

Fluorescent Film Sensor for Vapor-Phase Nitroaromatic Explosives via Monolayer Assembly of Oligo(diphenylsilane) on Glass Plate Surfaces

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A fluorescent film sensor was prepared by chemical assembly of oligo(diphenylsilane)s on a glass plate surface and was used for the detection of nitroaromatic compounds (NACs) in vapor phase. This design combines the advantages of fluorescent films based on single-layer chemistry and the signal amplification effect of conjugated polymers and provides an effective way to create novel fluorescence sensing films for NACs explosives. The advantages have been demonstrated experimentally by the super sensitive response of the above-mentioned film to the presence of trace amounts of NACs in vapor phase. Further experiments showed that the sensing process is reversible, and the commonly encountered interfering substances have no interference to the process. Fluorescence lifetime measurements revealed that the quenching is static in nature. The super sensitive response, and the reversibility and interference free of the sensing process, make the film a promising NACs sensor.

Introduction

Fast and sensitive detection of nitroaromatic compounds (NACs), in particular 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), is of major importance for finding hidden explosives in airport luggage and in mail, screening of personnel for concealed explosives, and detection of buried landmines.^{1,2} Up to now, only sniffers using advanced materials are able to locate explosives by detecting vapors of them. Among them, fluorescent film sensors fabricated in a spin coating way and using conjugated polymers as sensing materials are generally employed because of their sensitivity and simplicity.^{1a,b,3} The sensitivity comes from the so-called signal amplification effect because the backbone of these conjugated polymers acts as a molecular wire, enabling the rapid propagation of an exciton throughout the individual polymer chain.⁴

Considering the importance of explosives detection using conjugated polymers, it is important to develop new ways that can improve upon these methods. This is because the sensing performances of the films fabricated in a spin-coating way still have some limitations. For example, the thickness of the film has a significant effect upon the performance of

the sensors because of steric resistance to the diffusion of the analytes within the films⁵ and fluorescence self-quenching induced by energy migration between the conjugated polymer chains, which also affects the sensing performance of the films.⁶ Furthermore, the film sensors prepared in this way may not be suitable for solution-phase detection because of leakage of the polymers. Some of these limitations have been overcome or partially overcome by modification of the polymers,⁷ improving the fabricating techniques,⁸ or carefully selecting polymers.⁹ For examples, Swager and co-workers incorporated rigid three-dimensional pentiptycene moieties into the backbones of different poly(phenyleneethynylene)s. It was found that the presence of the rigid moieties prevented π -stacking or excimer formation between the polymers, and increased the porosity of the polymer films, and thereby significantly improved the sensing performances of the films to TNT.⁵ Schanze and co-workers studied the dependence of the NACs response rate of the thin film of poly[1-phenyl-

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2-(4-trimethylsilylphenyl)ethyne] to the thickness of the film, and concluded that the response rate could be increased by simply decreasing the film thickness.⁶ Adulteration of surfactant into the polymer layer is another way to improve the sensing performances of conjugated polymer sensors. It is believed that introduction of surfactant enhances the compatibility of the film to the analyte.⁷

Similar with conjugated organic polymers, conjugated inorganic polymers, in which the monomer units are silicon-, germanium-, or tin-containing metallacyclopentadienes, also exhibit high electron affinity and fast electron mobility.⁸ But the fluorescence emission of these polymers increases along with the aggregation of them, the so-called aggregation induced emission (AIE) effect.^{8,9,11} It is because of this reason that Trogler and co-workers fabricated fluorescent films in a spin coating way with the conjugated inorganic polymers as sensing materials, and found that the films are sensitive, particularly in solution, to NACs. Furthermore, compared to sensors prepared with conjugated organic polymers, conjugated inorganic polymer sensors are robust and insensitive to organic solvents, organic acids, oxygen, and other common interferents to NACs.¹⁰ As an example, Fujiki and co-workers fabricated a NAC chemsensor by using fluoro-alkylated polysilane as sensing material, and revealed that the sensor is very sensitive to NACs in THF and had no response to common interferents.¹² These results demonstrate clearly that both conjugated organic polymers and conjugated inorganic polymers are powerful sensing elements for the supersensitive detection of traces of NACs both in air and in solution. But there is still room for the improvement of their performances.

