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Photoluminescent metalloles for chemical sensing of nitroaromatic explosives and chromium(VI)

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Photoluminescent Metalloles for Chemical Sensing of Nitroaromatic Explosives and Chromium(VI)

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Chemistry by Sarah Josepha Toal

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2005
The dissertation of Sarah Josepha Toal is approved, and it is acceptable in quality and form for publication on microfilm.

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Karsten Deake

John B. Doolin

Kathi C. Troeger

Chair

University of California, San Diego

2005
DEDICATION

For my dad, for encouraging me to study philosophy, for showing me that the quest for wisdom must never end, and that we seek knowledge, not for its own sake, but for the power to do good;

For my mom, for teaching me that happiness is gained by serving others;

For my brothers, Ray and Adam, who always protected me as their little sister;

For my sister Mary, like whom I have always strived to be;

For Noëlle, Michael, and Joy, for bringing my siblings happiness, and whom I love as my own siblings.
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<tbody>
<tr>
<td>Å</td>
<td>Ångström</td>
</tr>
<tr>
<td>[A]</td>
<td>Analyte concentration</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2’-Azobisisobutyronitrile</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>BQ</td>
<td>benzoquinone</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
</tr>
<tr>
<td>CCDC</td>
<td>Cambridge Crystallographic Data Centre</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>°</td>
<td>degree</td>
</tr>
<tr>
<td>Δ</td>
<td>delta, heat, or change</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift; ppm</td>
</tr>
<tr>
<td>D</td>
<td>diameter</td>
</tr>
<tr>
<td>d</td>
<td>doublet or days</td>
</tr>
<tr>
<td>DEB</td>
<td>diethynylbenzene</td>
</tr>
<tr>
<td>DNB</td>
<td>dinitrobenzene</td>
</tr>
<tr>
<td>DNT</td>
<td>dinitrotoluene</td>
</tr>
<tr>
<td>e⁻</td>
<td>electron</td>
</tr>
<tr>
<td>ε</td>
<td>molar extinction coefficient; M⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>ε&lt;sub&gt;max&lt;/sub&gt;</td>
<td>molar extinction coefficient at wavelength of maximum absorption; M⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>E₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
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<tr>
<td>eV</td>
<td>Electron-Volt (1 eV = 1.6·10⁻¹⁹ Joules)</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
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<tr>
<td>Φ</td>
<td>fluorescence quantum yield</td>
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<td>Φ&lt;sub&gt;rel&lt;/sub&gt;</td>
<td>relative fluorescence quantum yield</td>
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<td>fg</td>
<td>femtogram</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz, s(^{-1})</td>
</tr>
<tr>
<td>I</td>
<td>fluorescence intensity</td>
</tr>
<tr>
<td>(I_0)</td>
<td>initial fluorescence intensity</td>
</tr>
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<td>IMS</td>
<td>ion mobility spectrometry, ion mobility spectrometer</td>
</tr>
<tr>
<td>INEPT</td>
<td>insensitive nuclei enhanced by polarization transfer</td>
</tr>
<tr>
<td>IR</td>
<td>infrared (spectroscopy or radiation)</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>(K_{SV})</td>
<td>Stern-Volmer constant</td>
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<tr>
<td>kHz</td>
<td>kilohertz</td>
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<tr>
<td>(\lambda)</td>
<td>wavelength, lambda</td>
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<td>wavelength of excitation, lambda</td>
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<tr>
<td>L</td>
<td>liter</td>
</tr>
<tr>
<td>LED</td>
<td>light emitting diode</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>M</td>
<td>molar; mol L(^{-1})</td>
</tr>
<tr>
<td>(M_w)</td>
<td>weight-averaged molecular weight</td>
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<tr>
<td>(M_N)</td>
<td>number-averaged molecular weight</td>
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<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>m(^3)</td>
<td>cubic meter</td>
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<td>MCL</td>
<td>maximum contaminant level</td>
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<tr>
<td>MeOH</td>
<td>methanol</td>
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<td>mg</td>
<td>milligram</td>
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<td>microgram</td>
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<td>mHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>MIP</td>
<td>molecularly imprinted polymer</td>
</tr>
<tr>
<td>(\mu L)</td>
<td>microliter</td>
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<td>mL</td>
<td>milliliter</td>
</tr>
<tr>
<td>(\mu m)</td>
<td>micrometer</td>
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<tr>
<td>(\mu M)</td>
<td>micromolar</td>
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<tr>
<td>mM</td>
<td>millimolar</td>
</tr>
<tr>
<td>(\mu mol)</td>
<td>micromole</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>mol</td>
<td>mole, 6.022(\cdot)10(^{23})</td>
</tr>
<tr>
<td>MP</td>
<td>melting point</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>ms</td>
<td>millisecond</td>
</tr>
<tr>
<td>MS(ES)</td>
<td>mass spectroscopy (electrospray)</td>
</tr>
<tr>
<td>NB</td>
<td>nitrobenzene</td>
</tr>
<tr>
<td>ng</td>
<td>nanogram</td>
</tr>
<tr>
<td>NHE</td>
<td>normal hydrogen electrode</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>ns</td>
<td>nanosecond</td>
</tr>
<tr>
<td>PA</td>
<td>picric acid</td>
</tr>
<tr>
<td>π</td>
<td>pi; bond or orbital</td>
</tr>
<tr>
<td>π*</td>
<td>pi-star; anti-bonding π orbital</td>
</tr>
<tr>
<td>PA</td>
<td>polyacetylene</td>
</tr>
<tr>
<td>pH</td>
<td>pH = -log[H⁺]</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>PPE</td>
<td>poly(ρ-phenylethenylene)</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>ppt</td>
<td>parts per trillion</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(ρ-phenylenevinylene)</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond</td>
</tr>
<tr>
<td>QD</td>
<td>quantum dot</td>
</tr>
<tr>
<td>r.t.</td>
<td>room temperature</td>
</tr>
<tr>
<td>σ</td>
<td>sigma; bond or orbital</td>
</tr>
<tr>
<td>σ⁺</td>
<td>Hammet parameter</td>
</tr>
<tr>
<td>σ⁻</td>
<td>Hammet parameter</td>
</tr>
<tr>
<td>σ*</td>
<td>sigma-star; anti-bonding σ orbital</td>
</tr>
<tr>
<td>s</td>
<td>singlet or seconds</td>
</tr>
<tr>
<td>SAW</td>
<td>surface acoustic wave</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>τ</td>
<td>tau, mean lifetime of emission</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl or trimethylsilane</td>
</tr>
<tr>
<td>TNB</td>
<td>trinitrobenzene</td>
</tr>
<tr>
<td>TNT</td>
<td>trinitrotoluene</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultra-violet – visible radiation</td>
</tr>
<tr>
<td>V</td>
<td>volts</td>
</tr>
<tr>
<td>v</td>
<td>wave number, cm⁻¹</td>
</tr>
<tr>
<td>W</td>
<td>Watts</td>
</tr>
<tr>
<td>w:v</td>
<td>weight:volume; g solute per 100 mL solvent</td>
</tr>
</tbody>
</table>
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Chapters Two, Four, and Five are reprints of material published as listed in the publication list on page xxi. Chapter Three is a print of material submitted for publication to the Journal of Forensic Sciences. Material in Chapter One will be submitted to the Journal of Materials Chemistry as a “Feature Article.” The dissertation author was the primary researcher and author in these publications.
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2002 – 2005 Achievement Rewards for College Scientists Scholar

2003  M.S., Chemistry, University of California, San Diego

2005  Ph.D., Chemistry, University of California, San Diego


ABSTRACT OF THE DISSERTATION

Photoluminescent Metalloles for Chemical Sensing of
Nitroaromatic Explosives and Chromium(VI)

by
Sarah Josepha Toal
Doctor of Philosophy in Chemistry
University of California, San Diego, 2005
Professor William C. Trogler, Chair

Photoluminescent metallacyclopentadienes, or metalloles, are shown to be highly sensitive and selective sensors for oxidant molecules. The method of detection is through electron-transfer quenching of the luminescence of the metallole by the electron-deficient analytes. The capability of metalloles to act as redox sensors results from their low energy LUMO and small HOMO-LUMO band gap energy.

An improved catalytic dehydrogenative coupling synthesis of the explosives sensing polysilole and polygermole is detailed. This new method requires less hazardous reagents and offers significantly improved product yields over traditional
Wurtz coupling syntheses. Addition of a hydrogen-accepting alkene co-reagent further improves polymer yield and molecular weight. Dehydrogenative coupling proceeds through either a catalytically homogeneous or heterogeneous mechanism, depending on the catalyst used. Homogeneous catalysts, RhCl(PPh\textsubscript{3})\textsubscript{3} and Pd(PPh\textsubscript{3})\textsubscript{4}, produce a significant amount (40%) of the silole dimer, thus limiting chain length and overall yield. The heterogeneous catalyst, H\textsubscript{2}PtCl\textsubscript{6}, produces higher molecular weight polymer product. Reaction mechanisms are proposed to account for this difference.

Polymetalloles and novel copolymers of diethynylbenzene and dihydrometalloles are investigated as detectors of solid-state nitroaromatic explosives, namely trinitrotoluene, dinitrotoluene, and picric acid. Thin films of the polymers are highly photoluminescent and show visual luminescence quenching in the presence of the explosives. Thin films are prepared via spray coating an organic solution of the polymers and the presence of explosives is confirmed by visual inspection of the film when illuminated with near UV radiation. Detection limits as low as 5 ng are possible.

Aqueous TNT detection is possible at 20 parts per billion (ppb) using colloidal polysilole nanoparticles. Fluorescence quenching efficiencies improve by 400% for the nanoparticles relative to the dissolved polymer. Nanoparticles, formed by the precipitation of an organic solution of the polymer with water, are approximately 80 nm in diameter, and have fluorescence lifetimes near 3.8 ns.

Functionalization of metalloles can produce redox sensors specific to other analytes. Thus, catalytic hydrosilation of allylamine by methylhydrosilole yields a
chemoselective chromate sensor. A colloid of siloleamine nanoparticles is able to detect 100 ppb CrO$_4^{2-}$. The sensor is selective to chromate and relatively insensitive to other oxoanion interferents commonly found in water supplies.
CHAPTER I

REVIEW OF METALLOLE CHEMISTRY, EXPLOSIVES DETECTION, AND CHROMIUM(VI) DETECTION

1.1 REVIEW OF METALLACYCLOPENTADIENES (METALLOLES)

1.1.1 Electronic Properties of Metalloles

Metallacyclopenta-2,4-dienes, or metalloles, are a class of organometallic compounds that are analogous to cyclopentadiene but have a Group 14 element (Si, Ge, Sn, Pb) substituted at the sp³ carbon (Figure 1-1).

![Metallole structure with position numbering](image)

M = Si, Ge, Sn, Pb

Figure 1-1 Metallole structure with position numbering

Metalloles are an interesting group of heterocyclic molecules because of their unique electronic structure. The highest occupied molecular orbital (HOMO) is depicted in
Figure 1-2A. The lowest unoccupied molecular orbital (LUMO) is of $\pi^*$ character and at low energy due to conjugation with the two exocyclic $\sigma^*$ orbitals on the metalloid atom (Figure 1-2B). This additional conjugation results in a lowering of the LUMO energy by 1.289 eV for 1,1-dihydrosilole as compared to cyclopentadiene.\(^1\)

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,\(^2\) electroluminescent devices,\(^3,4\) light emitting diodes (LEDs),\(^5\) and redox polymer sensors.\(^6\)

Figure 1-2  HOMO (A) and LUMO (B) of 2,5-diphenylsilole, $\text{Ph}_2\text{C}_4\text{SiH}_2$, from the \textit{ab initio} calculations at the HF/6-31G* level. Reprinted with permission from \textit{JACS}, 2003, 125, 3821; Copyright American Chemical Society

Functionalization of metalloles permits tuning of the HOMO-LUMO band gap energy. 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. 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.\textsuperscript{7} Functionalization of the 3,4 positions on the metallole ring also has a small effect on photophysical properties, but may be useful in fine-tuning of absorption and emission wavelengths.\textsuperscript{8} Substituents on the 2,5 positions of the metallole ring, however, have a much larger effect on the optoelectronic properties of the metallole.

The effects of 2,5-substituents on the photophysical and electronic properties of siloles have been studied extensively.\textsuperscript{9} The wavelengths of absorption and emission, and redox potentials of a series of nine 2,5-bis(mono substituted phenyls)-3,4-diphenylsiloles derivatives were characterized, three examples of which are shown in Figure 1-3. The substituents on the 2 and 5 phenyls were varied from electron donating groups, e.g. NMe\textsubscript{2} and OMe, to electron withdrawing groups, e.g. NO\textsubscript{2} and CF\textsubscript{3}. Absorption maxima range from 358 to 423 nm and fluorescence maxima range from 466 to 529 nm. The first oxidation (E\textsubscript{pa1}) and reduction (E\textsubscript{pc1}) potentials vary over a range of 1 V each. Emission maxima wavenumbers are linearly proportional to the difference in energy between E\textsubscript{pa1} and E\textsubscript{pc1}. These results illustrate the potential for tuning the HOMO-LUMO band gaps based on functionalization at the 2,5 positions. In addition, E\textsubscript{pa1} and E\textsubscript{pc1} exhibit a linear relationship with the Hammet parameters\textsuperscript{10} \(\sigma^+\) and \(\sigma^-\), respectively, suggesting that the wavelength of emission could be predicted for 2,5-bis(mono substituted phenyl)-3,4-diphenylsiloles derivatives. Thus, tuning of the HOMO-LUMO band gap is controllable and possible with 2,5-substitution of the metallole ring.
Table 1-3 Wavelengths of absorption ($\lambda_{\text{abs}}$) and emission ($\lambda_{\text{em}}$) in CHCl$_3$ and oxidation ($E_{\text{pa1}}$) and reduction ($E_{\text{pc1}}$) potentials for 1mM sample in n-Bu$_4$NCIO$_4$ (0.1 M) in CH$_3$CN for some 2,5-diaryl-3,4-diphenylsiloles

<table>
<thead>
<tr>
<th>R</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$E_{\text{pa1}}$ (V)</th>
<th>$E_{\text{pc1}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-NMe$_2$</td>
<td>423</td>
<td>529</td>
<td>+ 0.11</td>
<td>- 2.43</td>
</tr>
<tr>
<td>H</td>
<td>359</td>
<td>467</td>
<td>+ 1.02</td>
<td>- 2.27</td>
</tr>
<tr>
<td>$p$-NO$_2$</td>
<td>399</td>
<td>522</td>
<td>+ 1.28</td>
<td>- 1.44</td>
</tr>
</tbody>
</table>

Figure 1-3 Wavelengths of absorption ($\lambda_{\text{abs}}$) and emission ($\lambda_{\text{em}}$) in CHCl$_3$ and oxidation ($E_{\text{pa1}}$) and reduction ($E_{\text{pc1}}$) potentials for 1mM sample in n-Bu$_4$NCIO$_4$ (0.1 M) in CH$_3$CN for some 2,5-diaryl-3,4-diphenylsiloles

Functionalization of the metalloles with various aryl substituents at the 2,5 positions have revealed the extensive conjugation of the aryl groups and $\pi$-system of the butadiene moiety. For instance, the 2,5-distyrilsilole has a 76 nm red-shifted absorption maximum (435 nm) and a 60 nm red-shifted emission maximum (527 nm) relative to 2,5-diphenylsilole (Figure 1-4A). The 2,5-bithienylsilole (Figure 1-4B) has even further red shifted absorption (476) and emission (527) maxima. A restricted conformation of the backbone maintains planarity of the $\pi$-system and increases $\pi$-conjugation, which accounts for the red-shifts. Redox potentials of the molecules may be regulated by functionalization with various $\pi$-systems.
1.1.2 Syntheses of Metallole Monomers

The first metallole synthesized was hexaphenylsilole in 1959.\textsuperscript{11} The synthesis employed involves the reductive coupling diphenylacetylene with lithium metal to form 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, followed by addition of dichlorodiphenylsilane. This is a general means of preparation of tetraphenylmetalloles that are functionalized at the metalloid atom (Scheme 1-1). Zirconacyclopentadienes\textsuperscript{12} may also be used to form 1,1-difunctionalized siloles (Scheme 1-2). A general synthesis for 2,5-difunctionalized siloles entails the reaction of bis(phenylethynyl)silanes with lithium naphthalide (Scheme 1-3A).\textsuperscript{13} However, using a bis(phenylethynyl)diaminosilane allows for both 2,5-difunctionalization and 1,1-difunctionalization (Scheme 1-3B).\textsuperscript{14} There are now several known synthetic routes for metallole preparation.\textsuperscript{1,15}

![Scheme 1-1 Synthesis of tetraphenylsiloles with dilithiobutadiene](image-url)
Scheme 1-2  Zirconocene catalyzed synthesis of 1,1-difunctionalized siloles with substituted acetylenes

Scheme 1-3  Syntheses of siloles using bis(phenylethynyl)silanes

1.1.3 Polymetalloles and Metallole-Containing Polymers

1.1.3.1 Poly(2,5-metalloles) and Copolymers

Poly(2,5-metalloles) are polymers whose monomer units are connected through the α-carbons of the metallocycle ring. Direct coupling of a 2,5-disubstituted
silole to make polymer is difficult, and is only achievable if the monomer is sterically unhindered at the 3 and 4 positions.\textsuperscript{16}

Many copolymers linked through the 2 and 5 positions have been synthesized. Palladium (Pd) catalyzed cross-coupling reactions, using Pd(dba)\textsubscript{2} as the catalyst, are useful for this purpose. Silole-arene copolymers have been synthesized in this manner. Aryl linkers have also been incorporated as 2,5-bridging units between siloles from the coupling of 2,5-dihalosiloles and distanyldiethynylarenes (Scheme 1-4).\textsuperscript{17} These polymers typically exhibit longer absorption maxima than their corresponding monomers, indicating extensive delocalization of the $\pi$-system across the polymer backbone.

\begin{equation}
\begin{aligned}
\text{Bu}_3\text{Sn} \equiv & \text{SnBu}_3 \\
\text{Ph} \quad & \equiv \text{Ph} \\
\text{Ph} \quad & \equiv \text{Ph} \\
\text{Br} \quad & \equiv \text{Br} \\
\text{Si} \quad & \equiv \text{Si} \\
R \quad & \equiv R
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\text{Bu}_3\text{Sn} \equiv & \text{SnBu}_3 \\
\text{Ph} \quad & \equiv \text{Ph} \\
\text{Ph} \quad & \equiv \text{Ph} \\
\text{Si} \quad & \equiv \text{Si} \\
R \quad & \equiv R
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\text{Si} \quad & \equiv \text{Si} \\
\text{Br} \quad & \equiv \text{Br} \\
R \quad & \equiv R
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\text{Ph} \quad & \equiv \text{Ph} \\
\text{Ph} \quad & \equiv \text{Ph} \\
\text{Bu}_3\text{Sn} \equiv & \text{SnBu}_3 \\
\text{Si} \quad & \equiv \text{Si} \\
R \quad & \equiv R
\end{aligned}
\end{equation}

Scheme 1-4 Pd catalyzed cross coupling for synthesis of aryl-bridged silole polymers

1.1.3.2 Poly(1,1-metalloles) and Copolymers
Poly(1,1-metalloles) are polymers whose monomer units are connected at the metalloid center. One example is poly(tetraphenyl)silole, 1 (Figure 1-5), which possesses a Si-Si backbone surrounded and protected by the organic bulk of the phenyl substituents on the silacyclopentadiene ring. The structure of 1 is likely helical (Figure 1-5). In addition, the $\pi^*$ LUMO$^{18}$ is greatly lowered in energy because of $\sigma^*$-$\pi^*$ conjugation between the $\sigma^*$ orbitals of the polysilicon chain and the $\pi^*$ orbital of the butadiene moiety. This delocalized excited state provides an efficient pathway for electron transfer quenching by analytes that can penetrate the hydrophobic exterior. This conjugation also results in a near UV absorption (370 nm) and visible emission (~510 nm), whereas polysilanes typically absorb and emit at 320 nm and 340 nm, respectively.$^{19}$

![Figure 1-5](image.png)  
**Figure 1-5** Chemical structure and space filling model showing the helical structure of polysilole 1. Reprinted with permission from *JACS*, 2003, *125*, 3821; Copyright American Chemical Society
Polysilole and polygermole, 2, have been synthesized in 30-40% yield by Wurtz coupling of the corresponding metallole dichloride (Scheme 1-5A). Synthesis of co-polymers of metalloles and silanes, such as 3-11, prepared by Wurtz condensation of dichlorometalloles and dichlorosilanes, presents a means of tuning the HOMO-LUMO band gap while maintaining the $\sigma$-conjugation between metalloid atoms along the metalloid backbone (Scheme 1-5B).

