Fluorescent film sensors based on SAMs of pyrene derivatives for detecting nitroaromatics in aqueous solutions

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The detection of nitroaromatics in aqueous solutions by a novel pyrene-functionalized film has been investigated in the present study. The pyrene moieties were attached on the glass surface via a long flexible spacer based on self-assembled monolayer technique. Steady-state fluorescence measurements revealed that these surface-attached pyrene moieties exhibited both monomer and excimer emission. Nitroaromatics such as 2,4,6-trinitrotoluene, 2,4-dinitrotoluene, and 2,4,6-trinitrophenol (picric acid) were found to efficiently quench the fluorescence emission of this film. The quenching results demonstrated that the excimer emission of these surface-confined pyrene moieties is more sensitive to the presence of nitroaromatics than the monomer emission. The quenching mechanism was examined through fluorescence lifetime measurement and it revealed that the quenching is static in nature and may be caused by electron transfer from the polycyclic aromatics to the nitroaromatics. Furthermore, the response of the film to nitroaromatics is fast and reversible, and the obtained film shows promising potentials in detecting explosives in aqueous environment.

Introduction

The issues concerning explosive detection have been widely discussed for enormous demand in societal security area over the past two decades [1]. As one particular research field, environment monitoring has focused on identifying areas in soil, ground water, and seawater contaminated with nitroaromatics (NACs) especially TNT from past munitions manufacture, storage, disposal, and leakage from unexploded ordnance [2,3]. More disturbingly, ingestion of NACs may cause a series of health problems, such as liver damage, gastritis, aplastic anemia, cyanosis, and dermatitis [4,5]. As a matter of fact, various techniques have been employed, which include gas chromatography [6], mass spectrometry [7], ion mobility spectrometry [8], nuclear quadrupole resonance [9], electron capture detection [10], electrochemical methods [11], fluorescence [12], chemiluminescence [13], and capillary electrophoresis [14,15], etc. Fluorescence-based sensors have received growing interest in terms of sensitivity, selectivity, and multiple parameters as transduction signal [16,17]. Conjugated polymers (CPs) functioning as fluorescent active materials have been considerably employed in fabricating sensors mainly due to their so-called “molecular wire” effect, or “one point contact, multi-point response” effect, which impart them with amplified response [18].

Conjugated organic [19–22] and inorganic polymers [5,23,24] have been widely used to build potential fluorescent chemosensors for explosive NACs. Although these CP-based film sensors exhibited sensitive response to NACs, they encountered several serious problems in practical applications. This is mainly because most of these films were prepared by spin coating one of the desired polymers on a solid substrate surface. Polymer leaking to the medium is almost unavoidable, particularly when the film sensors are used in solution, which leads to contamination of analysis systems, and shortens the life time of the film sensors. Most of these CP-based films could not be used to directly detect TNT in water or seawater due to their poor stability. Therefore, the application of these CP-based films for detecting explosives is limited to monitor NACs in air phase.

Polycyclic aromatic hydrocarbons (PAHs) such as pyrene have been proved to be another important class of fluorophores sensitive to NACs [25]. Some recent applications in explosive detection utilizing homogeneous molecular sensors have been reported by Goodpaster and McGuffin [12] and Focsaneanu and Scaino [25]. Although the homogeneous sensors are rapid, simple, and show promise for near real-time evaluation of nitroaromatics in environmental samples, from the viewpoint of practical application, film sensors have a number of advantages such as reversibility, reusability, and ease to be made into devices [26]. PAHs are easily modified with functional groups and attached on reactive surfaces to prepare PAH-based films. In addition, pyrene derivatives are
505 nm is different from that monitored at the monomer emission peak such as 380 nm, where the former is longer than the latter, they should have similar variation trend upon the addition of the quencher.) Upon examination of the plots shown in Fig. 8, it is obvious that the lifetime of the sensing molecules did not change apparently along increasing the quencher concentration, a sharp contrast to that of the emission intensity. This reveals that the quenching process is static in nature, suggesting the formation of a non-fluorescent complex between the fluorophore and the quencher. This supports the assumption that an electron-transfer process occurred from the electron-rich PAH, pyrene, to the electron-poor compounds, NACs, resulting in quenching the fluorescence emission of the pyrene-modified film.

Reversibility and selectivity of the film to nitroaromatics

Reversibility is an important parameter for a film sensor in practical application, especially in the future development of apparatus [40]. Therefore, 2,4-DNT was chosen as a test analyte to examine the reversibility of the response of the film to NACs in aqueous solution. The film was alternatively exposed to a solution of DNT and pure water, and the corresponding fluorescence emission was measured. Firstly, in the absence of DNT, the fluorescence intensity of the film at 505 nm was recorded every 5 min for a period of 15 min, and the average data were termed as \(I_0\); then, a certain amount of DNT was added to the testing system, leading to DNT concentration at 0.08 mM; following this, the film fluorescence intensity at 505 nm was recorded again for three times over 15 min. All the measured data were treated as \(I\), and the value of \(I/I_0\) was used as reversibility parameter. After each measurement of the DNT solution, the film was rinsed with ethanol for several times and then with pure water for several times. It was found that the emission of the film could be well restored for at least five cycles and it is very fast for the system to reach equilibrium (c.f. Fig. 9). Moreover, like our other observations, the sensing performances of the film are not affected by common interferents including benzene, toluene, acrylamide and KI, etc. (the data are not shown) [29]. Therefore, the high sensitivity, selectivity, reversibility, and relatively short response time make this film a proper candidate material for determining NACs in aqueous environment.

Conclusion

In the present work, the sensing ability of a pyrene-functionalized SAM film to NACs was examined in aqueous solution. Fluorescence quenching studies showed that the film is sensitive and selective to the presence of nitroaromatics in aqueous solution due to their strong electron-withdrawing ability. The picric acid shows the highest quenching efficiency among the three analytes tested (picric acid, TNT, and DNT). Further examination showed that the responses of the film to nitroaromatics in aqueous solution are reversible and its sensing performances are not affected by common interferents including benzene, toluene, acrylamide and KI, etc. The sensitive response, reversibility of the sensing process, and freedom from commonly encountered interference of the specially designed film to nitroaromatics may qualify this material as promising fluorescent sensors for monitoring nitroaromatics in aqueous solution.

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