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► **To cite this version:**

Olivier Alévêque, Christelle Gautier, Eric Levillain. Real-time absorption spectroelectrochemistry: From solution to monolayer. *Current Opinion in Electrochemistry*, 2019, 15, pp.34-41. 10.1016/j.coelec.2019.03.015 . hal-02126917

**HAL Id: hal-02126917**

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Submitted on 20 Feb 2020

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# Accepted Manuscript

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PII: S2451-9103(19)30032-8

DOI: <https://doi.org/10.1016/j.coelec.2019.03.015>

Reference: COELEC 388

To appear in: *Current Opinion in Electrochemistry*

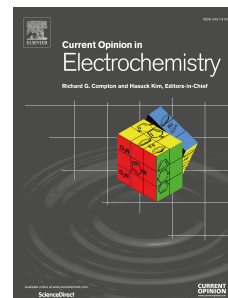
Received Date: 25 February 2019

Revised Date: 26 March 2019

Accepted Date: 30 March 2019

Please cite this article as: Alévêque O, Gautier C, Levillain E, Real-time absorption spectroelectrochemistry: from solution to monolayer, *Current Opinion in Electrochemistry*, <https://doi.org/10.1016/j.coelec.2019.03.015>.

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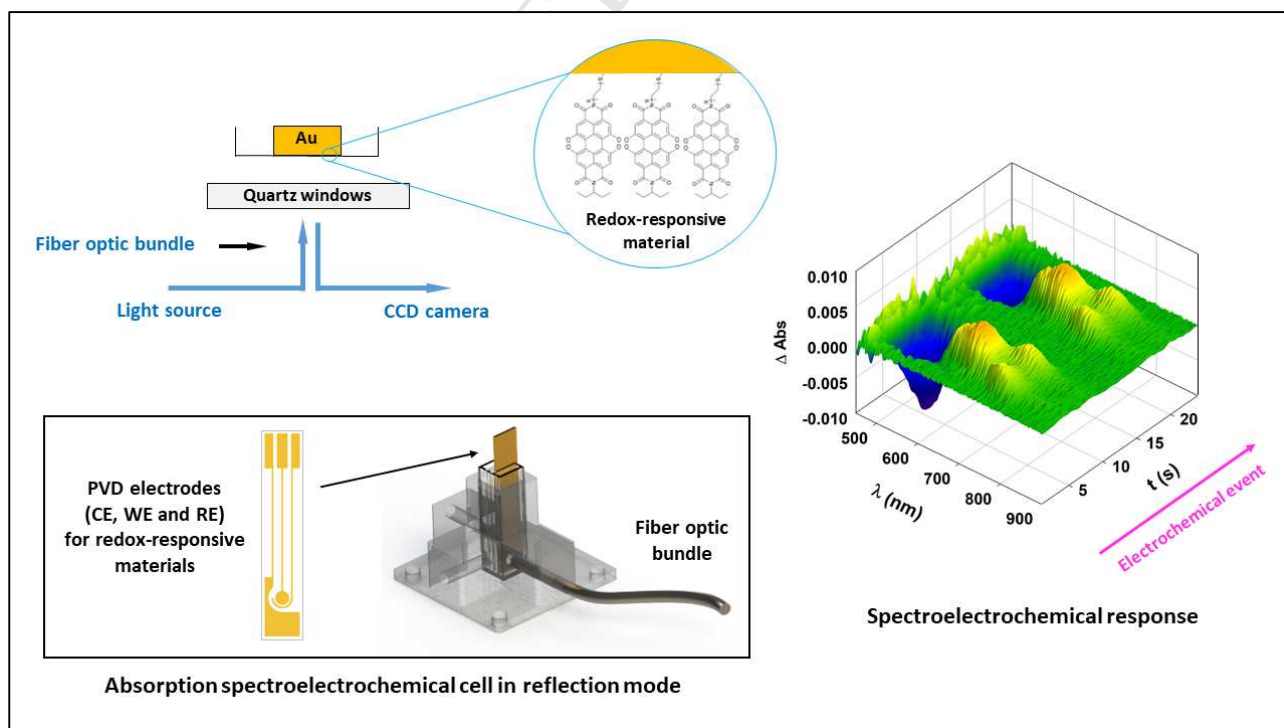
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## Highlights

- A short review to provide practical aspects of real-time absorption spectroelectrochemistry (A-SEC) devoted to monitoring low absorbance values.
- A brief overview of the seminal work of A-SEC performed on electroactive SAMs.
- A reflection mode is strongly suggested for monitoring redox-responsive materials and allows real-time emission spectroelectrochemistry (E-SEC).
- A-SEC at nanoscale enables the study of the grafting impact on heterogeneous reactions coupled to charge transfer.

