



# Preparation of a functionalized glass sensor and its sensing performances for nitroaromatics



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## ABSTRACT

A functionalized glass sensor **GS-P**, which was designed for detecting nitroaromatic compounds (NACs), has been prepared by grafting conjugated polymer **P** on the surface of a glass slide. For control, three spin-coated films (films I, II and III) with different thicknesses were also prepared. Interestingly, the grafted polymer film showed densely packed conical columns from atomic force microscopy. Quenching efficiency study showed that polymer **P** exhibited 92% quench toward 2,4-dinitrotoluene (DNT) in solution state while 82% quench toward DNT vapor in film state. Quenching kinetics showed that the fluorescence intensity of **GS-P** decreased significantly by 80% within first the 100 s, followed by gradually decreasing to a quenching equilibrium at 200 s. This was much faster than the other two thicker films (films I and II) whose emission intensities decreased only by 37% and 48% within 100 s, respectively. The **GS-P** exhibited similar quenching speed as the ultra-thin spin-coated film (film III) that had the similar thickness to **GS-P**. Reversibility study showed that **GS-P** exhibited good repeatability of quenching process after the three cycles, while the ultra-thin spin-coated film hardly showed any reversibility. These great differences indicated remarkable advantages of **GS-P** over the spin-coated film. Furthermore, the **GS-P** sensor exhibited good selectivity to the NACs such as DNT, 2,4,6-trinitrotoluene, picric acid, and nitrobenzene.

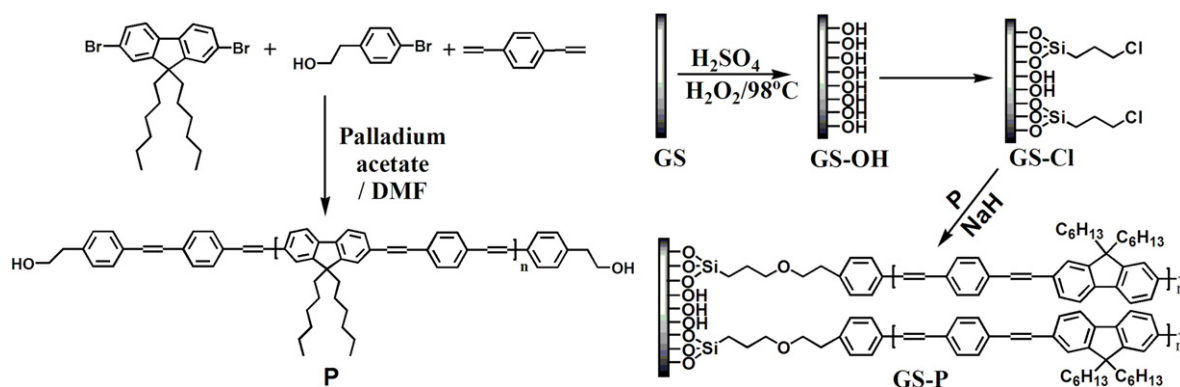
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## 1. Introduction

Nitroaromatic compounds (NACs) such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) are not only the main ingredients of explosives, but also environmental pollutants. Therefore, fast and in-field detection of NACs is of great significance for security, industrial process control, and environmental monitoring consideration [1,2]. Conjugated polymers (CPs), with the so-called molecular wire effect that allows the rapid propagation of excitons along the backbone of polymer chains, are endowed with signal amplification effect when they serve as sensing materials. Therefore, fluorescent CPs have been a hot topic in the field of chemical sensors, particularly in detecting traces of NACs. Until now, several CPs have been studied as the sensing materials for detecting NACs, such as pentyptycene-derived poly(phenylene ethynylene) and poly(*p*-phenylene vinylenes), etc [3–10]. They are usually processed into film sensors by directly spin-coating the polymers onto solid substrates. However, there will be two main disadvantages that restrict the practical application of these sensors. One is the high steric hindrance in thick film which reduces the diffusion of analyte. The other is the leakage of sensing materials due to none covalent binding between the sensing molecules and substrate surface. The former reduces the response speed, while the latter shortens the usage lifetime of the film sensor.

To overcome these disadvantages, researchers have prepared monolayer film sensors by chemically grafting fluorescent molecules onto a solid substrate surface. For example, self-assembled monolayer film sensors were obtained for detecting NACs by chemically immobilizing pyrene on the surface of a glass or mesoporous silica [11–14]. The resulting film sensors had advantages of high response speed due to their ultra-thin characteristic as well as good recyclable ability attributed to the chemical binding between the molecules and the surface of the substrate. Although self-assembled monolayer film sensors showed advantages described above, the fluorescence molecules grafted on the substrates are generally small molecules that lack signal amplification effect for detecting trace NACs. Recently, researchers began to graft various CPs onto substrate to prepare the thin film sensors for metal ions [15–16], so as to introduce the signal amplification effect of the CPs. The applications are only restricted in detecting metal ions. No reports based on the CPs-grafted glass sensor for detecting NACs have appeared till now.

Herein, a conjugated polymer **P** was prepared from 2,7-dibromo-9,9-dihexylfluorene and 1,4-diethynylbenzene by Sonogashira reaction. By grafting **P** onto the glass surface, a functionalized glass sensor **GS-P** for detecting NACs was obtained (Scheme 1). The sensor was expected to have the combined properties of the signal amplification effect of CPs, the high response speed and good recyclable ability.



Scheme 1. Synthetic routes of conjugated polymer **P** and functionalized glass sensor **GS-P**

## 2. Experimental

### 2.1. Materials and measurements

N,N-Dimethylformamide (DMF), Tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and toluene were obtained from Tianjin Fuyu Company. They were dried by molecular sieves (4 Å), sodium sands, and CaH<sub>2</sub> successively and distilled prior to use.

