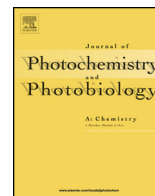




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## A selective fluorescent resonance energy transfer quenching and resonance light scattering enhancement dual-recognition probe for 2,4,6-trinitrotoluene



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## ABSTRACT

Fluorescein isothiocyanate (FITC) conjugated to polyethylenimine (PEI) (FITC&PEI) was synthesized and characterized. The nitrogen-containing organic groups played a key role in sensing nitroaromatic compounds that can bind 2,4,6-trinitrotoluene (TNT) to form TNT anions through an acid–base pairing interaction and FITC dye conjugation. The formation of TNT anions efficiently quenched the emission of FITC dye at 516 nm by fluorescent resonance energy transfer and induced the enhancement of a resonance light scattering (RLS) signal. A novel, dual-channel chemosensory FITC&PEI probe was thus constructed. Meanwhile, the FITC&PEI probe also exhibited highly selective fluorescence and RLS responses for TNT over other nitroaromatic compounds. Very good linearity was observed within the ranges of 3.0–150 nM TNT (detection limit down to 0.5 nM and RSD of 5.8%,  $n = 7$ ) for fluorescence and 1.0–150 nM TNT (detection limit down to 0.2 nM and RSD of 8.4%,  $n = 7$ ) for RLS. The proposed methods were well-suited for detecting and distinguishing trace amounts of TNT in aqueous solution.

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### 1. Introduction

Multi-signal response in one probe toward one target species is a current research hotspot [1]. Multi-signal output devices are usually constructed by chemically integrating multiple reporter units such as fluorescence, absorption and Raman in a molecule [2]. The multi-signal output occurs after a target species interacts with a probe molecule, allowing them to contact and affect each other. The generation of one signal can predict or demonstrate the existence or mechanism of other signals, and *vice versa*. The fluorescence technique bears the merits of high signal output, high sensitivity and simplicity. The endeavors have always been aiming at developing multi-signal responsive devices that incorporate fluorescence for the real-time determination of analytes in samples. Manganese (Mn)-doped zinc sulfide (ZnS) quantum dots (QDs) with synchronous short and long-lived emissions and scattering triple-channel sensing properties have been elegantly designed into a lab-on-a-nanoparticle [3]. Wu et al. [4] and Sang et al. [5] explored the nonspecific interactions of Mn doped ZnS QDs with proteins by reading out their triple channel optical properties to develop a sensor array for the proteins discrimination.

Similarly, dual-channel sensing systems for different analytes have been constructed through the integration of the optical responses of Mn-doped ZnS QDs (long-lived emission and scattering), recognizing trypsin, lysozyme and 2,4,6-trinitrotoluene (TNT) by phosphorescence, resonance light scattering (RLS) and dual-signal co-sensing, respectively [6,7].

TNT is a high explosive and environmentally detrimental substance that has become one of the major social concerns [8,9]. The United States Environmental Protection Agency lifetime health advisory guidance level and risk based concentration level of TNT in drinking water are both 2 ppb ( $\sim 8$  nM). Detection of trace explosives has been an important problem, and researchers from many scientific fields have been addressing for years. Therefore, the development of highly sensitive methods with tailored selectivity for the detection of TNT in environmental samples has attracted considerable research efforts in the recent years [10,11]. Given that subtle changes on the surface properties of photoluminescent materials can easily cause significant changes in their optical properties, the present designs for TNT sensing have focused on fluorescence quenching based on electron-deficient TNT molecule [12–24]. Among these methods, the transition metal ion doped QDs [6,13–15] and the combination of near-infrared and turn-on fluorescence [25] can greatly improve the detection sensitivity to efficiently eliminate the background signals from short wavelength emission in the samples and probe signals.

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The above approaches have led to significant contributions to respective target species assays. However, the essence of Mn doped ZnS QDs with low quantum yield (~4.5%) makes it unbeneficial to the improvement of the detection sensitivity [6]. A fluorescent lab-on-a-molecule-level device with multi-signal output may be well-suited for efficient and convenient analysis of TNT explosive. In this study, we report the design and synthesis of fluorescein isothiocyanate conjugated to branched polyethylenimine (FITC&PEI) with unusual TNT dual-recognition functions, and the study of its fluorescent and RLS sensing features in aqueous solution. The PEI can bind TNT species to form TNT anions through acid–base pairing interaction between electron-rich groups containing the nitrogen atom of PEI and the electron-deficient aromatic rings of TNT. The formation of TNT anions can aggregate the inter-PEI molecules, and induce RLS signal enhancement, as well as efficiently quench the fluorescence at 516 nm wavelength through fluorescence resonance energy transfer (FRET) pathways. Notably, FITC&PEI, a lab-on-a-molecule-level device, also displayed a highly selective fluorescent and RLS responses for TNT species.

