



Detection of biogenic amines using a nitrated conjugated polymer

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ABSTRACT

Nitrated polythiophene (NPT_h) was examined for the detection of amine vapors. When the polymer film was exposed to vapors of biogenic amines (BAs) such as ethylenediamine, putrescine, and cadaverine, its color darkened instantly. Accordingly, the ultraviolet-visible (UV-vis) absorption spectra showed a significant hyperchromic shift, indicating the formation of an intermolecular charge transfer complex (NPT_h^{δ+}-BA^{δ-}) between the polymer and analyte. On the other hand, the change in absorption was relatively small for non-BA vapors. The absorption response rates of NPT_h to the BAs were quite different because of the differences in their saturated vapor pressures. A linear relationship between vapor concentration (z) and absorption change (y : A/A_0 , where A and A_0 are the absorbances after and before exposure to the amine, respectively) was established, given by the equation $z = k(y-1)$, where $k = (\text{conc}_{\text{sat}}/t_{\text{eq}})/a$, conc_{sat} is the saturated vapor concentration, and t_{eq} is the exposure time necessary to reach an equilibrium in the absorption change. The k values for ethylenediamine, putrescine, and cadaverine were determined to be 5.01×10^3 , 0.83×10^3 , and 0.40×10^3 ppm, respectively. This equation can be used to determine the unknown BA vapor concentration by UV-vis spectroscopic analysis.

1. Introduction

Conjugated polymers (CPs) have been extensively utilized as functional active materials for optoelectronic devices and chemical sensors [1–6]. Especially, in the area of chemical sensing, CPs are one of the most powerful probes with highly sensitive optical (or electrical) responses to various kinds of analytes because they can reveal remarkable signal amplification as a result of the molecular wire effect based on their intrinsic conjugated cooperativity [7,8]. CPs are generally favorable for the detection of electron-deficient analytes because they usually exist in the π electron-rich state. Conversely, for efficient detection of electron-rich analytes, CPs should be entirely electron-poor all over the molecular wire backbone. Sensing of amines is relevant to this case because amines have a lone pair of electrons on the central nitrogen atom and possess electron-donating character. Cationic CPs combined with different counter-anions have been used for sensing amines [9]. The polymer array showed extremely high fluorescence responses in sensitivity and selectivity to a series of industrially relevant amine vapors. On the other hand, a carboxyl-containing CP generated a

very unique multidimensional response in absorption change upon analyte-induced aggregation with various amines [10]. However, such highly functionalized, electron-poor CPs that respond to amine vapors are still very rare [11]. Nitrated CPs constitute another promising candidate because of the powerful electron-withdrawing character of the nitro group. Nitrated CPs should readily form an intermolecular charge transfer complex with amines during the exposure to amine vapors. In this study, we examined the potential use of nitrated polythiophene (NPT_h, Fig. 1a) as a food freshness sensor for the sensing of biogenic amines (BAs, Fig. 1b) in comparison with non-BAs. NPT_h showed significant color darkening when exposed to vapors of the BAs because of the formation of a charge transfer complex between NPT_h and the BA. The absorption response rates were considerably different depending on the saturated vapor pressure of BA. Herein we describe the details of the sensing action based on spectroscopic analyses.

2. Results and discussion

NPT_h was prepared by the nitration of the parent polymer (poly-

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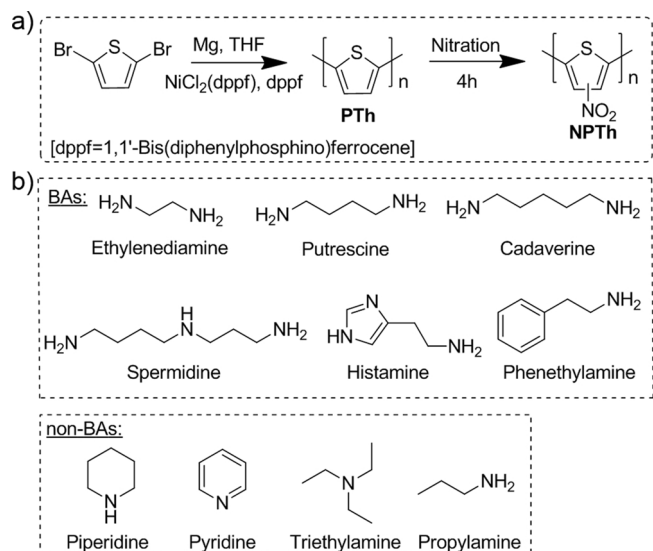


Fig. 1. (a) Synthetic route of nitrated polythiophene (NPTH). (b) Chemical structures of the amines used in this study.

thiophene, PTh), following a method previously reported in the literature [12]. The detailed synthetic method has been described in the experimental section. The reaction was performed for 4 h and monitored by IR spectroscopy (Fig. S1). The degree of nitration was determined to be 96% from the N/C molar ratio obtained by elemental analysis. The original metallic black color turned to a slightly light brown after the nitration (Fig. S2). Simultaneously, the solubility of the polymer was also drastically changed. NPTH dissolved very well in common organic solvents, such as toluene and tetrahydrofuran, while PTh was completely insoluble. Owing to its solubility, good-featured films with a smooth surface were readily obtained by the solvent casting method and used for spectroscopic analysis. The NPTH film showed a broad absorption band in a wide wavelength range of 300–700 nm.

