectroelectrochemical experiment

Electrochemistry and time-resolved spectroelectrochemistry in solution were performed using the already described home self-made cell [14, 15]. Electrochemical measurements were carried out using a platinum wire counter electrode and a silver wire as a quasi-reference electrode with a Biologic SP-150 potentiostat driven by the EC-Lab software including ohmic drop compensation. Experiments were recorded in dry HPLC-grade acetonitrile with tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, electrochemical grade, Fluka) as supporting electrolyte. All solutions were prepared and transferred into the spectroelectrochemical cell in a glove box containing dry, oxygen-free (<1 ppm) argon, at room temperature.

In order to use commercially available thermostated cell holders, the spectroelectrochemical cell dedicated to SAMs is dimensionally close to the conventional quartz cuvette (outer dimensions = 12.5 mm x 12.5 mm x 45 mm). The inner part of the cuvette (Hellma<sup>®</sup> Analytics) has been specially redesigned, in order to insert, parallel to the quartz windows, a home self-made interdigitated three Au electrodes with high precision (Figure 2).

Spectrophotometric measurements were carried out in direct reflexing mode on the working electrode (*i.e.* Pt or Au) with a homemade bench composed of different Princeton Instruments modules (light sources, fibers, monochromators, spectroscopy camera and software). The connection between the light source, the cell and the spectrophotometer is ensured through a “Y-shaped” optical fiber bundle: 18 fibers guide the light to the

cell, and 19 fibers collect the reflected light from the cell to visible (320-1080 nm / maximum acquisition frequency 2 MHz) and IR (900-1700 nm / maximum acquisition frequency 8 MHz) CCD detectors. The sensitivity of the spectroscopic measurement ( $< 3 e^-$  at 100 kHz and  $< 13 e^-$  at 2 MHz between 320 and 1080 nm;  $400 e^-$  (high gain) and 5000 électrons (low gain) between 900 nm and 1700 nm) allows performing a spectroelectrochemistry experiment under the usual conditions of electrochemistry.

### 3. Results and discussion

#### 3.1. Spectroelectrochemistry in solution

As expected [13], compound **1** presents a characteristic optical adsorption band with a lambda max of 340 nm ( $\sim 17\ 000\ M^{-1}\ cm^{-1}$  per redox unit) (Figure 1B) and exhibits a fully reversible one-electron process in positive direction (+0.49 V vs.  $Fc^+/Fc$ ) in 0.1 M  $Bu_4NPF_6/CH_2Cl_2$  (Figure 1C and 3B).

The oxidation of **1** is known to produce a reversible dimerization of the radical cation (*i.e.*  $EC_{Dim}$  process) leading to a  $\pi$  or  $\sigma$ -dimer. Spectroelectrochemical experiments (Figure 3C and 3D), performed to probe the oxidation process between 350 and 1700 nm, allowed characterizing two strong absorption bands (570 and 900 nm) and two shoulders (510 and 815 nm), as well as a weaker band close to 670 nm (Figure 3E).

In agreement with the work of Hapiot *et al.* in acetonitrile [16], the absorption bands close to 570, 815 and 900 nm (*i.e.* 490, 560, 800 and 880 nm in acetonitrile) are assigned to the radical cation and the absorption band close to 510 and 670 nm (*i.e.* 450-490 and 660 nm in acetonitrile) is typical to the dimer at 293 K.

#### 3.2. Electrochemistry and spectroelectrochemistry on SAMs

The main experimental difficulty is connected with the dimensionality of the studied material. Indeed, the intensity of the spectroscopic signatures depends on the amount of patterns immobilized on the metal surface ( $\Gamma$ ,  $mol.cm^{-2}$ ): the surface coverage is typically around  $10^{-10}\ mol.cm^{-2}$ !

In the case of an absorption measurement by reflexion (imposed by the spectroelectrochemical setup), Beer's law in a SAM can be expressed as follows:

$$\text{Absorbance} = 2 \cdot 1000 \cdot \varepsilon \cdot \Gamma \quad \text{with} \quad \begin{cases} \varepsilon, M^{-1}\ cm^{-1} \\ \Gamma, mol\ cm^{-2} \end{cases} \quad (1)$$

A simple numerical calculation shows that the absorbance on a monolayer is very low, around 0.002 for  $\Gamma = 10^{-10}\ mol.cm^{-2}$  and  $\varepsilon = 10\ 000\ M^{-1}.cm^{-1}$ . This limit imposes some constraints: (1) the molar extinction coefficients of the immobilized molecules must be high ( $> 10\ 000\ M^{-1}.cm^{-1}$ ), (2) the surface coverages must be high ( $> 10^{-10}\ mol.cm^{-2}$ ) and (3) the high sensitivity of the spectroscopic detectors and the resulting signal-to-noise ratio must the recording of voltabsorptograms possible.

