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A novel film of conjugated polymer grafted onto gelatin for detecting nitroaromatics vapor with excellent inhibiting photobleaching

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ABSTRACT

A novel sensing material (Gel-P) based on conjugated carbazole polymer grafted onto gelatin was successfully synthesized by spin-coating way. The grafting reaction between gelatin and Polymer P was confirmed by ATR-FTIR spectra of Polymer P and the content of residual amino group in gelatin solution. After UV irradiation for 30 min, the fluorescence intensity of Gel-P only reduced by 7.6%, while the polystyrene film doped with polymer P (Ps + P) decreased by 32.4%, indicating higher capability in inhibiting photobleaching for Gel-P due to the presence of tryptophan in gelatin and the fixation effect of gelatin molecules to polymer chains via hydrogen bonds between amino and hydroxyl. Exposed to saturated DNT vapor, the Gel-P sensor exhibited a high quenching efficiency (Q_f) of 60% after 50 s and the fluorescence of P in Gel-P film was completely quenched for 300 s owing to the plenty of NH_2 and OH groups in gelatin, which could effectively absorb nitroaromatics (NACs) by hydrogen bonding interaction between NACs and gelatin. After being exposed to saturated DNT vapor for 300 s, the Gel-P sensor showed good reversibility of quenching process.

1. Introduction

Fast and sensitive detection of nitroaromatic compounds (NACs) such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) in the air has attracted much attention because of their extensive security and pollution problems for humans and the ecosystem. The method for detection of NACs plays an essential role in finding hidden explosives in airport luggage or in mail, screening of personnel for concealed explosives, as well as the detection of buried landmines [1–5]. Compared with small molecules, conjugated polymers (CPs) possessed the so-called “molecular wire effect”, their backbone can act as a molecular wire, enabling the rapid propagation of an exciton throughout the individual polymer chain. Therefore, CPs as sensing materials for detection of NACs have been attracted considerable attention in recent years [6–13].

Although a large number of fluorescent sensing films have been reported, most of them were prepared by a simply spin-coating way onto solid substrates. It has been found that the response sensitivity of spin-coated film greatly depends on the film thickness. The thicker film exhibited lower sensitivity to NACs caused by poor permeability [14,15]. Generally, the quenching efficiency decreases as the film thickness increases. In order to obtain high sensing performance, the spin-coated films should be as thin as possible. However, majority of such thin films usually showed high photobleaching and poor repeatability of testability.

Considering the disadvantages of the fluorescent films above, our group has been seeking to develop a novel sensing films through spin-coating gelatin grafted with conjugated polymer on a solid substrate surface. In this study, a conjugated polymer P was prepared from 3,6-dibromocarbazole and 1,4-divinylbenzene by Heck reaction, then P was grafted onto gelatin (Scheme 1), finally forming a spin-coated film for detecting NACs. The novel method showed several advantages in preparing the sensing film: (i) Tryptophan and the fixation effect of gelatin molecules to polymer chains via hydrogen bonds between amino and hydroxyl could minimize the interference of photobleaching effects. The fluorescence emission of the film decreased slowly with UV light. (ii) The film showed high sensitivity to NACs owing to the enrichment effect of the amino and hydroxyl groups on the gelatin, which not only have a strong tendency to attract NACs, but also effectively promote the proton transfer [16–22]. The results demonstrated that the superiority of gelatin films in a spin coating way showed better sensing performance on the detection of NACs in the air.

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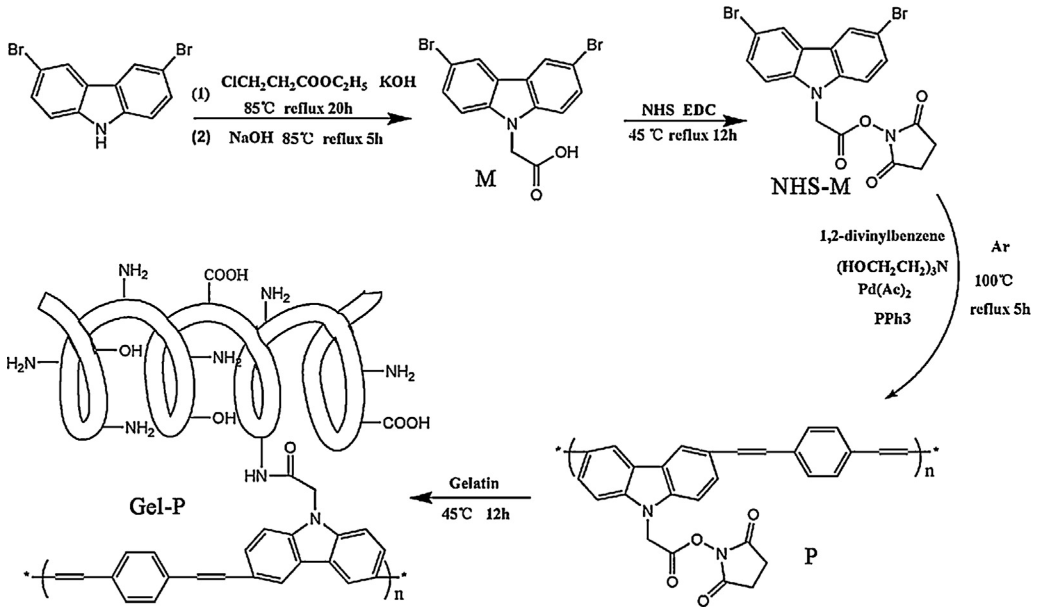


Scheme 1. Synthetic routes of conjugated polymer P grafted on gelatin.

