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Fluorescent Paper Strips for Highly Sensitive and Selective Detection of Nitroaromatic Analytes in Water Samples

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A portable, low-cost, flexible, sensitive and selective paper-based sensor was proposed for nitroaromatic explosive detection in water samples. The sensor was designed to achieve π - π stacking formation between emeraldine base polyaniline (PANI) and pyrene (Py) molecules. This π - π stacking formation enables a sensitive turn-off fluorescence quenching under the principle of photo-induced electron transfer (PET) mechanism. PANI–Py absorbed paper strips were immersed into the aqueous mediums of analytes and the fluorescence quenching was observed under a simple UV lamp by naked-

eye. Paper strips exhibited ~ 96% quenching efficiency and the limit of detection was calculated about 9.59 ng/ml. Self-quenching efficiency test showed that the sensor can be used for several weeks under the adequate storing conditions. In addition, experimental findings revealed that the paper-based PANI–Py strips work with high precision in real-samples such as tap water with ~ 85% quenching efficiency. Moreover the reusability investigations showed that PANI–Py paper-based sensor can be reused 5 times with 54% sensitivity.

Introduction

Nitroaromatic compounds (NACs) such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and their derivatives are well known explosives and environmental toxic pollutants. NACs are easily distributed in air, water and soil and can cause severe adverse effects on human health due to their high toxicity.^[1,2] Detection of NACs in water or soil is of great importance for both human and environment health. In the event of the presence of excess TNT amounts in water causes several important damages for human health such as liver, skin, and neurological problems.^[3] Therefore the fabrication of a rapid and reliable sensor platform for the detection of NACs in water samples is very important. Many advanced analytical methods^[4–6] have been used for the detection of NACs but the main problem of these advanced techniques is the requirement of expensive instruments and well-trained laboratory technicians.

In recent years, selective, facile, low-cost, and simple detection platforms are desired for the detecting NACs on-site usages. For this purpose several new techniques such as

fluorescence and colorimetric-based systems have been developed for detection of NACs.^[7–10] Especially, among these developed systems, paper-based systems have promising potential to fabricate desired portable and disposable sensor platforms.^[11–14] Taudte et al. reported pyrene (Py) deposited paper-based analytical devices (μ PADs). This Py deposited system is not selective and quenches against all of the NA explosives in the range of 100–600 ppm.^[15] Wang and coworkers reported a nanocomposite-based fluorescence paper sensor platform for selectively 2,4,6-trinitrophenol (TNP) sensing.^[16] They showed that the paper based fluorescent sensor exhibited sensitive and selective detection of down to 50 ng/mL of TNP in aqueous solution. Yu et al. prepared a colorimetric sensor system based on Meisenheimer complex with 3-aminopropyltriethoxysilane and TNT molecules both in solution and on solid phase.^[17] They showed that TNT forms a red-colored Meisenheimer complex with APTES on filter paper with the lowest detectable concentration of 1 μ M TNT.^[17]

Another approach towards the easy NA explosive detection is to utilize the π -stacking between the polymer chains and chromophore groups. Swager et al. proposed to use π -stacking polymer backbones which results in fluorescence quenching through the polymer-analyte interactions.^[18,19] Briefly, electron transfer occurs from the excited polymer to the analyte. It is well known that fluorescence of pyrene is quenched by nitroaromatic explosives through photo induced electron transfer (PET). Particularly, excimer emission of pyrene, which is observed in the presence of π - π^* stacking interaction between the excited and ground state pyrene molecules, is very sensitive towards nitroaromatics. This approach accelerated the turn-off sensor studies to produce selective and sensitive designs. In recent years, turn-off sensors were reported that relies on the PET mechanisms.^[20,21,22]

In our previous study, we prepared worm-like 3D structured thin film using Py doped polyethersulfone to sense NA