The electrochemical response of the SAMs of **1** in 0.1 M  $Bu_4NPF_6/CH_2Cl_2$  (Figure 4A and 4B) is consistent with a reversible redox system (+0.49 V (vs  $Fc^+/Fc$ )) confined at the Au electrode, as shown by the linearity of peak currents with the scan rate (up to  $50\ V\ s^{-1}$ ). As expected, the surface coverage ( $\Gamma$ ) reaches a value of  $2\ 10^{-10}\ mol\ cm^{-2}$  at 293 K.

Spectroelectrochemical experiments, probing the oxidation process between 350 and 1700 nm, were performed during two successive cycles (Figure 4C). First, the absorbance values are very low (*i.e.* some  $10^{-$

<sup>3</sup>), in agreement with equation 1. Second, the absorbance profile is different from the one obtained in solution, suggesting a change in the environment of the redox sites: three absorption bands emerge at around 515, 680 and 910 nm, suggesting only the dimer in attendance (Figure 4E) and no optical band was observed between 1000 and 1700 nm. Third, the absorption bands arise at each oxidation process with same values, showing the stability of the measurement. At Last, the good signal-to-noise ratio allows extracting, with the help of 2D digital filters [17] performed with SCILAB<sup>®</sup>, the derivative of the absorbance vs. time. For instance, the variation in the derivative of the absorbance at 680 nm vs. time fits with the one of the current vs. time during the two cycles (Figure 4D).

#### **4. Discussion and conclusion**

Based on this work, it appears possible to probe the spectroelectrochemical behavior of SAMs in visible and NIR ranges and, according to the signal-to-noise ratio, to extract voltabsorptograms. It is important to note that spectroelectrochemical measurements on SAMs are reliable, accurate and reproducible but they mainly depends on the sensitivity and the noise of the detectors, the quality of the calibrations and the maintenance of the bench.

This study shows that the confinement of redox sites in the material favors the presence of dimer in the case of an  $EC_{Dim}$  process, suggesting that a SAM could be viewed as a high concentrated solution. This interesting result will have to be confirmed by further work on other usual electrochemical mechanisms and on mixed SAMs [18, 19].

