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A dansyl-based fluorescent film: Preparation and sensitive detection of nitroaromatics in aqueous phase

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Abstract

A novel fluorescent film sensor for the detection of nitroaromatics in aqueous phase has been developed *via* chemical immobilization of dansyl chromophores on an epoxy-terminated self-assembled monolayer on glass slide surfaces. Chemical attachment of the chromophore on the substrate surface endows the present film a satisfying stability and avoids the leaching of the chromophores. Increase in the length of the spacer connecting the sensing element and the substrate results in a dramatic improvement in the performance of the film compared to those with similar structures. Fluorescence quenching experiments demonstrates that in aqueous medium, the emission of the film is more sensitive to nitrobenzene (NB) than to other nitroaromatics, including 2,4,6-trinitrotoluene, 2,4-dinitrotoluene, *p*-chloronitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, and *o*-chloronitrobenzene, etc. This exceptional result has been rationalized by considering the possible hindrance effect induced by the compact conformation of the long flexible spacer. It is also demonstrated that the NB quenching is static in nature, and the response of the film to NB is fast and reversible.

Keywords: Fluorescence quenching; Dansyl; Nitroaromatics; Film sensor

1. Introduction

The contamination of soil and water at sites where nitroaromatics were manufactured or used is a serious environmental problem. Ingestion of them may cause liver damage, gastritis, aplastic anemia, cyanosis, and dermatitis. Therefore, there is a demand for means of quick and reliable detection of these substances in aqueous phase and soil. As a matter of fact, a great variety of analytical methods, such as mass spectrometry [1], ion mobility spectrometry [2], electrochemical methods [3], fluorescence [4], chemiluminescence [5], capillary electrophoresis [6], immunoassay [7–13], electrochemical sensing [14], etc., have been developed for the detection and monitoring of them. Compared to other methods, fluorescent film sensors have become the one of the focus due to its sensitivity, selectivity, multiple choices in signals or parameters, and ease to be made into devices.

With respect to the fluorescent film sensors used for the detection of nitroaromatics, films with conjugated polymers as fluorescent active materials have received considerable attention due to their so-called "molecular wire", or "one point contact, multi-point response" effect [15]. Swager, Whitten and others have focused on the work for several years, and developed a number of fluorescent film sensors by using conjugated polymers as sensing materials [16,17]. It was proved that the films are photo-stable, and can be used effectively, particularly in air, for the sensitive detection of TNT and other nitroaromatics. It was also demonstrated that the performances of the films depend strongly on a number of factors including the permeability of analyte in the films, the thickness of the films, and the strength of the interaction between the analyte and the conjugated polymers, of which permeability is the bottleneck, even though it can be partially overcome by modification of the chain structures of the polymers [18,19], or by introducing surfactants into the films [20]. Furthermore, the films cannot be used for the detection of nitroaromatics in solution due to leaking problems.

Considering the high fluorescent quantum yields and the electron-poor property of nitroaromatics, an alternative

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methodology was proposed for the design and preparation of fluorescent film sensors. In this methodology, fluorescence active aromatics are employed as sensing elements, and are chemically attached on a self-assembled monolayer (SAM), which would endow a film sensor higher stability and absence of leaking problems. It is expected that the electron-rich nature of the aromatics will guarantee their special interaction with nitroaromatics due to the possible electron transfer process, which will definitely result in quenching of the fluorescence of the aromatics, and realizing detection of the nitroaromatics as discovered before [21].

In fact, this methodology has been used for the design of fluorescent film sensors of other analytes [22–26]. It has been found that the length of the spacer connecting the sensing element and the substrate has a great effect upon the sensing performance of a film [27–30]. Based upon the above considerations, a novel fluorescent film sensor has been specially designed by employing an even longer flexible spacer than our previous work, and the sensing performances for nitroaromatics in aqueous phase have been investigated. The details are reported in this article.

2. Experimental

2.1. General procedures

All fluorescence measurements were conducted on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) with a front face method. Infrared spectra (IR) were recorded with a Bruker Equinox 55 FTIR spectrometer. The ^{1}H NMR spectra of the samples were obtained on a Bruker AV 300 NMR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA PHI5400 (Perkin Elmer) photoelectron spectrometer using a monochromatic Mg Kα X-ray source. The contact angles of the film surfaces were measured by using a JY-82 contact angle goniometer.

