

Detection of Nitroaromatic Compounds Based on Fluorescent Silafluorene Chemosensors

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Abstract

A simple and rapid method is described for detecting nitroaromatic explosives in air or seawater with the use of photoluminescent organosilicon compounds. The synthesis, spectroscopic characterization, and fluorescence quenching efficiency of silafluorenes are reported. Silafluorenes were synthesized from the reduction of dilithiobiphenyl with dichlorosilanes. Two silafluorenes were used for the detection of nitroaromatic compounds. Detection of nitroaromatic molecules, such as 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and picric acid (PA), has been explored. A linear Stern-Volmer relationship was observed for the first three analytes. Fluorescence spectra of silafluorenes obtained in either toluene solutions or thin films displayed no shift in the maximum of the emission wavelength. The photoluminescence quenching occurs by a static mechanism.

Key words : Chemical sensors, Chemosensor, Fluorene, Nitrocompound

1. Introduction

The fast and on-site detection of 2,4,6-trinitrotoluene (TNT) and other nitroaromatic compounds would be one way to enhance the protection of society against terrorist attacks. Chemical sensors for explosives,^[1,2] which offer new approaches to the rapid detection of ultra-trace analytes from nitroaromatic compounds, have attracted attention because nitroaromatic compounds are important chemical species to detect^[3,4] in mine fields,^[5] military applications, munitions remediation sites, and homeland security applications.^[6] It is also important in forensic investigations, such as post-blast residue determinations.^[7,8] Metal detectors, widely used as portable instrumentation for field explosive detection, cannot locate the plastic casing of modern land mines. Trained dogs are expensive, difficult to maintain, and are easily fatigued. Physical detection methods for explosives include gas chromatography coupled with a mass spectrometer, surface-enhanced Raman spectroscopy, nuclear quadrupole resonance, energy-dispersive X-ray diffraction, neutron activation analysis, electron capture detection, and cyclic voltammetry.

These techniques are highly selective, but some are expensive and others are not easily fielded in a small, low-power package. Up to now only sniffers (sensors working as an artificial dog's nose) using advanced materials are able to search large areas and to locate explosives by smelling the compounds. Among these sniffers, fluorescence-based sensors were generally employed due to their sensitivity, selectivity, simplicity, and low cost in instrumentation. Materials used for the preparation of the fluorescent sensors include conjugated organic polymers^[9,10] and conjugated inorganic polymers.^[11] Swager and co-workers⁶ found that it is possible to improve the sensing performance of a conjugated polymer-based fluorescent film to nitroaromatic compounds by introducing bulky structures on the backbone of the polymer. For example, they incorporated rigid three-dimensional pentaerythritol moieties in the backbone of poly(phenylene-ethynylene) that prevent π -stacking or excimer formation, increase the porosity of the polymer films, and significantly improve the sensing response of the film to TNT.

Recently we have shown how luminescent polysiloles can be used as TNT and picric acid sensors.^[11,12] Inorganic polymers with Si-Si, Ge-Ge, and Si-Ge backbones, in which the monomer units are silicon-, germanium-, or tin-containing metallocyclopentadienes (metalloles), are other kinds of important conjugated poly-

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mers because they also exhibit high electron affinity and fast electron mobility. It has been demonstrated that the polymetalloles and metallole copolymers are effective materials for building up nitroaromatic compounds sensors used both in air and in solution. Unlike conjugated organic polymers, film sensors from conjugated inorganic polymers are robust and insensitive to common interferents, such as organic solvents, inorganic acids, and oxygen in air. In this paper, the synthesis, optical characterization of silafluorenes and their application as a chemosensor were reported.

2. Experimental

2.1. Materials

All synthesis manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were purified and degassed before use according to standard literature methods: diethylether, tetrahydrofuran (THF), methanol were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl. All other reagents (Aldrich) such as dibromobenzene, *n*-butyllithium, SiMeHCl₂, SiMe₂Cl₂, DNT, and picric acid were purchased and used without any purification. Spectroscopic grade THF from Fisher Scientific was used for the fluorescence measurements. Spectroscopy grade THF and water from Fisher Scientific were used for the fluorescence measurements. NMR grade deuteriochloroform was stored over 4 Å molecular sieves. NMR data were collected with 300 MHz spectrometer for ¹H NMR. Chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm. UV-vis absorption spectrum and fluorescence emission spectrum were recorded with the use of a Shimadzu UV-2401 spectrophotometer and a Perkin-Elmer luminescence spectrometer LS 50B, respectively. The solvents were determined to be free of emitting impurities prior to use. To avoid changing the concentrations of the emitting compound, the experiments were carried out with solution by preparing the quencher in the same solution of the emitting compound.