Considering the limitations of the conjugated polymer-based fluorescent film sensors, we started to develop a new family of fluorescent film sensors via monolayer assembly of polycyclic aromatics on substrate surfaces a few years ago. It was believed that in this strategy, the intrinsic deficiencies of the fluorescence film sensors fabricated by spin coating and using conjugated polymers as sensing materials should be overcome automatically. In fact, on the basis of this methodology, a series of fluorescent film sensors for various analytes including nitrite,¹⁵ nitromethane,¹⁶ dicarboxylic acids,¹⁷ organic copper salts,¹⁸ and nitrobenzene,¹⁹

in aqueous phase, for the composition of the mixtures of ethanol and water,²⁰ and for the purity of water,²¹ have been developed in our laboratory. As for NACs, a number of pyrene-based films were successfully created and used to detect them both in air and solution phase.²² Similar studies were conducted in other groups. Reinhoudt and co-workers prepared several fluorescent films by immobilizing dansyl, pyrene, or coumarin on glass surfaces in a monomolecular layer way and revealed their good sensing properties to Na^+ , Pb^{2+} , or β -cyclodextrin.²³ Gulino and co-workers reported a sensitive, reversible, and fast response optical NO_2 sensor by covalently immobilizing porphyrin onto a silica substrate surface.²⁴ Considering the works depicted above, it can be seen that monolayer assembly of fluorophores on substrate surfaces is a feasible way to fabricate fluorescent film sensors, and furthermore, combination of the advantages of this strategy and those of conjugated polymers may be a bright way to create novel fluorescent NAC film sensors. On the basis of this idea, oligo(diphenylsilane)s were specially prepared and monomolecularly immobilized on a glass plate surface. The sensing performances of this film to a variety of NACs in vapor phase were systematically investigated. This paper reports the details.

Experimental Section

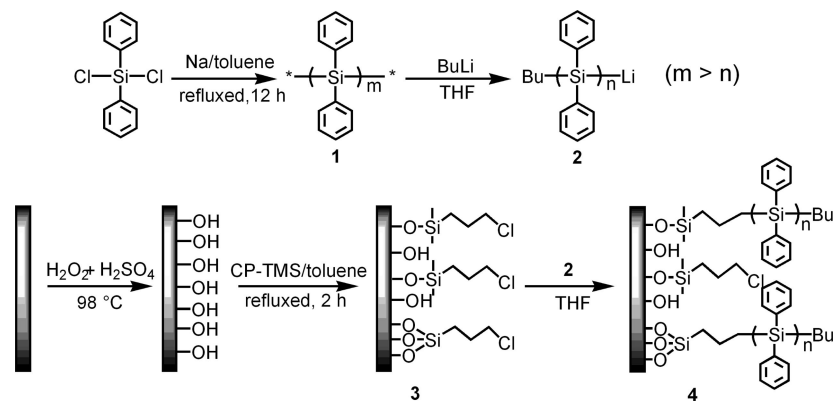
Materials. Diphenyldichlorosilane (Acros, 97%), (3-chloropropyl)trimethoxysilane (Aldrich, 98%), *n*-butyllithium (2.5 M in hexane, Alfa Aesar) were used as received. All manipulations for the preparation of the samples were performed using standard vacuum line and Schlenk techniques under a purified argon atmosphere. THF and toluene were distilled from sodium benzophenone ketyl under argon prior to use. NACs including TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene), NB (nitrobenzene), PA (2,4,6-trinitrophenol), and DNPH (2,4-dinitrophenyl-hydrazine) were of analytical grade and used directly without further purification. **Caution:** TNT and other NACs used in the present study are highly explosive and should be handled only in small quantities.