Glass wafers used in the experiment were microscope slides (25.4 mm × 76.2 mm, 1–1.2 mm thick) by cutting them into ∼0.9 cm × 2.5 cm pieces. Dansyl chloride (99%) and the silane coupling agent, 3-glycidoxypropyl-trimethoxysilane (GPTS, 97%), were both purchased from Acros and used directly without further purification. 1,6-Hexanediamine (99%), 2,4,6-trinitrotoluene (TNT), *m*-dinitrobenzene (*m*-DNB), 2,4-dinitrotoluene (DNT), nitrobenzene (NB), *p*-dinitro-benzene (*p*-DNB), and *p*-chloronitrobenzene (*p*-CNB) were of analytical grade. Water used throughout was de-ionized and then double distilled.

The amino derivative of dansyl was obtained by reacting 1,6-hexanediamine with dansyl chloride in CH_2Cl_2 according to a similar method for synthesizing 1,2-diaminoethylene derivative of dansyl [31]. The product, *N*-dansylhexanediamine (DHDA), was characterized by various techniques, and the results are listed below: IR (KBr): 3347 cm^{-1}, 3052 cm^{-1}, 2931 cm^{-1}, 2853 cm^{-1}, 1610 cm^{-1}, 1573 cm^{-1}, 1461 cm^{-1}, 1397 cm^{-1}, 1312 cm^{-1}, 1160 cm^{-1}, 1141 cm^{-1}, 1073 cm^{-1}, 936 cm^{-1}, 792 cm^{-1}, 623 cm^{-1}, 569 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.536 (d, 1H, ArH); δ 8.296 (d, 1H, ArH); δ 8.244 (d, 1H, ArH); δ 7.185 (d, 1H, ArH); δ 7.543 (m, 2H, ArH); δ 2.718 (m, 10H, $N(CH_3)_2$, SO_2NHCH_2 and CH_2NH_2); δ 1.308 (m, 8H, $CH_2CH_2CH_2CH_2CH_2NH_2$).

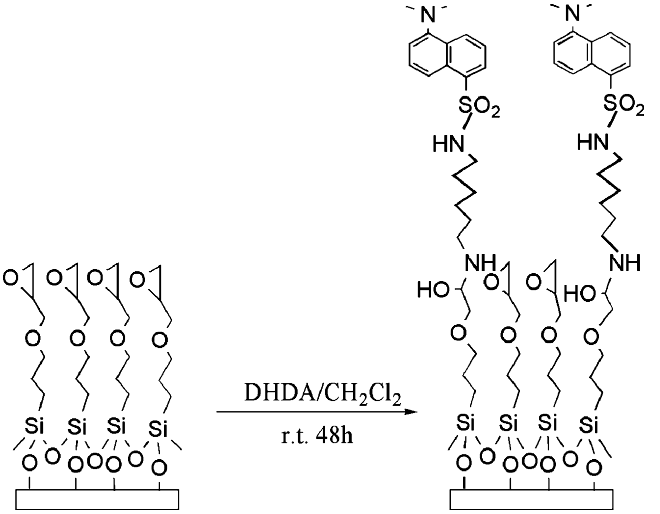

Fig. 1. Schematic representation of the dansyl-functionalized film by coupling dansyl derivative on epoxy-terminated SAM surface.

2.2. Preparation of dansyl-functionalized film sensor

The film was prepared in three steps as reported elsewhere [21] except using a different dansyl derivative, DHDA. The final dansyl-functionalized film is schematically shown in Fig. 1.