Scheme 1-5  (A) Wurtz coupling synthesis of polysilole 1 and polygermole 2; (B) Synthesis of copolymers 3 – 7: $M = Si$, $R_1 = H$, $Me$, $R_2 = Me$, $Et$, $Ph$; and copolymers 4 – 11: $M = Ge$, $R_1 = H$, $R_2 = Me$, $Ph$

Metallole units may also be incorporated into other polymers, such as polysilanes. Ring opening polymerization is one method to produce these polymers (Scheme 1-6). Interestingly, when the polysilane moiety is excited with 323 nm light, fluorescence near 510 nm is observed, corresponding to the emission of the silole
unit. This indicates efficient energy transfer from the silane to the silole and broad conjugation along the Si-Si backbone.

\[
\begin{align*}
\text{Si} \quad \text{Ph} & \quad \text{M} \quad \text{Si} \\
\text{Si} \quad \text{Si} & \quad \text{1) cat } n\text{-BuLi} \quad \text{2) EtOH} \\
\end{align*}
\]

**Scheme 1-6** Synthesis of poly(1,1-metalloles) by ring opening polymerizations: 
\( M = \text{Si or Ge} \)

Metallole units may also be linked through the metalloid atom through aryl bridging units. This may be done by the coupling of dilithiobutadiyne with a mono- or dihalometallole \(^{21}\) (Scheme 1-7A), or with a Pd/Cu catalyzed cross-coupling of 1,1-diethynilsilole with a dihaloaryl unit (Scheme 1-7B) \(^{22}\). A variety of bridging \( \pi \)-systems may be incorporated this way, presenting another means of varying the optoelectronic properties of these polymers \(^{23}\).

\[
\begin{align*}
\text{A.} & \quad \begin{array}{c}
\text{Ph} \quad \text{Si} \quad \text{Ph} \\
\text{H} \quad \text{Cl}
\end{array} + \begin{array}{c}
\text{Li} \quad \equiv \equiv \equiv \quad \text{Li}
\end{array} \rightarrow \begin{array}{c}
\text{Ph} \quad \text{Si} \quad \text{Ph}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{B.} & \quad \begin{array}{c}
\text{Ph} \quad \text{Si} \quad \text{Ph} \\
\text{Si} \quad \equiv \equiv \quad \equiv
\end{array} + \begin{array}{c}
\text{X} \quad \equiv \equiv \quad \equiv \quad \text{X}
\end{array} \rightarrow \begin{array}{c}
\text{Ph} \quad \text{Si} \quad \text{Ph}
\end{array}
\end{align*}
\]

\[X = \text{Br, I} \quad Z = p\text{-dibromobenzene, 4,4'-diiodonaphthal, 2,5-diiodothiophene, etc.}\]

**Scheme 1-7** Synthesis of poly(1,1-silole) copolymers via (A) dilithiobutadiyne coupling and (B) Pd/Cu catalyzed crosscoupling with aromatic dihalides
1.2 REVIEW OF EXPLOSIVES SENSING USING REDOX POLYMERS

1.2.1 The Explosives Threat

Chemical sensors for the rapid detection of explosives are important because they are relevant to military and humanitarian applications, such as demining, remediation of explosives manufacturing sites,\textsuperscript{24} and forensic and criminal investigations.\textsuperscript{25,26} Homeland security applications are attracting increased research, because terrorists frequently employ conventional explosive bombs. There are various methods of explosives detection currently available. Many simple techniques are often inefficient. Metal detectors, which are commonly used for explosives sensing, are limited to devices packaged in metal. The use of canine detectors is expensive because dogs require care and are easily fatigued.\textsuperscript{27} 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,\textsuperscript{28} surface enhanced Raman spectroscopy,\textsuperscript{29} nuclear quadrupole resonance,\textsuperscript{30} energy dispersive X-ray diffraction,\textsuperscript{31} neutron activation analysis, electron capture detection,\textsuperscript{24} and cyclic voltammetry.\textsuperscript{32} Ion mobility spectrometry, which is the most commonly used explosive detection system in airports, has sensitivity in the picogram to nanogram range, but is also expensive, operator dependent, prone to false positives and must be frequently calibrated.\textsuperscript{33}

High explosives consist of an intimate mixture of a chemical oxidant and reductant. Several nitroaromatic explosives are known, such as TNT, tetryl, and picric acid. Mixtures of high explosives are also commonly used. TNT, an inexpensive high
explosive is a component of fifteen explosive compositions.\textsuperscript{34} For example, TNT and DNT are widely used in industrial explosives containing ammonium nitrate. Tritonal is a mixture of TNT and Al powder. Amatol is a mixture of ammonium nitrate and TNT.\textsuperscript{35} Pentolite is a mixture of PETN and TNT and Composition B is a blend of RDX and TNT. Because of their widespread use and volatility, nitroaromatics comprise an important general class of explosives compounds for explosive vapor sensing. Chemical structures of a sample of nitroaromatic explosives are shown in Figure 1-6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of nitroaromatic and nitrate explosives}
\end{figure}

Both soil and water testing is necessary to locate unexploded mines;\textsuperscript{36-38} however, interference problems are troublesome in both media. Consequently, trace detection is often limited to vapor samples over soil. This narrows the focus to the
more volatile explosives, such as DNT and TNT, whose equilibrium vapor pressures are roughly 100 and 5 ppb, respectively. Concentrations of such volatile explosives may be 2-6 times less than their equilibrium vapor pressures due to their enclosure in a bomb casing, and because mixtures of explosive materials have lower vapor pressures than their pure compounds. Sensing of volatile components in soil headspace will also depend heavily on ambient temperature and humidity. For example, the vapor pressure of TNT quadruples between 20° and 30 °C. In addition, explosives have a tendency to adsorb onto surfaces, such as wood, paper, and soil. Water competes with TNT and DNT for binding sites on soil particles, thereby releasing more TNT and DNT into the headspace. Both dogs and chemical vapor sensors are more efficient when soil moisture content is high.

The low volatility of TNT and other explosives makes solid-state detection an attractive alternative to vapor detection. Surface detection of trace particles is important in forensic investigations for identifying unexploded residue subsequent to detonation. It is also known that explosive particles contaminate clothing and materials during preparation and packaging of explosive devices. For this reason, solid state detection may be useful for security screening procedures. Some solid-state explosives detection systems are already available. For instance, it is believed that canines detect explosives by inhalation of trace particulates. Many airport security systems detect explosives on persons by using an air “puffer,” which dislodges particles on hair and clothing and guides them into an IMS. Similarly, luggage may be swiped to adhere solid particles, which may then be sent to an IMS. These solid
state detection systems are bulky, expensive, and must be calibrated frequently. Commercially available colorimetric kits are able to detect a variety of explosive contaminants on surfaces with sensitivity at the tens of nanograms level; however, field tests have shown many false positives to occur with significantly higher detection limits (200 ng for TNT).

In addition to antiterror motivation, there are environmental health and safety concerns. Exposure to TNT is believed to cause anemia, abnormal liver function, and cataracts. Its toxicity and suspected carcinogenicity has led the EPA to establish a Health Advisory Standard, a non-mandatory technical guide for authorities, for TNT in drinking water at 2 parts per billion. Therefore, highly sensitive methods for detection of TNT and other nitro-based explosives in soil and groundwater is essential.

1.2.2 Fluorescent Organic Polymers for Redox Sensing of Explosives

One property of nitroaromatics which may be exploited in their detection is their electron acceptor capability. Substitution of the electron-withdrawing nitro groups on the benzene ring makes the $\pi$-system electron deficient, thereby making the compound a good electron acceptor. As expected, reduction potentials become more favorable (less negative) as nitro-substitution is increased, according to nitrobenzene (-1.15 V), DNT (-0.9 V), and TNT (-0.7 V), versus NHE. Conjugated polymers are promising candidates for redox sensing of explosives because they are usually
electron rich and may be easily oxidized. This reducing nature is further enhanced in their delocalized excited states.

1.2.2.1 Polyacetylenes

Polyacetylenes have been investigated as potential nitroaromatic sensors. For example, thin films of poly([1-phenyl-2-(4-trimethylsilylphenyl])acetylene (PTMSDPA) (Figure 1-7) have been shown to detect DNT vapor at low concentrations. Catalytic polymerization of the TMSDPA monomer with a TaCl₅/n-Bu₄Sn catalyst produces a high molecular weight polymer (Mₘ = 293,000) which is fluorescent at 520 nm, and has a relatively high quantum yield (Φ = 0.25) and a short lifetime (50 ps) in toluene solution. Casting the polymer into thin films (3-100 nm) shifts the emission only slightly to 533 nm, indicating 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. This structure also gives rise to a high fractional free volume of 0.26, which imparts permeability and allows analytes to penetrate quickly into the polymer and quench luminescence.

![Figure 1-7 Poly[1-phenyl-2-(4-trimethylsilylphenyl)ethyne] (PTMSDPA)]
Luminescence quenching may be monitored to detect small amounts (part per billion) of nitroaromatic analytes. Response times to various nitroaromatic quenchers decreases with increased vapor pressure 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 fluorescence quenching process. No shift in emission wavelength is observed upon analyte exposure, indicating that exciplexes are not formed. The emission intensity of exposed films is regained after standing in air or upon heating, indicating that binding of the analyte and the quenching process are reversible.

1.2.2.2 Poly(p-phenylenevinylenes)

Poly(p-phenylenevinylenes) (PPV) have also been explored as nitroaromatic sensors. These conjugated polymers, like polyacetylenes, are strongly luminescent and have high permeabilities to small molecule analytes, such as nitroaromatics. Figure 1-8 (A and B) shows two such polymers which undergo luminescence quenching with TNT and DNT vapor at the ppm level. As with the previously discussed polyacetylenes, the bulky phenyl substituents of these PPVs hinder π-stacking and self quenching. The MEH-PPV polymer (Figure 1-8A) shows greater quenching efficiency than DP10-PPV (Figure 1-8B). In this 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). One factor which may lead to 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 efficiency is that, according to molecular modeling calculations, the backbone of MEH-PPV is almost planar, while that of the 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 more effective exciton migration along the polymer backbone. For this reason, a non-polar polyacetylene (BuPA, Figure 1-8C), which contains a repeat unit rotational angle of 51°, has a quenching efficiency that is even lower than DP10-PPV. Both PPV polymers had larger quenching efficiencies with the saturated vapor from DNT than TNT, which is simply explained by its higher vapor pressure (~100 times that of TNT). A relatively weak response was observed with benzoquinone, even though BQ has the highest vapor pressure and is most easily reduced. Evidently, the polymers have a lower binding affinity for BQ 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 alone should only effect the time response.
The addition of surfactants to poly(p-phenylenevinylene) has also been explored as a means to improving polymer-analyte interactions. A water soluble anionic polymer, poly(2,5-methoxy-propyloxysulfonate phenylenevinylene) (MPS-PPV, Figure 1-8D), shows luminescence quenching 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 PPV polymer reduces the quenching efficiency 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. Thus, the surfactant acts to increase the association between neutral organic analytes and the polymer. The quenching efficiency of TNT, for example, in a 1:3 surfactant-polymer solution is amplified nearly ten-fold as compared to a DTA-free solution. A low concentration of TNT ($8.5 \times 10^{-6}$ M) effectively quenches MPS-PPV luminescence ($K_{SV} = 9.3 \times 10^4$ M). A similar amplification is observed with DNT as well.

Thin films of MPS-PPV also show efficient luminescence quenching upon exposure to DNT. The adsorption of DNT is not reversible, presumably due to strong coulombic interaction between the polymer and electron-deficient analyte. However, addition of a thin layer of the DTA surfactant over the polymer allows for reversibility in the DNT binding while maintaining sensor sensitivity. With only 10 minutes of heating an exposed polymer, 90% of the original luminescence is regained. The DTA layer provides a permeable barrier which allows for analyte penetration but limits the electrostatic interaction between the polymer and analyte.

1.2.2.3 Poly($p$-phenyleneethynlenes)

A related class of highly-conjugated fluorescent organic polymers which shows remarkable nitroaromatic detection capability is poly($p$-phenyeneethynlenes) (PPE). In particular, thin films of the PPE, developed by Swager and coworkers (Figure 1-9A), show rapid quenching of their blue luminescence (465 nm) when exposed to TNT vapor at sub part per trillion (ppt) levels. 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. This functional group also provides a porous packing arrangement in the solid state, which prevents interchain $\pi$ stacking and self-quenching of luminescence. 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%) upon heating or upon solvent washings. A further consequence of the porous packing arrangement is that it permits quenchers to penetrate rapidly into the film. A 25 Å film shows 50% quenching after a 30 s exposure to TNT vapor, and 75% at 60s. Response to DNT is even higher with 91% and 95% quenching observed at 30s and 60s, 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 $\pi-\pi$ interactions between the electron-rich polymer and BQ, which has a smaller electrostatic potential in the center of the aromatic ring relative to TNT and DNT. Polarizability and dipolar interactions dominate the interaction between analytes and polymeric sensors. In addition, BQ shows better quenching efficiency for thicker films; this is consistent
with a greater number of cavities in a thicker coating, which are more effective in trapping the more volatile analyte.

The pentaptycene-conjugated polymer has been fabricated into a semiselective sensor array for the tip of an optical fiber bundle. This sensor primarily detects the more volatile DNT. Short (200 ms) sampling times are needed to detect the explosives. Nomadics Inc. has fabricated and commercialized a landmine detector using this promising technology.

\[ \text{A: } R = C_{14}H_{29} \]

\[ \text{B: } R = C_{6}H_{12} \]

**Figure 1-9** Pentaptycene containing polymers: A) a poly(p-phenyleneethynlene) and B) copolymer with a dibenzochrysene

Swager and coworkers have also copolymerized the pentaptycene monomer with a dibenzochrysene monomer to yield a highly fluorescent polymeric material with greater sensitivity to TNT than the pentaptycene polymer (Figure 1-9B). Formation of the dibenzochrysene monomers proceeds through a novel 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 subnanosecond time scale.

1.2.2.4 Polymeric Porphyrins

Porphyrins functionalized with unsaturated substituents (Figure 1-10) have been crosslinked to form luminescent polymeric sensors with the ability to selectively bind explosives, such as TNT and trinitrobenzene (TNB). The method of detection relies on monitoring the change in optical absorption and/or emission following analyte binding. Selectivity is established during polymerization by utilizing the targeted analytes in the reaction mixture to serve as templating agents. After removal of the analytes, the polymers contain cavities which are permanently shaped like the targeted species. These are examples of “Molecularly Imprinted Polymers” (MIP).

For example, 1 weight % porphyrin with a stoichiometric amount of TNT, 83-88 mole % styrene, 5-10 weight % divinylbenzene (as a crosslinker), and 1 % percent 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. The resulting polymer is porous with shape selective cavities for TNT binding. The 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 (which will be discussed later). 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 specified for detection of a range of explosive analytes in both the vapor and solution phases.

![Figure 1-10 Porphyrins, polymerizable through R₁ functionality: R₁ = 4-vinylphenyl, styrene, etc.; R₂ = H, alkyl, aryl, halide](image)

1.2.3 Fluorescent Inorganic Polymers for Redox Sensing of Explosives

As described in section 1.2.2, electron rich conjugated organic polymers are good candidates for explosives detection because they may undergo electron transfer from their low lying excited state to the π* orbital of nitroaromatics. Electron rich conjugated inorganic polymers are also expected to exhibit similar behavior, and thus
may be good candidates for explosives sensors. Polysilanes comprise one such class of inorganic polymers.

Polysilanes are air-stable luminescent polymers with a Si-Si backbone. Their numerous applications include uses fluorescent materials for radiation detection, electroluminescent materials for display devices, and photorefractive materials for holographic data storage. Their unique electronic properties arise from $\sigma$-conjugation along the Si-Si chain, which gives polysilanes high hole mobility, high nonlinear optical susceptibility, and efficient emission in the UV spectral region. Such properties make polysilanes candidates for explosives detection as well. Two types of polysilanes that have shown the ability to detect nitroaromatics through luminescence quenching are rigid fluoroalkylated polysilanes and polymetalloles.

1.2.3.1 Fluoroalkylated Polysilanes

Poly(3,3,3-trifluoropropylmethysilane), 12, is shown in Figure 1-11. This rigid polymer exhibits photoluminescence quenching of its 335 nm emission ($\Phi = 0.36$ in THF) upon exposure to nitroaromatics in both THF solution or as a thin film in water. Detection limits lie in the ppm range for both. 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. Thus helical, or coil, shaped polysilanes have broad absorption bands due to their many segments in the $\sigma$-
conjugated Si backbone with different photoexcitation energies. In contrast, rod-like polysilanes have narrow absorptions due to a single photoexcitation state and enhanced emission due to greater energy migration along the linear conjugated backbone. Polysilane 12 shows both a broad absorption band at 285 nm and a narrow absorption band at 320 nm, indicating 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.

![Fluoroalkylated polysilane](image)

**Figure 1-11** Fluoroalkylated polysilane

Addition of nitroaromatics to a THF solution of 12 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 [$K_{SV} = (0.84 - 4.15) \times 10^4 \text{ M}^{-1}$] approximately 5-10 times higher than those obtained with polymetalloles. Polymer 12 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, in interacting with an adjacent Si of the backbone, stabilize the HOMO and LUMO. In addition, the electron-withdrawing effect may also increase the positive charge on silicon, thus increasing its ability to interact with the nitro groups of the explosives. A noncovalent interaction between the Si and the nitro group facilitates electron transfer from the electron rich Si backbone to the electron deficient nitroaromatic, thus causing photoluminescence quenching. Such interactions are supported by $^{29}$Si NMR data. A sample of 12 with picric acid is shifted slightly downfield (0.48 ppm) from a sample of 12 alone. This is consistent with the deshielding effect due to a weak interaction between the Si and the nitro group.

Thin films of 12 also detect nitroaromatics in water. Quenching efficiencies for PA and DNT more than double for the thin film over the THF solution, likely due to more efficient energy transfer in the solid state. In addition, the quenching is reversible. Washing an exposed film with MeOH or water allows for complete recovery of the luminescence. The first use of a film in detection shows 150% higher quenching efficiency than a MeOH or water treated film. 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 absorption, indicative of a helical film. However, UV data from the same film after exposure to PA and washing with MeOH or water shows a decrease in the 285 nm absorption and the appearance of the absorption band at 328 nm, consistent with a more ordered helical polymer film. A more ordered film will have smaller free volumes and quencher diffusion into the
film is more restricted, thus resulting in reduced quenching efficiencies. In addition, the polymer thin film is insensitive to various organic solvents (hexane, toluene, methanol), inorganic acids (sulfuric and hydrochloric) and oxygenated air.

1.2.3.2 Polymetalloles and Metallole-Silane Copolymers

The ability of polymetalloles and metallole-silane copolymers to detect nitroaromatics stems largely from their electronic, photophysical, and structural properties, which are discussed in section 1.1. Detection is achieved by observing luminescence quenching of the polymers by the electron deficient analyte under a long wave UV light. These polymers are highly sensitive. For example, thin films of 1 can detect 50 ppb of TNT in sea water in only 60 seconds.\(^5\)

Solution phase detection studies were done by measuring photoluminescence quenching of 1-11 (Scheme 1-5) in toluene with successive additions picric acid (PA), TNT, DNT, and NB analytes. Differences in quenching efficiency for various analytes in solution phase were quantified using the Stern-Volmer equation: \((I_0/I) - 1 = K_{SV}[A]\).\(^6\) A linear Stern-Volmer relationship is observed for polygermole, 2, and copolymers 3-7 for TNT and DNT, but the Stern-Volmer plot for quenching by picric acid exhibits an exponential dependence for concentrations above \(10^{-4}\) M.\(^6\) The 11 different polymers each exhibit a different response to picric acid, TNT, DNT, and NB, as well as a varied quenching ratio between analytes. This may be useful in construction of an “electronic nose” type sensor array to distinguish between a mixture of explosives.
The $K_{SV}$ of the analytes follows the order TNT $>$ DNT $>$ NB, which parallels analyte reduction potential. 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 mechanism of luminescence quenching (outer-sphere electron transfer). An alternative explanation might be that a charge transfer interaction between a polymer-quencher complex takes place (inner-sphere electron transfer); this would imply that the formation of such a complex becomes more favorable with increased electron acceptor ability of the analyte.

