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Fluoroalkylated Polysilane Film as a Chemosensor for Explosive Nitroaromatic Compounds

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The present paper reports a new type of polymer-based chemosensor made of stiff fluoroalkylated polysilane, poly(3,3,3-trifluoropropylmethylsilane) (**1**), which showed a remarkable sensitivity for explosive nitroaromatic compounds (NACs), such as 2,4,6-trinitrophenol (picric acid), 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (DNT), and *m*-dinitrobenzene (DNB), by a decrease in the photoluminescence (PL) intensity in the near-UV region with parts per million concentration of NACs in tetrahydrofuran (THF) solution and in the solid film in water. The PL intensity was completely reversible repeatedly after the removal of NACs from the thin film by rinsing with methanol (or water). A linear Stern−Volmer relationship was observed in all of the cases with high quenching constants. The PL quenching efficiency of **1** ($M_n = 3.12 \times 10^4$, PDI = 3.6, $K = 4.15 \times 10^4$ M^{-1}) for picric acid is 198 times better than that of nonfluoroalkylpolysilane, poly(*n*-propylmethylsilane) (**2**) ($M_n = 2.93 \times 10^4$, PDI = 2.1, $K = 2.09 \times 10^2$ M^{-1}). The weak noncovalent interaction between Si atoms of σ-conjugated polysilane and N and/or O atoms of electron-deficient NACs may be responsible for electron transfer from the excited state of the polysilane to the electron-deficient NACs, resulting in the PL quenching of **1** in solution and in the thin film by NACs.

Introduction

Recently, conjugated polymers have received a great deal of attention as fluorescent chemosensors, as these can provide signal amplification for the highly sensitive fluorimetric method.[1] The backbone of these luminescent polymers acts as a molecular wire, enabling the rapid propagation of an exciton throughout the polymer chain. Conjugated organic and inorganic polymers are realized to be potential fluorescent chemosensors for explosive NACs, being inexpensive and able to provide the portable detection devices.[2−7] The films of π-conjugated porous pentiptycene polymers[2,3] and polyacetylene[7] were reported as highly sensitive fluorescent chemosensors for the vapors of 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT). Recently, the σ-conjugated photoluminescent oligometalloles (M = Si, Ge), with a degree of polymerization of groups 10−16 metalloles units, were found to be effective in detecting NACs in organic solvents and water.[5,6] The sensitivity of such chemosensors can be enhanced by increasing the degree of polymerization as the high molecular weight polymers can provide multiple binding sites for the receptor. The binding constant of each receptor is multiplied by the degree of polymerization, thereby increasing the sensitivity by means of great amplification in the optical signals.[1]

Polysilanes have emerged as an important class of semiconducting inorganic polymers due to their unique optical and electronic properties.[8] The optical signals of polysilanes are highly sensitive to changes in torsion angle, segmentation, and the defects. Most of the polysilanes show a broad UV spectrum with narrow photoluminescence (PL) spectra due to many segments in the σ-conjugated silicon backbone with different photoexcitation energies.[8−10] In contrast, rodlike helical polysilanes show mirror images of UV and PL spectra due to a single photoexcitation state,[10] and the phenomenon of energy migration is enhanced in the case of rodlike polysilane.[11]

Recently, we reported rodlike fluoroalkylated polysilanes, in which rigidity was induced by the cooperative Si···F−C interactions operating between Si atoms in the backbone and F atoms in the side chains.[12,13] The conformation of polysilane can be controlled from rod- to coil-like by the proper

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choice of solvent and the molecular weight. The work described herein demonstrates a new type of chemosensor based on stiff fluoroalkylated poly(3,3,3-trifluoropropylmethylsilane) (**1**) for the detection of NACs by a decrease in the PL intensity. This chemosensor is highly sensitive and can detect NACs at parts per million concentrations in tetrahydrofuran (THF) solution and in the thin film of **1** in water.

