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Luminescent Polymeric Aggregate Sensors for Carcinogenic Chromate (VI) and Arsenate (V)

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The main goal of this work is to develop new selective sensors for chromium (VI) and arsenic (V) based on redox quenching of the photoluminescence of polymeric aggregate. The detection of carcinogenic chromium (VI) and arsenic (V) 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 linear relationship of Stern-Volmer plot for both chromium (VI) and arsenic (V) 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 selective and insensitive to common interferents in water, such as sulfate, phosphate, nitrate, nitrite, perchlorates, and chlorates. The detection limit for the polymeric aggregate is below 100 ppb for chromium (VI) and 500 ppb for arsenic (V), respectively.

Key words: detection, chromium, arsenic, photoluminescence, aggregate

1. Introduction

There has been considerable interest in the electronic properties of conducting polymers since the first discovery of a conjugated organic electroluminescent polymer by Burroughes *et al.* in 1988.[1,2] These conjugated polymers are organic 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.[3] These unusual optical and electrical properties can be useful in electronic devices, such as diodes, transistors,[1,4] light-emitting diodes (LEDs),[2] and large-area light-emitting displays.[5] These unique optoelectronical properties can be used for excellent candidates for luminescent chemical sensors. Recently we have shown how luminescent polysiloles can be used as TNT and picric acid sensors.[6,7] Yang and Swager have reported luminescent conjugated organic polymers for the detection of TNT from land mines.[8,9]

Metal ion pollutants in industrial wastewater cause a difficult problem in industrial process. The methods to detect metal ions in wastewater that instantly alert operators is required in metal working and electroplating industries. Chromium (VI) is an especially problematic contaminant in drinking water because it has been known as a human carcinogen. Chromate has an isostructure as sulfate. Sulfate transporting protein in the cell membrane facilitates the uptake of chromate (CrO_4^{2-}). which is the primary environmental species of chromium (VI). The oxidizing ability of chromium (VI) in the cell promotes damage to DNA.[10] Another contaminant, which is of serious concern for both toxicity and carcinogenicity, is arsenic in water. Therefore, sensors detecting chromium (VI) or arsenic (V) might be especially useful for the purpose of monitoring in water. Several chromium (VI) or arsenic (V) sensors were reported and based on polymer coated piezoelectrics[11] or luminescent bioassays employing reporter gene systems.[12,13]

We have previously developed polysilole sensors for TNT and other organic electron acceptors by using polysilole surfaces,[6] which readily bind the organic

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analyte so electron transfer quenching can occur. The polymer sensor was remarkably insensitive to simple inorganic oxidants. The polysilole consist of a long chain of silicon atoms surrounded by a bulky organic sheath. These polymers are incredibly stable and not susceptible to common interferents and biological organisms found in aquatic samples.

Polysilanes are well known as thermally stable polymers and they exhibit efficient emission in the UV region, high hole mobility, and high nonlinear optical susceptibility.[14] These novel properties arise from σ-π^* delocalization of σ electrons along the Si-Si backbones and quantum confinement of the conjugated electrons. Siloles, such as 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene, have recently received much attention[15] because of their unusual electronic properties, as well as their application in optoelectronics and as electron-transporting materials in display technologies, e.g. organic light-emitting diodes (LED's).[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] The polysiloles have a stabilizing sheath of organic groups surrounding a central Si-Si backbone. The backbone provides the correct electronic structure to allow migration of the excited state energy along the polymer chain. The organic sheath not only provides chemical protection needed to make the materials kinetically stable in air or water, but σ^*-π^* conjugation with the silole ring provides a pathway for electron transfer quenching at the edge of the organic sheath.

2. Experimental

2.1. Materials

Polysilole has been synthesized by the procedures described in the literature.[20] 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[24] using 90% water-THF mixtures. Potassium chromate and arsenic (V) oxide were purchased as analytical grade from Aldrich and used directly for the analysis without any purification.

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

3.1. Absorption and fluorescence studies

The UV-vis absorption and fluorescence spectra are measured for the polysilole in toluene. Polysilole exhibits three absorption bands, which are ascribed to the π-π^* (368 nm) transition in the silole ring and the σ-(σ_2^*+π^*) (314 nm) and σ-σ_1^* transitions in the Si-Si backbones. Fig. 1 shows a schematic energy-level diagram for polysilole. UV-vis absorption of polysilole aggregate exhibits nearly identical absorption band.

Fluorescence spectra for both polysilole and polysilole aggregate exhibit one emission band (λ_{max}, 513 nm) when excited at 340 nm. There is no shift in the maximum of the emission wavelength.

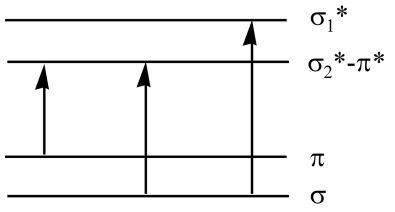

Fig. 1. schematic energy-level diagram for polysilole.

3.2. Fluorescence quenching studies with chromate (VI) and arsenate (V)

The detection method for chromium (VI) and arsenic (V) 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) and dictated quenching mechanism. Fluorescence spectra of a 90% water-THF mixture solution of the polysilole aggregate were obtained upon successive addition of aliquots of chromate (VI) and arsenate (V) in water. Photoluminescence quenching of the polysilole aggregate in 90% water-THF mixture solution with chromium (VI) and arsenic (V) were measured. Fig. 2 and 3 display the quenching of photoluminescence spectra of the polysilole aggregate upon addition of chromate (VI) and arsenate (V), respectively. Photoluminescence quenching efficiencies of polysilole are in the order of chromate (VI) > arsenate (V).