The stability and high selectivity of the helical silole polymers 1-11 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, nor to organic vapors (toluene, THF, MeOH), nor to the inorganic acids $\text{H}_2\text{SO}_4$ or HF. In addition, polysilole in organic solution exhibits a greater selectivity to nitroaromatic compounds than the pentiptycene conjugated polymer (Figure 1-9), while being less responsive to interferents. For instance, the Stern-Volmer constant for 1 with TNT ($4.34 \times 10^3 \text{ M}^{-1}$) is 644 % greater than that for benzoquinone ($K_{sv} = 674 \text{ M}^{-1}$). However, the pentiptycene polymer exhibits only 1.2 times greater sensitivity to TNT than to benzoquinone. Such selectivity may be accounted for by the helical structure of the silole, into which planar molecules may intercalate, but which would minimize interactions of other analytes with the shielded silole chromophores.
1.2.4 Resistive Sensing of Explosives Using Organic Polymers

Carbon black particles coated with different organic polymers and deposited into thin films across metallic leads show changes in resistance upon adsorption of vapors.\textsuperscript{69} The carbon black is necessary to impart electrical conductivity to an otherwise insulating organic polymer film. The resistance changes are simply due to the amount of swelling the polymer undergoes, and so, the presence of vapor components is detected. 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. Resistance signals are processed and analyzed to determine the composition of a complex mixture of analyte vapors. Arrays are made of inexpensive, commercially available polymers, such as polystyrene, polysulfone, polyvinylbutyl, polycaprolactone, polyvinylacetate, polymethylmethacrylate, etc. Each polymer has a different response to different analytes depending on the partition coefficients of the analytes. Analytes which absorb to a greater extent cause a higher increase in film resistance. A 20 sensor array is able to successfully distinguish H\textsubscript{2}O from D\textsubscript{2}O, as well as methanol, ethanol, acetone, acetonitrile and ethyl acetate. For nitroaromatic vapors, the rates of adsorption are slower than for other organics, though the array accurately distinguishes DNT, TNT, and toluene.

1.2.5 Polymeric Coatings on SAW Device Sensors
Surface acoustic wave (SAW) detectors have received much attention recently as chemical detectors, specifically for explosive compounds, because they may be designed to selectively respond to specific analytes of interest. A SAW device consists of two interdigitated transducers, comprised of interdigitated electrodes, on a piezoelectric substrate. After an applied voltage to the electrodes, the input transducer converts the electrical signal to an acoustic wave, which propagates through the substrate to the output transducer, whereby it is 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 which selectively adsorbs explosive vapors, the presence of such compounds could be achieved. Attempts to manufacture nitroaromatic sensing SAW devices have used silicone polymers,\textsuperscript{70} carbowax polymers,\textsuperscript{71} and cyclodextrin polymers.\textsuperscript{72}

A number of siloxane polymers have been tested and shown to preferentially adsorb nitroaromatic vapors over common interferents vapors, such as water and organic solvents, e.g. octane and toluene. Such selectivity is important to reduce false positives. One siloxane in particular which has shown a high sensitivity to nitrobenzene is SXPHFA (Figure 1-12A).\textsuperscript{70} The incorporation of the hexafluoroisopropanol (HFIP) substituent maximizes the polymers affinity to nitroaromatic adsorption. Aromatic nitro groups are electron-rich sites which possess hydrogen bonding basic sites (i.e. the oxygens). HFIP moieties along the polymer provide hydrogen bonding acidic groups in a similar spatial orientation. A SAW
device coated with 50 nm of the SXPHFA film with an operating frequency of 250 kHz shows a 90% drop in output frequency upon exposure to 30 ppm of nitrobenzene. Remarkably, this signal is seen in only 4 seconds. A reversible signal is obtained with DNT, whose detection limit is estimated to be 235 ppt.

Figure 1-12 Polymers for SAW device coatings

Carbowax-1000 (Figure 1-12B) is an organic polymer with hydrogen bonding acidic sites that has also been tested as a SAW device coating for nitroaromatics detection. Thin films (10 µm) may be prepared by drop coating organic solutions of the polymer onto the surface of the device. The solvent used in the coating process proved to be important in making smooth films. Benzene and chloroform solutions left rough films with cavities a few microns in diameter, which affect the adsorbate loading mass per area and signal output. Acetone and methanol yielded smoother films, although the high volatility of acetone creates a higher surface roughness. Wax films are stable and reversibly adsorb nitroaromatics up to 225 °C. Carbowax coated silica blends 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 μg/L DNT vapor, while 83% was adsorbed at 2.45 μg/L. Upon exposure to DNT, a SAW device coated with the carbowax shows a rapid (< 60s) frequency change of 130 Hz for 117 ppb DNT, 156 Hz for 253 ppb and 168 Hz, for 301 ppb. Thus, there is a linear frequency change response of about 0.2 Hz/ppb.

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 are naturally occurring ring structures of multiple linked glucose units, and comprise one class of host species that contains a rigid framework with a hydrophobic cavity. Functionalization of the cyclodextrin produces a larger cavity with a stronger affinity towards hydrophobic species. The ability to functionalize the cyclodextrin allows the cavity to be properly tailored to its desired guest. Cyclodextrins functionalized with electron-rich trimethylbenzyl aromatic rings selectively adsorb polar molecules, such as electron-deficient nitroaromatic explosives, with much higher sensitivity than nonpolar hydrocarbons. 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 hydrosilation with poly(methylhydro)siloxane, followed by a reaction with a vinyl-substituted, aromatic containing cyclodextrin. This step-wise growth, first using the siloxane polymer to immobilize the cyclodextrin host, creates a smooth surface of about 30 μm in thickness. Atomic Force Microscopy images shows there to be a surface roughness of about 3 μm. Spin coating methods produce a film
with a 15 µm surface roughness. A smooth surface is necessary for low noise in the optical transduction; thus, hydrosilation is 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, does not respond to 600 ppb of 2-nitrotoluene. The response is reversible and reproducible. Adsorption of DNT and TNT vapor is much faster than desorption, though saturation is not achieved after several minutes. It is possible that the thickness of the films is sufficiently high that it allows for permeation of the DNT and TNT deep into the film which contains the cyclodextrin cavities. A 60 s exposure time was 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.

1.2.6 Inorganic Nanoparticle Sensors

Inorganic nanoparticles have recently been applied to the detection of explosive compounds. These species include silicon nanoparticles, and cadmium selenide (CdSe) quantum dots with a zinc sulfide (ZnS) shell.

Fluorescent silicon nanoparticles have been utilized to detect explosive compounds through luminescence quenching. Silicon nanoparticles, whose size range 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.

Commercially available CdSe quantum dots (QD) protected with a ZnS shell are another example of fluorescent inorganic material with the ability to detect TNT by luminescence quenching. Emission from the QD may be stimulated with a femtosecond laser near the absorption band edge of TNT. The emission maxima of such QD are well characterized and dependent on the particle size. Exposure of the QD to TNT results in a quenching of luminescence as well as a shift in the emission maximum. 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. Interestingly, a similar solution of 2.4 nm diameter nanoparticles, emitting at 518 nm, is about 5 nm red-shifted upon TNT addition. Quenching may be due to a charge transfer mechanism between the QD and the analyte, or by the introduction of new trap states for QD relaxation. Adaptation of the QD may be carried out to apply these sensors to aqueous media.

1.2.7 Porous Silicon for Vapor-Phase Detection of Explosives

Porous silicon is a high surface area inorganic substance that exhibits luminescence quenching upon exposure to vapors of nitroaromatics at the ppb level. Porous silicon is fabricated by the electrochemical etching of a single-crystal silicon wafer with hydrogen fluoride in aqueous ethanol. This produces nanocrystallites of Si in the porous structure which are visibly photoluminescent due to quantum
confinement effects. Quantum efficiencies up to 5% are observed. The luminescence may be quenched by adsorption of charge acceptors onto the surface or by oxidation of the surface by corrosive materials, such as NO₂. At 5 minute exposure of porous silicon nanostructures to saturated vapor of NB, DNT, and TNT, detection limits as low as 500 ppb, 2 ppb, and 1 ppb, respectively, are obtained. Like other methods that utilize fluorescence quenching mechanisms, the lower detection limits scale with the oxidizing capabilities of the analytes. Surface adsorption is a diffusion controlled process, however, and therefore response times scale with the vapor pressure; hence, quenching is observed more quickly by DNT vapor than by TNT vapor. Quenching is unaffected by light, as samples irradiated at 480 nm and those handled in the dark do not vary in their detection abilities. After prolonged exposure to nitroaromatic vapors, the original photoluminescence intensity does not recover, even after air purging or solvent washing of the porous silicon wafer. For example, after 16 h of DNT exposure, 95% of the photoluminescence is quenched, and only 75% of the original photoluminescence is recovered after ethanol washing. This indicates an energy transfer mechanism for luminescence quenching, as well as irreversible oxidation of the silicon surface. Oxidation introduces non-radiative defects on the surface in place of the emissive Si nanocrystallites. This is confirmed by the appearance of Si-O stretching vibrations in the IR spectrum of the wafer.

1.2.8 Colorimetric Sensors for Solid-State Explosives Detection
Visual detection of trace particulates explosive residue can be achieved using colorimetry. One such method involves the use of a polymer imbedded with a cymantrene dye. Other methods have been commercialized to detect explosives in soil, water, and on surfaces.

A thin film of a divinyl/styrene copolymer embedded with 10-40% of the inorganic dye cymantrene (cyclopentadienylmanganese-tricarbonyl) demonstrates a noticeable color change upon contact with several nitroaromatics. 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 exhibit this color change. The presence of the nitroaromatic was quantified via optical absorption measurements at 680 nm. High quality finger print images are visible with this method. Detection limits are purported to be as low as 0.2 ng of DNT. The cymantrene imbedded polymer may also be spray coated on various substrates such as wood, leather, plastic, metal, paper, and luggage.

1.3 INTRODUCTION TO CHROMIUM(VI) TOXICITY AND DETECTION

1.3.1 Chromium Toxicity

Chromium is a naturally occurring element which can exist in oxidations states ranging from 0 to +6, though it is mainly found in the +3 and +6 states. Chromium(III) is a mineral essential for normal function of glucose, lipid, and protein metabolism, and is believed to be necessary in the glucose tolerance factor.
Therefore, dietary deficiencies of Cr(III) can lead to a reduced potency in insulin regulation and diabetes.\textsuperscript{80}

Hexavalent chromium (Cr(VI)), found largely in the environment as chromate, (CrO$_4^{2-}$), is known to be highly toxic. Chromate is isostructural with sulfate, SO$_4^{2-}$; consequently, sulfate transporter proteins carry CrO$_4^{2-}$ into cells.\textsuperscript{79} Therein, the chromate reacts with the tripeptide glutathione, is reduced to more active Cr(V) and Cr(IV), and forms a chromium-sulfur bond. This immobilizes and traps Cr in the cell. It proceeds to bind to and oxidize DNA, while reducing to Cr(III). Because Cr(III) is not known to be toxic to cells, facilitated transport is a key feature of the toxicity of Cr(VI). However, uptake of Cr(VI) into the cell is not necessary for cellular damage. Cr(VI) may also alter surface proteins of cells, thereby bringing about cell death with the aid of helper T-cells.\textsuperscript{81} DNA mutations, chromosomal damage, and protein destruction all can be effects from Cr(VI) exposure.\textsuperscript{82} Physical manifestations of excessive Cr(VI) exposure include nasal (CrO$_2$Cl$_2$ vapor), skin, and stomach ulcers, kidney and liver damage, respiratory problems, and even lung cancer. Because of its high toxicity, the EPA has set a maximum contaminant level for total chromium in drinking water at 100 ppb.\textsuperscript{83} Since Cr(VI) is the carcinogenic form, it would be helpful to directly monitor the amount of Cr in this active form.

1.3.2 Industrial Uses of Chromium

Chromium containing minerals and alloys have many industrial applications. One such use of chromium is in dyes and paints. For instance, chromium salts are
used to impart a green color in glass. Ruby is simply Cr-doped Al₂O₃. Chromium also gives rise to the lasing properties of rubies, which have found wide use in scientific research. Doping of chromium into steel, to form stainless steel, enhances the anti-corrosion properties of the alloy.

Chromium is used in the process of transforming raw hides into leather. The process, called chrome tanning, imparts softness and elasticity to leather. In addition, chrome-tanned leathers are more water-resistant than other leathers. Sodium dichromate (Na₂Cr₂O₇) is the starting chromium source, though under the acidic tanning conditions it is hydrolyzed to form the more active chromium sulfate Cr(OH)SO₄.

Lumber and timber are often preserved with agents containing dichromate salts, such as chromated copper arsenate, acid copper chromate, and chromated zinc chloride. Most often, hexavalent chromium is used. Potassium or sodium dichromate (K₂Cr₂O₄ and Na₂Cr₂O₄) or chromic anhydride (CrO₃) are commonly used. The chromium component serves two purposes. First, the chromium salt acts as a fixative, preventing the leaching of the copper sulfate or other preservative agents. Secondly, the chromium neutralizes the corrosivity of other added preservatives, especially copper sulfate.

Electroplating chromium on surfaces is a common practice in the automobile industry, as well as others. A thin layer of chromium is often applied to surfaces in order to impart a shiny, durable, and non-corrosive finish to materials, such as steel, copper, brass, and even plastic. The main source of the Cr metal is a concentrated
solution of chromic acid ($H_2CrO_4$). Chrome plating plants are subject to strict environmental protection regulations from the Occupational Safety and Health Administration due to the large quantities of toxic hexavalent chromium used. In addition to toxic liquid waste produced, aerosols containing hexavalent chromium compounds are also formed.

1.3.3 Chromium in the Environment

In the environment, chromium exists mainly in the inert trivalent form in mineral deposits, such as chromite, FeCr$_2$O$_4$, eskolaite, Cr$_2$O$_3$, Cr(OH)$_3$, and amorphous iron chromium hydroxides, [Fe(III)Cr(III)(OH)$_3$].$^{85}$ In natural waters, which usually have a pH between 4 and 8, aqueous species of Cr(III) predominately take the form of Cr(OH)$_{2+}$ and Cr(OH)$_3$, with lesser amounts of Cr$_{3+}$ and Cr(OH)$_2^+$.$^{85}$ Hexavalent chromium minerals, such as chromium oxide (CrO$_3$), are scarce in nature, and typically do not contribute significantly to Cr(VI) species in water. Instead, naturally occurring Cr(VI) compounds in water are usually formed by redox processes,$^{86}$ such as the oxidation of Cr(III) by dissolved oxygen.$^{86}$ Manganese(IV) oxide (MnO$_2$), also oxidizes Cr(III) to Cr(VI), and is predominantly responsible for toxic CrO$_4^{2-}$ in both water and soil. Because it is an extremely redox active metal, the specific soil or water conditions play a significant role in the ecological chromium cycle.$^{85}$ For instance, environments rich in the powerful MnO$_2$ oxidizer are richer in Cr(VI) products than they would be otherwise. Environments that are rich in Fe(II)
and organic matter contain predominantly trivalent chromium products, as these assist in Cr(VI) reduction.

Most of the toxic hexavalent chromium found in the environment results from processed industrial waste. Industrial processing of natural ore deposits with soda ash and lime (CaCO$_3$) produces the commercially useable hexavalent chromium, according to the equation: $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 2\text{CO}_2$. The industrial waste residue resulting from the manufacturing process contains toxic Cr(VI) byproducts, such as CaCrO$_4$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCrO}_4$, and Fe(OH)CrO$_4$. After waste disposal, the harmful water-insoluble chromate salts slowly leach into soil and groundwaters over many years.

### 1.3.4 Methods of Chromium(VI) Detection

There are several methods of detecting chromium in soil and groundwater. These include ion chromatography-chemiluminescence, resonance ionization mass spectrometry-laser desorption, atomic spectroscopy, capillary electrophoresis-atomic emission spectrometry, electron capture-gas chromatography, electrochemical methods, and recombinant bacterial sensors. These methods exhibit varying degrees of sensitivity, with some in the parts per trillion (ppt) range. However, most require bulky and costly instrumentation which prevents simple on-site analysis.

A sensitive method for detecting aqueous chromium is through the combination of ion-chromatography and chemiluminescence. An ion exchange column with an appropriate eluent (a $\text{KNO}_3/\text{K}_2\text{SO}_4$ blend) is able to successfully
separate Cr(III) from Cr(VI). The flow is then joined with a second flow of reducing agent, which serves to reduce the Cr(VI) to Cr(III). A third flow stream is introduced containing a mixture of luminol and hydrogen peroxide. It is known that the reaction of these two species with an oxidant, in this case Cr(III), produces a highly luminescent chemical. Luminescence may be monitored to quantify the amount of analyte presence. Detection limits as low as 0.12 µg/L (120 ppt) and 0.09 µg/L (90 ppt) for Cr(III) and Cr(VI), respectively.

Resonance ionization mass spectroscopy coupled with laser desorption is a highly sensitive procedure of chemical analysis.\(^9\) This process has found application in chromium detection, with detection limits as low as 10 femtograms.\(^9\) In this technique, atoms are electronically excited, thermally desorbed from a filament, and passed through a time of flight mass spectrometer. The advantage of the low detection limit is offset by the high expense of the equipment and the difficulty in obtaining useful calibration curves.

Absorption spectroscopy can be used to detect colored complexes of chromium.\(^2\) An example of spectrophotometric determination of chromium(VI) involves forming a green complex (\(\lambda_{em} = 560\) nm) of dichromate (Cr\(_2\)O\(_4^{2-}\)) with malachite green. The two species may be reacted in the presence of acetic acid, with the color change occurring after ~10 min reaction time. Due to the intensely colored complex, detection limits as low as 0.410 ppb are observed.

Several other characterization techniques exist for aqueous chromium detection as well. Capillary-electrophoresis coupled with inductively coupled plasma
and atomic emission spectrometry may detect total chromium levels with detection limits near 5 ppb.\textsuperscript{93} Electron capture gas chromatography can detect Cr(III), and total Cr concentrations after reduction of other species to Cr(III), with a 15 ppt detection limit.\textsuperscript{94} Electrochemical methods are also available that can easily detect the presence as well as the oxidation states of chromium contaminants, with some reaching a detection limit of 220 ppb.\textsuperscript{95,96}

One approach to chromium detection in soil is through the use of recombinant luminescence bacterial sensors.\textsuperscript{97} Bacterial sensors have the advantage of utilizing metal-specific regulatory units in nature.\textsuperscript{98} Bacteria altered with luminescent tags undergo luminescence quenching when exposed to specific analytes. The sensors are often selective to chromium complexes, but are activated by both Cr(VI) and Cr(III) species. Control studies found that a detection limit of 2.6 $\mu$g/L (2.6 ppb) was possible for $\text{CrO}_4^{2-}$, but analysis from environmental samples indicate that only about 46% of the analyte is bio-available, while the majority remains adsorbed to soil particles. Bacterial sensors have the capability of reporting the concentration of analytes actually available to organisms, rather than the true concentration, which may be useful for environmental and safety regulation planning.

\textbf{1.4 OBJECTIVES OF THE DISSERTATION}

The objective of the research presented herein is to demonstrate the potential utility of metalloles as chemical sensors, specifically, as chemical sensors for nitroaromatic explosives and chromium(VI). This work builds upon prior knowledge
of the unique electronic structure of metallole and metallole polymers. The electronic structure gives rise to their characteristic photophysical properties and makes them candidates for many practical applications, including chemosensors.

Chapter 2 provides an account of an improved synthetic method for the preparation of polymetalloles. This new catalytic dehydrocoupling procedure offers a less hazardous synthetic route and improved product yields over the traditional Wurtz coupling methods.

