

Research Article

New Ni-Anthracene Complex for Selective and Sensitive Detection of 2,4,6-Trinitrophenol

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Selective and sensitive detection of explosive materials through a simple approach is an attractive area of research having implications on public safety and homeland security. Considering this implication in mind, a new Ni-anthracene complex was designed and synthesized and has been demonstrated as an efficient fluorescence chemosensor for the selective and sensitive detection of 2,4,6-trinitrophenol. Firstly, a fluorescent anthracene ligand (**A**) was synthesized by treating anthracene-9-carboxaldehyde with 1,3-diaminopropane in presence of a weak acid. To achieve superior selectivity and great quenching efficiency for 2,4,6-trinitrophenol (TNP), a Ni complex, namely, $[\text{Ni}(\mu_2\text{-L})(\text{NO}_3)]$ (**B**), was synthesized via the reaction of **A** with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Complex **B** showed strong emission peak (λ_{max}) at 412 nm and exhibited high selectivity towards TNP among other nitroaromatics and anions. 100 equivalents of TNP made 95% fluorescence quenching of **B** and its detection limit for TNP was calculated as 2.8 μM .

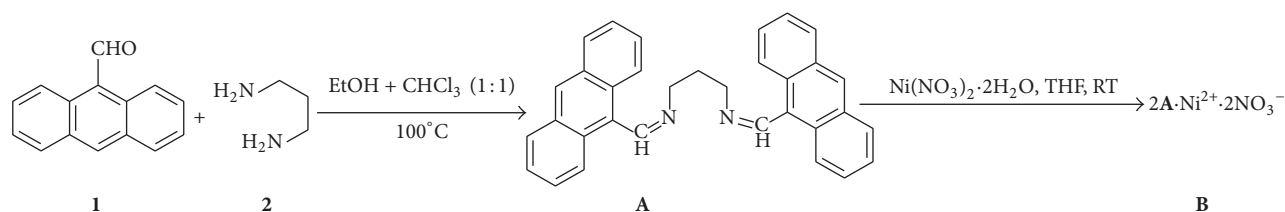
1. Introduction

Nitroaromatic compounds are generally used in many industries for the preparation of dyes, pharmaceuticals, rubber products, explosives, chemical fibres and pesticides, and so forth [1]. These nitroaromatic compounds were released into the environment as industrial wastage and are one of the main reasons for the pollution. Moreover, due to their poisonousness, carcinogenicity to living beings, and the risk to homeland safety, they cause serious intimidations to our lives [2]. 2,4,6-TNT; 2,4-DNT; 2,4-DNB; 2,6-DNT; and 2,4,6-TNP are the key constituents of environmental pollutants and explosive products [3]. Out of these compounds, TNP in particular creates health hazards and chronic, skin, and eye diseases and is used as a powerful explosive similar to TNT [4]. Furthermore, TNP is a more potent explosive than the more commonly used explosive TNT [5].

Various detection techniques such as electrochemical sensing, cyclic voltammetry, Raman spectroscopy, Liquid

chromatography-mass spectrometry (LC-MS), photoluminescence spectroscopy (PL), and several other techniques have been used to detect different types of explosives including TNP. Nevertheless, most of them are pretty sophisticated, time taking, and/or difficult to operate [6, 7]. Among these reported procedures, PL based method offers shorter response time and improved sensitivity and is economically worthwhile [7, 8]. Hence, with the above stated problems from TNP and the benefits of PL, TNP sensing through optical detection is highly needed.

Till now, many fluorescent sensors have been developed for the detection of nitroaromatic explosives [7–10]. Nitroaromatics are electron deficient in nature; due to this reason some electron-rich fluorescent probes can always produce nonfluorescent Meisenheimer or π -stacking complexes with nitroaromatics [11, 12]. Selective detection of TNP is very difficult as it has strong electron affinity [13]. Through donor-acceptor electron transfer mechanism, TNP can quench the fluorescence emission of various molecules such as metal

SCHEME 1: Synthetic route of nickel complex **B**.

complexes, conjugated polymers, organic molecules, and metal-organic frameworks [14–17].

Among various fluorophores used for designing of chemosensors, anthracene based compounds have been used for the detection of several analytes, due to their high chemical stability, richness of π -electrons and strong fluorescence [18, 19]. Mainly anthracene based compounds are widely used for the sensing of anions and cations. Nevertheless, there are very limited compounds reported for the detection of explosives/nitroaromatics [20–22]. In consequence, by considering the significance of the new photoluminescent material for TNP sensing, in this work, we synthesized a new anthracene based nickel complex with fluorescent activity for the detection of TNP. Solution phase spectral studies confirm the sensitivity of complex with TNP.

