



Comparison of fluorescence and QCM technologies: Example of explosives detection with a π -conjugated thin film

Simon Clavaguera^{a,b}, Pierre Montméat^{a,*}, Frederic Parret^a, Eric Pasquinet^a, Jean-Pierre Lère-Porte^b, Lionel Hairault^a

^a CEA Le Ripault, SMEO, BP 16, 37260 Monts, France

^b Laboratoire AM₂N, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

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ABSTRACT

A π -conjugated compound was synthesized as a sensitive material for explosives detection. The detection of vapors of 2,4-dinitrotoluene was demonstrated with quartz crystal microbalance (QCM) and fluorescence transduction methods. The fluorescence intensity monitoring shows a higher sensitivity and selectivity than the monitoring of the QCM frequency. Both methods appear to be synergic when used simultaneously as the sensor helps to discriminate interferent vapors from nitroaromatics.

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1. Introduction

Chemical sensors have been widely exploited over the past 15 years for the detection and the quantification of minute traces of explosives [1,2]. An effective approach for the unambiguous detection and identification of analytes such as volatile organic compounds is the multi-component sensing where several independent parameters of a sensitive layer are monitored and analyzed simultaneously. The most efficient option is to use separate transducers for the recording of orthogonal physical properties of one sensitive layer [3–5].

However, in the field of explosives identification and more particularly for the detection of nitroaromatic compounds (NACs), single-component sensing methods have only been described [1,2].

Among them, detection methods using piezoelectric transducers like quartz crystal microbalance (QCM), [6–11] surface acoustic wave device [12–14] or microcantilever [15,16] have been reported for vapour phase detection. Nevertheless, the method of choice for detecting minute traces of nitroaromatics is fluorescence quenching in regard to the extremely high sensitivity of this method

[17–19]. π -Conjugated compounds have received a great deal of attention as fluorescent chemosensors for NACs detection [20–23].

Single-component sensing methods might be an issue considering the importance of the high selectivity required for on-site monitoring devices. The humidity and also the presence of interferents have to be taken into account in order to distinguish their response from the NACs signature.

We report herein a new detection method to discriminate interferents (i.e. solvents) from target response using the same sensitive coating. Explosives sensor performances can be improved with the simultaneous monitoring of the fluorescence intensity of a sensitive coating deposited on a QCM and its resonance frequency. Compound **1** is a π -conjugated molecule sensitive towards NACs via fluorescence quenching. An original experiment based on the monitoring of the fluorescence intensity emission and the frequency of the QCM on which compound **1** was deposited onto was built to compare both detection technologies (i.e. QCM and fluorescence) and also to enhance the selectivity of this multisensory device (Chart 1).

2. Experimental

2.1. Synthesis of π -conjugated compounds; sensitive material

The synthesis of **1** is out-lined in Scheme 1 and the synthetic route is described in detail below.

Abbreviations: QCM, quartz crystal microbalance; NACs, nitroaromatic compounds; DNT, 2,4-dinitrotoluene; MEK, methylethylketone; TBAPF₆, tetrabutylammonium hexafluorophosphate.

* Corresponding author. Tel.: +33 2 47 34 56 79; fax: +33 2 47 34 51 42.

E-mail address: pierre.montmeat@wanadoo.fr (P. Montméat).

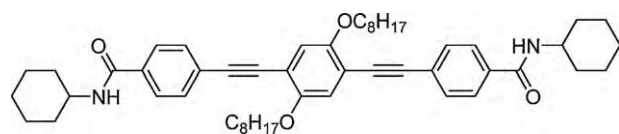


Chart 1. Molecular structure of compound 1.

The synthesis of intermediate **3** has been previously described [24].