Experimental Section

Measurements. UV and PL spectra were recorded on a JASCO V-570 spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. FT-NMR spectra (^{1}H, ^{13}C, ^{29}Si, and ^{19}F) were measured with a JEOL JNM-LA 400 NMR spectrometer. Chemical shifts were referenced to internal tetramethylsilane. Infrared spectra (scan = 32, resolution = 4 cm^{-1}) were obtained on a Horiba FT-730 infrared spectrometer by casting THF or toluene solutions of polysilane on a KBr plate. Molecular weight, polydispersity, and in-line absorption spectra of polysilanes were recorded on a Shimadzu A10 series HPLC apparatus (Polymer Laboratories PL gel 10 μM Mixed-B as a column, and HPLC-grade THF as eluent at 40 °C) with a photodiode array detector. The average molecular weights of polysilanes were measured relative to a calibration of polystyrene standards.

Polymer Preparation. All of the reactions were carried out in dried glassware under dry nitrogen atmosphere using Schlenk techniques. The polysilane (**1**) was synthesized by controlling the reaction conditions, as reported earlier.[14] To a mixture of 12 mL of dry *n*-octane (Aldrich) and 1.3 g (56.5 mmol) of sodium (Wako) was added dropwise 6.0 g (28.4 mmol) of methyl(3,3,3-trifluoropropyl)dichlorosilane (Shin-Etsu). The reaction mixture was stirred at 125 °C for 5 h and filtered through a 2.0 μm Teflon filter under nitrogen gas pressure. The crude polysilane was precipitated by careful successive addition of 2-propanol, ethanol, and methanol. Two fractionated samples of **1** with high ($M_n = 3.12 \times 10^4$, PDI = 3.6) and low ($M_n = 1.62 \times 10^4$, PDI = 1.22) molecular weight were isolated. The white precipitate was collected by centrifugation and dried overnight at 60 °C in a vacuum. Yield (3.6%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.29 (Si$-$*CH$_3$*, 3H); 1.01 (Si$-$*CH$_2$*, 2H); 2.05 (*CH$_2$*CF$_3$, 2H); 3.82 (*SiH* end group).^{13}C NMR (100.5 MHz, CDCl$_3$): δ $-$6.2 (br, Si$-$*CH$_3$*); 3.8 (br, Si$-$*CH$_2$*); 30.7 (q, *CH$_2$*-CF$_3$, $^2J_{\mathrm{C-F}} = 29.3$ Hz); 127.1 (q, *CF$_3$*, $^1J_{\mathrm{C-F}} = 276.2$ Hz). ^{19}F NMR (376.1 MHz, THF-d_8): δ $-$69.9.^{19}F NMR (376.1 MHz, toluene-d_8): δ $-$68.2. ^{29}Si NMR (79.4 MHz, THF-d_8): δ $-$31.4. ^{29}Si NMR (79.4 MHz, toluene-d_8): δ $-$33.2. IR (cm^{-1}): 2098 (ν_{SiH}); 1265 (δ_{SiMe}); 1211($\nu_{\mathrm{C-F\cdots Si}}$); 1199 ($\nu_{\mathrm{C-F}}$); 773($\delta_{\mathrm{C-F\cdots Si}}$); 749 ($\delta_{\mathrm{C-F}}$).