2. Materials and Methods

2.1. Materials. Anthracene-9-carboxaldehyde, 1,3-diaminopropane, nickel nitrate, tetra butyl ammonium salts of anions, Nitroaromatic compounds and other chemicals are purchased from Sigma-Aldrich, India and used without further purification.

2.2. Synthesis of A. Anthracene-9-carboxaldehyde (0.2 g, 0.97 mM) was dissolved in 10 mL of methanol. 1,3-Diaminopropane (0.036 g, 0.485 mM) and acetic acid (27.8 μ L, 0.485 mM) are added to the above solution while stirring. The yellow colored solution mixture was refluxed for 12 h. Upon cooling the yellow precipitate, (7E,19E)-N-((anthracen-10-yl)methylene)-N'-((anthracen-9-yl)methylene)propane-1,3-diamine, **A**, was separated by filtration under reduced pressure and then washed with excess methanol. The product was recrystallized from methanol. Yield: 85.32%. ^1H NMR (500 MHz, CDCl_3 , Me_4Si) δ 2.57–2.54 (t, 2H); δ 4.23–4.21 (m, 4H); δ 7.51–7.48 (m, 8H); δ 8.04–8.02 (d, 4H); δ 8.51 (s, 2H); δ 8.58–8.56 (d, 4H); δ 9.56 (s, 2H) (see supplementary Figure S1); ^{13}C NMR (CDCl_3): δ 160.74, 131.32, 130.05, 129.31, 128.88, 128.24, 126.71, 125.25, 124.80, 60.89, 32.48 (see supplementary Figure S2); HR-MS Data: $[\text{M} + 1]^+ = 450.86$.

2.3. Synthesis of B. To the solution of **A** (100 mg, 0.22 mM in THF), nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, 0.56 g, 1.93 mM] was added and stirred for two hours at room temperature. The yellowish green precipitate was separated out under reduced pressure. Yield: 83.96%. HR-MS $[\text{M} + 1]^+$ found 1082.34.

2.4. Characterizations. The ^1H and ^{13}C NMR spectra of the **A** have been recorded on a Bruker 400 MHz NMR

instrument. Mass spectra of the **B** have been recorded on Kratos PC Axima HR-Mass spectrometer in linear mode. The fluorescence quenching measurements were performed using Cary Eclipse Fluorescence spectrophotometer. The excitation and emission slit widths (each 10 nm) and scan rate (500 nm min^{-1}) were kept constant for all the measurements. The optical absorption spectral measurements were recorded using a Shimadzu UV-2450 spectrophotometer with a quartz cuvette (path length, 1 cm). Energy dispersive X-ray spectra (EDAX) were obtained using scanning electron microscope (SEM), FEI Nova Nano SEM-450.

3. Results and Discussion

Condensation of 1,3-diaminopropane **2** with anthracene-9-carboxaldehyde **1** produced a fluorescent ligand **A**, which gave a nickel complex **B** with the addition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at RT (Scheme 1). The as-synthesized complex was characterized by mass spectrometry, where the parent ion (m/z) peak appeared at 1082 corresponding to the species $[2\text{A} \cdot \text{Ni}(\text{NO}_3)_2]$ (see supplementary Figure S3). The presence of all the elements in complex **B** is confirmed through elemental analysis (see supplementary Figure S4). As we are developing a chemosensor for TNP, the main motivation behind the synthesis of compound **A** is that it was expected to become a nonfluorescent moiety as photoinduced electron transfer (PET) process can take place due to presence of imino nitrogen atom [23]. The binding of nickel ions to the imino nitrogen of compound **A** will prevent the PET process and it eventually results in the perseverance of fluorescence. Consequently, TNP can perhaps quench the fluorescence emission of **B** with electron transfer or energy transfer mechanism and could be sensed [24].

Complex **B** ($1 \mu\text{M}$) showed reasonably good emission intensity of anthracene monomeric species at 412 nm in THF : HEPES (9.5 : 0.5) when excited at $\lambda_{\text{ex}} = 365 \text{ nm}$ [25]. On addition of TNP ($150 \mu\text{M}$) to the solution of **B** ($1 \mu\text{M}$) in THF : HEPES (9.5 : 0.5), the emission band shows quenching of emission band (Figure 1). To observe the selectivity of **B** towards TNP, we carried out the fluorescence titration experiments with similar amount of $150 \mu\text{M}$ other nitroderivatives, namely, nitrotoluene (NT), 2,4-dinitrotoluene (2,4 DNT), and 1,4-dinitrobenzene (1,4 DNB) and anions (F^- , Cl^- , Br^- , I^- , OH^- , HSO_3^- , CN^- , NO_3^- , CH_3COO^- , ClO_4^- , and PO_4^{3-}) with tetrabutyl ammonium as counter ion, and observed no significant change in the emission spectrum of **B** depicting the selectivity of **B** (Figure 2). Detection limit (DL) was calculated using the equation: $\text{DL} = 3\alpha/K$, where α is the