Measurements. Fluorescence measurements were performed at room temperature on a time-correlated single photon counting Edinburgh FLS 920 fluorescence spectrometer with a front-face method. The fabricated film was inserted into a quartz cell with its surface facing the excitation light source. The cell was fixed in the solid sample holder of the instrument. The position of the film was kept constant during each set of measurements. Pressed KBr disks for the powder samples were used for the transmission infrared spectroscopy measurements, and their FTIR spectra were obtained with a Bio-Rad FTIR spectrometer. Contact angles of the films were measured on a dataphysics OCA20 contact-angle system at ambient temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCAPHI5400 photoelectron spectrometer

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Scheme 1. Schematics of Synthesis of Poly(diphenylsilane)s and Its Coupling onto a Glass Plate Surface



using a monochromatic Mg K α X-ray source. The ellipsometric thicknesses of the layers on glass plate substrate were measured on SpecEI-2000-VIS Spectroscopic Ellipsometer (Mikro Pack).

Synthesis of Poly(diphenylsilane). Poly(diphenylsilane) (1) was synthesized by a Wurtz type polycondensation reaction with slight modification.²⁵ A solution of diphenyldichlorosilane (0.04 mol, 10.458 g) in toluene (90 mL) was added dropwise over approximately 10 min to sodium dispersion (0.08 mol, 1.84 g) in toluene (90 mL), and the mixture was then refluxed for 12 h. A small amount of methanol was then added. Finally, the crude product was collected and successively washed with toluene, THF, and water. The average molecular mass of the polymer and the oligomer were determined, very roughly, by a self-designed thermogravimetric method, and the results are 1.86×10^4 and 3.1×10^3 g/mol, respectively (c.f. Supporting Information). The FTIR spectra of the monomer, polysilane, and oligosilane are also presented in the Supporting Information.

Activation and Silanization of the Glass Plate Surface. A glass plate (0.9 cm \times 2.5 cm) was treated in a "piranha solution" (7/3, V/V, 30% H₂O₂/98% H₂SO₄)²⁶ (**Warning:** *Piranha solution should be handled with extreme caution because it can react violently with organic matter.*) at 98 °C for 1 h, rinsed thoroughly with plenty of water, and finally dried at 100 °C in a dust-free oven for 1 h. The activated glass plate was placed in a flask charged with a toluene solution (20 mL) of (3-chloropropyl)-trimethoxysilane (0.2 mL), and the solution was refluxed for 2 h.²⁷ After being cooled to room temperature, the plate was removed from the flask, successively washed with copious amounts of toluene and ethanol, and then dried under a gentle stream of nitrogen.

Chemical Coupling of Poly(diphenylsilane) on a Glass Plate Surface. Chemical coupling of poly(diphenylsilane) on a glass plate surface was performed according to a modified literature method.²⁸ Poly(diphenylsilane) (0.04 g) was dispersed in THF (20 mL), and then stirred for 20 min. To the suspensions, a few drops of *n*-butyllithium were added under stirring. The scission reaction was

completed within a few minutes, and the solution was then poured onto the substrates with reactive anchors, and reacted for another 15 min. After coupling, the substrates were collected and rinsed repeatedly with THF and toluene. Further cleanout was conducted by immersing the substrates in toluene overnight, and then separated and refluxed in THF for 5 h to make sure that all physically adsorbed oligomer and other impurities are removed from the plate surface. The synthesis of poly(diphenylsilane) and its coupling onto a glass plate surface is schematically shown in Scheme 1.

Results and Discussion

Film Characterization. The films have been characterized by XPS and wettability measurements. Figure 1 shows the XPS spectra of the substrate of various surface compositions, of which the chemical structures changed from hydroxyl groups and chlorine groups to oligo(diphenylsilane)s along with the treatment (c.f. Scheme 1). It can be seen that the signal of C 1s became much stronger and the signal of Cl 2s appeared after silanization, a direct evidence for the

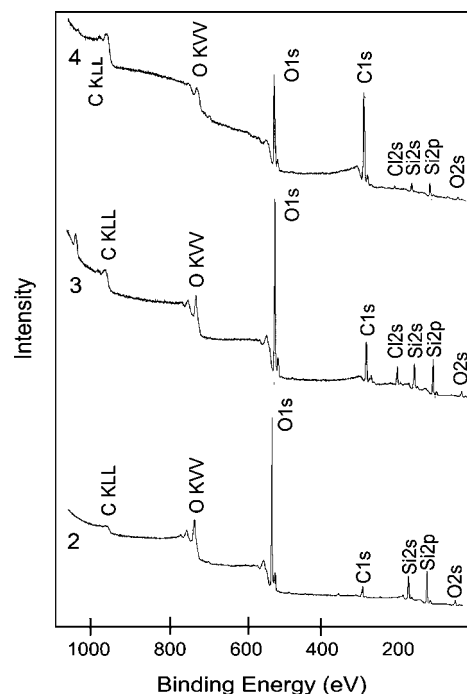


Figure 1. X-ray photoelectron spectra of the glass plates of various surface structures. The numbers of 2, 3, and 4 have similar meaning with those shown in Scheme 1.

