Fluorescent Calix[4]Arene-Based Polymer Chemosensor for Explosives Detection

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Abstract

A fluorescent calix[4]arene-based poly(phenylene-ethynylene) (**CALIX-*p*-PPE**) and an analogous poly(*p*-phenylene ethynylene) containing *p*-*t*-butyl-phenoxy-methyl side chains (**TBP-*p*-PPE**) showed high affinity to explosive-related analytes such as nitrobenzene (NB), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) in solution. Their chemosensing abilities were determined by a Stern-Volmer analysis. The corresponding quenching constants (K_{sv}) for **CALIX-*p*-PPE** ranged from 5.30×10^2 M^{-1} (NB) to 1.35×10^3 M^{-1} (DNT).

Keywords: Calixarene, Phenylene Ethynylene Polymer, Fluorescence, Sensing, Nitroaromatic Quenching.

Introduction

The design, synthesis and device development of chemical sensors for trace and ultra-trace detection of explosives is an active research area both in academia and industry owing to their potential applications in homeland security, detection of (buried) landmines and environmental remediation of munitions sites [1-7].

Although highly selective physical detection methods and techniques such as surface enhanced Raman spectroscopy, nuclear quadrupole resonance, energy-dispersive X-ray diffraction, cyclic voltammetry, gas chromatography-mass spectrometry and gas chromatography-electron capture detection are currently in use for the detection of explosive materials [8], most of these techniques are expensive and/or not easily portable to the field.

Macrocyclic receptors, either as side-chain or main-chain constituents of conjugated polymeric backbones, have been continuously screened as chemical and biological sensors [9-10]. In comparison to single receptor molecules, conjugated polymer-based sensors show higher sensitivity, leading to higher transduction signal amplification. Only a few studies have reported the use of calix[4]arenes as building blocks for this type of sensors [11-15].

On the other hand, fluorescence represents one of the most sensitive methods for explosives detection [7] [10].

Herein we report our preliminary results regarding the use of calix[4]arene-based conjugated polymers for explosives sensing.

Experimental

Materials and Methods

The calix[4]arene-based poly(phenylene-ethynylene) (**CALIX-*p*-PPE**) and the model polymer poly(*p*-phenylene ethynylene) containing *p*-*t*-butyl-phenoxy-methyl side chains (**TBP-*p*-PPE**) used in this work were synthesized by Sonogashira-Hagihara coupling methods, recently reported by us [16].

The nitrobenzene was used after distillation by standard methods, 2,4-dinitrotoluene was used as received (Fluka, OEKANAL – analytical standard), and 2,4,6-trinitrotoluene was prepared by a reported method [17]. Chloroform was of spectroscopic grade (Aldrich, ACS spectrophotometric grade).

UV-vis spectra were recorded on a Nicolet Evolution 300 spectrophotometer using 1-cm quartz cells.

Steady-state fluorescence spectra were recorded on a Perkin Elmer LS45 fluorimeter using a quartz cuvette with a path length of 1 cm in the right angle geometry at room temperature in air-equilibrated conditions; an excitation wavelength of 337 nm was used for the fluorescence quenching experiments.

During the quenching experiments, the concentration of the polymers was kept constant.

Solutions of **CALIX-*p*-PPE** and **TBP-*p*-PPE** in $CHCl_3$ at a concentration of 1.2×10^{-6} M were used. In a typical quenching experiment, 2.0 mL of polymer solution was placed in a 1 cm quartz fluorescence cell and the fluorescence spectrum recorded in the absence of quencher. Fluorescence and absorption spectra were then repeatedly acquired after each addition of microliter aliquots of a solution containing the polymer at 1.2×10^{-6} M concentration and the quencher (1.5×10^{-2} M). The fluorescence spectra were corrected for the absorption of the quencher at excitation wavelength.

Results and Discussion

The **CALIX-*p*-PPE** (Fig. 1) showed high photoluminescence with a quantum yield of 0.43 in $CHCl_3$ and solution lifetimes (320 ps) typical of PPE-type polymers [16].

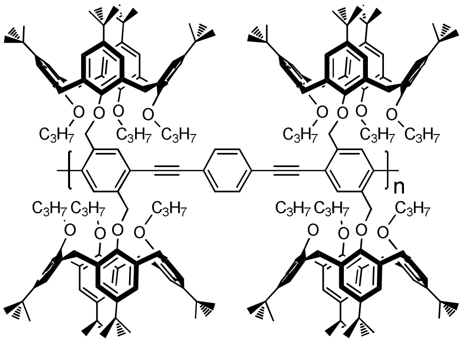

Figure 1: Conjugated fluorescent polymer (**CALIX-*p*-PPE**) used in explosives detection.

Similar optical properties were obtained for the model compound **TBP-*p*-PPE** with a quantum yield of 0.51 in $CHCl_3$ and solution lifetimes of 310 ps.

In order to study their ability to detect explosive materials, three nitroaromatic compounds (NAC; Fig. 2) commonly used in the explosives' industries were tested.

