PAPER

Ultra-sensitive detection of explosives in solution and film as well as the development of thicker film effectiveness by tetraphenylethene moiety in AIE active fluorescent conjugated polymer†

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A fluorescence sensory polymer (**P1**) consisting of pentiptycene and tetraphenylethene (TPE) units linked by acetylene was synthesized for direct detection of explosives in solution and air. At the same time, the effectiveness of thicker film in the presence of the TPE moiety for the detection of explosives was investigated. Fluorescence turn-off detection of picric acid (PA) was carried out in H_2O-THF mixture containing 90% water, where the TPE units of the polymer are in a highly emissive aggregation state. Polymer **P1** exhibits a fluorescence quenching response of 24% with addition of 4.36×10^{-8} M PA and 98% with the PA concentration at 4.7×10^{-6} M. For a thinner film (4 nm) of **P1** after exposure to dinitrotoluene for 10 s, the fluorescence intensity dropped 48% and it continued to drop 97% after 300 s, the corresponding values being 29% and 72% for thicker film (75 nm), respectively. These results indicate that **P1** is a promising material for direct detection of nitro explosives in air and solution at ppb levels, and the TPE moiety inside the polymer improves the sensitivity and effectiveness of thicker films.

Introduction

Nitroaromatic compounds are commonly used as explosives. Among them, 2,4,6-trinitrotoluene (TNT) is a main component in more than 10 types of bombs, especially those used in landmines.[1] Recent global terrorism has increased the attention paid to trace detection of explosives.[2] Low-level exposure to picric acid (PA), dinitrotoluene (DNT) and TNT can cause eye injury, red skin, liver damage and aplastic anemia.[3] The allowable contamination level of PA is not estimated; that of DNT is $0.2~\mu g~L^{-1}$ and TNT in water is 2 ppb.[4] This implies that the detection of explosive materials is greatly required for stopping unexpected terrorist activities and to ensure safe living. For the detection of explosives, there are many different techniques available like gas chromatography coupled with mass spectrometry,[5,6] surface-enhanced Raman spectroscopy,[7] ion mobility spectrometry,[8] energy dispersive X-ray diffraction,[9] metal detectors.[7] Though among the above mentioned methods some are highly sensitive to explosives, they are expensive, need to be calibrated frequently, require time-consuming procedures,[10] or are too sophisticated to handle and are not easily applied to on-field testing.[11] Besides these methods for onsite explosive detection, the use of dogs is one of the most common methods, but is totally dependent on the behavior of the dogs, and also the training and long-term care of dogs is expensive.[12] So, the development of efficient and cost-effective detection devices has become an urgent worldwide necessity.

Over the last two decades considerable research efforts have been devoted to fluorescence sensor polymers for accurate and rapid detection of nitro explosives by Swager and many other research groups, using pentiptycene, modified pentiptycene and tetraphenylethene (TPE) moieties as the key components in conjugated polymers.[2,13,14] Among them, several pentiptycene-based conjugated polymers are found to be highly sensitive towards nitroaromatic explosives.[2,13] We previously reported a series of highly sensitive sensory polymers containing pendent cholesteryl ester groups followed by fluorene and pentiptycene for detection of nitroaromatics.[15]

TPE-based polymers are aggregation-induced emission (AIE) active, AIE being a phenomenon where a non-emissive material in solution becomes highly luminescent upon aggregation.[16] Recently, TPE-based conjugated polymers for sensing of nitro explosives have become promising materials. Most of them are demonstrated in solution with rare examples in film.

Pentiptycene has a three-dimensional rigid and bulky structure, which prevents π-stacking or excimer formation in the excited state in the solid film; as a result, a gaseous analyte can easily interact with the surface and diffuse through the film

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causing fluorescence quenching.[13a,d] TPE polymer in solution forms highly emissive nanoaggregates; an analyte can enter the nanoaggregates and be captured, at the same time associating with the polymer by non-bonding electrostatic interactions or potential involvement of Lewis acid–base interactions, causing fluorescence quenching.[14a,b]

To detect an explosive in air with rapid response and a high sensitivity, a fluorescence polymer film that features a high degree of conjugation, large free volume, and high adsorption ability of gaseous analytes on the surface, with a fast diffusion rate and high solubility through the film would be an ideal system. Moreover, to detect an explosive in solution with rapid response and a high sensitivity, a fluorescence polymer that features strong luminescent amplification characteristics, *e.g.*, AIE enhancement with high degree of conjugation, would be an ideal system.

