

Detection of Nitroaromatic Explosives Based on Photoluminescent Polymers Containing Metalloles

Honglae Sohn, Michael J. Sailor,* Douglas Magde,* and William C. Trogler*

Contribution from the Department of Chemistry and Biochemistry, University of California at San Diego, 9500 Gilman Drive, San Diego, California 92093-0358

Received September 26, 2002; E-mail: wct@chem.ucsd.edu

Abstract: The synthesis, spectroscopic characterization, and fluorescence quenching efficiency of polymers and copolymers containing tetraphenylsilole or tetraphenylgermole with Si-Si, Ge-Ge, and Si-Ge backbones are reported. Poly(tetraphenyl)germole, 2, was synthesized from the reduction of dichloro-(tetraphenyl)germole with 2 equivs of Li. Silole-germole alternating copolymer 3 was synthesized by coupling dilithium salts of tetraphenylsilole dianion with dichloro(tetraphenyl)germole. Other tetraphenylmetallolesilane copolymers, 4-12, were synthesized through the Wurtz-type coupling of the dilithium salts of the tetraphenylmetallole dianion and corresponding dichloro(dialkyl)silanes. The molecular weights (Mw) of these metallole-silane copolymers are in the range of 4000~6000. Detection of nitroaromatic molecules, such as nitrobenzene (NB), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and picric acid (PA), has been explored. A linear Stern-Volmer relationship was observed for the first three analytes, but not for picric acid. Fluorescence spectra of polymetalloles or metallole-silane copolymers obtained in either toluene solutions or thin polymer films displayed no shift in the maximum of the emission wavelength. This suggests that the polymetalloles or metallole-silanes exhibit neither π -stacking of polymer chains nor excimer formation. Fluorescence lifetimes of polymetalloles and metallole-silanes were measured both in the presence and absence of TNT, and τ_0/τ is invariant. This requires that photoluminescence quenching occurs by a static mechanism.

Introduction

Chemical sensors for nitroaromatics,^{1,2} which offer new approaches to the rapid detection of ultra-trace anaytes from explosives, have attracted attention because explosives are important chemical species to detect^{3,4} in mine fields,⁵ military applications, munitions remediation sites, and homeland security applications.⁶ Other applications include forensic investigations, such as post-blast residue determinations.^{7,8} Metal detectors, widely used as portable instrumentation for field explosive detection, cannot locate the plastic casing of modern land mines. Trained dogs are expensive, difficult to maintain, and are easily fatigued.⁹ Physical detection methods for explosives include gas chromatography coupled with a mass spectrometer,¹⁰ surfaceenhanced Raman spectroscopy,¹¹ nuclear quadrupole reso-

- (1) McQuade, D. T.; Pullen, A. E.; Swager, T. M. Chem. Rev. 2000, 100, 2537-2574.
- (2) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. Chem. Rev. 2000, 100, 2595–2626.
- (3) Yinon, J. Forensic and Environmental Detection of Explosives; John Wiley & Sons Ltd: Chichester, 1999. (4) Steinfeld, J. I.; Wormhoudt, J. Annu. Rev. Phys. Chem. 1998, 49, 203-

- (5) Rouhi, A. M. Chem. Eng. News 1997, 75, 14–22.
 (6) Fainberg, A. Science 1992, 255, 1531–1537.
 (7) Barshick, S.-A. J. Forensic Sci. 1998, 43, 284–293.
- (8) Smith, K. D.; McCord, B. R.; McCrehan, W. A.; Mount, K.; Rowe, W. F.
- (b) Shindi, R. D., McCord, D. R., McCrenan, W. J. Forensic Sci. 1999, 44, 789–794.
 (9) Czarnik, A. W. Nature 1998, 394, 417–418.
- (10) Hakansson, K.; Coorey, R. V.; Zubarev, R. A.; Talrose, V. L.; Hakansson, P. J. Mass Spectrom 2000, 35, 337–346.
 (11) Sylvia, J. M.; Janni, J. A.; Klein, J. D.; Spencer, K. M. Anal. Chem. 2000, 72, 5834–5840.

10.1021/ja021214e CCC: \$25.00 © 2003 American Chemical Society

nance,¹² energy-dispersive X-ray diffraction,¹³ neutron activation analysis, electron capture detection,⁵ and cyclic voltammetry.¹⁴ These techniques are highly selective, but some are expensive and others are not easily fielded in a small, low-power package. Most detection methods for explosives are only applicable to vapor samples because of interference problems encountered in complex aqueous media. Sensing TNT in groundwater or seawater is important for the detection of buried unexploded ordnance and for locating underwater mines.^{15–17} There are also environmental applications for characterizing soil and groundwater contaminated with toxic TNT at military bases and munitions production and distribution facilities.¹⁸ Organic polymers and optical fibers¹⁹ have been previously studied to detect vapors of explosive analytes.^{1,2} The transduction methods used include absorption, fluorescence, conductivity, and so forth. Such simple techniques are promising, because they can be incorporated into inexpensive and portable microelectronic

- (12) Anferov, V. P.; Mozjoukhine, G. V.; Fisher, R. Rev. Sci. Instrum. 2000, 71, 1656-1659.
- (13) Luggar, R. D.; Farquharson, M. J.; Horrocks, J. A.; Lacey, R. J. J. X-ray Spectrom. 1998, 27, 87–94.
 (14) Krausa, M.; Schorb, K. J. Electroanal. Chem. 1999, 461, 10–13.
- (15) Krassa, M., Schork, K. J. Electroland. Chem. D97, 401, 10–13.
 (15) Shriver-Lake, L. C.; Donner, B. L.; Ligler, F. S. Environ. Sci. Technol. 1997, 31, 837–841.
 (16) Lu, J.; Zhang, Z. Analytica Chimica Acta 1996, 318, 175–179.
 (17) Dock, M.; Fisher, M.; Cumming, C. In Fifth International Symposium of
- Mine Warfare Association: Monterey, California, 2002, pp 1-8.
- (18) Approaches for the remediation of federal facility sites contaminated with explosive or radioactive wastes.; U. S. Environmental Protection Agency: Washington, D. C., 1993.
- (19) Albert, K. J.; Myrick, M. L.; Brown, S. B.; James, D. L.; Milanovich, F. P.; Walt, D. R. Environ. Sci. Technol. 2001, 35, 3193–3200.

devices. For example, a chemically selective silicone polymer layer on a SAW (surface acoustic wave) device has been shown to provide efficient detection for the nitroaromatic compounds.²⁰ The fluorescence of pentiptycene polymers^{21,22} and polyacetylene²³ are also highly sensitive to nitroaromatic molecules. Previously we communicated that the inorganic polymer, poly-(tetraphenyl)silole 1, is an excellent material for the detection of explosives by fluorescence quenching.²⁴ The work described herein describes a broad class of easily prepared luminescent inorganic polymer sensors for nitroaromatic compounds. Detection is based on photoluminescence quenching of polymers containing a metallole ring and Si-Si, Si-Ge, and Ge-Ge backbones.