In this study, several polyamines (BAs: ethylenediamine, putrescine, cadaverine, spermidine, phenethylamine, and histamine in Fig. 1b), and monoamines (non-BAs: piperidine, pyridine, triethylamine, and propylamine in Fig. 1b), with different saturated vapor pressures were tested as analytes for the detection of amine vapors and compared to non-amine compounds such as methanol, toluene, acetic acid, and propanethiol. Among the analytes used in this study, the aliphatic BAs such as ethylenediamine, putrescine, cadaverine, and spermidine which contain multiple primary amine groups, are typical putrefactive substances that are generated by the enzymatic decarboxylation of

amino acids during the processing and storage of food products [13]. A large amount of such BAs in foods can have a serious toxic effect in our body [14]. Therefore, it is very important to accurately detect low-ppm concentrations of such poisonous substances in order to maintain the quality and safety of the food products [15]. When the NPTH film (thickness: $\sim 2 \mu\text{m}$, solvent cast) was exposed to the aliphatic BA vapors at ambient temperature and pressure, except for the case of spermidine existing as solid, it quickly turned dark. Eventually, the brown color became considerably deep and dark (Fig. 2). This is because the bulk liquid BAs are vaporized in the air and subsequently diffuse into the polymer film to form charge transfer complexes with NPTH. This illustrates the high sensitivity of the NPTH film to BA vapors. However, it was quite difficult to accurately measure the variations in the ultraviolet-visible (UV-vis) absorption spectra using a thin NPTH film (thickness of $\sim 300 \text{ nm}$, spin-coating) because of the extremely fast response to BAs. Therefore, it was necessary to avoid a direct contact with BA liquids and release the vapors more slowly during the absorption measurement. To this end, the BAs were adsorbed on silica gels in a mixing ratio of 2:1 (silica gel wt%:BAs wt%) before spectroscopic analysis. This advance preparation was very helpful in lowering the release rates of the BA vapors. Therefore, a gas generator to provide a specific concentration was not required in our case. When the thin polymer film was exposed to the BA-adsorbed silica gels, the absorption band gradually increased over all wavelengths at a measurable speed to reach an equilibrium at an A/A_0 value of approximately 4.3–4.7 at 450 nm for ethylenediamine, putrescine, and cadaverine (Fig. 3a–c). This indicated a hyperchromic shift because of the formation of $\text{NPTH}^{\delta+}\text{-BA}^{\delta-}$ charge transfer complexes. The smaller the BA molecule, the higher the absorption response rate. This indicated the steric effect that a smaller BA molecule diffuses faster into the NPTH film. The slight difference in the A/A_0 value at equilibrium for the different BAs is probably because of the slight differences in their basicity. We also determined the limit of detection (LoD) for ethylenediamine, putrescine, and cadaverine. The values were 5.6, 0.92, and 0.45 ppm, respectively, which are almost same to those reported by other research groups who utilized fluorescent probe materials as an amine sensor [9,16]. On the other hand, NPTH did not reach an absorption enhancing equilibrium for spermidine within the exposure time owing to its extremely low saturated vapor pressure (Fig. 3d and Table S1). Owing to the same reason, NPTH also did not show any significant absorption changes in response to aromatic and heterocyclic BA vapors such as phenethylamine and histamine (Fig. 3e and f). Consequently, the absorption response rate of the NPTH film was proportional to the saturated vapor pressures of BAs (Fig. 4 and Table S1). This indicates that the rate of formation of the charge transfer complex between NPTH and BA is significantly dependent on the saturated vapor pressure of the BAs. On the other hand, the monoamines used in this study can be classified as non-BAs because BAs usually have at least one aliphatic primary amine group. Piperidine, pyridine, and triethylamine are

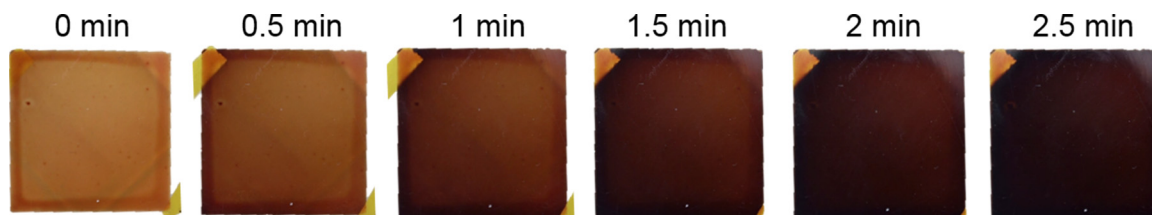


Fig. 2. Photographs of the NPTH film (solvent cast, thickness $\sim 2 \mu\text{m}$) when exposed to ethylenediamine vapors at room temperature and atmospheric pressure.

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