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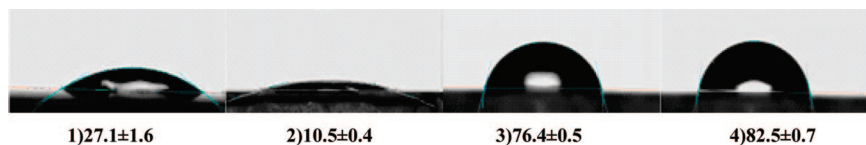


Figure 2. Advancing contact angles (θ) of various glass plate surfaces and water: (1) the original clean glass plate, (2) plate with a hydroxyl surface, (3) plate with a chlorine surface, and (4) plate with a oligosilane-coated surface.

Table 1. Ellipsometric Thickness of the Fluorescent Films on Oxidized Silicon Wafer

samples	thickness (\AA) ($\pm 0.5 \text{ \AA}$)
glass plate with chlorine surface	32
glass plate with oligo(diphenylsilane)-coated surface	49

successful coupling of the silanizing reagent on the glass plate surface. Immobilization of oligo(diphenylsilane) on the surface made C 1s signal even stronger, whereas the signals of Cl 2s almost disappeared because of reaction between end Cl groups of the silanization layer and the end-lithiated oligo(diphenylsilane), indicating that the oligomer had been successfully coupled on the glass plate surface. This conclusion was further confirmed by the results from surface wettability measurement.

Contact angles at ambient temperature of the surfaces of the substrates to water at different stages of the functionalization have been measured and shown in Figure 2. Reference to the figure reveals that the advancing contact angle decreased significantly from $27.1 \pm 1.6^\circ$ to $10.5 \pm 0.4^\circ$ after treatment with the “piranha solution”. Further treatment with (3-chloropropyl)trimethoxysilane resulted in a sharp increase in the data ($76.4 \pm 0.5^\circ$), indicating that the wettability of the surface has reversed. The angle increased further after treatment with the end-lithiated oligosilanes, and reached a value of $82.5 \pm 0.7^\circ$, a typical hydrophobic surface. These results are consistent with the expectation from the chemical composition of the surface, as shown in Scheme 1 and revealed by XPS measurement.

Success in the chemical coupling of the oligomers on the substrate surface was further investigated by monitoring the fluorescence emission of remained toluene after immersion of the film in the solvent, which had been filled in a quartz cell, for more than 18 h. The fact that no typical oligo(diphenylsilane) emission was found indicates that leaking of the oligomer from the substrate surface is negligible, and in other words, the oligomer had been chemically coupled on the substrate surface (c.f. Supporting Information).

Ellipsometry is a widely used optical technique for measuring the thickness of thin organic films. In this study, the measurements of the layers were made on glass plate assuming a refractive index of 1.5 for the layer over the substrate surface. Average values for the adlayers are summarized in Table 1. It is clear that the adlayer with chlorine as their end groups are not true monolayer because the thickness of a monolayer of (3-chloropropyl)trimethoxysilane should be ca. 12 \AA , on the basis of a calculation of the length and angles of the chemical bonds in the silanizing reagent. The difference between the experimental thickness and that predicted based on molecular dimension can be attributed to the use of a trialkoxysilane, which is known to

