한국환경분석학회지 제6권 (제4호) 271~274, 2003
J. of the Korea Society for Environmental Analysis

Luminescent Polymeric Aggregate Sensors for TNT

Honglae Sohn†

Department of Chemistry, Chosun University, 375 Seosuk-dong, Dong-gu, Gwangju 501-759, Korea

A new chemosensor for TNT using the photoluminescenct polymeric aggregate has been developed. The detection of TNT is achieved from the measuring of quenching photoluminescence of polymeric aggregate by adding the analyte. Photoluminescence quenching of polymeric aggregate was immediately observed in water. A nonlinear relationship of Stern-Volmer plot for TNT detection was obtained. The mechanism of quenching would involve electron transfer from the conduction band of polymeric aggregate to the analyte. The polymeric aggregate are highly insensitive to common interferents in water, such as sulfate, phosphate, nitrate, nitrite, perchlorates, and chlorates.

Key words: detection, TNT, photoluminescence, aggregate

1. Introduction

Chemical sensors, which are new approaches to the rapid detection of ultra-trace anaytes from explosives, have attracted a great deal of attention in recent years, because explosives are extremely important chemical species to detect in mine fields, military bases, remediation sites, and urban transportation areas.1) It is also important in forensic investigations such as post-blast residue determinations. Metal detectors, which are portable instrument for field explosive detection, cannot locate the plastic casing of modern land mines. Trained dogs are both expensive and difficult to maintain. Other detection methods for explosives use gas chromatography coupled with a mass spectrometer,2) surface-enhanced Raman,3) nuclear quadrupole resonance,4) energy-dispersive X-ray diffraction,5) neutron activation analysis, and electron capture detection.6) Most detection methods for explosives are only applicable to air samples due to interference problems encountered in complex aqueous media. Sensing TNT and picric acid in groundwater or seawater is important for the detection of buried unexploded ordnance and for locating underwater mines. There are also environmental applications for characterizing soil and groundwater contaminated with toxic TNT at military bases and munitions production and distribution facilities. Yang and Swager have shown that highly ð-conjugated, porous organic polymers can be used to detect vapors of electron deficient chemicals.7,8) However, these polymers require many steps to synthesize and are less sensitive to explosives. We also invented an inexpensive and highly efficient inorganic polymer sensor that can detect nitroaromatic compounds, such as picric acid, nitrobenzene, 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT) in air or seawater.9,10) The sensor employs a thin film of photoluminescent metallole copolymers, which are stable in air, water, acids, common organic solvents, and even seawater containing bioorganisms. An important aspect of the inorganic polymer sensors is their insensitivity to common environmental interferents. These conjugated polymers are organometallic semiconductors resulting from the π-molecular orbitals delocalized along the polymer chain. Both photoluminescence and electroluminescence originate from the radiative recombination of exciton states, in the former case formed by photoexcitation, and in the latter by combination of oppositely charged polarons generated by injection of electrons and holes.11) These unusual optical and electrical properties can be useful in electronic devices, such as diodes, transistors,12,14) light-emitting diodes (LEDs),13) and

---

† To whom correspondence should be addressed.

large-area light-emitting displays.[15] These unique optoelectronical properties can be used for excellent candidates for luminescent chemical sensors.

2. Experimental

2.1. Materials

Polysilole has been synthesized by the procedures described in the literature.[16] All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. Spectroscopic grade THF and water from Fisher Scientific were used for the fluorescence measurements. The polymeric aggregate of polysilole has been synthesized by the procedures described in the literature[17] using 90% water-THF mixtures. TNT was synthesized from the DNT purchased as analytical grade from Aldrich and purified by recrystallization from methanol three times before use.[10]

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.

2.2. Instrumentation and experimental conditions

Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer Luminescence Spectrometer LS 50B. The solvents were determined to be free of emitting impurities prior to use. To avoid changing the concentrations of the emitting compound, the experiments were carried out with solution by preparing the quencher in the same solution of the emitting compound. The concentration of polysilole aggregates for the quenching fluorescence measurement was 10 μM. Fluorescence spectra were taken right after injection of analyte. There was no change in intensity with time. The UV-vis spectra were obtained from Hewlett-Packard 8452A diode array spectrometer.