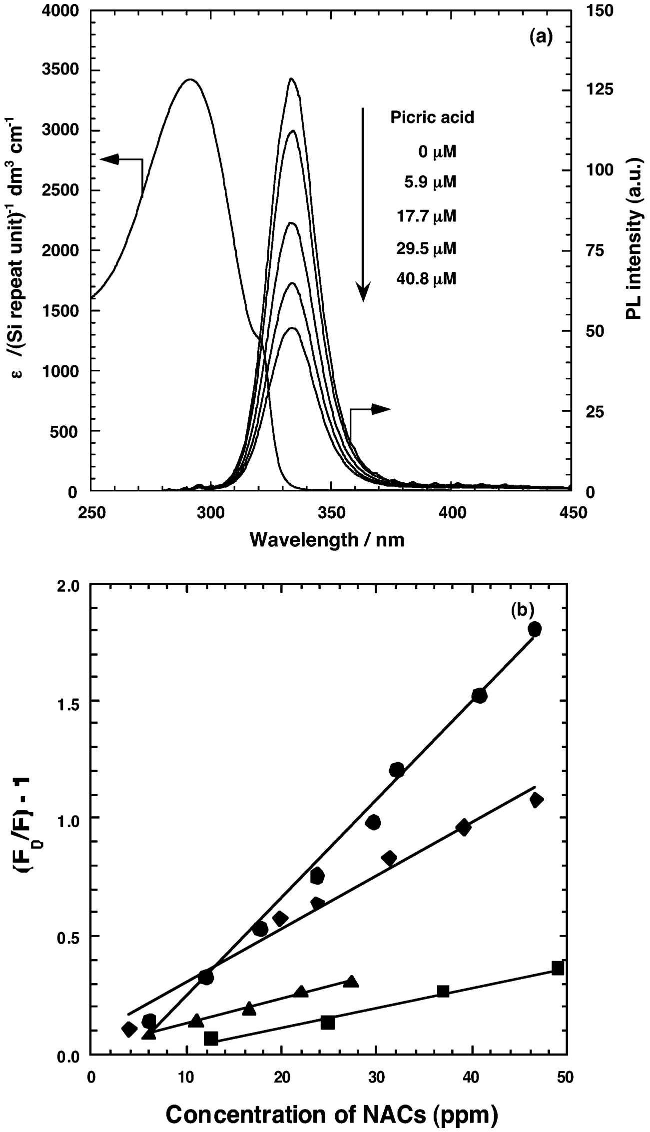

Figure 1. (a) UV and PL (excited at 280 nm) spectra of **1** ($M_n = 3.12 \times 10^4$, PDI = 3.6) in THF at 25 °C. PL spectra of THF solutions of **1** (4.4×10^{-5} M) were obtained by successive addition of aliquots of picric acid. (b) Stern$-$Volmer plot for the PL (excited at 280 nm) quenching of **1** ($\sim 4.0 \times 10^{-5}$ M) in THF by picric acid (●), DNT (■), TNB (◆), and DNB (□) at 25 °C.

Polymer **2** was obtained in the following manner. To a mixture of 12 mL of dry toluene (Wako) and 0.9 g (39.8 mmol) of sodium (Wako) was added dropwise 3.0 g (19.1 mmol) of methylpropyldichlorosilane (Shin-Etsu) under nitrogen atmosphere. The reaction mixture was stirred slowly for 2 h, and the hot reaction mixture was passed through a 2.0 μm Teflon filter under nitrogen gas pressure. To the filtrate were added ethanol and methanol, and the precipitates were collected by centrifugation and dried overnight at 60 °C under vacuum. Yield (12.4%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.26 (Si$-$*CH$_3$*, 3H); 0.82 (Si$-$*CH$_2$*$-$CH$_2$$-CH_3$, 2H); 0.98 (*CH$_3$* (Pr), 3H); 1.36 (Si$-CH_2$$-$*CH$_2$*$-CH_3$, 2H). ^{13}C NMR (100.5 MHz, CDCl$_3$): δ $-$4.6 (br, Si$-$*CH$_3$*); 17.8 (br, Si$-$*CH$_2$*$-$CH$_2$$-CH_3$); 19.1 (br, Si$-CH_2$$-CH_2$$-$*CH$_3$*); 20.5 (br, Si$-CH_2$$-$*CH$_2$*$-CH_3$). ^{29}Si NMR (79.4 MHz, CDCl$_3$): δ $-$32.1.

