

Polymer sensors for nitroaromatic explosives detection

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Several polymers have been used to detect nitroaromatic explosives by a variety of transduction schemes. Detection relies on both electronic and structural interactions between the sensing material and the analyte. Quenching of luminescent polymers by electron deficient nitroaromatic explosives, such as trinitrotoluene, may be monitored to detect explosives. Resistive sensing using carbon black particles that have been coated with different organic polymers and deposited across metallic leads can also be used to detect nitroaromatic vapors in an electronic nose approach. Frequency changes in surface acoustic wave devices may be monitored to detect nitroaromatics after their adsorption into polymer coatings. Luminescent polymetalloles have recently been investigated for sensing explosives in aqueous-based solutions and for improved visual detection of trace particulates on surfaces.

1. Introduction

Chemical sensors for the rapid detection of explosives are important because they have important potential applications, such as tactical and humanitarian demining, remediation of explosives manufacturing sites,¹ and forensic and criminal investigations.^{2,3} Homeland security applications are attracting increased research, because terrorists frequently employ explosive bombs. Various methods of explosives detection are currently available, but many simple techniques are often inefficient. Metal detectors are commonly used as an indirect technique for sensing explosive devices packaged in metal. This method is valuable for certain applications, such as for landmine and weapon detection, although many modern landmines employ plastic casings. Metal detectors, however, are not useful for other applications, such as for explosives screening in airports. Canines are considered the most reliable tool for the detection of explosive vapors; however, this method is expensive and not well-suited for continuous

monitoring, because dogs require care and are easily fatigued.⁴ Some methods, though highly sensitive, are expensive and require sophisticated instrumentation that is not easily applied to on-site field testing. Some such methods include gas chromatography coupled with mass spectrometry,⁵ surface enhanced Raman spectroscopy,⁶ nuclear quadrupole resonance,⁷ energy dispersive X-ray diffraction,⁸ neutron activation analysis, electron capture detection,¹ and cyclic voltammetry.⁹ Ion mobility spectrometry (IMS), which is a commonly used explosive detection system in airports, has sensitivity in the picogram to nanogram range, but it is also expensive, operator dependent, prone to false positives, and spectrometers must be frequently calibrated.¹⁰ A review of instrumentation for trace explosives detection has been published recently.¹¹

High explosives consist of an intimate mixture of a chemical oxidant and reductant that on initiation undergoes a highly exothermic decomposition to yield gaseous products. Several nitroaromatic explosives are known, such as trinitrotoluene (TNT), tetryl, and picric acid. Mixtures of high explosives are also commonly used, and TNT, an inexpensive compound, is a component found in fifteen explosive compositions.¹² For example, TNT and dinitrotoluene (DNT) are widely used in

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industrial explosives containing ammonium nitrate. Tritonal is a mixture of TNT and Al powder, and amatol contains ammonium nitrate and TNT.¹³ Pentolite is a mixture of pentaerythritoltetranitrate (PETN) and TNT, and Composition B is a blend of cyclotrimethylenetrinitramine (RDX) and TNT. Because of their widespread use and volatility, nitroaromatics comprise an important general class of explosives compounds for detection. Chemical structures of some nitroaromatic explosives are shown in Fig. 1.

Both soil and aqueous sampling are important for determining the location of unexploded landmines;^{14–16} however, interference problems are troublesome in complex media. Consequently, trace detection is often limited to collecting vapor samples over soil. This narrows the focus to the more volatile explosive components, such as DNT and TNT, whose equilibrium vapor pressures are roughly 100 and 5 ppb, respectively.¹⁷ DNT is present in TNT samples as an impurity resulting from the manufacturing process.¹⁸ Though present in such small quantities, the significantly higher vapor pressure of DNT often makes it the target molecule for detection. Vapor concentrations of volatile explosives near a bomb may be 2–6 orders of magnitude less than their equilibrium vapor pressures due to their enclosure in a casing, adsorption to soil particles, and because mixtures of explosive materials have lower vapor pressures than their pure compounds.¹⁹ Sensing of volatile components in soil headspace also depends heavily on ambient temperature and humidity. For example, the vapor pressure of TNT quadruples between 20° and 30 °C.²⁰ In addition, explosives have a tendency to adsorb strongly onto surfaces, such as wood, plastics, paper, and soil. Thus, moisture content plays a key role. Water competes with TNT and DNT for binding sites on soil particles, causing more TNT and DNT to be released into the vapor space as soil moisture content rises. Both dogs and chemical vapor sensors for landmine detection are more efficient at detection after rain.²¹ Due to the low volatility of explosives, absorptive materials, such as polymers, have been employed as explosive vapor sensors, with a variety of transduction schemes. When absorptive sensors continuously monitor the vapor space, explosive vapors accumulate in the sensing element through either condensation or analyte trapping in pores. Detection occurs once a certain mass threshold has been achieved.

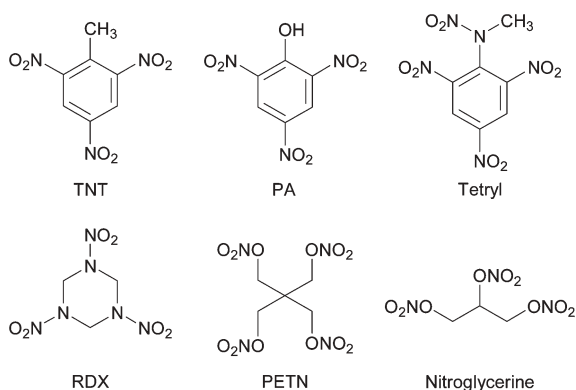


Fig. 1 Structures of nitroaromatic, nitramine, and nitrate ester explosives.

Thus, detection limits of many sensors are quoted in absolute mass limits rather than vapor concentration. Vapor concentration, then, predominantly affects sensor response times.

The low volatility of TNT and other explosives, coupled with their tendency to adhere to surfaces, makes direct trace particle detection an attractive alternative to vapor detection. Surface detection of explosive particles is important in forensic investigations for identifying unexploded residue after detonation. It is known that explosive particles contaminate hair, clothing, and other materials during preparation and packaging of explosive devices, and it is believed that canines detect some explosives by inhalation of trace particulates.^{22,23} For this reason, solid state detection approaches are potentially important security screening procedures. Some solid-state explosives detection systems are already available. Newer airport security systems detect explosives on persons by using an air “puffer,” which dislodges particles on hair and clothing and guides them into a heated inlet to an IMS.²⁴ Similarly, luggage may be swiped to collect solid particles, which may then be sent to an IMS.²⁴ These solid state detection systems are bulky, expensive, and must be calibrated frequently.¹⁰ Commercially available spray can kits are able to detect a variety of explosive contaminants on surfaces through chemical reactions of the explosives with applied reagents to produce colored products. Sensitivity at the tens of nanograms level is purported; however, field tests have shown many false positives to occur and practical detection limits are higher (200 ng for TNT).²⁵

In addition to bomb detection applications, there are environmental health and safety concerns relating to nitroaromatics. Exposure to TNT is believed to cause anemia, abnormal liver function, and cataracts.²⁶ Its toxicity and suspected carcinogenicity has led the Environmental Protection Agency to establish a Health Advisory Standard, a non-mandatory technical guide for authorities, for TNT in drinking water at 2 parts per billion.²⁷ Therefore, highly sensitive methods for detecting TNT and other nitro-based explosives in soil and groundwater are required.²⁸

2. Conjugated polymers for explosives detection

One property of nitroaromatics which may be exploited in detection schemes is their electron accepting capability. Substitution of the electron-withdrawing nitro groups on the aromatic ring lowers the energy of the empty π^* orbitals, thereby making these compounds good electron acceptors. As expected, reduction potentials become more favorable (less negative) as nitro substitution increases, according to nitrobenzene (−1.15 V), DNT (−0.9 V), and TNT (−0.7 V), *versus* NHE.²⁹ Conjugated polymers are promising candidates for redox sensing because they are electron donors.³⁰ Donor ability is further enhanced in their delocalized π^* excited states. Excited state delocalization is important because exciton migration increases the frequency of interaction with a bound quencher,^{31,32} which contributes to enhanced detection sensitivity. Fluorescent organic and inorganic conjugated polymers have therefore been applied to the detection of nitroaromatic explosives in solution and in the vapor phase; detection limits in the parts-per-billion, and even parts-per-trillion, range have

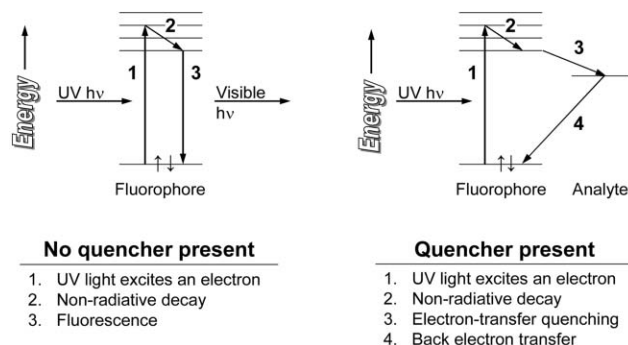


Fig. 2 Electron-transfer fluorescence quenching.

been observed. Fluorescence quenching is often achieved through an electron-transfer donor–acceptor mechanism, as depicted in Fig. 2. Electron deficient analytes, such as nitroaromatic explosives, can act as electron acceptors for photoexcited electrons of the polymers.