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## Abstracts

High sensitivity CCD cameras, efficient fiber optic bundles, high stable light source and 3D printing technologies now open large possibilities to probe redox species in solution and on confined surface by real-time absorption spectroelectrochemistry (A-SEC). This short review aims at providing an overview of the first work of A-SEC on redox-responsive self-assembled monolayers (SAM). Some practical aspects are emphasised to not underestimate the difficulties involved in set-up such instrumentation.

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## Introduction

Electronic (UV-visible and NIR) transmission and reflectance spectroelectrochemistry (SEC) already proved to be an effective approach for studying the redox chemistry of organic, inorganic and biological compounds. The *in-situ* simultaneous acquisition of spectroscopic and electrochemical information in an electrochemical cell (*i.e.* real-time SEC) for investigating reaction kinetics and mechanisms as well as exploring electrode surface phenomena indeed has a long-standing history.[1-9] The pioneering work was published in 1964 by Kuwana *et al.*, who reported a true technical feat for their time: the use of SnO<sub>2</sub> electrode to monitor the absorbance during an electrolysis at a given wavelength.[10] Half a century later, the improvement in CCD cameras (*i.e.* very sensitive and stable with low noise and large dynamics), light sources (*i.e.* stability vs. time), fiber optic bundles and 3D printing technologies have paved the way for the development of very efficient real-time SEC capable of probing redox-response nanomaterials at high sampling rate (*e.g.* 1 optical spectrum per millisecond with a high signal-to-noise ratio). By the way, León and Mozo provide a recent review dedicated to SEC and some major breakthroughs in the field with more than 300 references.[11]

In this short review, the first paragraph reminds some practical but essential aspects of real-time A-SEC for monitoring very low absorbance values. Then, a second paragraph will be dedicated to a textbook case A-SEC response: a perylenediimide (PDI) redox probe in solution and immobilized on Au substrate. Finally, the last paragraph gathers the very first results of A-SEC on self-assembled monolayers (SAM) extracted from the literature.

## A few practical reminders

In solution, Beer's law defines the usual relationship between concentration and absorbance as follows:

$$A = \epsilon \ell C \quad \text{with } \epsilon, \text{ the extinction coefficient (mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}\text{)}, \ell, \text{ the path length (cm) and } C, \text{ the concentration (mol}\cdot\text{L}^{-1}\text{)}.$$

For redox-responsive materials (*e.g.* a SAM), Beer's law can be expressed as:

$$A = 1000 \epsilon_{\text{APP}} \Gamma \quad \text{with } \Gamma, \text{ the surface coverage (mol}\cdot\text{cm}^{-2}\text{)} \text{ and } \epsilon_{\text{APP}}, \text{ the apparent extinction coefficient of the material.}$$

It is generally accepted that  $\epsilon_{\text{APP}}$  depends on the average tilt angle of immobilized molecules (*i.e.* the average dipole moment orientation vs. the light beam direction, perpendicular to the substrate) and readers should keep in mind that, in a borderline case, a zero value of tilt angle induces a zero value of  $\epsilon_{\text{APP}}$ . [12-21] Consequently, the measured absorbance is highly structure-dependent of the material.

Probing a SAM by A-SEC imposes to deal with very low absorbance values, close to 0.001 (with  $\Gamma \approx 10^{-10} \text{ mol.cm}^{-2}$  and  $\epsilon_{\text{APP}} = 10\,000 \text{ mol}^{-1} \cdot \text{L.cm}^{-1}$ ). This challenge seems huge but performing A-SEC in thin layer conditions can be equally problematic since all measurements need to be, at each step of potential, in an effective steady state to correlate spectroscopic and electrochemical data. In this case, a quite short conversion time ( $t$ ) close to 1s imposes a thin layer thickness ( $\ell$ ) of about ten micrometers (with  $\ell < (t \cdot D)^{1/2}$  and a diffusion coefficient  $D$  of *ca*  $5 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ ), resulting in low absorbance values (*e.g.*  $A = 0.01$  with  $\epsilon = 10\,000 \text{ mol}^{-1} \cdot \text{L.cm}^{-1}$ ,  $\ell = 10 \mu\text{m}$  and  $C = 1 \text{ mM}$ ). [6] It should be noted that A-SEC on SAM can lead to unusual hardships when the substrate strongly absorbs photon from the light source (*e.g.* vitreous carbon). In such a case, a careful spectroelectrochemical study of non-functionalised working electrodes is required to prevent unexpected signals, which could result in misleading or inaccurate interpretations.