Chapter 3 explores the usefulness of polymetalloles as solid state detectors of the nitroaromatic explosives TNT, DNT, and picric acid. A variety of metallole polymers and metallole-organic copolymers are examined, and detection limits in the low tens of nanograms are obtained.

Chapter 4 examines the photophysical properties of polysilole nanoparticles and their ability to detect aqueous TNT. A near 400-fold increase in luminescence quenching efficiency is observed for the nanoparticles over solution phase polysilole. Detection limits below 100 ppb are observed for TNT.

Chapter 5 extends the investigation of metallole chemosensors to silole monomers for chromium(VI) detection. Nanoparticles of silole monomers functionalized with hydrogen-bonding amine groups are able to detect chromate in water below the EPA MCL of 100 ppb. The photophysical properties of these nanoparticles are also presented.

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CHAPTER II

SYNTHESES OF OLIGOMETALLOLES BY CATALYTIC DEHYDROCOUPLING

2.1 ABSTRACT

The dehydrocoupling polycondensation of dihydro(tetraphenyl)metalloles (M = Si or Ge) with 0.2 mol % H$_2$PtCl$_6$·xH$_2$O and excess cyclohexene produces the respective oligometallole in high yield (>80%), where every silicon or germanium atom of the oligomer backbone is part of a silole or germole ring. Slightly less reactive catalyst systems of 1 mol % of Wilkinson’s catalyst, (RhCl(PPh$_3$)$_3$), or Pd(PPh$_3$)$_4$, yield the respective oligometallole in good yield (~60%). With these latter systems, and under less vigorous reflux conditions, the (tetraphenyl)silole dimer may be isolated in 40% yield. X-ray structural characterization of the dimer reveals a Si-Si bond length of 2.363(2) Å and an H-Si-Si-H torsion angle of 90(2)°. Using excess cyclohexene as a coreagent with RhCl(PPh$_3$)$_3$ increases the yield of oligomer and also eliminates dimer byproduct. The methyl-terminated dimer forms in the reaction between H$_2$PtCl$_6$·xH$_2$O and methylhydro(tetraphenyl)silole, but not in the similar reaction with the Rh and Pd catalysts. The methyl-terminated dimer has a Si-Si bond length of 2.375(1) Å and an H-Si-Si-H torsion angle of 92.3(1)°. Additionally, the oligosilole may be prepared by placing 1:2 dihydrosilole:cyclohexene and 1 mol % Wilkinson’s catalyst in an EmrysTM Optimizer microwave synthesizer for 2 h. The
molecular weight ($M_w$) of the oligometalloles ranges from 3000~7000. Even though the metallole possesses a secondary metalloid atom and contains bulky phenyl groups, polymerization may occur because the tetraphenylmetallole monomers have small angles at C-M-C (93.21° on C-Si-C and 90.14° on C-Ge-C), resulting in less steric hindrance at the metalloid center. Oligo(tetraphenyl)germole exhibits an absorption at 378 nm ($\varepsilon = 5400$ L/mol Ge·cm). The germole is photoluminescent in toluene solution, emitting blue-green light (498 nm, $\Phi = 0.01$). The hydrogen-terminated silole dimer shows a similar UV-vis absorption at 372 nm ($\varepsilon = 9600$ L/mol·cm), and luminesces green at 506 nm ($\Phi = 0.007$). The methyl-terminated dimer absorbs at 370 nm ($\varepsilon = 11800$ L/mol·cm) and luminesces blue at 468 nm ($\Phi = 0.004$).

### 2.2 INTRODUCTION

Siloles and germoles have attracted attention in recent years, because of their unusual electronic properties,\(^{1,2}\) and their applications as electron-transporting materials in electronic devices,\(^3\) polymer light-emitting diodes (PLED’s),\(^{4-6}\) and inorganic polymer sensors.\(^7\) Polymetalloles (M = Si or Ge) are unique in having both a M-M backbone and an unsaturated five-membered ring system. Characteristic features of the metallole unit are a low reduction potential and a low-lying LUMO, due to $\sigma^* - \pi^*$ conjugation from the interaction between the $\sigma^*$ orbital of the Si-Si or Ge-Ge chains and the $\pi^*$ orbital of the butadiene moiety of the ring.\(^{8,9}\) In addition, polymetalloles exhibit $\sigma - \sigma^*$ delocalization\(^{10}\) of the conjugated electrons along the M-M backbone.
Potential applications for polymetalloles have stimulated the search for more efficient synthetic methods. Current preparative routes use hazardous reagents and are of low efficiency. For example, poly(tetraphenyl)silole has been synthesized by Wurtz-type polycondensation of dichloro(tetraphenyl)silole; however, the reaction yields are low (ca. ~30%).

Catalytic dehydrocoupling of dihydrosilole is an attractive alternative, since Wurtz-type coupling is also problematic in large scale syntheses. Bis(cyclopentadienyl) complexes of Group 4 have been extensively studied and are shown to catalyze the dehydrocoupling of hydrosilanes to polysilanes in the formation of Si-Si bonds; however, only primary organosilanes are polymerized. Secondary and tertiary silanes afford dimers or oligomers in low yields. It has been reported that the reactivity decreases dramatically with increasing substitution at the silicon atom, since reactions catalyzed by metallocenes are typically very sensitive to steric effects. Mechanisms for dehydrocoupling of silanes with metallocenes have also been extensively investigated and involve $\sigma$-bond metathesis.

Studies using Wilkinson’s catalyst for dehydrogenative coupling of primary silanes show that only short chain oligomers are formed. A platinum-complex catalyzed dehydrocoupling polymerization of a silafluorene has been reported using 4 mol % catalyst, yielding a bimodal weight distribution, in equal proportions, as determined by GPC ($M_n = 8100$ and 3000, relative to polystyrene). Silafluorene has also been polymerized via dehydrocoupling with $\text{Cp}_2\text{ZrMe}_2$, $\text{Cp}_2\text{TiMe}_2$, $\text{Cp}_2\text{ZrCl}_2$/n-BuLi, and Wilkinson’s catalyst. However, only the dimer and trimer are formed in significant yields, along with minor amounts of short chain oligomers. Inorganic hydrides have
also been used to effect the dehydrocoupling of dihydrosilole to form polysilole ($M_w = 4000-6000$).\textsuperscript{23}

### 2.3 RESULTS AND DISCUSSION

#### 2.3.1 Catalytic Dehydrocoupling Syntheses

Herein is reported the dehydrocoupling polycondensation of dihydro(tetraphenyl)metalloles, where every silicon or germanium atom of the oligomer backbone is part of a silole or germole ring (Figure 2-1). Dehydrocoupling of dihydro(tetraphenyl)silole (1) and dihydro(tetraphenyl)germole (2) with 0.2 mol % H$_2$PtCl$_6$·xH$_2$O and 2 eq cyclohexene produces the oligomers 3\textit{a} and 4\textit{a} in 88% and 81% isolated yields, respectively. An alternative catalyst system of 1 mol % of Wilkinson’s catalyst, RhCl(PPh$_3$)$_3$, or Pd(PPh$_3$)$_4$ catalyst, yields the respective oligosiloles 3\textit{b,c} and oligogermoles 4\textit{b,c} in good yield (~60%). Adding cyclohexene along with Wilkinson’s catalyst improves the yield of oligosilole 3\textit{d} to 82%, though the yield of oligogermole 4\textit{d} does not change. The dihydrometallole is completely consumed in the reaction for each catalyst system, as observed by $^1$H NMR spectroscopy, and Si-29 NMR spectra are consistent with those previously reported for poly(tetraphenyl)silole.\textsuperscript{23} Catalytic dehydrocoupling significantly improves isolated oligomer yields over traditional Wurtz type coupling.
If less vigorous reflux conditions are used with only the RhCl(PPh$_3$)$_3$ or Pd(PPh$_3$)$_4$ catalyst, or if the solvent is not sufficiently degassed, the silole dimer (5) (n=2) is observed to form in ~40% yield. This product is slightly soluble in hot toluene and precipitates from the reaction mixture during reflux, and even more so upon cooling. Addition of 2 eq of cyclohexene with the RhCl(PPh$_3$)$_3$ catalyst, however, prevents dimer formation and aids in the further polymerization of the shorter chain oligomers. Wilkinson’s catalyst is known to be a hydrogenation catalyst, and it is likely that addition of the alkene provides a means for more efficient hydrogen removal by the catalysts. When 1-hexene or 1-dodecene is used as the alkene coreagent, however, competing reactions of polymerization and hydrosilation are observed, with hydrosilation being dominant. This is not surprising...
since Wilkinson’s reagent is also a hydrosilation catalyst.\textsuperscript{25} The steric bulk of the internal alkene, cyclohexene, favors hydrogenation over hydrosilation and dehydrocoupling predominates, though a minor amount of hydrosilation is sometimes visible by \textsuperscript{1}H NMR.

Similar results are observed with H\textsubscript{2}PtCl\textsubscript{6}·xH\textsubscript{2}O. In the absence of an alkene coreagent, large amounts of dimer and lesser amounts of oligomer exist after 24 h reflux. The addition of cyclohexene produces oligomers of higher molecular weights than the syntheses with Wilkinson’s catalyst, and no hydrosilation products are observed. Both hydrosilation and polymerization products are observed when 1-hexene is used with H\textsubscript{2}PtCl\textsubscript{6}·xH\textsubscript{2}O, as observed with Wilkinson’s catalyst.\textsuperscript{25} One advantage of the Pt catalyst is that polymerization proceeds much more quickly (one day versus three days for Wilkinson’s catalyst). Additionally, removal of the heterogeneous catalyst formed from the H\textsubscript{2}PtCl\textsubscript{6} is simpler. After reflux, black particles are seen in solution and are easily removed by filtration. Most likely the particles are Pt colloids, the proposed active catalytic species for H\textsubscript{2}PtCl\textsubscript{6} catalyzed hydrosilation.\textsuperscript{26,27}

The synthesis of oligosilole, under each catalytic system, was also carried out with the use of an Emrys\textsuperscript{TM} Optimizer microwave synthesizer. Polymerization occurs in only 2 h at 170 °C with Wilkinson’s catalyst when cyclohexene is present (3e). When no alkene is present, only limited polymerization takes place, and mostly monomer and dimer are observed by NMR after 2 h reaction time. Microwave synthesis offers the advantage of more rapid polymerizations, although lower $M_w$ are
obtained. Microwave syntheses with Pd(PPh$_3$)$_4$ and H$_2$PtCl$_6$ catalysts were not successful. A summary of reaction conditions and results is shown in Table 2-1.

Table 2-1 Results of dehydrocoupling syntheses of oligo(tetraphenyl)metalloles

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Catalyst (1 mol %)</th>
<th>Alkene (2 eq)</th>
<th>Method</th>
<th>Yield %</th>
<th>$M_N$ (IR)</th>
<th>$M_N$ (NMR)</th>
<th>$M_w$ ($M_w/M_N$) (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>H$_2$PtCl$_6$</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>Reflux 24 h</td>
<td>88</td>
<td>6500</td>
<td>6500</td>
<td>5600 (1.1), 2400 (1.1), 1300 (1.0)</td>
</tr>
<tr>
<td>3b</td>
<td>Wilkinson</td>
<td>none</td>
<td>Reflux 72 h</td>
<td>62</td>
<td>3500</td>
<td>4100</td>
<td>4800 (1.2), 1800 (1.0), 1200 (1.0)</td>
</tr>
<tr>
<td>3c</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>none</td>
<td>Reflux 72 h</td>
<td>58</td>
<td>3500</td>
<td>4800</td>
<td>4800 (1.2), 1700 (1.0), 1200 (1.0)</td>
</tr>
<tr>
<td>3d</td>
<td>Wilkinson</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>Reflux 72 h</td>
<td>82</td>
<td>4000</td>
<td>5200</td>
<td>5100 (1.1), 2100 (1.0), 1300 (1.0)</td>
</tr>
<tr>
<td>3e</td>
<td>Wilkinson</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>Micro 2 h</td>
<td>78</td>
<td>2700</td>
<td>2800</td>
<td>3300 (1.3), 1200 (1.0)</td>
</tr>
<tr>
<td>4a</td>
<td>H$_2$PtCl$_6$</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>Reflux 24 h</td>
<td>81</td>
<td>3600</td>
<td>4000</td>
<td>3400 (1.1), 1300 (1.0)</td>
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<tr>
<td>4b</td>
<td>Wilkinson</td>
<td>none</td>
<td>Reflux 72 h</td>
<td>50</td>
<td>3400</td>
<td>3800</td>
<td>4000 (3.3), 1200 (1.0)</td>
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<tr>
<td>4c</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>none</td>
<td>Reflux 72 h</td>
<td>67</td>
<td>5500</td>
<td>6900</td>
<td>4800 (1.9), 1200 (1.0)</td>
</tr>
<tr>
<td>4d</td>
<td>Wilkinson</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>Reflux 72 h</td>
<td>49</td>
<td>5600</td>
<td>5700</td>
<td>3600 (1.3), 1200 (1.0)</td>
</tr>
</tbody>
</table>

$^a$ Catalytic concentration of 0.2 mol % used
2.3.2 Molecular Weights

The molecular weight ($M_w$) of the oligosilole is in the range of 3000–7000, even though the silole possesses a secondary silicon atom and contains bulky phenyl groups (Table 2-1). The oligomers obtained are slightly lower in $M_w$ than those obtained from Wurtz-coupling polycondensation. A similar result is also obtained from the catalytic dehydrocoupling of dihydro(tetraphenyl)germole. The molecular weights of the oligometalloles were estimated in three ways. First, $M_N$ were calculated using infrared spectroscopy by integrating the phenyl C-H stretch region relative to the Si-H or Ge-H stretch, and comparing to the ratio in the dihydro monomers. Similarly, NMR was used to calculate $M_N$, by integrating the phenyl protons relative to the Si-H or Ge-H endgroups. Finally the $M_w$ was determined by gel permeation chromatography (GPC). For the siloles, higher molecular weights are obtained using the H$_2$PtCl$_6$ catalyst, followed by Wilkinson’s catalyst with the alkene coreagent, Pd(PPh$_3$)$_4$, and then Wilkinson’s catalyst alone. For the germoles, highest molecular weights are obtained using Pd(PPh$_3$)$_4$, followed by Wilkinson’s catalyst with the alkene coreagent, H$_2$PtCl$_6$, and then Wilkinson’s catalyst alone. Molecular weights determined by IR were slightly higher than those determined by GPC, and the NMR measurements yielded the highest molecular weight estimates.

NMR is the most reliable method for determining actual molecular weights because it does not, as GPC does, calculate $M_w$ based on the size exclusion of individual polymer strands relative to an external standard. The Si-H endgroup of the dimer appears at $\delta = 5.3$ ppm, and endroups of the oligomers appears to shift
increasingly downfield as chain length increases, arising near $\delta = 5.5$ ppm for $3b,e$, near 5.6 for $3c,d$, and 5.7 for $3a$. For the oligogeromoles, the endgroup Ge-H resonance appears at $\delta = 5.37$ ppm for $3a$, and 5.45 for $3b,c,d$, shifting downfield with increasing molecular weight. GPC, however, reveals the size distribution of the polymer. Polysiloles $3a-d$ are trimodal in weight distribution, and $3e$ and polygermoles $4a-d$ are bimodal, each in roughly equal proportion, plus or minus 5%.

2.3.3 Molecular Structure as Driving Force for Dehydrocoupling

Polymerization may take place for the disubstituted silicon or germanium since the tetraphenylmetalloles have small angles at C-M-C in the metallacyclopentadiene ring, which results in less steric hindrance at the metalloid center. The angles of C-M-C of dihydro(tetraphenyl)silole (1) (Figure 2-2) and dihydro(tetraphenyl)germole (2) (Figure 2-3) are 93.21° and 90.14°, respectively. In addition, no polymer is observed using an H atom abstracting reagent, such as AIBN, which suggests that the monomers are not simply undergoing free radical polymerization. The bulky phenyl groups of the silole might reduce the formation of a cyclic hexamer, which is often problematic in polysilane syntheses. Nevertheless, the GPC profiles of the oligomers prepared by each method show a peak centered around $M_w = 1200$ with a low polydispersity of 1.0. This may indicate the formation of a cyclic species or a low molecular weight oligomer. In addition to the Si-29 resonances of polysilole at $\delta = -34.2$ (terminal Si) and -40.1 (internal Si), a small resonance at $\delta = -32.0$ is sometimes visible, which may indicate a cyclic species or low $M_w$ oligomer. The NMR spectra contains a broad
phenyl region with very small Si-H resonances, suggesting that the low molecular weight fraction is probably cyclic.

Figure 2-2  Thermal ellipsoid plot of 1 at 50% probability level. Selected bond lengths, (Å): Si1-C1 1.856(2), Si1-C4 1.866(1), C1-C2 1.358(2), C2-C3 1.506(2), C3-C4 1.359(2), Si1-H1 1.40(2), Si1-H2 1.37(2); and angles, (deg): C1-Si1-C4 93.21(6), Si1-C1-C2 107.4(1), Si1-C4-C3 107.0(1), C1-C2-C3 116.1(1), C2-C3-C4 116.3(1), H1-Si1-H2 109(1)
The reaction of 1-methyl-1-hydro(tetraphenyl)silole with 1 mol % of Wilkinson’s catalyst, RhCl(PPh$_3$)$_3$, or Pd(PPh$_3$)$_4$ catalyst yielded no dimer, C$_4$H$_7$Si(CH$_3$)$_3$-(CH$_3$)SiC$_4$Ph$_4$, with or without added cyclohexene. However, the same reaction with H$_2$PtCl$_6$·xH$_2$O catalyst does yield the methyl-terminated dimer (6) in 40% isolated yield. This demonstrates the higher reactivity of the Pt catalyst, as do the higher $M_w$ silole oligomers obtained. Scheme 2-1 shows a proposed reaction mechanism for the homogeneous catalysts (Rh and Pd catalysts) with a putative
silylene intermediate formed after oxidative addition of the Si-H bond to the metal center. Electronic stabilization of the silylene intermediate by π-conjugation with the silole ring may contribute to the unexpected observation of catalytic dehydrocoupling for a secondary silane. This scheme is consistent with the fact that no dimer is observed with the methylhydrosilole because an Si-Me bond would not oxidatively add to the metal center to form the silylene intermediate. However, dimerization of the methylhydrosilole is observed using the Pt catalyst. This suggests that the surface catalyzed reaction on the Pt colloid proceeds by oxidative addition of the Si-H of the silole, followed by reductive elimination of H₂ and dimer (Scheme 2-2).

**Scheme 2-1** Proposed dehydrocoupling mechanism for Rh and Pd catalyzed oligosilole synthesis
Crystal structures for both the hydrogen-terminated and methyl-terminated dimers were obtained. The H-terminated dimer (5) has a H1-Si1-Si2-H2 torsion angle of 90(2)° (Figure 2-4) and the Me-terminated dimer (6) has a similar torsion angle of 92.3(1)° (Figure 2-5). This torsion angle is larger than that of the 51.2° observed for the chlorosilole dimer. This deviation is obviously not due to steric, as Me and Cl ligands are of similar size, but perhaps arises from electronic effects of the interaction of the π system with the halide. The torsion angles suggest that the structure of the oligomers is helical, as previously proposed, and as established for several disubstituted polysilanes.
Figure 2-4  Thermal ellipsoid plot for 5 at 50% probability level. Selected bond lengths, (Å): Si1-Si2 2.363(2), Si1-H1 1.47(4), Si2-H2 1.48(4), Si1-C1 1.870(5), C1-C2 1.363(7), C2-C3 1.503(7); and bond angles, (deg): H1-Si1-Si2 106(2), Si1-Si2-H2 107(2), C1-Si1-C4 92.8(2); and torsion angles, (deg): H1-Si1-Si2-H2 90(2), C1-Si1-Si2-C32 94.6(2)
Figure 2-5 Thermal ellipsoid plot for 6 at 50% probability level. Selected bond lengths, (Å): Si1-Si2 2.375(1), Si1-C5 1.867(2), Si2-C10 1.873(2), Si1-C1 1.881(2), C1-C2 1.355(2), C2-C3 1.502(2); and bond angles, (deg): C5-Si1-Si2 109.32(6), Si1-Si2-C10 108.80(6), C1-Si1-C4 91.99(7); and torsion angles, (deg): C5-Si1-Si2-C10 -92.3(1), C1-Si1-Si2-C9 164.88(8), C4-Si2-Si1-C6 10.09(8)

2.3.4 Fluorescence of Silole Monomers, Dimers, and Polymers

The hydrogen-terminated dimer has a UV-vis absorption at 372 nm, similar to that of the dihydro monomer at 368 nm, which is assigned to the $\pi-\pi^*$ transition of the silole ring. The dimeric compound is strongly luminescent, much more so than the monomer, emitting green light at 506 nm when excited at 360 nm (Figure 2-6).
Similarly the Me-terminated dimer is much more luminescent than both methylhydrosilole and dimethylsilole, emitting at 468 nm. Fluorescence spectra of 20 mg/L metallole samples in toluene are shown in Figure 2-6. The broad emission spectra could possibly be due to the overlapping of emission from the $\pi-\pi^*$ and $\sigma-\pi^*$ transitions. Absorbance and fluorescence data are summarized in Table 2-2.

