Fluorescence "Turn-On" Indicator Displacement Assay-Based Sensing of Nitroexplosive 2,4,6-Trinitrophenol in Aqueous Media via a Polyelectrolyte and Dye Complex

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ABSTRACT: A water-soluble nonfluorescent cationic conjugated polyelectrolyte poly(1,1′-(1,4-phenylenebis(oxo))bis-(propane-3,1-diy1))bis(pyridin-1-ium)bromide (PPPy) was specifically synthesized via an economical method of oxidative coupling polymerization in high yields. PPPy selectively recognized nitroexplosive picric acid (PA) by fluorescence "turn-on" in the presence of closely related nitroexplosive compounds, namely, 2,4,6-trinitrotoluene, 2,4-dinitrophenol, and 4-nitrophenol via fluorescence indicator displacement assay (IDA) technique in water at pH 7.0. The polymer PPPy was characterized by NMR spectroscopy, gel permeable chromatography, UV–vis spectroscopy. The polymer PPPy forms an electrostatic complex with uranine dye. This ensemble scheme was utilized to detect PA with a limit of detection value of 295 nM (solution state) and 0.22 ppm (vapor state) through IDA, a phenomenon that is very different from the widely reported Förster resonance energy transfer, photoinduced electron transfer, ground-state charge transfer and inner filter effect based probes used for nitroexplosive PA detection.

INTRODUCTION

2,4,6-Trinitrophenol, commonly referred as picric acid (PA), has been categorized as a strong nitroexplosive compound (Scheme S1). The potential explosive power of PA is remarkably superior than that of other competitive and interfering nitroexplosives 2,4,6-trinitrotoluene (TNT). Thus, its detection is of immense significance for homeland security and forensic investigation.2,3 Owing to its high solubility in water and extensive use in dye, leather, drugs, matchbox, and firework industries, it can easily contaminate land and water resources.3 PA is a well-known environmental pollutant that has lower degradation rate in biosystems and can cause severe health problems such as cancer, abnormal liver functions, sycosis, and damage to kidney as well as respiratory organs.4,5 Furthermore, during metabolism, PA is transformed into picramic acid, which has even much higher mutagenic activity than PA.6 Therefore, there is an urgent need to develop superior methods with high selectivity, rapid detection probes, and high sensitivity for PA detection with respect to environmental issues and terrorist threats.

Host/guest chemistry is a very active area of research in supramolecular chemistry.7–11 The changes in the response of host/dye complex property after the addition of particular analyte has been extensively investigated to build a selective and sensitive chemosensor.12–25 Fluorescent dyes possess high affinity for macrocyclic host and significant change in fluorescence is observed after the host/dye complex formation in water medium.9,15,22 When an analyte is introduced into the host/dye complex, it selectively displaces the dye from the host and forms a host/analyte complex with an initial fluorescence recovery. This phenomenon is generally termed as indicator displacement assay (IDA). There is competition between the analyte and the indicator for the selective binding of the host.10,17 Several host/dye complex-based sensing with a variety of hosts used, such as calixarenes,9,10,20,22 cyclodextrins,15 cucurbiturils,10,19,22 and pillararene,21 have been reported. However, no report is available till date with a cationic conjugate polymer as a host. Notably, the IDA technique has been widely used for selective sensing of biological and environmental analytes such as basic amino acids,19 adrafinil,24 heparin,25 carbohydrate,26 citrate,27,28 phosphate,29–31 tartarate,32,33 nitrate,34 and so on.

Several literature methods are available for the sensitive detection of PA; however, most of them use organic media15–41 and fluorescence "turn-off" and lack good selectivity toward PA37,42–44 with selected reports available based on fluorescence "turn-on" sensing.45–51 The mechanisms of sensing involved in the previous reports are majorly photoinduced electron transfer and/or energy transfer process52 and inner filter effect.53 To the best of our knowledge, there are no reports available for the
sensitive PA (solution and vapor) detection based on fluorescence turn-on via IDA. In this work, we introduce a straightforward method to synthesize pyridinium receptor containing nonfluorescent cationic conjugated polymer poly-\((1,1'\text{-((1,4-phenylenebis(oxy))bis(propane-3,1-diyl))bis(pyridin-1-ium)bromide (PPPy) (Scheme 1)}\), which shows selective fluorescence turn-on sensing of PA over 2,4-dinitrophenol (2,4-DNP), 4-nitrophenol (4-NP), and TNT through the IDA technique in water at pH 7.0 for the first time (Scheme 2).