Metalloles are silicon or germanium-containing metallacyclopentadienes.²⁵ Silole and germole dianions (RC)₄Si²⁻ and (RC)₄Ge²⁻, R=Ph and Me, have been studied by X-ray crystallography^{26,27} and found to be extensively delocalized. Siloles and germoles are of considerable current interest,^{26–30} both because of their unusual electronic and optical properties^{31,32} and because of their possible application as electron transporting materials in devices.³³ Polysilanes and polygermanes containing a metal-metal backbone emit in the near UV spectral region, exhibit high hole mobility, and show high nonlinear optical susceptibility, which makes them efficient photoemission candidates for a variety of optoelectronics applications.³⁴ These properties arise from $\sigma - \sigma^*$ delocalization along the M-M backbones and confinement of the conjugated electrons along the backbone. Polymetalloles and metallolesilane copolymers are unique in having both a M-M backbone as well as an unsaturated five-membered ring system. These polymers are highly photoluminescent,³⁵ and used as lightemitting diodes (LED's)^{36,37} or as chemical sensors.²⁴ Characteristic features of polymetalloles and metallole-silane copolymers include a low reduction potential and a low-lying LUMO due to $\sigma^* - \pi^*$ conjugation arising from the interaction between the σ^* orbital of silicon or germanium, and the π^* orbital of the butadiene moiety of the five membered ring.^{38,39} In addition,

- (20) McGill, R. A.; Mlsna, T. E.; Mowery, R. In IEEE International Frequency

- 7452-7455.
- (24) Sohn, H.; Calhoun, R. M.; Sailor, M. J.; Trogler, W. C. Angew. Chem., Int. Ed. Engl. 2001, 40, 2104–2105.
 (25) Tamao, K.; Kawachi, A. Adv. Organomet. Chem. 1995, 38, 1–58.
 (26) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apelog, Y.; Mueller, T. J. Am. Chem. Soc. 1995, 117, 11 608–11 609.
 (27) W. H. D. M. H. D. M. H. D. M. H. T. A. Lin, Y. A. C. Chem. 2010.
- (27) West, R.; Sohn, H.; Powell, D. R.; Mueller, T.; Apeloig, Y. Angew. Chem.,
- Int. Ed. Engl. 1996, 35, 1002-1004.
- (28) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. J. Organomet. Chem. 1995, 499, C7–C9.
- (29) Freeman, W. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. Angew. Chem., Int. Ed. Engl. 1996, 35, 882.
 (30) Hong, J. H.; Boudjhouk, P.; Castellino, S. Organometallics 1994, 13, 27.
 (31) Yamaguchi, S.; Tamao, K. J. Chem. Soc., Dalton Trans. 1998, 3693-2709.
- 3702 Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem. Eur. J.* **2000**, *6*, 1683–1692. (32)
- (33) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. J. Am. Chem. Soc. 1996, 118, 11 974–11 975.
- (34) West, R. In *Comprehensive Organometallic Chemistry II*; Davies, A. G., Ed.; Pergamon: Oxford, 1995; pp 77–110.
 (35) Sanji, T.; Sakai, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* 1998, *120*, 4552–4553.
- (36) Sohn, H.; Huddleston, R. R.; Powell, D. R.; West, R. J. Am. Chem. Soc. 1999, 121, 2935-2936.
- (37) Xu, Y.; Fujino, T.; Naito, H.; Dohmaru, T.; Oka, K.; Sohn, H.; West, R. Jpn. J. Appl. Phys. 1999, 38, 6915-6918.
- (38) Yamaguchi, Y. Synthetic Met. 1996, 82, 149–153.
 (39) Yamaguchi, S.; Tamao, K. Bull. Chem. Soc. Jpn. 1996, 69, 2327–2334.



Figure 1. Space-filling model of polysilole 1.

the M–M backbones exhibit σ – σ * delocalization, which further delocalizes the conjugated metallole π electrons along the backbone.³⁴ Electron delocalization in these polymers provides one means of amplification, because interaction of an analyte molecule at any position along the polymer chain quenches an excited state or exciton delocalized along the chain. A space filling model structure of **1** is shown in Figure 1. This structure features a Si-Si backbone inside a conjugated ring system of side chains closely packed to yield a helical arrangement. A similar means of amplification is available to quantum-confined semiconductor nanocrystallites, via a three-dimensional crystalline network, where the electron and hole wave functions are delocalized throughout the nanocrystal.⁴⁰

Result and Discussion

Syntheses of Polymetalloles and Metallole Copolymers. The syntheses of dichloro(tetraphenyl)silole, dichloro(tetraphenyl)germole,²⁷ and polysilole 1³⁶ were reported previously. The synthesis of polygermole 2, shown in eq 1, is analogous to the synthesis of polysilole 1, which employs a Wurtz-type polycondensation. An alternative synthesis of the polysilole and polygermole can be effected by catalytic dehydrocoupling polycondensation of dihydro(tetraphenyl)silole or dihydro-(tetraphenyl)germole with 1 mol % of Wilkinson's catalyst, Rh-(PPh₃)₃Cl, or Pd(PPh₃)₄.⁴¹ The latter reactions yield the respective polysilole and polygermole in high yield (ca. 80-90%) and give molecular weights (M_w) of 4000~6000, similar to those of the Wurtz-type polycondensation (ca. \sim 30%).