3. Results and discussion

3.1. Characterization of the dansyl-functionalized film

Contact angle measurement is one of the efficient characterization methods for surface properties, which examines the wettability of surfaces and provides some useful information about the structure and composition of surfaces [32]. The results from the contact angle measurements for the slide surfaces in preparing the dansyl-functionalized film are shown in Table 1, where water was used to provide the droplet. Activation by "piranha solution" provides more hydrophilic hydroxyl groups on the slide surface as the values decreased from 15.8° to 2.5° after activation. Treatment with silanes resulted in a larger contact angle, which was 20.4°, indicating formation of a relatively

Table 1
The advancing water contact angles (θ) of the glass slide surfaces

Surfaces[a]	θ (°)
(a)	15.8 ± 5.6
(b)	2.5 ± 1.0
(c)	20.4 ± 0.6
(d)	27.3 ± 3.8

[a] Stands for surfaces of (a) original glass slide, (b) slide activated by "piranha solution", (c) slide coupled with SCAs, and (d) slide modified with dansyl moieties.

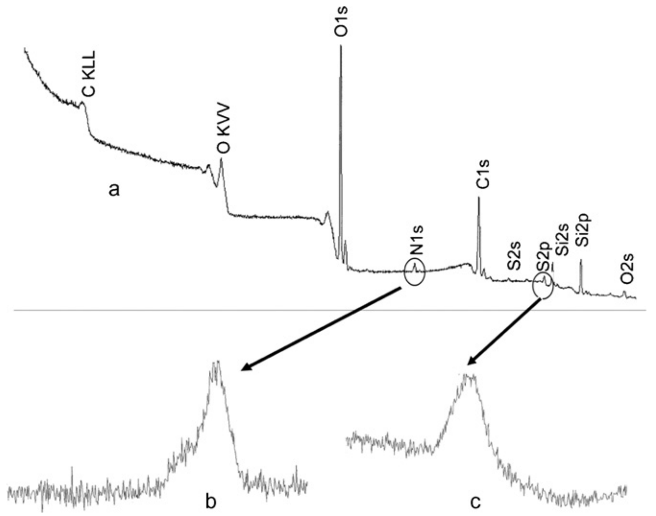

Fig. 2. XPS spectra of the dansyl-functionalized film.

hydrophobic surface. Finally, the introduction of dansyl moieties to the surface further increased the contact angle to an even higher value as 27.3°. These results are consistent with the expectation from the chemical compositions of the slide surfaces treated in different steps.

The results of XPS studies further confirmed that the fluorophores were successfully attached on the glass slide surface. Fig. 2 illustrates the X-ray photoelectron spectra of the functional film with fluorescent dyes. And the signals of elements N_{1s} (Fig. 2b), and S_{2p} (Fig. 2c) appeared, which should come from the nitrogen and sulfur elements in the amino derivatives of dansyl moieties, DHDA, indicating successful attachment of dansyl moieties on the substrate surface.

UV–vis spectroscopy was employed to evaluate the density of dansyl groups according to Ref. [22]. The absorption at 350 nm was used to estimate the surface density of the fluorophore (ρ) from the Beer–Lambert law ($\rho = A\varepsilon^{-1}$), using the experimentally determined absorption coefficient of dansyl chloride in CH_2Cl_2 ($\varepsilon = 4765\ M^{-1}\ cm^{-1}$). The resulting density is 3.8 dansyl groups/100 Å^2, which is about 65% of the theoretical value [33].

3.2. Steady-state fluorescence spectra of dansyl-functionalized film

The steady-state fluorescence excitation and emission spectra of the film in water (Fig. 3) were recorded by varying the analysis and the excitation wavelengths and found to show similar behaviors as the previous dansyl-functionalized films reported elsewhere [21]. The fluorescence emission was stable and did not change very much along with time. The leaking problem was examined by investigating the fluorescence emission of the solvent in which the functional film had been immersed for 24 h. Since there was no evidence of existence of dansyl in the solvent, it may be concluded that the leaking of dansyl from the slide surface was negligible and should not affect the follow-up measurements.

