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Phenothiazine-based oligomers as novel fluorescence probes for detecting vapor-phase nitro compounds

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ABSTRACT

To meet the need for rapid and low-cost chemical sensing of explosive, new fluorescence chemosensors based on oligophenothiazines for probing vapor-phase nitro compounds have been developed. The phenothiazine-based trimer **P3** and pentamer **P5** have been synthesized via Heck and Wittig reactions by convergent approach. It was found that they can detect the vapors of nitro compounds, including *p*-nitrotoluene (***p*-NT**), 2,4-dinitrotoluene (**DNT**), 2,4,6-trinitrotoluene (**TNT**) with good sensitivity and reversibility. And the sensor of **P3** film gave a linear fluorescence quenching response to 7–800 ppb **TNT** with the detection limit of 4 ppb. For **DNT** vapor, a linear working range of the sensor was 2–24 ppm with the detection limit of 40 ppb. Meanwhile, the interferents, including common organic solvents, *p*-nitrophenol and 2,4-dinitrophenylhydrazine cannot lead to obvious fluorescence quenching, meaning that the film based on oligophenothiazines exhibited good specificity of fluorescence response to explosive. Based on the fluorescence lifetime and UV–vis absorption measurements, we suggested that the fluorescence quenching of oligophenothiazine-based films exposed to the vapors of nitro compounds was due to the formation of non-fluorescent charge-transfer complex between oligophenothiazine and nitro compounds.

1. Introduction

Fast and sensitive detection of the vapor-phase nitroaromatics, such as 2,4,6-trinitrotoluene (**TNT**), and 2,4-dinitrotoluene (**DNT**), etc., is of vital importance in national security and evaluation of environmental pollution [1–4]. The presently used detections of nitroaromatics include gas chromatography coupled with a mass spectrometer, surface enhanced Raman spectroscopy [5,6], optofluidic ring resonator [7], electrochemical techniques [8–10], and ion mobility spectrometry, etc. [11], which are usually expensive and not easily fielded in a small, low-power package. Therefore, the development of chemosensors with high sensitivity and selectivity for the real-time detecting nitroaromatics has received much attention in recent years. Since Swager et al. reported the amplified fluorescence quenching of the conjugated polymers with pentiptycene moieties towards the nitroaromatic binding events in the film [12–15], fluorescence chemsensors have been of importance in the detection of nitroaromatics on account of the high signal output and detection simplicity. Up to date, lots of fluorescent materials such as poly(silole) [16–18], poly(silafluorene-fluorene) [19], poly(tetraphenylgermole) [20], oligo(diphenylsilane) [21], oligopyrene [22,23], 1,4-substtituted pentiptycenes [24], functional silica nanoparticles [25,26], and organic nanofibril film [27–31] have been used for fluorescence detection of nitro compounds. Although the reported fluorescent response to nitroaromatic exhibits high sensitivity, the reversibility is usually bad. So it is still a great challenge to design new sensory materials with high sensitivity and good reversibility.

It was known that the fluorescence quenching of the probing molecules in detection of nitro compounds could be attributed to photoinduced charge transfer (PET) or the formation of the charge-transfer complex in most cases [13,21], so the compounds with electron-rich units might become ideal fluorescent sensing materials for nitroaromatics [14]. Previously, we have synthesized a series of vinyl-substituted oligophenothiazines [32], which are electron-rich systems with low oxidation potentials and can emit intense green light [33–35]. With these results in mind, we designed new linear vinyl-substituted phenothiazine-based trimer **P3** and pentamer **P5** as fluorescence probing molecules for nitroaromatics. To the best of our knowledge, there is no example of detecting nitroaromatics with phenothiazine-based oligomers. It was found that the films of phenothiazine-based oligomers were good candidates in fluorescence detection of vapor-phase nitro compounds with good sensitivity and fairish reversibility.

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2. Experimental

2.1. Materials

10-Octyl-3-vinyl-10H-phenothiazine (**1**), 3,7-dibromo-10-octyl-10H-phenothiazine (**2**), 10-octyl-3-((E)-2-(10-octyl-3-vinyl-10H-phenothiazin-7-yl)vinyl)-10H-phenothiazine (**3**) were prepared according to the methods we reported previously [32]. DMF was distilled from phosphorous pentoxide, dichloromethane was distilled from NaH. Toluene had been purified by reflux with sodium for several hours under nitrogen and then distilled to remove trace water. Nitroaromatics including ***p*-NT**, **DNT**, and **TNT** were of analytical grade and used directly without further purification. *Caution*: Nitroaromatics used in the present study are highly explosive and should be handled only in small quantities. The films based on **P3** and **P5** were fabricated by spin-casting of CH_2Cl_2 solutions (1.0 mM) onto glass substrates, followed by drying in vacuum at room temperature for 1 h. The thickness of the films was measured as 30 nm for **P3** and **P5** on average.

2.2. Instruments and characterization

^{1}H NMR spectra were recorded on a Mercury plus 500 MHz using $CDCl_3$ as solvent in all cases. UV–vis spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. Photoluminescence (PL) spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer. Fluorescence lifetimes were measured using the time correlated single photon counting technique with FL920 fluorescence lifetime spectrometer. The excitation source was an nF900 ns flashlamp. Lifetimes were obtained by deconvolution of the decay curves. FT-IR spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr pellet. Cyclic voltammetry was performed at room temperature under nitrogen in three electrode cells in dichloromethane + 0.1 M Bu_4NPF_6. The reference electrode was Ag/AgCl, and working electrode was Pt, using ferrocene as internal standard, scan rate was maintained at 100 mV/s on BAS 100W Bioanalytical Systems. Mass spectra were performed on AXIMA CFR MALDI/TOF matrix assisted laser desorption ionization/time-of-flight) MS (COMPACT). C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The thickness of the film was measured using Veeco Dektak 150 Surface Profiler.