Results and Discussion

Figure 1 shows the UV and PL spectra of **1** ($M_n = 3.12 \times 10^4$, PDI = 3.6) in THF. The UV spectrum reveals a broad absorption band at 285 nm with a shoulder at 320 nm,

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(13) Saxena, A.; Fujiki, M.; Naito, M.; Okoshi, K.; Kwak, G. *Macromolecules* **2004**, *37*, 5873. The polysilane **1** showed unusual molecular weight chromism in THF. The UV spectrum of **1** revealed two absorption bands in THF, which are assumed to originate from two different global/local conformations: the narrow 320 nm-absorption is attributed to the "locked" rigid helical conformation of **1** due to Si$\cdots$F$-$C backbone-side chain interaction, and the broad 285 nm-band is due to "unlocked" coil-like conformation, in which no interaction is present between the side chain and polymer backbone. The intensity of the absorption band at 285 nm decreases with increasing molecular weight, with a concomitant rise of the narrow band ($\lambda_{\max} = 320$ nm) characterizing the helical rodlike population. A fully formed rodlike helical architecture was realized with high molecular weight samples ($M_n = 1.03 \times 10^5$; PDI = 3.3, viscosity index (α) = 0.81) in THF, whereas only a broad absorption band at 285 nm in THF was observed with low molecular weight samples ($M_n = 1.54 \times 10^4$, PDI = 1.3, $\alpha = 0.27$), signifying the dominant conformation to be disordered coil. Population of rodlike and random coil conformations of **1** in THF thus depends on the molecular weight; however, it slightly varies in different polymerization runs.

(14) Fujino, M.; Hisaki, T.; Fujiki, M.; Matsumoto, N. *Macromolecules* **1992**, *25*, 1079.

suggesting the presence of disordered coil and stiff conformation of **1** within the same polymer backbone.[13] The PL spectrum of **1** was recorded in THF by monitoring the excitation wavelength at 280 nm. The spectrum shows a photoemission band at 335 nm with a full-width at half-maximum height (fwhm) of 20 nm. This stiff polysilane is a highly emissive material with a high quantum yield of 0.36, which is comparable to other rodlike dialkylpolysilanes.[8b]

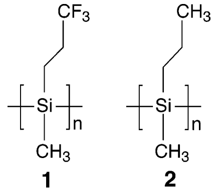
The electron-deficient NACs such as 2,4,6-trinitrophenol (picric acid), 1,3,5-trinitrobenzene (TNB), DNT, and *m*-dinitrobenzene (DNB) were detected in a THF solution of **1** by the attenuation of PL intensity.[15] The PL spectra were obtained by successive additions of aliquots of picric acid, TNB, DNT, and DNB. Figure 1a features the quenching of PL intensity of **1** upon the addition of picric acid.

The Stern–Volmer equation was utilized to evaluate the difference in quenching efficiency for different analytes.[16] The Stern–Volmer plots of **1** for each analyte are shown in Figure 1b. A linear Stern–Volmer relationship was obtained in all of the cases with high quenching constants [$K = (0.84-4.15) \times 10^4$ M^{-1}]], which are approximately 5–10 times higher in magnitude than the previously reported conjugated polymers in solution.[5,6]

This phenomenon can be explained on the basis of a model proposed by Swager and co-workers on the molecular wire approach for sensing.[1] The optical properties of polysilanes are highly sensitive toward the conformation of backbone and defects.[8,10] The polysilane **1** consists of nearly 225 silicon atoms.[17] Each silicon atom in the polymer acts as a receptor for an analyte. The wiring of the receptor provides a means of great amplification in optical signals because the interaction of an analyte molecule with polymer is communicated in the entire backbone through energy migration in the delocalized polymer. Thus, the binding constant for each receptor is additive, which results in an overall high binding constant.