## 2. Materials and methods

### 2.1. Materials

TNT, 2,4-dinitrotoluene (DNT) and 4-trinitrotoluene (NT) were generously given by Professor Zhao-Wu Shen (University of Science and Technology of China, Hefei, China) and used as recrystallized from methanol–water (2:1, v/v) mixture. Fluorescein isothiocyanate (FITC, purity >95%) is a product of Alfa Aesar (Tianjin, China). 4-Nitrophenol (4-NP, purity >99.5%) and branched polyethylenimine (PEI, purity 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. and Aladdin Reagent Inc. (Shanghai, China), respectively. The stock solutions of TNT, DNT, NT and 4-NP were prepared by dissolving in ethanol with a concentration of  $1 \times 10^{-3}$  M for TNT, and  $2 \times 10^{-2}$  M for others. The concentration of FITC&PEI in ethanol/water mixed solution (20/80, v/v) was about  $2 \times 10^{-5}$  g/L. Double distilled water (DDW) was prepared in Elix 5 pure water system (Millipore, Milwood, MA, USA). All other reagents were of analytical grade and used without further purification.

### 2.2. Apparatus

The ultraviolet visible (UV–vis) absorption spectra were obtained using a UV-3600 UV–vis spectrophotometer (Shimadzu, Tokyo, Japan). The fluorescence and RLS spectra were recorded on an F-4600 (Hitachi, Tokyo, Japan). The measurements were performed equipping with a plotter unit and a quartz cell (1 cm  $\times$  1 cm). The contents of mineral ions in real water samples were analyzed with an OPTIMA 5300DV ICP-OES (Perkin-Elmer, Norwalk, CT, USA). The morphology and microstructure of the aggregation between TNT and FITC&PEI polymer were characterized by high resolution transmission electron microscopy on a JEM-200CX (JEOL, Tokyo, Japan) microscope operating at a 200 kV accelerating voltage. The samples for TEM were obtained by drying the sample droplets from ethanol dispersion onto a 300-mesh Cu grid coated with a lacey carbon film, which was then allowed to dry prior to imaging.

### 2.3. Spectroscopic measurements and imaging

Spectral measurements were performed with excitation and emission slit widths of 10 nm for the fluorescent and synchronous modes. For the photomultiplier tube voltage, 700 V and 400 V were set for fluorescence and RLS, respectively. Fluorescence at an emission wavelength of 516 nm with an excitation wavelength of

475 nm and RLS at a wavelength range of 200–700 nm were monitored. The camera for imaging was located 20 cm apart from the sample cell on the UV lamp box.

### 2.4. Synthesis of FITC&PEI polymer

FITC&PEI polymer was prepared according to the reported procedures in the literature [17]. Typically, 5.0 mg of FITC was dissolved in anhydrous alcohol (5 mL) and then added dropwise into the anhydrous alcohol solution (25 mL) containing PEI (1.0 g). The resultant solution was kept under mechanical stirring in the dark for 24 h under a dry nitrogen atmosphere at room temperature, which led to the formation of the FITC&PEI polymer. The productions were dissolved in 25 mL DDW after vacuum dried at room temperature, and then repeatedly extracted by 25 mL hexane to totally remove the unbound FITC. To evaluate the loading amount of FITC to PEI backbone, the fluorescence spectra of anhydrous alcohol containing 0.005 mg of FITC stirred for 24 h in the dark and the above residual solution extracted by hexane were measured at the same time. Finally, the productions were placed in a refrigerator for further use prior to being diluted to the desirable concentration.

### 2.5. Analysis of a real sample

The water samples were collected in a precleaned glass bottle from a pond in the south area of Anhui Jianzhu University (Hefei, Anhui, China). The samples were filtered through 0.45  $\mu$ m Supor filters and stored in a refrigerator after the addition of ethanol (water/ethanol, 1:1, v/v). TNT was not detected by the proposed method in the collected water samples, thus a recovery test was carried out on the samples spiked with 50, 75 and 100 nM TNT to evaluate its reliability after the pH of the filtered water sample was adjusted to 7.5.

## 3. Results and discussion

### 3.1. Synthesis and emission characterization of FITC&PEI polymer

Electron-rich molecules can easily interact with electron-deficient TNT molecules to form Meisenheimer complexes (MHCs) through acid–base pairing and hydrogen bond assistance interaction or TNT anions through acid–base pairing interaction. In the reports on TNT assays, amine-containing molecules are commonly selected as the electron donor of TNT for the design of either sensitive sensing platform through fluorescence quenching [12–25] or molecularly imprinted polymers to achieve tailored selectivity [26–28]. Different amine-containing molecules can couple with dye or anchor at the surface of fluorescent nanomaterials to form multifunctional nanocomposites. For example, mercaptoethylamine (MEA) and L-cysteine (L-cys) can tightly bind at the surface of bare ZnS QDs or Au nanoparticles through the mercapto groups [12,25]. PEI is a polymer molecule containing multi-amine and imino groups (Fig. 1A). When conjugated with a suited signal reporting unit such as fluorescence, Raman and electrochemiluminescence, the resulting polymer molecule would be an excellent sensing platform and features a good capture property [1].

In the present work, the FITC dye was utilized as signal reporting unit because its emission wavelength is close to the peak absorption of TNT anions. The PEI was conjugated with FITC in anhydrous ethanol for 24 h in the dark at room temperature (Step 1 in Fig. 1B). During the course of the reaction, humidity was excluded by the input of dry nitrogen to prevent the hydrolysis of the FITC dye. The resulting FITC&PEI can emit strong fluorescence at 516 nm, indicating that the FITC dye was successfully conjugated with PEI (Fig. 2A). About 0.45 wt% of fluorophore was loaded to PEI polymer backbone.

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