2.3. Synthesis of ***P3*** and ***P5***

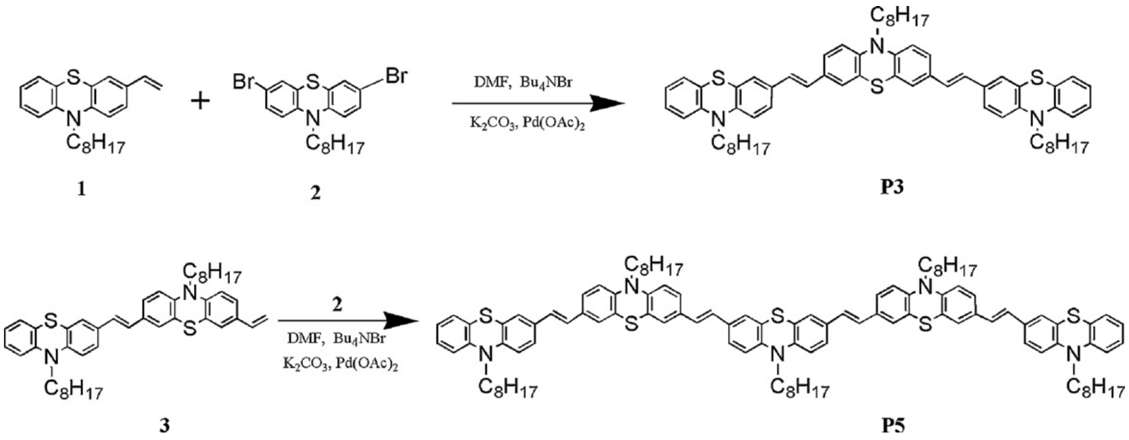
In our previous report, we have synthesized linear vinylene-linked oligophenothiazines by Heck and Wittig reactions via divergent approach. In order to improve the synthetic efficiency, we design the synthetic routes with less steps for new phenothiazine-based oligomers **P3** and **P5** by convergent approach (Scheme 1).

10-Octyl-3-((1E)-2-(10-octyl-3-((E)-2-(10-octyl-10H-phenothiazin-7-yl)vinyl)-10H-phenothiazin-7-yl)vinyl)-10H-phenothiazine (**P3**): A mixture of 0.86 g (2.2 mmol) compound **1**, 0.47 g (1 mmol) 3,7-dibromo-10-octyl-10H-phenothiazine **2**, 0.31 g (2.2 mmol) anhydrous potassium carbonate, 0.71 g tetrabutylammonium bromide, and 12 mg $Pd(OAc)_2$ in 20 mL dry DMF under N_2 atmosphere was stirred at 120 °C for 24 h. Then, the mixture was cooled to room temperature and poured into 300 mL water with stirring. After extracted with CH_2Cl_2 (3× 50 mL), the organic phase was washed with brine and dried with anhydrous magnesium sulfate. The solvent was removed and the residue was purified by column chromatography using petroleum ether/dichloromethane (v/v = 2/1) as the eluent, followed by recrystallization from the mixed solvents of dichloromethane and light petroleum to give yellow solid with a yield of 62%. mp: 93.0–94.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ = 7.28–7.24 (8 H, m), 7.18–7.14 (4 H, m), 6.93 (2 H, t), 6.89–6.82 (10 H, m), 3.85 (6 H, t), 1.85–1.79 (6 H, m), 1.46–1.42 (6 H, m), 1.32–1.27 (24 H, m), 0.89 (9 H, t) (see Fig. S1). IR (KBr, cm^{-1}): 2921, 2850, 1598, 1575, 1466, 1363, 1248, 1039, 955, 874, 745. MS, *m*/*z*: cal: 982.5, found: 981.5 (see Fig. S2). Elemental analysis: cal. for $C_{64}H_{75}N_3S_3$: C, 78.24; H, 7.69; N, 4.28; S, 9.79. Found: C, 78.26; H, 7.74; N, 4.22.

10-Octyl-3-((E)-2-(10-octyl-10H-phenothiazin-3-yl)vinyl)-7-((1E)-2-(10-octyl-3-((1E)-2-(10-octyl-3-((E)-2-(10-octyl-10H-phenothiazin-7-yl)vinyl)-10H-phenothiazin-7-yl)vinyl)-10H-phenothiazin-7-yl)vinyl)-10H-phenothiazine (**P5**): The synthetic method for **P5** was similar to that of **P3** except that compound **3** 1.48 g (2.2 mmol) was used as reagent. Finally, we got yellow solid in a yield of 53%. mp: 129.0–131.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ = 7.26–7.21 (16 H, m), 7.16–7.13 (4 H, m), 6.91 (2 H, t), 6.87–6.79 (18 H, t), 3.83 (10 H, t), 1.83–1.77 (10 H, m), 1.44–1.40 (10 H, m), 1.30–1.26 (40 H, m), 0.89–0.86 (15 H, m) (see Fig. S3). IR (KBr, cm^{-1}): 2923, 2852, 1599, 1580, 1473, 1362, 1251, 1040, 957, 873, 746. MS, *m*/*z*: cal: 1653.5, found: 1652.7 (see Fig. S4). Elemental analysis: cal. for $C_{108}H_{125}N_5S_5$: C, 78.45; H, 7.62; N, 4.24; S, 9.70. Found: C, 78.48; H, 7.67; N, 4.19.