2.1 Fluorescent organic polymers for redox sensing

2.1.1 Polyacetylenes. Polyacetylenes have been investigated as potential nitroaromatic sensors.³³ For example, thin films of poly([1-phenyl-2-(4-trimethylsilylphenyl)]acetylene) (PTMSDPA) (Fig. 3) have been shown to detect DNT vapor. The polymer was prepared from the TMSDPA monomer with a $\text{TaCl}_5/\text{n-Bu}_4\text{Sn}$ catalyst,³⁴ which yields a high molecular weight polymer ($M_w = 293\,000$). It fluoresces at 520 nm, and has a relatively high quantum yield ($\Phi = 0.25$) and a short lifetime (50 ps) in toluene solution. Casting the polymer into thin films (3–100 nm thick) shifts the emission only slightly to 533 nm, which reflects a small amount of aggregation in the solid state. The rigid backbone and bulky phenyl side groups prevent chain stacking and self-quenching of luminescence, as is often observed for solid state conjugated polymers. This structure also produces a high fractional free volume of 0.26, which imparts permeability and allows analyte vapors to penetrate quickly into the polymer. Luminescence quenching is observed with as little as part per billion concentrations of nitroaromatic analytes.³³ Response times to various nitroaromatic quenchers decrease with increasing vapor pressures of the analyte (1,4-DNT < 2,6-DNT < 1,3-dinitrobenzene < 4-nitrotoluene). Formation of a charge transfer complex between the nitroaromatic analyte and the electron-rich polyacetylene chain is postulated as important in the

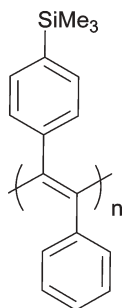


Fig. 3 Poly([1-phenyl-2-(4-trimethylsilylphenyl)]acetylene) (PTMSDPA).

fluorescence quenching process; however, no shift in emission wavelength occurs upon analyte exposure, indicating that exciplexes are not formed. The emission intensity of exposed films is regained after standing in air or on heating, which shows that binding of the analyte and the quenching process are reversible.

2.1.2 Poly(*p*-phenylenevinylenes). Poly(*p*-phenylenevinylenes) (PPV), like polyacetylenes, are strongly luminescent conjugated polymers with high permeabilities to small molecule analytes, such as nitroaromatics. Fig. 4 (A and B) shows two such polymers which undergo luminescence quenching on exposure to TNT and DNT vapor at the ppm level.³⁵ As with the previously discussed polyacetylenes, the bulky phenyl substituents of these PPVs hinder π -stacking and self quenching. In one study, 25 Å thick films of the polymer were exposed to saturated vapors of TNT, 2,4-DNT, 2,6-DNT, 4-nitrotoluene, and benzoquinone (BQ). The MEH-PPV polymer (Fig. 4A) shows greater quenching efficiency than DP10-PPV (Fig. 4B). One factor determining the difference in polymer response is that the dialkoxy-substituted aromatic ring of MEH-PPV is more electron rich than the diphenyl-substituted aromatic ring of DP10-PPV, thus allowing for stronger coulombic interactions between the electron-donating MEH-PPV and the electron-accepting nitroaromatics. A second factor in the improved response is that, according to molecular modeling calculations, the backbone of MEH-PPV is almost planar, while that of DP10-PPV is slightly twisted; the rotational angle between repeat units is 180° for the former and 175° for the latter. A higher degree of planarity allows for

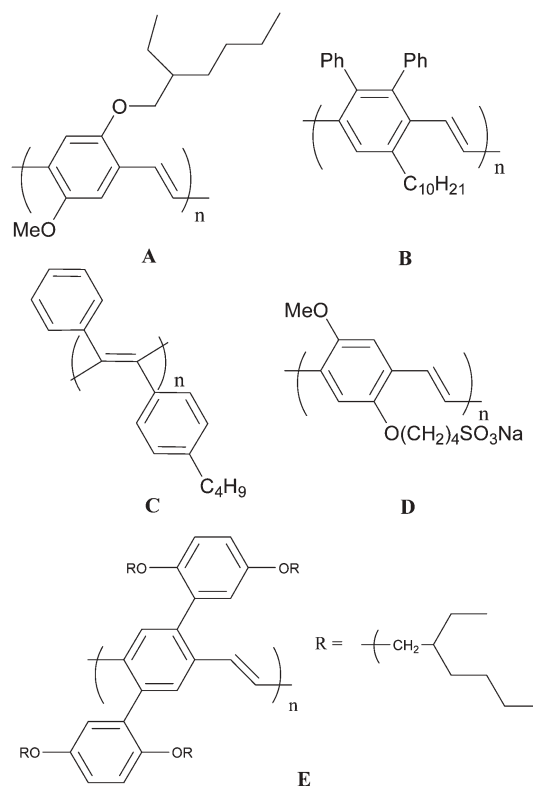


Fig. 4 Poly(*p*-phenylenevinylenes): (A) MEH-PPV, (B) DP10-PPV, (C) BuPA (polyacetylene), (D) MPS-PPV, (E) DADP-PPV.

more effective exciton migration along the polymer backbone. For example, a non-polar polyacetylene (BuPA, Fig. 4C), which contains a repeat unit rotational angle of 51° , has a quenching efficiency that is even lower than that of DP10-PPV. Both PPV polymers have larger quenching efficiencies with the saturated vapor from DNT than TNT, which is explained by its higher vapor pressure (~ 100 times that of TNT). A relatively weak response is observed with benzoquinone, even though it has the highest vapor pressure and is the most easily reduced. Evidently, the polymers have a lower binding affinity for benzoquinone than for nitroaromatics. In addition, reduced sensitivity is observed when thicker films (200 Å) of the polymers were exposed to the analytes. This suggests that luminescent regions of thicker films may not be completely accessible to vapor diffusion of analytes, as diffusion effects should only affect the time response.

The addition of surfactants to poly(*p*-phenylenevinylenes) has also been explored as a means to improving polymer-analyte interactions.³⁶ A water soluble anionic polymer, poly(2,5-methoxy-propyloxysulfonate phenylenevinylene) (MPS-PPV, Fig. 4D), shows luminescence quenching in solution by cationic methyl viologen, but it is insensitive to neutral nitroaromatics. However, addition of 0.4 equivalents of the cationic surfactant dodecyltrimethylammonium bromide (DTA) to an aqueous solution of the anionic PPV polymer reduces the quenching efficiency of methyl viologen by three orders of magnitude. The surfactant competes electrostatically for polymer binding and hence reduces quenching efficiency. Another effect of the DTA, however, is to assemble around the polymer in a pseudo-micellar arrangement, creating local hydrophobic environments. The surfactant thereby acts to increase the association between neutral organic analytes and the polymer. The quenching efficiency of TNT in a 1 : 3 surfactant-polymer solution is thereby amplified nearly ten-fold as compared to a DTA-free solution, as an 8.5×10^{-6} M TNT solution effectively quenches MPS-PPV luminescence ($K_{SV} = 9.3 \times 10^4$ M).

