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Fluorescent thiazol-substituted pyrazoline nanoparticles for sensitive and highly selective sensing of explosive 2,4,6-trinitrophenol in aqueous medium

Mukhtiar Ahmed[a], Shahid Hameed[a], Ayesha Ihsan[b], Muhammad Moazzam Naseer[a,*]

[a] Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan
[b] Nanobiotechnology group, National Institute for Biotechnology and Genetic Engineering (NIBGE), P.O. Box 577, Jhang Road, Faisalabad, Pakistan

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ABSTRACT

2,4,6-Trinitrophenol (TNP), also known as picric acid is an explosive material that pose hazard to human safety and health, therefore its selective and efficient detection is extremely important. By knowing the good optical properties of pyrazoline derivatives, thiazol-substituted pyrazoline (**1**)-based organic fluorescent nanoparticles (**N1**) were employed for the highly selective sensing of TNP over a number of other nitroaromatics in aqueous medium. The quenching efficiency of **N1** is proportional to the concentration of TNP over 0 μM–6 μM concentration range and it efficiently detects TNP with a detection limit of 0.002 ppm. The fast, sensitive and highly selective detection of trinitrophenol (TNP) on the basis of fluorescence quenching in contrast to other nitro-explosives and structurally-related compounds in aqueous medium by the fluorescent probe **N1** is attributed to the acid-base interaction induced electron transfer process.

1. Introduction

Nitroaromatic compounds, in general, represent the most important chemicals that are heavily used for the production of various products in industry [1–3]. Unfortunately, their extensive use has led to the large release of these compounds into environment resulting in the contamination of soil and groundwater [4–6]. Other than having environmental concerns which directly affect human health, most of these nitroaromatics has detonation properties [7]. The nitro compounds that are well-known for such properties are nitrophenol derivatives in addition to most widely used nitro-explosive, 2,4,6-trinitrotoluene (TNT). The nitro group not only increases the acidity of phenols, but also augments detonation [7]. Due to this reason, 2,4,6-trinitrophenol (TNP) also known as picric acid is another superior explosive material along with TNT having highest detonation tendency/explosive nature; therefore widely used in World War I [8]. Furthermore, TNP being highly acidic and soluble in water have the highest possibility of polluting the ground water and irrigation land. In this way, it causes severe health issues in human beings [9]. Moreover, 2-amino-4,6-dinitrophenol (metabolite of TNP) is found to be 10 times more mutagenic compared to TNP [10]. Therefore, the fast, efficient and selective detection of trace amounts of TNP in an ambient environment is very crucial not only for homeland security but also for human safety and health [11].

Most of the current analytical methods such as X-ray diffraction [12], surface enhanced Raman spectroscopy [13], mass spectrometry [14], surface plasmon resonance [15], colorimetry [16], electrochemistry [17], LC–MS [18], GC–MS [19], HPLC[20], ion mobility spectrometry [21], and proton transfer reaction-mass spectrometry (PTR-MS) [22] for the detection of TNP are not easily accessible because of the requirements for costly and bulky equipment, complicated manipulations, and laborious procedures. As an alternate, fluorescence sensors based on conjugated polymers [23], semiconductor quantum dots [24], carbon dots [25], metal−organic frameworks (MOF) [26], ionic liquid [27], small molecular fluorophores [28] and metal nanoclusters [29] are developed and have advantages of low cost, high sensitivity and utmost convenience. But majority of these fluorescent sensors for TNP detection still suffer from various limitations such as interference from other nitroaromatics, tedious multistep synthesis of conjugated polymers, and health/environment-related hazards associated with semiconductor quantum dots and MOFs [11].

Herein, as continuation of our recent interest in pyrazoline skeleton [30–35], we report a thiazol-substituted pyrazoline (**1**) probe, synthesized by a simple one-pot three component

* Corresponding author.
E-mail address: moazzam@qau.edu.pk (M.M. Naseer).

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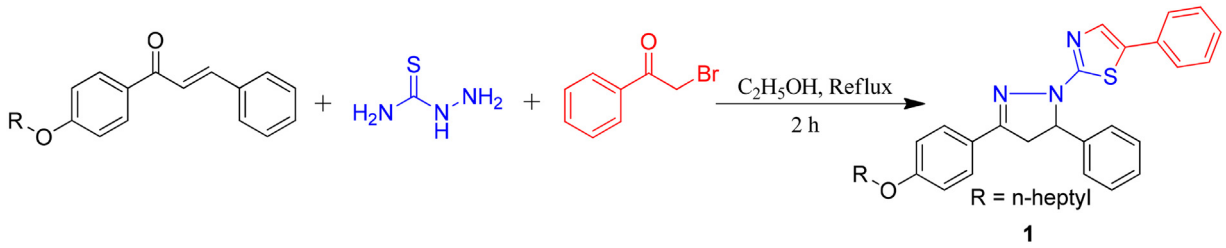

Scheme 1. Synthesis of thiazol-substituted pyrazoline **1.**

reaction involving thiosemicabazide, phenecyl bromide and (*E*)-1-(4-(heptyloxy)phenyl)-3-phenylprop-2-en-1-one and fabricated into organic nanoparticles (**N1**) to investigate its sensing potential in water. The organic fluorescent nanoparticles (OFN) (**N1**) has the admirable sensing ability of TNP in aqueous medium having fast, sensitive and highly selective detection of 2,4,6-trinitrophenol (TNP) over a number of nitro-explosives and structurally-related compounds on the basis of fluorescence quenching. To best of our knowledge, this is the first sensor developed based on small molecule organic fluorescent nanoparticles (OFNs) that has the ability to selectively sense TNP in aqueous medium.