Silole-germole alternating copolymer 3, in which every other silicon or germanium atom in the polymer chain is also part of a silole or germole ring, was synthesized from the coupling of dichloro(tetraphenyl)germole²⁷ and dilithio(tetraphenyl)silole.²⁶ The latter is obtained in 39% yield from dichlorotetraphenyl-

⁽⁴⁰⁾ Content, S.; Trogler, W. C.; Sailor, M. J. Chem. Eur. J. 2000, 6, 2205-2213 (41) Sohn, H.; Trogler, W. C., manuscript submitted 2002.



silole by reduction with lithium (equation 2). The molecular weight of silole–germole copolymer **3**, $M_w = 5.5 \times 10^3$, $M_n = 5.0 \times 10^3$ determined by SEC (size exclusion chromatography) with polystyrene standards, is similar to that of polysilole or polygermoles. All the polymetalloles are extended oligomers with a degree of polymerization of about 10 to 16, rather than a true high M_w polymer; however, they can be cast into a thin film from solution and show polymer-like properties.



Silole-silane alternating copolymers **4**–**8** were also prepared from coupling of the silole dianion, (Ph₄C₄Si)Li₂,²⁶ with the corresponding silanes. Germole-silane alternating copolymers **9–12** were synthesized from the coupling of the germole dianion, (Ph₄C₄Ge)Li₂,²⁷ with the corresponding silanes (eq 3). These reactions generally employ reflux conditions in tetrahydrofuran under an argon atmosphere for 72 h. Some silolesilane copolymers have been synthesized previously by the West and Sakurai groups,^{35,42} and shown to be electroluminescent. The molecular weight of metallole-silane copolymers, $M_w =$ $4.1 \times 10^3 \sim 6.2 \times 10^3$, $M_n = 4.1 \times 10^3 \sim 5.4 \times 10^3$ determined by SEC, is similar to that of the polymetalloles.

The molecular weight properties of polymers 1-12 determined by GPC (gel permeation chromatography) are listed in Table 1. These polymers are soluble in organic solvents, such as tetrahydrofuran, diethyl ether, toluene, and chloroform.

Absorption and Fluorescence Studies. The UV-vis absorption and fluorescence spectral data for 1–12 are reported in Table 1. The poly(tetraphenyl)metalloles 1–3 and tetraphenyl-metallole-silane copolymers 4–12 exhibit three absorption bands, which are ascribed to the $\pi^*(\sigma_2 + \pi^*)$ transition in the metallole ring and the $\sigma - (\sigma_2^* + \pi^*)$ and $\sigma - \sigma_1^*$ transitions in the M–M backbones.³⁷

A schematic energy-level diagram for polymetalloles and metallole-silane copolymers is shown in Figure 2. UV-vis

ARTICLES



absorption spectra in THF (solid line) and fluorescence spectra in toluene (dotted line) for (A) poly(tetraphenylgermole) **2**, (B) silole-silane copolymer **4**, and (C) germole-silane copolymer **9** are shown in Figure 3.

Absorptions at a wavelength of about 370 nm for the poly-(tetraphenylmetallole)s **1–3** and tetraphenylmetallole-silane copolymers **4–12** are assigned to the metallole $\pi - \pi^*$, which are about 89 to 95 nm red-shifted relative to that of oligo[1,1-(2,3,4,5-tetramethylsilole)] ($\lambda_{max} = 275 \text{ nm}$)⁴³ and are about 75 to 81 nm red-shifted relative to that of oligo[1,1-(2,5-dimethyl-3,4-diphenylsilole)] ($\lambda_{max} = 289 \text{ nm}$).⁴⁴ These red shifts are attributed to an increasing main chain length⁴³ and partial conjugation of the phenyl groups to the silole ring.

Figure 4 shows the HOMO (A) and LUMO (B) of 2,5diphenylsilole, Ph₂C₄SiH₂, from the ab initio calculations at the HF/6-31G* level. Phenyl substituents at the 2,5 metallole ring positions may π -conjugate with the metallole ring LUMO. Second absorptions at wavelengths of 304 to 320 nm for the poly(tetraphenylmetallole)s **2**–**3** and tetraphenylmetallole-silane copolymers **4**–**12** are assigned to the $\sigma - (\sigma_2^* + \pi^*)$ transition, which parallels that of the poly(tetraphenyl)silole **1**.

Polymetallole 1-2 and silole-silane copolymers 4-7 exhibit one emission band (λ_{max} , 486 to 513 nm) when excited at 340 nm, whereas the others exhibit two emission bands with λ_{max} of 480-510 nm and 385-402 nm. The ratios of the two emission intensities are not concentration dependent, which indicates that the transition does not derive from an excimer. Emission peaks for germole-silane copolymers 9-12 are only 2 to 33 nm blue-shifted compared to the other polymers. Figure 5 shows fluorescence spectra of the poly(tetraphenyl)silole in toluene solution (solid line) and in the solid state (dotted line). The bandwidth of the emission spectrum in solution is slightly larger than in the solid state. There is no shift in the maximum of the emission wavelength. This suggests that the polysilole exhibits neither π -stacking of polymer chains nor excimer formation.

Fluorescence Quenching Studies with Nitroaromatic Analytes. The detection method involves measurement of the quenching of photoluminescence of the polymetalloles 1-3 and metallole-silane copolymers 4-12 by the analyte (using a

⁽⁴²⁾ Sohn, H.; West, R., unpublished studies.

 ⁽⁴³⁾ Kanno, K.; Ichinohe, M.; Kabuto, C.; Kira, M. Chem. Lett. 1998, 99.
 (44) Yamaguchi, S.; Jin, R.; Tamao, K. Organometallics 1997, 16, 2486.

Table 1. Summary of Molecular Weights, Photophysical Data,^a Stern–Volmer Quenching Constants with Picric Acid, TNT, DNT, and Nitrobenzene Analytes, and Mean Lifetimes of Emission^b for Polymers 1–12 at 293 K