2.4. General methods

In steady-state emission, the quenching data fit the Stern–Volmer model well. $I_0/I = 1 + K_{sv}$ [*Q*], where I_0 and *I* are the fluorescence emission intensity of the sensory material before and after adding of the quencher, respectively, and [*Q*] is the concentration of the quencher. The constant K_{sv} defines the



Scheme 1. The synthetic routes for oligophenothiazines **P3** and **P5**.

efficiency of quenching. The sensitivity of **P3** and **P5** towards **TNT**, **DNT** and ***p*-NT** was recorded by micro-titration in toluene. The concentration of **P3** and **P5** was maintained at 1×10^{-6} M. The fluorescence intensity was monitored at 500 nm excited at 306 nm.

The sensing performance of the oligophenothiazine-based films to vapor nitro compounds was studied in a way adopted by Swager and others [14]. Specifically, the film to be tested was inserted into a sealed vial at room temperature containing an analyte and cotton gauze which prevents the direct contact of the film and the analyte, and helps to maintain a constant vapor pressure. The time-dependent fluorescence spectra of the film were measured after immersing the film into the sealed vial immediately or for a certain time. By monitoring the changes of the fluorescence intensity at 520 nm (λ_{ex} = 306 nm) of the film with increasing the exposure time to vapor-phase analyte, the time-dependent fluorescence quenching efficiency was obtained.

The reversibility of the sensing process was examined using **P3** film as an example. Firstly, the fluorescent spectrum of the film exposed to the saturated vapor of ***p*-NT** at room temperature for 10 s, or to **DNT** as well as **TNT** vapors for 600 s, was recorded. Then, the non-fluorescent film containing the complex of **P3** and ***p*-NT** (or **DNT**) was blown by hairdryer for 10 s (or 60 s), and that containing the complex of **P3** and **TNT** was immersed into a saturated vapor of hydrazine (ca. 140 ppm) for 10 s to recover the fluorescence emission. The above process was repeated for several times.

In addition, the fluorescence quenching efficiency of the film for sensing to the vapor of nitro compound at different concentrations was obtained by tuning the tested temperature of the sealed cell containing an analyte and cotton gauze since the vapor pressure of the nitro compound at different temperatures can be referred [36–38]. After the equilibrium vapor pressure of the analyte was reached at different temperatures, the film was immersed in the sealed cell for 30 s, followed by monitoring the fluorescence intensity. Thus, the concentration-dependent fluorescence quenching efficiency of **P3** film was obtained.

The standard deviation of the quenching efficiency was less than ±4% in all cases.

3. Results and discussion

3.1. Photophysical and electrochemical data of *P3* and *P5*

Photophysical and electrochemical data of oligophenothiazines **P3** and **P5** are shown in Table 1, we can find that **P3** gave the absorptions at 306 nm and 408 nm in toluene, which red-shift to 308 nm and 426 nm, respectively, in the film due to the aggregation. Similarly, two absorption bands at 308 nm and 419 nm are detected for **P5** in solution, which also red-shift to 311 nm and 438 nm in the film (see Fig. S5). In addition, the absorption bands of **P5** appeared in the longer wavelength region compared with **P3** is on account of the larger conjugated length of **P5**. Moreover, the two compounds can emit strong fluorescence irradiated by UV light. As shown in Fig. 1, we can find that in toluene the fluorescent band of **P3** is located at 500 nm, and that of **P5** appears at 509 nm. They red-shifted to 524 nm and 529 nm in film for **P3** and **P5**, respectively. The fluorescence quantum yields of **P3** and **P5** in toluene were 0.33 and 0.38 using quinine sulfate in 0.1 H_2SO_4 (Φ_F = 0.546) as the standard. The energy levels of HOMO of **P3** and **P5** were estimated as −5.01 eV and −4.97 eV, respectively, according to the electrochemical results, meaning that the two oligomers were typical electron-rich systems. Strong fluorescence emitting as well as electron-donating characters made it possible that **P3** and **P5** might be candidates for fluorescence chemosensors for nitroaromatics.

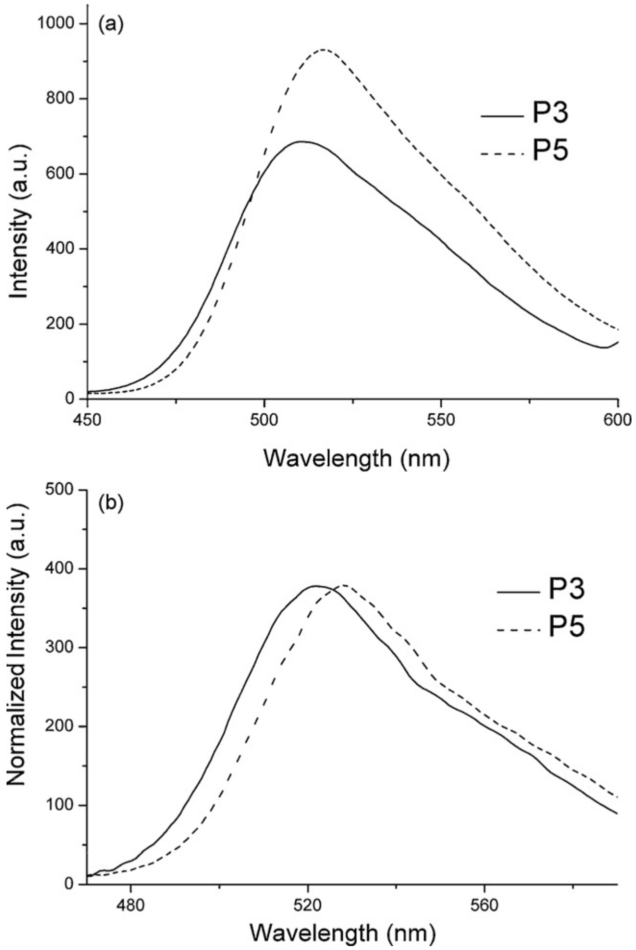


Fig. 1. (a) Fluorescence spectra of **P3** and **P5** in toluene (1×10^{-6} M, λ_{ex} = 306 nm) and (b) normalized fluorescence spectra of **P3** and **P5** in the films (λ_{ex} = 306 nm).