**Figure 2-6** Fluorescence spectra of 20 mg/L toluene solutions of (a) methyl dimer, (b) oligogermole, (c) hydrogen dimer, (d) oligosilole, (e) dihydrogermole (THF), (f) methylhydrosilole, and (g) dihydrosilole on excitation at 360 nm
Table 2-2 Summary of Absorbance (THF) and Fluorescence (toluene) data of various metalloles

<table>
<thead>
<tr>
<th>Metallole</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\varepsilon_{max}^a$ (L/mol·cm)</th>
<th>$\lambda_{flu}^e$ (nm)</th>
<th>Fluorescence Quantum Yield ($\Phi^f$)</th>
<th>Relative $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydrosilole</td>
<td>368</td>
<td>9500</td>
<td>495</td>
<td>0.83 x 10^-3</td>
<td>1.0</td>
</tr>
<tr>
<td>Dideuterosilole</td>
<td>370</td>
<td>10,500</td>
<td>484</td>
<td>0.79 x 10^-3</td>
<td>0.95</td>
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<td>Methylhydrosilole$^a$</td>
<td>368</td>
<td>10,250</td>
<td>495</td>
<td>0.75 x 10^-3</td>
<td>0.90</td>
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<tr>
<td>Dimethylsilole$^a$</td>
<td>362</td>
<td>9500</td>
<td>473</td>
<td>1.0 x 10^-3</td>
<td>1.2</td>
</tr>
<tr>
<td>Hydrogen Dimer$^b$</td>
<td>372</td>
<td>4800</td>
<td>506</td>
<td>6.9 x 10^-3</td>
<td>8.3</td>
</tr>
<tr>
<td>Methyl Dimer$^{b,c}$</td>
<td>370</td>
<td>5900</td>
<td>468</td>
<td>3.6 x 10^-5</td>
<td>4.3</td>
</tr>
<tr>
<td>Oligosilole</td>
<td>370</td>
<td>2230</td>
<td>510</td>
<td>11 x 10^-3</td>
<td>13</td>
</tr>
<tr>
<td>Dihydrogermole$^d$</td>
<td>360</td>
<td>11,200</td>
<td>469</td>
<td>1.4 x 10^-3</td>
<td>1.7</td>
</tr>
<tr>
<td>Dideuterogermole$^a$</td>
<td>362</td>
<td>9200</td>
<td>470</td>
<td>2.1 x 10^-3</td>
<td>2.5</td>
</tr>
<tr>
<td>Oligogeremole$^a$</td>
<td>378</td>
<td>5400</td>
<td>498</td>
<td>13 x 10^-5</td>
<td>16</td>
</tr>
</tbody>
</table>

$^a$UV-vis taken in toluene; $^b$Absorptivities are reported per mole of metalloid; actual molar absorptivities of dimers are twice the reported value; $^c$UV-vis data taken in CHCl$_3$; $^d$Fluorescence taken in THF; $^e$$\lambda_{ex}$ = 360 nm; $^f$±30%, relative to 9,10-diphenylanthracene$^{31}$, $\lambda_{ex}$ = 360 nm

2.3.5 Fluorescence Quantum Yields

Fluorescence quantum yields (\(\Phi\)) of the metalloles were measured relative to a diphenylanthracene (DPA) standard and are listed in Table 2-2.$^{31}$ The $\Phi_{rel}$ of the
oligogermole is roughly ten times greater than dihydrogermole and the quantum yield of the siloles follow the order oligosilole > H-dimer > dihydrosilole. One possible explanation of this series order is the fact that coupling of the excited state to high frequency (Si-H or Ge-H) vibrations of the ground state increases the efficiency of non-radiative decay processes. In order to test this hypothesis, the dideuterometallole monomers were prepared, along with dimethylsilole and methylhydrosilole in order to vary the vibrational frequencies directly coupled to the metallocene chromophore. Infrared spectra of dideuterosilole (7) and dideuterogermole (8) show the decrease in vibrational frequencies of the metal-deuterium stretches ($\nu = 1543 \text{ cm}^{-1}$ for Si-D and 1476 cm$^{-1}$ for Ge-D) relative to the metal-hydrogen analogues ($\nu = 2140 \text{ cm}^{-1}$ for Si-H and 2053 cm$^{-1}$ for Ge-H), which is consistent with the increase in the reduced mass. Dideuterogermole has a slightly higher $\Phi_{rel}$ than the dihydrogermole, but dihydrosilole has a very slightly higher $\Phi_{rel}$ than dideutersilole. The dimethyl and methylhydrosiloles have comparable quantum yields to the other silole monomers. Because emission intensity and quantum yield are not significantly affected by the varying vibrational frequencies coupled to the chromophore, vibrational relaxation does not appear to be the dominant pathway in determining the variation in metallocene fluorescence quantum yields. Interestingly, the hydrogen terminated dimer is more than 8 times more luminescent than the monomer, while the oligomer is about 13 times more luminescent. The enhanced quantum yields of the dimer and oligomer may possibly be attributed to restricted conformations about the Si-Si bond. It may also result from shielding of the metallocene excited state from
solvent. Polysilole and siloles are dramatically more luminescent in the solid state than in fluid solution.\textsuperscript{7cd,33}

### 2.3.6 Polygermole Compared to Polysilole

The UV-vis absorption spectrum of oligo(tetraphenyl)germole has an absorption at 378 nm, which is slightly red shifted compared to the absorption of the corresponding oligosilole (370 nm). This absorption is assigned to both the $\sigma-\sigma^*$ transition of the germanium-germanium backbone chain and the $\pi-\pi^*$ transition of the germole ring. Like oligosilole, the oligoger mole is highly photoluminescent in the solid state. When excited at 360 nm, the polymer emits blue-green light at 498 nm, which is 12 nm blue shifted compared to the emission of the oligosilole (510 nm). Germole species are noticeably more intensely photoluminescent than the corresponding siloles. The wavelengths of fluorescence red shift with increasing chain length, which is consistent with the lowering of the LUMO energy due to $\sigma-\sigma^*$ conjugation along the metalloid backbone.
### Table 2-3  Summary of X-ray Crystallographic Data

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<th>1</th>
<th>2</th>
<th>5</th>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;Si</td>
<td>C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;22&lt;/sub&gt;Ge</td>
<td>C&lt;sub&gt;56&lt;/sub&gt;H&lt;sub&gt;42&lt;/sub&gt;Si&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;58&lt;/sub&gt;H&lt;sub&gt;46&lt;/sub&gt;Si&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
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</tr>
<tr>
<td><strong>Space group</strong></td>
<td>I&lt;sub&gt;4&lt;/sub&gt;/a</td>
<td>I&lt;sub&gt;4&lt;/sub&gt;/a</td>
<td>P&lt;sub&gt;1&lt;/sub&gt;</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;1&lt;/sub&gt;/c</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>26.5859(7)</td>
<td>26.457(2)</td>
<td>10.023(2)</td>
<td>12.4024(9)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>26.5859(7)</td>
<td>26.457(2)</td>
<td>12.806(2)</td>
<td>19.9497(14)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>11.9092(7)</td>
<td>11.846(2)</td>
<td>17.695(3)</td>
<td>18.2523(13)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>--</td>
<td>--</td>
<td>89.440(3)</td>
<td>--</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>--</td>
<td>--</td>
<td>88.558(3)</td>
<td>104.951(1)</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>--</td>
<td>--</td>
<td>71.737(3)</td>
<td>--</td>
</tr>
<tr>
<td><strong>V, Å&lt;sup&gt;3&lt;/sup&gt;</strong></td>
<td>8417.5(6)</td>
<td>8292(2)</td>
<td>2156.1(6)</td>
<td>4363.2(5)</td>
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<tr>
<td><strong>Z, Z'</strong></td>
<td>16, 1</td>
<td>16, 1</td>
<td>2, 1</td>
<td>4, 1</td>
</tr>
<tr>
<td><strong>Crystal color, habit</strong></td>
<td>yellow, block</td>
<td>colorless, plate</td>
<td>green, block</td>
<td>yellow, block</td>
</tr>
<tr>
<td><strong>ρ(calc), g cm&lt;sup&gt;-3&lt;/sup&gt;</strong></td>
<td>1.220</td>
<td>1.381</td>
<td>1.188</td>
<td>1.217</td>
</tr>
<tr>
<td><strong>μ(MoKα), mm&lt;sup&gt;-1&lt;/sup&gt;</strong></td>
<td>0.123</td>
<td>1.489</td>
<td>0.120</td>
<td>0.121</td>
</tr>
<tr>
<td><strong>Temp, K</strong></td>
<td>213(2)</td>
<td>100(2)</td>
<td>218(2)</td>
<td>213(2)</td>
</tr>
<tr>
<td><strong>Reflections measured</strong></td>
<td>29964</td>
<td>26461</td>
<td>10251</td>
<td>26441</td>
</tr>
<tr>
<td><strong>Reflections ind.</strong></td>
<td>5040 [R&lt;sub&gt;int&lt;/sub&gt;=0.0338]</td>
<td>5045 [R&lt;sub&gt;int&lt;/sub&gt;=0.0495]</td>
<td>6627 [R&lt;sub&gt;int&lt;/sub&gt;=0.0291]</td>
<td>9645 [R&lt;sub&gt;int&lt;/sub&gt;=0.0303]</td>
</tr>
<tr>
<td><strong>R(F) (I &gt; 2σ(I))&lt;sup&gt;a&lt;/sup&gt;</strong></td>
<td>0.0423</td>
<td>0.0390</td>
<td>0.0860</td>
<td>0.0493</td>
</tr>
<tr>
<td><strong>R(wF&lt;sup&gt;2&lt;/sup&gt;) (I &gt; 2σ(I))&lt;sup&gt;b&lt;/sup&gt;</strong></td>
<td>0.1111</td>
<td>0.0855</td>
<td>0.2774</td>
<td>0.1195</td>
</tr>
</tbody>
</table>

<sup>a</sup> R=∑||F<sub>o</sub>|-|F<sub>c</sub>||/ ∑|F<sub>o</sub>|

<sup>b</sup> R(ωF<sup>2</sup>)={∑[ω(F<sub>o</sub>²-F<sub>c</sub>²)]²/∑[ω(F<sub>o</sub>²)]<sup>1/2</sup>; ω=1/[σ²(F<sub>o</sub>²)+(aP)²+bP], P=[2F<sub>c</sub>²+max(F<sub,o</sub>,0)]/3
2.4 EXPERIMENTAL

2.4.1 General Synthetic Techniques

All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard Schlenk techniques. Solvents were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl. NMR data were collected with a Varian Unity 300 or 500 MHz spectrometers (300.1 MHz for $^1$H, 77.5 MHz for $^{13}$C, and 99.4 MHz for $^{29}$Si NMR). Infrared spectra were obtained with the use of a Nicolet Magna-IR$^\text{TM}$ Spectrometer 550. GPC data were obtained with the use of a Viscotek GPCmax VE 2001 GPC and a Viscotek VE 3580 refractive index detector. A calibration curve was obtained using 1, 5, and three polysilole samples calibrated by Viscotek using RI, viscosity, and light scattering detectors (this triple detection method yields absolute molecular weights). Fluorescence emission and excitation spectra were recorded with the use of a Perkin-Elmer Luminescence Spectrometer LS 50B. UV-vis spectra were obtained with the use of a Hewlett-Packard 8452A diode array spectrometer.

2.4.2 X-ray Crystal Structure Determinations

Diffraction intensity data were collected with a Bruker P4/CCD diffractometer at 213 K (1, 6) and 218 K (5) and a Bruker P4/CCD Smart Apex CCD diffractometer at 100 K (2). Crystal, data collection, and refinement parameters are given in the Table 2-3. The space groups were chosen based on the systematic absences (1, 2, 6) and intensity statistics (5). The structures were solved by direct methods, completed by
subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on $F^2$. SADABS absorption corrections were applied to all data. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All H atoms in 1, 2, 6 and the H atoms bonded to the Si atoms in 5 were found on the difference maps and refined with isotropic thermal parameters. Other H atoms in 5 were treated as idealized contributions. The structures of 7 and 8 were also determined and are isomorphous with their protio analogues. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

2.4.3 Synthesis of 1,1-Dihydro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (Dihydrosilole) (1): Diphenylacetylene (18 g, 0.10 mol) and Li (0.25 mol) in dry ether (130 mL) were stirred for 2.5 h and then frozen with liquid nitrogen. Dichlorosilane (25% in xylenes, 20 mL, 0.20 mol) was added and the solution was thawed and stirred for 4 h at room temperature. The solvent was evaporated and the solid was extracted with toluene, washed with water, and recrystallized from toluene to afford bright yellow crystals (10.3 g, 53%). MP: 205-206 °C (Lit: 209-210 °C);

$^1$H NMR (300.133 MHz, CDCl$_3$): $\delta$ = 6.80-6.85 and 7.00-7.24 (br. m, 20H, Ph), 4.90 (s, 2H, SiH$_2$); $^{13}$C NMR (75.403 MHz, CDCl$_3$): $\delta$ = 157.50, 138.74, 135.20, 131.63, 129.62, 129.36, 128.09, 127.72, 126.63, 126.23; $^{29}$Si NMR (99.36 MHz, INEPT, CDCl$_3$, TMS ($\delta = 0.0$)): $\delta$ = -35.03; IR (KBr): $\nu_{Si-H}$ = 2140 cm$^{-1}$. 
2.4.4 1,1-Dihydro-2,3,4,5-tetraphenyl-1-germaclopenta-2,4-diene

(Dihydrogermole) (2): The dichlorogermole starting material was prepared according to the literature.\textsuperscript{7b} To a dry THF (100 mL) solution of dichlorogermole (1.0 g, 2 mmol) was added LiAlH\textsubscript{4} (1 M in THF, 2 mL, 2 mmol). The solution was quenched with methanol, evaporated to dryness, and the product was extracted and recrystallized from hexanes to afford pale yellow crystals (0.44 g, 51%). MP: 190-192 °C (Lit: 192-193 °C\textsuperscript{35}); \textsuperscript{1}H NMR (300.133 MHz, CDCl\textsubscript{3}): δ = 6.80-6.84 and 6.95-7.07 (br. m, 20H, Ph), 5.36 (s, 2H, GeH\textsubscript{2}); \textsuperscript{13}C NMR (75.403 MHz, CDCl\textsubscript{3}): δ = 153.54, 139.33, 138.99, 138.01, 129.72, 129.43, 127.85, 127.55, 126.28, 126.01; IR (KBr): ν\textsubscript{Ge-H} = 2053 cm\textsuperscript{-1} (Lit: 2060\textsuperscript{35}).

2.4.5 Oligo(tetraphenyl)silole (3)

(3a): 1 (1.0 g, 2.59 mmol) and 0.2 mol % H\textsubscript{2}PtCl\textsubscript{6}·xH\textsubscript{2}O and 2 mol equivalents of cyclohexene in toluene (10 mL) were vigorously refluxed for 24 h. The solution was passed through a sintered glass frit and evaporated to dryness under an Ar atmosphere. Dissolution with THF (1 mL) and precipitation with methanol (10 mL) yielded the oligosilole in (88%).

(3b,c,d): 1 (1.0 g, 2.59 mmol) and 1 mol % of RhCl(PPh\textsubscript{3})\textsubscript{3} (3b) or Pd(PPh\textsubscript{3})\textsubscript{4} (3c) in toluene (10 mL) were placed under an Ar atmosphere and degassed through freeze-pump-thaw cycles. The reaction mixture was then vigorously refluxed for 72 h and then evaporated to dryness. THF (1 mL) was added to the reaction mixture and
the resulting solution was then poured into 10 mL of methanol. Polysilole was obtained as a pale yellow powder after filtration and freeze-drying. Addition of 2 eq of cyclohexene with RhCl(PPh$_3$)$_3$ (3d) eliminates dimer precipitation and increases yield. 3b: 62%, 3c: 58%, 3d: 82%. 3: $^1$H NMR (300.133 MHz, CDCl$_3$): δ = 6.60-7.40 (br, m, Ph); $^{13}$C NMR (75.403 MHz, CDCl$_3$ (δ = 77.00)): δ = 125-132 (br, m, Ph), 137-147 (silole carbons); $^{29}$Si NMR (99.37 MHz, INEPT, CDCl$_3$, TMS (δ = 0.0)): δ = -31.8 (end groups), -40.0 (backbone); IR (KBr): ν$_{Si-H}$ = 2146 cm$^{-1}$; CHN Analysis: Calc: C: 87.4, H: 5.24; Found: C: 86.9, H: 5.19.

(3e): 1 (0.5 g, 1.3 mmol), 1 mol % RhCl(PPh$_3$)$_3$, cyclohexene (2.6 mmol), and 5 mL toluene into an Emrys$^{TM}$ Optimizer microwave synthesizer for 2 h at 170 °C and 120 W. The solution was then evaporated to dryness. Dissolution with THF (1 mL) and precipitation with methanol (10 mL) yielded the oligosilole (78%).

2.4.6 Oligo(tetraphenyl)germole (4a,b,c,d)

Reaction conditions for preparing the oligogermole are the same as those for oligosilole. 4a: 81%, 4b: 50%, 4c: 67%, 4d: 49%. 4: $^1$H NMR (300.133 MHz, CDCl$_3$): δ = 6.30-7.90 (br, m, Ph); $^{13}$C NMR (75.403 MHz, CDCl$_3$ (δ = 77.00)): δ = 124-130 (br, m, Ph), 131-139 (germole carbons); IR (KBr): ν$_{Ge-H}$ = 2063 cm$^{-1}$; CHN Analysis: Calc: C: 78.4, H: 4.70; Found: C: 78.2, H: 4.60.

2.4.7 Dihydrosilole Dimer (5)
1 (1.0 g, 2.59 mmol) and 1 mol % of RhCl(PPh₃)₃ in toluene (10 mL) were placed under an Ar atmosphere and degassed through freeze-pump-thaw cycles. The reaction mixture was vigorously refluxed for 72 h. The solid that precipitates during cooling was filtered and recrystallized from xylenes to afford bright yellow crystals (0.38 g, 38%). MP ≥ 250 °C; ¹H NMR (300 MHz, CDCl₃ (δ = 7.26)): δ = 6.4-7.4 (m, 40H, Ph), δ = 5.30 (s, 2H); ¹³C NMR (99.40 MHz, CD₂Cl₂ (δ = 54.00)): δ = 157.13, 139.27, 139.22, 137.99, 130.23, 129.95, 128.41, 127.76, 126.81, 126.52; ²⁹Si NMR (100 MHz, CDCl₃, TMS (δ = 0.0)): δ = -33.81 (dd, J₁₁-H₁ = 200 Hz, J₁₁-H₂ = 8.4 Hz); CHN Analysis: Calc: C: 87.22, H: 5.49; Found: C: 86.67, H: 6.18; IR (KBr): νSi-H = 2112 cm⁻¹.

