Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 871–874

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A selective fluorescent and colorimetric dual-responses chemosensor for streptomycin based on polythiophene derivative

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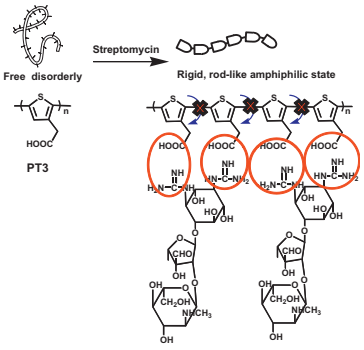
HIGHLIGHTS

- A new polythiophene-based chemosensor for streptomycin has been developed.
- **PT3** displays colorimetric and fluorescent dual-responses toward streptomycin.
- The sensing mechanism may be the conformational change of **PT3** induced by streptomycin binding.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 May 2014
Received in revised form 23 July 2014
Accepted 24 September 2014
Available online 2 October 2014

Keywords:
Colorimetric sensor
Fluorescent
Polythiophene
Conformational change
Streptomycin

ABSTRACT

A colorimetric and fluorescent dual-responses chemosensor (**PT3**, a water-soluble polythiophene) for streptomycin was designed and synthesized. The structure of **PT3** was characterized by using infrared spectroscopy, ^{1}H NMR and gel-permeation chromatography analyses. The conformational change of **PT3** induced by streptomycin resulted in the red shift of absorption spectra and fluorescent quenching. Moreover, **PT3** showed excellent selectivity for streptomycin over other antibiotics and biomolecules. **PT3** could quantificationally detect streptomycin in the range of 2–70 μM with a detection limit of 0.2 μM (116 ppb), which is lower than the maximum residue limit defined by World Health Organization (200 ppb).

Introduction

Antibiotics, such as penicillin, neomycin, and streptomycin have been widely used in veterinary practice for treating the bacterial infections of domestic animals and dairy cattle. They are also used as a pesticide, to combat the growth of bacteria, fungi, and algae. Human also often take antibiotics based drug to treat infectious diseases [1]. Thus, antibiotic residues are often encountered in animal-derived food products, drinking water, and even in human body; these residues are now becoming one of the most serious threats to human health [2,3]. For example, the emergence of antibacterial-resistant super bacteria which has killed thousands of people around the word arises from abuse of antibiotics. Thus, there is a high demand for a selective and efficient approach to track the residual antibiotics. To date, various analytical methods, such as microbiological methods [4,5], immunochemical methods [6,7], high-performance liquid chromatography [8–10], and spec-

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http://dx.doi.org/10.1016/j.saa.2014.09.106
1386-1425/

tral analysis have been developed to detect antibiotic residues [11,12]. Among these, spectral analysis such as UV–vis and fluorescence spectroscopy is widely used due to its distinctive advantage, such as high selectivity, high sensitivity, short response time, conveniently and on line detection [13–15]. However, few successful examples were satisfied to practical application. Therefore, development of new approaches for quantitative detection of antibiotics with high sensitivity and selectivity is an important topic from both scientific and technical views.

As an emerging sensory material, water-soluble conjugated polythiophenes have been receiving much research interest and have been designed for probing many biological relevant targets, such as LPS, DNA, proteins, and ATP [16–21]. The conjugated polythiophenes are able to bind analytes through noncovalent bonding, such as the electrostatic interaction, hydrophobic interaction, hydrogen bonds, which is proved to cause conformational changes [22,23]. When the conjugated polythiophene chain was in nonplanar state, the absorption wavelength is about 400 nm. However, the absorption wavelength of polythiophene can be red shifted due to more planar conformation of the conjugated chain. Therefore, water soluble polythiophene based chemosensors have the advantages over other conjugated polymers in visual detection [24–27]. Additionally, the conformational changes of the polythiophene chain can also result in fluorescent quenching and a redshift in the emission wavelength after binding the target.

Along with our continuing efforts in the exploration of chemosensors for the selective detection of antibiotics based on both small molecule and polythiophenes [28–30], herein, we reported poly(3-thiophene acetic acid) (**PT3**) as a colorimetric and fluorescent dual-responses chemosensor for streptomycin. The details of streptomycin binding characteristics of the **PT3** have been investigated by UV–vis and fluorescence spectroscopy. The selective and sensitive of **PT3** toward streptomycin arise from the strong electrostatic interaction bonds between carboxyl group and guanidyl group. The limit of detection was calculated to be 0.2 μM (116 ppb), which is lower than maximum residue limits defined by World Health Organization (200 ppb) [31].