3.2. Fluorescence quenching of *P3* and *P5* by nitro compounds in solution

In order to investigate the fluorescence sensibility of phenothiazine-based oligomers for detecting nitroaromatics, fluorescence titration of **P3** and **P5** by ***p*-NT** (E_{red} = −1.2 V), **DNT**

Table 1
Photophysical and electrochemical data of **P3** and **P5**.

Oligomers	Solutions[a]			Films		E^{ox}_{onset} (eV)[c]	HOMO (eV)[d]	LUMO (eV)[e]
	λ^{abs}_{max} (nm)	λ^{em}_{max} (nm)	Φ_F [b]	λ^{abs}_{max} (nm)	λ^{em}_{max} (nm)			
P3	306, 408	500	0.33	308, 426	524	0.33	−5.01	−2.35
P5	308, 419	509	0.38	311, 438	529	0.29	−4.97	−2.40

[a] In toluene (1 μM).
[b] Using quinine sulfate in 0.1 H_2SO_4 (Φ_F = 0.546) as the standard.
[c] Using E^{ox}_{onset} is the onset oxidation potential.
[d] Using HOMO = $-(E^{ox}_{onset} + 4.68)$ eV.
[e] LUMO = HOMO − E_g, E_g is determined from the onset of the absorption at the lower energy band edge.

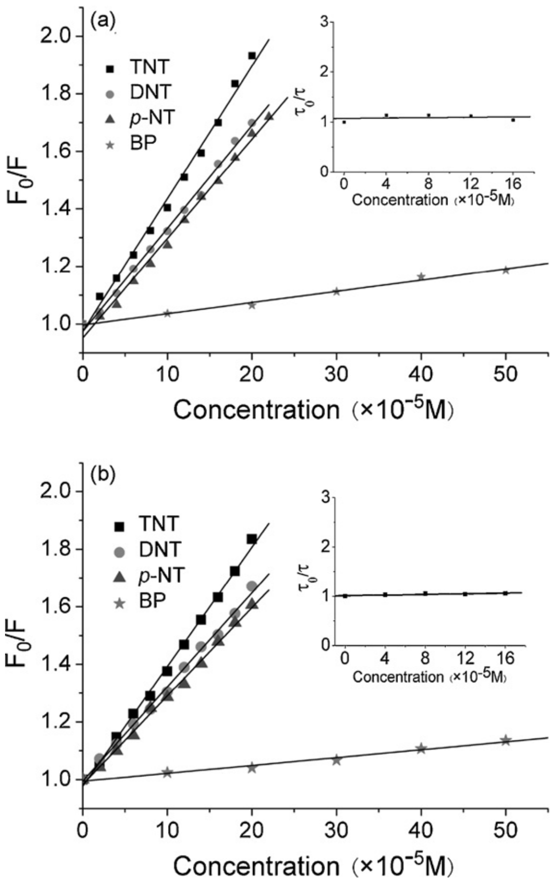


Fig. 2. Stern–Volmer plots for **P3** (a) and **P5** (b) in response to **TNT** (square), **DNT** (circle), ***p*-NT** (triangle) and **BP** (pentagon), the concentration of **P3** and **P5** was maintained at 1×10^{-6} M. The fluorescence intensity was monitored at 500 nm for **P3** and **P5** (λ_{ex} = 306 nm). The insets were τ_0/τ as a function of the concentration of **DNT**.

(E_{red} = −1.0 V), **TNT** (E_{red} = −0.7 V), and **BP** (benzophenone), (which was used as a reference due to its weaker electron-deficiency, E_{red} = −1.6 V) in toluene was recorded [14]. It was clear that the fluorescent emission intensity of the phenothiazine-based oligomers decreased obviously by increasing the content of nitro compounds. Stern–Volmer plots for **P3** as well as **P5** (monitored at 500 nm) and various nitroaromatics in toluene at room temperature were shown in Fig. 2, and we can find a linear fluorescence quenching response. The apparent quenching constants K_{sv} was estimated by fits of the first linear part of the Stern–Volmer plots, and the K_{sv} values of **P3** were 4607 M^{-1}, 3576 M^{-1}, 3451 M^{-1}, 389 M^{-1}, and of **P5** were 4149 M^{-1}, 3271 M^{-1}, 3070 M^{-1}, 272 M^{-1}, for **TNT**, **DNT**, ***p*-NT** and **BP**, respectively. It was obvious that **P3** exhibited a little high sensibility than **P5** due to its lower free energy change (ΔG°) in fluorescence quenching process. ΔG° is approximated by the equation of $\Delta G^{\circ} = E(P/P^{+\bullet}) - \Delta E_{0-0} - E(Q/Q^{\bullet -})$, where $E(P/P^{+\bullet})$, ΔE_{0-0}, and $E(Q/Q^{\bullet -})$ are the oxidation potential of oligomer $P \rightarrow P^{+\bullet}$, the lowest singlet 0–0 excitation energy of the oligomer, and the reduction potential of quencher $Q \rightarrow Q^{\bullet -}$, respectively [14]. The values of $E(P/P^{+\bullet})$ and ΔE_{0-0} for **P3** are −5.01 eV, 3.04 eV, and for **P5** are −4.97 eV, 2.96 eV, and the values of $E(Q/Q^{\bullet -})$ for **TNT**, **DNT** and ***p*-NT** are −3.8 eV, −3.3 eV and −3.1 eV, respectively [39]. Therefore, the values of ΔG° were −4.25 eV and −4.13 eV in the fluorescence quenching of **P3** and **P5** by **TNT**, respectively. Moreover, the quenching constants of phenothiazine-based oligomers for **TNT** are higher than the ones of reported functional compounds [20,24], meaning that **P3** and **P5** were ideal fluorescence probes for nitro compounds.