| Scheme 1. (1) Synthesis of the Polymer PPPy and Monomer M2 and Chemical Structures of (2) Uranine Dye (UD) and (3) PA\(^a\) |
|---|
| (1) | (2) |
| (a) 1,3-Dibromopropane, dry acetone, K\(_2\)CO\(_3\) reflux, 24 h. (b) FeCl\(_3\), nitrobenzene (NB), room temperature (rt), 36 h, (c) pyridine, dimethylformamide (DMF), 70 °C, 24 h, and (d) pyridine, acetonitrile, reflux, overnight. |

\(\text{UD (Scheme 1)}\)

\(\text{PPPy (Scheme 1)}\)

\(\text{M2 (Scheme 1)}\)

\(\text{PA (Scheme 1)}\)

**RESULTS AND DISCUSSION**

The cationic polymer PPPy was obtained via postfunctionalization polymerization method (Scheme 1 and Figures S1–S8). Pyridinium group strapped along the side chains of the PPPy makes the polymer highly soluble in polar solvents such as methanol, water, and so on, and also provides specific recognition site for PA because of attractive electrostatic interactions. The cationic polymer PPPy shows an absorbance maximum at 319 nm and does not emit any kind of fluorescence in water buffered with 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES, pH 7.0, 0.01 M). The indicator used in the IDA studies is UD (Scheme 1), which has the absorbance and fluorescence maxima at 490 and 513 nm (excitation 490 nm), respectively, in water buffered with HEPES (pH 7.0, 0.01 M). The concentration of UD for every titration experiment was fixed at \(6.6 \times 10^{-6}\) M. In the preliminary experiment, the fluorescence of UD \(6.6 \times 10^{-6}\) M in water buffered with HEPES (pH 7.0, 0.01 M) was measured in the presence of various concentrations of PPPy \((1.6 \times 10^{-6}, 3.3 \times 10^{-6}, 5.0 \times 10^{-6}, 6.66 \times 10^{-6}, 8.3 \times 10^{-6}, 10.0 \times 10^{-6}, 11.6 \times 10^{-6}, 13.3 \times 10^{-6}, 15.0 \times 10^{-6}, \text{and 16.6} \times 10^{-6}\) M) (Figure 1a). The fluorescence intensity of UD gradually quenched on further addition of PPPy, and 86% of the quenching occurred after the addition of PPPy in \(16.6 \times 10^{-6}\) M concentration. It should be noted that the addition of monomer M2 (Scheme 1) to the solution of UD barely affected its...
Figure 1. (a) Photoluminescence (PL) spectra of UD (6.6 × 10⁻⁶ M) with increasing concentrations of PPPy in water buffered with HEPES (0.01 M, pH 7.0). (b) UV–vis spectra of UD (6.6 × 10⁻⁶ M) with increasing concentrations of PPPy in water buffered with HEPES (0.01 M, pH 7.0).

Figure 2. (a) PL spectrum of PPPy (16.6 × 10⁻⁶ M) and UD (6.6 × 10⁻⁶ M) complex with increasing concentrations of PA (166.6 × 10⁻⁶ M) in water buffered with HEPES (pH 7.0, 0.01 M). (b) UV–vis spectra of UD (6.6 × 10⁻⁶ M) and PPPy (16.6 × 10⁻⁶ M) complex with increasing concentrations of PA (166.6 × 10⁻⁶ M) in water buffered with HEPES (pH 7.0, 0.01 M).

fluorescence intensity (Figure S9). This proved the high affinity of PPPy toward UD. The UV–vis spectra of UD were studied after adding PPPy in varying concentrations (1.6 × 10⁻⁶, 3.3 × 10⁻⁶, 5.0 × 10⁻⁶, 6.66 × 10⁻⁶, 8.3 × 10⁻⁶, 10.0 × 10⁻⁶, 11.6 × 10⁻⁶, 13.3 × 10⁻⁶, 15.0 × 10⁻⁶, and 16.6 × 10⁻⁶ M) (Figure 1b). The absorbance maxima of UD (490 nm) was red shifted by 12 nm to 502 nm. This new peak at 502 nm in the UV–vis spectrum was indicative of the host/dye complex, that is, the PPPy/UD complex.