Since nitroaromatic explosive compounds are electron deficient in nature, with highly conjugated electron-rich polymers they are able to make π-stacking complexes, and by the photoinduced electron transfer process the fluorescence intensity of polymer sensors can be quenched.[17,18] Highly fluorescent AIE active polymers are also able to be quenched by nitroaromatics through energy transfer. With these basic requirements in mind, we have designed a polymer (**P1**) which consists of pentiptycene diacetylene (**1**) and 1,2-bis(4-bromophenyl)-1,2-diphenylene (**2**) as monomers making the polymer highly conjugated and electron rich. This polymer showed high sensitivity towards isocyanates and can detect them at ppt levels.[19] Though isocyanates are less electron deficient than the explosive compounds, we expect polymer **P1** to have very high sensitivity towards nitroaromatic explosives. In this paper we report the detection of nitroaromatic compounds in air and solution as well as the effectiveness of a thicker polymer film. We also hypothesized that the TPE moiety would increase the cavity of the film as well as the conjugation, thus enhancing the performance of the thicker film.

Measurements

^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance Digital 300 and 400 MHz (300, 400 MHz and 75, 100 MHz for ^{1}H and ^{13}C NMR, respectively). Resonances were quoted on the δ scale relative to tetramethylsilane (TMS, $\delta = 0$) as an internal standard. For ^{1}H NMR spectra, the following abbreviations have been used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared measurements were performed with a Varian 1000 FT-IR Scirinitar series spectrophotometer. The following abbreviations have been used for IR spectra: s = strong, m = medium, w = weak, br. = broad, sh = sharp. The measuring mode was percentage transmittance (%T). The band positions were expressed per centimeter (cm^{-1}). Mass spectra were measured with a Micromass Quattro LC ESI (EI). UV-Vis spectra were recorded with a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer at room temperature. The fluorescence spectra of all samples were measured in a quartz cuvette with a path length of 1 cm using a Shimadzu RF-1501 spectrofluorometer.

Preparation of fluorometric titration solutions

Stock THF solutions of the polymer **P1** with a concentration of 1.17×10^{-3} M in 10 mL were prepared and then 1 mL of the solution was transferred into a 20 mL vial to further dilution by 9 mL of THF as experimental solution. After adding an appropriate amount of the experimental solution into a 20 mL vial, water was added under vigorous stirring to prepare H$_2$O–THF mixture of different fractions ($f_w = 0$–95) by volume. A stock PA solution was prepared at a concentration of 4.36×10^{-3} M in 10 mL THF. The fluorescence spectroscopic titration was carried out by sequentially adding 0.1, 0.2, 0.3 and up to 10.8 µL of PA solution to 10 mL of **P1** in H$_2$O–THF mixture containing 90% of water. The solution of **P1** with PA was stirred for 1 minute and then placed into a quartz cuvette. The fluorescence spectra of the resultant mixtures were then recorded immediately at room temperature with excitation wavelength of 365 nm. During the titrations the instrument sensitivity was kept low, otherwise it went beyond the range.

Film formation

Films coated on glass substrates were prepared by the spin-coating process. Polymer films were spin-coated from 1,1,2,2-tetrachloroethane solutions onto a glass plate (microscope slide, 20 × 20 × 1 mm) and spun at 1000 rpm by using a Chemat KW-4B spin-Coater. Then the films were dried overnight at 80 °C under argon atmosphere. To prepare 4–80 nm thick films, 5–10 mg of polymer in 1.5 mL of solvent were used. The thickness of the films ranged from 4 to 80 nm, as measured using a Tencor Instrument Alpha-Step 200 surface profiler (uncertainty ± 0.01 Å) and by atomic force microscopy (AFM) (uncertainty ± 0.2 nm).