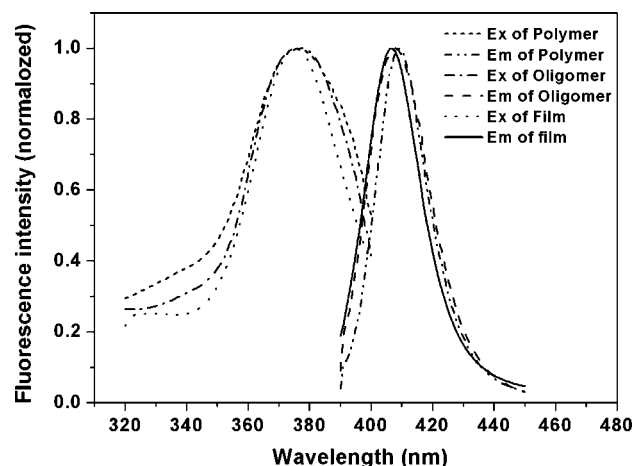


Figure 3. Excitation and emission spectra of the polymer, oligomer in toluene, and oligomer-functionalized film in dry state ($\lambda_{\text{ex}} = 370 \text{ nm}$, $\lambda_{\text{em}} = 408 \text{ nm}$).

form polysilanol readily, and then to polymerize with other polysilanol, resulting in multilayer structures on the surface. After coupling the oligomer, the thickness of the film increased to 4.9 nm , a net increase of 1.7 nm , which is a value significantly shorter than 2.5 nm , a theoretical data obtained by modeling the oligomer with Materials Studio 3.0. This is not a surprising result considering that the oligomer could not stand perpendicularly on the substrate surface.

Steady-State Excitation and Emission Spectra of the Film. The excitation and emission spectra of the polymer, oligomer in toluene, and oligomer-functionalized film in dry state are shown in Figure 3. The maximum excitation and emission of the polymer appeared at 370 and 410 nm , respectively. After scission reaction, the maximum emission blue-shifted a few nanometers, but the maximum excitation does not change significantly. With a comparison of the profile and position of the excitation and emission spectra of the oligomer in solution and those in immobilized state (c.f. Figure 3), it is safe to say that chemical immobilization does not affect the fundamental fluorescence properties of the oligomer.

Fluorescence Quenching Studies with NACs. The sensing performance of the present film to NACs in vapor phase was studied in a way adopted by Swager and others.⁵ Specifically, the film to be tested was inserted into a sealed vial (20 mL size) at room temperature containing an analyte and cotton gauze, which prevents direct film analyte contact and helps to maintain a constant vapor pressure. The fluorescence emission spectrum of the film was recorded immediately after the film was exposed to the analyte for a specific time. Figure 4 shows the time-dependent fluorescence emission spectra of the film upon exposure to TNT vapor at room temperature. It is clear that for TNT, 10 s

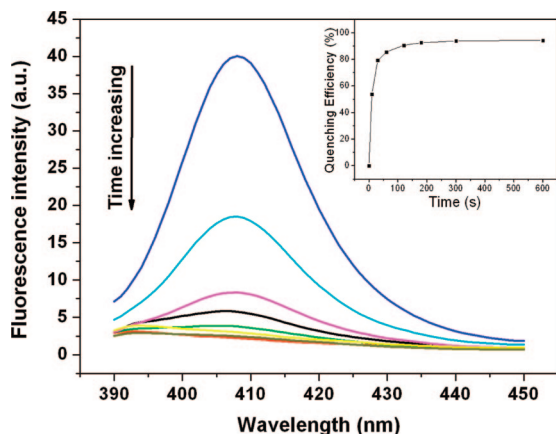


Figure 4. Time-dependent fluorescence emission spectra of the oligomer functionalized film upon exposure to TNT vapor (room temperature) at 0, 10, 30, 60, 120, 180, 300, and 600 s (top to bottom) and the fluorescence quenching (%) against time (inset).

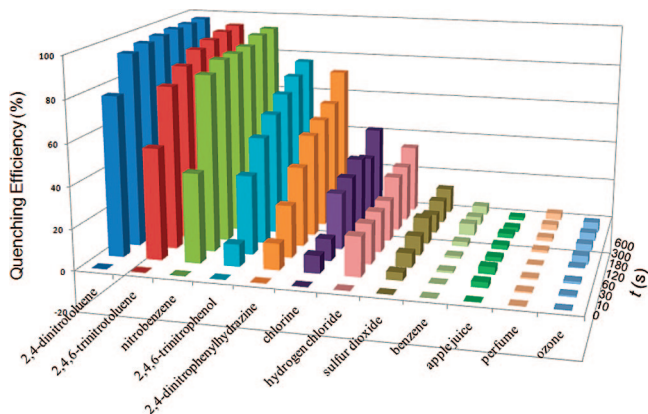


Figure 5. Quenching efficiencies of various NACs vapors to the fluorescence emission of the oligo(diphenylsilane)-functionalized film and interferences of common interferents to the sensing process.