The relative efficiency of PL quenching of **1** was found to be 4.9:2.7:1.2:1.0 for picric acid, TNB, DNB, and DNT, respectively, which was calculated by the quenching constant, obtained from the slopes of Stern–Volmer plots. For comparison, a similar experiment was carried out with poly(*n*-propylmethylsilane) (**2**), which is analogous to nonfluoroalkylpolysilane (Chart 1). No significant change in the PL spectra of **2**, even with 80 times more NACs than observed with **1**, was observed. The PL quenching efficiency of **1** ($M_n = 3.12 \times 10^4$, PDI = 3.6, $K = 4.15 \times 10^4$ M^{-1}) for picric acid is 198 times better than that of **2** ($M_n = 2.93 \times 10^4$, PDI = 2.1, $K = 2.09 \times 10^2$ M^{-1}).

Chart 1. Chemical Structures of 1 and 2



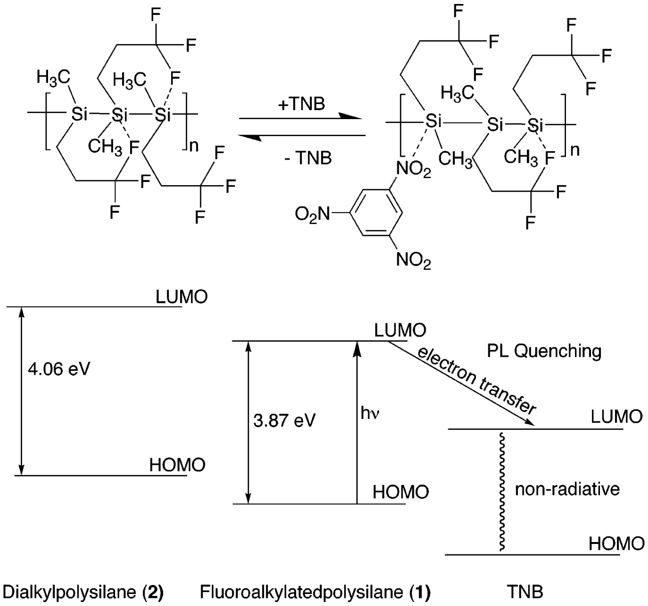


Figure 2. Schematic representation of the electron-transfer mechanism for PL quenching of **1** by NACs.

This phenomenon could be explained by the electron-withdrawing behavior of CF_3 groups. Electron-withdrawing groups will lead to stabilize the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1**.[18] The electron-withdrawing CF_3 groups may increase the positive charge on the silicon atom in the backbone, facilitating the interaction between nitro group and silicone atom. Recently, we reported a very weak and dynamic noncovalent interaction between Si atoms and F atoms in **1**.[12,13] The weak noncovalent interaction between Si atoms of σ-conjugated polysilane and N and/or O atoms of electron-deficient NACs may be responsible for electron transfer from the excited state of polymer to the LUMO of electron-deficient NACs, resulting in an effective PL quenching of **1** on addition of NACs in its THF solution. Figure 2 shows the schematic representation of the electron-transfer mechanism for the quenching of PL of **1** with NACs.

The ^{19}F NMR spectrum of **1** in $CDCl_3$ revealed a broad signal centered at δ −68.75 due to the presence of CF_3 groups in the side chains (Figure 3a). Figure 3b shows the ^{19}F NMR spectrum of **1** in $CDCl_3$ after addition of picric acid. The spectrum showed a downfield chemical shift by 0.52 ppm in comparison to the parent polysilane and a new signal appeared at δ −68.30, probably due to the competition between dynamic intramolecular Si···F–C interactions in **1** and intermolecular weak Si···N and/or Si···O interactions

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(15) Among the various known polysilanes, poly(phenylmethyl)silane was found to be an electron donor to an electron-deficient fullerene. It was believed that fullerene formed a weak complex with π-electrons of phenyl groups, which facilitates electron transfer. Wang, Y.; West, R.; Yuan, C.-H. *J. Am. Chem. Soc.* **1993**, *115*, 3884.

(16) $I_0/I) - 1 = K$ [concentration], where I_0 and I are the fluorescence intensity without and with analyte, respectively. Lakowicz, J. R., Ed. *Principles of fluorescence spectroscopy*; Plenum Press: New York, 1986.