Thin films of MPS-PPV show similar efficient luminescence quenching on exposure to DNT. The adsorption of DNT is irreversible, presumably due to a strong dipolar or charge transfer interaction between the polymer and electron-deficient analyte. However, coating the polymer with a thin layer of the DTA surfactant allows for reversible DNT binding while maintaining sensitivity. With 10 min of heating an exposed polymer, 90% of the original luminescence is regained. The DTA layer provides a permeable barrier that allows analyte penetration but reduces the electrostatic interaction between the polymer and analyte.

Recently, it was reported that an enhanced sensitivity to nitroaromatic detection is possible through the lasing action of organic polymers.¹⁷ This mechanism was shown using the poly(*p*-phenylenevinylene) DADP-PPV (Fig. 4E). DADP-PPV has a high thin film quantum yield (0.80), relatively short fluorescence lifetime (650 ps), and an emission maximum at 500 nm (corresponding to the (0,0) transition). The pendant phenyl groups with branched alkoxy substituents encapsulate the polymer backbone, which protects it from self-quenching and, potentially, from photooxidation. Thin films (30–400 nm) of DADP-PPV may be fabricated into simple waveguides, or

coated on distributed feedback grates or optical fibers. Optical excitation with a 4 ns pulsed nitrogen laser ($\lambda = 337$ nm) at a frequency of 30 Hz induces the lasing action of the polymer and a multimode amplified emission at 535 nm, which corresponds to the first vibronic transition (0,1). Advantageously, the threshold pump energy of 40 nJ cm^{-2} that is needed to generate emission in a 40 nm thick film is insufficient to cause significant photobleaching.

Upon exposure to DNT vapor, luminescence quenching is observed in thin films of DADP-PPV for both the spontaneous emission at 500 nm and the stimulated laser emission at 535 nm. After a 2 min exposure to saturated vapor, the 500 nm peak displays twofold enhanced quenching independent of the laser power. Quenching of the 535 nm peak, however, depends markedly on laser power. After 2 minutes of analyte exposure, there is a tenfold drop in intensity. Remarkably, a response to analyte vapor is observed in the lasing emission after only 1 second of exposure to DNT, which is more than 30 times more sensitive than the response from the spontaneous emission peak. Response to TNT vapor is less reproducible than with DNT, due to the lower volatility of TNT, its tendency to adhere to the film surface, and its inability to quench excitons deep in the polymer film. However, on the surface of an optical fiber, exposure to 5 ppb of TNT vapor is sufficient to cause attenuation in the lasing emission, while the spontaneous emission remains unchanged. The magnitude of quenching, and detection sensitivity, improves with increasing laser power; however, photobleaching results at exposure times longer than 1 min. Nevertheless, these findings suggest attenuated lasing in luminescent organic polymers is a promising field in the development of chemical sensors.

2.1.3 Poly(*p*-phenyleneethynylenes). Related highly-conjugated fluorescent organic polymers showing remarkable nitroaromatic detection capability are poly(*p*-phenyleneethynylenes) (PPE). In particular, thin films of the PPE, developed by Yang and Swager (Fig. 5A), show rapid quenching of their blue luminescence (465 nm) when exposed to TNT vapor at sub-part-per-trillion (ppt) levels.³⁷ This polymer contains two bulky pentiptycene moieties on each alternating phenyl unit of the backbone. The long polymer chain lengths ($M_N = 56\,000$) provide exciton delocalization along the chain, which contributes to the exceptional sensitivity. The pentiptycene groups also provide a porous packing arrangement in the solid state, which prevents interchain π stacking and self-quenching of luminescence.

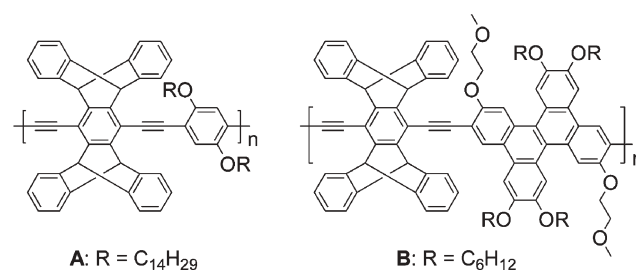


Fig. 5 Pentiptycene containing polymers: (A) a poly(*p*-phenyleneethynylene), and (B) copolymer with a dibenzochrysene.

In addition, this steric bulk, which prevents direct contact of the polymer backbones, contributes to greater photochemical stability of thin films. Fluorescence intensity does not change significantly (<10%) with heating or solvent washings. A further consequence of the porous structure is that it permits quenchers to penetrate rapidly into the film. A 25 Å film shows 50% quenching after 30 s exposure to TNT vapor, and 75% at 60 s. Response to DNT is even faster with 91% and 95% quenching observed at 30 s and 60 s, respectively. Again, this is attributable to the higher equilibrium vapor pressure of DNT relative to TNT. Not surprisingly, the response depends on film thickness, as for PPA and PPV films. The sensitivity to other quenchers also depends on structural and electronic properties. Thin films are much less sensitive to benzoquinone (only 8% quenching at 60 s exposure time), even though BQ has a higher equilibrium vapor pressure and oxidative power. This is most likely due to weaker π - π interactions between the electron-rich polymer and BQ. Dipolar interactions dominate the interaction between analytes and polymeric sensors.³⁸ The polarizabilities of *p*-benzoquinone and *p*-dinitrobenzene are $14.5 \times 10^{-24} \text{ cm}^3$ and $18.4 \times 10^{-24} \text{ cm}^3$, respectively. The higher polarizability of nitroaromatics is one factor which contributes to the higher detection sensitivity of the polymer to TNT and DNT relative to BQ.³⁹ Benzoquinone, however, shows better quenching efficiency in thicker films; this is consistent with there being a greater number of cavities in a thicker coating, which are more effective in trapping volatile analytes.

The pentiptycene-conjugated polymer has been fabricated into a semiselective nitroaromatic sensor array for the tip of an optical fiber bundle.^{40,41} This sensor primarily detects the more volatile DNT vapor from landmines. Short (200 ms) sampling times are needed to detect explosives. Nomadics Inc. has fabricated and commercialized a landmine detector using this promising technology using alternative thin film flow cell designs.⁴²

Yamaguchi and Swager have also copolymerized the pentiptycene monomer with a dibenzochrysene monomer to yield a highly fluorescent polymeric material (Fig. 5B) with greater sensitivity to TNT than the parent pentiptycene.⁴³ Formation of the dibenzochrysene monomers proceeds through an intramolecular oxidative acetylene cyclization mechanism. These copolymers absorb in the visible (444–453 nm) spectral region and emit near 474–480 nm, which is about 10–15 nm red-shifted from the pentiptycene polymer. In addition, they have long fluorescent lifetimes (~ 2 ns) compared to other π -conjugated polymers, such as PPEs and PPVs, whose lifetimes are on the sub-nanosecond time scale.

Recent work in Swager's lab has extended the application of conjugated polymers for detection of less powerful electron accepting analytes, such as 2,3-dimethyl-2,3-dinitrobutane (DMNB), which is a volatile taggant added to manufactured explosives to facilitate vapor detection of less volatile explosives.⁴⁴ For example, RDX has such low volatility that its direct detection by ambient vapor sampling is not practical.¹² Detection of DMNB was observed using polyphenylenes, which have excited-state oxidation potentials lower than those of the poly(*p*-phenylenevinyls). This was possible because of the high energy LUMOs and large

band-gap energies of polyphenylenes. Improved binding interactions between the nonplanar DMNB and these polymers should improve quenching efficiencies and detection limits.

2.1.4 Polymeric porphyrins. Porphyrins functionalized with unsaturated substituents (Fig. 6) have been crosslinked to form luminescent polymeric sensors with the ability to selectively bind explosives, such as TNT and trinitrobenzene (TNB).⁴⁵ The detection method relies on monitoring changes in optical absorption and/or emission after analyte binding. Selectivity is established during polymerization by utilizing the targeted analytes as templates in the reaction mixture. After removal of the analytes, the polymers contain cavities that are shaped like the targeted species. These are examples of "Molecularly Imprinted Polymers" (MIP). For example, 1 wt% porphyrin with a stoichiometric amount of TNT, 83–88 mol% styrene, 5–10 wt% divinylbenzene (as a crosslinker), and 1% AIBN (as a free-radical initiator) may be polymerized in ethanol. The polymer is then cured under mild conditions (60 °C) and washed with solvent to remove the TNT templating agent. The resulting polymer is porous with shape selective cavities for TNT binding. An unassigned emission band at 710 nm increases in intensity with TNT binding, which is accompanied by a decrease in intensity of the porphyrin emission band at 660 nm. These polymers may also be manufactured on fiber optic sensors, or even surface acoustic wave devices (see section 5). Physical properties of the polymers, such as porosity, stability, rigidity, and hydrophilicity, may be tuned by varying porphyrin functionalities, crosslinking reagents, and reaction conditions. This would allow the manufacturing of a series of chemical-recognition sensors specific for explosive analytes in both the vapor and solution phases.

