Selective detection and discrimination of nitro explosive vapors using an array of three luminescent sensory solid organic and hybrid polymer membranes

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ABSTRACT

Three fluorogenic sensory polymer membranes, film shaped (one organic and two hybrids containing complexes of Tb(III) and Sm(III)) based on a dicoumarol motif were designed and prepared for use as sensory matrices to selectively detect nitro explosives (TNT, RDX and PETN) in the environment. Thus, the exposure of these membranes to these explosives and to 6 explosive mimics gave rise to variations in the fluorescence spectra of the materials as a function of the type of vapor and exposure time. Therefore, the fluorescence intensity recorded over the wavelength range from 381 to 575 nm and at times of 5, 10, 15 and 30 min for each of the 3 membranes had a highly defined internal structure. Thus, the principal component analysis (PCA) showed that only 3 principal components (PCs) were needed for each membrane for its description (9 PCs in total compared with the 195 wavelengths). The PCA allows for both discrimination between explosives and their mimics and for distinction between the 3 explosives. A SIMCA (soft independent modeling of class analogy) model was built using the scores from the PCs to a confidence level of 95%, which is completely specific (100%) for the vapors of each explosive and explosive mimic. Furthermore, the 3 explosive models and the model built using the 6 explosive mimics have a sensitivity of 100% and 95.8%, respectively. The modeling power and discriminant capability from the 9 PCs show that no membrane could be removed to build these models. Using a multilinear regression with the 9 PCs as predictor variables and binary responses, it was possible to model the fitted response using a normal distribution for each class (explosives and explosive mimics). There is a probability of 1.5×10^{-9} that a sample is not an explosive when actually it is and a probability of 0.05 that a sample is an explosive when it is an explosive mimic.

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1. Introduction

Explosives are a major societal concern, and their rapid, easy and cheap detection is challenging for a number of fields, including military endeavors, homeland security, forensic and criminal investigations, humanitarian efforts, and environmental control and remediation.

Trace explosive vapor detection has been conventionally performed using gas chromatography, high performance liquid chromatography, and ion mobility spectroscopy, among other analytical techniques. However, these techniques are time consuming and expensive, require bulky instrumentation and must be operated by skilled and specialized personnel [1–3]. Within this context, chemical sensing has emerged as a powerful and highly promising field of research with current and forthcoming applications in explosive detection [4], and among the different outputs, optical sensing using color or fluorescence changes is a topic of important and increasing research interest [5–7]. A number of colorimetric and fluorescence probes have been developed that provide good time response, high sensitivity and simple instrumentation [4,8,9].

In the explosive sensory field, vapor detection is especially challenging and stimulating due to the extremely low vapor pressures of these chemicals, e.g., 9.2 ppb$_v$ for TNT (2,4,6-trinitrotoluene), 1.1×10^{-2} ppb$_v$ for PETN (pentaerythritol tetranitrate) and 4.9×10^{-3} ppb$_v$ for RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) [10]. Thus, it is not straightforward to design and prepare optical sensors that possess inherent sensitivity and

selectivity. The sensitivity and selectivity challenges have been approached, for example, using amplifying fluorescent conjugated polymers [11–14], and array sensing [1,2,15–17], respectively.

With this in mind, we have approached the sensing of explosive vapors by preparing 3 novel fluorescent polymeric sensory membranes, one organic and two hybrid, shaped as films, based on a new acrylic dicoumarol derivative as an explosive sensory motif and its complexes with terbium(III) and samarium(III). The 3 sensory materials matrices were exposed to explosive vapors, and the fluorescence variation, both "turn-on" and "turn-off", were recorded and the matrix data containing the spectral data (fluorescence intensity *vs.* wavelength) as a function of time were simultaneous treated using multivariate techniques, thus permitting both the differentiation of the explosives from explosive mimics or interferents and discrimination between explosives and the ability to assess the probability of false non-detection of an explosive and probability of false detection. Within the different commercial explosive families, we have jointly studied three of them, i.e., nitroaromatics (TNT), nitramines (RDX) and nitrate esters (PETN). Along with these, we have also analyzed other molecules that are not explosives by themselves but are intermediates in their synthesis or have an explosive-like structure with a much higher vapor pressure and may interfere in the detection of explosive vapor. The explosive mimics that we have considered are 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), 1-chloro-4-nitrobenzene (ClNB), 4-nitrotoluene (4-NT), 2-nitro-*m*-xylene (NX), and 2-nitrotoluene (2-NT) [18].