To examine the displacement of the indicator, UD, from the cationic conjugated polymer PPPy, the IDA studies were done for PA, carried out in cuvettes, keeping the fixed concentration of resulting solution of PPPy (16.6 × 10⁻⁶ M)/UD (6.6 × 10⁻⁶ M) complex in water buffered with HEPES (pH 7.0, 0.01 M) by varying the concentration of PA. In typical IDA studies, fluorescence spectra of PPPy (16.6 × 10⁻⁶ M)/UD (6.6 × 10⁻⁶ M) complex were recorded at various concentrations of analyte PA (16.6 × 10⁻⁶, 33.3 × 10⁻⁶, 50.0 × 10⁻⁶, 66.6 × 10⁻⁶, 83.3 × 10⁻⁶, 100.0 × 10⁻⁶, 116.6 × 10⁻⁶, 133.3 × 10⁻⁶, 150.0 × 10⁻⁶, and 166.6 × 10⁻⁶ M) (Figure 2a). The fluorescence intensity increased gradually with the addition of PA, and 86% dequenching occurred after the addition of PA in 166.6 × 10⁻⁶ M concentration. The UV–vis spectra of PPPy (16.6 × 10⁻⁶ M)/UD (6.6 × 10⁻⁶ M) complex were recorded upon the addition of various concentrations of PA (16.6 × 10⁻⁶, 33.3 × 10⁻⁶, 50.0 × 10⁻⁶, 66.6 × 10⁻⁶, 83.3 × 10⁻⁶, 100.0 × 10⁻⁶, 116.6 × 10⁻⁶, 133.3 × 10⁻⁶, 150.0 × 10⁻⁶, and 166.6 × 10⁻⁶ M) (Figure 2b). The absorbance maximum of UD/PPPy complex (502 nm) is blue shifted back to 490 nm, indicating the displacement of UD from the PPPy/UD complex.

To elucidate the selectivity, fluorescent IDA studies were performed by adding various common interfering analytes, namely, 2,4-DNP, 4-NP, TNT, research department explosive (RDX), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 4-nitrotoluene (4-NT), 1,3-dinitrobenzene (1,3-DNB), benzoic acid (BA), NB, and phenol to the solution of PPPy (16.6 × 10⁻⁶ M)/UD (6.6 × 10⁻⁶ M) complex in water buffered with HEPES (pH 7.0, 0.01 M) (Figures 4a and S11). Interestingly, no significant change was seen in the PL spectra of PPPy/UD complex after the addition of these analytes. Furthermore, other
metal ions (Fe$^{3+}$, Cd$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Pd$^{2+}$, and Mn$^{2+}$) as well as anions (H$_2$PO$_4$$^{-}$, HPO$_4$$^{2-}$, PO$_4$$^{3-}$, I$^{-}$, Cl$^{-}$, F$^{-}$, NO$_3$$^{-}$, N$_3$$^{-}$, BF$_4$$^{-}$, and AcO$^{-}$) did not have any effect on the fluorescence of PPPy/UD complex (Figures 4b,c, S12, and S13), which confirms the high selectivity of PPPy toward PA in the IDA studies. Sensing studies were also done in a competitive environment. In a typical set of experiment, a solution of 2,4-DNP (166.6 $\times$ 10$^{-6}$ M) was added initially to the solution of PPPy (16.6 $\times$ 10$^{-6}$ M)/UD (6.6 $\times$ 10$^{-6}$ M) complex in water buffered with HEPES (pH 7.0, 0.01 M), but no substantial change in the emission intensity was seen (Figure S14). The solution of PA (166.6 $\times$ 10$^{-6}$ M) was then introduced to the same solution, which resulted in significant enhancement in fluorescence. The same sets of experiments were repeated with other nitroaromatic compounds and similar fluorescence turn-on response was obtained after the addition of PA (Figures S15–S24). It is worth mentioning that most of the existing chemosensor systems developed for the detection of PA suffered from a large interference by several other electron-deficient nitroaromatic compounds, particularly 2,4-DNP, 4-NP, and TNT. The present method provides a simple, rapid, reliable, and highly specific detection of PA even in a competitive environment.