			$\lambda_{ m abs}\pi-\pi^*$,						
			$\sigma - \sigma_2^* + \pi^*$		K_{sv} (M ⁻¹)	K _{sv} (M ⁻¹)	K _{sv} (M ⁻¹)	$K_{\rm sv}$ (M ⁻¹)	
polymers	M_{w}	Mn	(nm)	$\lambda_{ m fluo}$ (nm)	PA	TNT	DNT	NB	<i>t</i> (× 10 ⁻⁹ s)
1	6.2×10^{3}	5.4×10^{3}	368, 314	513	11 000	4340	2420	1200	0.70^{c}
2	4.6×10^{3}	4.4×10^{3}	368, 302	499	6710	2050	1010	320	0.28^{d}
3	5.5×10^{3}	5.0×10^{3}	364, 302	510, 385	8910	3050	1730	753	0.43
4	4.4×10^{3}	4.2×10^{3}	370, 318	491	9120	3520	2060	1150	2.33
5	4.5×10^{3}	4.1×10^{3}	370, 320	488	10 700	3940	2380	1230	1.34
6	4.8×10^{3}	4.1×10^{3}	368, 320	489	8420	3030	2010	735	2.20
7	5.0×10^{3}	4.8×10^{3}	368, 318	493	10 800	3430	2330	965	0.62
8	4.6×10^{3}	4.0×10^{3}	366, 324	505, 385	9350	3680	2340	864	2.70
9	4.9×10^{3}	4.4×10^{3}	364, 304	483, 400	10 300	3990	2570	1140	0.27
10	4.4×10^{3}	4.2×10^{3}	364, 304	486, 400	9990	3330	2000	965	0.35
11	4.1×10^{3}	3.9×10^{3}	364, 304	484, 400	8740	3430	2210	986	0.26
12	5.4×10^{3}	5.0×10^{3}	364, 306	480, 402	9840	3340	2150	936	0.22

^{*a*} Absorption and fluorescence spectra were taken at the concentrations of 2 mg/L in THF and 10 mg/L in toluene, respectively. ^{*b*} Repeatability is about 5% but not less than ± 0.04 nanoseconds. ^{*c*} 1.77 ns (solid state). ^{*d*} 1.17 ns (solid state)



Figure 2. Schematic energy-level diagram for polymetalloles and metallole-silane copolymers.



Figure 3. UV-vis absorption spectra in THF (solid line) and fluorescence spectra in toluene (dotted line) for (A) poly(tetraphenyl)germole **2**, (B) silole–silane copolymer **4**, and (C) germole–silane copolymer **9**.

Perkin-Elmer LS 50B fluorescence spectrometer, 340 nm excitation wavelength). Fluorescence spectra of toluene solutions of the polymers 1-12 were obtained by successive addition of



Figure 4. HOMO (A) and LUMO (B) of 2,5-diphenylsilole, Ph₂C₄SiH₂ from the ab initio calculations at the HF/6-31G* level.

aliquots of picric acid (purchased from Aldrich and recrystallized from ethanol solution before use), TNT (prepared from DNT⁴⁵ and recrystallized twice from methanol), DNT, and nitrobenzene. Photoluminescence quenching of the polymers **1**–**12** in toluene solutions with picric acid, TNT, DNT, and nitrobenzene were measured. Figure 6 displays the quenching of photoluminescence spectra of the silole-silane copolymer **5** upon addition of (A) nitrobenzene, (B) DNT, (C) TNT, and (D) picric acid. Photoluminescence quenching efficiencies of the polymetalloles **1**–**3** and metallole-silane copolymers **4**–**12** are in the order of picric acid > TNT > DNT > nitrobenzene.

The purity of the TNT sample was found to be important to obtain reproducible results. It was synthesized by nitration of dinitrotoluene and recrystallized twice from methanol. A third recrystallization produces the same results as the twice-recrystallized material. When the quenching experiment was undertaken without recrystallization of TNT, higher (ca. $10 \times$) quenching percentages are obtained. Presumably, impurities with higher quenching efficiencies are present in crude TNT.

⁽⁴⁵⁾ W. H. Dennis, J.; Rosenblatt, D. H.; Blucher, W. G.; Coon, C. L. J. Chem. Eng. Data 1975, 20, 202–203.



Figure 5. Fluorescence spectra of polysilole 1 in toluene solution (solid line) and in thin solid film (dotted line).



Figure 6. Quenching of photoluminescence spectra of silole-silane copolymer **5** with (A) nitrobenzene, from top 2.0×10^{-5} M, 3.9×10^{-5} M, 7.8×10^{-5} M, and 11.5×10^{-5} M, (B) DNT, from top 1.4×10^{-5} M, 3.9×10^{-5} M, 3.9×10^{-5} M, and 12.4×10^{-5} M, (C) TNT, from top 2.1×10^{-5} M, 4.2×10^{-5} M, 8.1×10^{-5} M, and 12.6×10^{-5} M, (D) picric acid, from top 2.1×10^{-5} M, 4.2×10^{-5} M, 8.0×10^{-5} M, and 12.6×10^{-5} M.

The Stern–Volmer equation was used to quantify the differences in quenching efficiency for various analytes.⁴⁶ In

this equation, I_0 is the initial fluorescence intensity without analyte, I is the fluorescence intensity with added analyte of concentration [A], and K_{sv} is the Stern–Volmer constant

$$(I_{\rm o}/I) - 1 = K_{\rm sv}$$
 [A]

Figure 7 shows the Stern–Volmer plots of polysilole 1, polygermole 2, and silole–silane copolymer 8 for each analyte. A linear Stern–Volmer relationship is observed in all cases, but the Stern–Volmer plot for picric acid exhibits a nonlinear dependence when its concentration is higher than 1.0×10^{-4} M. A linear Stern–Volmer relationship may be observed if either a static or dynamic quenching process is dominant. Thus, in the case of higher concentrations of picric acid, the two processes may be competitive, which results in a nonlinear Stern–Volmer relationship. This could also arise from aggregation of analyte with chromophore.

Photoluminescence quenching may arise from either a static process, by the quenching of a bound complex, or a dynamic process, by a bimolecular quenching of the excited state.^{47,48} For the former case, K_{sv} is an association constant due to the analyte-preassociated receptor sites. Thus, the collision rate of the analyte is not involved in static quenching and the fluorescence lifetime is invariant with the concentration of analyte. With dynamic quenching, the fluorescence lifetime should diminish as quencher is added.

A single "mean" characteristic lifetime (τ) for polymetalloles and metallole-silane copolymers 1-12 has been measured and summarized in Table 1. Luminescence decays were not singleexponential in all cases. Three lifetimes were needed to provide an acceptable fit over the first few nanoseconds. The amplitudes of the three components were of comparable importance (the solvent blank made no contribution). These features suggest that the complete description of the fluorescence is actually a continuous distribution of decay rates from a heterogeneous collection of chromophore sites. Because the oligomers span a size distribution, this behavior is not surprising. The mean lifetime parameter reported is an average of the three lifetimes determined by the fitting procedure, weighted by their relative amplitudes. This is the appropriate average for comparison with the "amount" of light emitted by different samples under different quenching conditions, as has been treated in the literature.⁴⁹ Given this heterogeneity, we were concerned about possible long-lived luminescence that might be particularly vulnerable to quenching. However, measurements with a separate nanosecond laser system confirmed that there were no longer-lived processes other than those captured by the timecorrelated photon counting measurement and incorporated into Table 1.

