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Study of calixarenes thin films as chemical sensors for the detection of explosives

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ABSTRACT

Calix(n)arenes ($n = 4$, 6, 8) are used as sensitive coatings for Quartz Crystal Microbalance (QCM)-based chemical sensors, and specially for the detection of dinitrotoluene as a model explosive molecule. Calix(n)arenes complex organic architectures were deposited by spray on gold-coated wafer surfaces, and DNT detection tests were performed by measuring both frequency changes and IR spectra during exposure to DNT vapours. The adsorption of DNT on calixarenes surface is proved by Polarisation Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) experiments, which brings a chemical characterisation of the sensing surfaces. Kinetics of interaction of DNT with the surface was measured by QCM. When deposited onto QCM, calixarenes showed an excellent sensitivity to DNT vapours; no significant effect of the size of the cage was observed.

The main drawback is the poor reversibility of these sensors, possibly due to a too strong interaction of dinitrotoluene inside the cage of the calixarenes, or to a loss of the ternary structure of these molecules, which in turn induces a loss of interaction strength with host molecules.

1. Introduction

With the increased use of explosives in terrorist attacks, law enforcement agencies have to face the problem of detecting hidden bombs in luggage, cars and aircrafts. Because of the million unexploded landmines, another concern involving explosives is the detection of contaminated land mines. For these reasons, the development of efficient, portable and low-cost explosive detection devices has become an urgent worldwide issue.

In recent years there has been a growing interest in quartz crystal microbalance (QCM) set-ups, not only as highly sensitive and selective detectors of various pollutants (like explosives vapour) but also as simple, low cost and portable devices which are even small enough to be carried in a worker's pocket. QCM sensors consist of a piezoelectric quartz crystal on which is deposited a sensitive and selective coating that serves as an adsorptive surface. The QCM possesses a natural resonant frequency that is disturbed by any mass change occurring, such as the adsorption of molecules, onto the coating. The frequency shift in the resonant frequency is used as the sensor output. In chemical gas sensors, the vibration frequency decreases because a gaseous pollutant is selectively adsorbed by a coating on the crystal [1]. The decrease in frequency is proportional to the increase in mass due to the presence of gas adsorbed on the coating.

The detection of explosives such as nitroaromatic compounds with QCM has been widely studied [2–10]. From these studies, it appears that the coating of organic molecules, constituting a strongly adsorbing material, is the most promising technology.

As example, the detection of nitrobenzene over the range 2–10 ppm (parts per million) was demonstrated to be efficient by thin films of amine derivatives [8]. Host-guest chemistry has also been widely studied for detecting nitroaromatics. The first study, dealing with the behaviour of epoxyoctacosahydrocyclacene [2], reported that a selective detection of nitrotoluene and nitrobenzene could be achieved with such a macromolecule. Cavitands [5] have also been assessed as coatings for the selective detection of nitrobenzene with respect to other aromatic vapours. Finally, the selective detection of other nitroaromatics has been achieved with specific thiols [6] or metalloporphyrins [4].

The coatings of thin films of polymers have also been investigated. First of all, commercial polymers were screened for their ability to adsorb dinitrotoluene [3]: polymethacrylate has been found to be the best candidate compared to polystyrene. Various studies investigated the detection of nitrotoluene. The first two studies pointed out the interest of polyethylene glycol [8,10]. The third one demonstrated the detection of such a nitroaromatic compound with aminopropyltriethoxysilane [7]. The detection of nitrobenzene [9] was achieved with polyphenylene dendrimers.

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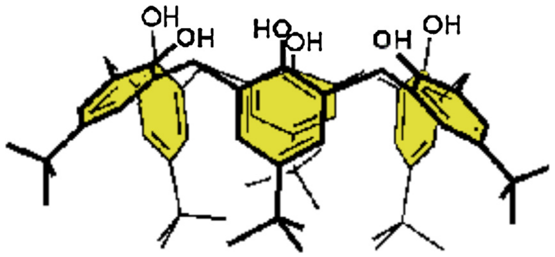

Fig. 1. tBu-calix(6)arene.

Another original study involving polymers used the plasma-polymerised copper phthalocyanine [11]. The resulting poly (Pc)Cu film has been found very sensitive but not selective to nitrobenzene. Commercial polysiloxanes are also very promising materials because of their sensitivity and selectivity to dinitrotoluene derivatives, and specially polycyanopropylmethylsiloxane [12].

In this work, the detection of 2,4 dinitrotoluene (DNT) using calixarene sensors is studied. Indeed, the latter are frequently studied for various VOCs [13] or other gas detection, like methanol [14], NOx [15], ketones [16], amines [17], chloroform [18] or pesticides [19], and also in molecular recognition for cation separation [20]. The interest of calix(n)arenes comes for their ability to occlude guest molecules in their cavities [21,22]. To evaluate the interest of such molecules for building explosive sensors, we first deposited them as thin films on the gold surfaces of QCM quartz, or of Polarisation Modulation-Infrared Reflection Absorption Spectroscopy adequate samples. The combination of these two techniques enables first to check the deposit of calixarenes and then, to monitor the interactions between thin films of calix(n)arene (with different cavity sizes, n = 4, 6, 8) and DNT vapours. The detection efficiency was evaluated using a quartz crystal microbalance (QCM), while the chemical modifications of the sensing films were characterised by PM-IRRAS.