2.4.8 Methylsilole Dimer (6)

Methylhydrosilole³⁶ (1.0 g, 2.5 mmol) and 0.2 mol % H₂PtCl₆·xH₂O and 2 mol equivalents of cyclohexene in toluene (10 mL) were vigorously refluxed for 24 h. The solid that precipitates during cooling was filtered and recrystallized from toluene to afford bright yellow crystals (0.41 g, 40%). MP ≥ 250 °C; ¹H NMR (300 MHz, CDCl₃ (δ = 7.26)): δ = 6.7-6.8 and 6.9-7.2 (m, 40H, Ph), δ = 0.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃ (δ = 77.00)): δ = 154.6, 143.4, 139.9, 138.8, 130.3, 129.4, 127.9, 127.4, 126.3, 125.6, -6.0; ²⁹Si NMR (99.37 MHz, INEPT, CDCl₃, TMS (δ = 0.0)): -9.34; CHN Analysis: Calc: C: 87.16, H: 5.49; Found: C: 86.84, H: 5.87.

2.4.9 1,1-Dideuterosilole (7) and 1,1-Dideuterogermole (8)
Methods for synthesizing 7 and 8 are identical to the procedure described for preparing 2, beginning with either dichlorosilole or dichlorogermole and reducing with LiAlD₄, and recrystallizing from toluene (7) or hexanes (8). 7: 58%; CHN Analysis: Calc: C: 86.55, H: 6.22; Found: C: 86.35, H: 6.37; MP = 204-206 °C; IR (KBr): ν_{Si-D} = 1543 cm⁻¹. 8: 52%; CHN Analysis: Calc: C: 77.65, H: 5.58; Found: C: 77.62, H: 5.74; MP = 191-193 °C; IR (KBr): ν_{Ge-D} = 1476 cm⁻¹.

2.5 ACKNOWLEDGEMENT

This chapter is a reprint of the material as it appears in Organometallics, 2005, 24(13), 3081-3087. With H. Sohn, L.N. Zakarov, W.S. Kassel, J.A. Golen, A.L. Rheingold, and W.C. Trogler. Crystallographic information files for compounds 1, 2, 5, 6, 7, and 8 are available on the internet at pubs.acs.org as “Supporting Information” to this publication.

2.6 REFERENCES


(9) Yamaguchi, Y. Synthetic Met. 1996, 82, 149.


(13) Grimmond, B. J.; Corey, J. Y. Organometallics 2000, 19, 3776.


## 2.7 APPENDIX

### 2.7.1 Crystal Data and Structure Refinement for Dihydrosilole (1)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
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<td>Temperature</td>
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</tr>
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<td>Wavelength</td>
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</tr>
<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>I4(1)/a</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
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</tr>
<tr>
<td>b = 26.5859(7) Å</td>
<td>β = 90°</td>
</tr>
<tr>
<td>c = 11.9092(7) Å</td>
<td>γ = 90°</td>
</tr>
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<td>Volume</td>
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</tr>
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<td>Crystal size</td>
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<td>29964</td>
</tr>
<tr>
<td>Independent reflections</td>
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<tr>
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</tr>
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<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.000 and 0.810</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.023</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0423, wR2 = 0.1111</td>
</tr>
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<td>R indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.323 and -0.178 e.Å⁻³</td>
</tr>
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</table>
2.7.2 Crystal Data and Structure Refinement for Dihygermole (2)

Empirical formula C28 H22 Ge  
Formula weight 431.05  
Temperature 100(2) K  
Wavelength 0.71073 Å  
Crystal system Tetragonal  
Space group I4(1)/a  
Unit cell dimensions
\[ a = 26.457(2) \text{ Å} \quad \alpha = 90^\circ \]
\[ b = 26.457(2) \text{ Å} \quad \beta = 90^\circ \]
\[ c = 11.846(2) \text{ Å} \quad \gamma = 90^\circ \]
Volume 8292.1(18) Å³  
Z 16  
Density (calculated) 1.381 g/cm³  
Absorption coefficient 1.489 mm⁻¹  
F(000) 3552  
Crystal size 0.35 x 0.10 x 0.03 mm³  
Theta range for data collection 1.54 to 28.25°  
Index ranges -30<=h<=34, -34<=k<=33, -14<=l<=15  
Reflections collected 26461  
Independent reflections 5045 [R(int) = 0.0495]  
Completeness to theta = 28.25° 98.2 %  
Absorption correction Semi-empirical from equivalents  
Max. and min. transmission 1.000 and 0.801  
Refinement method Full-matrix least-squares on F²  
Data / restraints / parameters 5045 / 0 / 350  
Goodness-of-fit on F² 1.059  
Final R indices [I>2sigma(I)] R1 = 0.0390, wR2 = 0.0855  
R indices (all data) R1 = 0.0523, wR2 = 0.0910  
Largest diff. peak and hole 0.579 and -0.269 e Å⁻³
### 2.7.3 Crystal Data and Structure Refinement for Dihydrosilole Dimer (5)

<table>
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</tr>
<tr>
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<td>218(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.0229(17) Å, b = 12.806(2) Å, c = 17.695(3) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>2156.1(6) Å</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.188 Mg/m³</td>
</tr>
<tr>
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<td>0.120 mm⁻¹</td>
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<td>F(000)</td>
<td>812</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.25 x 0.20 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.67 to 24.00°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11&lt;=h&lt;=10, -14&lt;=k&lt;=14, -16&lt;=l&lt;=20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>10251</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6627 [R(int) = 0.0291]</td>
</tr>
<tr>
<td>Completeness to theta = 24.00°</td>
<td>97.6 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9765 and 0.9650</td>
</tr>
<tr>
<td>Refinement method</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>6627 / 0 / 531</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.099</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0860, wR² = 0.2774</td>
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<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1012, wR² = 0.2904</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.863 and -0.337 e.Å⁻³</td>
</tr>
</tbody>
</table>
2.7.4 Crystal Data and Structure Refinement for Methylsilole Dimer (6)

Empirical formula: C58 H46 Si2
Formula weight: 799.13
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: P2(1)/c
Unit cell dimensions:
\[ a = 12.4024(9) \text{ Å}, \quad \alpha = 90^\circ. \]
\[ b = 19.9497(14) \text{ Å}, \quad \beta = 104.951(1)^\circ. \]
\[ c = 18.2523(13) \text{ Å}, \quad \gamma = 90^\circ. \]
Volume: 4363.2(5) Å³
Z: 4
Density (calculated): 1.217 Mg/m³
Absorption coefficient: 0.121 mm⁻¹
F(000): 1688
Crystal size: 0.28 x 0.21 x 0.12 mm³
Theta range for data collection: 1.54 to 27.50°.
Index ranges: -15 ≤ h ≤ 16, -21 ≤ k ≤ 25, -23 ≤ l ≤ 21
Reflections collected: 26441
Independent reflections: 9645 [R(int) = 0.0303]
Completeness to theta = 27.50°: 96.3 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.000 and 0.719
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 9645 / 0 / 725
Goodness-of-fit on F²: 1.047
Final R indices [I>2σ(I)]: R1 = 0.0493, wR2 = 0.1195
R indices (all data): R1 = 0.0578, wR2 = 0.1249
Largest diff. peak and hole: 0.704 and -0.321 e.Å⁻³
CHAPTER III

VISUAL DETECTION OF TRACE NITROAROMATIC EXPLOSIVE RESIDUE USING PHOTOLUMINESCENT METALLOLE-CONTAINING POLYMERS

3.1 ABSTRACT

The detection of trace explosives is important for forensic military and homeland security applications. Detection of widely-used nitroaromatic explosives was carried out using photoluminescent metallole-containing polymers. The method of detection is through the quenching of fluorescence of thin films of the polymer by the explosive analyte. Visual quenching of luminescence in the presence of the explosive is seen immediately upon illumination with near UV light. Detection limits were observed to be as low as 5 ng for TNT, 20 ng for DNT, and 5 ng for picric acid. In addition, experiments with normal production line explosives and their components show this technology is also able to detect Composition B, Pyrodex®, and nitromethane. This method offers a convenient and sensitive method of detection of trace nitroaromatic explosive residue.

3.2 Introduction

The interest in explosives detection is important for forensic investigation (1), military applications (2), minefield remediation (3), and homeland security purposes
The effort to detect trace explosive residue is made more compelling given the rising threat of global terrorism. After the collapse of the Soviet Union, a large black market for explosives, particularly military grade trinitrotoluene (TNT), developed in central and southern Europe (5). In addition, TNT is an inexpensive component of at least 15 other explosive blends (6). For instance, Tritonal is a mixture of TNT and Al powder, Amatol is a mixture of TNT and ammonium nitrate, Pentolite is a mixture of TNT and PETN, and Composition B is a blend of TNT and RDX. The widespread use and availability of TNT makes it an explosive of concern, and subsequently makes it an important target molecule for detection.

There are several physical methods for trace detection of nitroaromatics with low detection limits. These include gas chromatography coupled with mass spectrometry (7), gas chromatography-electron capture detection (3), surface-enhanced Raman spectroscopy (8), mass spectrometry (9), and ion mobility spectrometry (10). These methods are unsuitable for manufacture into an inexpensive, low-power portable device for in situ detection. In addition, many are limited to sampling the vapor phase, which is problematic given the low volatility of many explosives. For instance, the vapor pressure of TNT (5 ppb (11) at room temperature) may be up to 6 times lower when enclosed in a bomb or mine casing or when present in mixtures with other explosives (12). For this reason, solid state sensing may be desirable for trace residue detection on contaminated surfaces. It is known that trace amounts of explosives often adhere to the surface of packaging materials and clothing present when preparing explosive devices. One commercially available solid-state
detection kit is ExPray, which is a three-step colorimetric explosives detection system for a wide range of explosive compounds, with sensitivity purported down to the tens-of-nanogram level; however, performance evaluation tests by Sandia National Laboratories show a practical detection level for TNT at 200 ng, and many false positives are known to occur (13).

Nitroaromatics, such as trinitrotoluene, are oxidizers due to a low energy unoccupied \( \pi^* \) orbital, which can accept an electron from the excited state of luminescent polymers (14). The detection of nitroaromatic vapor has been achieved using fluorescent polymers, including various functionalized organic polyacetylenes (15), polyphenylenevinylene (16), and polyphenylethynylene (17), as well as inorganic polysilanes (18) and poly(phenylenevinylene) (19). Polymetalloles have been shown to detect nitroaromatics in organic solution (19), and nanoparticles of polysilole can detect TNT in aqueous media (20), through electron-transfer photoluminescence quenching. Reported herein is the visual detection of trace residue on surfaces of the nitroaromatics TNT, 2,4-dinitrotoluene (DNT), and picric acid (PA) using thin films of luminescent metallole-containing polymers. Detection limits as low as 5 ng are observed. Polymetalloles have the advantage of being inexpensive, easily prepared, and their application uses simple equipment readily fielded for on-site explosives detection.

3.3 Explosives Detection Technique
The method of explosives detection is through luminescence quenching of the polymetalloles by the nitroaromatic analyte. Three common explosives were tested, trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and picric acid (PA). Six metallole polymers were used, including polysilole and polygermole previously discussed in Chapters 1 and 2, and shown in Scheme 1-5A. Polysilafluorene21 is a known polymetallol with ring systems fused to the silole ring (Figure 3-1A). The other three polymers examined, PDEBSi, PDEBGe, and PDEBSF (Figure 3-1 B, C and D) are novel metallole-organic copolymers prepared by the H2PtCl6 catalyzed hydrosilation of diethylsilylbenzene (DEB) by a dihydrometallole.22

![Figure 3-1 Chemical structures of PSF, PDEBSi, PDEBGe, and PDEBSF](image-url)

Stock solutions of the explosives were prepared in toluene. Aliquots (1-5 μL) of the stock (containing 5 to 100 ng analyte) were syringed onto either Whatman filter paper or a CoorsTek® porcelain spot plate with well sizes of 2.0 cm in diameter, and
allowed to dry completely. The spots were between 3 and 10 mm in diameter, producing a surface concentration of not more than 64 ng/cm$^2$ and not less than 17 ng/cm$^2$. Solutions of the polymers (0.5–1 % w:v) were prepared in acetone (PSi, PGe), 1:1 toluene:acetone (PDEBGe), 2:1 toluene:acetone (PDEBSi, PSF), or toluene (PDEBSF). A thin film of a polymer, amounting to approximately 2.5 µg/cm$^2$, was applied to the substrate by spray coating a polymeric solution with an air brush onto the substrate and air drying. The coated substrates were placed under a black light ($\lambda_{ex}$ ~ 340 nm) to excite the polymer fluorescence. Dark spots in the film indicate luminescence quenching of the polymer by the analyte.

Illuminated plates were examined by an independent observer to determine if quenching was discernable. Detection limits are reported as the lowest amount of explosive necessary for the independent observer to notice quenching visually. The blind detection study was carried out five times for the three explosive analytes with each polymer on both substrates. Digital images were recorded with a Cannon Powershot 110 2.0 Megapixel digital camera, or a Sony 2.0 Megapixel digital camera as black and white images. No representative images of the silafluorene polymers (PSF and PDEBSF) were obtained due to their low fluorescence yield in the visible and the difficulty to image with the use of a conventional digital camera.

The ability of the polymers PSi and PDEBSi to detect normal production line explosives and their components through luminescence quenching was also researched at a Department of Defense approved explosives testing range operated by Newtec Services Group, Inc. The nitro-based explosives tested were TNT, Comp B,
Pyrodex®, and nitromethane. Contaminated filter paper samples were prepared by contacting a gloved hand with an explosive (either solid, pellet, or powder form, or liquid swab for nitromethane), removing the excess on the glove, and then contacting the filter paper. A thin film of a polymer was applied to the filter paper by airbrushing an acetone or toluene solution, and quenching was visually observed under near UV illumination from a black light.

3.4 RESULTS AND DISCUSSION

The detection of nanogram quantities of the explosives is possible using thin films of the luminescent polymers. Detection is achieved through luminescence quenching by the nitroaromatics. The silole and germole polymers fluoresce green, with $\lambda_{\text{max}}$ of emission at 510 nm for PSi, 495 nm for PDEBSi, 500 nm for PGe, and 475 nm for PDEBGe. The metallole rings of the silafluorenes, PSF and PDEBSF, are functionalized differently than the siloles and germoles, which results in $\lambda_{\text{max}}$ of emission at 360 nm. Illumination with near UV radiation from a black light ($\lambda_{\text{ex}} \sim 340$ nm) excites the fluorescence of all polymers. The blue luminescence of the silafluorenes is weak in the visible, 390 - 420 nm, but is sufficient to observe quenching by eye. Luminescence quenching in the presence of the explosives is observed immediately upon illumination. The polymers are photodegradable, however, and luminescence begins to fade after a few minutes of continual UV exposure. Regardless, detection of the explosives is effected immediately. Figure 3-2 shows sample black and white digital images of the luminescence quenching of four
Figure 3-2  Luminescence quenching of polymers PSi, PDEBSi, and PGe, by 200, 100, 50, and 10 ng TNT on porcelain plates with well sizes of 2.0 cm in diameter

polymers by TNT observed on a porcelain plate, at TNT concentrations of 200 ng, 100 ng, 50 ng, and 10 ng, respectively. Quenching was observed at 10 ng for each polymer. Figures 3-3 and 3-4 show photoluminescence quenching on porcelain plates of the same four polymers by DNT and PA, respectively, at the same analyte concentrations. Quenching was observed as low as 50 ng for all polymers. Detection limits depend on the nitroaromatic analyte, the substrate (porcelain or filter paper), and on the polymer used. Table 3-1 summarizes the detection limits of TNT, DNT, and PA using the six metallole-containing polymers synthesized - PSi, PDEBSi, PGe, PDEBGe, PSF, and PDEBSF.
Figure 3-3  Luminescence quenching of polymers PSi, PDEBSi, and PGe, by 200, 100, 50, and 10 ng DNT on porcelain plates with well sizes of 2.0 cm in diameter.
Visual detection studies were performed by preparing substrates that were spotted four times, including three spots of an explosive solution and one spot of a solvent blank. An independent observer was asked to identify dark spots in the polymer thin film. Detection limits were noted as the lowest concentration of explosives that enabled the independent observer to notice quenching. The detection limits depend on the quality of the polymer thin film. Film quality depends on the concentration of the polymer in solution and the quality of the airbrush. The independent observer was able to correctly identify the presence of explosives at the
detection limits reported in Table 3-1, on average for all analytes, more than 75% of the time when film quality was poor, with an approximate false positive rate of 10%. However, in cases when high quality, uniform films are prepared, quenching is more clearly discernable. A probability of detection >90% was obtained at the detection limits reported in Table 3-1; probabilities of detection at the detection limit are also listed parenthetically in Table 3-1. At contamination levels 10 ng above the reported detection limits, 100% probability of detection was achieved, with no false positives.

**Table 3-1** Detection limits (ng) and probabilities of detection (listed parenthetically) of nitroaromatic explosives (TNT, DNT, PA) with luminescent metallole-containing polymers

<table>
<thead>
<tr>
<th></th>
<th>TNT</th>
<th></th>
<th></th>
<th>DNT</th>
<th></th>
<th></th>
<th>PA</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Paper</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSi</td>
<td>10 (100%)</td>
<td>30 (100%)</td>
<td>40 (100%)</td>
<td>50 (100%)</td>
<td>40 (93%)</td>
<td>40 (93%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDEBSi</td>
<td>10 (100%)</td>
<td>30 (100%)</td>
<td>20 (100%)</td>
<td>50 (100%)</td>
<td>20 (87%)</td>
<td>30 (93%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGe</td>
<td>5 (93%)</td>
<td>30 (100%)</td>
<td>30 (87%)</td>
<td>50 (100%)</td>
<td>30 (100%)</td>
<td>30 (93%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDEBGGe</td>
<td>10 (100%)</td>
<td>30 (87%)</td>
<td>50 (100%)</td>
<td>50 (93%)</td>
<td>30 (87%)</td>
<td>3 (93%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSF</td>
<td>5 (87%)</td>
<td>30 (93%)</td>
<td>20 (87%)</td>
<td>40 (93%)</td>
<td>5 (100%)</td>
<td>5 (100%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDEBSF</td>
<td>10 (93%)</td>
<td>20 (93%)</td>
<td>20 (93%)</td>
<td>40 (93%)</td>
<td>5 (100%)</td>
<td>5 (100%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In all cases, the detection limits observed on porcelain were as low or lower than those observed on paper. This is not surprising since the dissolved analyte may be carried deep into the paper fibers during deposition, thus lowering the amount of explosive analyte available on the surface after solvent evaporation. Less of the explosive would therefore be present to visibly quench the luminescence from the thin film of polymer on the surface. This situation will be less of a problem in real applications, because explosive traces are expected to be in the form of residual particulates from the solid phase rather than from solution.

Since the method of detection is through electron-transfer luminescence quenching of the polymer luminescence by the analytes, the ability of the polymers to detect explosives depends on the oxidizing power of the analytes. The oxidation potentials of the analytes follow the order TNT > PA > DNT. Both TNT and PA have three electron-withdrawing nitro substituents on the aromatic ring that account for their higher oxidizing and quenching potential relative to DNT, which has only two nitroaromatic substituents. PA has a lower oxidation potential than TNT due to the electron donating power of the hydroxy substituent.

Fluorometric detection is highly sensitive, and these polymers offer a method to detect nitroaromatic explosives at detection limits lower than those obtained from performance evaluation tests using the colorimetric detection system ExPray. The first step in the ExPray system detects nitroaromatics, while the second and third steps encompass nitramines, nitrate esters and inorganic nitrates. One advantage of polymetalloles is that, like many commercial colorimetric schemes including ExPray,
they may potentially be combined with other detection methods as part of a more comprehensive explosives detection system, encompassing non-nitroaromatics, while enabling a much higher sensitivity to nitroaromatics.

Detection studies were performed at an explosives testing range in order to observe the behavior of this technology in experiments closer to what might be expected in the real-world. The explosives available at the range are as they exist in their commonly used form, rather than in their purified form as used in the laboratory studies, for instance, with impurities, plasticizers, etc. that would be part of the chemical composition of the explosives as they are actually used. In these range experiments, the solid forms of the explosives were used to contaminate the filter paper, rather than organic solutions of the explosives. Therefore, although no quantitative data on the amount of explosive present could be determined, the resultant contamination resembles that which might be expected in real-world applications, as far as surface coverage, particulate size, and size distribution.