3. Results and Discussion

Polysilanes exhibit efficient emission in the UV region, high hole mobility, and high nonlinear optical susceptibility.[14] These novel properties arise from σ-σ^* delocalization of 6 electrons along the Si-Si backbones. Siloles have recently received much attention[15] because of their unusual electronic properties, as well as their application in optoelectronics and in display technologies.[16] The most characteristic feature of siloles is a low reduction potential and a low-lying LUMO due to σ^*-π^* conjugation arising from the interaction between the σ^* orbital of the s-bonded silicon atom and the π^* orbital of the butadiene moiety of the five membered ring.[17,18] Polysiloles, such as 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene, also possess a Si-Si backbone[19] but the unsaturated five-membered ring of the silole shifts their optical absorption and emission spectra into the visible spectral region.[20] These polysiloles exhibit quantum yields of photoluminescence near unity.[21,22]

3.1. Fluorescence studies

The fluorescence spectra are measured for the polysilole in toluene. Polysilole exhibits one emission band at 520 nm. Fig. 1 shows fluorescence spectra of polysilole in solid and toluene solution.

Polysilole aggregate exhibits nearly identical emission band. Fig. 2 shows the fluorescence spectra in water-THF mixture for polysilole aggregate exhibiting one emission band (λ_{max}, 513 nm) when excited at 340 nm. Emission band of polysilole aggregate in water-THF mixture shifts 7 nm to the blue wavelength

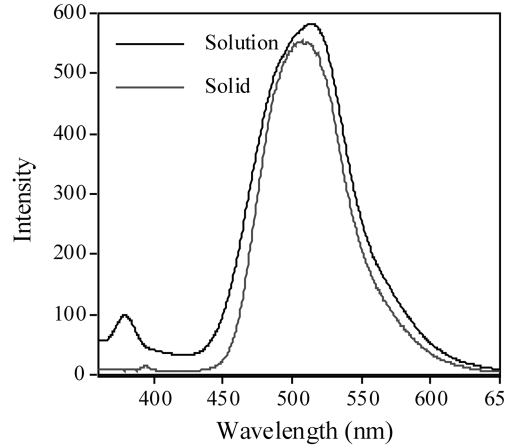

Fig. 1. Fluorescence spectra of polysilole (top; in solution, bottom; in solid).

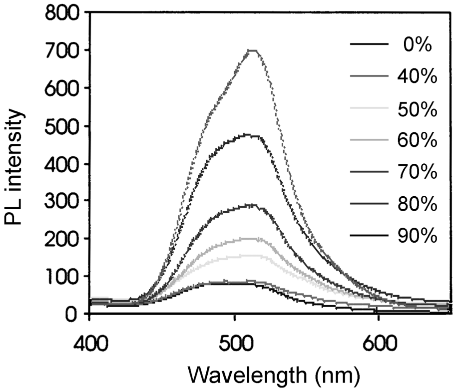

Fig. 2. Fluorescence spectra of polysilole aggregate. (water fraction from top; 90%, 80%, 70%, 60%, 50%, 40%, 0%)

compare to that of polysilole in toluene. As increasing water fraction, the emission intensity of polysilole aggregate increases dramatically. There is no shift in the maximum of the emission wavelength. In the range of water fraction between 0% and 40%, the emission intensity of polysilole increases slightly. However, the intensity of emission band increases 1100%, when the ratio of water to THF is 9:1. Luo et al. reported similar behavior for the silole aggregate.[17] Fig. 3 shows the plot for the relative intensity of polysilole aggregate *vs* content of water fraction.

3.2 Fluorescence quenching studies with TNT

The detection method for TNT involves measurement of the quenching of photoluminescence of the polysilole aggregate by adding analytes (using a Perkin-Elmer LS 50B fluorescence spectrometer, 340 nm excitation wavelength). Quenching photoluminescence spectra of polysilole aggregate in 90% water-THF mixture solution were obtained upon successive addition of aliquots of TNT in water. The Stern-Volmer equation was used to quantify the differences in quenching efficiency for TNT. Fig. 4 display Stern-Volmer plot for both polysilole aggregate and polysilole with TNT. A linear Stern-Volmer relationship is observed for polysilole, but the Stern-Volmer plot for for polysilole aggregate exhibits an exponential dependence. A linear Stern-Volmer relationship may be observed if either static or dynamic quenching process is dominant. Thus, in the case of polysilole aggregate, the two processes may be competitive, which results in a nonlinear Stern-Volmer relationship. Photoluminescence quenching efficiencies of polysilole aggregate with TNT are greater than that of polysilole. Polysilole ggregates exhibits 340% better quenching efficiency than polysilole at 2.5 ppm of TNT.