Vapor-phase detection of PA was also carried out by using PPPy. Fixed volumes of PA vapors of concentration (0.018 ppm, 50 mL) were purged through the UD/PPPy complex using a leak-proof syringe. The PL spectra were recorded after the purging of PA vapors in the cuvette and the increase in the emission maxima observed with each addition (Figures 5 and S25) were recorded. Furthermore, the LOD value was calculated to be 0.220 ppm based on the change in the emission spectrum of the PPPy (16.6 $\times$ 10$^{-6}$ M)/UD (6.6 $\times$ 10$^{-6}$ M) complex at various concentrations of PA vapors (0.316, 0.632, 0.948, 1.264, 1.580, and 1.896 ppm) using the equation 3$\sigma$/K (Figure S26). Thus, the present method established a rapid and specific detection of PA in the vapor phase as well, which remains a highly challenging and an exciting area of research.

## CONCLUSIONS

In conclusion, a nonfluorescent cationic conjugated polymer was demonstrated to selectively detect PA among other closely related electron-deficient nitroaromatic compounds like 2,4-DNP, 4-NP, and TNT via fluorescent turn-on IDA using UD as
the indicator for the first time. The ensemble system could be used to detect PA with a LOD of 295 nM in water buffered with HEPES (pH 7.0, 0.01 M) and 0.22 ppm in the vapor state. The addition of PA thus led to a quick fluorescence turn-on response of the PPPy/UD complex even at very low concentrations. This fluorescence turn-on based system avoids the erroneous false signals and significantly improves the detection sensitivity as compared with the assays that work on the fluorescence quenching methods.

**EXPERIMENTAL SECTION**

**Caution!** The nitroaromatics used in the study, especially PA, TNT, and RDX, are highly explosive in nature and should be handled with utmost caution and in minor quantities with appropriate safety measures to avoid any explosion.

**Materials and Methods.** Nitroexplosives, namely, 4-NT, 1,3-DNB, 2,4-DNT, and 2,6-DNT, were purchased from Aldrich Chemicals. RDX and TNT were purchased from AccuStandard. PA was purchased from Loba Chemie Pvt. Ltd. HEPES buffer was purchased from Sigma-Aldrich Chemicals. Various other reagents and chemicals and were purchased from Merck and Alfa-Aesar and used without further purification. 

**Synthesis of PPPy.** Poly(1,4-bis(3-bromopropoxy)benzene) (PPBr). In a three-necked RBF, ferric chloride (anhydrous) (1.84 g, 11.36 mmol) was solubilized in NB (10 mL) under continuous nitrogen flow. Monomer M1 (1.0 g, 2.84 mmol) (solubilized in NB (15 mL)) was added to flask dropwise. After that, the reaction mixture flask was kept for 36 h under stirring at rt, followed by precipitation in methanol. The solution was centrifuged and precipitates were washed with methanol (repeated thrice). The resulting precipitates were lastly dried under vacuum to obtain a brown polymer with 66% yield. The GPC using polystyrene as the standard in CHCl₃: Mₚ = 2.07 × 10⁶; polydispersity index = 4.1. 

**Synthesis of PPPy.** Polymer PPBr (0.067 g) was dissolved in dry DMF (2 mL) and then pyridine (0.306 mL) was added to the reaction mixture under inert condition. Then, the reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was then poured into excess of chloroform and stirred for 1 h to get a precipitate. The process was repeated thrice to remove excess pyridine, DMF, and PPBr. The solution was centrifuged and the precipitates were collected by drying under reduced pressure to get a dark brown sticky product with 70% yield. 