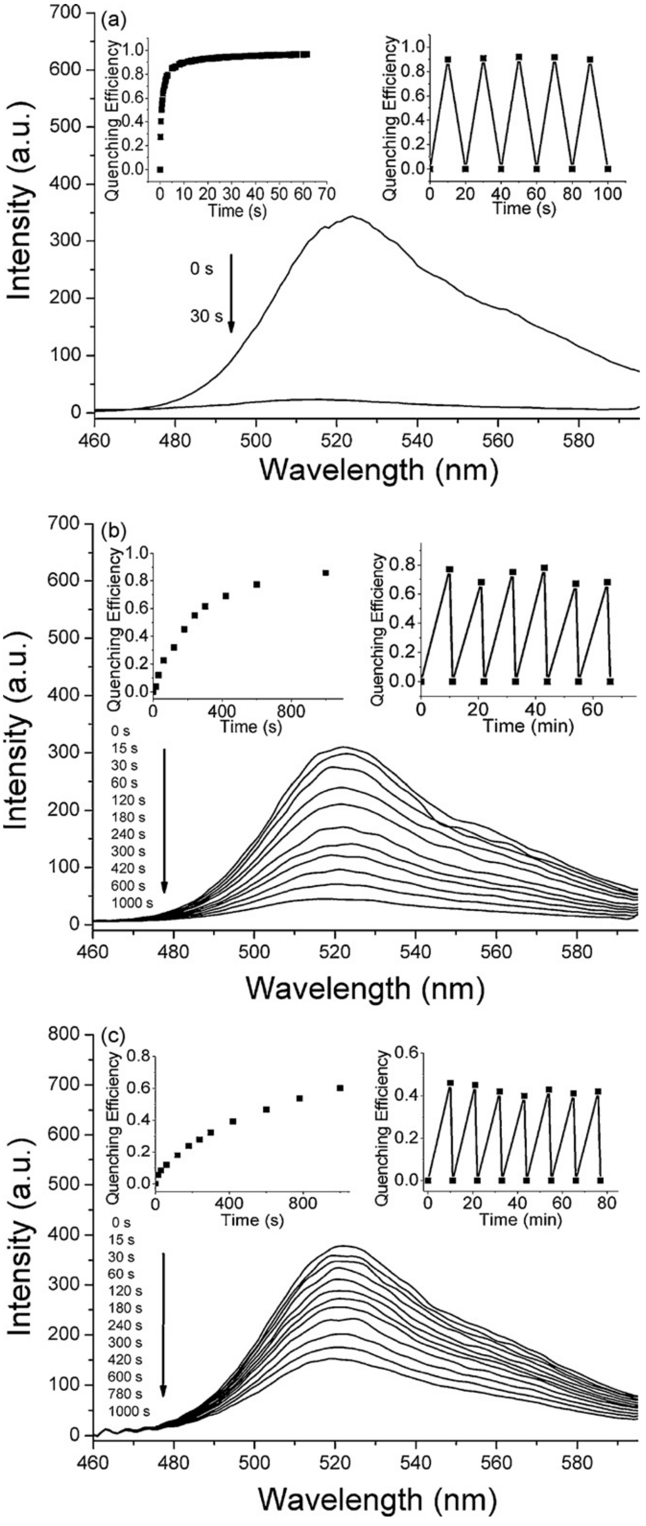


Fig. 3. Time-dependent fluorescence emission spectra of **P3** film (λ_{ex} = 306 nm) exposed to the vapors of (a) ***p*-NT**, (b) **DNT**, and (c) **TNT**. The inset was the fluorescence quenching efficiency against time and the reversibility of the responses of **P3** film.

*3.3. Fluorescence quenching of the films based on **P3** and **P5** by the vapors of nitro compounds*

Fig. 3 shows the time-dependent fluorescence emission spectra and reversibility of the responses of **P3** films upon exposure to the saturated vapor of ***p*-NT** (200 ppm), **DNT** (180 ppb) and **TNT**

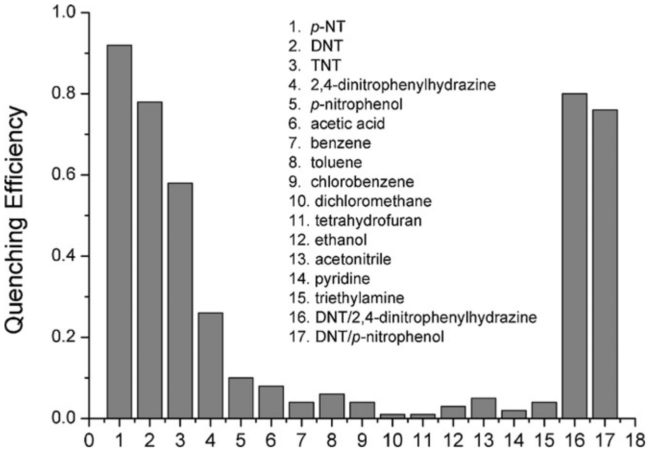


Fig. 4. Fluorescence response of **P3** film to the saturated vapors of ***p*-NT**, **DNT**, **TNT**, some organic solvents, *p*-nitrophenol, 2,4-dinitrophenylhydrazine, and the mixtures of **DNT**/*p*-nitrophenol as well as **DNT**/2,4-dinitrophenylhydrazine for 600 s.