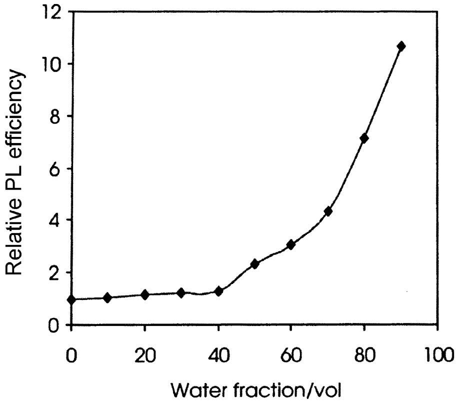

Fig. 3. Plot for the relative intensity of polysilole aggregate *vs* content of water fraction.

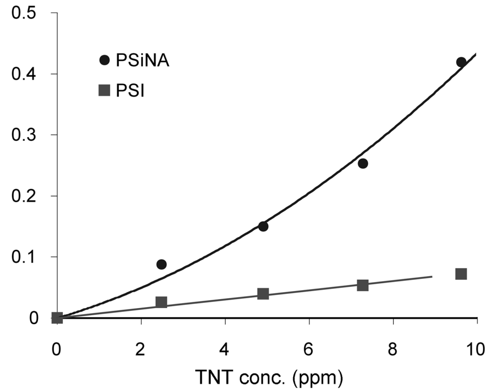

Fig. 4. Stern-Volmer plot of polysilole aggregate (■) and polysilole (■) with TNT.

Control experiments using polysilole aggregate with oxygenated air displayed no change in the photoluminescence spectrum. The quenching efficiency of polysilole aggregate with TNT shows that the quenching efficiency is greater in aggregate.

Conclusion

New polymeric aggregate has been synthesized and characterized by photoluminescence spectroscopy. The polymeric aggregate shows much greater intensity of photoluminescence, when the content of water fraction in water-THF mixture increases. The polymeric aggregate used for the detection of TNT and shows greater sensitivity compared with polysilole in toluene.

Reference

1. A. R. Maureen,. *C&EN News* **1997**, 14-22.
2. K. Hakansson, R. V. Coorey, R. A. Zubarev, V. L. Talrose and P. J. Hakansson, *Mass Spectrom* **2000**, 35, 337-346.
3. J. M. Sylvia, J. A. Janni, J. D. Klein and K. M. Spencer, *Anal. Chem.* **2000**, 72, 5834-5840.
4. V. P. Anferov, G. V. Mozjoukhine and R. Fisher, *Rev. Sci. Instrum.* **2000**, 71, 1656-1659.
5. R. D. Luggar, M. J. Farquharson, J. A. Horrocks and R. J. J. Lacey, *X-ray Spectrom.* **1998**, 27, 87-94.
6. A. M. Rouhi, *Chem. Eng. News* **1997**, 75, 14-22.
7. J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.* **1998**, 120, 11864-11873.
8. J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.* **1998**, 120, 5321-5322.
9. H. Sohn, R. M. Calhoun, M. J. Sailor and W. C. Trogler, *Angew. Chem. Int. Ed.*, **2001**, 11, 2104-2105.
10. H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, *J. Am. Chem. Soc.* **2003**, 125, 3821-3830.
11. D. D. C. Bradley, *Chem. Brit.* **1991**, 27, 719-723.
12. J. H. Burroughes, C. A. Jones and R. H. Friend, *Nature* **1988**, 335, 137-141.
13. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature* **1990**, 347, 539-541.
14. Y. Yang and A. J. Heeger, *Nature* **1994**, 372, 344-346.
15. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. D. Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature* **1999**, 397, 121-128.
16. H. Sohn, R. R. Huddleston, D. R. Powell and R. West, *J. Am. Chem. Soc.* **1999**, 121, 2935-2936.
17. J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, S. H. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun,* **2001**, 18, 1740-1741.

14. R. West, “*Comprehensive Organometallic Chemistry II*”, **1995**, pp 77-110, A. G. Davies, Ed., Pergamon, Oxford.
15. R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apelog and T. Mueller, *J. Am. Chem. Soc.* **1995**, 117, 11608-11609.
16. K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa and S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, 118, 11974-11975.
17. Y. Yamaguchi, *Synthetic Met.* **1996**, 82, 149-153.
18. S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.* **1996**, 69, 2327-2334.
19. Y. Xu, T. Fujino, H. Naito, T. Dohmaru, K. Oka, H. Sohn, R. West, *Jpn. J. Appl. Phys.* **1999**, 38, 6915-6918.

21. S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa and K. Tamao, *Chem. Eur. J.* **2000**, 6, 1683-1692.
22. T. Sanji, T. Sakai, C. Kabut and H. Sakurai, *J. Am. Chem. Soc.* **1998**, 120, 4552-4553.

참고문헌 14~17번호가 반복되었습니다.

확인하여 주십시오.