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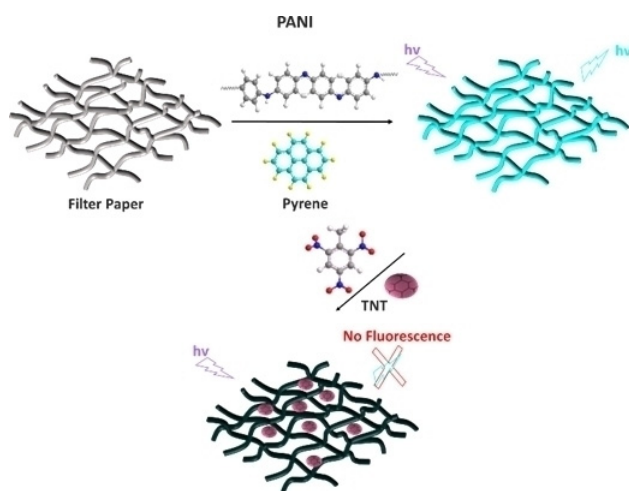
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vapours.^[23] We reported that this 3D and porous structure of the thin polymer film exhibits an efficient quenching performance owing to the easy diffusion of NA explosives throughout the film. Most of these kinds of studies are reported to detect nitroaromatic explosives in the vapour phase or in organic solvents. The detection of NAC in water samples using the materials with pyrene excimer emission are very rare and also the detection limit in aqueous phase is generally at μM levels.^[24]

Recently, Fang et al. synthesized two different pyrene-containing fluorescent polymer films for the TNT sensing in water samples.^[24] They reported that these thin fluorescent polymer thin films exhibited very sensitive sensing performance to the presence of TNT in aqueous medium. Besides the selective and sensitive turn-off sensors, there are very few examples to detect nitroaromatic explosives in real-samples such as, beach water, tap water, or drinking water.^[24–27]

Here we have developed a sensitive and selective fluorescence turn-off sensor based on the π - π stacking formation between PANI and fluorescent Py molecules for NA explosive sensing for nanogram concentration in aqueous medium as seen in Scheme 1.

The quenching performance of fluorescent PANI–Py paper-based sensor was tested for detecting of explosives including 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and nitrobenzene (NB) in aqueous medium. PANI–Py paper-based system was exhibited both good sensitivity and selectivity against TNT. This study shows new insights into the development of fluorescent paper-based explosive sensors with high performance.



Scheme 1. Schematic demonstration of the preparation and the working principle of fluorescent PANI–Py paper strips for detection of TNT.

Results and Discussion

PANI is the best known conducting and conjugated polymer. It is widely used in electrochemical sensing platform owing to its

tremendous properties such as mechanical flexibility, low operating temperature, tunable conductivity and doping.^[28–30] In addition, PANI also shows an efficient π - π stacking formation capability.^[31,32] These properties of PANI polymer is very important for the development of the fluorescence quenching based sensor platforms. We used the compound pyrene (Py) to prepare the π -stacking formation fluorescent-based sensor system. Because Py is a kind of organic dye with high fluorescence quantum yield and also it shows an efficient binding performance to NACs by electron donation and acceptation interaction.

Here, we prepared PANI–Py fluorescent polymer system to detect the NA explosives via photo-induced electron transfer (PET) sensing mechanism. In this sensing mechanism, the electron-transfer occurs from the electron rich PANI–Py fluorescent polymer to the electron deficient aromatic NA molecules. As known that the LUMO levels of 2,4,6-trinitrotoluene (TNT), 2,4-dinitrobenzene (DNT) and nitrobenzene (NB) molecules are very close to each other as seen in Figure 1A,