It is notable that polysilole 1 and silole-silane copolymers 4-8 have about 3 to 11 times longer fluorescence lifetimes than polygermole 2 and germole-silane copolymers 9-12. Fluorescence lifetimes in the thin films (solid state) for polysilole 1 and polygermole 2 are 2.5 and 4.2 times longer than in toluene

⁽⁴⁶⁾ Turro, N. J. Modern Molecular Photochemistry; University Science Books: Sausalito, California, 1991.

 ⁽⁴⁷⁾ Connors, K. A. Binding Constants: The Measurement of Molecular Complex Stability; Wiley-Interscience: New York, 1987.
 (48) Lakowicz, J. R. Principles of Fluorescence Spectroscopy: Plenum Press;

 ⁽⁴⁸⁾ Lakowicz, J. R. Principles of Fluorescence Spectroscopy, Plenum Press: New York, 1986.
 (40) Silva A. Facelbarnick, Y. Photocham. and Photokick 1008, 67, 475 –

⁽⁴⁹⁾ Sillen, A.; Engelboroughs, Y. Photochem. and Photobiol. 1998, 67, 475– 486.



Figure 7. Stern-Volmer plots; from top polysilole 1, polygermole 2, and silole-silane copolymer 8; \blacklozenge (picric acid), \blacksquare (TNT), \blacktriangle (DNT), \blacklozenge (nitrobenzene); the plots of fluorescence lifetime (τ_0/τ), shown as inset, are independent of added TNT.

solution, respectively. The fluorescence lifetimes as a function of TNT concentration were also measured and are shown in Sohn et al.



Figure 8. Fluorescence decays of polysilole 1 for different concentrations of TNT: 0 M, 4.24×10^{-5} M, 9.09×10^{-5} M, 1.82×10^{-4} M.



Figure 9. Stern-Volmer plots of polymers; ♦ (polymer 1), ■ (polymer 5), ▲ (polymer 4), ● (polymer 6), * (polymer 2), and - (organic pentiptycenederived polymer 13), for TNT.

the inset of Figure 7 for polymers 1, 2, and 8. No change of mean lifetime was observed by adding TNT, indicating that the static quenching process is dominant for polymetalloles and metallole-silane copolymers 1-12 (Figure 8). Some issues with such analyses have been discussed in the literature.⁵⁰ This result suggests that the polymetallole might act as a receptor and a TNT molecule would intercalate between phenyl substituents of the metallole moieties (Figure 1).

For chemosensor applications, it is useful to have sensors with varied responses. Each of the 12 polymers exhibits a different ratio of the photoluminescence quenching for picric acid, TNT, DNT, and nitrobenzene and a different response with the same analyte. The use of sensor arrays is inspired by the performance of the olfactory system to specify an analyte.² Figure 9 displays the Stern–Volmer plots of polymers 1, 2, 4, 5, and 6 for TNT, indicating that the range of photoluminescence quenching efficiency for TNT is between 2.05×10^3 and 4.34 \times 10³ M⁻¹. The relative efficiencies of photoluminescence quenching of poly(tetraphenylmetallole)s 1-3 and tetraphenylmetallole-silane copolymers 4-12 were obtained for picric acid, TNT, DNT, and nitrobenzene, as indicated by the values of K_{sv} determined from the slopes of the steady-state Stern-Volmer plots and summarized in Table 1. We have also synthesized polymer 13, an organic pentiptycene-derived polymer for

⁽⁵⁰⁾ Webber, S. E. Photochem. and Photobiol. 1997, 65, 33-38.



Figure 10. Highest and lowest photoluminescence quenching efficiency for picric acid (purple), TNT (yellow), DNT (green), and nitrobenzene (blue) showing how the varying polymer response to analyte could be used to distinguish analytes from each other.

comparison.^{21,22} The metallole copolymers are more sensitive to TNT than the organic pentiptycene-derived polymers in toluene solution.^{21,22} For example, polysilole **1** ($4.34 \times 10^3 \text{ M}^{-1}$) has about a 370% better quenching efficiency with TNT than organic pentiptycene-derived polymer ($1.17 \times 10^3 \text{ M}^{-1}$).



The trend in Stern-Volmer constants usually reflects an enhanced charge-transfer interaction from metallole polymer to analyte. For example, the relative efficiency of photoluminescence quenching of polysilole 1 is about 9.2:3.6:2.0:1.0 for picric acid, TNT, DNT, and nitrobenzene, respectively. Although polysilole 1 shows best photoluminescence quenching efficiency for picric acid and TNT, polymer 9 and 5 exhibit best quenching efficiency for DNT and nitrobenzene, respectively.(Figure 10) Polygermole 2 has the lowest quenching efficiency for all analytes. Since the polymers 1-12 have similar molecular weights, the range of quenching efficiencies with the same analyte would be expected to be small. Polysilole 1 (11.02 \times 10^3 M^{-1} and $4.34 \times 10^3 \text{ M}^{-1}$) exhibits 164% and 212% better quenching efficiency than polygermole 2 (6.71 \times 10³ M⁻¹ and 2.05×10^3 M⁻¹) with picric acid and TNT, respectively. Polymer 9 (2.57 \times 10³ M⁻¹) has 253% better quenching efficiency than polymer 2 ($1.01 \times 10^3 \text{ M}^{-1}$) with DNT. Polymer 5 (1.23 \times 10³ M⁻¹) has 385% better quenching efficiency than metallole polymer 2 ($0.32 \times 10^3 \,\mathrm{M}^{-1}$) with nitrobenzene. Figure 11 illustrates how an analyte might be specified using an array of multi-sensors.



Figure 11. Comparison of the photoluminescence quenching constants (from Stern–Volmer plots) of polymers 1-12 with different nitroaromatic analytes.



Figure 12. Plot of log *K* vs reduction potential of analytes; \blacklozenge (polymer 1), \blacksquare (polymer 2), \blacktriangle (polymer 3), \blacklozenge (polymer 4), * (polymer 5), and – (polymer 10).