In addition, it should also be kept in mind that, under such conditions, performing A-SEC in transmission mode has proven, so far, to be very difficult via a commercial or homemade TLCV cell because  $\ell$  is at best close to 200  $\mu\text{m}$ . Therefore, a reflection mode turns out to be a method of choice because it (i) provides an optimal control of the optical path length (via a micrometric screw, a spacer, etc...), (ii) doubles the absorbance (*i.e.* the light beam passes through the thin film twice meaning that  $A = 2 \epsilon \ell C$ ), (iii) minimises the light signal attenuation and, icing on the cake, (iv) enables a photoluminescence monitoring via a perpendicular excitation to the electrode surface by real-time emission spectroelectrochemistry (E-SEC). [22-25] By the way, a recent review of Dan Bizzotto provides a general overview of E-SEC on SAM. [26]

Last but not least, a high sensitivity CCD camera with a signal-to-noise ratio (S/N) above 1 000 (*i.e.*  $S/N = (\text{Gain} \cdot I)^{1/2}$  with  $I$ , the number of counts and Gain, the conversion between the number of electrons recorded by the CCD and the number of digital units contained in the CCD image) and a high stable light source over time are required to monitor such extremely low absorbance variation. Moreover, the large dynamic range of up-to-date CCD cameras leads to sampling frequencies around a few MHz (on 16 or 32 bits) and so a real-time monitoring of redox process and possible chemical reactions accompanying it on millisecond scale or even less. However, reaching such a time scale strongly depends on CCD camera settings and a compromise between the number of points and the lag time is required to optimize either the dynamic or the sensitivity.

One last point that is often problematic: the choice of reference spectrum (*i.e.* the radiant flux  $I_0(\lambda)$  received by the sample) is crucial to extract very low absorbance or transmittance values because real-time A-SEC imposes a single-beam scanning bench. In order to minimize the noise propagation, the radiant flux  $I_0$  must be at the steady state (*e.g.*  $I_0 = \text{an average of the first measured frames}$ ) and thus A-SEC experiments monitor an absorbance variation ( $\Delta A$ ) and not an absorbance value (*i.e.*  $\Delta A = \log(I/I_0) = A - A_0$  with  $A_0 = \text{absorbance at steady state}$ ). Consequently, an electrochemical consumption of a steady state species results in a negative absorbance and the generation of a redox species and products arising from redox reaction leads to a positive one.

Nowadays, a fine-tuned real-time spectroelectrochemical bench, equipped with the above mentioned instrumentations, allows monitoring optical spectra at high sampling rate (typically between 10 and 100 Hz at 100  $\text{mV} \cdot \text{s}^{-1}$  for CV experiments) with an experimental noise lower than 0.0005 (Figure 1).

**A-SEC of perylenediimide derivatives, a textbook case**

A perylenediimide (PDI) derivative, known to be an efficient redox chromophore, is suitable for illustrating the procedure for performing A-SEC on SAM. At this stage, it is worth remembering that, before probing an electroactive SAM by A-SEC, the molecule has to be studied first in solution.

In non-aqueous solvents, PDI derivatives exhibit two successive fully reversible one-electron processes in negative direction, absorb most visible light in the blue and green regions (*i.e.*  $\lambda_{\text{max}}$  between 450 and 500 nm with a  $\epsilon$  of *ca* 40 000 mol<sup>-1</sup>.L.cm<sup>-1</sup>) and produce a green light when excited at  $\lambda_{\text{max}}$  with a photoluminescence quantum yield close to 100 %. A-SEC in thin layer conditions at several scan rates and concentrations may help to check the absence of any homogeneous or heterogeneous reactions coupled to charge transfer while identifying the spectral signatures of the radical anion and dianion arising from the reduction of PDI in solution (Figure 2).[22,23]

Several synthesis steps are required to afford graftable PDI derivatives involved in the formation of PDI-based SAMs on Au substrates. Furthermore, the chemical and electrochemical stability of redox-responsive nanomaterials must be ensured to avoid any molecular desorption during A-SEC experiments. The absence of mass transfer by diffusion in SAM allow performing fast and reliable A-SEC experiments in a large range of scan rates and facilitates the monitoring of optical spectra of redox species and/or products arising from redox reaction. The sensitivity of CCD cameras and the high signal-to-noise ratio makes the derivative cyclic voltabsorptogram (DCVA) possible on SAM in a large range of surface coverage (Figure 3).[27]

The study of mixed PDI-based SAMs by A-sec revealed a Beer's law issue (Figure 4). The absorbance maxima of PDI species indeed varies non-linearly with surface coverage. In other words, the more the surface coverage increases, the more the absorbance deviates from Beer's law, which has been interpreted (but still not confirmed so far) by a surface coverage dependence of the tilt angle of PDI moieties, inducing a direction change of dipolar moments.[28]

Decreasing the number of PDI immobilized induced by the formation of mixed PDI-based SAMs provided an estimation of the detection limit (LOD) in absorbance value. According to the wavelength range (from 320 to 1650 nm) and the type of CCD camera (*i.e.* visible or NIR), the LOD-value varies between 10<sup>-5</sup> and 10<sup>-3</sup>.