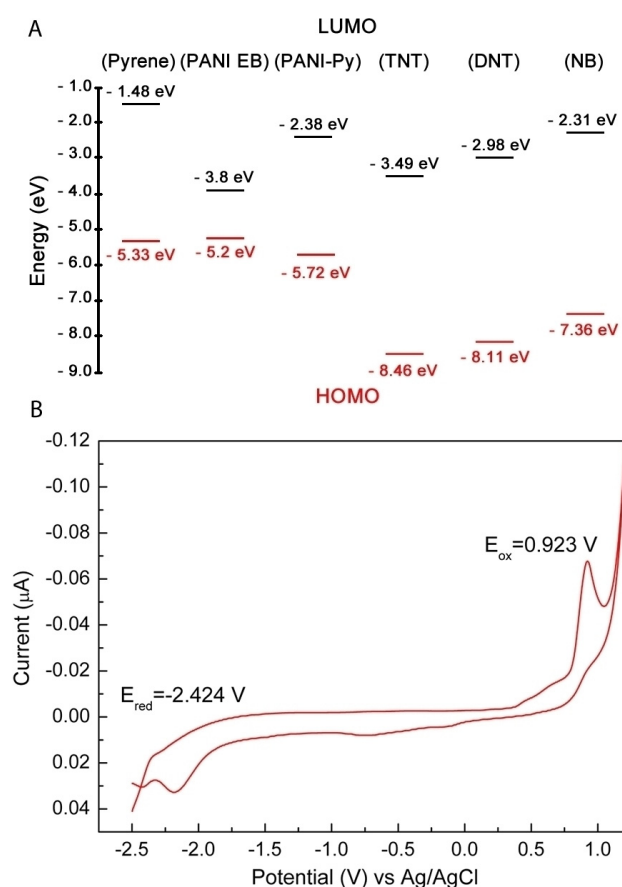


Figure 1. Determination of the PANI–Py system energy levels. A) HOMO-LUMO energy diagram of the main aromatic compounds are given.^[24] HOMO-LUMO levels of the PANI–Py system were calculated using the onset oxidation/reduction voltages of the CV measurement, B) Cyclic voltammogram of the PANI–Py system is given, which was measured using Ag/AgCl reference electrode.

therefore it is very difficult to distinguish them from each other. This phenomenon is very important for the selectivity and sensitivity of PET-based sensor systems. For this purpose, to reveal the selectivity and working mechanism of PANI-Py paper-based sensor, we calculated HOMO/LUMO energy levels of the PANI-Py system by cyclic voltammetry (CV) measurement as seen in Figure 1B.

CV measurement is one of the widely used experimental approaches.^[33–35] Onset oxidation and reduction potentials are used to estimate the HOMO and LUMO levels using an empirical formulation. In our experiments, ferrocene is used as the reference, which is a common reference with the known ferrocene value of -4.4 eV.^[36] HOMO and LUMO energies were calculated as given in the Equation 1 and 2, respectively.^[37]

$$E_{\text{HOMO}}(\text{eV}) = -e[E_{\text{ox}}^{\text{onset}} + 4.4] \quad (1)$$

$$E_{\text{LUMO}}(\text{eV}) = -e[E_{\text{red}}^{\text{onset}} + 4.4] \quad (2)$$

Based on the cyclic voltammetry results (Figure 1B) and Equation 1 and 2, HOMO and LUMO values of PANI-Py system were determined to be -5.72 eV and -2.38 eV, respectively with band gap energy (E_g) of 3.34 eV and HOMO/LUMO levels of the PANI-Py system and the main aromatic compounds are given in the Figure 1A.^[24,34] According to these results, it can be said that these values may be suitable for the detection of TNT via PANI-Py fluorescent polymer. For this purpose we prepared PANI-Py paper strips. Firstly, simple filter paper strips were immersed into PANI-Py solution and dried at vacuum at room temperature. SEM images of the PANI-Py uncoated and coated filter papers are given in Figure 2A–B. There is not observed any significant difference between the coated and uncoated samples. Images exhibit that PANI-Py solution is homogeneously coated on the cellulosic substrate and does not form any aggregated particular formation. It can be said that the polymer coating on the paper is very uniform.

We tested the interactions between the PANI-Py paper-strip and TNT molecules using fluorescence spectrometer. As seen in Figure 2C, monomeric fluorescence emission peaks ($\sim 374, 380, 385, 418$ nm) of Py molecule and an additional excimer peak at ~ 471 nm were observed for the PANI-Py paper strips. The presence of monomer and excimer emissions from the Py-PANI polymer shows that the loading of pyrene is high enough that π -stacked dimers have formed but not that high as not to also allow for the presence of isolated pyrene molecules.^[38] The excimer peak was disappeared after the paper-strip was exposed to 1×10^{-4} M TNT solution. Excimer emission was quenched significantly, while there was not observed any considerable decrease for monomeric Py emission peaks. Basically, the illumination of the PANI-Py system results in the electron excitation from HOMO to LUMO level of the system. Then, electron transfer occurs from the LUMO level of the PANI-Py to the electron-deficient NA explosives and fluorescence quenching is observed. This finding supports the proposed PET quenching mechanism.

