



# Fluorescence chemical sensor for determining trace levels of nitroaromatic explosives in water based on conjugated polymer with guanidinium side groups



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## ABSTRACT

A novel fluorescent conjugated polymer (poly(2-amino-N-(2-((4-ethynylphenyl) ethynyl) phenyl)-5-guanidinopentanamide)-1,4-phenylethynylene-1,4-phenyleneethynylene, PPE-Arg) was synthesized in this paper. We found that PPE-Arg could be quenched by picric acid (PA). Photoinduced electron transfer (PET) mechanism can be used to describe the fluorescence quenching of PPE-Arg. It could be speculated that the photo-induced electrons may be transferred from PPE-Arg to nitroaromatic explosives. In this paper, the experiment conditions and detection performance of PPE-Arg were systematically studied. The experiment results demonstrate PPE-Arg as a sensor for PA has a good linear range from  $5 \times 10^{-7}$  to  $6 \times 10^{-5}$  mol L<sup>-1</sup> with the calculated limit of detection (LOD) to be  $1.0 \times 10^{-7}$  mol L<sup>-1</sup>. Meanwhile, reaction time between PPE-Arg and PA is less than 1 min. This proposed sensor was applied to rapidly detect nitroaromatic explosives in environmental water samples and satisfactory results were obtained.

## 1. Introduction

Nowadays, public security has attracted more and more concern but how to simply and quickly detect the explosives is always a serious problem for many scientific researchers. The nitroaromatic compounds as goal matters have been studied by many researchers because of their implementation as principal constituents in the preparation of explosives [1,2]. Picric acid (PA), a representative nitroaromatic compounds, has been used as a military explosive with strong explosion ability [3,4]. Besides, it has widely applications in dyes, fireworks, leather and medicine industries [5–7]. Due to its higher water solubility, it will contaminate groundwater once it is released into the environment. The contaminated groundwater can irritate the skin, eyes and respiratory system and even cause severe health problems, such as anemia, male infertility and respiratory organs [8,9]. In view of the significance and perniciousness of PA in the area of national security and environment, it is highly desired to develop a simple and rapid analytical method for detection of PA.

Recently, many techniques and methods for qualitative and quantitative analysis of PA have been developed and utilized, include fluorescence method [9], plasma desorption mass spectrometry [10], surface enhanced Raman spectroscopy [11] and nuclear quadrupole resonance [12], and so on. However, these methods suffer from several

limitations, such as time-consuming, high-cost, less sensitive and require complicated instruments [13]. Recently, fluorescence-based detection methods with nanomaterials, organic small molecules and conjugated polymers (CPs), have drawn much more attention owing to their sensitivity, short response time and convenient visual detection [14,15]. Among all these materials, CPs due to efficient electron delocalization and exciton migration over long distances show more sensitive response than the others [16]. Swager et al. had synthesized pentiptycene-derived phenyleneethynylene polymers and used them to make polymer films as a sensor for 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) [17,18].

In this study, arginine was used to functionalize CPs because it has a good water solubility. A new fluorescent conjugated polymer (poly(2-amino-N-(2-((4-ethynylphenyl) ethynyl) phenyl)-5-guanidinopentanamide)-1,4-ph-enylethynylene-1,4-phenyleneethynylene, PPE-Arg) was synthesized, which can be used for detecting PA in water samples. The advantage of PPE-Arg is that it not only has hydrophilic property and unaffected by acidity, but also can rapidly detect PA because the fluorescence intensity of PPE-Arg rapidly decreases and gets equilibrium within 40 s when PPE-Arg interacts with PA. The experiment results show that PPE-Arg has good linear range, high sensitivity and low detection limit for detection of PA. It is significant that PPE-Arg can provide a new choice for rapid detection of PA in environmental water samples.