(10 ppb) at room temperature [14]. It was not surprising that **P3** film showed stronger fluorescence quenching efficiency for ***p*-NT** than **DNT** and **TNT** vapor, which could be ascribed to different vapor pressure and redox potential of nitro compounds. Generally speaking, the greater of the vapor pressure or the higher of the redox potential of nitro compounds, the stronger of its binding ability to probing molecules [21]. Clearly, the fluorescence emission of **P3** could be almost quenched completely after exposed to ***p*-NT** vapor for 15 s due to high saturated vapor pressure. The response time of **P3** to ***p*-NT** vapor was estimated as 1.12 s by fitting a single exponential decay (Fig. S6). As to **DNT**, exposure of **P3** film to its saturated vapor for 300 s and 600 s resulted in 60 and 76% reduction of the emission intensity, respectively. In addition, 32 and 47% reduction of the emission intensity of **P3** film was detected when exposed to saturated vapor of **TNT** for 300 s and 600 s. Similarly, **P5** films also gave the more sensitive fluorescence response to ***p*-NT** than **DNT** and **TNT** (Figs. S7–S9). Although **P3** and **P5** exhibited higher sensitivity to the explosive in toluene than pentiptycene-based polymer [20], the sensitivity of the films to the explosive vapors was not as good as that reported by Swager and Yang [15]. It could be explained that large cavities in the film could be easily generated from pentiptycene-derived polymer with three-dimensional rigid structure, and favored the explosive binding and diffusion within the matrix.

3.4. *Effect of interferents*

The effect of some interferents, such as some organic solvents, *p*-nitrophenol, and 2,4-dinitrophenylhydrazine on the specificity of fluorescence response for **P3** film to explosive was investigated. No significant changes of the fluorescence emission intensity at 520 nm of **P3** film were observed upon exposing the film to the saturated vapors of some organic solvents, including benzene, toluene, chlorobenzene, dichloromethane, THF, ethanol, acetonitrile, pyridine, and triethylamine at room temperature for 600 s (Fig. 4). Although the vapors of *p*-nitrophenol, 2,4-dinitrophenylhydrazine and acetic acid could lead to slight decrease of the emission intensity of **P3** film, the fluorescence quenching efficiencies were less than those of ***p*-NT**, **DNT** and **TNT** significantly. In addition, we also found that the presence of some interferents, such as *p*-nitrophenol, 2,4-dinitrophenylhydrazine cannot affect the fluorescence response to **DNT**, so the film based on oligophenothiazines can exhibit good specificity of fluorescence response to explosive.

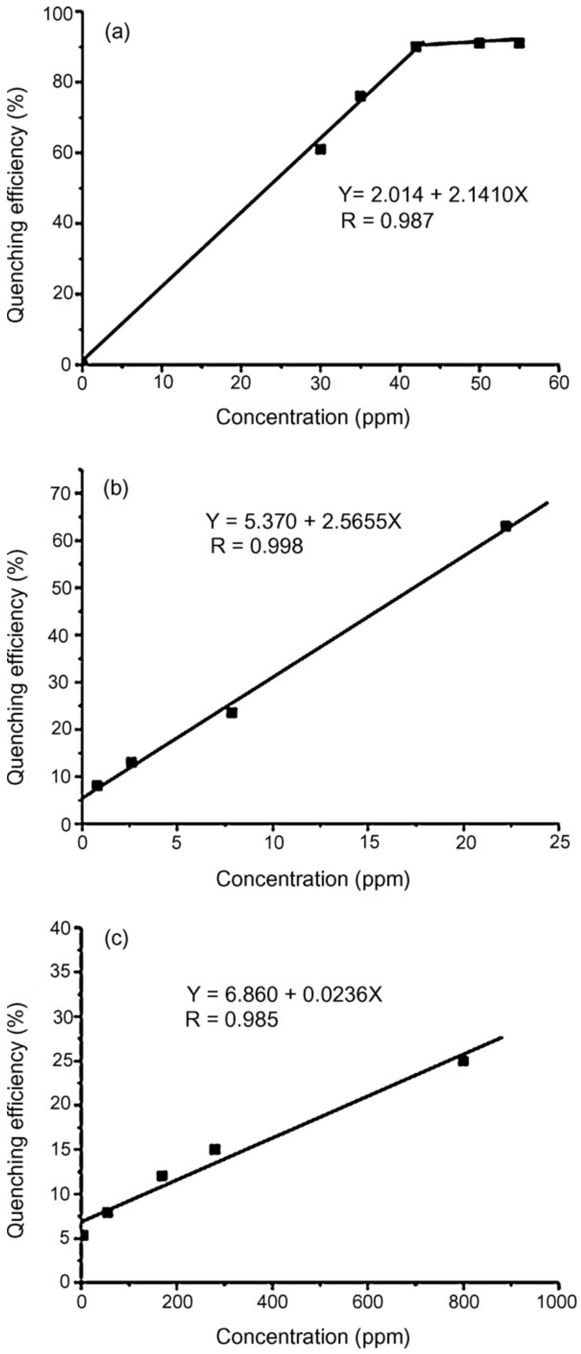


Fig. 5. The concentration-dependent fluorescence quenching efficiency of **P3** film exposed to (a) ***p*-NT**, (b) **DNT**, and (c) **TNT** for 30 s.

3.5. *Calibration curve and detection limits*

To explore the detection limit for the nitro compounds, the concentration-dependent fluorescence quenching efficiencies of **P3** film exposed to ***p*-NT**, **DNT** and **TNT** for 30 s were shown in Fig. 5. It was clear that there is a good linear relationship between the quenching efficiencies ($1 - F/F_0$) and the concentrations in the ranges of 4–42 ppm for ***p*-NT**, 2–24 ppm for **DNT** and 7–800 ppb for **TNT**. Considering the fact that a well-calibrated photodetector can detect the intensity change as small as 0.1% or below [40], we suggested that the detection limit of **P3** film is 4 ppb, 40 ppb and 48 ppb for **TNT**, **DNT** and ***p*-NT**, respectively.