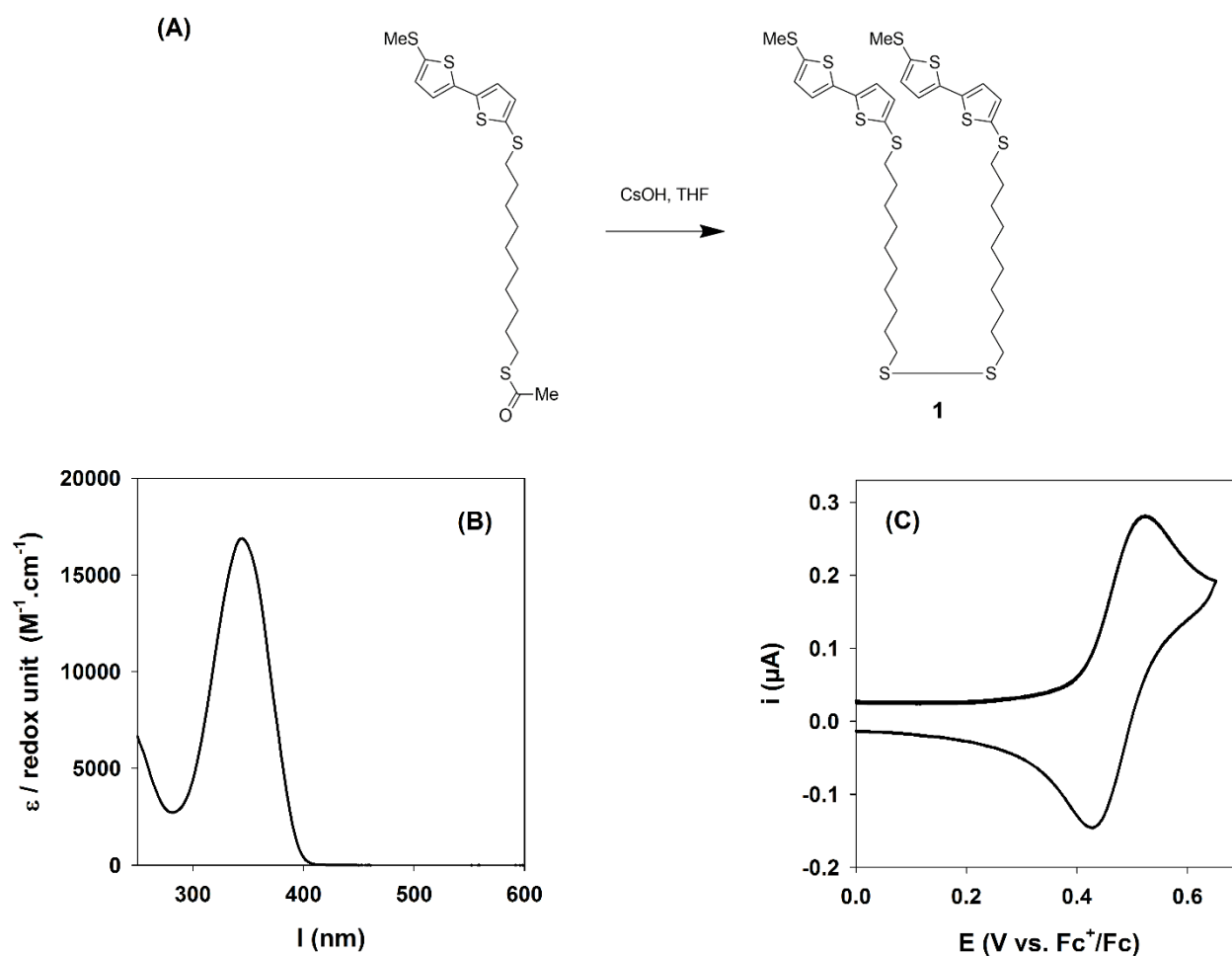
To conclude, we hope this new spectroelectrochemical bench, also dedicated to fluorescence measurements, will provide tools to assist in establishing detailed structure-reactivity relationships for interfacial reactions on SAMs and on mixed SAMs and, will help to explain why the reactivity of some reactions on the surface are amplified or inhibited.

#### **Acknowledgments**

The authors thank Hellma<sup>®</sup> Analytics and Princeton Instruments companies for the quality of their products and services. This work was supported by the Contrat Plan État Région 2007-2013 (Pays de la Loire - France). The authors thank Flavy Alévêque for her critical reading of the manuscript.

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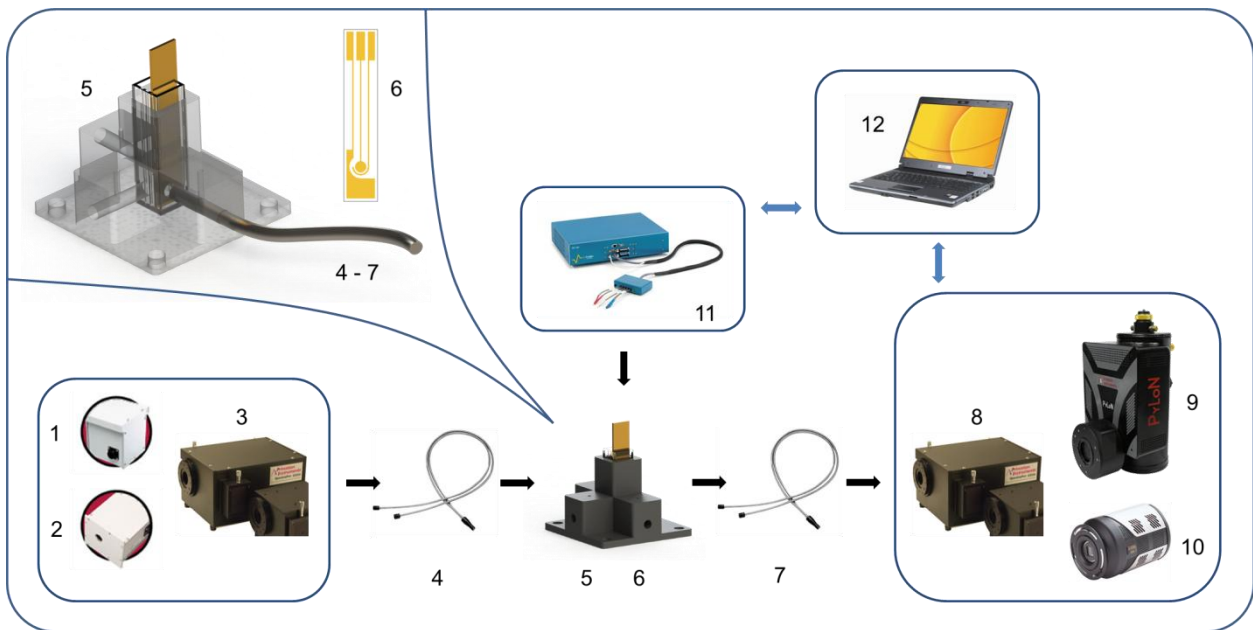