(17) The number-average molecular weight was used to estimate the degree of polymerization ($M_n = 3.12 \times 10^4$, PDI = 3.6, DP = 225).

(18) Electron-withdrawing groups can lower the energies HUMO and LUMO of conjugated polymer. (a) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480. (b) Jin, Y.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2004**, *37*, 6711. (c) Salzner, U. *J. Phys. Chem. B* **2003**, *107*, 1129.

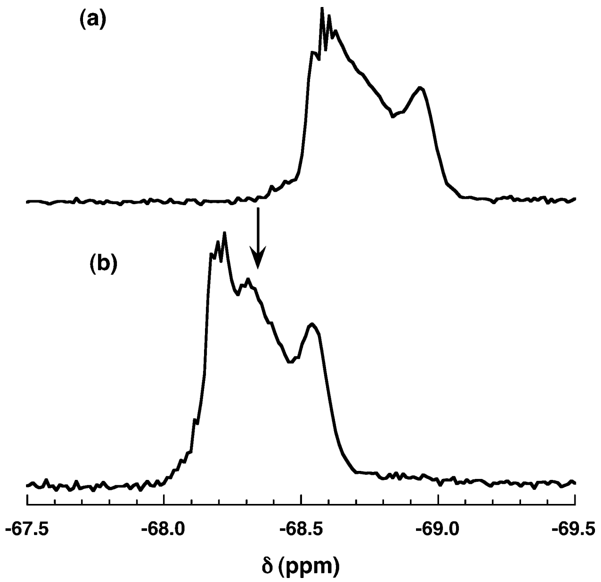

Figure 3. ^{19}F NMR spectra (376.4 MHz) of **1** at 25 °C (a) in $CDCl_3$; (b) with picric acid in $CDCl_3$ and a few drops of toluene.

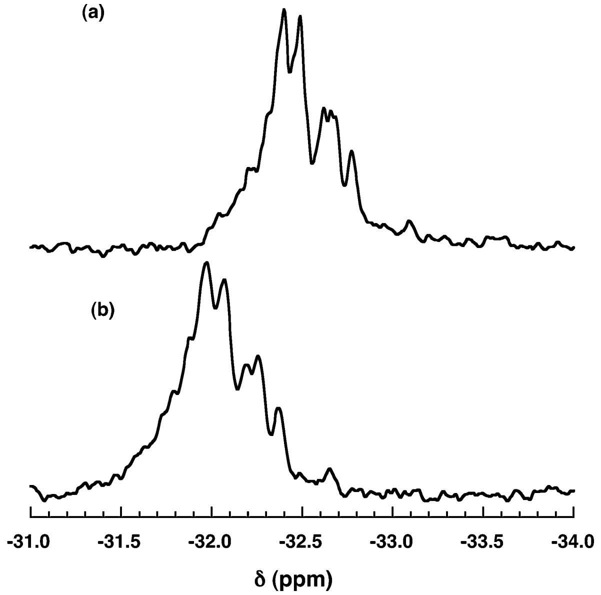

Figure 4. ^{29}Si NMR spectra (79.6 MHz) of **1** at 25 °C (a) in $CDCl_3$; (b) with picric acid in $CDCl_3$ and a few drops of toluene.

between Si atoms in polymer backbone and N and/or O atoms of NACs.[12,13] The ^{29}Si NMR spectrum of **1** in $CDCl_3$ revealed broad resonances centered at δ −32.52 due to the silicon catenated polymer backbone. The ^{29}Si NMR spectrum showed a downfield chemical shift by 0.48 ppm in $CDCl_3$ after the addition of picric acid due to deshielding of Si atoms in the polymer backbone (Figure 4). These small changes in the chemical shifts suggested a very weak interaction between Si and N and/or O atoms.[12,13,19]

It is noteworthy that **1** can also detect NACs in water. The detection of picric acid was carried out using a thin film of **1** (M_n = 1.62 × 10^4, PDI = 1.22) in water. The films were prepared by casting the THF solution of **1** ((1.0−8.0)