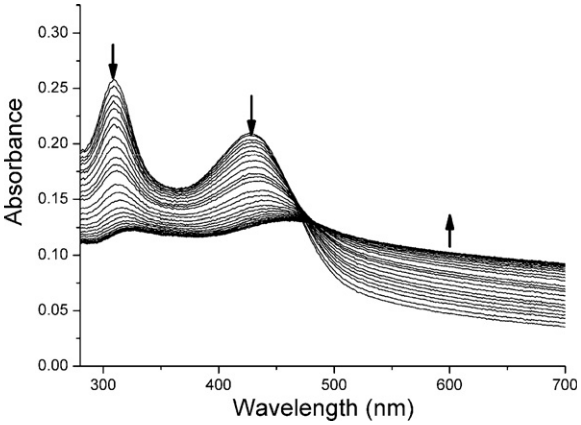


Fig. 6. Time-dependent absorption spectra of **P3** film exposed to **DNT** vapor (the time interval for each curve is 1 min).

3.6. Investigation of fluorescence quenching mechanism

In order to reveal the fluorescence quenching mechanism of **P3** and **P5** in detecting nitro compounds, the fluorescence lifetimes of oligomers before (τ_0) and after (τ) addition of different amount of quenchers were measured. We found that the fluorescence lifetime (τ_0) of **P3** was 1.86 ns and that of **P5** was 1.48 ns, respectively (Figs. S10 and S11). Notably, the τ_0/τ values were invariant against the concentration of nitro compounds (insets in Fig. 2). Therefore, we suggested that the fluorescence quenching was caused by formation of a non-fluorescent charge-transfer complex through a static process in our systems [20,21], which could be further confirmed by the time-dependent absorption spectra of **P3** film exposed to **DNT** vapor. As shown in Fig. 6, we could find the absorption bands for **P3** in the film appeared at 308 and 426 nm, which red-shifted gradually accompanying with the declining of the absorption intensity when prolonging the time of **P3** film exposed to **DNT** vapor, for instance, they shifted to 323 nm and 466 nm after **P3** film was exposed in **DNT** vapor for 30 min (see Fig. 6). Notably, the enhancement of the absorption above 500 nm suggested the formation of charge-transfer complex between **P3** and **DNT**.

3.7. Reversibility of the fluorescence response of *P3* film to the vapors of nitro compounds

The reversibility of the fluorescence response of **P3** for ***p*-NT**, **DNT**, **TNT** was also studied. We could find from the right inset of Fig. 3a that the fluorescence emission of **P3** could be recovered immediately after blowing the non-fluorescent film containing the complex of **P3** and ***p*-NT** by hairdryer for 10 s, and such fluorescence quenching and recovery could be repeated for many times without fatigue. On the other hand, **P3** also exhibited good reversibility of fluorescence response in detecting **DNT** except for long recovery time via blowing for 60 s (right inset of Fig. 3b). The reason is that **DNT** exhibited stronger binding ability to **P3** than ***p*-NT** due to its higher reduction potential, whereas, the strong interaction between **P3** and **TNT** made it difficult to recover the emission of **P3** by blowing the non-fluorescent film. However, the fluorescence emission can be reproduced by immersing the non-fluorescent film containing the complex of **P3** and **TNT** in a saturated vapor of hydrazine (ca. 140 ppm) for 10 s [27,28], and good repeatability can also be achieved (right inset of Fig. 3c). Therefore, the fluorescence sensing process of **P3** for vapor-phase nitroaromatics are well reversible.

3.8. The stability of *P3* film under analytical conditions

The photostability of **P3** film under analytical conditions was recorded as shown in Fig. S12, and it was found that only a slight decrease of the fluorescence emission intensity at 520 nm upon exposure to natural light for 200 min, meaning that the photostability of **P3** film allowed it to be used as candidate in fluorescence probe for detecting nitro compounds.

4. Conclusion

We have synthesized two vinyl-substituted oligophenothiazines **P3** and **P5**, which could be used as efficient fluorescence probing molecules for detection of the vapor of ***p*-NT**, **DNT** and **TNT**. Stern–Volmer plots revealed that phenothiazine-based oligomers exhibited high sensitivity to nitro compounds compared to other reported polymers in solution. Notably, **P3** and **P5** films could detect the vapor-phase nitro compounds with high sensitivity and fairish reversibility. **P3** film gave a linear fluorescence quenching response to **TNT** in the range of 7–800 ppb with the detection limit of 4 ppb, and the detection limit to **DNT** and ***p*-NT** was 40 ppb and 48 ppb, respectively. It was also found that the interferents, including common organic solvents, *p*-nitrophenol and 2,4-dinitrophenylhydrazine cannot lead to obvious fluorescence quenching, meaning that the film based on oligophenothiazines exhibited good specificity of fluorescence response to explosive. Furthermore, the fluorescence lifetimes of **P3** and **P5** did not change with addition of **DNT** illustrated that the fluorescence quenching was caused by formation of a non-fluorescent charge-transfer complex, which was further confirmed by the UV–vis absorption spectral changes of **P3** before and after exposed to **DNT**. Therefore, as electron-rich systems, oligophenothiazines and related compounds should be ideal candidates of sensory materials for detection of nitroaromatics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.08.016.