Figure 12 shows a plot of log K_{sv} vs reduction potential of analytes. All metallole polymers exhibit a linear relationship, even though they have different ratios of photoluminescence quenching efficiency to analytes. This result indicates that the mechanism of photoluminescence quenching is primarily attributable to electron transfer from the excited metallole polymers to the LUMO of the analyte. Because the reduction potential of TNT (-0.7 V vs NHE)²² is less negative than that of either DNT (-0.9 V vs NHE) or nitrobenzene (-1.15 V vs NHE), it is detected with highest sensitivity. A schematic diagram of the electron-transfer mechanism for the quenching of photoluminescence of the metallole polymers with analyte is shown in Figure 13. Optical excitation produces an electronhole pair, which is delocalized through the metallole copolymers. When an electron deficient molecule, such as TNT is present, electron-transfer quenching occurs from the excited metallole copolymer to the LUMO of the analyte. The observed dependence of K_{sv} on analyte reduction potential suggests that for the static quenching mechanism, the polymer-quencher complex luminescence intensity depends on the electron acceptor ability of the quencher. An alternative explanation would be that the formation constant (K_{sv}) of the polymer-quencher complex is



Figure 13. Schematic diagram of electron-transfer mechanism for quenching the photoluminescence of polymetallole by analyte.



Figure 14. Quenching of photoluminescence polysilole **1** with 4 parts per hundred of THF.

dominated by a charge-transfer interaction between polymer and quencher and that the formation constant increases with quencher electron acceptor ability.

An important aspect of the metallole copolymers is their relative insensitivity to common interferents. Control experiments using both solutions and thin films of metallole copolymers (deposited on glass substrates) with air displayed no change in the photoluminescence spectrum. Similarly, exposure of metallole copolymers both as solutions and thin films to organic solvents such as toluene, THF, and methanol or the aqueous inorganic acids H₂SO₄ and HF produced no significant decrease in photoluminescence intensity. Figure 14 shows that the photoluminescence spectra of polysilole 1 in toluene solution display no quenching of fluorescence with 4 parts per hundred of THF. The ratio of quenching efficiency of polysilole 1 with TNT vs benzoquinone is much greater than that of polymer 13. The $K_{\rm sv}$ value of 4.34 \times 10³ M⁻¹ of polysilole 1 for TNT is 640% greater than that for benzoquinone ($K_{sv} = 674 \text{ M}^{-1}$). The organic polymer 13, however, only exhibits a slightly better quenching efficiency for TNT ($K_{sv} = 1.17 \times 10^3 \text{ M}^{-1}$) (ca. 120%) compared to that ($K_{sv} = 998 \text{ M}^{-1}$) for benzoquinone. This result indicates that polysilole **1** exhibits less response to interferences and greater response to nitroaromatic compounds compared to the pentiptycene-derived polymer **13**.

Conclusions

The polymetalloles and metallole copolymers have been synthesized and used for the detection of nitroaromatics, such as picric acid, TNT, DNT, and nitrobenzene. These polymers are extended oligomers with a degree of polymerization of about 10 to 16 metallole units and similar molecular weights. Quenching of photoluminescence is a static process, because τ_0/τ is invariant with quencher concentration. Each metallole polymer has a unique ratio of quenching efficiency to the corresponding analyte and each analyte has a variety of different responses to different metallole polymers, which could be utilized to specify the analyte by pattern recognition methods. The metallole copolymers are robust and insensitive to common interferents, such as organic solvents and inorganic acids. The polymetalloles and metallole copolymers exhibit 2 to 5 times better quenching efficiencies than the organic pentiptycenederived polymer^{21,22} in toluene solution; however, the organic pentiptycene-derived polymer offers superior sensitivity as a solid-state sensor because of its higher molecular weight and more efficient energy migration in the solid state.

Experimental Section

General. Caution: TNT and picric acid are high explosives and should be handled only in small quantities. Picric acid also forms shock sensitive compounds with heavy metals. All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were degassed and purified before use according to standard literature methods: diethyl ether, hexanes, tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl. Spectroscopic grade toluene from Fisher Scientific was used for the fluorescence measurements. NMR grade deuteriochloroform was stored over 4 Å molecular sieves. All other reagents (Aldrich, Gelest) were used as received or distilled before use. NMR data were collected with Varian Unity 300, 400, or 500 MHz spectrometers (300.1 MHz for ¹H NMR, 75.5 MHz for ¹³C NMR and 99.2 MHz for ²⁹Si NMR). Chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm. The 1H and 13C chemical shifts were referenced relative to CHCl₃ (δ = 77.0 ppm) as an internal standard, and the ²⁹Si chemical shifts were referenced to an external TMS standard. Samples were dissolved in CDCl₃ unless otherwise stated. ¹³C NMR were recorded as proton decoupled spectra, and ²⁹Si NMR spectra were acquired using an inverse gate pulse sequence with a relaxation delay of 30 s. Molecular weights were measured by gel permeation chromatography using a Waters Associates model 6000A liquid chromatograph equipped with three American Polymer Standards Corp. Ultrastyragel columns in series with porosity indices of 10³, 10⁴, and 10⁵ Å (freshly distilled THF as eluent). The polymer was detected with a Waters Model 440 ultraviolet absorbance detector at a wavelength of 254 nm, and the data were manipulated using a Waters model 745 data module. Molecular weights were calibrated by polystyrene standards. Fluorescence emission and excitation spectra were recorded with the use of a Perkin-Elmer Luminescence Spectrometer LS 50B. The solvents were determined to be free of emitting impurities prior to use. The concentration of metallole copolymers for the fluorescence quenching measurements was 10 mg/1L, which is about 2.0×10^{-6} M. Fluorescence spectra were taken immediately after injection of analyte. There was no change in intensity with time. The UV-vis spectra were obtained with the use of Hewlett-Packard 8452A diode array spectrometer. Monomers, 1,1-dichloro-2,3,4,5-tetraphenylsilole, 1,1-dichloro-2,3,4,5-tetraphenylgermole, 1,1-dilithio-2,3,4,5-tetraphenylsilole, and 1,1-dilithio-2,3,4,5-tetraphenylgermole were synthesized by following the procedures described in the literature.^{26-28,52} These reactions were performed under an argon atmosphere. Polymer 13 was synthesized and characterized according to the literature procedures.²²