The concentration of thiophene pentiptycene polymers and their aggregates for the fluorescence measurement was 1 mg/1 L = 1 ppm. Caution: TNT and picric acid are high explosives and should be handled only in

small quantities. Picric acid also forms shock sensitive compounds with heavy metals. TNT was synthesized as described elsewhere^[13] and purified by recrystallization twice from methanol and dried overnight in a vacuum. Purity was confirmed by NMR spectroscopy.

2.2. Synthesis of 2,2-dibromobiphenyl

To a solution of 250 mL of anhydrous tetrahydrofuran, 24 g (0.1 mole) of 1,2-dibromobenzene was added and stirred in -78°C. An ethereal solution containing 0.05 mole of *n*-butyllithium was added at such a rate that the temperature was not allowed to rise more than 5°C during the addition. A white suspension developed in the pale yellow solution, after only a few drops of *n*-butyllithium had been added. The main product isolated after work-up in the usual manner was an ether insoluble white solid. ¹H-NMR (300 MHz, CDCl₃) δ 7.67 (d, 2H), 7.45 (d, 2H), 7.34 (d, 2H), 7.28 (d, 2H)

2.3. Synthesis of 1,1-methylhydrosilafluorene

To a solution of 5 g (0.016 mole) of 2,2-dibromobiphenyl in 120 mL of anhydrous diethyle ether cooled to -78°C by a dry ice-acetone bath, was added dropwise 20 mL of 0.032 mole *n*-butyllithium. After the addition, the reaction mixture was allowed to warm up to room temperature. It then was stirred at room temperature for an additional 3 h. The reaction solution was then cooled to -197°C by a liquid nitrogen, Dichloromethylsilane 1.65 mL (0.016 mole) was then added. After addition of dichloromethylsilane, the reaction mixture was allowed to warm up to room temperature. The reaction mixture was stirred at room temperature for 12 h. After the reaction, all volatile liquids are removed under the reduced pressure. The remaining solid was washed with methanol several times. The pale yellow solid, 1,1-methylhydrosilafluorene, was obtained. ¹H-NMR (300 MHz, CDCl₃) δ 7.82 (d, 2H), 7.61 (d, 2H), 7.44 (t, 3H), 7.24 (t, 3H), 4.54 (s, 1H) 0.44 (s, 3H), ¹³C-NMR (75 MHz, CDCl₃) δ 147.77, 138.90, 131.86, 130.15, 127.65, 120.79, 1.02.

2.4. Synthesis of 1,1-dimethylsilafluorene

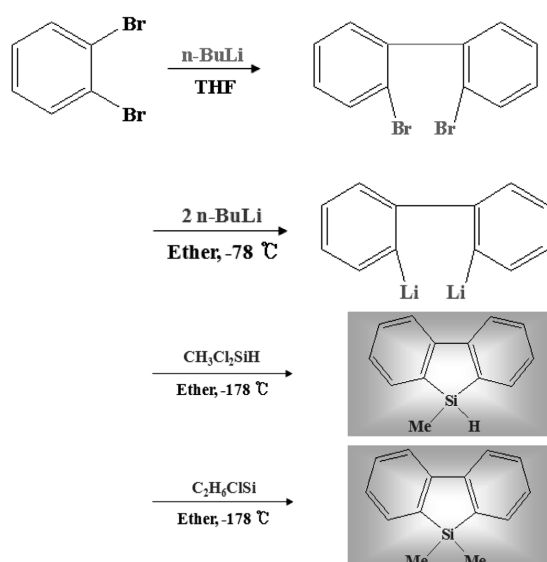
To a solution of 5 g (0.016 mole) of 2,2-dibromobiphenyl in 120 mL of anhydrous diethyle ether cooled to -78°C by a dry ice-acetone bath, was added dropwise 20 mL of 0.032 mole *n*-butyllithium. After the addition, the reaction mixture was allowed to warm up to