**Figure 1**

(A) Synthesis of compound **1** (1,2-bis(5-((5'-(methylthio)-[2,2'-bithiophen]-5-yl)thio)decyl)disulfane): A degassed solution of monohydrate cesium hydroxide (0.72mg, 4.3 mmol) in dry MeOH (1 ml) was added to a freshly degassed solution of 5-(Méthylsulfanyl)-5'-(12-Oxo-11-thiatridecylsulfanyl)-2,2'-bithiophène (0.66g, 1.4 mmol) in dry THF (30 ml) under nitrogen atmosphere at 0°C [13]. The reaction mixture was left under stirring for 30 min at this temperature, quenched by adding water, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. After removal of the solvent, the crude product is purified by flash chromatography (i.e. silica gel with CH<sub>2</sub>Cl<sub>2</sub>/Petroleum ether (1/2) as eluent) to afford the desired compound (0.41g; 69%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ=7.01-6.91 (m, 4H); 2.80 (t, J = 7.3 Hz, 2H); 2.67 (t, J = 7.3 Hz, 2H); 2.50 (s, 3H); 1.62 (q, J = 7.3 Hz, 2H); 1.44-1.22 ppm (m, 14H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ= 139.9; 139.1; 136.7; 134.4; 134.0; 131.7; 123.9; 123.8; 39.2; 38.9; 29.7; 29.4-29.3; 29.2; 29.1; 28.5; 28.4; 22.1 ppm.

(B) Spectrophotometry: 0.1 mM of **1** in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> at 293 K.