2.1.1. 4-Nitrophenyl-4-iodobenzoate (**2**)

p-Nitrophenol (1.39 g, 0.01 mol) was dissolved in 25 mL THF, then 1.4 mL triethylamine (0.01 mol) were added. 4-Iodobenzoic acid chloride (2.19 g, 0.01 mol) dissolved in 15 mL THF was poured dropwise. The reaction mixture was filtered after 4 h stirring at room temperature. After concentration, the product was recrystallized from THF/pentane and gave **2** as a white powder (75%). ¹H NMR (CDCl₃, 400 MHz) δ(ppm) 7.41 (m, 1H), 7.90 (m, 2H), 8.32 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ(ppm) 102.5, 122.6, 125.32, 128.0, 131.6, 138.2, 145.6, 155.5, 163.8; IR (KBr pellet) ν(cm⁻¹) 3113, 3084, 1737, 1615, 1588, 1514, 1488, 1351, 1263, 1212, 1177, 1067, 1008, 878, 859, 740, 674.

2.1.2. 4,4'-(2,5-Bis(octyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)bis(*N*-cyclohexylbenzamide) (**1**)

Pd(PPh₃)₄ (46 mg, 0.04 mmol), CuI (8 mg, 0.04 mmol), compound **2** (738 mg, 2 mmol) and compound **3** (383 mg, 1 mmol) were introduced in a schlenk tube under nitrogen. 40 mL THF and 20 mL triethylamine were added. After 2 days stirring at room temperature, the reaction mixture was filtered and concentrated. The intermediate is precipitated from CH₂Cl₂ with pentane. That compound is solubilized with 30 mL THF in a 50 mL round-bottom flask. Then, cyclohexylamine (0.2 mL, 2.6 mmol) were added. After one night stirring at room temperature under nitrogen, the product precipitates. After washing with THF, **1** was obtained as a yellow solid (28%). ¹H NMR (DMSO-*d*₆, 250 MHz) δ(ppm) 0.83 (m, 6H), 1.2–1.9

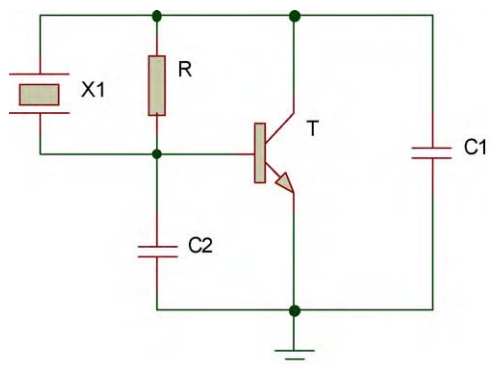


Fig. 1. Schematic diagram of the QCM.

(m, 44H), 3.80 (m, 2H), 4.07 (m, 4H), 7.19 (s, 2H), 7.57 (d, 4H, *J* = 7.7 Hz), 7.90 (d, 4H, *J* = 7.7 Hz), 8.18 (s, 2H); IR (KBr pellet) ν(cm⁻¹) 3292, 2924, 2854, 2066, 1630, 1535, 1511, 1468, 1415, 1330, 1216, 1153, 1062, 853, 770.