The fluorescence spectra were recorded with a fluorimeter immediately after exposing the polymer film to the analyte, 2,4-DNT, for a specific period of time. Fluorescence quenching response (FQR) is defined as $I_0 - I/I_0 \times 100$, where I_0 and I are the fluorescence intensity prior to and after exposure to analyte (DNT) vapor, respectively.

Results and discussion

The synthetic route to the target sensory polymer **P1** is shown in Scheme 1. The Sonogashira cross-coupling reaction of compound **1** with compound **2** affords polymer **P1** in 71% yield which we have recently published. Its characterization by spectroscopic method has been mentioned in that literature.[19]

The backbone of polymer **P1** contains the TPE unit, which is AIE active. The emission property of the polymer and its AIE behavior were investigated in THF and in H$_2$O–THF mixture solutions (Fig. 1). Tang has revealed that TPE-containing polyenes are non-emissive in solution but become luminescent afterwards due to AIE with the addition of poor solvent. This emission gradually increased with the formation of aggregates and reached its maximum in 90% aqueous solution.[14a,b,16]
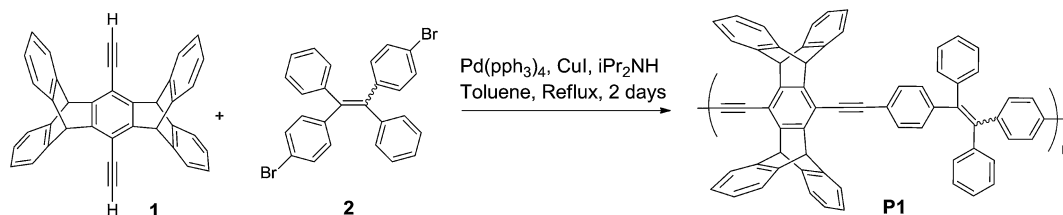
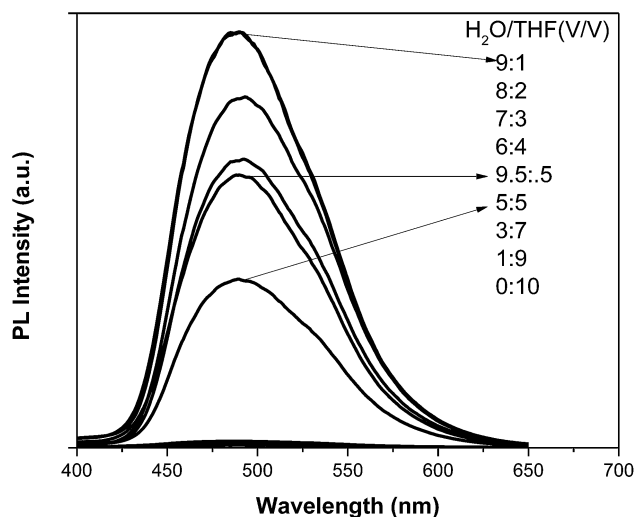**Scheme 1** Synthesis of polymer **P1** by the Sonogashira cross-coupling reaction.

Fig. 1 Photoluminescence spectra of polymer **P1** in H_2O–THF mixtures with different water contents. Excitation wavelength: 365 nm.

Fig. 2 Fluorescence response of **P1** (1.17×10^{-5} mol L^{-1}) to the addition of different amounts of picric acid (PA) into the H_2O–THF mixture solution with a water fraction of 90%. Excitation wavelength: 365 nm.

A similar phenomenon was observed for polymer **P1** in THF and in H_2O–THF solutions. Polymer **P1** is non-emissive or very weakly emissive in THF or in H_2O–THF mixture when the water content is below 30%, but upon further addition of water the photoluminescence (PL) intensity gradually increases at around 490 nm.

The photograph of Fig. S1† clearly indicates that in H_2O–THF solution with lower water fraction, polymer **P1** emits no light; the emission becomes stronger afterwards due to aggregation.