The impact of nanoscale grafting such as the molecular structure change and/or an increasing of intermolecular interactions can be studied by comparing A-SEC data in solution with those of recorded on confined species. Hence, A-SEC performed on PDI-based SAMs did not provide evidence of significant spectral change for the confined PDI derivative and his reduced forms.

The grafting impact on the photoluminescence of PDI moieties has also been studied by E-SEC and, as expected, no light emission was detected because of a quenching of molecular fluorescence on Au substrate via an energy transfer (*i.e.* Förster resonance energy transfer).[26,27,29]

**Grafting impact on EDIM mechanism**

A-SEC at the nanoscale enables the study of the grafting impact on heterogeneous reactions coupled to charge transfer. In this context, the initial work aimed at probing the grafting impact on EDIM mechanism.

Some short thiophene or thienylenevinylene derivatives are known to produce a reversible dimerization of the radical cation, leading to a  $\pi$ -dimer. In non-aqueous solvents, fully reversible EDIM and EDIME mechanisms were established via an expected linear dependence of apparent potential with log (C) (*i.e.* a slope of +/- 29 mV/log unit at 293 K) and the equilibrium constant of dimerization ( $K_{\text{DIM}}$ ) is greater than 10<sup>4</sup>. Consequently, the absorption bands of cation radical and  $\pi$ -dimer were identified from a systematic A-SEC study as a function of concentration (Figure 5 A).[30-34]

A-SEC study of 5,5'-disubstituted-2,2'-bithiophene-based SAMs (*i.e.* EDIM mechanism) provided evidence of the  $\pi$ -dimer optical signatures, due to an expected increase of intermolecular interactions in confined nanometer-scale spaces (Figure 5 B).[35,36]

Electrochemical and spectroelectrochemical studies on mixed SAMs of a 2,5-bis(methylthio)-thienylenevinylene dialkyl disulfide derivative and dodecanethiol were provided to study the surface coverage impact on EDIME process.[37] In agreement with electrochemical simulations performed with KISSA-1D<sup>®</sup> software,[38] electrochemical data have suggested a conservation of EDIME process for immobilized molecules. Then, A-SEC studies have confirmed the predominance of  $\pi$ -dimer in a wide range of surface coverage (*i.e.* a dilution factor of 20). Nevertheless, the emergence of the signature of radical cation has been monitored at low surface coverage by chronoamperometry coupled to absorption spectroscopy.

These first results suggest that a SAM could be seen as a high concentrated solution but that is to be confirmed through studying various electrochemical mechanisms.

## Conclusion

Only a very few work are dedicated so far to real-time A-SEC on SAM in literature because such an equipment is very expensive and requires numerous repetitive and time-consuming fine adjustments. Nevertheless, a real-time A-SEC devoted to very low absorbance measurements is undoubtedly an asset for examining more thoroughly electrochemical mechanism in solution (*e.g.* see reference [39]) within redox-responsive materials (*e.g.* see reference [40]) or in surface-confined redox species [27,28,35,37] and it should facilitate the establishment of detailed structure-properties and structure-reactivity relationships at nanoscale. Lastly, it is important to bear in mind that a fine study of current-voltage characteristics, supported, where possible, by efficient electrochemical simulations (*e.g.* DigiElch or KISSA-1D<sup>®</sup>), should be initiated prior to performing A-SEC experiments on electroactive molecules in solution or on redox-responsive materials.

What about the real-time A-SEC future? The improvement in CCD cameras (*e.g.* deep depletion back-illuminated CCD cameras) and light sources (*e.g.* laser-driven light sources that enable extreme high brightness with a relatively flat spectrum, from UV to NIR) paves the way for better signal-to-noise ratios and smaller time scale monitoring in a few years. However, it is likely that signal processing will bring about a huge improvement. Indeed, rapid advances in facial recognition have enhanced the alternating least squares algorithm for principal components analysis, opening up a whole range of possibilities for extracting very weak spectroscopic signals from noise.[41,42]

## Acknowledgments

The authors thank Hellma<sup>®</sup> Analytics and Princeton Instruments companies for the quality of their products and their technical assistance and the "Contrat Plan État Région" 2007-2013 and 2014-2020 (Pays de la Loire, France, Europe) for the financial supports. The authors thank Yohann Morille for his expertise in Matlab<sup>®</sup> programming and Clément Cabanetos for his critical reading of the manuscript.