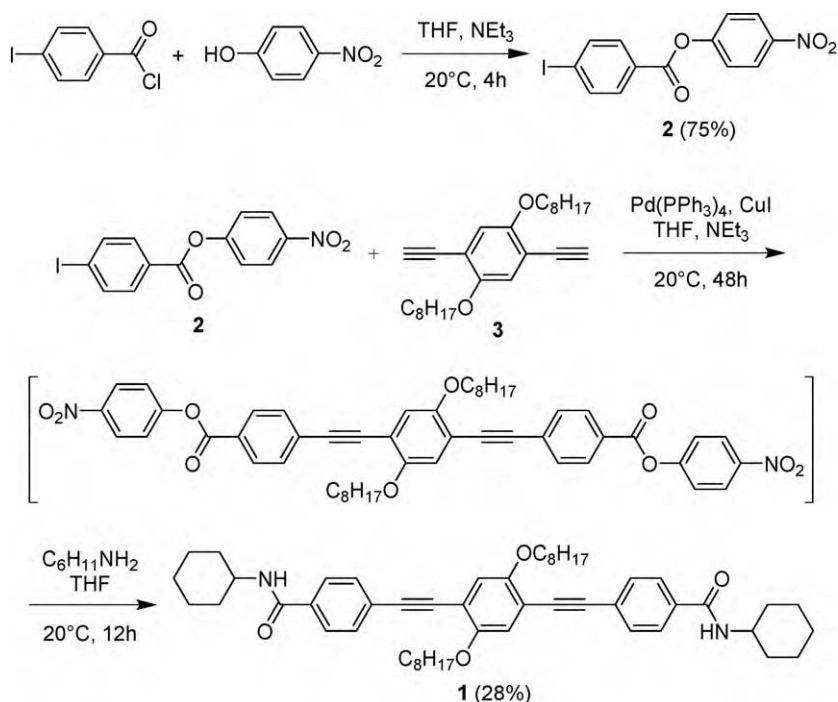
2.2. Sensors preparation

All the solvents (analytical grade) were purchased from Sigma–Aldrich. They were used without any further purification. The 2,4-dinitrotoluene (DNT) was purchased from Sigma–Aldrich and used after recrystallization in dry ethanol.

The piezoelectric crystals (Fig. 2) used were 9 MHz AT-cut quartz crystals (polished surface) with gold-plated metal electrodes on both sides (AMETEK, model QA-A9M-AU M). One side of a 9 MHz quartz microbalance was coated with the sensitive material.

In order to satisfy the Barkhausen criterion, the quartz crystal resonator was inserted in an electronic oscillator loop (Fig. 1). This electronic feedback was a typical Colpitts oscillator based on transistor built in common emitter.

The measurement oscillator frequency was achieved by a frequency counter with an accuracy of ±1 Hz. For the piezoelectric quartz used herein, the Sauerbrey equation [25] was defined



Scheme 1.

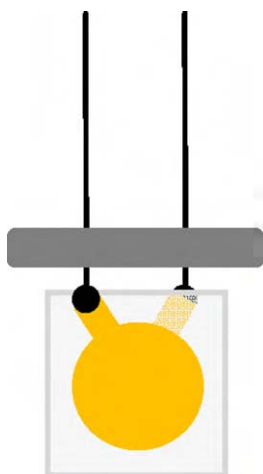


Fig. 2. Quartz crystal microbalance: 9 MHz AT-cut quartz crystals with gold-plated metal electrodes on both sides.

according to Eq. (1):

$$\Delta m = -0.44 \times 10^6 \times A \times \frac{\Delta F}{F_0^2} \quad (1)$$

where Δm is the adsorbed mass in g; ΔF is the frequency shift in Hz; F_0 is the fundamental frequency of the quartz: 9×10^6 Hz; A is the total sensitive surface of the electrodes: 0.39 cm^2 . The constant 0.44×10^6 has units of g Hz cm^{-2} .

The sensitive layers were prepared by spray coating using dilute solution of compound **1** in THF (5 mg/mL). The dilute solution was filtered, introduced in the spray coating instrument (Dosage 2000 – FRANCE) and deposited onto the substrates. The spray coating instrument was calibrated to yield approximately 5 kHz QCM frequency shift (equivalent to $10 \mu\text{g}$ deposition according to Sauerbrey equation) on QCM substrate with twenty pulses.

The substrate used for fluorescence experiments was a quartz substrate (Thuét Biechelin – France) $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$.

2.3. Tests of detection

2.3.1. Detection with the single QCM

The detection performances of the coated piezoelectric quartz crystal were tested with DNT at room temperature. The interferents were chosen as representatives of a broad range of chemicals: chloroform, dichloromethane, ethanol, methylethylketone and toluene. During the exposure, the QCM was located in the upper part of a flask containing the analyte or the interferent. As a result, the partial pressure of the chemical in the headspace of the flask was closed to the vapor pressure of each compound at 25°C (Table 1).

During a typical experiment, the QCM was exposed to ambient air, organic vapors for 10 min and again ambient air. This procedure was repeated for every compound and the sensor response as a function of time was expressed as a frequency shift $\Delta F(\text{vapor})$ in Hz for a 10 min exposure. To investigate the selectivity and to compare the sensor output, for each vapor, the sensor response was

Table 1
Vapor pressure of DNT and interferents [26,27].

	Vapor pressure at 25°C in ppm
2,4-Dinitrotoluene (DNT)	0.28
Chloroform (CHCl_3)	262,000
Dichloromethane (CH_2Cl_2)	526,000
Ethanol (EtOH)	79,000
Methylethylketone (MEK)	132,000
Toluene	20,000

assessed from the frequency shift divided by the vapor pressure of the analyte used.

