Detection of TNT and Picric Acid on Surfaces and in Seawater by Using Photoluminescent Polysiloles**

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Polysilanes exhibit high hole mobility and high nonlinear optical susceptibility in the UV region which makes them efficient photoemission candidates for a variety of optoelectronics applications.[1] These properties arise from $\sigma-\sigma^*$ delocalization of σ electrons along the Si–Si backbones and confinement of the conjugated electrons along the backbone. Polysiloles, such as poly(2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene), also possess a Si–Si backbone, but the unsaturated five-membered ring of the silole shifts their optical absorption and emission spectra into the visible spectral region.[2] Thus polysiloles have been examined as materials for organic light-emitting diodes (LED's).[3] The most characteristic feature of siloles is a low reduction potential and a low-lying lowest unoccupied molecular orbital (LUMO). These features result from the $\sigma^*-\pi^*$ conjugation arising from the interaction between the σ^* orbital of the silicon chain and the π^* orbital of the butadiene moiety of the five-membered ring.[4, 5]

Polytetraphenyl-1,1-silole, $(C_4Ph_4Si)_n$, which was used in this study, has a helical structure along the Si–Si backbone[6] and a highly conjugated ring system in the side chains. It also exhibits a high luminescence quantum yield.[7] Recently Yang and Swager showed that highly π-conjugated, porous organic polymers can be used to detect vapors of electron-deficient chemicals.[8, 9] Electron delocalization in these polymers provides a means of amplification, since interaction of an analyte molecule at any position along the polymer chain is communicated throughout the chain. A similar means of amplification is available to quantum-confined semiconductor nanocrystallites, where the electron and hole wave functions are delocalized throughout the nanocrystal.[10]

Most methods for the detection of explosives are only applicable to air samples as a consequence of interference problems encountered in complex aqueous media. Sensing 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (picric acid) in groundwater or seawater is important for the detection of buried unexploded ordnance and for locating underwater mines.[11, 12] There are also environmental applications for characterizing soil and groundwater contaminated with toxic TNT at military bases as well as at munitions production and distribution facilities.[13] Here we report an inexpensive and highly efficient inorganic polymer sensor that can detect nitroaromatic compounds, such as picric acid, nitrobenzene, 2,4-dinitrotoluene (DNT), and TNT in air or seawater. The sensor employs a thin film of photoluminescent polysilole, which is stable to air, water, acids, common organic solvents, and even seawater-containing bioorganisms.

Polytetraphenylsilole[14] was coated as a thin film on substrates such as commercial filter paper, borosilicate glass cover slips, porous silicon chips,[15] and silicon wafers. Samples were prepared by soaking the substrates in a toluene solution of polysilole after filtration through a 0.2-μm PTFE filter. Thin films of polysilole were also deposited on glass or silicon wafer substrates by spin coating. These samples were dried in a vacuum before use. Samples were then placed either in a cylindrical quartz flow cell ($d = 2.5$ cm, $h = 2.0$ cm) under flowing air or in a quartz cell ($1.5 \times 1.5 \times 2.5$ cm^3) filled with seawater that contained the analyte for the detection experiment.

The detection method involves measuring the quenching of the photoluminescence of the polysilole by the analyte (by using a Perkin–Elmer LS 50B fluorescence spectrometer, 340 nm excitation wavelength). The fluorescence spectra of a toluene solution of the polysilole were obtained upon successive addition of aliquots of TNT. The quenching of the photoluminescence of the polysilole in toluene solutions of nitrobenzene, DNT, TNT (prepared from DNT[16]), and picric acid were measured. A linear Stern–Volmer relationship was observed in the first three cases, but not for picric acid (Figure 1; $(I_0/I) - 1 = K[\text{analyte}]$). This latter observation may result from slight irreversibility in the case of picric acid. The fluorescence spectra of polysilole from either toluene solutions or thin polymer films displayed no shift in the maximum of the emission wavelength. This observation suggests that neither π stacking of the polymer chains nor excimer formation occurs with the polysilole.

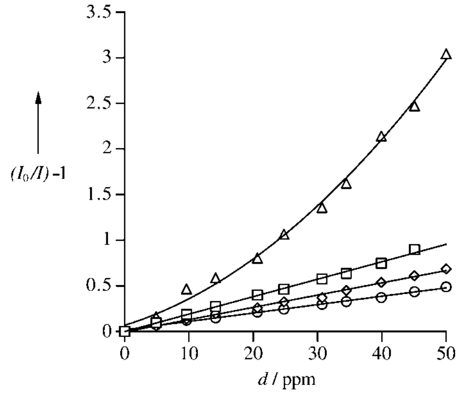

Figure 1. Stern–Volmer plots for the quenching of polysilole luminescence by nitrobenzene (○), DNT (◇), TNT (□), and picric acid (△).