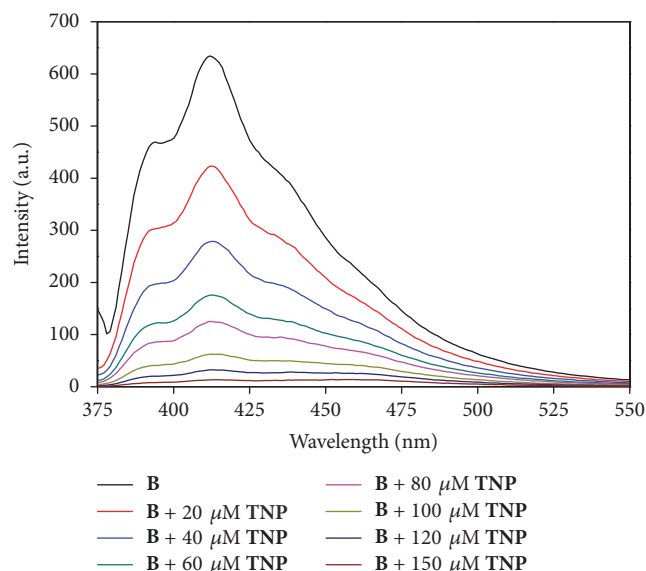


FIGURE 1: Change in emission spectrum of **B** (1 μM) on addition of **TNP** (150 μM) in THF:HEPES (9.5:0.5) (v/v).

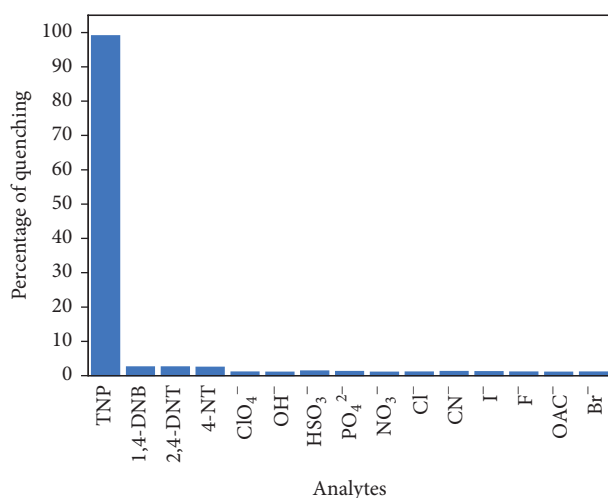


FIGURE 2: Fluorescence response of **B** (1 μM) in THF:HEPES (9.5:0.5) (v/v) among various nitroaromatics and anions. All analytes are tested in the same molar ratio to **B**.

standard deviation calculated by measuring the fluorescence intensity of complex **B** for more than 15 times and K presents the slope of fitting curve between variation of the fluorescence intensity ($I_0 - I$) and the added amount of **TNP** at low concentration. According to the linear fitting curve (Figure S5 shown in supporting information), the detection limit of complex **B** for sensing of **TNP** was found to be 2.857 μM [26]. The complex **B** DL in sensing of **TNP** is as comparable with the existing materials (see Table S1 in supporting information).

We also examined the meddling of other anions and nitroaromatics towards the sensing of **TNP** (Figure 3) and it was confirmed that the **B** was detecting **TNP** even in the presence of other potential analytes. The emission plot of **B**

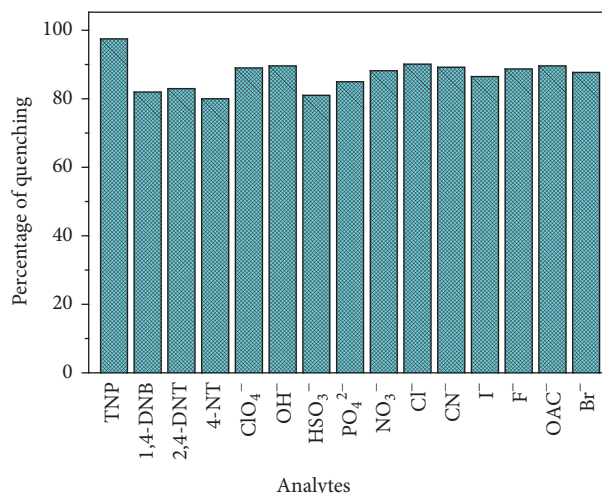


FIGURE 3: Fluorescence quenching in **B** with the addition of **TNP** alone and **TNP** in the presence of other analytes. The molar ratio to **B** used in each case is 100 equivalents.