Explosive detection by polymer nanoaggregates

We used PA as a model explosive of TNT in this work. The sensitivity of polymer **P1** towards PA was determined by fluorescence spectroscopic titration experiment. Fig. 2 displays the fluorescence turn-off detection of different concentrations of PA using **P1** (1.17×10^{-5} M) in H_2O–THF mixture containing 90% of water. Upon the addition of PA into **P1** aggregate solution, the emission intensity decreased quickly and the FQR reached over 98% with the PA concentration at 4.71×10^{-6} M. The inset photograph (bottom) shows that polymer **P1** is highly emissive, but after addition of PA emission decreases, which is also detectable by the naked eye (inset photograph (top)).

The FQR was 24% with addition of 4.36×10^{-8} M PA to the nanoaggregates of **P1**, which confirmed the nanoaggregates of

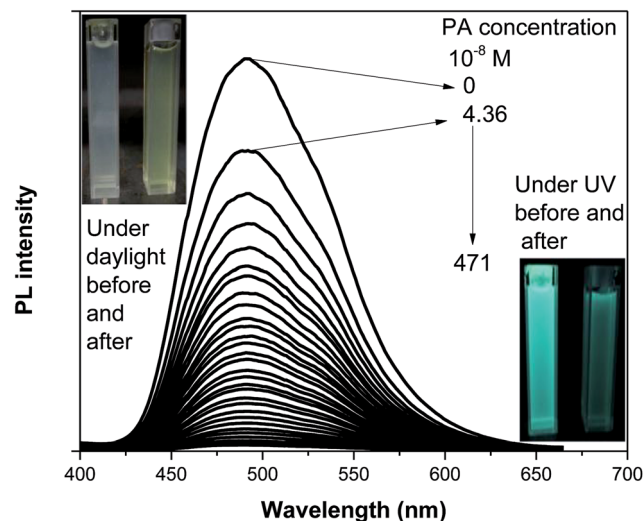**P1** could be a very sensitive sensor for the detection of nitro-aromatic explosives at ppb levels in solution. Fig. S3† reveals that polymer **P1** exhibits high sensitivity towards PA with the association constant between the host and guest being 37×10^{-8} M^{-1}, deduced by the Stern–Volmer equation, which is lower than that reported for TPE-based fluorescence sensor polymers.[14a,b] This can be explained by the fact that in the turn-off detection system where water content is high, the AIE active TPE units are in an aggregated state, which gives intense fluorescence. In addition, pentiptycene is a large compound and maintains a large free volume inside the polymer allowing the analyte to enter into the polymer. This large cavity in the nanoaggregated state helps to bind with more PA thus making the quenching a highly efficient process for polymer **P1**.[17,20] This can also be explained by the Lewis acid–base interaction between the electron-rich polymer **P1** and the electron-deficient PA molecules as well as the photoinduced electron transfer from the higher lowest unoccupied molecular orbital (LUMO) energy level of **P1** nanoaggregates to PA which plays a key role in the quenching process. Cyclic voltammetry (CV) was carried out for this polymer to determine the highest occupied molecular orbital (HOMO) and LUMO energy levels (Fig. S4 in ESI†). From CV we only got the noticeable oxidation process (2.02 V) since our synthesized polymer is electron rich. This oxidation

potential value provides the HOMO energy level of 6.81 eV.[21] Calculation of LUMO from optical energy band gap tends to give large error; therefore, the calculated LUMO would not be accurate. Addition of trace analytes to the polymer aggregates leads to quenching, indicating that surely the LUMO of the polymer is much higher than the LUMO of analytes (PA and DNT) which facilitates electron transfer from the excited polymer to analytes. Fig. S5 in the ESI† illustrates that there is an overlap between the absorption spectrum of PA and the emission spectrum of the polymer aggregates, but this was not possible for DNT. Therefore, in solution the quenching mechanism can be dominated by charge or energy transfer or both, depending on the overlap of the absorption of nitroaromatics and emission of polymer at the highest aggregation state.[14c,e,22]

Study of DNT quenching of polymer P1 film fluorescence

DNT was used as an analyte in our study, because of its higher equilibrium vapor pressure (1.47×10^{-4} mmHg at 22 °C) than TNT (8.06×10^{-6} mmHg at 25 °C)[7] as well as its availability. Fig. 3 shows the changes in fluorescence intensity of the P1 film (16 nm thick) upon exposure to DNT vapor over several different time periods. With a 10 s exposure, fluorescence intensity dropped 43% and after 360 s intensity dropped 92.0%.