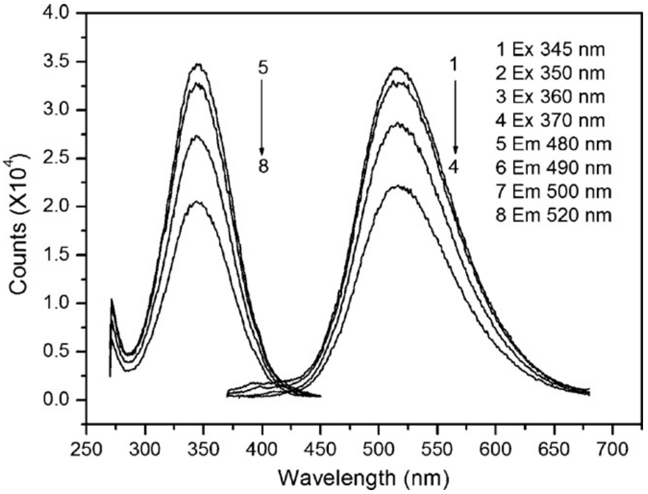

Fig. 3. Excitation and emission spectra of the dansyl-functionalized film sensor in water.

3.3. Sensing properties of the present film to nitroaromatics

As is well known, nitroaromatics are effective fluorescence quenchers of most fluorophores [34]. Accordingly, the effects of a series of nitroaromatics (such as TNT, *m*-DNB, DNT, NB, *p*-DNB, *p*-CDNB) to the fluorescence emission of the film were examined. In the experiment, the film was adhered to one inner-side of a quartz cell with a volume of ca. 3.5 cm^3 firstly. Then, solvent with a volume of 2.5 cm^3 was added into the cell. Finally, the spectra were recorded when the fluorescence intensity kept being stable after injecting the nitroaromatics into the cell. As expected, all the nitroaromatics quenched, with different efficiency, the emission of the dansyl-based film. As an example, Fig. 4 shows the fluorescence emission spectra of the film as a function of the concentration of NB. Clearly, the emission of the film decreased significantly with increasing NB concentration. The results from lifetime measurements were illustrated in Fig. 5. It is obvious that the lifetime of the sensing molecules does not change very much with increasing concentration of

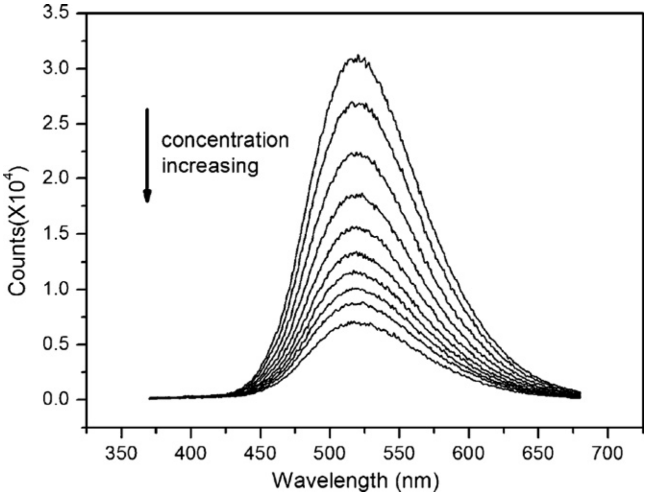

Fig. 4. Fluorescence emission spectra of the dansyl-functionalized film in the presence of nitrobenzene at different concentrations ($\lambda_{ex} = 350$ nm).

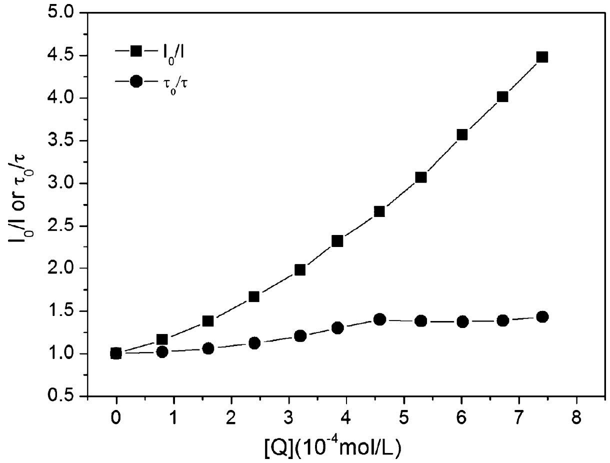

Fig. 5. Quenching plots of the fluorescence intensity and fluorescence lifetime of the film in aqueous medium at room temperature.

nitrobenzene and τ_0/τ is equal to 1 where τ_0 and τ stand for the lifetime of the surface-bound fluorophore in the absence and presence of the quencher, respectively. This indicates that the quenching is mainly caused by formation of a nonfluorescent complex (F–Q), which is the result of charge transfer from the electron-rich dansyl group to the electron-poor nitrobenzene. So the quenching mechanism of nitrobenzene to the film was static in nature, as discovered previously [21].