Fluorescence Lifetime Measurements. Fluorescence decay constants in the range 0.05 to 20 ns were characterized by time-correlated single photon counting (TCSPC). A neodymium:vanadate laser at 530 nm (Coherent Verdi) pumped a home-built titanium:sapphire laser that generated femtosecond mode-locked pulses by self-phase-locking. Harmonic doubling provided excitation pulses near 400 nm. A portion of the beam was sent to a photodiode to provide "stop" pulses. Emission from solutions in ordinary 1 cm luminescence cells or from solid polymer films was collected and sent through a half-meter monochromator (Spex 1870) to a microchannelplate photomultiplier (Hamamatsu 1564U-01). After amplification (Philips 774), pulses were recognized by a constant-fraction discriminator (Tennelec TC454) to provide "start" signals to the time analyzer (Canberra 2044). The "stop" pulses came from the photodiode through a separate discriminator (EGG-Ortec 934). Electronic gating⁵³ was employed to avoid pile-up at the time analyzer. The histogram of the delay times between fluorescence and excitation was collected by a multichannel pulse height analyzer (Norland 5300) and transferred to a microcomputer for processing. The instrument response function to instantaneous emission was measured using a colloidal suspension. Deconvolution was carried out using iterative reconvolution within a least-squares routine based on the Marquardt method.⁵⁴ The program, developed in-house, incorporates some insights from Grinvald and Steinberg.55 It also accommodates an infinite sequence of excitation pulses producing decays longer than the repetition period; for exponential decays, this involves only summing a simple geometric series for each fitted component. A general introduction to the methodology, along with other details of the apparatus, was provided previously.56 The use of an internal reference,56 is not necessary with the new laser system.

Preparation of Polymetalloles (1,2). Synthesis of polygermole 2 is similar to that of polysilole 1.36 1,1-Dichloro-2,3,4,5-tetraphenylgermole (3.0 g, 6.0 mmol) in THF (130 mL) was stirred with 2 equiv Li under Ar atmosphere. After the mixture was refluxed for 3 d, 4 mL of methanol was added to the reaction mixture. After removal of solvent, the residual solid was dissolved in 5 mL of THF and then poured into 400 mL of methanol. Polygermole 2 was obtained as pale yellow powder after the third cycle of dissolving-precipitation followed by freeze-drying. 2: (1.11 g, 43%, $M_{\rm w} = 4600$, determined by SEC with polystyrene standards); ¹H NMR (300.133 MHz, CDCl₃): $\delta = 6.80-$ 7.40 (br, m, Ph), 3.60 (br, OMe); ¹³C{H} NMR (75.403 MHz, CDCl₃ $(\delta = 77.00)$): $\delta = 125-132$ (br, m, Ph) and 136-151 (br, m, germole ring carbon).

Preparation of Silole-Germole Alternating Copolymer 3. Stirring 1,1-dichloro-2,3,4,5-tetraphenylsilole (3.0 g, 6.6 mmol) with lithium (0.9 g, 129.7 mmol) in THF (120 mL) for 8 h at room temperature gave a dark yellow solution of silole dianion. After removal of excess lithium, 1,1-dichloro-2,3,4,5-tetraphenylgermole (3.3 g, 6.6 mmol) was added to a solution of tetraphenylsilole dianion, and stirred at room temperature for 2 h. The resulting mixture was refluxed for 3 d. The reaction mixture was cooled to room temperature and quenched with methanol. Then the volatiles were removed under reduced pressure. THF (20 mL) was added to the residue and polymer was precipitated by slow addition of the solution into 500 mL of methanol. The third cycle of dissolving-precipitation followed by freeze-drying gave the polymer as yellow powder. 3: (2.10 g, 39%, $M_w = 5500$, determined by SEC with polystyrene standards); ¹H NMR (300.133 MHz, CDCl₃): $\delta = 6.30-7.40$ (br, m, Ph), 3.56 (br, OMe); ¹³C{H} NMR $(75.403 \text{ MHz}, \text{CDCl}_3 (\delta = 77.00)): \delta = 125-130 \text{ (br, m, Ph) and}$ 138-152 (br, m, silole and germole ring carbon).

Preparation of Silole-Silane Copolymers, (Silole-SiR¹R²)_n. Stirring of 1,1-dichloro-2,3,4,5-tetraphenylsilole (5.0 g, 11.0 mmol) with lithium (0.9 g, 129.7 mmol) in THF (120 mL) for 8 h at room temperature gave a dark yellow solution of silole dianion. After removal of excess lithium, 1 mol equiv of corresponding silanes, R1R2SiCl2-(11.0 mmol) was added slowly to a solution of tetraphenylsilole dianion, and stirred at room temperature for 2 h. The resulting mixture was refluxed for 3 d. The reaction mixture was cooled to room temperature and quenched with methanol. Then the volatiles were removed under reduced pressure. THF (20 mL) was added to the residue and the polymer was precipitated by slow addition of the solution into 700 mL of methanol. The third cycle of dissolving-precipitation followed by freeze-drying gave the polymer as yellow powder.

For (silole)_n(SiMeH)_m(SiPhH)_a, each 5.5 mmol of SiMeHCl₂ and SiPhHCl₂ were slowly added into a THF solution containing 11 mmol of silole dianion. In the case of $(silole-SiH_2)_m$, after addition of the xylene solution of SiH₂Cl₂ (11.0 mmol), the resulting mixture was stirred for 3 d at room-temperature instead of refluxing.

Selected data for (silole-SiMeH)_n, 4; Yield = 2.10 g (44.5%); ¹H NMR (300.134 MHz, CDCl₃): $\delta = -0.88 - 0.60$ (br. 3H, Me), 3.06-4.89 (br. 1H, SiH), 6.16-7.45 (br. 20H, Ph); ¹³C{H} NMR (75.469 MHz, CDCl₃): $\delta = 0.61 - 1.69$ (br. Me), 123.87 - 131.75, 137.84 -145.42 (br. m, Ph), 153.07-156.73 (br. m, silole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): $\delta = -29.22$ (br. silole), -66.61 (br. SiMeH). GPC: $M_w = 4400$, determined by SEC with polystyrene standards.

Selected data for (silole-SiPhH)_n, 5; Yield = 2.00 g (37.0%); ¹H NMR (300.134 MHz, CDCl₃): $\delta = 3.00-4.00$ (br. 1H, SiH), 6.02-7.97 (br. 20H, Ph); ${}^{13}C{H}$ NMR (75.469 MHz, CDCl₃): $\delta = 123.64 -$ 143.98 (br. m, Ph), 152.60-157.59 (br. m, silole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): $\delta = -37.51$ (br. silole), -71.61 (br. SiPhH). GPC: $M_{\rm w} = 4500$, determined by SEC with polystyrene standards.