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## 2. Experimental

### 2.1. Reagents and chemicals

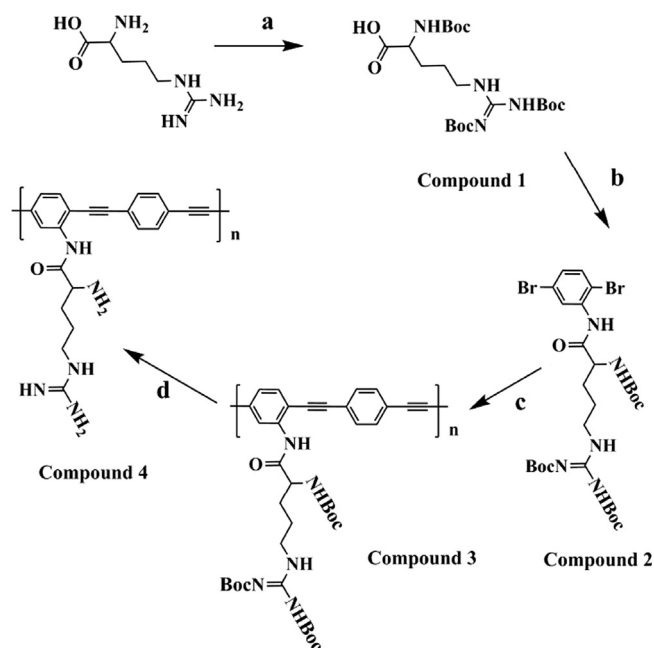
1, 4-Diethynylbenzene (96%),  $(\text{PPh}_3)_4\text{Pd}$  (99%), di-tert-butyl dicarbonate (99%), trifluoroacetic acid (TFA) (99.9%), 2, 5-dibromoaniline (98%), arginine (Arg, 99%), (3-dimethylaminopropyl)-ethyl-carbodiimid monohydrochloride (EDCI, 98%) and N-hydroxybenzotriazole (HOBT, 99%) were purchased from J&K SCIENTIFIC LTD (Beijing, China). NaCl, HCl, NaOH, citric acid,  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{CH}_3\text{COOH}$  and  $\text{H}_3\text{BO}_3$  were purchased from Beijing Chemical Works (Beijing, China). Tris(hydroxymethyl)aminomethane (Tris), tert-butanol, 3-nitroaniline (3-NA), 2-chloronitrobenzene (2-ClNB), 2,4-dinitrotoluene (2, 4-DNT), picric acid (PA), nitrobenzene (NB), 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT) and 4-nitrobenzoic acid (4-NBA) were purchased from Energy chemical technology co., LTD (Shanghai, China). Triethylamine and diisopropylamine were purchased from Tianjin Fu Yu Chemical Co., Ltd. (Tianjin, China). Dichloromethane, methanol, ethanol, tetrahydrofuran, dimethyl formamide, acetonitrile, tetrahydrofuran, dichloromethane, acetone and acetic ether purchased from Tianjin Tiantai Fine Chemical Co., Ltd. (Tianjin, China). Anhydrous magnesium sulfate was purchased from Tianjin Dong Li Big Chemical Reagent Factory (Tianjin, China). Thin layer chromatography (TLC) was carried out using silica gel 60 F254, and column chromatography was conducted over silica gel (300–400 mesh), both of which were obtained from the Qingdao Ocean Chemicals (Qingdao, China). Twice-distilled water was used throughout all experiments. All chemicals were used without further treatment. For the practicality experiments, lake water 1, lake water 2 and tap water were obtained from Yan Lake in Changchun, Peony Garden in Changchun and tap water in our laboratory. Water samples were filtered by 0.45  $\mu\text{m}$  filter membrane and stored in 100 mL flask, respectively.

### 2.2. Instrumentations

The nuclear magnetic resonance spectroscopy (NMR) of compounds were identified by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (Varian Mercury YH-400 NMR spectrometer), using tetramethylsilane (TMS) as an internal standard. Infrared spectroscopy (IR) spectra were recorded using Spectrometer One (Perkin-Elmer Corporation, America). ESI Mass spectra were obtained using a Q-Trap 2000 (Applied Biosystems Corporation, American) without using the liquid phase part. All fluorescence measurements were carried out in a 1 cm path length quartz cuvette with a Hitachi F-2700 spectrometer (Shimadzu Corporation, Japan). Fluorescence quantum yields and fluorescence lifetime were carried out with a FLS920 steady state and transient state fluorescence spectrometer (Edinburgh Instrument). All pH measurements were tested with a Sartorius PB-10 digital pH meter. All the optical measurements were carried out at room temperature (298 K) under ambient conditions.