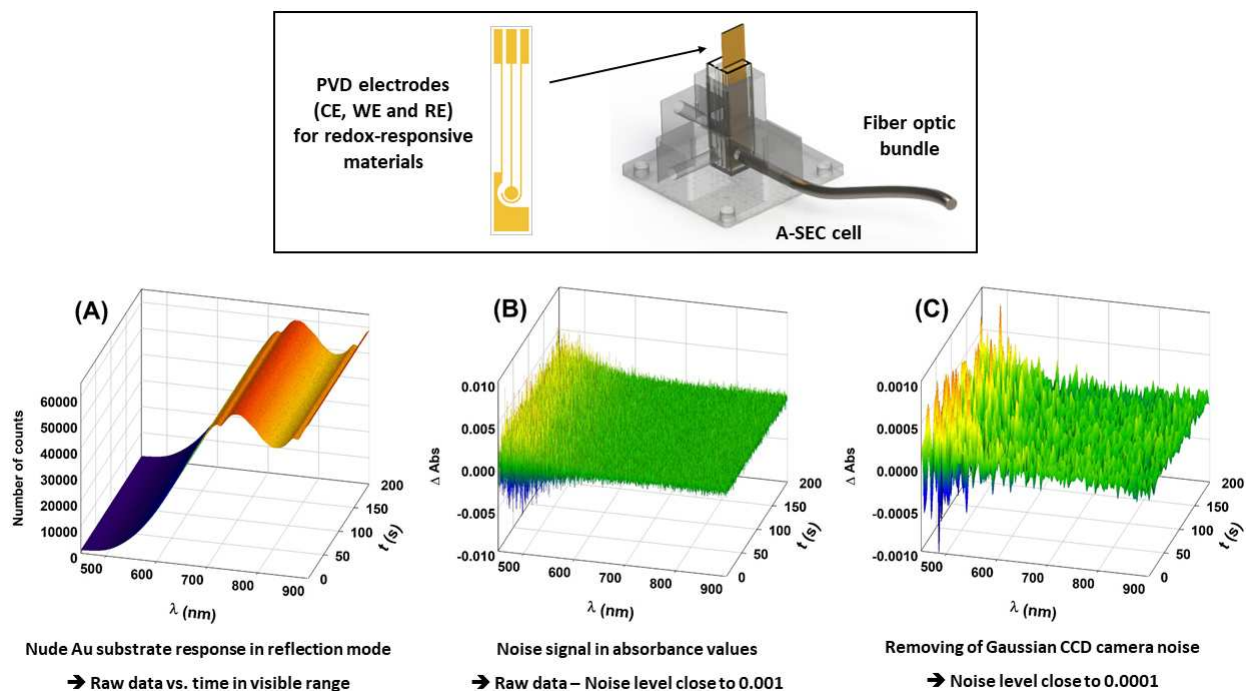


Figure 1. (Top) A-SEC cell dedicated to redox-responsive materials: Disposable electrodes are made by physical vapour deposition (PVD), leading to a reproducible geometry and a low roughness (*i.e.*  $R_a \approx 2$  nm). Produced by 3D-printer, the cuvette holder is designed to minimize the light signal attenuation and accommodate the electrode placement in the optical cuvette, thereby offering a perpendicular light path for reflection and fluorescence measurements. (Bottom) Repeatability of A-SEC bench on nude Au substrate versus time: the numbers of counts ( $I$ ) measured by the CCD camera are monitored over time (*i.e.* 200 s at a sampling rate of 100 Hz) in real-time A-SEC conditions (3D-graph A). Note that the number of counts depends on wavelength range. The values of the absorbance variation over the whole wavelength range (*i.e.* 450 - 900 nm) are calculated from the usual equation  $\Delta Abs = \log(I_0/I)$  with  $I_0$ , the average of all the frames. The noise level reaches a wavelength-dependent value close to 0.001 (3D-graph B). According to experimental data, the Gaussian noise can be removed via some specific 2-D convolution operators to reach a noise level 10 times lower than the previous one (3D-graph C). Note that the reliability and relevance of this procedure are highly dependent on the sensitivity CCD cameras, the quality of the calibrations and the maintenance of the A-SEC bench.