In order to detect the sensitivity of the paper-based sensor, we prepared aqueous TNT solutions at different concentrations.

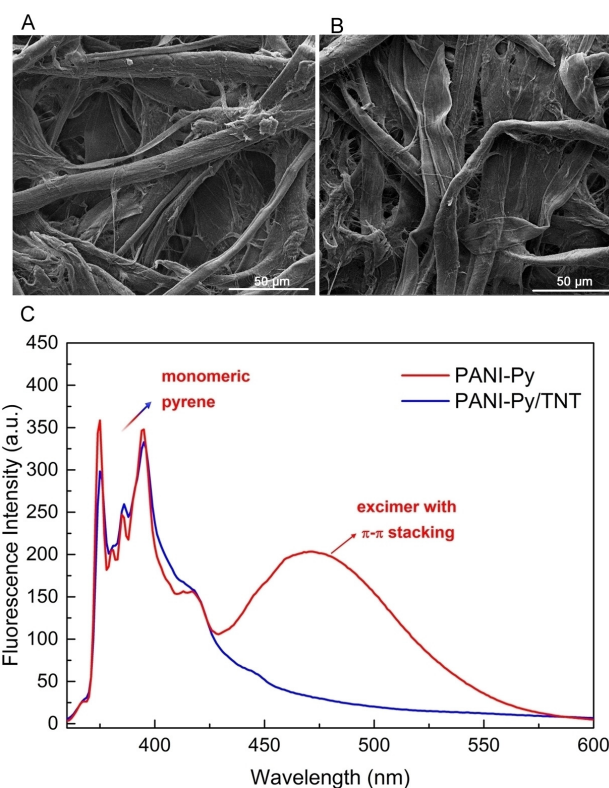


Figure 2. SEM images of PANI-Py A) uncoated and B) coated filter paper, C) Fluorescence spectrum of the PANI-Py coated paper is given before (PANI-Py) and after (PANI-Py/TNT) immersed into the 1×10^{-4} M TNT solution.

PANI-Py paper strips were immersed into these solutions for 15 minutes. Dipped paper strips were illuminated by 364 nm UV light and imaged. Images were analysed using ImageJ program and quenching efficiencies (%) of samples are given in Figure 3. Sensor achieves $\sim 96\%$ quenching efficiency at 10^{-4} M level.

The quenching behavior of PANI-Py paper strips was characterized by the normalized fluorescence intensity (I_0/I) and quenching constant (K_{SV}) using the Stern–Volmer (S–V) equation, $I_0/I = 1 + K_{SV}[Q]$ where I_0 is the initial fluorescence intensity in the absence of analytes, I is the fluorescence intensity in the presence of TNT, $[Q]$ is the molar concentration of TNT, and K_{SV} is the quenching constant (M^{-1}). The fluorescence intensities of sensor showed linear relationship ($R^2 > 0.99$) at lower than $1 \mu\text{M}$ concentration as seen Stern-Volmer plot in Figure 3 (inset). The K_{SV} value was calculated as $4.54 \times 10^5 M^{-1}$ and the detection limit (LOD) for TNT was calculated^[37] to be 9.6 ng/mL. It can be also said that PANI-Py paper strips exhibit a visual sensitivity to nM concentration of TNT as seen in Figure 3 inset.