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

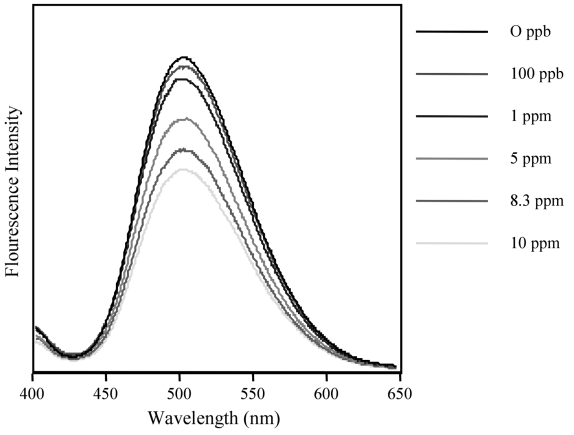

Fig. 2. Quenching of photoluminescence spectra of polysilole aggregate with chromate (VI).

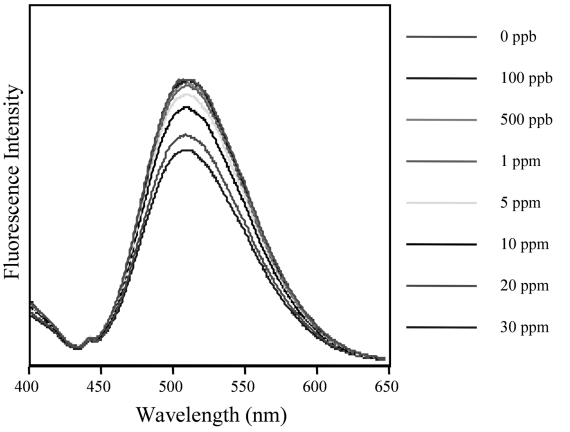

Fig. 3. Quenching of photoluminescence spectra of polysilole aggregate with arsenate (V).

In this equation, I_o is the initial fluorescence intensity without analyte, I is the fluorescence intensity with added analyte of concentration [A], and Ksv is the Stern-Volmer constant.

$$(I_o/I) - 1 = Ksv[A]a$$

Fig. 4 and 5 show the Stern-Volmer plots of polysilole aggregate for chromate (VI) and arsenate (V), respectively. A linear Stern-Volmer relationship is observed for both cases, but the Stern-Volmer plot for arsenate (V) exhibits an exponential dependence when its concentration is lower than 2 ppm. A linear Stern-Volmer relationship may be observed if either static or dynamic

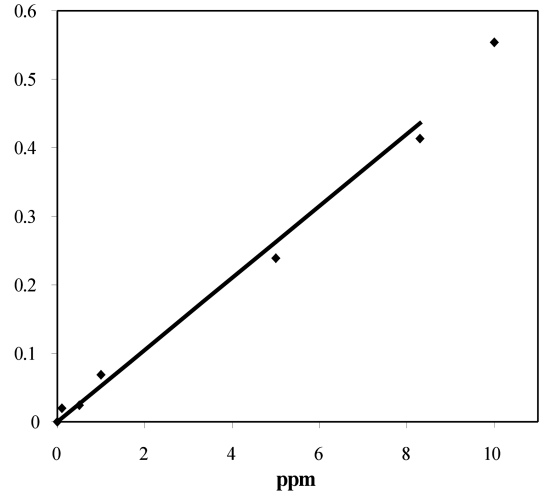

Fig. 4. Stern-Volmer plots of polysilole aggregate for chromate (VI).

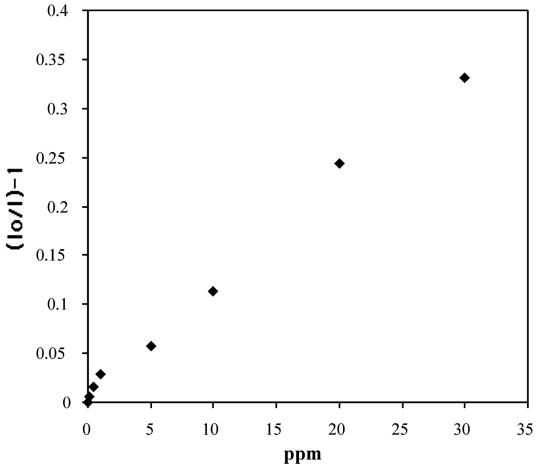

Fig. 5. Stern-Volmer plots of polysilole aggregate for arsenate (V).

quenching process is dominant. Thus, in the case of lower 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.

Control experiments using polysilole aggregate with oxygenated air displayed no change in the photoluminescence spectrum. The quenching efficiency of polysilole aggregate with chromate (VI) vs. arsenate (V) shows that the quenching efficiency of chromate (VI) is 5 times greater than that of arsenate (V). The detection limit by luminescence quenching for the polymeric nano-aggregate is below 100 ppb for chromate (VI) and 500 ppb for arsenate (V), respectively.

Conclusion

New polymeric aggregate has been synthesized and characterized by photoluminescence UV-vis spectroscopy. The polymeric aggregate having photoluminescence used for the detection of carcinogenic chromate (VI) and arsenate (V). The quenching efficiency of polysilole aggregate with chromate (VI) vs. arsenate (V) shows that the quenching efficiency of chromate (VI) is greater than that of arsenate (V).

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