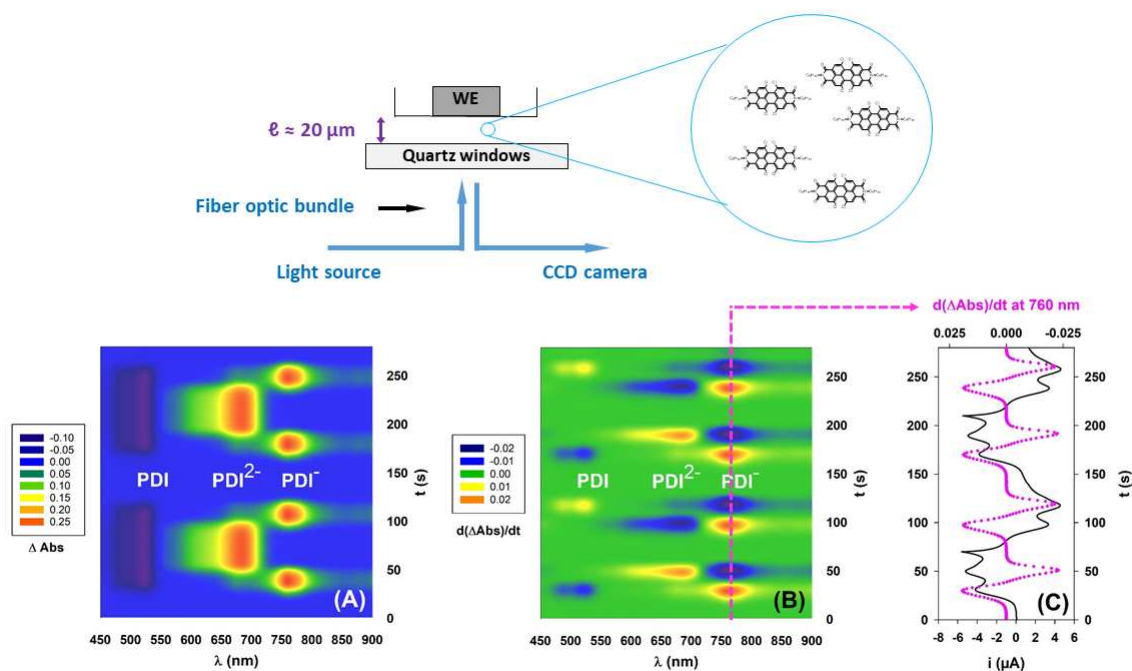


Figure 2. Schematic layout of real-time A-SEC in reflection mode for monitoring spectroelectrochemical behavior in solution (Top). In non-aqueous solvents, PDI derivative exhibits two successive reductions in thin layer conditions ( $l \approx 20 \mu\text{m}$ ,  $C = 1 \text{ mM}$  in  $0.1 \text{ M TBAHP/CH}_2\text{Cl}_2$  on Pt electrode at  $5 \text{ mV}\cdot\text{s}^{-1}$ ) (see 2D-graph C - current vs. time on two electrochemical cycles) and A-SEC response at a sampling rate of 5 Hz is displayed in 3D-graph A. Note that an electrochemical consumption of a steady state species leads to observe a negative absorbance and vice versa (Reminder:  $\Delta A = A - A_0$  and consequently  $d(\Delta A)/dt = d(A)/dt$ ). The first time derivative of the absorbance variation of A-SEC response (see 3D-Graph B) allows the extraction of all the derivative cyclic voltabsorptograms over wavelength (see, for instance, the extraction at 760 nm on 2D-graph C) and, thereby, facilitates an effective assignation of the optical bands monitored during the two reduction processes of PDI in solution.[22]