Fig. 4 and 5 display the FQR for different time intervals upon exposure of DNT analyte to different thicknesses of polymer film. For a 4 nm film, the FQR after exposure for 30 s is 70%; however this reduces to 37% for a film of 80 nm in thickness. This result is consistent with the time intervals within 60 s exposure to DNT vapor: our experimental work shows that thinner films give a higher response than thicker films, especially in the first 30 s. A similar phenomenon was observed for 1–5 min of DNT exposure (Fig. 5). However, after 5 min exposure to DNT, films around 35–75 nm in thickness gave almost the same FQR (77–73%). This rapid response to the analyte indicates that the DNT molecules have better nonbonding
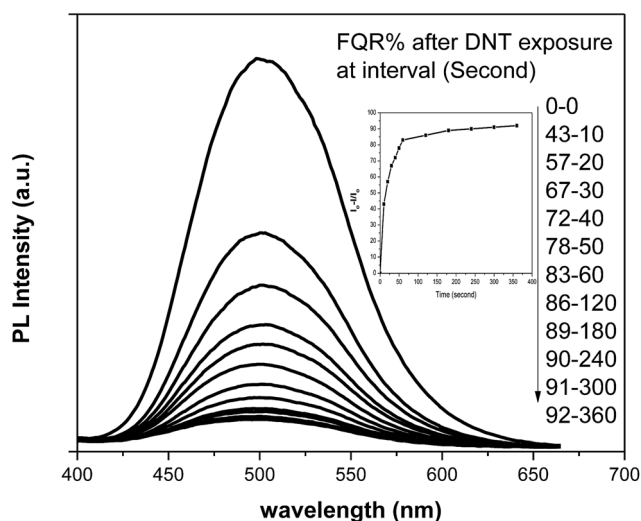
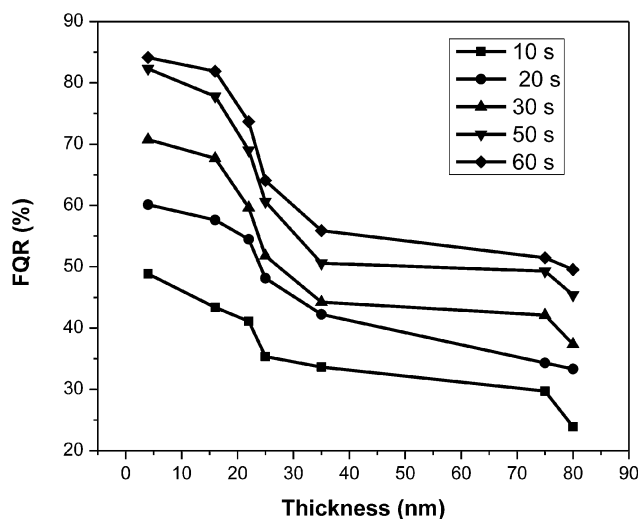