Experimental

Materials and general methods

Dry $FeCl_3$, 3-thiophene acetic acid, phosphate, pyrophosphate, adipic acid, aspartic acid, and glutamic acid were purchased form Alfa Aesar. Carbenicillin, chloromycetin, penicillin, neomycin, erythromycin, ampicillin, and streptomycin were purchased from INALCO. Other reagents were purchased from Beijing Chemical Regent Co. All reagents and chemicals were AR grade and used directly without further purification unless otherwise noted. $CHCl_3$ was distilled from CaH_2 under nitrogen. The water was purified by Millipore filtration system.

All UV–vis and fluorescence spectra in this work were recorded in Hitachi U3010 and Hitachi F4500 fluorescence spectrometers at 25 °C. All spectral characteristics were carried out in DMF/ HEPES buffer (5/95, v/v) solution. The stock solution of **PT3** was prepared in DMF (1.0×10^{-3} M), stored at room temperature in the dark before use. The antibiotics solutions (1.0×10^{-2} M) were prepared in HEPES buffer solution. To a quartz cell (1 cm of optical path length) filled with 2 mL of **PT3** (DMF/HEPES buffer (5/95, v/v) solution) was added with the stock solution of antibiotics dropwise using a micro-syring. The volume of these added antibiotics stock solutions was less than 100 μL to remain the concentration of **PT3** unchanged. All pH measurements were made with a Sartorius basic pH-meter PB-10. ^{1}H NMR (400 MHz) spectrum was determined on a Bruker Advance-400 spectrometer with chemical shifts reported as ppm (tetramethylsilane as internal standard). The gel-permeation chromatography (GPC) was performed using Polystyrene as the standard, and THF was employed as eluent. FT-IR spectrum in KBr was collected on a Varian Excalibur 3100 FTIR spectrometer.

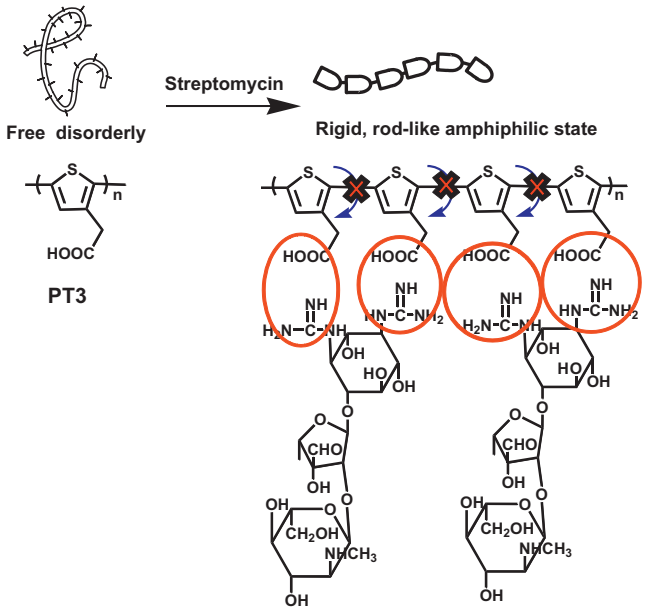
Synthesis

6.6 g dry $FeCl_3$ was dissolved in 30 mL of dry $CHCl_3$ under nitrogen, and then 1.42 g 3-thiophene acetic acid dissolved in 20 mL dry $CHCl_3$ was added dropwise. The reaction mixture was stirred at room temperature for 2 days. The resulting precipitate was collected, wash with methanol, and finally dried under vacuum to give the desired polythiophene as a brown solid (0.85 g, Yield: 59.8%). ^{1}H NMR (400 MHz, NaOD-D_2O, TMS, ppm): δ 3.23–3.82 (br), 6.83–7.32 (br). IR (KBr pellet, cm^{-1}) 3430, 2924, 1706, 1628, 1398, 1200. Gel-permeation chromatography analysis (GPC): Mn = 32,952 g mol^{-1}, PDI = 1.67.

Results and discussion

*The design and synthesis of chemosensor **PT3***

Water-soluble polythiophene-based chemosensors transduced by simply conformational change upon binding target molecule provide an ideal platform for the design of colorimetric sensors [32,33]. A streptomycin molecule bears two guanidyl groups with p*Ka* values up to 13.5, which means that the groups can bear positive charge in the aqueous solution [34]. Moreover, the extreme affinity of carboxyl group to guanidyl group over other cation could improve the selectivity and specificity of polythiophene-based chemosensors for streptomycin [31,35]. Based on the above considerations, we designed a simple but selective and sensitive chemosensor for streptomycin sensing on the basis of strong electrostatic interaction between carboxyl-modified polythiophene and streptomycin. As shown in Scheme 1, the conformation of **PT3** in aqueous solution (5% DMF) is freed disorderly. Upon complexation with streptomycin, the electrostatic interaction between carboxyl and guanidyl groups may induce the conformational



Scheme 1. Molecular structures of **PT3**, streptomycin, and the proposed interaction mechanism between **PT3** and streptomycin.