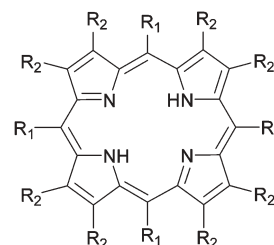


Fig. 6 Porphyrins, polymerizable through R_1 functionality: R_1 = 4-vinylphenyl, styrene, *etc.*; R_2 = H, alkyl, aryl, halide.

2.2 Fluorescent inorganic polymers for redox sensing

2.2.1 Polysilanes. Polysilanes are air-stable luminescent polymers with a Si–Si backbone. Their applications include use as fluorescent materials for radiation detection, electroluminescent materials for display devices, and photorefractive materials for holographic data storage.⁴⁶ Their unique electronic properties arise from σ -conjugation along the Si–Si chain which gives polysilanes high hole mobility, high nonlinear optical susceptibility, and efficient emission in the UV spectral region.⁴⁶ Such properties make polysilanes candidates for explosives detection as well.

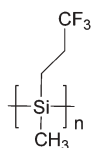
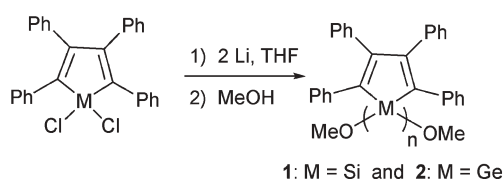


Fig. 7 Fluoroalkylated polysilane (PTFPMS).

Poly(3,3,3-trifluoropropylmethylsilane), PTFPMS, is shown in Fig. 7.⁴⁷ This rigid polymer exhibits photoluminescence quenching of its 335 nm emission ($\Phi = 0.36$ in THF) in the presence of nitroaromatics. A thin film wafer of the polymer can be used to detect nitroaromatics in water, as well as for sensing the vapor phase. Detection limits lie in the ppm range for vapor sensing. The rigidity of the polymer is imposed by the interaction between the Si atom of the backbone and an F atom of an adjacent pendent group. This interaction imparts long-range ordering of the polymer into a rod-like chain. It has been reported that the optical signals of polysilanes are sensitive to changes in torsion angles around the Si–Si bond.⁴⁸ Therefore, helical or coil-shaped polysilanes have broad absorption bands due to the many segments in the σ -conjugated Si backbone. In contrast, rod-like polysilanes have narrow absorptions, due to a single photoexcitation state,⁴⁹ and exhibit enhanced emission, due to greater energy migration along the linear conjugated backbone.⁵⁰ PTFPMS shows both a broad absorption at 285 nm and a narrow feature at 320 nm, suggesting the presence of both coil-like and rod-like components. The amount of each phase is dependent on solvent and on molecular weight. High molecular weight polymer ($M_N = 103\,000$) is rod-like while low molecular weight polymer ($M_N = 15\,400$) is helical.

Addition of nitroaromatics to a THF solution of PTFPMS causes photoluminescence quenching. Relative quenching efficiencies are 4.9 : 2.7 : 1.2 : 1.0 for PA, TNB, DNB, and DNT, respectively. Linear Stern–Volmer relationships are observed, with quenching constants [$K_{SV} = (0.84\text{--}4.15) \times 10^4 \text{ M}^{-1}$] approximately 5–10 times higher than those obtained with polymetalloles (Scheme 1 and section 2.2.2).⁵¹ PTFPMS is 200 times more sensitive to PA than its nonfluorinated analogue, poly(methylpropylsilane). Such sensitivity is attributed to the electron withdrawing CF_3 groups, which stabilize the HOMO and LUMO. In addition, the electron-withdrawing effect may increase the positive charge on silicon, thereby increasing its ability to interact with the nitro groups of the explosives. A noncovalent interaction between the silicon and the nitro group facilitates electron transfer from the electron rich polysilicon backbone to the electron deficient nitroaromatic, and enhances photoluminescence quenching. The presence of such interactions is supported by ^{29}Si NMR



Scheme 1 Wurtz coupling synthesis of polysilole 1 ($M = \text{Si}$) and polygermole 2 ($M = \text{Ge}$).

data. The Si resonances in the presence of picric acid are shifted slightly downfield (0.48 ppm) from a sample of the polymer alone. This is consistent with deshielding caused by a weak interaction between Si and the nitro group.

Thin films of PTFPMS may be used to detect nitroaromatics in water. Quenching efficiencies for PA and DNT more than double for the thin film over those in THF solution, which is attributed to more efficient energy transfer in the solid state. In addition, the quenching is reversible. Washing an exposed film with methanol or water allows for complete recovery of the luminescence, but reduces detection sensitivity in subsequent exposures. This may be attributed to a reduction in the fractional free volume of the film after washing. A film initially cast from a THF ($M_N = 16\,200$) solution shows a broad 285 nm absorption, indicative of a helical film. However, UV data from the same film, after exposure to PA and washing with methanol or water, show a decrease in the 285 nm absorption and the appearance of a 328 nm absorption, consistent with a rod-like polymer film. A more ordered film will have smaller free volumes and quencher diffusion into the film is restricted, thus reducing quenching efficiencies. The polymer thin film is insensitive to various organic solvents (hexane, toluene, methanol), inorganic acids (sulfuric and hydrochloric) and air.

2.2.2 Polymetalloles and metallole–silane copolymers.

Metallacyclopenta-2,4-dienes, or metalloles, are a class of unsaturated organometallic compounds that are analogous to cyclopentadiene but have a Group 14 element (Si, Ge, Sn, Pb) substituted at the sp^3 carbon (Fig. 8A). Metalloles are an interesting group of heterocyclic molecules because of their unique electronic structure. The lowest unoccupied molecular orbital (LUMO) is of π^* character and at unusually low energy due to conjugation with the two exocyclic σ^* orbitals on the metalloid atom (Fig. 8B). This additional conjugation results in a lowering of the LUMO energy by 1.289 eV for 1,1-dihydrosilole as compared to cyclopentadiene.⁵² This also reduces the HOMO–LUMO band gap, which makes metalloles highly fluorescent materials and potential candidates for several optoelectronic devices, including electron transporting materials,⁵³ electroluminescent devices,^{54,55} light emitting diodes (LEDs),⁵⁶ and redox polymer sensors.⁵¹

Functionalization of metalloles permits tuning of the HOMO–LUMO band gap energy. Functionalization of the metalloid atom has little effect on the electronic properties of metalloles, though the absorption maximum red-shifts slightly as substituents become increasingly electronegative.⁵⁷ Functionalization of the 3,4 positions on the metallole ring

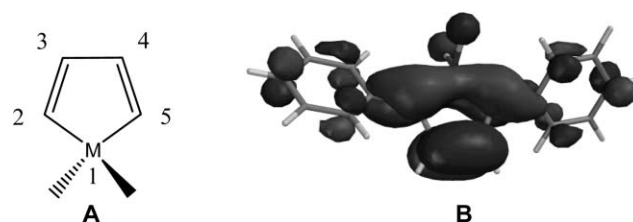


Fig. 8 (A) Structure of metallole molecule, $M = \text{Si, Ge, Sn, Pb}$; (B) LUMO of 2,5-diphenylsilole.