Fig. 4 Fluorescence quenching response of films of P1 of different thicknesses after exposure to DNT vapor for 10−60 s.
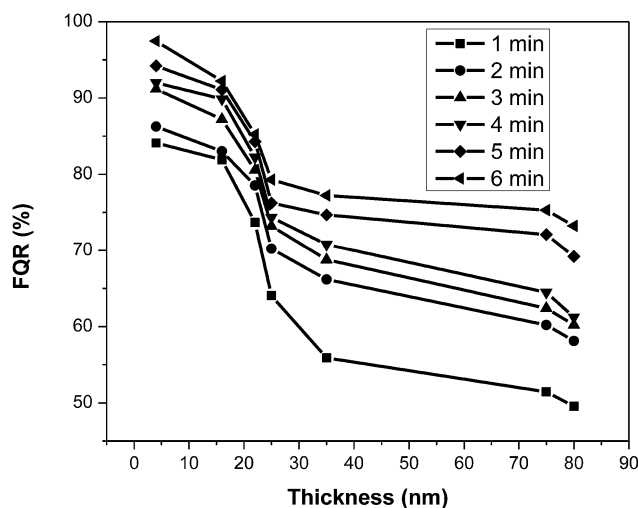

Fig. 5 Fluorescence quenching response of films of P1 of different thicknesses after exposure to DNT vapor for 1−6 min.

electrostatic interactions with the electron-rich polymer.[9] Thinner films, 4–30 nm, show a better FQR (85–64%) within 60 s for our synthesized polymer P1. These results can be explained by the cavity of the polymer backbone and diffusion rate of the analyte through the polymer in the solid state. The pentiptycene and TPE moieties make the polymer more electron rich, thus leading to a high FQR within a short period of exposure. These two moieties also create a large number of cavities or free volume in the polymer film which permits a high diffusion rate for explosive molecules to enter and solubilize in the polymer film, thus giving a window for higher FQR in a longer period of exposure. Moreover, the rigid pentiptycene moiety in the polymer prevents significant π-stacking interactions between polymer backbones, thereby weakening the interpolymer interactions. As a result, the polymer will provide a very quick response regardless of thickness and, due to the morphological

Fig. 3 Time-dependent PL spectra of a spin-coated film of P1 upon exposure to DNT vapor at room temperature for 0−360 s. Film thickness: 16 nm; excitation wavelength: 375 nm.

change in the polymer film, it will provide a better response with time for thicker films. Experimentally, the fluorescence signals decrease noticeably within only 10 s of DNT exposure regardless of the thickness of the film and reach equilibrium after 5 min. The FQR value is always higher for thinner films and also it improves for thicker films with time, which indicates that the DNT molecules have strong interactions with film surface, and can easily diffuse and solubilize through the bulk of the film. These results indicate that the TPE moiety enhances the formation of cavities along with the pentiptycene moiety in the solid state as well as increasing the conjugation, thus significantly improving the FQR for thicker films, though the thinner films have higher FQR. Our experimental result was relevant to our hypothesis and the polymer gave a better response than in our previous work.[16] Therefore, our polymer is more suitable for the detection of nitroaromatic vapor.