Both PSi and PDEBSi positively identify the presence of TNT and Comp B, which contains TNT in addition to RDX, through luminescence quenching. In addition, nitromethane and Pyrodex are detected by PDEBSi. As stated above, these polymers may potentially be used in conjunction with other detection methods to broaden the range of detectable explosives to nitrate esters and nitramines, while obtaining the high sensitivity of the polymetalloles with respect to nitroaromatics. Overall, polymetalloles present an inexpensive, simple and rapid visual detection method that reliably identifies low nanogram levels of nitroaromatic explosives.
3.5 EXPERIMENTAL

**Polysilole (PSi) and Polygermole (PGe):** PSi and PGe were prepared according to the literature, and as described in section 2.4.

**Poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylsilole (PDEBSi), Poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylgermole (PDEBGe), Poly(1,4-diethynylbenzene)silafluorene (PDEBSF), and Polysilafluorene (PSF):** The syntheses of these new metallole-organic copolymers proceeds via catalytic hydrosilation of diethynylbenzene by a dihydrometallole. Details will be made known in an upcoming publication.

3.6 ACKNOWLEDGEMENT

This chapter is a reprint of the material which has been submitted to Journal of Forensic Sciences. With J. Sanchez, R.E. Dugan, and W.C. Trogler. Newtec Services Group, Inc. is acknowledged for providing production line explosives and for the use of their facilities for this research. Sara A. Urbas and Victoria Crockett are acknowledged for their help in the synthesis and laboratory studies.

3.7 REFERENCES


(22) The synthesis and characterization of these polymers will be made known in a forthcoming publication, by Sanchez, J.; Urbas, S.A.; Toal, S.J.; Trogler, W.C.

CHAPTER IV

LUMINESCENT OLIGO(TETRAPHENYL)SILOLE NANOPARTICLES AS CHEMICAL SENSORS FOR AQUEOUS TNT

4.1 ABSTRACT

Colloidal oligo(tetraphenyl)nanoparticles in THF/H₂O suspensions show increased luminescence and offer a method to detect the explosive TNT in an aqueous environment. The colloid is prepared by the rapid addition of water to a THF solution of the polymer. A minimum volume fraction of 60% water is necessary to precipitate the colloid, as evidenced by a sharp rise in photoluminescence of the colloid over an organic solution of the polymer. Highest luminescence yield is achieved with 90% water, with lower yields at 95% and 99% water, possibly due to solvent trapping by the particles during their formation. Colloids with higher water content (>80%) show little to no change in luminescence over 5 days, indicating good particle stability. Dynamic light scattering data shows the particles to exhibit a minimum size of 60 nm in diameter at 90% water, with somewhat larger particles at higher and lower water fractions. Essentially all of the silole is aggregated at water fractions above 80%. The nanoparticles exhibit non-exponential fluorescence decay, and fluorescence lifetimes are dependent on water fraction. The lifetime of the polymer in solution and colloid are 0.59 ns and ~3.8 ns, respectively. The method of TNT detection is through electron transfer quenching of the excited state of the silole by the analyte.
of the colloid is not dependent on analyte concentration, indicating static quenching. The colloids are more than 400% more sensitive to TNT compared to the polymer in organic solution, as determined from Stern-Volmer quenching efficiencies.

4.2 INTRODUCTION

Aggregation-induced emission of silole species has been recently observed.\textsuperscript{1,2} The large increase in luminescence from tetraphenylsilole aggregates has been attributed to the restricted rotation of the phenyl rings, which limits the nonradiative decay pathways;\textsuperscript{3} however, the inhibition of solvent assisted quenching resulting from aggregation is another possible explanation.\textsuperscript{4} Lifetime measurements show dramatically lengthened emission lifetimes in the solid state.\textsuperscript{3,4} Siloles have also been shown to have potential as chemosensors for detecting oxidizing species, such as chromate\textsuperscript{4,5} and explosives.\textsuperscript{6,7} For example, poly(tetraphenyl)silole, 1, has been shown to detect nitroaromatics, including TNT, with high sensitivity in organic solution.\textsuperscript{7} Methods using capillary electrophoresis with sample preconcentration\textsuperscript{8} have been developed to detect TNT well below the low to mid ppb concentration found in ground water near some military facilities.\textsuperscript{9} Concentrations in ground water near unexploded ordinance have been measured as high as 500 ppb,\textsuperscript{10} while concentrations in soil are often near 1000-5000 ppm.\textsuperscript{11} The US Environmental Protection Agency has issued a Health Advisory Standard of 2 ppb for TNT.\textsuperscript{12} Commercially available colorimetric kits are able to detect TNT above 500 ppb in soil, and in the 20-45 ppb range in water.\textsuperscript{13} We report herein the sensing of TNT in aqueous media using
nanoparticles of oligo(tetraphenyl)silole, produced by the precipitation of an organic solution of the oligomer with water. Photophysical properties of the nanoparticles are also discussed.

4.3 RESULTS AND DISCUSSION

4.3.1 Colloid Preparation and Luminescence

The luminescence properties of the nanoparticles depend greatly on the solution in which they are suspended. A colloid of 1 is prepared by the rapid precipitation from a THF solution by the addition of water. A minimum volume-fraction of 60% water is needed to effect a sizable increase in luminescence, which indicates the onset of aggregation (Figure 4-1). This critical water concentration is similar to that observed with other silole monomers, but less than the 80% needed to aggregate the more hydrophilic siloleamine. The luminescence of colloids precipitated with 80 and 90% water are very similar, but the luminescence decreases if the volume fraction of water is increased to 95%, and more so at 99% water. No change in the $\lambda_{\text{max}}$ of emission is observed between the nanoparticles and dissolved species, unlike the monomeric silole amine nanoparticles which undergo a 10 nm red-shift in fluorescence relative to the dissolved species. This may indicate that the majority of the silole rings in the oligomer are protected from solvent, because of the helical structure. This may also explain the much longer lifetime observed for the oligomer in solution (590 ps) as compared to the monomeric silole amine (26 ps).
Figure 4-1  Left: oligo(tetraphenyl)silole; Right: Fluorescence spectra of oligosilole aggregates in THF:H$_2$O suspensions with %H$_2$O, from top, equal to 90, 80, 95, 99, 70, 60, 50, and 0%

Nanoparticles formed with higher water volume fractions ($\geq 80\%$) are quite stable. Fluorescence spectra taken on 6 mg/L nanoparticles stored in amber vials (to protect from photobleaching) showed little to no change ($<5\%$) in fluorescence intensity over 5 days time.

4.3.2 Particle Sizing

Colloids of 1 consist of particles on the order of 80 nm in diameter, as determined by dynamic light scattering measurements.$^{14}$ Particle diameter appears to vary somewhat with water fraction, but to be more or less monodisperse ($\pm 20\%$) for any given suspension (Table 4-1).
Table 4-1  Summary of percent aggregated silole, particle diameter (D) mean lifetimes of emission (τ), and Stern-Volmer constants (K_{SV}), for nanoparticle suspensions of I (6 mg/L) at various water percentages

<table>
<thead>
<tr>
<th>% H₂O</th>
<th>% aggregates</th>
<th>D (nm)</th>
<th>τ (ns)</th>
<th>K_{SV}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0^a</td>
<td>&lt;1</td>
<td>--</td>
<td>0.590</td>
<td>970</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
<td>--</td>
<td>0.625</td>
<td>2800</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
<td>90</td>
<td>1.43</td>
<td>3400</td>
</tr>
<tr>
<td>70</td>
<td>55</td>
<td>90</td>
<td>2.48</td>
<td>3300</td>
</tr>
<tr>
<td>80</td>
<td>&gt;95</td>
<td>70</td>
<td>3.64</td>
<td>5000</td>
</tr>
<tr>
<td>90</td>
<td>&gt;95</td>
<td>60</td>
<td>3.84</td>
<td>4100</td>
</tr>
<tr>
<td>95</td>
<td>&gt;95</td>
<td>70</td>
<td>3.48</td>
<td>4300</td>
</tr>
<tr>
<td>99</td>
<td>&gt;95</td>
<td>100</td>
<td>3.26</td>
<td>4500</td>
</tr>
</tbody>
</table>

^a In THF

4.3.3 Fluorescence Lifetimes

Flourescence lifetimes^{14} of the nanoparticles were measured and compared to those of the solid oligomer as well as to a THF solution of the oligomer. Three exponentials were needed to obtain an adequate fit of the fluorescence decay. The oligomers exhibit a trimodal distribution of molecular weights^{15} and are not expected to respond as a single chromophore. In addition, the nanoparticles vary somewhat in size. Even a 20 - 30% variation in diameter amounts to a 170 - 220% change in volume, and, potentially, a 290 – 480% variation in the duration of random energy migrations to quenching sites. The distribution of quenching sites may show
heterogeneity itself. Even the solid oligomer, with a mean lifetime of 4.08 ns does not follow a single exponential decay, indicating the possibility of multiple decay pathways in the oligomer chain.

Mean lifetimes\textsuperscript{16} also depend on the water fraction in the suspensions (Figure 4-2). The mean lifetime of oligosilole nanoparticles in 90% water have the longest lifetime, 3.84 ns, followed by the 80%, 95%, and 99% water suspensions (Table 4-1). This trend follows the steady state fluorescence, in that the more intensely luminescent samples are longer lived. The large difference in mean lifetime between 50% water (0.625 ns) and 60% water (1.43 ns) further supports the conclusion that 60% water is the onset of aggregation, as suggested by the steady state fluorescence changes (Figure 4-1).

**Figure 4-2** Semilog plots of fluorescence decay versus time for nanoparticle suspensions in (a) 0%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, (f) 90%, (g) 95%, (h) 99% water, and (i) solid oligosilole
The percentage of silole existing in the suspension as aggregates was calculated from the fluorescence lifetime decay curves (Table 4-1). The nonexponential fluorescence decay from the unaggregated polymer is not easily distinguished from the fluorescence decay of the aggregates, imposing some limit on the certainty of the fit. Only 3% of silole is aggregated at 50% water, but the value rises to 30% at 60% water, coinciding with the rise in luminescence at these water fractions. Nearly all (>95%) of the silole is aggregated for suspensions consisting of 80% water and above. The decay curves of 80% water and above are essentially identical with the decay curve for the solid silole, demonstrating that most or all of the silole in the suspension is aggregated.

The lower fluorescence yields of the 95% and 99% water suspensions may be due to the kinetics of aggregation in the precipitation of the colloids. It is possible that during rapid precipitation with large amounts of water, solvent is trapped within the particles. This would account for the larger particle sizes observed, as well as the slightly shorter lifetimes observed. The behaviour of this system is in contrast to the silole amine nanoparticle suspensions,\(^4\) whose large increase in luminescence for 95% and 99% water fraction colloids correlates with a higher percentage of the silole being precipitated as nanoparticles at these higher water fractions.

4.3.4 TNT Detection

The ability of the oligosilole nanoparticles to detect TNT through luminescence quenching was investigated by adding successive aliquots of a THF
stock solution of TNT to the nanoparticles. The decrease in luminescence was monitored as a function of added TNT. Luminescence quenching is observed as low as 100 ppb in pH 7 buffered solution. The response to quenching of various colloids was analyzed using the Stern-Volmer equation: \[ \frac{I_0}{I} = K_{SV}[A] + 1. \] Linear Stern-Volmer relationships are observed for both the colloidal and solvated oligosilole in the ppm range. Linear relationships may arise from either a static or dynamic quenching mechanism. In the case of dynamic quenching, bimolecular collisions of the quencher and fluorophore occur; hence, lifetimes vary proportionally with quencher concentration. In the case of static quenching, quenching occurs through a bound complex of quencher and fluorophore, and lifetimes are invariant with quencher concentration. \[ \text{Fluorescence lifetimes of nanoparticle suspensions of various water percentages were measured and were largely unchanged by added TNT (Figure 4-3). This indicates a static quenching mechanism, as previously observed for TNT and oligosilole in toluene solution.} \] It was hypothesized that the planar TNT molecule intercalates between the phenyl substituents around the silole ring, a mechanism which may likewise account for the static quenching of the oligosilole nanoparticles. Since intercalation may upset aggregate structure, especially at high quencher concentration, there may be small changes in excitation migration through the aggregates that is reflected by the small changes in lifetimes observed at high TNT concentration.
Figure 4-3  Semilog plots of fluorescence decay versus time for a nanoparticle suspension of 1 in 90% water with, from top, 0, 2, 4, 6, 8, 10, and 20 ppm added TNT. Curves have been offset for clarity.

The Stern-Volmer analysis also allows a comparison of the quenching efficiencies of TNT on the various colloids (Figure 4-4). Quenching experiments were performed on nanoparticle suspensions, as well as on 1 dissolved in THF. Quenching efficiencies improved more than 400% for the nanoparticles relative to the dissolved oligosilole (Table 4-1). The $K_{SV}$ were similar for nanoparticle suspensions consisting of a minimum of 80% water, which is consistent with their similar size and lifetime. At water percentages below 80%, when the silole is not significantly aggregated,
quenching efficiencies drop noticeably. Thus, aggregation to form nanoparticles is favorable for TNT detection in aqueous solution.

![Figure 4-4](image.jpg)

**Figure 4-4** Stern-Volmer plots of luminescence quenching of nanoparticle suspensions of I in various water percentages by TNT

In the case of static quenching, the Stern-Volmer constant ($K_{SV}$) is an association constant between the quencher and fluorophore receptor sites. It was found that vigorous shaking or stirring of the colloid after addition of TNT more than doubled the quenching efficiency. Such bulk mixing of the sample may aid in the adsorption of analyte into polymer. Under these conditions, quenching comparable to the sensitivity of commercially available colorimetric kits is easily observed below 20 ppb.
4.4 ACKNOWLEDGEMENT

This chapter is a reprint of the material as it appears in Chemical Communications, 2005, 43, 5465-5467. With D. Magde and W.C. Trogler.

4.5 NOTES AND REFERENCES


(14) Experimental setup and procedures for fluorescence lifetimes and dynamic light scattering can be found in reference 4 and 7, respectively.


(16) Mean lifetime is calculated as the amplitude-weighted mean of the three lifetimes used in fitting. This is the definition of mean that correlates with fluorescence yield.


CHAPTER V

LUMINESCENT SILOLE NANOPARTICLES AS CHEMOSELECTIVE SENSORS FOR CHROMIUM(VI)

5.1 ABSTRACT

Colloidal suspensions of 3-aminopropyl-methyl(tetraphenyl)silole nanoparticles can be used as selective chemosensors for carcinogenic chromium(VI) analyte. Methylhydrosilole is functionalized by hydrosilation of allylamine and the colloid is prepared by the rapid addition of water to a THF solution of the silole. The method of detection is through electron-transfer quenching of the fluorescence of the silole colloid ($\lambda_{em} = 485$ nm at 360 nm excitation) by the analytes, with hundred ppb detection limits. Stern Volmer plots are linear up to 10 ppm in the case of chromium, but exhibit saturation behavior near 5-10 ppm for arsenic. Dynamic light scattering experiments and AFM measurements show the particle sizes to be around 100 nm in diameter, and dependent on solvent composition, with a particle size dispersity of ± 25%. The fluorescence lifetimes of the silole in solution and colloid are ~31 ps and ~4.3 ns, respectively, while the silole has a lifetime of 6 ns in the bulk solid. A minimum volume fraction of 80% water is necessary to precipitate the colloid from THF, and the luminescence continues to rise with higher water fractions. Colloids in a pH 7 phosphate buffered suspension show both higher sensitivity and greater
selectivity (100-fold) for CrO$_4^{2-}$ detection than for other o xoanion interferents, NO$_3^-$, NO$_2^-$, SO$_4^{2-}$, and ClO$_4^-$. 

5.2 INTRODUCTION

Detection of chromium(VI) and arsenic(V) in drinking water is important because both species pose serious health risks and are regulated by the U.S. Environmental Protection Agency. In aqueous solutions at pH 7, CrO$_4^{2-}$, which is isostructural with the sulfate ion, SO$_4^{2-}$, is carried into mammalian cells by sulfate transporters, where the CrO$_4^{2-}$ oxidatively damages DNA. Similarly, the predominant environmental form of As(V) in oxygenated water, AsO$_4^{3-}$, competes in cellular uptake with isoelectronic phosphate, PO$_4^{3-}$. Both chromate and arsenate may be introduced into drinking water through industrial processes, as well as by environmental erosion. The EPA has set the Maximum Contaminant Level Goals (MCLG) for total chromium and arsenic concentrations in drinking water at 100 ppb and 10 ppb, respectively. For chromium, it would be advantageous to be able to distinguish harmful Cr(VI) from benign Cr(III). There are currently several physical detection methods used to identify the presence of chromium and arsenic in aqueous media, including high performance liquid chromatography coupled with atomic absorption spectrometry, fiber optic wave sensors, ion-chromatography, inductively coupled plasma-MS, electrochemical processes, and electron capture-GC. Methods using luminescence quenching for detecting chromate have also been used. These include bacterial sensors with detection limits as low as 2.6
ppb. Dynamic quenching of luminescence in lanthanide complexes by chromate and nitrite using ion chromatography can detect 13 ppb of the anions. A synchronous absorbance and fluorescence analysis of dynamic liquid drops at the end of a flow injection capillary, monitoring the decrease in fluorescence caused by the reaction between chromate and 3,3',5,5'-tetramethylbenzidine dichloride, can detect chromate at the femtomolar level.

Both chromate and arsenate are oxidants, a property that may be exploited to detect their presence in water. Recently, it was reported that silole-containing polymers are selective sensors for nitroaromatic oxidants, including TNT. Detection is achieved though fluorescence quenching of the silole by the electron-deficient analyte. The silole luminescence is due to a $\sigma^*-\pi^*$ LUMO stabilized though conjugation of the $\sigma^*$ orbital of the silicon chain with the $\pi^*$ orbital of the butadiene moiety. The selectivity of the sensor is due to the polymer’s helical structure, which permits intercalation of planar nitroaromatics. The aim of the research reported herein is to make a luminescent silole sensor for aqueous $\text{CrO}_4^{2-}$ and $\text{AsO}_4^{3-}$ by functionalization of a silole monomer with anion binding groups. Recently, it has been reported that colloidal suspensions of methylphenylsilole may be prepared by the rapid addition of water to an ethanolic silole solution, and that the colloid exhibits as much as a 300-fold increase in fluorescence intensity as compared to the organic solution. Other silole colloids have since been prepared and characterized. As most nanoparticles characterized in the literature are either purely inorganic, such as semiconductor quantum dots, or purely organic (e.g. carotenes and dendrimers),
the silole organometallic nanoparticles are of particular interest for their unique photophysical and structural properties, as well as for their sensor applications. Fluorescent inorganic quantum dots have been shown to be widely useful in sensing applications.\textsuperscript{30,31} This paper describes the potential utility of luminescent silole nanoparticles in redox sensing applications. An attractive feature of these molecular based materials is their ease of functionalization for analyte recognition.

5.3 RESULTS AND DISCUSSION

5.3.1 Synthesis and Physical Properties of Siloleamine Chemosensor

In order to make the silole nanoparticles bind oxoanions such as \( \text{CrO}_4^{2-} \) and \( \text{AsO}_4^{3-} \), a hydrogen-bonding amine functionality was incorporated into the monomer via a chloroplatinic acid (\( \text{H}_2\text{PtCl}_6 \)) catalyzed hydrosilation\textsuperscript{32-34} of allylamine with methylhydrosilole, 1, yielding the siloleamine, 2, in 90\% yield (Scheme 5-1).

\begin{center}
\textbf{Scheme 5-1} Synthesis of siloleamine chemosensor.
\end{center}
The UV-vis absorption at 360 nm ($\varepsilon = 7900 \text{ L/mol·cm}$), assigned to the $\pi-\pi^*$ transition of the silole moiety, is typical of tetraphenylsilole monomers.\textsuperscript{35} A powder sample of 2 luminesces a bright yellow-green at 480 nm when excited at 360 nm; however, a THF solution of 2 is only weakly luminescent at 475 nm. The fluorescence quantum yield of 2 in toluene, measured relative to 9,10-diphenylanthracene,\textsuperscript{36} is only 1.15 (±0.35) x 10\textsuperscript{-3}, which is similar to the quantum yields of other silole monomers.\textsuperscript{37} However, a dramatic increase in luminescence is observed for colloids of 2, which are prepared by adding water rapidly to a THF solution of 2. This rise in luminescence is accompanied by a 10 nm red shift in emission wavelength to 485 nm.