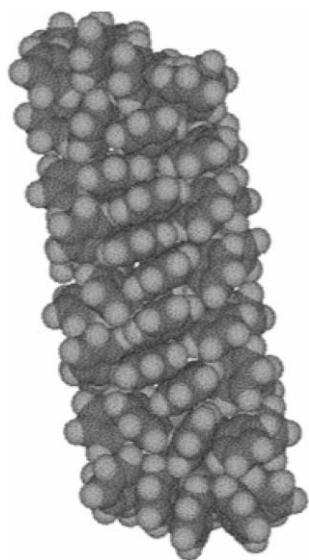


Fig. 9 Helical structure of polysilole 1.

also has a small effect on photophysical properties, but may be useful in fine-tuning absorption and emission wavelengths.⁵⁸ However, substituents on the 2,5 positions of the metallole ring have a large effect on the optoelectronic properties of the metallole. This is relevant for practical applications, for instance, in wavelength selection of LEDs or perhaps in some sensor optimization designs by matching the reduction potential of the metallole to the oxidizing potential of the targeted analyte.

One example of a poly(1,1-metallole) is poly(tetraphenyl)silole, **1**, which possesses a Si–Si backbone surrounded and protected by the organic bulk of the phenyl substituents on the silacyclopentadiene ring (Fig. 9). The structure of **1** is likely helical, as suggested by the 90° H–Si–Si–H torsion angle of the hydrogen dimer (Fig. 10) and the 92° Me–Si–Si–Me torsion angle of the methyl dimer.⁵⁹ In addition, the π^* LUMO⁶⁰ is greatly lowered in energy because of $\sigma^*-\pi^*$ conjugation between the σ^* orbitals of the polysilicon chain and the π^* orbital of the butadiene moiety. The delocalized excited state provides an efficient pathway for electron transfer quenching by analytes that can penetrate the hydrophobic exterior of the helix. This conjugation also results in a near UV absorption

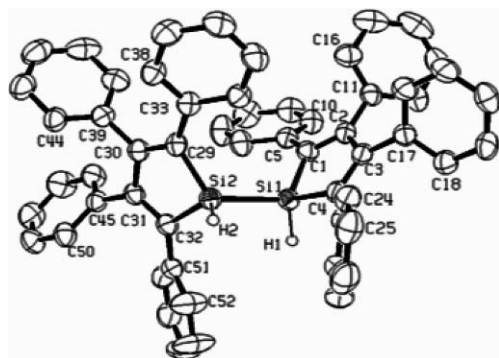
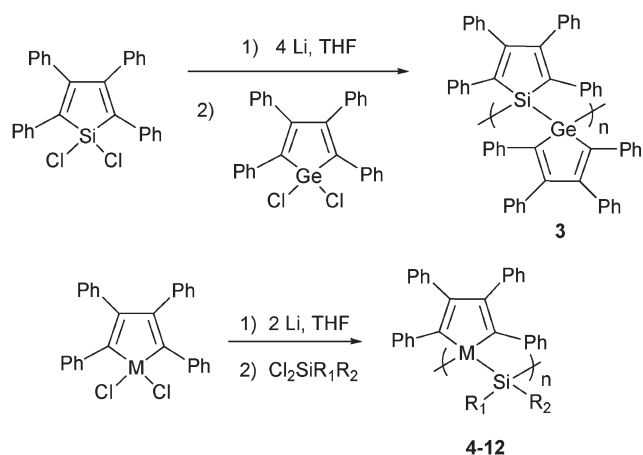


Fig. 10 X-Ray crystal structure of silole dimer shows H1A–Si1–Si2–H2A torsion angle of 90.2(2)°.

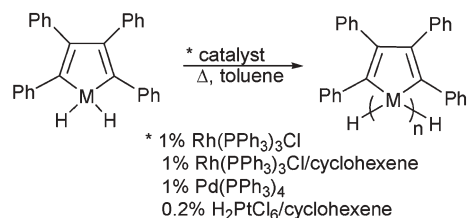


Scheme 2 Synthesis of copolymers **3**; **4–9**: M = Si, R₁ = H, Me, R₂ = Me, Et, Ph; and copolymers **10–12**: M = Ge, R₁ = H, R₂ = Me, Ph.

(370 nm) and visible emission (~ 510 nm), whereas polysilanes typically absorb and emit at 320 nm and 340 nm, respectively.⁶¹ The hydrophobic exterior also serves to separate the metallole chains and prevent self-quenching in the solid state. Polysiloles are usually much more luminescent in the solid state than in solution.

Polysilole and polygermole, **2**, have been synthesized in 30–40% yield by Wurtz coupling of the corresponding dichlorometallole (Scheme 1). Synthesis of co-polymers of metalloles and silanes, such as **4–12**,⁵¹ prepared by Wurtz condensation of dichlorometalloles and dichlorosilanes (Scheme 2), presents a means of tuning the HOMO–LUMO band gap while maintaining the σ -conjugation between metallole atoms along the metallole backbone.⁶² Recently, catalytic dehydrocoupling of the dihydrometallole monomer has been shown to produce the polymetalloles in 60–80% yield (Scheme 3), with similar molecular weights ($M_N = 3000$ –7000) as those polymers prepared by Wurtz type polymerizations.⁵⁹ Previous attempts to polymerize dialkylsilanes *via* dehydrocoupling reactions yielded only dimers and short chain oligomers.⁶³

The helicity of the polymetalloles and metallole–silane copolymer backbone creates a structure that should be selective in allowing intercalation of planar molecules, such as nitroaromatics. This suggests further that these polymers are attractive candidates for fluorescent nitroaromatic chemosensors. For instance, thin films of **1** can be used to detect 50 ppb of TNT in sea water in about 60 s.²⁹ Quenching increases with time as TNT is adsorbed by the polymers.



Scheme 3 Catalytic dehydrocoupling synthesis of polysilole **1** and polygermole **2**.

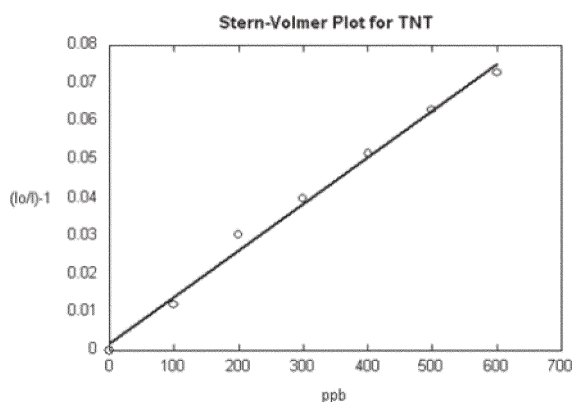


Fig. 11 Quenching efficiency defined by the Stern–Volmer relationship for TNT.

Solution phase detection studies were done by measuring photoluminescence quenching of **1–12** in toluene with successive additions of picric acid (PA), TNT, DNT, and NB analytes.⁶⁴ Fig. 11 shows the Stern–Volmer plot for luminescence quenching of a toluene solution of polysilole, **1**, by TNT.⁵¹ A linear Stern–Volmer relationship is observed for TNT with polysilole and polygermole, and copolymers **3–8**, but the Stern–Volmer plot for quenching by picric acid exhibits an exponential dependence for concentrations above 10^{-4} M.⁵¹ The 12 different luminescent polymers each exhibit a different response to picric acid, TNT, DNT, and NB as well as a varied quenching ratio between analytes (Fig. 12). This suggests construction of an electronic nose type sensor array^{65,66} to distinguish between a mixture of explosives, in which each vapor analyte produces a characteristic “fingerprint” response.

The K_{SV} of the analytes follows the order TNT > DNT > NB, which parallels the analyte reduction potentials. The fact that the quenching efficiency is related to the electron acceptor ability of the analyte suggests that electron transfer from the polymer to the analyte is the dominant mechanism of luminescence quenching. An alternative explanation might be that a charge transfer interaction between a polymer–quencher complex takes place; this would imply that the formation of such a complex becomes more favorable with increased

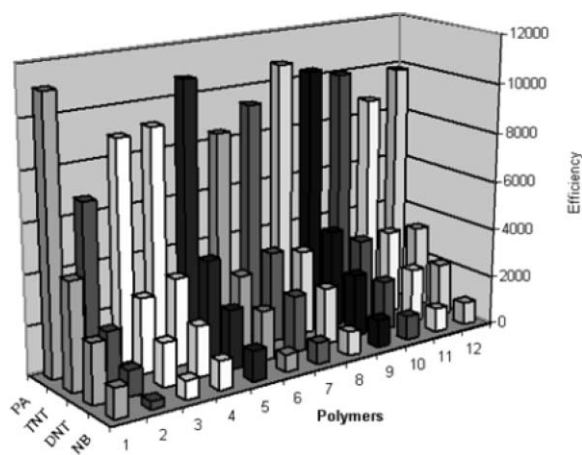


Fig. 12 Quenching efficiencies of polymers **1–12**.

electron acceptor ability of the analyte. However, there is no evidence for such a charge transfer complex in the absorption spectra.