2. Experimental

Selected calix(n)arene are tBu-calix(n)arene (n = 4, 6, 8) from Acros (Fig. 1). DNT is supplied by Aldrich, and used without further purification.

2.1. Quartz crystal microbalance

In this study, the piezoelectric crystals used were 9 MHz AT-cut quartz crystals (polished surface) with gold-plated metal electrodes on both sides (AMETEK, model QA-A9M-AU-M). The microbalance instrument was homemade and the frequency output was measured by a frequency counter with a resolution of 0.1 Hz (Racal DANA, model 1999). For our piezoelectric quartz, the Sauerbrey equation is defined according to:

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

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.

2.2. Surface coatings

For both PM-IRRAS measurements and QCM measurements, the various t-Bu calixarenes have been deposited onto the gold surfaces by spraying.

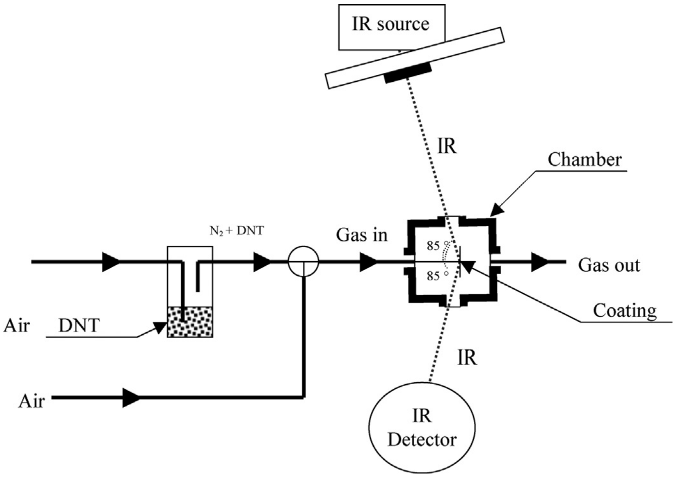

Fig. 2. Schematic diagram of infrared experimental cell.

A dilute solution of the coating selected material, calix(n)arene (n = 4, 6 or 8) was prepared in $CHCl_3$ (5 mg/mL) and was deposited by the spray technique (DOSAGE 2000) on the QCM devices. This deposition was achieved on both sides of the quartz. The resulting coating caused a decrease of 10 kHz (Equivalent to a 5 kHz decrease for each side), corresponding to a total mass deposit of 20 μg on the quartz, estimated by using the Sauerbrey equation.

For PM-IRRAS measurement, the calixarenes were coated onto gold coated substrates (ARRANDEE) using the same procedure. For these analyses, only 1 μg was deposited on the gold-covered slides.

2.3. Surface infrared analysis

Polarisation Modulation Infrared Reflection-Absorption spectra (PM-IRRAS) were recorded on a commercial NICOLET Nexus spectrometer. The external beam was focused on the sample, with a mirror, at an optimal incident angle, 80°. A ZnSe grid polariser and a ZnSe photoelastic modulator to modulate the incident beam between p and s polarisations (HINDS Instruments, PEM 90, modulation frequency = 37 kHz) were placed prior to the sample. The light reflected at the sample was then focussed on a liquid nitrogen-cooled MCT detector. The detector output was sent to a two channel electronic device that generates the sum and difference interferograms. Those were processed and Fourier-transformed to lead to the differential reflectivity $\Delta R/R = (R_p - R_s)/(R_p + R_s)$ which is the PM-IRRAS signal.

Thanks to the PM-IRRAS technique, no reference spectrum was needed; this enabled a good and reproducible characterisation of the films right after their elaboration.

All the spectra reported below were recorded at an 8 cm^{-1} resolution by co-adding 64 scans.

For evaluating the adsorption of the nitroaromatic pollutant as well as the possible chemical changes of the sensor, induced by the presence of DNT, a special cell was built that enables real-time *in situ* characterisation of the sensor surface (Fig. 2). Before admission into the cell, the nitrogen gas flow was saturated with DNT by passing through a pure nitroaromatic solution. The resulting pressure is close to the vapour pressure of the DNT.

As for solvents, dichloromethane and toluene, they were diluted in air at a concentration of 1000 ppm. These dilute solvents (in air, 1000 ppm) are supplied by Air Liquide (commercially available).

2.4. Tests of detection by QCM

The detection performances of the coated piezoelectric quartz crystal were tested against DNT vapour in the air. In addition to