# Electrochemically monitored fluorescence on plasmonic gratings: A first step toward smart displays with multiple inputs

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## ARTICLE INFO

## ABSTRACT

This paper describes one of the first examples of triple coupling between electrochemistry, fluorescence and plasmon resonance, through the investigation of the electrofluorochromic properties of a tetrazine derivative on gold plasmonic gratings used as working electrodes. Fluorescence enhancement is observed when the plasmon resonance band is excited and overlaps the emission of the fluorophore. The electrochemically driven fluorescence switch shows a similar trend as on a classical electrode when plasmon resonance is not excited, or when the fluorescence is recorded outside of the grating. A switch in the opposite direction is observed when the light is recorded on the gold nanoarray opening the way to smart multiple input devices.

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## 1. Introduction

There is a great interest in the research of new low energy consuming displays, as well as smart devices for information coding. Electrochemically monitored luminescence (called "electrofluorochromism") can be a valuable concept for both by enabling a voltage controlled light switch while maintaining the excitation source. A recent review reports the various ways to achieve this phenomenon [1]. From the instrumental point of view, the recent development of fluorescence microscopy in various modes (TIRF, confocal) and its coupling with an electrochemical cell has proven to be an expedient way to analyze the fluorescence behavior of various types of molecules or cells under electrochemical control [2–6].

On the other hand, plasmonics is also an interesting way to offer an external additional control on the luminescence properties. It is indeed well known that plasmon resonance arising from metallic nanoparticles or ultrathin metallic layers can either quench or enhance the luminescence depending on various parameters like spectral overlap, distance or relative positions of the associated dipoles [7–9]. Discrimination between quenching and enhancement cases can be rationalized using the concept of radiating plasmons and lead to the conclusion that small colloidal particles are usually quenchers because absorption is dominant over scattering, whereas larger particles made by physical means

(lithography, ion beam) may behave as enhancers [10]. This latter effect was developed in the frame of metal enhanced fluorescence (MEF) induced by various plasmonic systems based on metallic arrays [11,12], core–shell metal-dielectric nanoparticles [13] or quantum dots [14,15]. Hence a plamon-controlled fluorescence is likely to be observed especially when the emission spectrum of the fluorescent moiety matches the plasmon resonance band of the nano-object [16]. This concept finds several applications in biological issues where ultra-bright systems are of valuable interest.

On their own side, interplay between plasmonics and electrochemistry has been the subject of various studies from the pioneering work of Murray et al. on gold nanoclusters [17]. One of the challenges is among others to induce large shifts in the plasmon resonance which was accomplished using either large oxidation voltages [18] or the insulating-conducting transition in conjugated polymers [19,20]. These variations in the plasmon resonance may in turn induce a switch in the luminescence properties of interacting species [21]. However, there is almost no example of this triple electrochemical–fluorescence–plasmon coupling in the literature at that time, except one involving the luminescence of quantum dots coated on a plasmonic metallic layer whose potential was varied [22]. Only a few other recent examples of redox switch influencing the nanoparticle induced Raman enhanced response (SHINERS) are also worth mentioning [23].

In this paper, we present an example of such a coupling using gold nanodots gratings of various sizes obtained by electron beam lithography (EBL). EBL is now a widespread technique to build nanoarrays of plasmonic materials of various shapes on various substrates [24], since it was demonstrated that plasmon resonance

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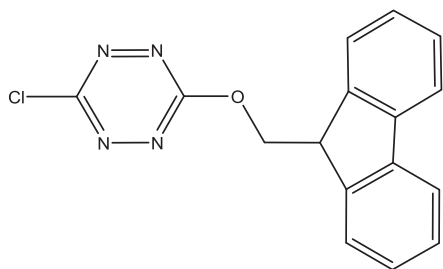
**Scheme 1.** Chemical formula of the tetrazine derivative used as an electrofluorochromic compound.

can be tuned according to the grating features (size and spacing) [25]. The luminescence and electrochemical behaviors analyzed in this paper are those of an electrofluorochromic compound, i.e. a dye whose luminescence can be reversibly tuned according to its redox state. We chose a tetrazine derivative for this purpose due to its unique photophysical properties [26] coupled to reversible reduction into a stable anion radical in an accessible potential range where the plasmonic gold nanoarrays are perfectly stable. The chosen compound (see Scheme 1) was synthesized by monosubstitution of (3,6)-dichloro-(1,2,4,5)-tetrazine by fluorenemethanol according to a previously published protocol [27]:

This compound was selected in the now widespread family of accessible tetrazine derivatives due to its emission wavelength (see below) that is likely to match the plasmon resonance of the gold gratings used. Moreover, like most chloroalkoxytetrazines, this molecule is reversibly reduced into its anion radical in acetonitrile at a potential of ca. $-0.8\,V$ vs. $Ag^+/Ag$. Thus it is expected that its fluorescence might be reversibly tuned when applying potential steps surrounding this value.

The set-up used to investigate this electrofluorochromic behavior is an epifluorescence microscope coupled to an electrochemical cell with a stationary white light excitation, instead of the laser source used in similar studies [3,4,28]. In the first part, the electrofluorochromic behavior of the dye is analyzed on a 'classical' platinum working electrode. Then the same properties are investigated but with the plasmonic electrode made of the gold nanoarray to highlight the crucial role of the plasmon resonance on the electrofluorochromic response.