The fluorescence lifetime of **1** is invariant as a function of quenching.⁵¹ This fact, in conjunction with linear Stern–Volmer plots, indicates that the mechanism is predominantly static quenching. In this case, K_{SV} represents an association constant between analyte and its receptor sites in the polymer chain. The helical structure of the polymers is proposed to provide stable intercalation sites for the planar nitroaromatics. The stability and selectivity of the silole polymers **1–12** is an attractive feature for their use as nitroaromatic sensors. Thin films of the polymers show no significant change in luminescence after prolonged exposure to oxygenated air or organic vapors (toluene, THF, MeOH). The selectivity of luminescence quenching of polysilole for TNT in solution is 644 % greater than that for benzoquinone.⁵¹

3. Resistive sensing of explosives using nonconducting organic polymers

Carbon black particles have been coated with an organic polymer and deposited as a thin film across metallic leads. This simple device shows changes in resistance on adsorption of analyte vapors.⁶⁷ The carbon black is necessary to impart electrical conductivity to an otherwise insulating organic polymer film. Resistance changes are simply due to the amount of swelling the polymer undergoes on absorbing organic vapor, which changes the effective concentration of conducting carbon particles. By manufacturing an array of sensing elements, each with a different polymer or polymer blend coating, a characteristic signal from specific analytes can be obtained in an electronic nose approach.^{65,66} Arrays are made of inexpensive, commercially available polymers, such as polystyrene, polysulfone, polyvinylbutyl, polycaprolactone, polyvinylacetate, polymethylmethacrylate, *etc.* Each polymer has a different response to an analyte depending on the partition coefficient of the analyte. Analytes which absorb to a greater extent cause a higher increase in film resistance. A 20 sensor array is able to successfully distinguish mixtures, such as H_2O from D_2O , as well as part per thousand concentrations of methanol, ethanol, acetone, acetonitrile and ethyl acetate.⁶⁸ For nitroaromatic vapors, the rates of adsorption are slower than for other organics, though the array accurately distinguishes DNT, TNT, and toluene. Detection limits for DNT vapor in the low ppb range are observed.⁶⁷

4. Polymeric coatings on SAW device sensors

Surface acoustic wave (SAW) detectors have received much attention as chemical sensors, specifically for explosive compounds, because they may be designed to selectively respond to analytes of interest. A SAW device consists of interdigitated electrodes on a piezoelectric substrate. Upon application of a voltage to the electrodes, the input transducer converts the electrical signal to an acoustic wave, which propagates through the substrate to the output transducer, where it is then reconverted into an electric signal. Chemically selective thin film coatings may be applied to the substrate,

which shift the frequency of the SAW. Adsorption of chemicals into the thin films further shifts the propagation velocity, which causes a change in the electrical output. By choosing a coating that selectively adsorbs explosive vapors, such compounds may be detected. Nitroaromatic sensing SAW devices have been prepared with silicone polymers,⁶⁹ carbowax polymers,⁷⁰ and cyclodextrin polymers.⁷¹

4.1 Inorganic silicone polymers

A number of siloxane polymers have been tested and shown to preferentially absorb nitroaromatic vapors over common interferent vapors, such as water and organic solvents (*e.g.* octane and toluene). Such selectivity is important to reduce false positives. One siloxane, which has shown a high sensitivity to nitrobenzene, is SXPFA (Fig. 13A).⁶⁹ The incorporation of the hexafluoroisopropanol (HFIP) substituent maximizes the polymer's affinity for nitroaromatic analytes. Aromatic nitro groups are electron-rich sites which possess hydrogen bonding basic sites (*i.e.* the lone pair electrons on oxygen). HFIP moieties along the polymer provide hydrogen bonding acidic groups in a similar spatial orientation. Since the HFIP oxygen lone pairs are not basic, water (two acidic H atoms) does not bind favorably. Therefore, this overcomes the problem of background humidity, which is an interferent in many absorptive sensors for polar analytes. A SAW device coated with 50 nm of the SXPFA film, operating at a 250 kHz frequency, shows a 90% drop in output frequency after exposure to 30 ppm of nitrobenzene. Remarkably, this signal is seen in only 4 s. A reversible signal is obtained with DNT, whose detection limit is estimated to be 235 ppt. Interferents include other molecules with basic H-bonding sites, such as organophosphonates.

4.2 Carbowax and carbowax–silica blends

Carbowax-1000 (Fig. 13B) is another organic polymer that has also been tested as a SAW device coating for nitroaromatics detection.⁷⁰ Thin films (10 μm) may be prepared by drop coating organic solutions of the polymer onto the device surface. The solvent used in the coating process is important in making smooth films. Benzene and chloroform solutions leave rough films with cavities of a few microns in diameter. Such large cavities affect the adsorbate loading mass and signal output. Acetone and methanol yield smoother films, although the high volatility of acetone creates a higher surface roughness. The terminal hydrogens in Carbowax-1000 provide hydrogen bonding acid groups, which may interact with the oxygen basic sites on the nitro groups of nitroaromatics. Wax films are stable and reversibly adsorb nitroaromatics up to 225 $^{\circ}\text{C}$. Carbowax coated silica blends also have the ability to

adsorb DNT vapor with higher adsorption rates at higher vapor concentrations. Only 30% of the vapor is adsorbed at 0.95 $\mu\text{g L}^{-1}$ DNT vapor, while 83% is adsorbed at 2.45 $\mu\text{g L}^{-1}$. Upon exposure to DNT, a SAW device coated with carbowax shows a rapid (<60 s) frequency change of 130 Hz for 117 ppb DNT, 156 Hz for 253 ppb and 168 Hz for 301 ppb. There is a linear frequency change response of about 0.2 Hz ppb^{-1} .

4.3 Cyclodextrins

Another strategy for using polymer coated SAW devices as explosive detectors is to embed analyte host cavities into the polymer films, rather than relying on hydrogen bonding acid/base interactions. Cyclodextrins, which are naturally occurring barrel-shaped ring structures of glucose units, are host species that contain a rigid framework with a hydrophobic cavity. Functionalization of the cyclodextrin produces a cavity with an enhanced affinity for hydrophobic species. Cyclodextrins functionalized with electron-rich trimethylbenzyl aromatic rings selectively adsorb polar molecules, such as electron-deficient nitroaromatic explosives, with much higher selectivity than nonpolar hydrocarbons.⁷¹ In order to deposit the host molecules in a uniform film, a vinyl-functionalized transducer surface must first be prepared on the SAW device. Surface conditioning involves coating the SAW device with poly(methylhydro)siloxane, followed by hydrosilation of a vinyl-substituted aromatic containing cyclodextrin. This step-wise preparation, which uses the siloxane polymer to immobilize the cyclodextrin host, creates a smooth 30 μm thick surface coating. Atomic force microscopy images show a surface roughness of about 3 μm , as compared to a 15 μm surface roughness obtained by the simple spin coating of cyclodextrins. A smooth surface reduces noise in the sensor, making surface attachment by hydrosilation the preferred method of film growth. The coated device shows a 75 Hz frequency change response in the presence of 2 ppb of 2-nitrotoluene. In contrast, a SAW device coated with the siloxane polymer alone, without the cyclodextrin, shows no response to 600 ppb of 2-nitrotoluene. The response is also reversible and reproducible. Adsorption of DNT and TNT vapor is much faster than desorption, although saturation is not achieved after several minutes. It is possible that the thickness of the films allows for permeation of the DNT and TNT deep into the film which contains the cyclodextrin cavities. A 60 s exposure time is necessary to effect a 100 Hz frequency change. The slow desorption rate may explain the higher sensitivity to nitroaromatics than to more volatile compounds like water, octane, and toluene. In addition, it is possible that a sensor array may be manufactured using several SAW devices with various functionalized cyclodextrins to develop characteristic response patterns for analyte identification.