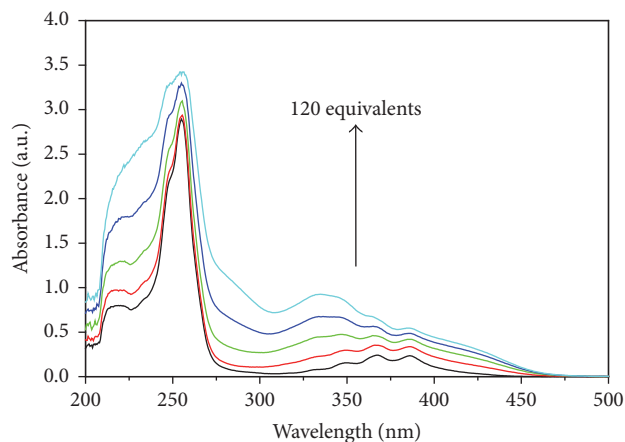


FIGURE 4: Change in absorption spectra of **4** (1 μM) with the addition of **TNP** in a mixed aqueous medium of THF:HEPES (9.5:0.5) (v/v).

in the presence of TNP was studied using Stern-Volmer relationship. Stern-Volmer plot seemed like a hyperbolic curve (see supplementary Figure S6) which may be accredited to the combination of static and dynamic (collision) quenching [27].

We have also detected these variations with the assistance of UV-vis analysis. Nickel complex **B** (1 μM) in THF:HEPES (9.5:0.5) showed an absorbance band at 260 nm (Figure 4). On addition of **TNP** (120 μM) along with the formation of band at 340 nm corresponding to **TNP** (Figure 4), there was subsequent increase in the band at 260 nm presenting that there is some photochemical process happening between **B** and **TNP**. To have a deep insight into the mechanism, we made plot between the absorbance spectrum of **TNP** and emission spectrum of **B** (Figure 5). The overlap between the two plots suggests an energy transfer mechanism from photoexcited π -electron-rich derivative **B** to ground state

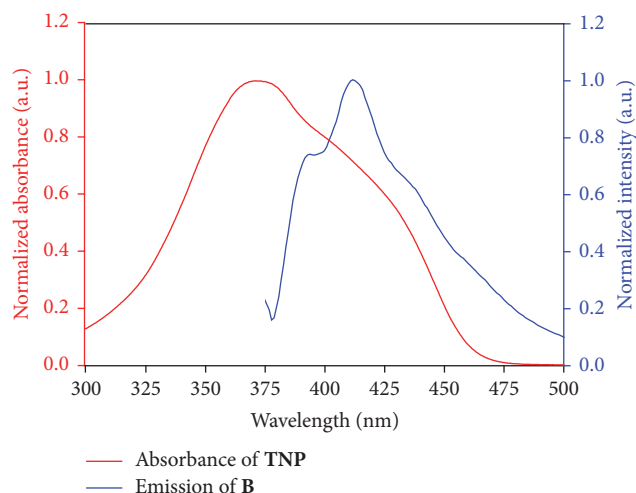


FIGURE 5: Spectral overlap of the absorption of TNP (red line) with the emission spectrum of **B** (blue line).

electron-deficient TNP. Thus, the changes occurring in the optical properties of **B** on addition of TNP are attributed to the energy transfer process.

4. Conclusions

In conclusion, we have designed and synthesized a new photoluminescent Ni-anthracene complex. The luminescence behaviour of the complex was assessed towards different nitroaromatics and other analytes. The synthesized Ni-anthracene complex shows selective and sensitive detection of TNP and could be a helpful tool for the people working in forensic sciences.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this article.

Acknowledgments

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Supplementary Materials

Figure S1: ^1H NMR spectrum of **A**. Figure S2: ^{13}C NMR spectrum of **A**. Figure S3: mass spectrum of complex **B**. Figure S4: energy dispersive X-ray spectrum (EDAX) of complex **B**. Figure S5: change in fluorescence intensity of complex **B** at low concentrations of TNP. Figure S6: Stern-Volmer plot for the quenching of the fluorescence of **B** upon the addition of $120\ \mu\text{M}$ of TNP. Table S1: comparison of detection limit with different reported materials. (*Supplementary Materials*)

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