2. Experiment

2.1. Materials and measurements

3,6-Dibromocarbazole (aladdin, 98%), divinylbenzene (aladdin, 80%), gelatin (sinopharm, CP), ethyl chloroacetate (aladdin, 98%), *N*-hydroxysuccinimide (energy, 98%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (energy, 98%) were used without further purification. DMF was generally dried by molecular sieves (4 Å), sodium sands and CaH_2 successively, and distilled prior to use. The analytes for fluorescence quenching studies obtained from aldrich, 2,4,6-trinitrotoluene (TNT) was prepared according to the method of Richard's group [23].

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

The ^1H NMR spectra were recorded on AVANCZ II 400 spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. The FTIR spectra were measured by Nicolet NEXUS 470 FT-IR spectrometer. DSC spectra were performed on a NETSCH (DSC-204) unit at a heating rate of 10 °C min^{-1} under nitrogen. The fluorescence spectra were measured with F-4600 fluorescence spectrophotometer.

2.2. Synthesis of M

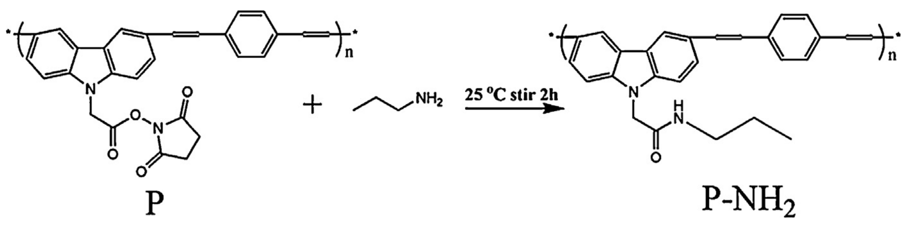
3,6-Dibromocarbazole (1.63 g, 5.00 mmol), potassium hydroxide (1.00 g, 17.80 mmol), and tetrabutyl ammonium bromide (0.05 g, 0.16 mmol) were dissolved in DMF (40 mL) in a 100 mL single-aperture flask, and stirred for 20 min. Ethyl chloroacetate (1.23 g, 10.00 mmol) was added to the flask above, and the mixture was refluxed at 85 °C for another 20 h, after cooling, the mixed solution was filtered. Sodium hydroxide (0.80 g, 20.00 mmol) solution was added to the filtrate, and refluxed at 85 °C for 5 h. The reaction mixture above was added to distilled water (400 mL) and filtered. The filtrate obtained was neutralized to pH 2–3 with HCl, which formed a white deposit. The deposit was filtered and dried under a vacuum. The product was afforded as a white solid (Yield 90%). ^1H NMR: (DMSO-d_6, 400 MHz), δ (ppm): 8.46 (s, 2*H*), 7.52–7.58 (q, 4*H*), 13.00 (s, 1*H*).

2.3. Synthesis of NHS-M

The crosslinker NHS-M was synthesized according to the method of Chen et al. [24] with some modification. Mixed solution was prepared by dissolving 2.80 mmol M and 5.60 mmol NHS together in 15 mL DMF. EDC (5.60 mmol) was added to the mixed solution, and the reaction mixture was gently stirred at 25 °C for 12 h. After reaction, DMF was washed out by water extraction (ethyl acetate) and purified through chromatography (silicone, ethyl acetate/petroleum ether = 10: 1) [25,26], then dried under vacuum at 60 °C. The product was afforded as a white solid. ^1H NMR: (DMSO-d_6, 400 MHz), δ (ppm): 8.50 (s, 2*H*), 7.65 (s, 4*H*), 5.96 (s, 2*H*), 2.77 (s, 4*H*).

2.4. Synthesis of conjugated polymer P

A 100 mL flask was charged with 5 mL DMF, monomer M (0.48 g, 1.00 mmol), divinylbenzene (0.13 g, 1.00 mmol), triethanolamine (0.35 mL), Pd $(OAc)_2$ (9.00 mg, 0.04 mmol) and tri(*o*-tolyl) phosphine (60.90 mg, 0.20 mmol). The reaction mixture was refluxed



Scheme 2. Synthetic of conjugated polymer P-NH_2. P-NH_2 represents the product by stirring the mixture of P and *n*-propylamine at 25 °C for 2 h.