2,7-Dibromo-9,9-dihexylfluorene (98%) and 4-bromophenethyl alcohol (99%) were obtained from Energy Reagent Company; divinylbenzene (80%) and (3-chloropropyl)triethoxysilane (98%) were obtained from Aladdin Reagent Company; styrene (98%) was obtained from Guang Fu Reagent Company. The analytes for fluorescence quenching studies such as DNT (99%), picric acid (PA, 99%), nitrobenzene (NB, 99%), and *p*-benzoquinone (BQ, 99%) were obtained from Aldrich Reagent Company. All the reagents were used as received without further purification. A small amount of TNT with a purity of 99% was prepared in our laboratory. The common cover-glass used for microscope (Sail brande, 18 × 18 mm) was bought from Aladdin Reagent Company. The chemical composition of the glass is Na<sub>2</sub>O · CaO · 6SiO<sub>2</sub> and the main ingredient is SiO<sub>2</sub>.

**Caution:** TNT and other NACs used in the present study are highly explosive, they should be stored in refrigerating chamber and be handled only in small quantities.

<sup>1</sup>HNMR spectra were measured using a Bruker AVANCE II400 Nuclear Magnetic Resonance (NMR) spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA Phi-5300 (Perkin-Elmer) photoelectron spectrometer using a monochromatic Mg Kα X-ray source. Water contact angles were measured using a DSA 100 instrument at ambient temperature. The absorption spectra were recorded using a UV-2500 spectrophotometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the standard. Atomic force microscopy (AFM) images were obtained using a Bruker Multi-mode 8 Nanoscope V system atomic force microscope in the peak force tapping mode.

Fluorescence measurements were performed using a Hitachi F-4600 fluorescence spectrophotometer. The quenching efficiency of **GS-P** in saturated vapor of each analyte at quenching equilibrium was measured according to the following procedures: To a quartz cell with a lid, either 100 mg solid analyte or a cotton ball absorbing 100 mg liquid analyte, was added, with a piece of filter paper covering upon the analyte to prevent direct contact between the analyte and the film. The cell was laid aside for 1 h at room temperature to obtain saturated vapor of the analyte. Then, the film sensor was inserted into the cell with the film surface facing the excitation light, and the emission spectra were measured.

### 2.2. Synthesis of poly[2,7-di(*p*-divinylidene benzene)-9,9-dihexylfluorene] (**P**)

To a 100 mL flask with 5 mL DMF, 2,7-dibromo-9,9-dihexylfluorene (0.48 g, 1 mmol), 1,4-diethynylbenzene (0.13 g, 1 mmol), 4-bromophenethyl alcohol (0.2 g, 1 mmol), triethanolamine (0.35 mL), Pd(OAc)<sub>2</sub> (9.0 mg, 0.04 mmol), and tri(*o*-tolyl)phosphine (60.9 mg, 0.2 mmol) were added. After reacting at 100 °C for 2 h, the resulting mixture was poured into 30 mL water and extracted with 30 mL dichloromethane three times. The organic phase was concentrated by rotary evaporation. The polymer was precipitated by adding excess methanol to the organic phase [17–18]. Then, the obtained raw product was reprecipitated using dichloromethane/methanol and extracted with methanol using a Soxhlet extractor for 24 h to remove the excess monomer. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400), δ (ppm): 0.561–0.664 (m, 4 H), 0.756–0.812 (m, 6 H), 1.069–1.146 (m, 12 H), 1.903–2.051 (m, 4 H), 7.162–7.231 (m, 2 H), 7.162–7.686 (m, 10 H). GPC: *M*<sub>n</sub> = 4.262 × 10<sup>3</sup>, *M*<sub>w</sub> = 4.825 × 10<sup>3</sup>, *PDI* = 1.13.

### 2.3. Immobilization of **P** on the glass surface

The functionalization of a glass slide by immobilizing polymer **P** on the glass surface was completed in three steps as follows:

- Activation of the glass surface (**GS-OH**): A common glass slide (**GS**) (0.9 × 1.8 cm<sup>2</sup>) was calcined in a muffle furnace at 500 °C for 3 h to remove the organic impurities and then treated with a “piranha solution” (30% H<sub>2</sub>O<sub>2</sub>/98% H<sub>2</sub>SO<sub>4</sub>, 7:3, v/v) at 98 °C for 1 h. Then, the glass slide was washed with sufficient water [19].
- Silanization of the glass surface (**GS-Cl**): The activated glass **GS-OH** was placed in a solution of 1 mL (3-chloropropyl)trimethoxysilane (CPTS) in 10 mL toluene and refluxed at 50 °C for 12 h. After cooling to room temperature, the glass **GS-Cl** was washed with sufficient ethanol in an ultrasonic bath for 10 min to remove the excess CPTS.
- Functionalization of the glass surface by polymer **P** (**GS-P**): The glass **GS-Cl** was placed in a 50 mL flask containing a solution of **P** (0.01 g, 2.23 × 10<sup>-5</sup> mol) and NaH (0.096 g, 4 × 10<sup>-3</sup> mol) in 10 mL toluene. The solution was warmed at 60 °C for 12 h along with periodical shaking. Then the glass was washed with CH<sub>2</sub>Cl<sub>2</sub> in an ultrasonic bath for 10 min to remove the polymers physically adsorbed on the glass. After the above procedures, the obtained functionalized glass (**GS-P**) was stored in THF, and they were dried by air blower for 5 min before they were used in measurements of quenching and detection of nitroaromatics both in gas and liquid media.

### 2.4. Preparation of spin-coated films (SC-P)

Three spin-coated films (films I, II and III) on glass slides (10 × 20 × 1 mm<sup>3</sup>) were prepared using a Spin Coater KW-4A instrument. A

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