2.3.2. Detection with the single fluorescence sensor

The detection performances of the fluorescence sensor were investigated for the same targets (DNT, dichloromethane, ethanol, methylethylketone and toluene). The experiments were performed at a constant temperature (i.e. 20°C) on a Fluoromax 3 spectrofluorometer (Jobin Yvon) with a specific airtight chamber designed specifically for our purpose. This instrument allows the placement of the sensor under controlled atmosphere (air, DNT or interferents) and measures the fluorescence emission at $\lambda_{\text{em}} = 460 \text{ nm}$ of the thin film as a function of time when excited at $\lambda_{\text{ex}} = 410 \text{ nm}$ (Fig. 3).

The 300 mL chamber was connected to a digitally controlled system providing the possibility to inject the desired gas at variable concentrations with a 330 mL/min flowrate. Dry air and solvent vapors calibrated at 100 ppm in dry air were purchased in gas cylinder from Air Liquide.

DNT charged airflow is generated by passing dry air over the headspace of DNT powder (Fig. 4). A recirculating chiller that pumped water through water-jacket around the chamber regulated the temperature to $20 \pm 0.1^\circ\text{C}$ in order to produce a stable concentration of DNT in air. The DNT vapor concentration was estimated to be around 120 ppb in air from bubbling experiments through acetonitrile solution trap. During a typical experiment, the sensor response was first monitored under air, then under DNT or solvent vapors for 10 min and then air again.

2.3.3. Simultaneous detection with the QCM and fluorescence sensor

The sensitive material was deposited onto a QCM positioned in the center of the chamber described in Fig. 4. The QCM was oriented accurately in order to maximize the fluorescence emission intensity. Electrical connexions have been added to the airtight chamber in order to connect the QCM to the oscillating circuit and to measure the frequency (Fig. 3). During a typical experiment, two orthogonal sensor responses were monitored simultaneously (i.e. frequency and fluorescence intensity at $\lambda_{\text{ex}} = 410 \text{ nm}$ and $\lambda_{\text{em}} = 460 \text{ nm}$) from the coated QCM.

2.4. Cyclic voltamperometry measurement

Electrochemical measurements were performed with a standard three-electrode system consisting of a Pt working electrode, a Pt wire counter electrode, and an Ag/Ag^+ reference electrode in a 0.1 M TBAPF₆ solution made with freshly distilled acetonitrile.

3. Results and discussion

3.1. Detection with the single QCM

The sensitive layer mass change upon exposure to analyte vapors is exploited in electronic olfactory systems based on QCM sensors [6]. The analyte sorption on the sensitive overlayer deposited onto the quartz crystal causes its mass changes and, in turn, changes in the fundamental oscillation frequency F_0 , in accordance with the Sauerbrey Eq. (1) [25].

The frequency of a $10 \mu\text{g}$ coating of compound **1** decreased slowly when exposed to a saturated vapour pressure of DNT (280 ppb). A 70 Hz frequency shift was noticed for 10 min exposure (Fig. 5a). The reversibility was then investigated under air. 70% of the initial signal is recovered after 10 min under air.

QCM frequency changes upon exposure to solvent vapors are illustrated in Fig. 5b. The tendency of the sensor response when exposed to organic vapors was a sharp decrease of the quartz