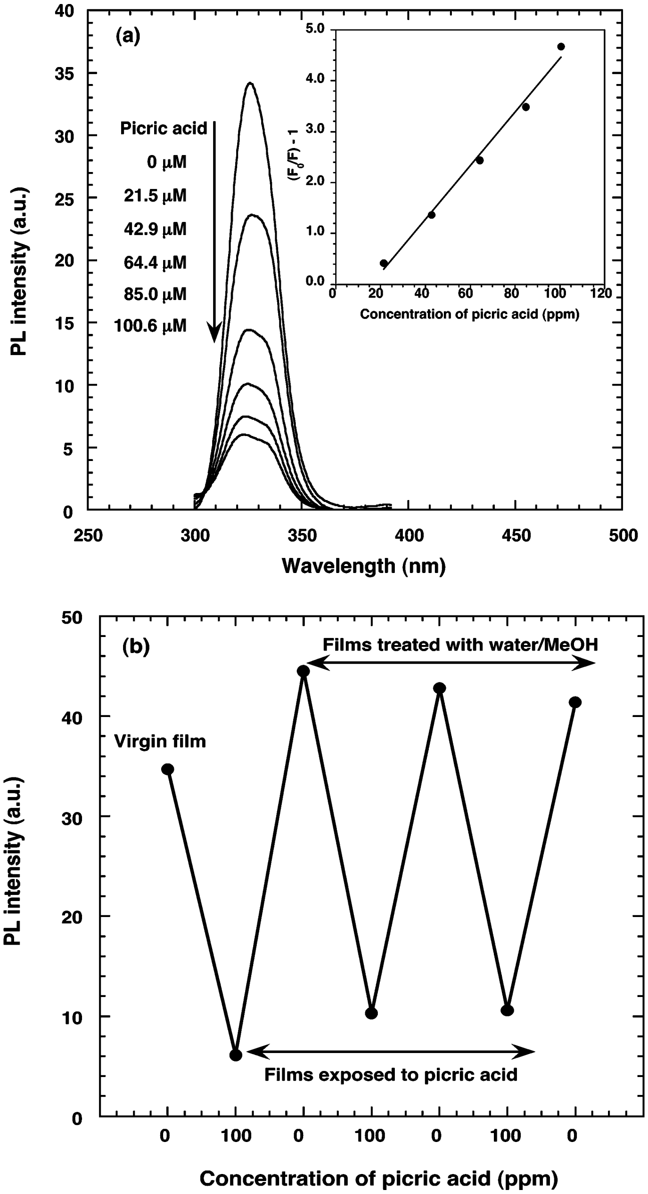

Figure 5. (a) PL spectra (excited at 280 nm) of **1** thin film in water. PL spectra of a thin film of **1** (M_n = 1.62 × 10^4, PDI = 1.22) were obtained by successive addition of aliquots of picric acid in water. The thin film was prepared by casting the THF solution of **1** (2.0 × 10^{-3} M) onto quartz substrate and drying in air. (b) Dependence of the PL intensity of a thin film (30 nm) of **1** on the repeated changes in the concentration of picric acid between 0 and 100 ppm.

× 10^{-3} M) on a freshly cleaned and dried quartz disk. The UV spectrum of the thin film (estimated to be 30 nm thick) of **1** shows a broad band at 285 nm.[20] The PL spectrum (excited at 280 nm) shows a broad photoemission band at 334 nm with a fwhm of 27 nm (Figure 5a). The 10 parts per million concentration of picric acid in water decreases the 14% PL intensity of polymer film. A linear Stern−Volmer relationship was observed for picric acid and DNT with high quenching constants of 5.28 × 10^4 and 1.31 × 10^4 M^{-1}, respectively, shown in the inset of Figure 4a. The quenching

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(19) (a) Bourke, S. C.; Jakle, F.; Vejzovic, E.; Lam, K.-C.; Rheingold, A. L.; Lough, A. J.; Manners, I. *Chem.-Eur. J.* **2003**, *9*, 3042. (b) Bassindale, A. R.; Pourny, M.; Taylor, P. G.; Hursthouse, M. B.; Light, M. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3488.