room temperature. It then was stirred at room temperature for an additional 3 h. The reaction solution was then cooled to -197°C by a liquid nitrogen, 16 mmol of dichlorodimethylsilane was then added. After addition of dichloromethylsilane, the reaction mixture was allowed to warm up to room temperature. The reaction mixture was stirred at room temperature for 12 h. After the reaction, all volatile liquids are removed under the reduced pressure. The remaining solid was washed with methanol several times. The pale yellow solid, 1,1-methylhydrosilafluorene, was obtained. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.82 (d, 2H), 7.61 (d, 2H), 7.44 (t, 3H), 7.24 (t, 3H), 0.44 (s, 3H), $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 147.77, 138.90, 131.86, 130.15, 127.65, 120.79, 1.02.

3. Result and Discussion

The synthetic routes of methylhydrosilafluorene and dimethylsilafluorene were displayed in Scheme 1. Characteristic features of silafluorene include a low reduction potential and a low-lying LUMO due to $\sigma^*-\pi^*$ conjugation arising from the interaction between the σ^* orbital of silicon, and the π^* orbital of the butadiene moiety of the five membered ring.

The UV-vis absorption and fluorescence spectral data for methylhydrosilafluorene are reported in Fig. 1. Absorptions at a wavelength of about 320 nm for the



Scheme 1. Synthesis of methylhydrosilafluorene and dimethylsilafluorene.

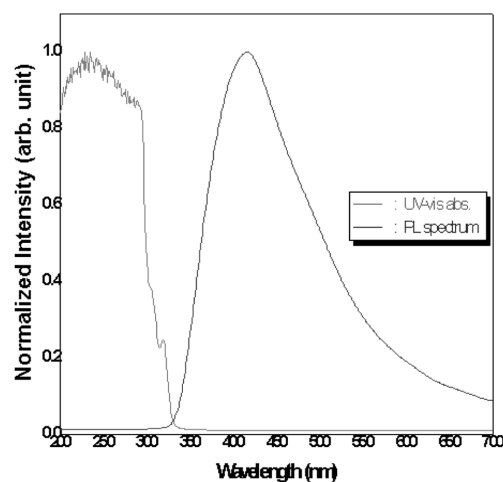


Fig. 1. UV-vis absorption and fluorescence spectra of methylhydrosilafluorene.

methylhydrosilafluorene is assigned to the silafluorene the $\pi^*-(\sigma_2^*+\pi^*)$ transition in the silafluorene ring. Methylhydrosilafluorene exhibit one emission band (λ_{max} , 430 nm) when excited at 320 nm.

Fluorescence quenching studies with nitroaromatic analytes were achieved in 1 mg of silafluorene/1 L of toluene solution. The detection method involves measurement of the quenching of photoluminescence of methylhydrosilafluorene by the analyte (using a Perkin-Elmer LS 50B fluorescence spectrometer, 320 nm excitation wavelength). Fluorescence spectra of toluene solutions of the methylhydrosilafluorene were obtained by successive addition of aliquots of picric acid (purchased from Aldrich and recrystallized from ethanol solution before use), TNT (prepared from DNT and recrystallized twice from methanol), DNT, and nitrobenzene. Photoluminescence quenching of methylhydrosilafluorene in toluene solutions with picric acid, TNT, and DNT were measured. Fig. 2 displays the quenching of photoluminescence spectra of methylhydrosilafluorene upon addition of picric acid.

The Stern-Volmer equation was used to quantify the differences in quenching efficiency for various analytes. In this equation, I_0 is the initial fluorescence intensity without analyte, I is the fluorescence intensity with added analyte of concentration $[A]$, and K_{sv} is the Stern-Volmer constant.