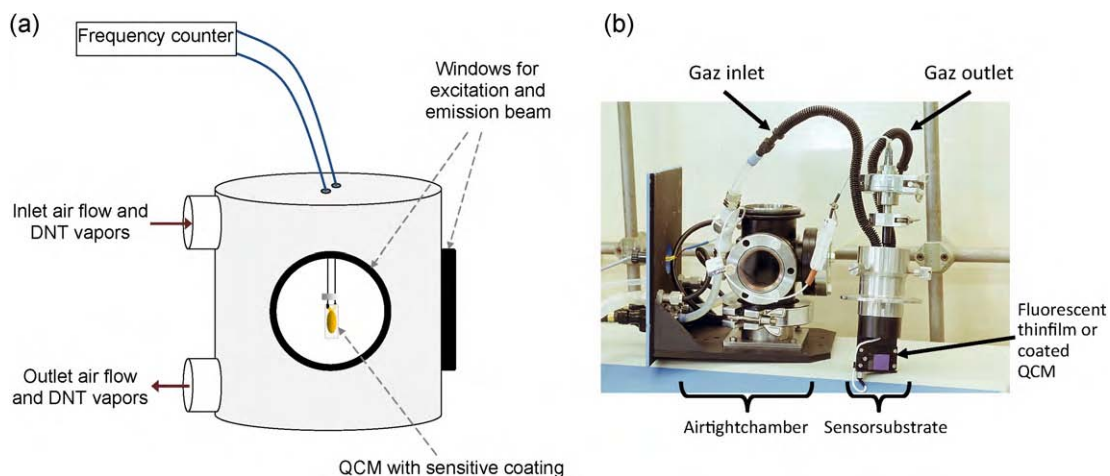


Fig. 3. (a) Schematic of the airtight chamber allowing the simultaneous measurement of the fluorescence intensity and QCM frequency of the sensor in a controlled atmosphere. (b) Picture of the opened cell with the sample holder out of the airtight chamber.

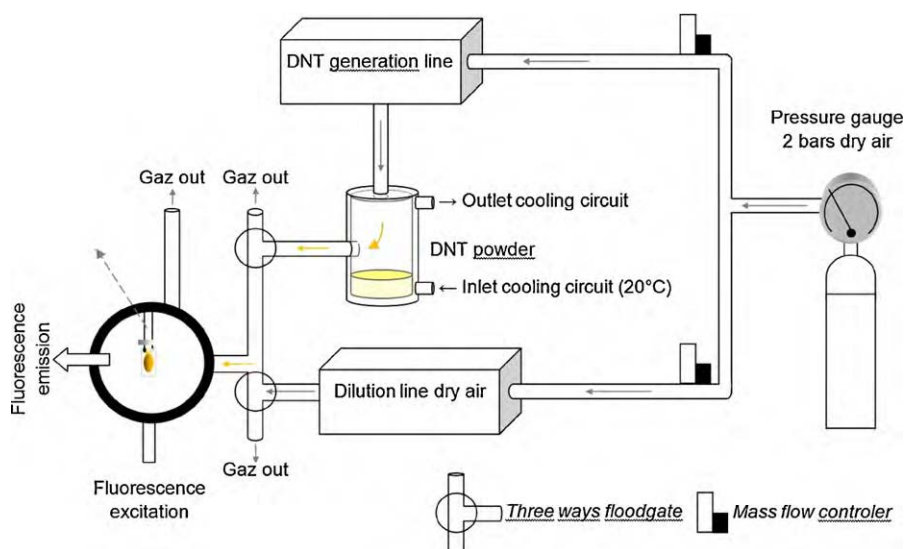


Fig. 4. Schematic diagram of the experimental setup for the DNT sensing.

vibration frequency. The reversibility was also satisfactory with a complete recovery of the initial vibration frequency of the device within few seconds after the end of the exposure. Chloroform (CHCl_3) produced the highest frequency shift (540 Hz) while dichloromethane (CH_2Cl_2), toluene and ethanol (EtOH) exposures gave respectively 350, 320 and 200 Hz. The lowest frequency shift was observed for the methylethylketone (MEK) exposure: 200 Hz. It has to be noted that a 10 min exposure of uncoated quartz to every

vapors (DNT and interferences) was evaluated and a slight decrease inferior to 2 Hz was recorded for every vapor. Therefore, the sensitivity of the device is inherent to the coating of compound **1** on the quartz.

As defined below, the response for each exposure to DNT or interferences are presented in Table 2. The DNT response was the highest one: 230 Hz/ppm. The responses obtained for the other organic solvents were inferior to 0.01 Hz/ppm.