(20) The thickness of polysilane films was estimated by the absorbance−thickness relationship on the basis of the following publications. (a) Despotopoulou, M. M.; Frank, C. W.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1995**, *28*, 6687. (b) Saxena, A.; Guo, G.; Fujiki, M.; Yang, Y.; Ohira, A.; Okoshi, K.; Naito, M. *Macromolecules* **2004**, *37*, 3081.

efficiency of the thin film of **1** was found to be 128% and 155% better for picric acid and DNT, respectively, than in solution probably due to more efficient energy transfer in the solid state.

Most notably, the changes in PL intensity of the thin film of **1** were fully recovered after the complete removal of NACs from the film by rinsing with water or methanol (MeOH). Figure 5b shows three alternating cycles for the exposure of film to picric acid in water and the recovery of its PL intensity by washing with water/MeOH. After each cycle, the PL intensity reveals that the chemosensing of NACs is highly reversible.

UV spectra of the thin film (estimated to be 30 nm) of **1** after washing with water (or MeOH) and/or the thick film (estimated to be 180 nm) casted from THF solution (8.0×10^{-3} M) show an additional narrow absorption band at 328 nm with a decrease in intensity of 285 nm band, probably due to a partially formed ordered phase of **1** with an extended conformation (see Supporting Information, Figure 1).[20a] Also, in the PL spectra (excited at 320 nm) of the water treated thin film and/or thick film, a red-shifted (by 12 nm) narrow photoemission band with a fwhm of 13 nm at 346 nm was observed (see Supporting Information, Figure 1). As the 328-nm absorption and the 346-nm PL bands are typical for 7_3 helical conformation of **1**,[8b,10,13] the photoexcited energy will be relaxed to the most energetically lowest ordered phase existing in these films.[20a] In this case, because the λ_{max} of the 346-nm PL band remains unchanged, a possibility of excimer formation with addition of NACs in the thin film and in solution ($\lambda_{max} = 335$ nm) is ruled out.

The PL quenching efficiency of the pristine thin film from casting a THF solution of **1** was about 150% better for picric acid than the water/MeOH treated thin film and the thick film. This may be related to the degree of free volumes of **1** in these films, although **1** has a lower glass transition temperature (−4 °C), the pristine thin film includes sufficient free volumes, but the thin film treated with water/MeOH and the thick film do not possess free volumes. Therefore, analytes can easily penetrate into the virgin film and diffuse into water phase reversibly, whereas they may not move into the thick film and the water-treated film, due to insufficient free volumes of **1** in the densely packed state, as demonstrated by the red-shifts in UV and PL spectra.

To test the effect of common interferents and environmental contaminants, control experiments using a thin film of **1** were carried out. No significant change in PL intensity of **1** was observed with organic solvents (e.g., toluene, hexane, and MeOH), aqueous inorganic acids (e.g., sulfuric acid and hydrochloric acid), and oxygenated air, revealing the insensitivity of this polymer to such interferents.

Conclusions

The present paper highlighted the highly sensitive chemosensing behavior of stiff σ-conjugated fluoroalkylated polysilane toward the detection of NACs, such as picric acid, TNB, DNT, and DNB in THF solution and in the thin film state in water. The system showed the complete repeated reversibility of change in the PL intensity after the removal of NACs from the thin film by rinsing with water/MeOH.

Supporting Information Available: UV and PL spectra of thin film of **1** after washing with water/MeOH. PL spectra of a thin film (after washing; second cycle) of **1**, obtained by successive addition of aliquots of picric acid in water and changes in PL intensity with time. This material is available free of charge via the Internet at http://pubs.acs.org.

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