The relative efficiencies of photoluminescence quenching of polysilole are 3.8:2.2:1.0 for TNT, DNT, and nitrobenzene (NB), respectively, as indicated by the values of K determined from the slopes of the steady-state Stern–Volmer plots. The quenching efficiency of photoluminescence for picric acid is 77 % greater than that for TNT at 50 ppb. Figure 2 shows that a plot of $\lg K$ versus the reduction potential of the analytes exhibits a linear relationship, which indicates that the

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[**] This work was supported through DARPA's Tactical Sensors Program through a Space and Naval Warfare Systems Center Contract (N66001-98-C-8514) and the National Science Foundation, Division of Material Research (Grant No. DMR 9900034). The technical point of contact for this DARPA program is Dr. Edward Carapezza.

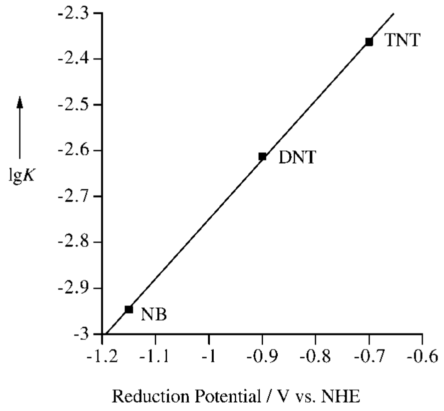

Figure 2. Plot of lg$K$ versus the reduction potential of the analytes.

mechanism of quenching is attributable to electron transfer from the excited polysilole to the LUMO of the analyte. Since the reduction potential of TNT (−0.7 V versus the normal hydrogen electrode (NHE))[9] is less negative than that of either DNT (−0.9 V versus NHE) or nitrobenzene (−1.15 V versus NHE), it is detected with high sensitivity.

Photoluminescence quenching of the oligomeric tersilole, $Cl(C_4Ph_4Si)_3Cl$, by TNT was also measured. The K value of $(4.34 \pm 0.12) \times 10^3\,M^{-1}$ for a polysilole, which has about 15 repeat units,[14] is 38% greater than that for the oligomer tersilole ($K = (3.14 \pm 0.04) \times 10^3\,M^{-1}$). This result suggests that polysilole produces an excited state that is delocalized over many repeat units. The sensitivity of the photoluminescence quenching technique for the detection of analytes by organic polymers depends not only on the molecular weight of the polymer but also on the diffusion length of excitation.[17]

An important aspect of the inorganic polymer sensors is their insensitivity to common interferents. Control experiments using thin films of polysiloles (deposited on glass substrates) with oxygenated air displayed no change in the photoluminescence spectrum. Similarly, exposure to organic solvents such as toluene, tetrahydrofuran, and methanol or the aqueous inorganic acids H_2SO_4 and HF produced no significant decrease in the photoluminescence intensity. However, 4 ppb of TNT vapor in air (air stream flowing at a rate of 100 mL min^{-1}) was detected as an 8.2% decrease in the photoluminescence intensity within 10 min.

The detection of TNT and picric acid in seawater (collected off Scripps Pier, La Jolla, CA) was measured using thin films of polysilole. No quenching of the photoluminescence was observed until the seawater was spiked with 50 ppb of TNT. Quenching was detected instantly and the amount of quenching was stable with time. The efficiency of the photoluminescence quenching by picric acid is greater than that for TNT and we obtained a 6 ppb detection limit for picric acid in seawater using the thin films. Ionic oxidants, such as aqueous CrO_4^{2-}, are inefficient electron transfer quenchers of the hydrophobic polymer luminescence under similar conditions.

The effect of TNT exposure on polysilole-coated substrates is readily visible to the naked eye when the samples are illuminated with a small ultraviolet (UV) lamp. Thus, polysilole can be used as a convenient indicator reagent for TNT residues. Trace amounts of TNT deposited by a glove that was used to handle TNT, and then wiped clean, show up as an easily viewed change in the photoluminescence (Figure 3).

Figure 3. TNT residue hand print visualized as quenched luminescence on paper developed with polysilole and illuminated with an ultraviolet light. The left hand (nitrile gloved) had been rubbed with about 0.1 g of TNT, and the glove was brushed to remove all visible TNT particles before being pressed onto the paper sheet. The right hand (nitrile gloved) was not exposed to TNT and serves as a control. The paper was then lightly coated with a fine mist of polysilole (0.1 mM in toluene) from an airbrush. The image taken under ultraviolet light demonstrates the utility of polysiloles for visualizing trace residues of TNT.

Received: December 18, 2000
Revised: March 16, 2001 [Z 16295]

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