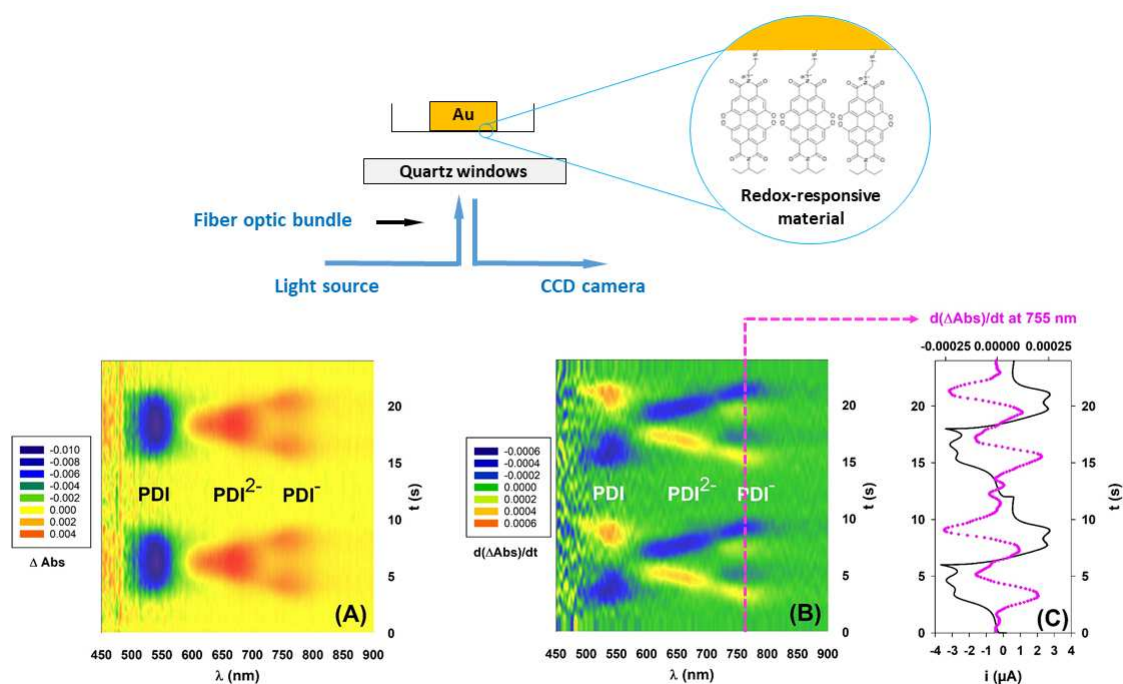


Figure 3. Schematic layout of real-time A-SEC in reflection mode for monitoring spectroelectrochemical behavior of surface-confined redox species (Top). In non-aqueous solvents, a PDI-based SAM exhibits two successive reductions ( $\Gamma \approx 2 \cdot 10^{-10} \text{ mol.cm}^{-2}$ , in 0.1 M TBAHP/ $\text{CH}_2\text{Cl}_2$  at  $100 \text{ mV.s}^{-1}$ ) (see 2D-graph C - current vs. time on two electrochemical cycles) and A-SEC response at a sampling rate of 100 Hz is displayed in 3D-graph A. Note that an electrochemical consumption of steady state species leads to observe a negative absorbance and vice versa (Reminder:  $\Delta A = A - A_0$  and consequently  $d(\Delta A)/dt = d(A)/dt$ ). As previously, the first time derivative of the absorbance variation of A-SEC response (see 3D-Graph B) allows the extraction of all the derivative cyclic voltabsorptograms over wavelength (see, for instance, the extraction at 755 nm on 2D-graph C) and, thereby, facilitates an effective assignation of the optical bands monitored during the two reduction processes. Note that a colour scale represents the 3D-graph Z-axis.[27]