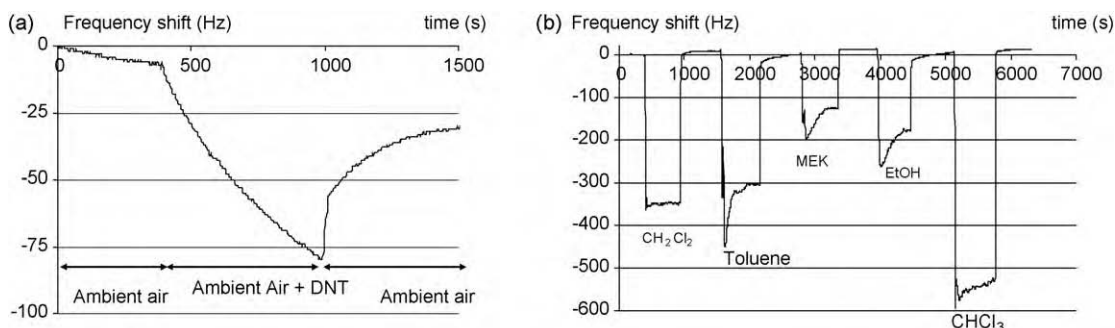


Fig. 5. Frequency of the QCM as a function of time (a) with a 10 min DNT exposure (280 ppb); (b) with a 10 min interferences exposure (vapor pressure).

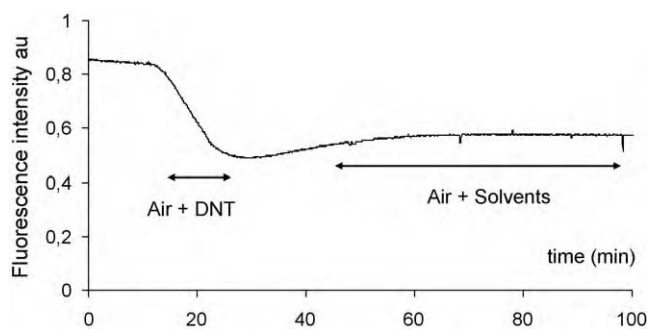


Fig. 6. Fluorescence emission intensity as a function of the atmosphere of the sensor.

Since the exposure of vapors of DNT on the coated QCM produced a significant response (up to 70 Hz), the material could be considered as a sensitive coating to DNT and its family the nitroaromatic compounds at a larger extent. The adsorption process on the solid appeared to be very slow, which might indicate that the detection of the nitroaromatic involves not only a surface process but also bulk diffusion which is not the case with solvent exposure and their U-shaped response. The moderate reversibility of the process was the consequence of weak interactions (i.e. π -stacking) in the bulk of the coating between the nitroaromatic and the sensitive material. The response of the sensor after solvent exposure was also significant (>100 Hz for each interferent). The adsorption and desorption processes, in that case, were very fast (i.e. U-shaped response), which might indicate that the detection process only involve weak interactions at the surface. The response values (Table 2) pointed out a very large selectivity of the coating to DNT with regards to other organic vapors at a same concentration in air. The response of the sensor to the nitroaromatic compound was at least four orders of magnitude larger than that observed for the solvents. This specificity was a consequence of the undergoing π - π interactions between the electron-deficient DNT and the electron-rich aryl rings of the sensitive compound **1** in the bulk of the coating. Hydrogen bond between the amide NH and the oxygen lone pairs of the DNT nitro substituents might also act as a favorable interaction to bind DNT to the sensitive coating.

QCM experiments have demonstrated the very large affinity of the sensitive material for the adsorption of DNT. The effects of the adsorption of various vapors on the fluorescence of the sensor were also investigated in order to study the synergy of QCM and fluorescence transductions.

3.2. Detection with the single fluorescence sensor

Fluorescence monitoring as a function of time of the sensitive coating under various atmospheres is depicted in Fig. 6. Under interferent vapor exposure, the fluorescence emission of the thin film remained constant, meaning the coating is not sensitive to those solvent vapors via fluorescence transduction. On the contrary, the device shows a clear sensitivity towards NACs as the fluorescence intensity decreases by 15% within 10 min of exposure to 120 ppb of vapors of DNT.

Table 2

Compound **1** response towards various organic compounds.