As expected, the quenching efficiency of NB to the emission of the present film is much more efficient than to the emission of the films reported earlier [21]. In order to make a comparison, the dansyl-functionalized films containing propanediamine and butanediamine as subunits were also fabricated and defined as Film 1 and Film 2. The present film with hexanediamine as subunit was defined as Film 3. The concentration of NB needed for quenching half of the initial fluorescence of the three films as well as the detection limit (DL) was determined. Detection limit of the present film was determined according to the following functions:

$$s_b = \sqrt{\frac{\sum_{i-1}^{n}(I_i - \bar{I})^2}{n-1}} \quad (1)$$

$$S = \frac{\Delta I}{\Delta c} \quad (2)$$

$$\mathrm{DL} = \frac{3s_b}{S} \quad (3)$$

Firstly, the standard deviation (s_b) was calculated by measuring the intensity of the dansyl-functionalized film in blank solution for more than 10 times and then got the average intensity ($\bar{I}$). By fitting the data into Function 1, the value of standard deviation (s_b) was obtained. Secondly, a certain amount of nitrobenzene (among the concentration range of linear response shown in Fig. 6) was added into the blank solution and the resulting variation of the intensity (Δc) was recorded. By fitting the data into Function 2, where ΔI is the variation of intensity, and Δc is the variation of quencher concentration, the value of precision S was calculated. Finally the detection limit, DL, was calculated according to Function 3.

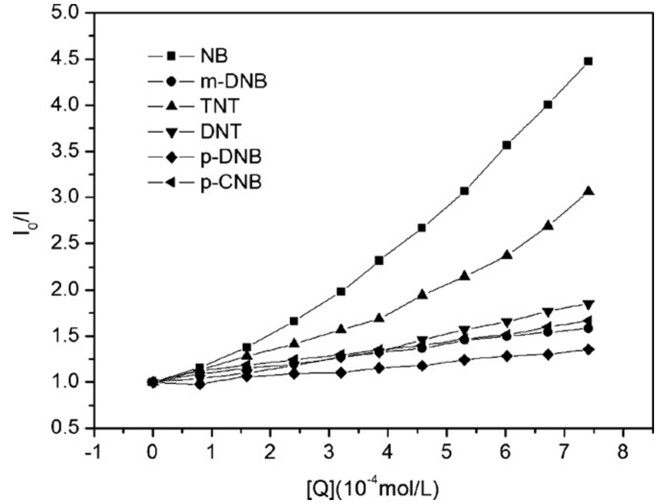

Fig. 6. Response of the dansyl-functionalized film to various nitroaromatics in water ($\lambda_{ex} = 350$ nm, $\lambda_{em} = 518$ nm).

The results are shown in Table 2. It can be seen that the sensitivity of the film sensors to NB increases along with increasing the length of the spacers. In particular, for the present film, the two values depicted in the table are one or two orders lower than those of the corresponding films, indicating that the lengths of the spacers connecting the sensing molecules and the substrates have a significant effect upon the sensing performances of the films designed in the present strategy. Similar phenomenon was observed in the studies of other film sensors, of which different sensing molecules had been employed [29,30].

Fig. 6 depicts the plots of I_0/I against the concentration of each nitroaromatic compound, where I_0 and I stand for the maximum fluorescence intensities of the film in the absence and presence of the nitroaromatics, respectively. Each data was recorded 20 min later after the injection of the quencher. According to the ability of drawing electrons, it is expected that TNT might have the highest quenching efficiency to the emission of the films due to the existence of three nitro-groups on the benzene ring that make the ring have lowest electron density if compared with other nitroaromatics. However, it was surprisingly found that it was NB not TNT or other nitroaromatics with more than one nitro-group that showed highest quenching efficiency to the emission of the present film provided the quenching studies were conducted in aqueous phase.