$$(I_0/I) - 1 = K_{\text{sv}}[A]$$

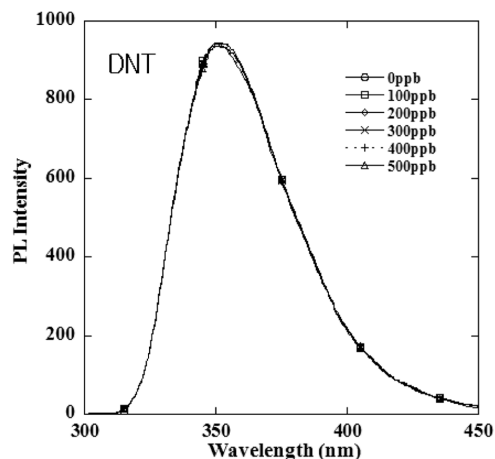
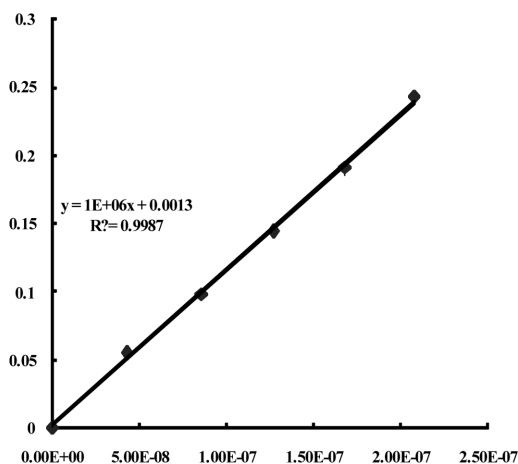
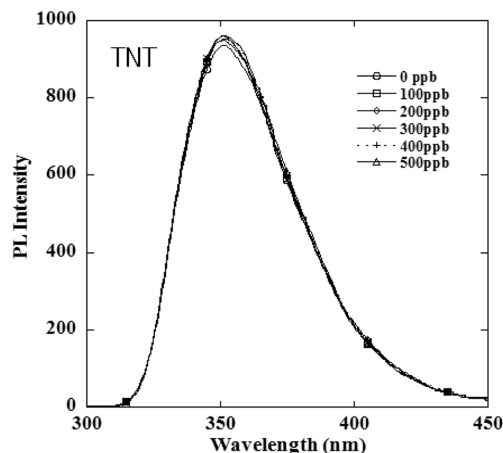
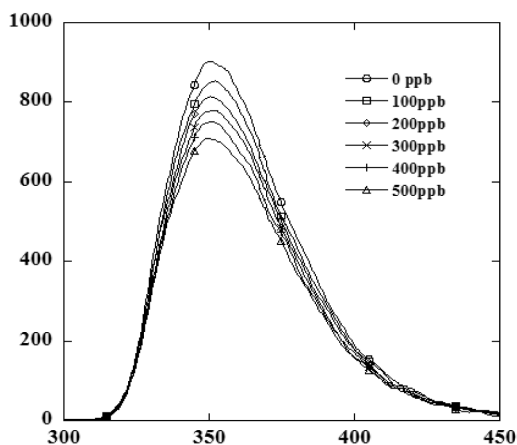


Fig. 2. Quenching photoluminescence spectra and Stern-Volmer plot of methylhydroxylfluorene for picric acid.

Fig. 3. Quenching photoluminescence spectra and Stern-Volmer plot of methylhydroxylfluorene for TNT and DNT.

Fig. 3 displays the quenching of photoluminescence spectra of methylhydroxylfluorene upon addition of TNT and DNT. Photoluminescence quenching efficiencies of methylhydroxylfluorene are in the order of picric acid > TNT > DNT. The purity of the TNT sample was found to be important to obtain reproducible results. It was synthesized by nitration of dinitrotoluene and recrystallized twice from methanol. A third recrystallization produces the same results as the twicerecrystallized material. When the quenching experiment was undertaken without recrystallization of TNT, higher (ca. 10x) quenching percentages are obtained. Presumably, impurities with higher quenching efficiencies are present in crude TNT.

A linear Stern-Volmer relationship is observed in all cases. A linear Stern-Volmer relationship may be

observed if either a static or dynamic quenching process is dominant. Thus, in the case of higher concentrations of picric acid, the two processes may be competitive, which results in a nonlinear Stern-Volmer relationship. Photoluminescence quenching may arise from either a static process, by the quenching of a bound complex, or a dynamic process, by a bimolecular quenching of the excited state.

4. Conclusion

New method for sensing nitroaromatic compounds has been developed by the measurement of photoluminescence of silafluorene. The silafluorenes have been synthesized and used for the detection of nitroaromatics, such as picric acid, TNT, and DNT. The silafluorenes

are robust and insensitive to common interferents, such as organic solvents and inorganic acids.

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