Vapor	QCM frequency in Hz	QCM response in Hz/ppm
DNT	70	230
CHCl ₃	540	0.002
CH ₂ Cl ₂	350	0.002
EtOH	200	0.003
MEK	130	0.001
Toluene	320	0.009

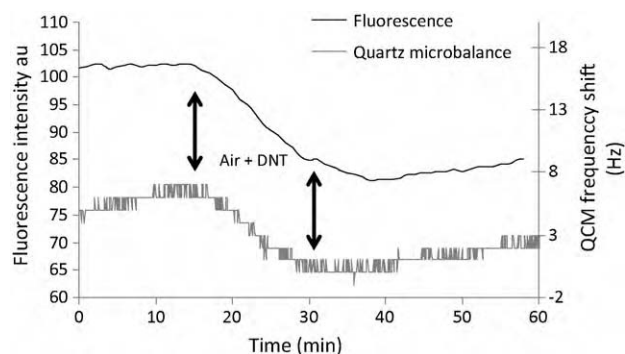


Fig. 7. Simultaneous monitoring of the fluorescence intensity and the QCM frequency of the same substrate coated with **1**.

The fluorescence quenching of a thin layer of **1** by DNT vapor can be attributed to a photoinduced electron transfer from the electron-rich sensitive material to the electron-deficient analyte. Sensing largely relies upon the relative redox potentials of the ground-state analyte (low-lying LUMO) and excited-state fluorophore (high energy SOMO*) [19,20]. HOMO and LUMO levels of the sensitive compound **1**, determined by cyclic voltammetry to be respectively, at -5.62 eV and -2.59 eV, compared with the DNT LUMO level at -3.60 eV, are consistent with the aforementioned photoinduced electron transfer. Mechanism of fluorescence quenching by rotational relaxation induced by solvent vapor molecules [28] and by hydrogen bonding [12,29] are not occurring because the fluorescence intensity remained stable in the presence of solvent vapors. As a consequence, the fluorescence transduction technique shows a strong sensitivity and a high selectivity of the sensitive coating towards vapors of DNT. The sensitivity of the thin film was then monitored towards vapors of DNT with two different transduction techniques in order to study their synergy simultaneously.

3.3. Simultaneous detection with the QCM and fluorescence sensor

Adsorption and fluorescence quenching measurements have been performed simultaneously by exposing the QCM sensor to vapors of DNT within a spectrofluorimeter. The results obtained are depicted in Fig. 7, where the responses of both acoustic and optical transducers are reported.

Accordingly to the previous experiments with QCM transduction, the vibration frequency of the coated QCM was decreasing under exposure of 120 ppb vapors of DNT. At the same time, a decrease in fluorescence emission intensity is also monitored. This experiment shows that while the sensitive coating mass is loaded by DNT, the fluorescence of the thin film is consequently quenched. After 15 min under DNT, the frequency shift was 5 Hz, and 13% of fluorescence quenching was observed. The slightest signal which could be detected by the QCM device or by the fluorescence system was 2 Hz and 2%, respectively. Thus the ratio signal/noise for DNT vapors was 2.5 for QCM and 6.5 for fluorescence sensor. The fluorescence sensor was thus much more sensitive than the QCM sensor.

This synergic approach can be helpful to first discriminate interferents (moisture, vapors of solvents) from nitroaromatics and also to investigate the fluorescence response of the sensor in a complex mixture of vapors of nitroaromatics and interferents solvents. Nitroaromatic explosives can be detected with QCM and fluorescence sensors while solvents can be detected only with the QCM sensor.

4. Conclusion

The use of an original π -conjugated compound has been evaluated as nitroaromatic multi-component sensor with the simultaneous QCM frequency and fluorescence intensity monitoring. Both transduction methods taken separately present drawbacks and advantages, but they are synergic when monitored at the same time. Hence, the fluorescence sensors based on this material has exhibited a perfect selectivity towards DNT, when common solvents are used as interferents. The fluorescence sensor appears to be much selective and sensitive than a QCM sensor. However, the correlation between acoustic and optical sensors data could be very useful in order to enhance the features extraction from a hybrid system employing complementary transducers by mean of pattern recognition methods. We foresee a growing interest in the development of such a synergic approach where selectivity and sensitivity can be enhanced allowing the discrimination of interferent vapors to analyte response (i.e. minute traces of explosives in polluted air).

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