Actually, TNT was found to have the highest quenching efficiency to the emission of Film 1 and Film 2, which contained propanediamine and butanediamine as subunits. For example, when Film 1 was tested in a 2 mM of each nitroaromatic compound aqueous solution, TNT quenched nearly 76.5% of the initial intensity of the film, and those aromatics containing two nitro-groups like *m*-DNB and DNT-induced 62.4% and 54%

Table 2
Comparison of the sensing properties of the three dansyl-functionalized films

Film	Film 1	Film 2	Film 3
[NB] for $I_0/I = 2$ (M)	2.8×10^{-3}	2.0×10^{-3}	3.2×10^{-4}
DL (M)	8.2×10^{-5}	2.0×10^{-5}	2.0×10^{-7}

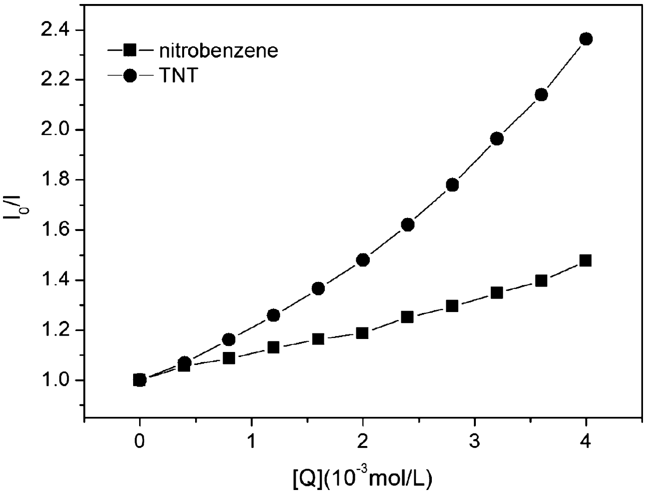

Fig. 7. Responses of the dansyl-functionalized film to nitrobenzene and TNT in ethanol.

quenching of the fluorescence of the film. However, NB with only one nitro-group quenched only 34.1%. Furthermore, some non-nitroaromatics like benzene and toluene did not quench the fluorescence of the film at all. These results further confirmed electron transfer was the main reason for the quenching of these dansyl-functionalized films and the quenching efficiency was dominated by the electron-drawing ability of the nitroaromatics.

The uncommon phenomenon found for the present film (Film 3) may be understood by considering the possible microenvironment surrounding dansyl moieties on the substrate surface. As discovered before [21,33] the long, hydrophobic and flexible spacers shown in Fig. 1 tended to adopt compact coiled conformation when the film was immersed in a polar solvent like water. The sensing molecules, dansyl moieties, were expected to incorporate into the compact coiled conformation, as they prefer to stay in a relatively hydrophobic microenvironment. In the present case, however, the length of the spacer is four-methylene subunits longer than the ones previously employed [21] and seemed to form a more compact conformation around the fluorophore moieties when the film was used in aqueous phase, resulting in a hindrance effect on the accessibility of nitroaromatics to the fluorophore moieties incorporated in the spacer layer. No doubt, nitroaromatics having smaller sizes may have more chances to enter into the spacer layer and thereby result in greater quenching efficiency. This may explains why NB quenches the fluorescence emission of the film more efficiently than TNT and other nitroaromatics. This explanation is partially supported by the results of solvent effect studies.

3.4. Solvent effect and anisotropy studies

In order to confirm the assumption, a titration experiment in ethanol was conducted. The result is shown in Fig. 7. It can be seen that the order of the quenching efficiency for NB and TNT to the emission of the film is reversed in this case if compared with that conducted in aqueous phase. This result may be understood by considering that ethanol is a relatively hydrophobic solvent, and the less polar spacers should adopt more open conformations in it, resulting in less compact spacer layer, or less compact spacer clusters. In this case, it is the nature, the degree of electron deficiency, not the size of the quencher that plays crucial role upon its quenching efficiency to the emission of the film. And thereby, TNT showed greater quenching efficiency to the emission of the film than NB in ethanol. In addition, it takes ca. 15 min for the quenchers to be saturated after being added into the tested solution, and this is shorter than it dose in aqueous solution. It can be concluded that by subtly utilizing the effect of spacer's conformation one can design selective, efficient fluorescent film sensors in the manner of the strategy presented in present work and those reported before [21].