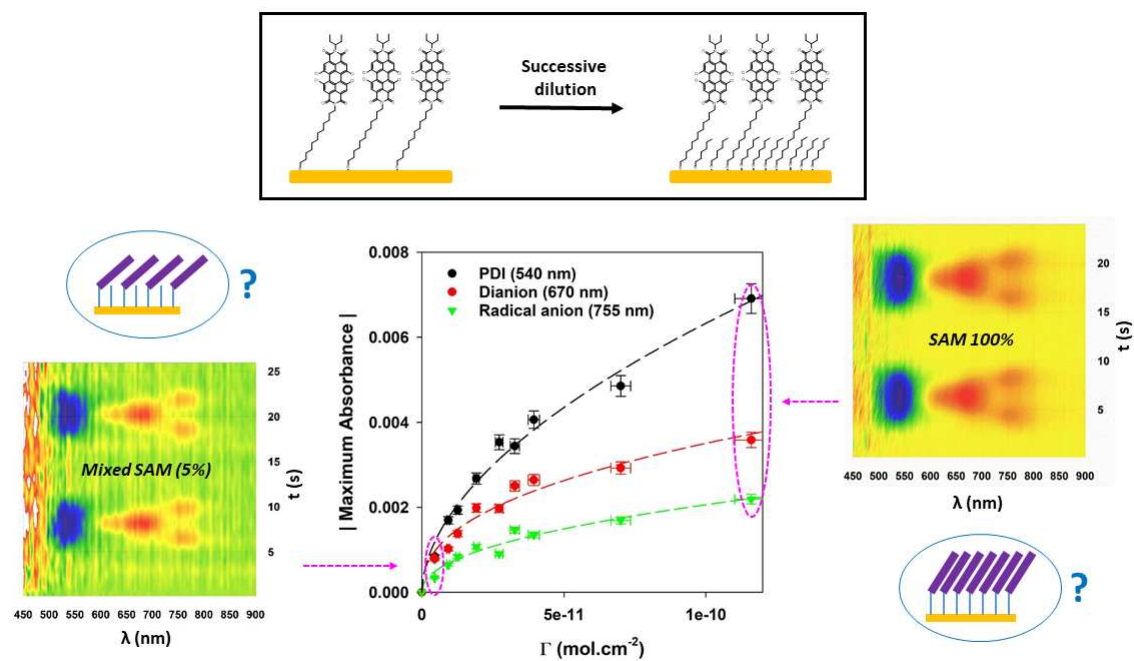


Figure 4. Maximum absorbance at 540, 670 and 755 nm have been extracted from A-SEC experiments of mixed SAMs in 0.1 M TBAHP/CH<sub>2</sub>Cl<sub>2</sub> at 10 mV.s<sup>-1</sup> and 303 K. The dash lines are trend curves. Note that the experimental absorbance values at 540 nm (*i.e.* DPI) are negative but they are displayed in absolute value. The extraction of the maxima at low surface coverage is the main drawback and the Levenberg-Marquardt least-squares minimization technique to fit absorption spectra is a successful way.[28]

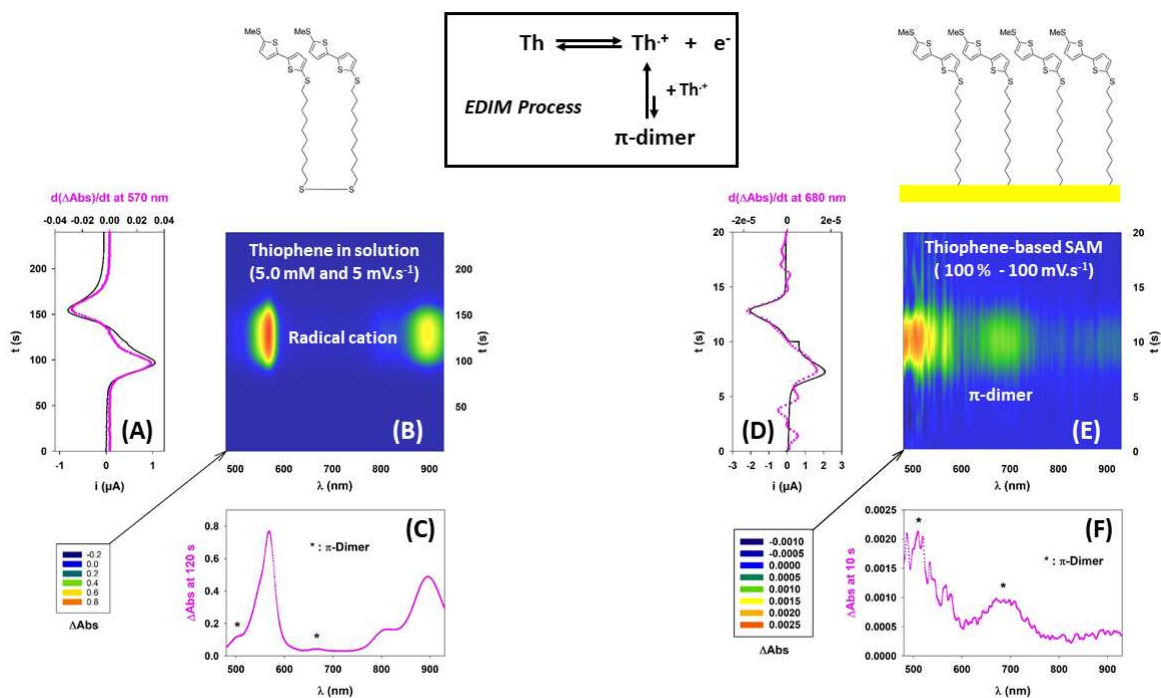


Figure 5. The electrochemical behaviour of a 5,5'-disubstituted-2,2'-bithiophene in 0.1 M TBAHP/ $\text{CH}_2\text{Cl}_2$  at 100  $\text{mV}\cdot\text{s}^{-1}$  on a Pt working electrode involves a EDIM process in positive direction (A and D), supported by a linear variation of the apparent potential with  $\log(c)$  (*i.e.* a slope of -29 mV/log unit). The invariance of apparent potentials with scan rate between 0.10 and 100  $\text{V}\cdot\text{s}^{-1}$  indicates that the dimerization equilibrium is fast. A-SEC experiment performed in solution and investigated at several concentrations does not provide a clear evidence of the development of the characteristic spectral features of the  $\pi$ -dimer in the visible region (B and C). A-SEC experiment on thiophene-based SAMs has shown that the confinement of thiophene moieties on Au-substrate favours intermolecular interactions and thereby the formation of  $\pi$ -dimer (E and F).[35,37]

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