## 2. Experimental

The synthesis of the selected fluorophore is described elsewhere [27]. Its photophysical and electrochemical properties are displayed in Supplementary Information. The maximum absorption and emission wavelengths in acetonitrile are equal respectively to 511 and 553 nm. The emission spectrum was checked in a quartz cuvette with a Horiba spectrofluorimeter (Fluorolog 3) prior to the electrofluorochromic measurements.

All the experiments are performed with a 0.7 mM solution of the fluorophore in acetonitrile (SDS, spectro grade) with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, puriss.) as the supporting electrolyte. Solutions are deaerated by argon bubbling for 5 min before starting the experiments. The CV recorded on a platinum disk electrode (1 mm diameter) is shown in Supplementary Information and displays a fully reversible wave at a standard potential of $-0.84\,V$ vs. $Ag^+/Ag$.

The working electrode is either a microscope coverslip (170 μm) coated with a thin (ca. 25 nm) platinum layer in the first part, or an ITO coverslip (ca. 400 μm thin) coated by the gold nanodots in the second part (see details below). Counter and pseudo-reference electrodes are Pt and Ag wires respectively. The home-made cell containing the electroactive fluorophore is connected to a potentiostat (CHI600, CH Instruments).

The gold nanodots are made by EBL according to the following procedure: first, the ITO surface was covered with a positive resist (PMMA) by spin coating. Lithography system (NPGS© control coupled to a Zeiss SUPRA 40 Scanning Electronic Microscope) was used to design the array of gold nanodots. After development a thin gold layer was deposited onto the PMMA-ITO substrate with a Plassys MEB550S metallic evaporator, followed by a lift-off procedure. The footprint of each array is $80\,\mu m \times 80\,\mu m$. The diameter of each nanodot is either 160 or 200 nm, with a 50 nm height. The spacing between the nanodots in each grating is 400 nm. The plasmon resonance maximum wavelength is checked in air by recording the absorption spectrum with a HR4000 Ocean Optics spectrophotometer coupled to an Olympus BX51 optical microscope.

The epifluorescence microscope used in the electrochemically monitored luminescence study is an inverted microscope (Nikon, Ti-U) equipped with either a $100\times$ objective (numerical aperture NA: 1.49) for TIRF, or a $40\times$ objective (numerical aperture: 0.75) for direct excitation measurements. Excitation can be injected either perpendicularly to the substrate (direct excitation) or with a large angle through the high NA objective to induce total reflection at the solution interface (TIRF excitation mode [29]). The set-up is similar to the already published one [3] except the excitation source, which is a white mercury lamp (130 W) emitting from 300 to 700 nm. Wavelength selection is operated through filters and a dichroic mirror. The spectral features of the lamp and filters used are shown in Supplementary Information. Their emission and transmission spectra are acquired with a UV–vis Spectrometer SD2000 (5 nm (FWHM) resolution) from Ocean Optics coupled with the microscope by a P600 UV–vis optical fiber (300–800 nm, NA 0.22, 600 μm) with a direct spatial filtering in the image space. Note that the electrofluorochromic experiments on plasmonic gratings are performed without excitation filter.

The fluorescence intensity is recorded by a single photon avalanche diode (MPD-CCTC Single Photon Counting APD from Picoquant) coupled to the microscope by a Multimode Fiber GI
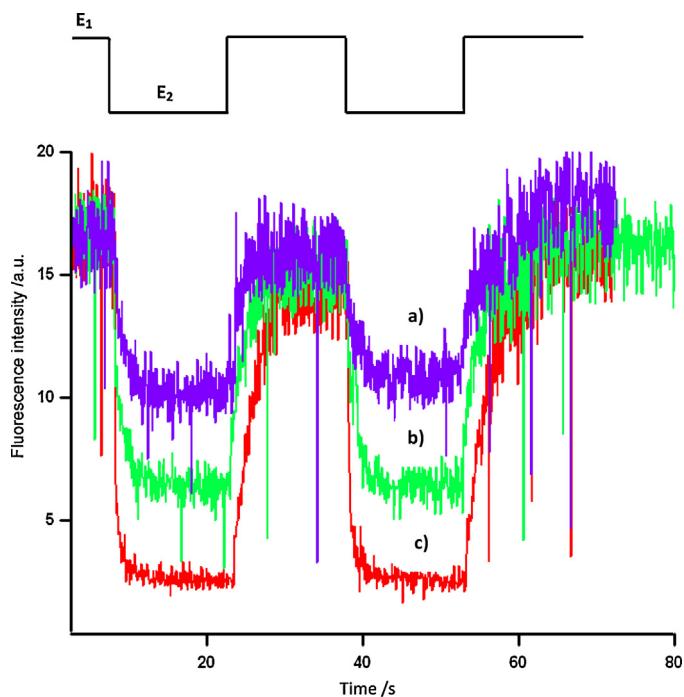


**Fig. 1.** Fluorescence intensity of the tetrazine derivative (3 mM in acetonitrile + TBAPF$_6$) upon potential steps from $E_1 = 0\,V$ to the following values $E_2$ (in V vs. Ag): (a) $-0.6$, (b) $-0.8$, (c) $-1.0$. TIRF excitation with a mercury lamp (300–700 nm). Excitation filter: $482 \pm 35$ nm. Emission recorded through a long pass filter (see Supplementary Information 1 for the spectral features of the filters used).