exposure resulted in 55% reduction of the fluorescence emission, and further 30 s exposure made the reduction exceed 83%. It is to be noted that the film is not only responsible to TNT but also to the vapors of other NACs. As for NB, exposure of the film to its saturated vapor for 10 and 30 s resulted in 44 and 85% reduction of the emission, respectively. The quenching reached its maximum, 92%, after 100–200 s exposure to the vapor. On comparison, the emission of the film to DNT vapor is much more sensitive than to TNT and other NACs vapors, specifically, nearly 80% reduction and 94% reduction for 10 and 30 s exposures, respectively. The responses of the film to 2,4,6-trinitrophenol (PA) and 2,4-dinitrophenyl-hydrazine (DNPH), however, are much slower than to other NACs tested. The quenching efficiencies of them are 38 and 25%, respectively, for exposure time of 30 s. Clearly, the quenching follows the order of DNT > TNT > NB > PA > PHDH (Figure 5).

The differences in the quenching efficiency and response of the film to different NACs and interferents should be a result of the differences of them in vapor pressure, redox potential, and even the concentration of them on the film surface, and thereby the result may be understood by considering these factors. Generally speaking, for fluorescence quenching of conjugated polymers in vapor phase, the greater of the vapor pressure, the higher of the redox

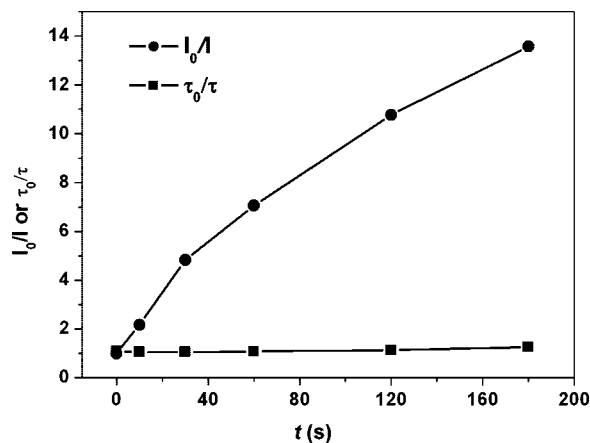


Figure 6. Plots of the ratios of I_0/I and τ_0/τ against the exposure time of the film in TNT vapor.

potential, the more of the concentration of a nitro-aromatic compound, the greater of its quenching efficiency is. More detailed discussions can be found in Swager and co-workers' publication.^{5b} For the present system, the redox potentials of DNT and TNT are -1.0 and -0.7 V, respectively, and their vapor pressures are 1.74×10^{-4} and 8.02×10^{-6} mmHg, respectively at 25°C .²⁹ Clearly, the considerable faster and greater response of the film to DNT than to TNT could be attributed to the higher vapor pressure of DNT (21: 1). This rationalization can be also applied to other NACs systems. For example, the vapor pressures of PA and DNPH are 5.80×10^{-9} and 1.26×10^{-9} mmHg, respectively, at 25°C .²⁹ Accordingly, their quenching efficiencies are getting lower and lower. As for NB, however, its quenching efficiency is not as great as that expected even though it possesses higher vapor pressure than others. A detailed mathematical description of vapor pressure effect upon the sensing performance of a fluorescent film was provided in an earlier study of the sensing performances of pyrene-functionalized films to NACs.²² For benzene, however, its lower quenching efficiency could be attributed to its much lower redox potential (<-2.7 v). Considering that selectivity is a crucial criterion for the practical uses of a sensing film, it should be of value to study the response of the film to other chemicals that may affect the detection of NACs.

Interference from Other Chemicals. Interestingly, no significant change in fluorescence emission was observed upon exposing the film to the vapors of common organic solvents, daily chemicals, and fruit juice, such as benzene, toluene, methanol, ethanol, perfume (Chanel), and apple juice (c.f. Figure 5). Similarly, smoke and ozone also showed little effect upon the emission of the film. All these results revealed the insensitivity of the film to such interferents. However, exposure of the film to chlorine, HCl, and SO_2 gas did result in some decrease in the fluorescence emission of the film, but the response is weaker and slower if compared with those of NACs.