DNT detection study by using APTES undercoated and top-coated films of P1

Fig. 6 displays FQR for different time intervals upon exposure of DNT analyte to different thicknesses of polymer film undercoated by (3-aminopropyl)triethoxysilane (APTES). APTES is a surface promoter for a variety of substances such as glass, silicon and plastics, and is able to form an ultrathin layer containing free amino groups on the surface. The polar electron-donating group ($-NH_2$) in APTES has an ability to bind electron-deficient nitroaromatic compounds through the electron donor and acceptor interaction. The purpose of using APTES in our experiment was to get a quick response compared to the uncoated polymer. However, Fig. 6 clearly shows that the polymer films with the APTES undercoating gave lower FQR than those without the undercoating for different time intervals. Thus, this indicates that the undercoating decreases the sensitivity of polymer P1. Fig. 7 displays the fluorescence turn-off detection of DNT using P1 top-coated with APTES. This shows lower FQR for different time intervals compared to the
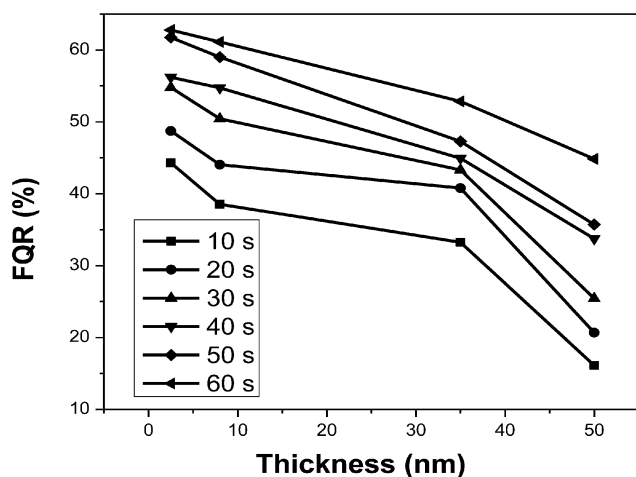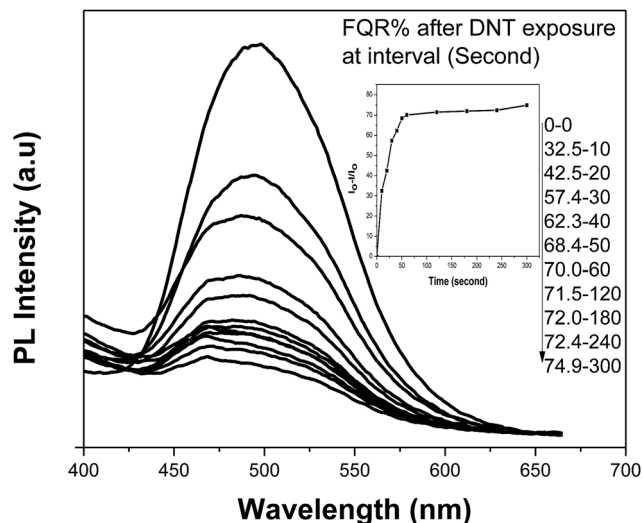

Fig. 7 Time-dependent PL spectra of spin-coated film of P1 with APTES top-coating upon exposure to DNT vapor at room temperature for 0–300 s. Film thickness: 4 nm; excitation wavelength: 375 nm.

Table 1 Comparison of the fluorescence quenching response (FQR) of P1 films (4 nm) on glass plates with APTES undercoating and top-coating

Time (s)	10	30	60
With under-coated film[a]	10.31	20.33	23.75
With top-coated film[b]	16.38	13.41	14.79

[a] Change in FQR = $F_1 - F_2$, where F_1 is the FQR without undercoating and F_2 is the FQR with APTES undercoating. [b] Change in FQR = $F_1 - F_2$, where F_1 is the FQR without top-coating and F_2 is the FQR with APTES top-coating.

uncoated film, indicating that the top coating also decreases the sensitivity of polymer P1.

Table 1 shows the level of fluorescence quenching after 10 s, 30 s and 60 s for a 4 nm P1 film with undercoated and top-coated surfaces with respect to that without APTES. There is a noticeable difference among them; initially the undercoated film shows better response upon exposure than the top-coated one. After 60 s exposure of DNT vapor to the top-coated film, it shows higher FQR compared to the undercoated film. The polymer film without APTES gave higher FQR response for different time intervals than that with APTES coating. This indicates that the polymer itself has enough cavities to allow sufficient diffusion of DNT vapor through the film. Moreover, with the presence of APTES, the interaction with the analyte is more hindered, which leads to a slight decrease of FQR.

Conclusion

In this work, a conjugated fluorescent polymer (P1) consisting of pentiptycene and TPE moieties that are linked with acetylene was successfully used as an explosive chemosensor both in the

Fig. 6 Fluorescence quenching response of films of P1 of different thicknesses undercoated with APTES after exposure to DNT vapor for 10–60 s.

aggregated and solid states. **P1** showed high sensitivity towards nitroaromatic explosives. In the aggregated state the detection limit can reach the ppb level; while for a solid film with a thickness of 4 nm, 85% FQR has been recorded within 60 s. Moreover, in the presence of TPE moieties, the polymer itself has enough cavities that facilitate better FQR for thicker films as well. The presence of a top-coating or undercoating did not improve the FQR. The experimental data indicated that **P1** self-supporting films can be used as a promising sensor material for the detection of nitroaromatic explosives without the need for any further film modifications.

Acknowledgements

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