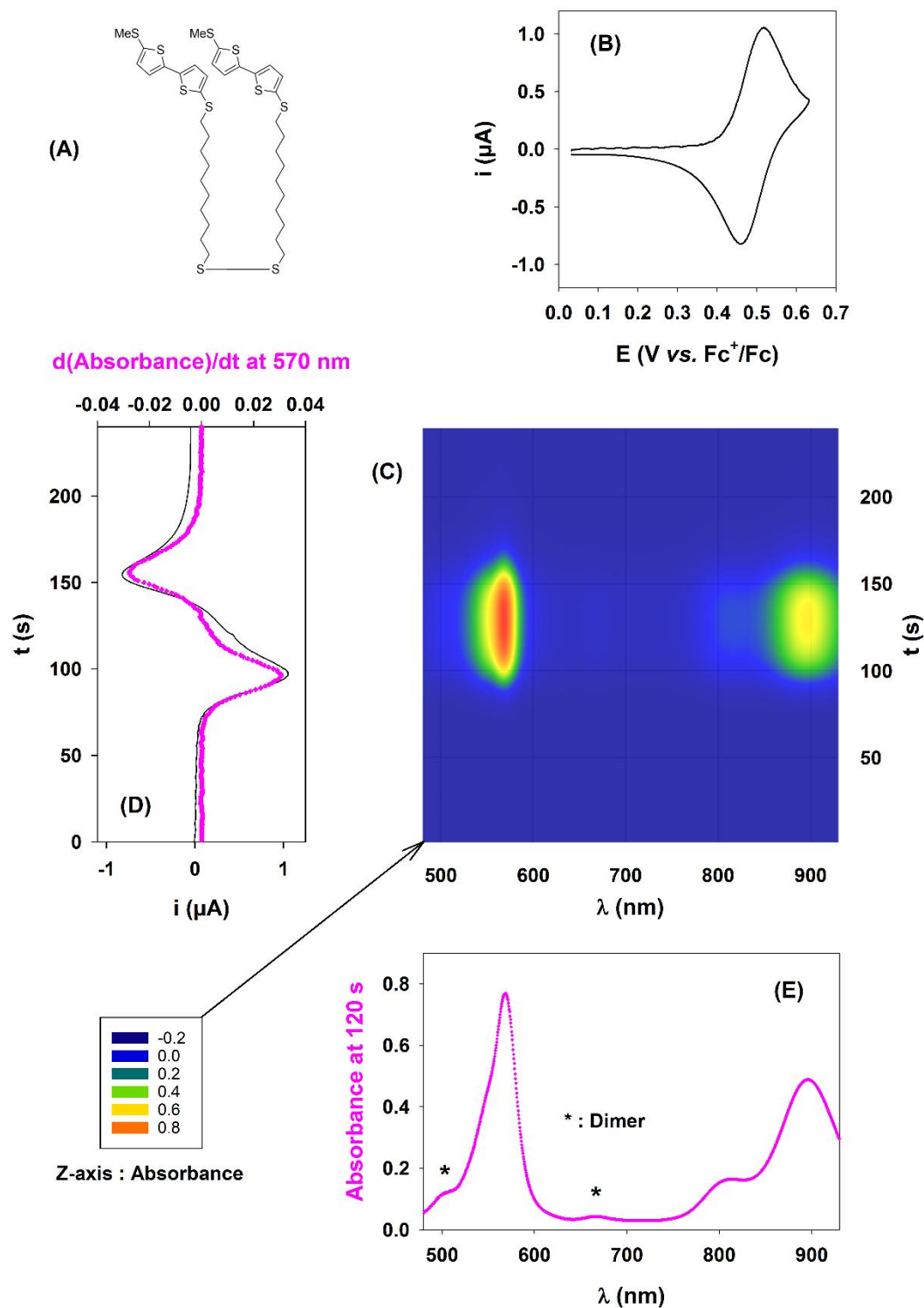
(C) Cyclic voltammetry: 0.1 mM of **1** in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> at 100 mV.s<sup>-1</sup> and 293 K on Pt electrode.