Selected data for $(silole)_n(SiMeH)_{0.5n}(SiPhH)_{0.5n}$, 6; Yield = 2.10 g (41.5%); ¹H NMR (300.134 MHz, CDCl₃): $\delta = -0.67 - 0.40$ (br. 3H, Me), 3.08–4.98 (br. 2H, SiH), 6.00–7.82 (br. 55H, Ph); ¹³C{H} NMR $(75.469 \text{ MHz}, \text{CDCl}_3): \delta = -0.85 - 1.76 \text{ (br. Me)}, 122.06 - 147.25$ (br. m, Ph), 153.11-157.26 (br. m, silole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): $\delta = -28.61$ (br. silole), -59.88 (br. SiMeH and SiPhH). GPC: $M_w = 4800$, determined by SEC with polystyrene standards.

Selected data for (silole-SiPh₂)_n, 7; Yield = 2.93 g (47.0%); ¹H NMR $(300.134 \text{ MHz}, \text{CDCl}_3): \delta = 6.14 - 7.82 \text{ (br. 20H, Ph)}; {}^{13}\text{C}\{\text{H}\} \text{ NMR}$ $(75.469 \text{ MHz}, \text{CDCl}_3): \delta = 122.08 - 146.25 \text{ (br. m, Ph)}, 152.81 - 160.07$ (silole ring carbon); GPC: $M_{\rm w} = 5248$, determined by SEC with polystyrene standards.

Selected data for (silole-SiH₂)_n, 8; Yield = 2.05 g (45%); ¹H NMR $(300.134 \text{ MHz}, \text{CDCl}_3): \delta = 3.00-4.96 \text{ (br. 2H, Si}H_2), 6.12-7.72$ (br. 20H, Ph); ${}^{13}C{H}$ NMR (75.469 MHz, CDCl₃): $\delta = 122.08-$ 132.78, 136.92-146.25 (br. m, Ph), 152.81-160.07 (br. m, silole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): $\delta = -30.95$ (br. silole), -51.33 (br. SiH₂), ratio of n: m = 1.00:0.80; GPC: $M_{\rm w} = 4600$, determined by SEC with polystyrene standards.

Preparation of Germole-Silane Copolymers, (Germole-SiR¹R²)_n. The procedure for synthesizing all germole-silane copolymers was similar to that for silole-silane copolymers. For (germole)_n(SiMeH)_{0.5n}-(SiPhH)_{0.5n}, each 5.0 mmol of SiMeHCl₂ and SiPhHCl₂ were added

⁽⁵¹⁾ Zhou, Q.; Swager, T. M. J. Am. Chem. Soc. 1995, 117, 7017-7018.

⁽⁵²⁾ Sohn, H. In New Chemistry of Siloles and Germoles, Ph.D. thesis; University

of Wisconsin: Madison, 1997; pp 1-310. (53) Laws, W. R.; Potter, D. W.; Sutherland, J. C. Rev. Sci. Instrum. 1984, 55, 1564.

⁽⁵⁴⁾ Marquardt, D. W. J. Soc. Indust. Appl. Math. 1963, 11, 431-441.

 ⁽⁵⁵⁾ Grinvald, A.; Steinberg, I. Z. Anal. Biochem. 1974, 59, 583–598.
 (56) Magde, D.; Campbell, B. F. SPIE 1989, 1054, 61–68.

slowly into a THF solution containing 11 mmol of germole dianion. The resulting mixture was stirred for 3 days at room temperature.

Selected data for (germole-SiMeH)_n, **9**; Yield = 2.03 g (43%); ¹H NMR (300.134 MHz, CDCl₃): $\delta = -0.21-0.45$ (br. 2.4H, Me), 5.14–5.40 (br. 0.8H, Si*H*), 6.53–7.54 (br. 20H, Ph); ¹³C{H} NMR (75.469 MHz, CDCl₃): $\delta = -9.70 - 8.15$ (br. Me), 125.29–130.94, 139.08–148.12 (br. m, Ph), 151.29–152.88 (br. m, germole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): $\delta = -50.40$ (br. *Si*MeH); GPC: $M_{\rm w} = 4900$, determined by SEC with polystyrene standards.

Selected data for (germole-SiPhH)_n **10**; Yield = 2.13 g (40%); ¹H NMR (300.134 MHz, CDCl₃): δ = 4.71 (br. 1.0H, Si*H*), 6.30–7.60 (br. 25H, Ph); ¹³C{H} NMR (75.469 MHz, CDCl₃): δ = 125.50–144.50 (br. m, Ph), 151.50–153.00 (br. m, germole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): δ = -56.81 (br. *SiPhH*).; GPC: $M_{\rm w}$ = 4400, determined by SEC with polystyrene standards.

Selected data for (germole)_{*n*}(SiMeH)_{0.5*n*}(SiPhH)_{0.5*n*}, **11**; Yield = 2.01 g(40%); ¹H NMR (300.134 MHz, CDCl₃): $\delta = -0.04-0.42$ (br. 3H,

Me), 4.94 (br. 2H, Si*H*), 6.33–7.66 (br. 25H, Ph); ¹³C{H} NMR (75.469 MHz, CDCl₃): $\delta = 124.31-130.66$ (br. m, Ph), 138.43–152.54 (br. m, germole ring carbon); ²⁹Si NMR (71.548 MHz, inversed gated decoupling, CDCl₃): $\delta = -63.01$ (br. *Si*MeH and *Si*PhH): 0.71; GPC: $M_{\rm w} = 4100$, determined by SEC with polystyrene standards.

Selected data for (germole-SiPh₂)_{*n*}, **12**; Yield = 3.23 g (48%); ¹H NMR (300.134 MHz, CDCl₃): $\delta = 6.21-7.68$ (br. 30H, Ph); ¹³C{H} NMR (75.469 MHz, CDCl₃): $\delta = 125.15-141.40$ (br. m, Ph), 151.12–153.99 (germole ring carbon); GPC: $M_{\rm w} = 5377$, determined by SEC with polystyrene standards.

Acknowledgment. This work is supported by the National Science Foundation (Grant CHE-0111376) and DARPA's Tactical Sensors Program via a Space and Naval Warfare Systems Center Contract (N66001-98-C-8514).

JA021214E