### 2.3. Synthesis of PPE-Arg

PPE-Arg was synthesized through Cassar-Heck-Sonogashira reaction. The synthetic route of PPE-Arg was shown in Scheme 1. At first, amino group in arginine was protected using di-tert-butyl dicarbonate ( $\text{Boc}_2\text{O}$ ) [19] and compound 1 was obtained. And then, compound 2 was obtained by acylation between compound 1 and 2,5-dibromoaniline. Later, 1,4-diethynylbenzene and compound 2 were reacted through Cassar-Heck-Sonogashira reaction [20] and compound 3 was synthesized. In the end, the Boc-protecting groups of amino group were removed by trifluoroacetic acid (TFA) to yield target compound 4 [21]. Intermediates and the final product were characterized by liquid chromatography-mass spectrometry (LC-MS), IR and NMR described in detail (see Fig. S1–S7).



**Scheme 1.** Synthetic routes of PPE-Arg. Reagents and conditions: (a) tert-butanol/water, di-tert-butyl dicarbonate, arginine, NaOH, stirred 48 h, 25 °C (92%); (b) anhydrous  $\text{CH}_2\text{Cl}_2$ , Boc-Arg-(Boc) $_2$ -OH, EDCI, HOBT,  $\text{Et}_3\text{N}$ , 24 h, 0 °C→25 °C (12%); (c)  $\text{CHCl}_3$ , triethylamine, diisopropylamine, 1,4-diethynylbenzene, stirring under oil bath, 24 h, 60 °C (35%); (d) anhydrous  $\text{CH}_2\text{Cl}_2$ , trifluoroacetic acid, under argon, 3 h, 0 °C→25 °C (46%).

#### 2.3.1. Synthesis of compound 1 (Boc-Arg-(Boc) $_2$ -OH)

Arginine (3.484 g, 20 mmol) was added into a solution of tert-butanol (60 mL) and water (60 mL) in a 250 mL round-bottom flask. The mixture was cooled to 0 °C in an ice bath and sodium hydroxide (2.8 g, 70 mmol) was added. The solution was stirred for 5 min at 0 °C. Then, di-tert-butyl dicarbonate (18.4 mL, 80 mmol) was added to the mixed solution in portions. The reaction mixture was stirred for 48 h at room temperature and monitored by TLC ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 15:1, v/v). The tert-butanol (60 mL) was evaporated under reduced pressure and the residue was acidified with citric acid to pH 3. The above solution extracted with ethyl ether. The extracted solution was divided into two layers in the separating funnel. The upper layer was collected and the extracted solution was extracted with ethyl acetate (30 mL) for 3 times. The extractant was dried with anhydrous sodium sulfate and evaporated in a vacuum. The white solid (9.2621 g, 92% yield) was obtained after dried in a vacuum oven.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 1.37 (s, 9 H), 1.40 (s, 9 H), 1.48 (s, 9 H), 1.91(s, 2 H), 3.09 (m, 2 H), 3.76–3.88 (m, 2 H), 4.65 (s, 1 H), 6.94 (d,  $J = 9.0$  Hz, 1 H), 8.24–8.28 (m, 1 H), 9.05 (s, 1 H), 11.51 (s, 1 H). MS (ESI $^+$ )  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{38}\text{N}_4\text{O}_8$ , 474.27, found 473.3.

#### 2.3.2. Synthesis of compound 2

Compound 1 (0.19 g, 0.4 mmol) was added in 10 mL of anhydrous  $\text{CH}_2\text{Cl}_2$  and stirred at 0 °C for 20 min. Then, triethylamine (0.252 mL, 0.9 mmol), HOBT (0.121 g, 0.4 mmol) and EDCI (0.0767 g, 0.4 mmol) were added and the mixture was stirred at 0 °C for 30 min 2,5-dibromoaniline (0.1000 g, 0.4 mmol) in 10 mL of anhydrous  $\text{CH}_2\text{Cl}_2$  was dropwise added into the above mixed solution. After stirring overnight at room temperature, water was added to the reaction mixture. The reaction mixture was adjusted to pH 12 by 10% NaOH solution and extracted 3 times with ethyl ether. The organic layer was dried using anhydrous  $\text{MgSO}_4$  and evaporated in a vacuum. The crude product was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 10:1, v/v). The final product was evaporated in vacuum and collected as white powder (12% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 1.61–1.01 (m,

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