References

[1] D.T. McQuade, A.E. Pullen, T.M. Swager, Chem. Rev. 100 (2000) 2537–2574.
[2] S. Singh, J. Hazard. Mater. 144 (2007) 15–28.
[3] L. Senesac, T.G. Thundat, Mater. Today 11 (2008) 28–36.
[4] M.E. Germain, M.J. Knapp, Chem. Soc. Rev. 38 (2009) 2543–2555.
[5] S.S.R. Dasary, A.K. Singh, D. Senapati, H.T. Yu, P.C. Ray, J. Am. Chem. Soc. 131 (2009) 13806–13812.
[6] T. Kawaguchi, D.R. Shankaran, S.J. Kim, K.V. Gobi, K. Matsumoto, K. Toko, N. Miura, Talanta 72 (2007) 554–560.
[7] Y.Z. Sun, J. Liu, G. Frye-Mason, S. Ja, A.K. Thompson, X.D. Fan, Analyst 134 (2009) 1386–1391.
[8] J. Wang, Electroanalysis 19 (2007) 415–423.
[9] F. Wang, W.B. Wang, B.H. Liu, Z. Wang, Z.P. Zhang, Talanta 79 (2009) 376–382.
[10] S.-Y. Ly, D.-H. Kim, M.-H. Kim, Talanta 58 (2002) 919–926.
[11] P. Kolla, Angew. Chem., Int. Ed. 36 (1997) 800–811.
[12] T.M. Swager, Acc. Chem. Res. 41 (2008) 1181–1189.
[13] S.W. Thomas, G.D. Joly, T.M. Swager, Chem. Rev. 107 (2007) 1339–1386.
[14] J.-S. Yang, T.M. Swager, J. Am. Chem. Soc. 120 (1998) 11864–11873.
[15] J.-S. Yang, T.M. Swager, J. Am. Chem. Soc. 120 (1998) 5321–5322.
[16] S.J. Total, D. Magde, W.C. Trogler, Chem. Commun. (2005) 5465–5467.

[17] H. Sohn, R.M. Calhoun, M.J. Sailor, W.C. Trogler, Angew. Chem., Int. Ed. 40 (2001) 2104–2105.
[18] A. Saxena, M. Fujiki, R. Rai, G. Kwak, Chem. Mater. 17 (2005) 2181–2185.
[19] J.C. Sanchez, W.C. Trogler, J. Mater. Chem. 18 (2008) 3143–3156.
[20] H. Sohn, M.J. Sailor, D. Magde, W.C. Trogler, J. Am. Chem. Soc. 125 (2003) 3821–3830.
[21] G. He, G.F. Zhang, F. Lü, Y. Fang, Chem. Mater. 21 (2009) 1494–1499.
[22] S.J. Zhang, F.T. Lü, L.N. Gao, L.P. Ding, Y. Fang, Langmuir 23 (2007) 1584–1590.
[23] H. Bai, C. Li, G.Q. Shi, Sens. Actuators B 130 (2008) 777–782.
[24] G.V Zyryanov, M.A. Palacios, P. Anzenbacher Jr., Org. Lett. 10 (2008) 3681–3684.
[25] D.M. Gao, Z.P. Zhang, M.H. Wu, C.G. Xie, G.J. Guan, D.P. Wang, J. Am. Chem. Soc. 129 (2007) 7859–7866.
[26] Q.L. Fang, J.L. Geng, B.H. Liu, D.M. Gao, F. Li, Z.Y. Wang, G.J. Guan, Z.P. Zhang, Chem. Eur. J. 15 (2009) 11507–11514.
[27] T. Naddo, Y.K. Che, W. Zhang, K. Balakrishnan, X.M. Yang, M. Yen, J.C. Zhao, J.S. Moore, L. Zang, J. Am. Chem. Soc. 129 (2007) 6978–6979.
[28] X.G. Yang, X.-X. Du, J.X. Shi, B. Swanson, Talanta 54 (2001) 439–445.
[29] S.Y. Tao, G.T. Li, J.X. Yin, J. Mater. Chem. 17 (2007) 2730–2736.
[30] Y.Y. Long, H.B. Chen, Y. Yang, H.M. Wang, Y.F. Yang, N. Li, K. Li, J. Pei, F. Liu, Macromolecules 42 (2009) 6501–6509.
[31] C. Vijayakumar, G. Tobin, W. Schmitt, M.-J. Kim, M. Takeuchi, Chem. Commun. 46 (2010) 874–876.
[32] X.P. Qiu, R. Lu, H.P. Zhou, X.F. Zhang, T.H. Xu, X.L. Liu, Y.Y. Zhao, Tetrahedron Lett. 48 (2007) 7582–7585.
[33] T. Okamoto, M. Kuratsu, M. Kozaki, K. Hirotsu, A. Ichimura, T. Matsushita, K. Okada, Org. Lett. 6 (2004) 3493–3496.
[34] C.S. Krämer, K. Zeitler, T.J.J. Müller, Org. Lett. 2 (2000) 3723–3726.
[35] A.W. Franz, F. Rominger, T.J.J. Müller, J. Org. Chem. 73 (2008) 1795–1802.
[36] J.A. Widegren, T.J. Bruno, J. Chem. Eng. Data 55 (2010) 159–164.
[37] L. Rittfeldt, Anal. Chem. 73 (2001) 2405–2411.
[38] M.B. Pushkarsky, I.G. Dunayevskiy, M. Prasanna, A.G. Tsekoun, R. Go, PANS 103 (2006) 19630–19634.
[39] C.Y. Zhang, Y.K. Che, X.M. Yang, B.R. Bunes, L. Zang, Chem. Commun. 46 (2010) 5560–5562.
[40] C.J. Cumming, C. Aker, M. Fisher, M. Fox, M.J.L. Grone, D. Reust, M.G. Rockley, T.M. Swager, E. Towers, V. Williams, IEEE Trans. Geosci. Remote Sensing 39 (2001) 1119–1128.