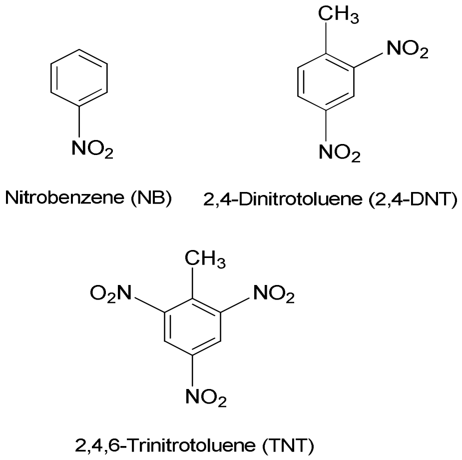

Figure 2: Nitroaromatic compounds (NAC) used in the study.

The fluorescence quenching studies were conducted in $CHCl_3$ solution using different concentrations of NAC analytes (Fig. 3; DNT shown).

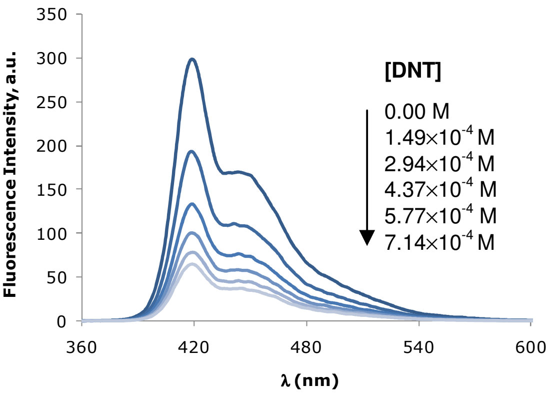

Figure 3: Photoluminescence spectra of **CALIX-*p*-PPE** after successive additions of DNT (up 7.14 X 10^{-4} M).

To determine the degree of fluorescence quenching of **CALIX-*p*-PPE** and **TBP-*p*-PPE** as a function of NAC concentration, the Stern-Volmer analysis was performed on the resulting data (Fig. 4), using the Stern-Volmer relationship:

$$F_0/F = 1 + K_{sv}[Q]$$

where F_0 is the fluorescence intensity without added quencher, F is the fluorescence intensity with added quencher, [Q] is the quencher concentration and K_{sv} is the Stern-Volmer constant.

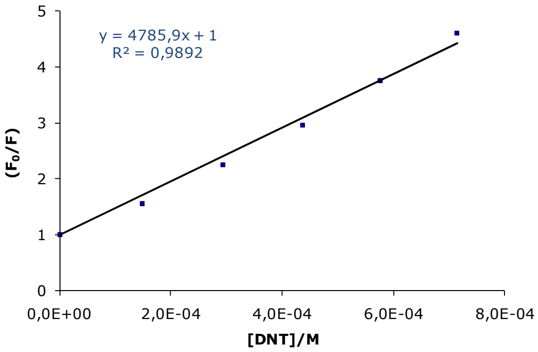

Figure 4: Stern-Volmer plot of **CALIX-*p*-PPE** for DNT (uncorrected for the absorption of the quencher at excitation wavelength).

The absorption spectra of the solutions upon sequential additions of the quencher showed significant absorption by the quencher at the excitation wavelength. All raw data were thus corrected for this effect giving $K_{sv\ corr}$ [18].
The K_{sv}'s (uncorrected and corrected) are presented in Table 1.

Table 1 - Stern-Volmer constants for polymer **CALIX-*p*-PPE**.

CALIX-*p*-PPE	NB	2,4-DNT	2,4,6-TNT
K_{sv}/M^{-1}	1.58×10^3	$4.79\text{x}10^3$	$5.77\text{x}10^3$
$K_{sv\ corr}$/M^{-1}	$5.30\text{x}10^2$	$1.35\text{x}10^3$	$1.14\text{x}10^3$

Similar quenching studies were also undertaken with the model PPE polymer lacking the calixarene units (**TBP-*p*-PPE**) in order to address the involvement of the macrocycle in the sensing event.

The K_{sv}'s (uncorrected and corrected) are presented in Table 2.

Table 2 - Stern-Volmer constants for polymer **TBP-*p*-PPE**.

TBP-*p*-PPE	NB	2,4-DNT	2,4,6-TNT
K_{sv}/M^{-1}	1.42×10^3	$3.70\text{x}10^3$	$5.50\text{x}10^3$
$K_{sv\ corr}$/M^{-1}	$3.69\text{x}10^2$	$7.82\text{x}10^2$	$1.06\text{x}10^3$

It was found that, in general, **CALIX-*p*-PPE** shows higher K_{sv} than **TBP-*p*-PPE** which is indicative of its superior sensitivity for the detection of all the NAC used in this work.

The sensitivity of **CALIX-*p*-PPE** to DNT is 1.7 times larger than that seen for **TBP-*p*-PPE**. For NB **CALIX-p-PPE** continues to perform better whereas for TNT similar sensitivities were found.

The high K_{sv} observed and the subsequent study of fluorescence lifetimes of these polymers in the quencher concentration range used in the experiments showed that a static mechanism is operating.
Further studies with other analytes are in progress and will be presented elsewhere.

Conclusions

CALIX-*p*-PPE is an extremely efficient chemical sensor for NAC used in explosive materials showing high quenching efficiencies for TNT, DNT and NB in solution. The preliminary evaluation of its sensing abilities in solid state has also shown its remarkable sensitivity for NAC [19].

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