The response time of the sensors is very important to apply them in real-environment measurements. Fluorescence intensity of PANI-Py strips at 2.5×10^{-4} M, 1×10^{-5} M and 1×10^{-7} M concentrations were analyzed depending on immersion time. Paper strips quenched dramatically in 1 minute and reached their maximum performance in 7 minutes (Figure 4A). In addition, immersion time was prolonged to 30 minutes but

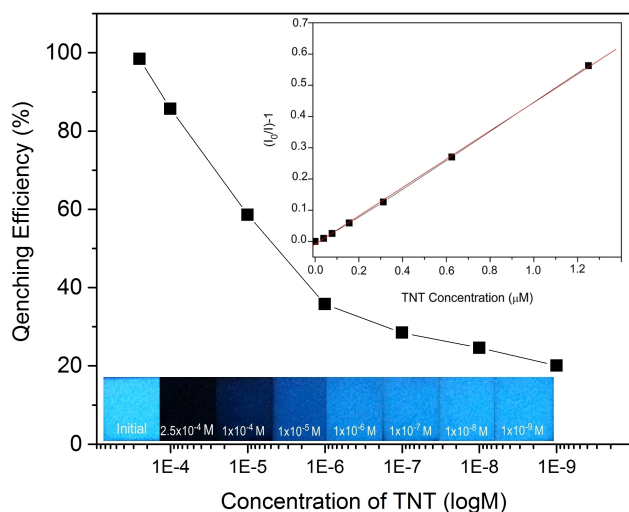


Figure 3. Quenching efficiency of the PANI–Py paper sensor is given depending on the analyte (TNT) concentration. Inset figures show the paper strip samples which were used for this detection and the Stern–Volmer plot for the quenching efficiencies at different TNT concentration.

fluorescence intensity did not change after 10 minutes. This stable quenching efficiency after 10 minutes suggests that PANI–Py paper strips response is fast and reliable for on-site usage.

Furthermore we also tested the stability of the sensor system for 30 days at ambient conditions as seen in Figure 4B. Same sample were recorded for 30 days. Insets show the sample photos which were used to measure fluorescence intensity with respect to the measurement time. Even after 30 days, only 17% intensity fall is observed and paper strips still demonstrate high fluorescence in visual. Therefore, these paper based sensor has a promising potential to safety use for several weeks.

The real-environment measurements are very important to reveal the performance of the sensor for on-site usage. Especially it is very challenging for sensors which work under the principles of fluorescence quenching to analyze real samples because of potential unknown effects such as ionic conditions. The real water environment such as tap water is very complex system owing to presence of many kinds of ions. Electron transfer mechanism can be affected by ionic conditions of the environment. In this study, we tested fluorescent PANI–Py strips in TNT solutions which were prepared in deionized water and random tap water samples. For this purpose, deionized and tap water samples were spiked with different concentration of TNT to compare and to mimic the real-environment measurements as seen in Figure 5.

We achieved 96% and 85% quenching efficiency for deionized water and tap water, respectively. As expected, the sensor exhibited lower sensitivity for spiked tap water samples than spiked deionized water samples due to the effect of the presence of different kind of ions.^[26] As a result, it can be clearly said that PANI–Py paper-based sensor is reliable and applicable for TNT detection in complex real water samples.