(29) (a) The vapor pressures of NB, DNT, TNT, PA, and DNPH are 2.70×10^{-1} , 1.74×10^{-4} , 8.02×10^{-6} , 5.80×10^{-9} , and 1.26×10^{-9} mmHg, respectively, at 25°C (the first three data were obtained from ref 22. The fourth was obtained from: (b) Bruschini, C. *Subsurface Sensing Technologies and Applications* **2001**, 2, 299–336. The last one came from: (c) Behrens, R.; Wiese-Smith, D.; Johnston, L.; Maharrey, S. *Sandia Report*, **2004**.

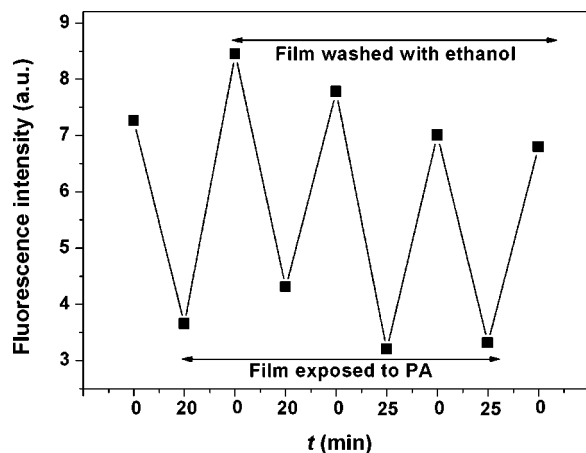


Figure 7. Reversibility of the responses of oligo(diphenylsilane) functionalized film to the vapor of PA ($\lambda_{\text{ex}} = 370$ nm, $\lambda_{\text{em}} = 410$ nm).

The interference from oxygen was also conducted, but in this case, the film was treated with pure nitrogen in a glovebox for more than 1 h and then transferred into a tightly sealed cell. Finally, the fluorescence emission was recorded. From the result, it was revealed that elimination of oxygen enhanced the fluorescence emission of the film (<5%). The results presented are in good agreement with those obtained by Trogler and others in their studies of spin-coated fluorescent films of polysiloles.^{10–12,30}

Quenching Mechanism of the Sensing. The quenching mechanism of the sensing was studied by comparing the quenching results from static measurement and those from fluorescence lifetime measurement (c.f. Figure 6). It is obvious that the average fluorescence lifetime (1.06 ns) of the film did not change significantly along with increasing exposure time of the film in TNT vapor. The emission intensity, however, changed a lot during the measurement, suggesting that the quenching was mainly caused by formation of a nonfluorescent complex, in support of the assumption that conjugated polymers possess specific affinity to

NACs and form nonfluorescent donor–acceptor complexes with them.^{10,12}

Reversibility of the Quenching Process. The reversibility of the sensing process was examined with PA as an example NAC. The film was first exposed to the saturated vapor of PA at room temperature for 20 min and then the fluorescence emission was measured. After the measurement, the film was washed with ethanol several times and air-dried. The fluorescence emission of the film was measured again. This sensing and washing process was repeated several times, and the results are shown in Figure 7. Clearly, the sensing process is basically reversible.

Conclusion

The superquenching, fast response, and interference free of oligo(diphenylsilane)-functionalized film to TNT and DNT vapors demonstrated clearly that combination of the advantages of fluorescent films based on single-layer chemistry and those based on conjugated polymers is an effective and feasible way to create novel fluorescent film sensors. Further experiments revealed that the quenching of NACs to the fluorescence emission of the film is static in nature, and the quenching process is basically reversible. Considering the fast, sensitive, and selective response of the film to DNT and TNT vapors, the two most significant signal compounds of common explosives, it is safe to conclude that the oligomer-functionalized film should be a strong candidate of explosive sensory materials.

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Supporting Information Available: Details of stability of the fluorescent films and preparation, scission, molecular mass determination, and fluorescence quantum yield of the polymer (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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