**Figure 2:** Schematic diagram of the bench

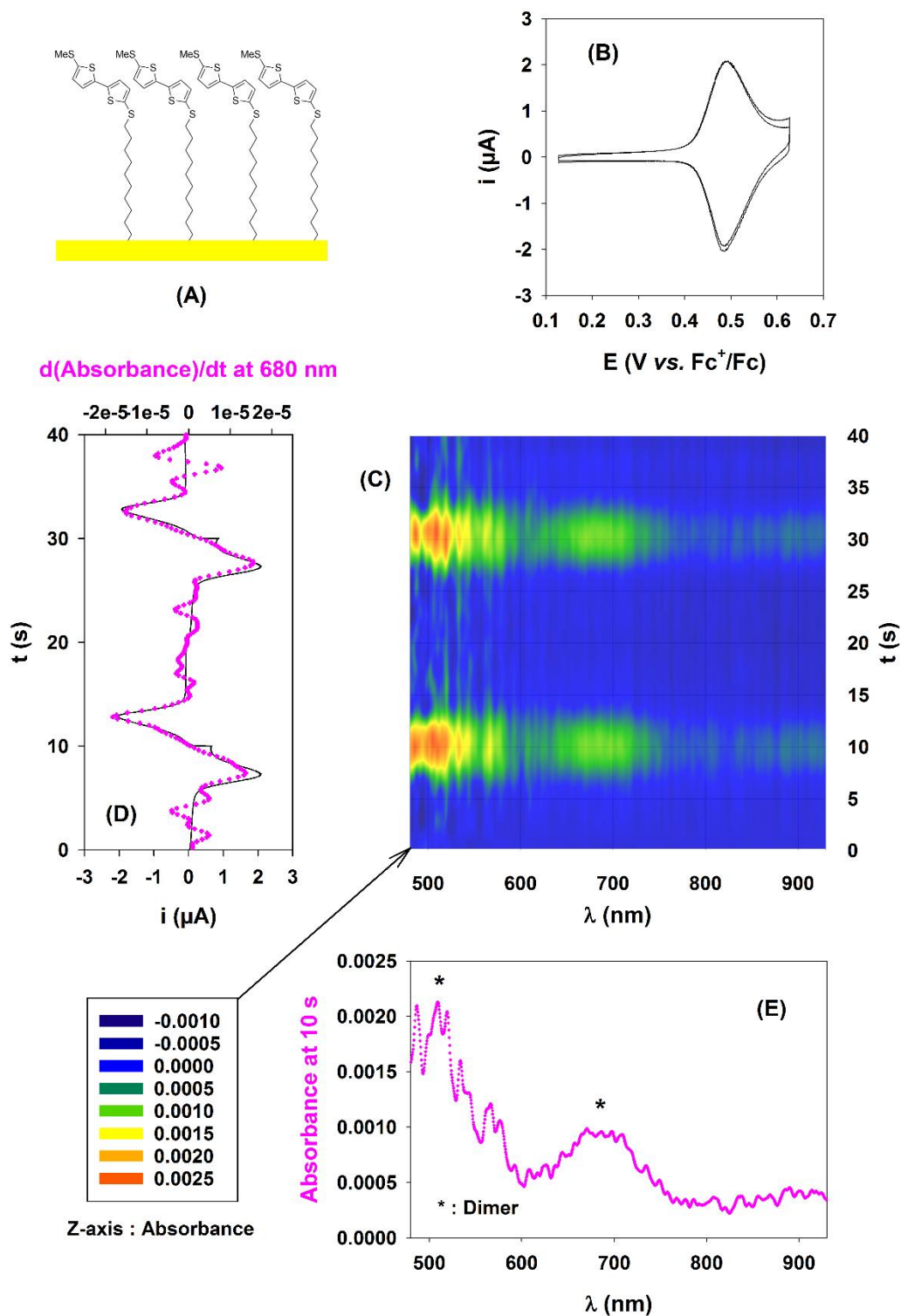
- |   |                                   |    |                                       |
|---|-----------------------------------|----|---------------------------------------|
| 1 | UV source (Tungsten lamp)         | 7  | Fiber optics                          |
| 2 | Visible-NIR source (Halogen lamp) | 8  | Spectrometer (ACTON SP2360i)          |
| 3 | Spectrometer (ACTON SP2155)       | 9  | NIR detector (PyLoN-IR-1024-1.7)      |
| 4 | Fiber optics                      | 10 | Visible detector (PIXIS-100B-eXcelon) |
| 5 | Analysis cell                     | 11 | Potentiostat (Biologic SP150)         |
| 6 | Modified electrode                | 12 | Control and signal processing         |





**Figure 3:** Spectroelectrochemical experiment in solution.

- (A) Target = compound 1
- (B) Cyclic voltammogram of 1 mM of 1 in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$  at  $5 \text{ mV}\cdot\text{s}^{-1}$  and 293 K on Pt electrode in thin layer conditions (close to  $50 \mu\text{m}$ ).
- (C) 3D representation: X-axis = wavelength, Y-axis = time and Z-axis = absorbance.
- (D) Comparison between  $i$  vs.  $t$  and  $d(\text{Absorbance})/dt$  vs.  $t$ . at 570nm, characteristic of radical cation.
- (E) Absorbance at 120 s (i.e. 0.625 V vs.  $\text{Fc}^+/\text{Fc}$ ) extracted from figure 3C, characterizing the oxidized state (the radical cation, for the most part).



**Figure 4:** Spectroelectrochemical experiment on electroactive SAMs.

- (A) Target = SAM from compound 1 on Au substrate.  
 (B) Cyclic voltammogram in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$  at  $50 \text{ mV}\cdot\text{s}^{-1}$  and 293 K on "Au electrode".  
 (C) 3D representation: X-axis = wavelength, Y-axis = time and Z-axis = absorbance.  
 (D) Comparison between  $i$  vs.  $t$  and  $d(\text{Absorbance})/dt$  vs.  $t$ . at 680nm, characteristic of dimer.  
 (E) Absorbance at 10 s (i.e. 0.625 V vs.  $\text{Fc}^+/\text{Fc}$ ) extracted from figure 4C, characterizing the oxidized state (the dimer, for the most part).