Table 3
Fluorescence anisotropies of the film in different solvents ($\lambda_{ex}/\lambda_{em}$ = 350/518 nm)

Solvents	*r*
Water	0.23 ± 0.04
Ethanol	0.14 ± 0.01

The assumption that the spacer in the present film might adopt compact coil conformation when it was used in aqueous phase was further confirmed by fluorescence anisotropy measurements, which can provide information on the mobilities of the fluorophores in the test [35]. The anisotropy values (*r*) of the fluorophore moieties immobilized on the substrate surfaces of the film examined in water and ethanol are given, respectively, in Table 3. The fact that the value in water is significantly greater than that in ethanol indicates directly that the dansyl moieties are less mobile in water than that in ethanol, suggesting that the long spacer is more compact in water, and thus the dansyl moieties might be protected by the compact spacer coil or the clusters, and even the layer.

3.5. Reversibility of the response of the film to NB

The reversibility of the film to NB was examined in a standard way [36]. That is exposing the film to the aqueous solution of

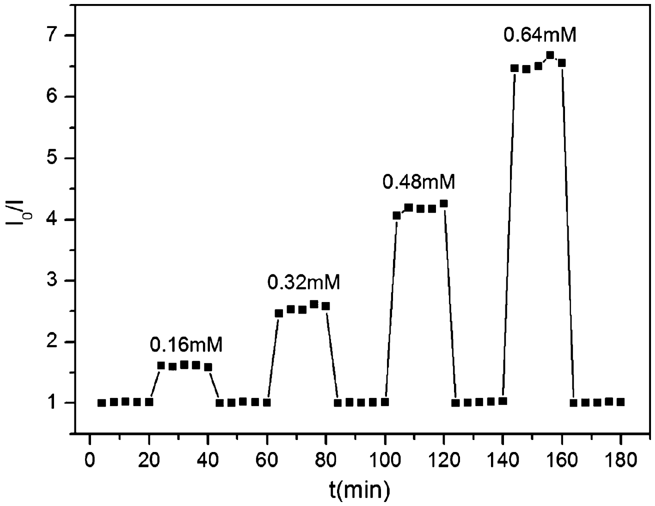

Fig. 8. Reversible responding of the dansyl-functionalized film to nitrobenzene with different concentration (λ_{ex} = 350 nm, λ_{em} = 518 nm).

the analyte first, then, recording the maximum emission intensity of the film, and then adding proper amount of NB solution in ethanol to the solution, finally, the emission intensity of the film was measured every 3 min for 5 times. After the measurement, the film was washed with ethanol, and then with pure water for several times. The measurement was repeated for 4 times with different concentrations of the analyte. The results are shown in Fig. 8. A close look of the figure reveals that the response of the film to different concentrations of NB is fully reversible. Furthermore, the time needed for reaching equilibrium of the response is less than 3 min, a rather fast response.

4. Conclusion

A new fluorescent film sensor for nitroaromatics, particularly for NB, was developed by chemically immobilization of dansyl moieties onto epoxy-terminated SAM surfaces *via* a long, flexible, and relatively hydrophobic spacer containing 1,6-hexanediamine subunit. It was demonstrated that the fluorescence emission of the film is sensitive to the presence of nitroaromatics in aqueous phase. Among them, NB is a much more efficient quencher to the emission of the film than to others. This exceptional result was ascribed to the hindrance effect induced by the compact conformation of the present long flexible spacer. To the best of our knowledge, this is the first report that a film sensor is more sensitive to NB than to other nitroaromatics, and the detection limit of 2.0×10^{-7} mol L^{-1} is the lowest one reported in the literatures till now. Considering the sensitivity, the reversibility, and the fast response of the present film in the detection of NB, it can be expected that the film may find uses in the monitoring of contamination of NB to water, soil and even air.

Acknowledgments

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