**Synthesis of Poly(1,4-bis(3-bromopropoxy)benzene) (PPPy).** A mixture of pyridine (0.046 mL, 0.568 mmol) and 1,4-bis(3-bromopropoxy)benzene (M1) (0.100 g, 0.284 mmol) was dissolved in acetonitrile and refluxed overnight. On cooling, yellow crystals were obtained. These crystals were filtered and washed with chloroform to get pure shiny yellow crystal (yield = 85%). 

**Sensing Studies in Aqueous Solution.** The stock solutions of the polymer PPPy and other analytes, namely, NB, nitromethane, BA, 4-NP, phenol, and 2,4-DNP, were prepared in Milli-Q water at concentrations of 1 × 10⁻⁶ and 1 × 10⁻⁵ M, respectively. Stock solutions of other nitroaromatics, namely, 2,6-DNT, 2,4-DNT, 4-NT, and 1,3-DNB, were prepared at concentration of 1 × 10⁻⁶ M in high-performance liquid chromatography grade tetrahydrofuran. Stock solutions of TNT and RDX were prepared at concentration of 1 × 10⁻⁵ M in 1:1 CH₃CN/MeOH. The absorption measurements and the PL titrations of UD (6.6 × 10⁻⁶ M) at different concentrations of the polymer PPPy were carried out by sequentially adding various concentrations of the polymer PPPy (1.6 × 10⁻³, 3.3 × 10⁻⁶, 5.0 × 10⁻⁶, 6.66 × 10⁻⁶, 8.3 × 10⁻⁶, 10.0 × 10⁻⁶, 11.6 × 10⁻⁶, 13.3 × 10⁻⁶, 15.0 × 10⁻⁶, and 16.6 × 10⁻⁶ M) to a 3 mL water medium buffered with HEPES (0.01 M, pH 7.0) containing 6.6 × 10⁻⁶ M of UD in a quartz cuvette of 10 mm path length. The resulting mixtures were mixed thoroughly before recording the spectra at rt.

**Figure 5.** PL spectrum of PPPy (16.6 × 10⁻⁶ M) and UD (6.6 × 10⁻⁶ M) complex with increasing concentration of PA vapors in water buffered with HEPES (pH 7.0, 0.01 M).
Titration Conditions. All of the UV—vis and PL titrations were carried out in aqueous solutions buffered with HEPES (pH 7.0, 0.01 M). The concentration of the fluorophore—UD was kept constant at 6.6 × 10−6 M throughout the fluorescence titrations.

Calculation of Detection Limit. For calculating the detection limit, different solutions of the polymer PPPy (16.6 × 10−6 M) and UD (6.6 × 10−6 M) each containing PA (3.3 × 10−6, 6.6 × 10−6, 10.0 × 10−6, 13.3 × 10−6, 16.6 × 10−6, and 20.0 × 10−6 M) were taken individually in HEPES buffer (pH 7.0, 0.01 M) and then the emission spectrum was obtained for individual sample by exciting at 490 nm. A calibration plot was obtained between the fluorescence intensity and the increasing concentration of PA to get a regression curve equation. From the calibration curve, the LOD was evaluated using the equation 3σ/ K, where σ denotes the standard deviation for the intensity of UD and PPPy in the absence of PA and K is the slope of the curve.

Vapor-Phase Detection. Hundred milligrams of dried PA was taken in an airtight flask and kept for 2 days at rt and maintained at 40 °C for 15 min before titration so that the air inside the flask gets completely saturated with PA vapors. The vapor pressure (P) of PA was calculated using the integrated form of Clausius—Clapeyron equation (log10 P = A − B/T).56,57 Here, A and B are the two conventionally used fitting parameters. Furthermore, the concentration of PA vapors was also calculated by the following equation: saturation concentration (ppm) = P (mmHg)/760 mmHg × 106, where P represents the vapor pressure of PA.57 For each titration, the concentration of PA vapors was kept constant (i.e., 0.018 ppm, 50 mL) and purged through cuvette using a leak-proof syringe.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00765.

Chemical structures of various nitroexplosives used in the study; characterization data (1H NMR and 13C NMR, high-resolution mass spectrometry) of various synthesized compounds, detection limit plot for PA, table for comparison, PL spectra for selectivity and sensing in competitive interfering nitroexplosive environment (PDF)

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Notes
The authors declare no competing financial interest.

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