

Solid State Sensing of Explosives by a Photoluminescent Calix[4]arene-Based Polymer

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Abstract

The fluorescence quenching behavior of a fluorescent calix[4]arene-based poly(phenylene-ethynylene) (**CALIX-*p*-PPE**) and an analogous poly(*p*-phenylene ethynylene) containing *p-t*-butylphenoxy-methyl side chains (**TBP-*p*-PPE**) in solid state is reported. The films of these polymers were obtained through a drop-coating technique and upon exposure to nitroaromatic compounds vapors (NB and DNT) an efficient response was retrieved.

The sensitivity of **CALIX-*p*-PPE** to quenching by nitroaromatic compounds is 1.5 times larger than that seen for **TBP-*p*-PPE**. The incorporation of calix[4]arene units into conjugated polymer backbones offers several advantages for solid-state (thin-film) fluorescent sensory materials, such as preventing π -stacking or excimer formation of the polymer backbones and the cavities generated between adjacent polymer chains are sufficiently large to allow diffusion of small organic molecules into the films. The advantages are apparent from comparison of the fluorescence quenching behaviour of **CALIX-*p*-PPE** to an analogous **TBP-*p*-PPE**.

The rapid fluorescence response (quenching) of **CALIX-*p*-PPE** to nitroaromatic compounds in solid state qualifies this material as promising explosives chemosensory material.

Keywords: Calixarene, Phenylene Ethynylene Polymer, Fluorescence Quenching, Sensor, Nitroaromatic, Thin Films.

Introduction

Development of fast and portable chemical sensors for trace and ultra-trace detection of explosive materials, namely those based on nitroaromatic compounds (NAC), is a current topic of intense research mainly due to the need of enhance the general homeland security, locating buried landmines on mine fields, remediation of munitions sites and determination of post-blast residues in forensic investigations [1-8]. Current physical detection methods and techniques (eg. surface enhanced Raman spectroscopy, nuclear quadrupole resonance, energy-dispersive X-ray diffraction, gas chromatography-mass spectrometry and gas chromatography-electron capture detection) suffer from poor portability and expensiveness [9].

Chemical sensing by fluorescence quenching is one of the most sensitive methods for explosives detection.

In this communication we report on the solid state chemosensing ability of **CALIX-*p*-PPE** for aromatic-based explosives.

Experimental

Materials and Methods

The 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**) used in this work were synthesized by Sonogashira-Hagihara coupling methods, recently reported by us [11].

The nitrobenzene was used after distillation by standard method, 2,4-dinitrotoluene was used as received (Fluka, OEKANAL), and 2,4,6-trinitrotoluene was prepared by a reported method [12]. Chloroform was of spectroscopic grade (Aldrich, ACS spectroscopic 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, an excitation wavelength of 337 nm was used for the fluorescence quenching experiments.

The films were prepared by drop-coating from chloroform solutions of the polymers onto a quartz substrate (4×0.8cm), leading to thicknesses between 25 and 100 nm, followed by vacuum drying at 60°C for 3h before use. The films thicknesses were determined using a profilometer Veeco Dektak 6M.

The quencher (nitrobenzene (NB) or 2,4-dinitrotoluene (2,4-DNT)) was placed into a sealed quartz cell at room temperature (15-18°C) containing cotton gauze, which provides a high surface area to maintain a constant vapor pressure, previously saturated for at least 12h. The fluorescence spectra were recorded immediately after exposing the polymer films to the vapor of analyte for a specific period of time.

Results and Discussion

In previous work, the **CALIX-*p*-PPE** (Fig. 1) showed high ability to detect explosive materials. Three nitroaromatic compounds (NAC), NB, 2,4-DNT and 2,4,6-trinitrotoluene (TNT) were selected and their quenching efficiency in solution evaluated by a Stern-Volmer analysis [10].

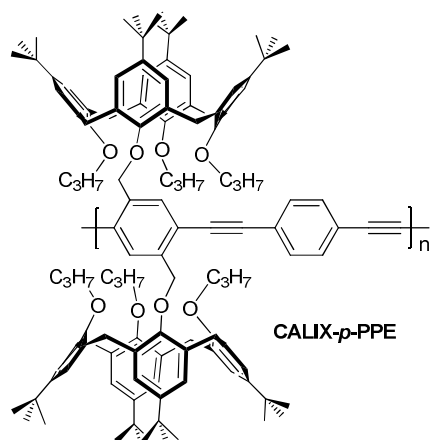


Figure 1: Conjugated fluorescent polymer (**CALIX-*p*-PPE**) used in explosives sensing.

The fluorescence spectra of **CALIX-*p*-PPE** and **TBP-*p*-PPE** in CHCl_3 and film are shown in Figure 2.

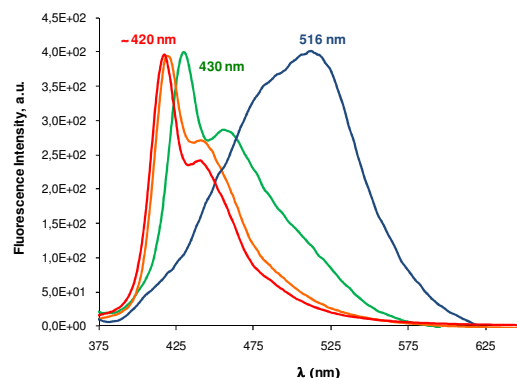


Figure 2: The fluorescence spectra of **CALIX-*p*-PPE** and **TBP-*p*-PPE** in CHCl_3 (orange and red line, respectively) and in drop-cast films (green and blue line, respectively).