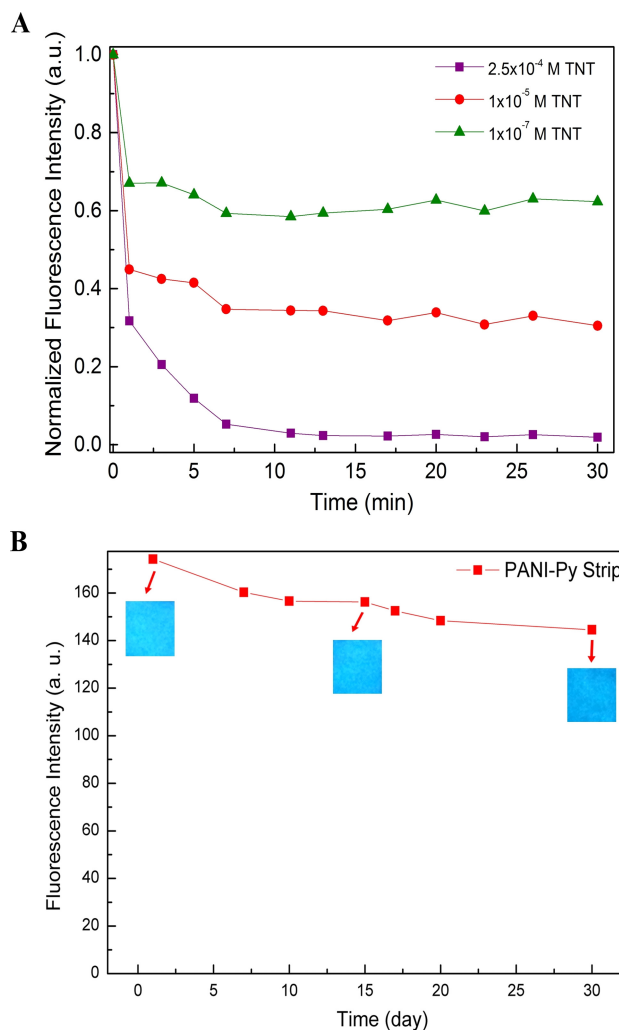


Figure 4. A) Time-dependent manner of the PANI–Py strips were investigated for 2.5×10^{-4} M, 1×10^{-5} M and 1×10^{-7} M concentration of TNT solutions, B) Stability of the PANI–Py paper strips was analyzed. Same sample were recorded for 30 days. Insets show the sample photos which were used to measure fluorescence intensity with respect to the measurement time.

Selectivity is one of the vital issues that define a sensor as reliable. Here, we tested our PANI–Py paper-based sensor against the different aromatic compounds, which have very close chemical structure to TNT molecule. Quenching efficiencies (%) of selectivity measurements are given in Figure 6.

The PANI–Py sensor is quenched by 96% for 0.25 mM TNT, while this value decreases to 68% and 24% of DNT and NB, respectively (Figure 6). The sensor exhibited higher selectivity against TNT and the sensitivity order of the sensor is observed as TNT > DNT > NB. It can be said that these quenching efficiencies correspond to the relative electron deficiency of the NACs that is mainly determined by the number of nitro-groups present.^[38] We also investigated the selectivity response of the PANI–Py paper strips against other aromatic compounds. PANI–Py paper-based sensor failed to provide any quenching response against electron-neutral (toluene) or electron rich compounds (aniline and phenol) due to the lack of capability

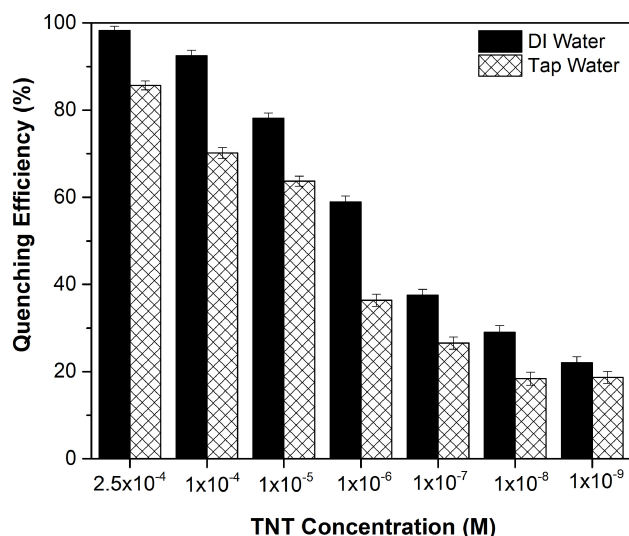


Figure 5. Quenching efficiency (%) of PANI-Py paper strips against different concentrations of TNT in deionized water (DI) and tap water.