2. Experimental

2.1. Materials

All materials and solvents were commercially available and used as received, unless otherwise indicated. They included the following: 4-hydroxycoumarin (Alfa Aesar, >98%), 4-nitrobenzaldehyde (Alfa Aesar, 99%), Pd/C (Aldrich, 10%), methacryloyl chloride (Fluka, 97%), *N*-methyl-2-pyrrolidone (NMP) (Fluka, 99.5%), lithium chloride (Aldrich, 99%), terbium (III) nitrate pentahydrate (Aldrich, 99.9%), Samarium (III) nitrate pentahydrate (HPLC grade, Alfa Aesar), 1-chloro-4-nitrobenzene (ClNB) (Aldrich, 99%), 2-nitro-*m*-xylene (NX) (Aldrich, 99%), 1,3-dinitrobenzene (1,3-DNB) (Aldrich, 99%), 2-nitrotoluene (2-NT) (Aldrich, 99%), 4-nitrotoluene (4-NT) (Aldrich, 99%), 2,4-dinitrotoluene (2,4-DNT) (Aldrich, 99%), sodium hydroxide (Aldrich, 99%), DMSO (Merck, 99%), ethanol absolute (GPR Rectapur), acetone (Aldrich, 99%), acetonitrile (Aldrich, 99%), DMA (Aldrich, 99%), hexane (Aldrich, 99%), diethyl ether (VWR, 99.99%), 1-vinyl-2-pyrrolidone (Aldrich, 99%), ethylene glycol dimethacrylate (**EGDMMA**, Aldrich, 99%), 2-hydroxyethyl acrylate (**2HEA**, Aldrich, 99%), dimethoxy-2-phenyl acetophenone (Aldrich, 99%). 2,4,6-Trinitrotoluene (TNT), pentaerythritol tetranitrate (penthrite, PENT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) were prepared and synthesized at a milligram scale following previously described procedures [18,19]. 2,4,6-Trinitrotoluene (TNT) was recrystallized from ethanol (CAUTION: TNT is an explosive, and although it is insensitive to shock and friction and can be milled and melted at 82 °C, it must be handled with care. Only small quantities of TNT were prepared – 500 mg – to avoid risks; PETN and RDX are also explosives, to avoid risks, 500 mg of each were prepared and stored as a water suspension. Small quantities were dried at rt and dissolved in acetone previous use).

2.2. Instrumentation and software

^{1}H and ^{13}C NMR spectra were recorded at 399.92 and 100.57 MHz, respectively on a Varian Unity Inova 400 MHz

spectrometer. All NMR data were recorded at 25 °C in deuterated dimethyl sulfoxide (DMSO-d_6), and both ^{1}H and ^{13}C chemical shifts were referenced to the residual signal of this solvent (δ_{TMS} 0.0 ppm). ^{1}H and ^{13}C resonances were assigned based on signal multiplicities and intensities in 1D spectra and correlation peaks in 2D NMR spectra: ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC.

Infrared spectra (FTIR) were recorded using a Nicolet Impact spectrometer, a JASCO FT/IT-4100 fitted with a PIKE TECH "Miracle" ATR, or a JASCO FT-6300.

Thermogravimetric analysis (TGA) data were recorded using 4–5 mg of sample under a nitrogen atmosphere on a TA Instrument Q50 TGA analyzer at a scan rate of 10 °C min^{-1}.

Fluorescence spectra were recorded using an F-7000 Hitachi Fluorescence spectrophotometer.

FAB mass spectra were measured on a VG Autospec spectrometer in positive ion mode using m-nitrobenzyl alcohol (NBA) as the matrix.

HRMS spectra were obtained in a hybrid spectrometer API QSTAR® XL Hybrid system (Applied, Biosystems) using ESI of high resolution with DMSO as the solvent.

Elemental analysis was obtained using a LECO CHNS-932 analyzer and a VTF-900 equipped with an ultra-microbalance SARTORIUS M2P (accuracy ± 0.001 mg).

The data were analyzed using the statistical program PARVUS [20] for building the SIMCA model and STATGRAPHICS [21] for the *PCA*, the multilinear binary regression and its validation, and the probabilistic distributional features of the fitted values. The probability, α, of erroneously affirming that the sample is not an explosive and the probability, β, of erroneously affirming that a sample is an explosive were calculated using a MATLAB function, version 7.12.0.635 (R2011a) (MathWorks), written in-house.

2.3. Measurements

Fluorescence sensing measurements of nitro-compounds were performed according to a previously described procedure [22]: first, 0.1 M solutions of each nitro-compound were prepared in acetonitrile. Next, 1 mL of each solution was dropped onto a ∼40–60 mg piece of cotton gauze and dried at room temperature overnight. Subsequently, the cotton gauze was heated in an open glass vial at 100 °C for 10 min to eliminate traces of humidity and, finally, for 1 h in a closed glass vial, thus allowing the vapor molecules to bind to the cotton fibers. Finally, it was cooled at room temperature for 5 min and rapidly placed into a sealed quartz cuvette containing the solid sensory disk, 5 mm in diameter, cut from the membrane using a puncher. Then, fluorescence spectra were acquired every 30 s to 1 min at 25 °C. The excitation wavelength was 360 nm, and the excitation/emission slits for the membranes **Mem3**, **Mem3a** and **Mem3b** were 5/5, 2.5/5, and 10/10 nm, respectively.

The solvent-swelling percentage (SSP) of the membrane was obtained from the weights of a dry sample membrane (ω_d) and a solvent-swelled sample membrane (ω_s) (the membrane was immersed in pure solvent at 20 °C until the swelling equilibrium was achieved) as follows: $100 \times [(\omega_s - \omega_d)/\omega_d]$.

2.4. Synthesis of the intermediates

The intermediates and sensory monomers were synthesized following the reaction conditions described in Scheme 1.

Synthesis of 3,3′-((4-nitrophenyl)methylene)bis(4-hydroxychromen-2-one) (**1**): 30.83 mmol (5.00 g) of 4-hydroxycoumarin were dissolved in 50 mL of absolute ethanol. 15.21 mmol (2.30 g) of 4-nitrobenzaldehyde were added to the solution. The mixture was heated under stirring at reflux until the appearance of an insoluble strong yellow precipitate. After cooling, the product was filtered