In CHCl_3 the fluorescence spectra are similar for both polymers. However, in thin films the **TBP-*p*-PPE** displays a substantial red shift (ca. 96 nm) relative to solution spectrum showing a broad structureless emission band. This clearly suggests the formation of excimeric species resulting from co-facial π - π -stacking between the main-chain units. On the other hand, the emission spectrum of **CALIX-*p*-PPE** is quite similar to the fluid solution meaning that the calix[4]arene units prevent interchain interactions thus precluding any excimer formation.

The following preliminary results report the fluorescence response (quenching) of drop-cast films of **CALIX-*p*-PPE** and **TBP-*p*-PPE** to NB and DNT.

The Figures 3 and 5 show the time-dependent fluorescence intensity of **CALIX-*p*-PPE** films upon exposure to NB and DNT vapors.

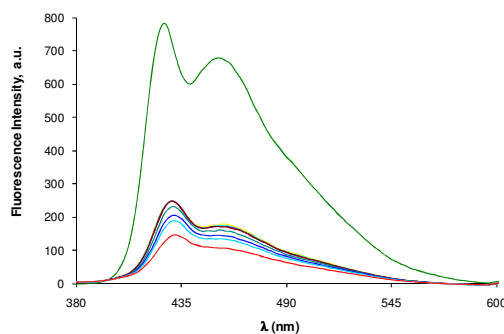


Figure 3: Fluorescence intensity decay of a **CALIX-*p*-PPE** film (OD= 0.097 at 337 nm) with NB vapor ($P=2.45 \times 10^{-1}$ mmHg, 322 ppm at 25°C). Traces from 0 to 30 min.

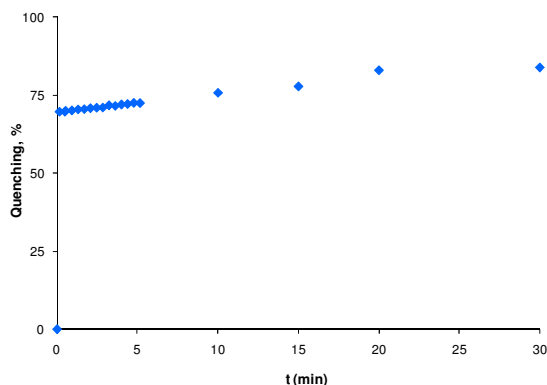


Figure 4: Time-dependent fluorescence quenching of a **CALIX-p-PPE** film (25-100 nm) with NB.

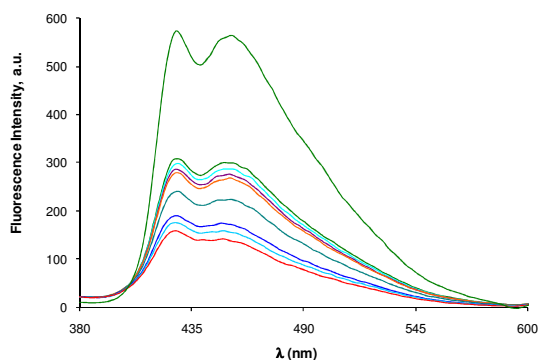


Figure 5: Fluorescence intensity decay of a **CALIX-p-PPE** film (OD= 0.089 at 337 nm) with DNT vapor ($P=1.74 \times 10^{-4}$ mmHg, 229 ppb at 25°C). Traces from 0 to 30 min.

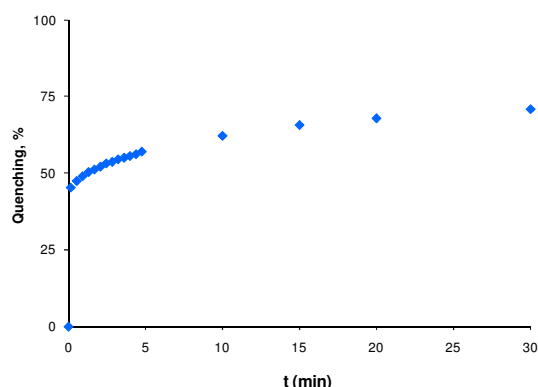


Figure 6: Time-dependent fluorescence quenching of a **CALIX-p-PPE** film (25-100 nm) with DNT.

The fluorescence of **CALIX-p-PPE** in drop-cast film responds rapidly to the vapors of NB and DNT

(Fig. 4 and 6), reaching ca. 70 and 45% for NB and DNT, respectively, in only 10s albeit the large and inhomogeneous thickness of the polymer films.

Under the same conditions, the **TBP-p-PPE** showed a lower response to NB and DNT (48 and 34%, respectively). The sensitivity of **CALIX-p-PPE** to quenching by nitroaromatic compounds is 1.5 times larger than that seen in **TBP-p-PPE**.

The response of both films to NB vapor is faster and can be attributed to the higher equilibrium vapor pressure of NB ($P=2.45 \times 10^{-1}$ mmHg, at 25°C) relative to DNT ($P=1.74 \times 10^{-4}$ mmHg, at 25°C).

Further studies aiming to determine the influence of films thickness in the quenching response are in progress in our laboratory and will be presented elsewhere.

Conclusions

The results obtained qualify **CALIX-p-PPE** as an excellent fluorescent chemosensor for the detection of electron-deficient unsaturated species such as NB and DNT used as explosives. The superior response observed for **CALIX-p-PPE** as compared to **TBP-p-PPE** may be due the nature of substituents covalently linked to the rigid-rod polymer main chains and the enhanced diffusion ability of the quenchers through polymer films.

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