5.3.2 Colloid Preparation and Luminescence

Luminescence of the colloid is highly dependent on solvent composition, specifically the amount of water used to precipitate 2. Solutions containing 2, 4, and 6 mg/L of 2 in THF/H\textsubscript{2}O were prepared at various water percentages. The concentration represents the total mass of silole, not the mass of the nanoparticles. A minimum volume fraction of 80% water is necessary to effect a detectable increase in luminescence (Figure 5-1). The luminescence continues to increase with 90, 95, and 99% water. For the 99% water samples, fluorescence rose by a factor of 15x for 2 mg/L, 36x for 4 mg/L, and 46x for 6 mg/L as compared with pure THF solutions of the respective concentration.
5.3.3 Particle Sizing

The colloids consist of particles on the order of 100 nm in size, as determined by dynamic light scattering measurements. Best fits to the data suggest a polydispersity of not more than ± 25%. AFM images of settled particles show similar particle sizes. The colloid particles exhibit a minimum in size at 90% water, with somewhat larger sizes at both greater and lesser volume fractions of water. One possible explanation is that at higher water concentrations the organic silole molecules aggregate to a higher extent in the hydrophilic environment. The larger colloid particles observed at lower water concentrations may possibly be explained by THF absorbing into the particles causing them to swell.
5.3.4 Fluorescence Lifetimes

Fluorescent lifetime measurements were performed to compare the dissolved silole and the silole in colloidal suspensions. In toluene solution, the fluorescence lifetime of 2 is only 31 ± 2 ps, which is somewhat longer than the lifetimes of both dimethyl(tetraphenyl)silole at 17.5 ± 2.5 ps, and hexaphenylsilole, whose reported lifetime in acetone is 20 ps. Intramolecular quenching of the π-π* excited state of the silole by the donor amino moiety is therefore not responsible for the short lifetime in the siloleamine. Indeed, the luminescence of polysiloles is quenched by electron acceptors, rather than by electron donors. The lifetime of 2 is about 20 times shorter than observed for poly(tetraphenyl)silole at 700 ps. The polysilole adopts a helical structure and solvent access to the face of the silole π system is restricted. This may account for the long fluorescence lifetime observed for the polymer and for siloles in the solid state. Other workers have attributed the increased lifetime of silole monomers in the solid state to restricted rotation of the phenyl substituents. As water is added and the nanoparticles begin to form, fluorescence emission lifetimes become longer and are clearly non-exponential. Multi-exponential fits of fluorescence decay curves show a fast decay component from unaggregated species still present in the colloidal suspension, along with additional longer decay time components from the nanoparticle aggregates. Figure 5-2 shows semi-log plots of the fluorescence decay curves of 6 mg/L solutions at various water concentrations. The nanoparticles have mean lifetimes of 4.0, 4.3, and 4.6 ns in 90%, 95%, and 99% water solutions.
respectively. The lifetime reported is an average of two exponentials needed to obtain an appropriate fit to the nanoaggregate decay. This is not surprising, as the particles are not uniform in size, but span a size distribution. The longest lived nanoparticles observed have a fluorescence lifetime of 6 ns, which is also the lifetime of 2 in the solid state.

**Figure 5-2** Semi-log plots of fluorescence lifetime decay of 2, 6 mg/L, in THF/water solutions for a) 0%, b) 80%, c) 90%, d) 95% and e) 99% water. Amplitudes are normalized, so all curves begin at 1.

The unaggregated 2 is readily distinguished in Figure 5-2 because of its very short lifetime as compared to the nanoparticles. In an 80% water suspension, 92% of the silole remains dissolved, as can be seen in Figure 5-3b with the sharp initial decay.
In 90% water, 83% silole remains dissolved and in 95% water, 65% of the silole remains dissolved. In a 99% water suspension, less than 10% of 2 is in solution.\textsuperscript{39}

The luminescence intensity is also directly proportional to the percent of aggregated silole (Figure 5-3), as determined from the lifetime analysis. The nonzero intercept in Figure 5-3 corresponds to the weak fluorescence contribution arising from the solution phase silole.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5_3.png}
\caption{Fluorescence intensity as a function of percent aggregated 2 for a 6 mg/L colloid. The percentage of aggregated silole was determined from the fluorescence decay curves.}
\end{figure}
5.3.5 CrO$_4^{2-}$ and AsO$_4^{3-}$ Detection

The ability of the siloleamine to detect the carcinogens CrO$_4^{2-}$ and AsO$_4^{3-}$ was investigated by adding successive aliquots of aqueous stock solutions of the analytes to nanoparticle suspensions of 2 and monitoring the decrease in fluorescence intensity (Figure 5-4 and 5-5 (top), respectively). Quenching of photoluminescence is observed at the EPA action level of 0.1 ppm CrO$_4^{2-}$. Not surprisingly, since AsO$_4^{3-}$ is a weaker oxidant than CrO$_4^{2-}$, it is a weaker quencher as well (standard reduction potentials vs. NHE are -0.68 V and -0.13 V, respectively, and at pH 7 they are +0.15 and +0.56 V, respectively).\(^{40}\) This supports the hypothesis that the quenching of photoluminescence of siloles is due to electron transfer from the excited state of the silole to the analyte.
Figure 5-4 Photoluminescence quenching of 4mg/L 2 by CrO$_4^{2-}$: Top, quenching by, from top, 0, 0.1, 0.5, 1, 2.5, 5, and 10 ppm quencher in 99% water; Bottom: Stern-Volmer plots of photoluminescence quenching in various water percentages
Figure 5-5 Photoluminescence quenching of 4mg/L 2 by AsO$_4^{3-}$: Top, quenching by, from top, 0, 0.5, 1, 2.25, 5, 10, 20, 30 and 40 ppm quencher in 95% water; Bottom: Stern-Volmer plots of photoluminescence quenching in various water percentages.

Quenching efficiencies were fit to the Stern-Volmer equation, $I_0/I = K_{SV} [A] + 1$, which relates the fluorescence intensity, $I$, at different concentrations of analyte quencher, $[A]$, where $I_0$ is the intensity at $[A] = 0$, and $K_{SV}$ is the Stern-Volmer constant. A plot of CrO$_4^{2-}$ quenching efficiency is linear up to 10 ppm, at which point there is a rise in quenching efficiency (Figure 5-4 bottom). Since chromate ion
absorbs at 360 nm, the apparent increase in quenching seen in Stern-Volmer plots is an artifact that does not represent real quenching but rather an inner filter effect. However, a Stern-Volmer plot of AsO$_4^{3-}$ quenching saturates above 10 ppm (Figure 5-5 bottom). The nonlinear relationship observed for arsenate may indicate saturation of the surface-binding sites, since the nanoparticle concentration per liter is approximately $6 \times 10^{12}$, which is less than the analyte molecular concentration per liter of approximately $4 \times 10^{18}$ at 1 ppm AsO$_4^{3-}$. It also suggests that the lower driving force for electron transfer with AsO$_4^{3-}$ does not permit complete quenching at saturation coverage of the nanoparticles.

The selectivity of the colloid sensor was tested by performing quenching experiments in pH 7 phosphate buffered suspensions, using both CrO$_4^{2-}$ and AsO$_4^{3-}$, as well as common aqueous interferents, NO$_3^-$, NO$_2^-$, SO$_4^{2-}$, and ClO$_4^-$. Colloids prepared in the buffer were almost twice as luminescent as those prepared in distilled water, since the presence of phosphate alone led to an increase in nanoparticle luminescence. The buffer was used in the interferent quenching studies in order to prevent variations in the fluorescence intensity caused by changes in ionic strength from quenchers at higher concentrations (>50 ppm). Sensitivity to Cr(VI) detection more than doubled in the buffered aqueous colloid as compared to the unbuffered suspensions. Even though phosphate anions may compete with chromate for surface hydrogen bonding sites, the increased luminescence intensity more than compensates for any sensitivity loss. Stern-Volmer plots of Cr(VI) quenching in the buffered aqueous colloid are linear only up to 1 ppm, after which there is a sharp rise in
sensitivity. This may be due to competition between the chromate quencher and phosphate buffer for binding sites at lower chromate concentrations. However, sensitivity to arsenate decreased about 20-fold for the buffered colloid, which suggests that phosphate effectively competes with arsenate. Much higher concentrations of the interferent analytes (NO$_3^-$, NO$_2^-$, SO$_4^{2-}$, and ClO$_4^-$) were needed to observe quenching. Comparison of the slopes of Stern-Volmer plots gives relative sensitivities to analyte detection. For instance, the buffered colloid is 120 times more sensitive to chromate than to nitrate. A summary of the relative sensitivities is shown in Table 5-1. The net result is that preparation of the colloid of 2 with a pH 7 phosphate buffer produces a highly selective chromate sensor.

**Table 5-1**  Stern-Volmer constants and relative sensitivities of a pH 7 phosphate buffered colloid of 2 to various aqueous anions

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Stern-Volmer Constant (M$^{-1}$)</th>
<th>Relative Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>87</td>
<td>1.0</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>140</td>
<td>1.6</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>170</td>
<td>2.0</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>780</td>
<td>9.0</td>
</tr>
<tr>
<td>AsO$_4^{3-}$</td>
<td>1300</td>
<td>15</td>
</tr>
<tr>
<td>CrO$_4^{2-}$</td>
<td>10,900</td>
<td>120</td>
</tr>
</tbody>
</table>
Quenching experiments were also carried out on environmental water samples to determine the ability of the silole to detect chromate in the presence of ambient interferents at actual environmental concentrations. Quenching efficiencies for chromate spiked in San Diego tap water were identical to those measured in distilled water, and efficiencies for chromate spiked in La Jolla sea water were only slightly higher (Figure 5-6). The higher sensitivity to chromate in the saline sea water, with its high ionic strength, is in agreement with the observation that buffered suspensions also provide more sensitive chromate detection.

**Figure 5-6** Stern-Volmer plots of luminescence quenching of 2, 4 mg/L, in 90% water suspension, by chromate
5.4 EXPERIMENTAL

5.4.1 General Synthetic Techniques

All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard Schlenk techniques. Solvents were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl. NMR data were collected with a Varian Unity 300 or 500 MHz spectrometers (300.1 MHz for $^1$H, 77.5 MHz for $^{13}$C, and 99.4 MHz for $^{29}$Si NMR). Fluorescence emission and excitation spectra were recorded with the use of a Perkin-Elmer LS 50B Luminescence Spectrometer. UV-vis spectra were obtained with the use of a Hewlett-Packard 8452A diode array spectrometer. Atomic Force Microscopy images of particles settled on glass slides were obtained with the use of a Digital Instruments Nanoscope IIIa. Fluorescence lifetimes were measured using time-correlated photon counting, following excitation by the frequency-doubled output of a mode-locked Ti:sapphire laser, as described previously. Dynamic light scattering used an argon-ion laser line at 514.5 nm, with detection at 90° in a solid angle of one or two coherence areas. Individual photons were detected and recorded in bin-widths of 10 µs and correlation functions calculated by digital computer, assuming spherical particles. Although the particle diffusion can be obtained through first principles, the calibration was verified by measuring latex spheres of known diameters.

5.4.2 Synthesis of 1-methyl-1-(3-aminopropyl)-2,3,4,5-tetraphenylsilole
Methylhydrosilole\textsuperscript{42} (1.0 g, 2.5 mmol), allylamine (0.36 mL, 5.0 mmol), and H\textsubscript{2}PtCl\textsubscript{6}·xH\textsubscript{2}O (2.5 mg, 5 µmol) and freshly distilled toluene (10 mL) were placed under an Ar atmosphere and refluxed for 20 h. The solution was cooled, passed through a sintered glass frit, and evaporated to dryness. The product was dissolved in ether and precipitated with hexanes and filtered. The precipitate was collected as a yellow powder: (1.1 g, 90 %); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3} δ = 7.26): δ = 6.7-7.3 (m, 20H, Ph), δ = 2.64 (t, 2H), δ = 1.53 (m, 2H), δ = 1.01 (m, 2H), δ = 0.49 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3} δ = 77.00): δ = 154.638, 140.784, 139.691, 138.523, 129.802, 128.685, 127.838, 127.254, 126.079, 125.419, 44.847, 27.367, 10.593, 4.587; \textsuperscript{29}Si NMR (99.36 MHz, INEPT, CDCl\textsubscript{3}, TMS (δ = 0.0)): δ = 9.5; MS(ES): m/z 458.8 [M+1]; CHN (w/ O\textsubscript{2} purge): C\textsubscript{32}H\textsubscript{31}SiN·H\textsubscript{2}O: Calc: C 80.79, H 6.99, N 2.94, Found: C 81.40, H 6.99, N 2.80.

5.5 ACKNOWLEDGEMENT

This chapter is a reprint of the material as it appears in the Journal of the American Chemical Society, 2005, 127(33), 11661-11665. With K.A. Jones, D. Magde, and W.C. Trogler.

5.6 NOTES AND REFERENCES


(39) This assumes the quantum yields of the aggregates and unaggregated silole are proportional to $\tau_{\text{obs}}/\tau_{\text{rad}}$, where $\tau_{\text{obs}}$ is the observed lifetime and $\tau_{\text{rad}}$ is the radiative lifetime. The radiative lifetimes are assumed to be the same for both species, because their absorption and emission spectra are nearly identical.


The unique electronic structure of metalloles and metallole polymers has attracted research on employing these compounds for a variety of applications, including electron transporting materials, light emitting diodes, and, recently, chemical sensors. The $\pi^*$ LUMO of the butadiene ring in metalloles is stabilized through conjugation with the two exocyclic $\sigma^*$ orbitals on the metalloid atom, which further results in a reduction in the HOMO-LUMO band gap energy. Metalloles, therefore, are highly luminescent materials in the solid state, with excitation energies in the near UV spectral region.

This electronic structure is useful for sensor applications because the low-lying LUMO allows for electron-transfer quenching of excited state siloles by electron-deficient analytes. The research described in this dissertation aims to illustrate the utility of metalloles as chemoselective sensors for nitroaromatic explosives and carcinogenic chromate. The sensitivity and selectivity of the sensors depend on functionalizing the metallole appropriately for analyte binding specificity.

Chapter 2 describes an improved catalytic dehydrocoupling synthetic method for poly(1,1-metalloles) which reduces reaction time and complexity, uses less hazardous reagents, and significantly increases product yield over Wurtz-type
polycondensation by more than 50%. An improved synthesis was desired because these polymers had been previously shown to be sensitive nitroaromatic detectors. The polysiloles and polygermoles were prepared in 60-90% yield using dehydrocoupling transition metal catalysts and hydrogen accepting alkene coreagents. Although secondary polysilanes do not undergo dehydrocoupling to give more than trimers, the secondary metalloles may dehydrocouple to give extended oligomers due to the reduced steric hindrance at the metalloid center. The heterogenous catalyst, $\text{H}_2\text{PtCl}_6$, provides the highest yield and easier workup, as opposed to the homogenous catalyst which are more difficult to remove during product purification. One consequence with this new approach is the minor amount of hydrosilation of alkene coreagents by polymer chain Si-H or Ge-H endgroups. This result is not terribly frustrating, as endgroup hydrosilation does not affect the electronic conjugation over the Si-Si or Ge-Ge chains (as evidenced by the Fluorescence and UV-vis data). It may, however, limit product chain length by serving as a termination step in the polymerization.

Further investigations into additional transition metal catalysts may be warranted to increase chain length and electronic conjugation. Heterogeneous catalysts which are good hydrogenation catalysts, but poor hydrosilation catalysts, would be ideal. Metalloocene catalysts, such as $\text{Cp}_2\text{ZrMe}_2$ and $\text{Cp}_2\text{TiMe}_2$, used for polysilane and polysilafluorene dehydrogenative coupling may effectively couple metalloles due to the reduced steric hindrance at the metalloid center. The addition of a hydrogen acceptor, such as cyclohexene, may also improve product yield and
molecular weight. This research also showed that metalloles and polymetalloles will indeed undergo hydrosilation, just as polysilanes do, a reaction that had not been previously reported. This may be of use in polymer endgroup functionalization, for instance with trimethylsilylacetylene, for molecular weight determination, or for sensor application in engineering analyte-specific binding oligometalloles. It also revealed possibility of making metallole-organic copolymers through hydrosilation of unsaturated organic compounds by dihydrometalloles. Such compounds were synthesized in our lab and used for solid state detection of TNT, as described in Chapter 3.

Chapter 3 illustrates the effectiveness of fluorescent metallole-containing polymers as sensitive and selective sensors of nitroaromatic explosives, particularly TNT, DNT and picric acid (PA). Detection through electron-transfer luminescence quenching for thin films of polysilole and polygermole shows remarkable sensitivity, with detection limits as low as 5 ng for TNT, and 30 ng for DNT and PA. In addition, metallole-organic copolymers were prepared by the hydrosilation of diehtynylbenzene (DEB) with dihydrosilole, dihydrogermole, and dihydrosilafluorene. Sensitivity of the DEB silole and germole are comparable to or slightly lower than the analogous polysilole and polygermole. Significant improvements in sensitivity to PA were obtained using the silafluorene polymer and copolymer, with detection limits observed as low as 5 ng.

The high sensitivity of picric acid detection with the silafluorenes may give insight into the mechanism of quenching. It is possible that the two species have a
high binding affinity, or LUMOs of similar energy whose orbital overlap provides a means for efficient electron transfer. However, for all other polymers, detection limits follow the trend in oxidation potential, where the more oxidizing analyte (TNT) proved to be a better quencher than the least oxidizing analyte (DNT). This indicates that the driving force for luminescence quenching is the redox potentials of the analytes. A detailed electrochemical study of the metallole polymers and copolymers, and several oxidizing analytes, nitroaromatic and otherwise, would be useful in elucidating the quenching mechanism. Such an understanding of the detection mechanism may aid in synthetically tailoring fluorescent metalloles for more selective and sensitive explosives detection.

Chapter 4 furthers the investigation of polysilole as an explosives detector to aqueous TNT. Nanoparticles of the polymer may be made by the rapid addition of water to an organic solution of the polymer. The increase in luminescence for the colloid over an organic solution has been attributed to the restriction of phenyl ring rotation, which prevents non-radiative decay pathways. Prevention of solvent-assisted quenching may also contribute to the fluorescence rise. When all the silole is aggregated, particles on the order of 80 nm are formed, with fluorescence lifetimes near 4 ns, the lifetime of the polymer solid. Detection limits well below 100 ppb are observed. Longer mixing times allow for analyte adsorption into the polymer and detection limits improve. These silole nanoparticles present an interesting photophysical system, which has not, as yet, been much researched. One area to
explore is energy migration and electron transport through the polymer in the colloid, as compared to polymer in solution and polymer thin films.

Chapter 5 extends the discussion of silole chemosensors functionalized silole monomers and carcinogenic chromate. A $\text{H}_2\text{PtCl}_6$ catalyzed hydrosilation of allylamine by methylhydrosilole produces the siloleamine, which has an hydrogen-bonding amino substituent specific for oxoanion binding. Nanoparticles of the siloleamine may be formed in a manner similar to the polysilole nanoparticles. A higher water fraction is necessary for siloleamine nanoparticle precipitation due to its more hydrophilic character. Particles are on the order of 100 nm, with fluorescence lifetimes of the longest lived particles near the lifetime of the solid at 6 ns. Chromate detection limits below the EPA maximum contaminant level of 100 ppb are obtainable through redox fluorescence quenching. One attractive feature of this detector is the chemoselectivity of the sensors. Chromate has a 120 times higher quenching efficiency than nitrate, and much larger quenching efficiencies than several common oxoanion contaminants. Experiments with environmental samples show that the quenching efficiency of chromate is not diminished by ambient aqueous contaminants.

The colloid of functionalized monomers presents another system for future photophysical investigation. Exploration of excited state characteristics, energy migration, and analyte quenching mechanisms will give insight into the electronic properties of the colloid, as compared to an organic solution. Differences in polymeric versus monomeric colloids would be an interesting comparison. Synthetic manipulation of monomers and oligomers with more efficient or multiple hydrogen
bonding units may increase sensitivity to chromate detection. Chelation substituents
are one such avenue to explore.

Metallole polymers, copolymers, and functionalized monomers have been
shown to be relevant for chemosensor applications. The utilization of catalytic
hydrosilation allows for synthetic flexibility and targeted analyte binding. Metalloles
present an attractive starting point for the redox sensing of explosives and carcinogens
through fluorescence detection.