5. Polymer nanoparticles as redox sensors

There is much interest in the potential applications of nanoparticles, even chemical sensors. Fluorescent inorganic nanoparticles have recently been applied to the detection of explosive compounds through luminescence quenching. For example, fluorescent silicon nanoparticles, whose sizes range

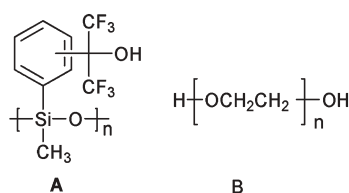


Fig. 13 Polymers for SAW device coatings.

from about 1–100 nm, may be dispersed in an aerosol onto a substrate suspected of being contaminated with an explosive. If explosive vapors are present and adsorb onto the nanoparticle, a subsequent decrease in luminescence intensity is observed. Porous silicon is a high surface area inorganic substance that exhibits luminescence quenching on exposure to vapors of nitroaromatics at the ppb level.⁷² At 5 min exposure of porous silicon nanocrystallites to saturated vapor of NB, DNT, and TNT, detection limits as low as 500 ppb, 2 ppb, and 1 ppb, respectively, are obtained. Commercially available CdSe quantum dots (QD) protected with a ZnS shell are another example of a fluorescent inorganic material with the ability to detect TNT in solution by luminescence quenching.⁷³ Emission from the QD may be stimulated with a femtosecond laser near the absorption band edge of TNT; upon exposure to TNT there is a shift in the emission maximum accompanied by a quenching of luminescence. For example, a toluene solution of 3.2 nm diameter CdSe/ZnS nanoparticles emits around 567 nm; its emission is blue-shifted ~10 nm with the addition of ppb levels of TNT. Adaptation of the QD may be carried out to apply these sensors to detection in aqueous media. In addition to these inorganic nanoparticles, nanoparticles of organometallic polymers have also been investigated as detectors of TNT in aqueous media.

5.1 Polysilole nanoparticles

Colloidal solutions of tetraphenylsilole compounds, prepared by the rapid precipitation of an organic solution (ethanol, THF) with water, show significantly enhanced (up to 300 ×) luminescence over their organic solutions.⁷⁴ A colloid of poly(tetraphenyl)silole, **1**, which has been shown to detect nitroaromatics when dissolved in organic solvents,⁵¹ may be precipitated to detect TNT in aqueous media.⁷⁵ A minimum of 60% water is necessary to form the colloid, as indicated by a sharp rise in luminescence (Fig. 14). The amount of aggregated polymer depends on the volume fraction of the water in the resulting colloid. At 50% water fraction, only 3% of silole is aggregated, but the value rises to 30% at 60% water, paralleling the rise in luminescence at these water fractions (Table 1). At 80% water and above, nearly all (>95%) of the polysilole is aggregated. Dynamic light scattering measurements show that the colloid consists of particles about 80 nm in diameter, with a polydispersity of about 20%.

In a pH 7 buffered colloid, luminescence quenching is observed with as low as 100 ppb TNT.⁶⁹ Linear Stern–Volmer

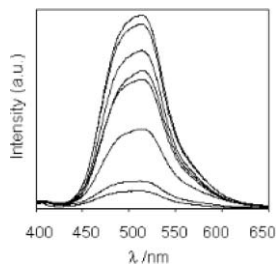


Fig. 14 Fluorescence spectra of polysilole aggregates in THF : H₂O suspensions with %H₂O, from top, equal to 90, 80, 95, 99, 70, 60, 50, and 0%.

Table 1 Summary of percentage of aggregated silole, particle diameters (*D*), mean lifetimes of emission (τ), and Stern–Volmer constants (K_{SV}), for nanoparticle suspensions of **1** (6 mg L^{−1}) at various water fractions

% H ₂ O	<i>D</i> /nm	% aggregated	τ /ns	K_{SV}
0 ^a	—	<1	0.590	970
50	—	3	0.625	2800
60	90	30	1.43	3400
70	90	55	2.48	3300
80	70	>95	3.64	5000
90	60	>95	3.84	4100
95	70	>95	3.48	4300
99	100	>95	3.26	4500

^a In THF.

relationships are observed for both the colloidal and solvated polysilole in the ppm range. Fluorescence lifetimes of nanoparticle suspensions are largely unchanged by added TNT, indicating a static quenching mechanism, as previously observed for TNT and polysilole in toluene solution.⁵¹ It is hypothesized that the TNT molecule preadsorbs into the polysilole nanoparticles.

Quenching efficiencies of TNT on the various colloids may also be analyzed using the Stern–Volmer equation. A 4-fold improvement in quenching efficiency is observed for the nanoparticles relative to the polysilole dissolved in THF (Table 1). In addition, shaking of the colloid with TNT for longer times more than doubles the quenching efficiency and detection limits as low as 20 ppb are observed. Shaking may aid in the bulk mixing of the sample and the interaction of the nanoparticle and analyte. Chemical modification can be used to incorporate anion binding groups so that silole nanoparticles may be used to detect CrO₄^{2−} and other oxidizing anions in the aqueous phase.⁷⁰

6. Visual detection of solid-state nitroaromatic explosives

Highly sensitive visual detection of trace explosive particles can be achieved using techniques that rely on a chemical reaction between a detector molecule and an explosive compound that produces a colored product. As described in section 1, the low volatility of many explosives makes vapor detection approaches problematic. The tendency of explosives to adhere to surfaces makes solid state detection an attractive alternative. Surface contamination may arise from spillage during bomb making, transfer to surfaces from contaminated hands or clothing, or even from unexploded residue post-detonation. Colorimetry is a method of detection that generates a colored dye upon reaction of detector molecule and analyte. Colorimetric sensors have been commercialized for detecting explosives in soil, water, and on surfaces, including the forensic test for a person who recently handled explosives. Although many of these methods do not utilize polymers in their detection schemes, they are discussed because their ease of use makes them attractive candidates for the inexpensive and rapid detection of explosives. Such simple methods are urgently needed for field-deployable detector systems. Colorimetric and fluorescent methods for the visual

detection of explosives are beginning to be developed based on polymeric systems.

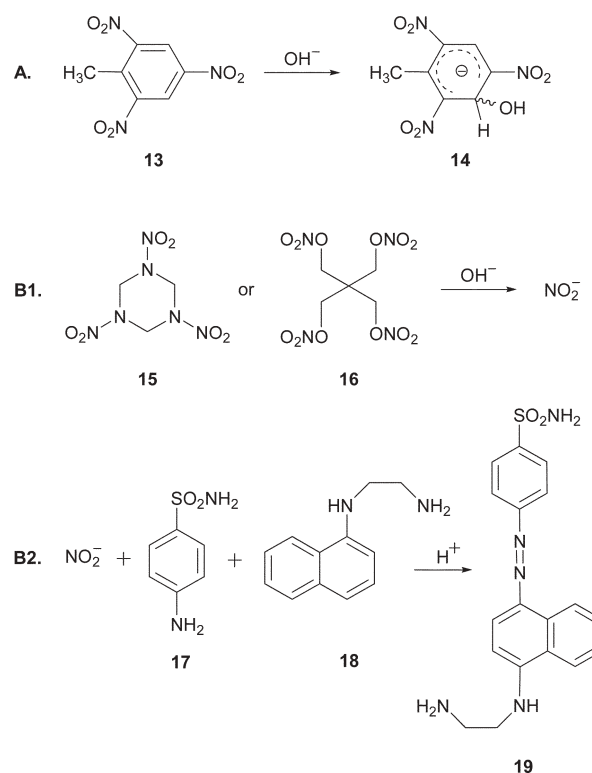
6.1 Colorimetric detection

One highly sensitive colorimetric detection system uses a thin film of a divinyl/styrene copolymer embedded with 10–40% of the inorganic cymantrene (cyclopentadienylmanganesetri-carbonyl) dye, which exhibits a color change on contact with several nitroaromatics.⁷⁶ A 3 μm film, prepared by spin coating a toluene solution of the polymer onto glass slides, turns blue–green after 1–3 minutes of UV irradiation after contact with a fingertip contaminated with DNT, DNB, or NT. Films not exposed to the explosive do not display this color change. The presence of the nitroaromatic can be quantified by optical absorption measurements at 680 nm. High quality fingerprint images are visible with this method, and detection limits as low as 0.2 ng of DNT have been obtained. The cymantrene-embedded polymer may also be spray coated on various substrates such as wood, leather, plastic, metal, paper, and luggage.