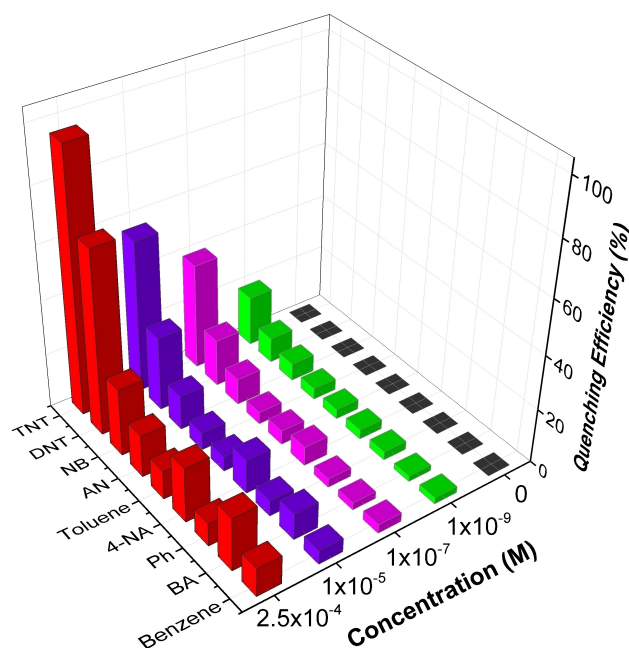


Figure 6. Quenching efficiency of PANI-Py sensor against different concentration of various analyte solutions (Benzene, Benzoic acid (BA), Phenol (Ph), 4-Nitroaniline (4-NA), Toluene, Aniline (AN), nitrobenzene (NB), 2,4-Dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT)).

for PET-type energy transfer processes.^[39] According to these results, it can be said that PANI-Py strips display high selectivity towards to TNT molecules.

Moreover we have tested the reusability of the PANI-Py paper strips. For this purpose, firstly the initial fluorescence value of strip was measured and then the strip was immersed 1×10^{-4} M TNT solution for 15 min and fluorescence intensity was recorded again. After the measurement, the strip was immersed in ethanol for 10 min, and then washed with distilled

water for several times and dried at rt. The strip was reused and the whole process was repeated for five cycles as seen in Figure 7. Although the PANI-Py paper strip could not reach the

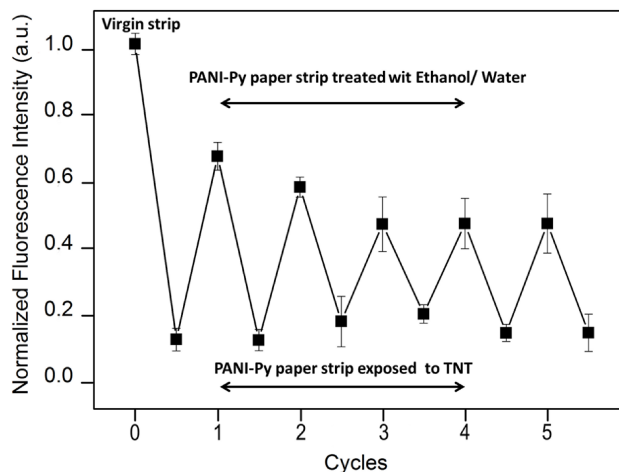


Figure 7. The reusability cycles of PANI-Py paper strip.

initial fluorescence intensity value but the sensor exhibited ~ 54% sensitivity after repeat treatments 5 times.

Conclusions

In conclusion, we propose and demonstrate a low cost, facile, sensitive and selective paper-based sensor for the detection of TNT. The PANI-Py sensor works under the principles of the photo-induced electron transfer mechanism. PANI-Py paper-based sensor exhibits very high selectivity and sensitivity against the presence of TNT in water samples. The lowest detection limit has been found to be 9.59 ng/ml. PANI-Py paper-based sensor detects the presence of TNT within 1 min and the quenching of the sensor has been noticed in visual by naked-eye under a simple UV lamp. The sensor also exhibits very high stability for several weeks in ambient conditions. Besides the high sensitivity and selectivity, PANI-Py strips also represent high performance in real water samples. Moreover the reusability results showed that the sensor can be used for 5 times with ~ 54% sensitivity. According to results it can be said that this developed new paper-based sensor has a promising potential to detect TNT in real-environment and on-site investigation for public safety, human health, waste water treatment and homeland security. We are also trying to fabricate different type of polymer-Py systems to enhance the sensitivity of the paper-based sensor system for visual sensing performance for ongoing studies.

Supporting Information Summary

Experimental details are given in SI.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Fluorescent sensor · Paper-based · PANI · Pyrene · TNT

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