2. Experimental

2.1. General

All chemicals used in this work were purchased from Sigma-Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectrum were recorded on a Burker AM-300 which operates at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR, TMS as internal standard; chemical shifts are expressed in ppm. The absorption spectra were recorded on Pharmac UV-1800 UV–vis Spectrophotometer Shimadzu (Japan); Quartz cells with 1 cm path length were used for running samples. Fluorescence measurements were performed on a Perkin Elmer LS55 Luminescence spectrophotometer, the slit width for the excitation and emission was set at 10 nm and scan speed was maintained at 200 scans per second throughout the study. The TEM images were recorded on Hitachi (H-7500) instrument worked at 120 kV. This instrument has the resolution of 0.36 nm (point to point) with 40–120 kV operating voltage. A 400-mesh formvar carbon-coated copper grid was used for sample preparation. Melting points were determined on Gallenkamp melting point apparatus and were uncorrected.

2.2. Synthesis of thiazol-substituted pyrazoline (1)

1-(4-(Heptyloxy)phenyl)-3-phenylprop-2-en-1-one [36] (0.322 g, 0.001 mol), thiosemicarbazide (0.091 g, 0.001 mol) and phenecylbromide (0.197 g, 0.001 mol) were dissolved in ethanol at room temperature and the reaction mixture was then heated under reflux for 2 h. The progress of reaction was monitored by TLC (n-hexane: ethyl acetate 7: 3). Upon completion of reaction, the reaction mixture was cooled down to room temperature resulting in the formation of precipitates. The thanol and finally recrystallized in ethanol to get light yellow crystals, m.p 97–99 °C, Yield 78%, Rf = 0.29 (n-hexane: ethyl acetate 7: 3), **^{1}H NMR** (300 MHz, DMSO-*d6)* δ values: 0.81 (t, 3H, *J* = 7.0 Hz, –O–$(CH_2)_6$–C***H***$_3$), 1.22–1.33 (m, 8H, –O–CH_2–CH_2–$(CH_2)_4$–CH_3), 1.77 (qn, 2H, *J* = 7.0 Hz, –O–CH_2–C***H***$_2$–C_5H_{11}), 3.33 (dd, 1H, *J* = 6.3, 7.2 Hz, Pyr), 3.88 (t, 2H, *J* = 6.6 Hz, –O–C***H***$_2$–), 3.98 (dd, 1H, *J* = 11.5, 12.0 Hz, Pyr), 5.62 (dd, 1H, *J* = 6.6, 6.3 Hz, Pyr), 6.86 (d, 2H, *J* = 8.40 Hz, Ar), 7.22–7.26 (m, 2H, Ar), 7.29 (s, 1H, Ar), 7.32–7.34 (m, 2H, Ar), 7.34–7.37 (m, 1H, Ar), 7.46-7.51 (m, 2H, Ar), 7.47-7.51 (m, 1H, Ar), 7.73 (d, 2H, *J* = 7.77 Hz, Ar), 7.77–7.79 (m, 2H, Ar). **^{13}C NMR** (75 MHz, DMSO-*d6*) δ values: 14.3, 22.5, 25.9, 28.8, 29.1, 31.6, 43.4, 64.1, 67.8, 104.7, 114.7 (2C), 125.9, 126.8 (2C), 127.9 (2C), 128.4 (2C), 128.9, 129.2 (2C), 130.3 (2C), 131.4, 134.0, 134.9, 150.9, 153.1, 158.5, 164.7.

2.3. Fabrication of 1 into organic nanoparticles (N1)

A single step reprecipitation method [37] was used for the fabrication of **1** into its nanoparticles. The 15 μl of sensor solution in DMF was injected into 50 ml of water and sonicated for 6 h resulting in the formation of evenly sized nano-particles. The driving force for the formation of nanoparticles is the difference of solubility of solvents. The organic solution diffuses into the aqueous cores and enters inside after crossing the interfacial film, in next stage organic molecules get precipitated due to insolubility in water which encourage the nucleation of organic molecule. This is followed by solvent displacement and exchange of organic matter between the aqueous cores on collisions between different droplets. At last, the nuclei tend to grow in size. Several parameters that influence the size and shape of nanoparticles include, for instance, nature of the organic compound involved, the selection of organic phase, aqueous phase, ratio of organic phase to aqueous phase, concentration, agitation speed and time, and injection rate. The constancy of our synthesized organic nanoparticles **N1** was checked over a period of time. The fluorescence spectra were recorded over a period of 7 days and it was observed that the fluorescence emission profile remained unpretentious during this time, thus approving the stability of the organic nanoparticles.

2.4. Sensing properties of N1

The sensing studies were performed at 25 ± 1 °C. The stock solution of **N1** (4 μM) was prepared in water. The interaction of **N1** with nitroaromatics was studied by adding appropriate volume of 2 μM aqueous solutions of nitroaromatics into N1 stock solution and fluorescence was recorded without any delay. For titrations, different solutions (0.2, 0.4, 0.6, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.8, 4.4, 5, and 6 μM) of TNP were individually added to volumetric flasks containing organic nanoparticles **N1** (4 μM) and emission spectra were recorded after each aliquot addition of TNP. The possible interference due to different nitroaromatics was checked by the addition of interfering nitroaromatic (2 μM) to the nanoparticles solution containing TNP (2 μM). The sensitivity of nanoparticles towards TNP was checked by adding the solution of TNP (2 μM) to the nanoparticles solution **N1** (4 μM), and emission profile was recorded at as function of a time after small intervals (10, 20, 30, 40, 50, 60, 70, 80 and 90 s).

2.5. Calculation of detection limit (LOD)

The detection limit (LOD) was calculated according to the IUPAC definition [38]; using the following equation.

$$LOD = 3.3\sigma/K$$