Several commercially available solid-state chemical detection kits are able to detect explosives through colorimetry, with sensitivity purported down to the tens-of-nanogram level. Detection of nitroaromatics is achieved, as depicted in Scheme 4A (TNT, **13**, is representative of nitroaromatic compounds). The chemical specificity relies on the reaction of the aromatic ring with a strong base, which produces a colored Meisenheimer complex, **14** (e.g. reddish-brown for TNT and yellow for PA). Detection of nitramines (e.g. RDX, **15**) and nitrate esters (e.g. PETN, **16**) is achieved by adding a second reagent, to the same area as the first, containing an aromatic amine and an aromatic nucleophile (Scheme 4B). The first reaction with base produces nitrite ions. The second step involves a Griess reaction in an acidic medium with the liberated nitrite and the aromatic amine (e.g. sulfanilamide, **17**) followed by a coupling reaction with the aromatic nucleophile (e.g. *N*-1-naphthylethylenediamine, **18**). This reaction produces an intensely pink-colored azo dye (e.g. **19**). A third step may be used to detect inorganic nitrates, such as ammonium nitrate. A reducing agent, such as zinc dust, reduces nitrate ions to nitrite ions, which then undergo the Griess reaction with the compounds applied in the second step. Despite high sensitivity in the laboratory, performance evaluation tests by Sandia National Laboratory in the field show a practical detection level for TNT of 200 ng, and many false positives are known to occur.²⁵ Colorimetric detection has also been extended to chlorate and bromate type explosives using aniline salts in an acidic medium.⁷⁷ Reaction of aniline sulfate with chlorates produces a dark blue color, while reaction with bromates produces a blue–pink colored product.

6.2 Fluorimetric detection of trace explosive residue

One attractive use of luminescent polymers is in imaging explosive contaminants on surfaces.⁷⁸ Polysilole (**1**), polygermole (**2**), polysilafluorene (Fig. 15) and related metallole-containing copolymers (Fig. 16), prepared by hydrosilation of diethynylbenzene by dihydrometalloles,⁷⁹ are useful for this purpose. Thin films of the polymers may be applied to



Scheme 4 Reactions for colorimetric detections of explosives in commercial spray can kits. A: Base reacts with nitroaromatics to produce colored Meisenheimer complexes. B1: Base reacts with nitramines or nitrate esters to liberate nitrite ion. B2: Nitrite ion reacts with an aromatic amine and an aromatic nucleophile to produce an azo dye.

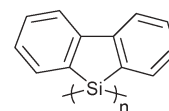


Fig. 15 Polysilafluorene (PSF).

contaminated surfaces by spray coating an acetone or toluene solution of the polymer on the surface followed by drying. A simple black light ($\lambda_{\text{ex}} \sim 340 \text{ nm}$) is used to excite the polymer, which fluoresces (near 490–510 nm for siloles, 470–500 for germoles, and 360–400 nm for silafluorenes). Dark spots in the luminescent image indicate the presence of an analyte quencher under the film and are visible immediately. Visible

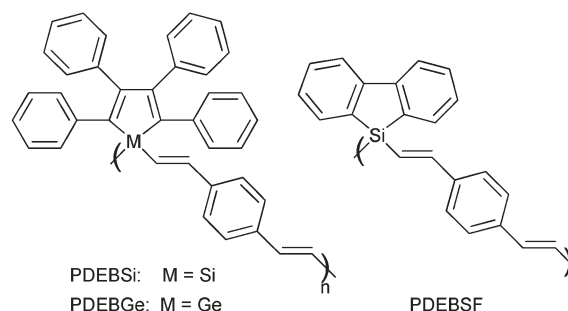


Fig. 16 Copolymers of metalloles and diethynylbenzene used for surface detection of nitroaromatics.

Table 2 Solid-state detection limits (ng) of nitroaromatic explosives on porcelain, using thin films of metallole-containing polymers

	TNT	DNT	PA
PSi	10	40	40
PDEBSi	10	20	20
PGe	5	30	30
PDEBGe	10	50	30
PSF	5	20	5
PDEBSF	10	20	5

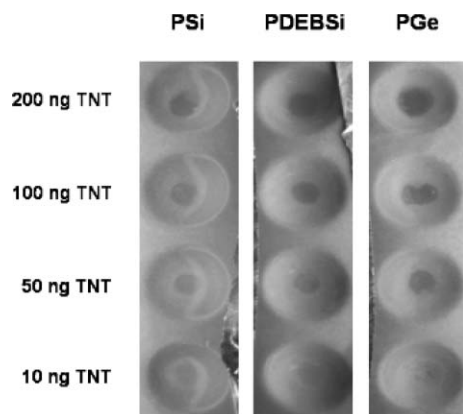


Fig. 17 Luminescence quenching of polymers PSi, PDEBSi, and PGe, by 200, 100, 50, and 10 ng TNT on porcelain plates.

detection limits on porcelain plates as low as 5 ng are obtained for TNT and picric acid and limits as low as 10–20 ng are obtained for DNT (Table 2). Detection limits are determined as the lowest amount of explosive necessary for an independent observer to detect quenching by eye. Fig. 17 shows a black and white image of visible quenching of polysilole luminescence in the presence of 200, 100, 50, and 10 ng of TNT. Detection limits are listed in Table 2, and are comparable to or exceed many commercially available colorimetric detection systems.

Detection studies at an explosives testing range were performed to observe the ability of polymers **1** and PDEBSi (Fig. 16) to detect real-world explosives, rather than purified laboratory explosive samples.⁷⁴ Experiments were performed by contacting a gloved hand to a solid explosive, removing any excess solid, and then contacting filter paper with the contaminated glove. This procedure allows testing of the polymers applicability in detecting trace contamination as it would be found in the real world, *i.e.* as solid particulates from the solid phase of the explosive, rather than as deposited from solution. Both polymers are able to detect military-grade TNT and Comp B, which is a TNT/RDX blend.

There is promise for the application of many luminescent polymers to the visual imaging of nitroaromatic explosives using this fluorimetric technique. Polymers that emit in the green are attractive for this purpose because the human eye is most sensitive in this spectral region. However, polymers that emit more in the blue spectral region may be of use in detecting less powerful oxidizers due to their larger HOMO–LUMO band gaps. UV-imaging equipment may be helpful in supplementing visualization where the human eye is less sensitive.

7. Future directions and challenges

Luminescent polymers have shown adaptability for detecting a variety of explosives under a variety of conditions. In some cases, excellent sensitivity has been achieved with reasonable specificity. Specificity derives from the binding interaction that occurs between the polymer and analyte, as well energetic considerations in the redox-based quenching process. Additional factors include kinetic considerations for electron transfer quenching. Most systems are limited to detection of nitroaromatic-based explosives. Extension of detection to other classes (*e.g.*, nitramine, nitrate, and peroxide) remains an area in need of further progress. Sensitivity is another issue, which depends on some of the same factors described above, as well as on issues such as the extent of exciton delocalization along the polymer chain or between adjacent chains in solids. Although data are not available for the use of luminescent polymers in imaging trace explosive residues, other than for metallole polymers, this is a fertile area of research. Laser action in polymer sensing films offers another potential method for significant sensitivity enhancement. Many polymer sensors for explosives rely on fluorescence quenching mechanisms; however, greater sensitivity might be achieved by nonfluorescent materials that become fluorescent in the presence of explosives. Improved specificity in absorptive SAW-based polymer sensors might best be achieved by using them as semispecific sensors at the back end of a micro- or miniature gas chromatograph.

The feasibility of using polymer sensors in specific methods of detection involves considerations such as ease of synthesis, cost, and toxicity. For highly sensitive detection of explosive vapors in electronic devices, sensitivity is the overriding issue because of the small amount of polymer sensing film needed. For applications in chemical test kits for monitoring ground water, sensitivity and cost become more important. For applications in trace particle detection *in situ*, cost and toxicity of the reagent are crucial. Biodegradability is another important consideration when detection schemes use direct application of the sensing material. Finally, stability of materials to air, oxygen, water and other environmental variables is important not only for issues of long-term storage and use, but these factors also often determine the limits of the stability of the sensor.

Acknowledgements

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