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Dansyl-based fluorescent film sensor for nitroaromatics in aqueous solution

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Abstract

We demonstrate the preparation, characterization and performance evaluation of a fluorescent film sensor for the specific detection of nitroaromatics in aqueous solution. The film sensor was fabricated by covalent immobilization of a fluorophore, dansyl, on a glass slide surface via reaction with diaminopropane and then with an epoxide-terminated self-assembled monolayer. Nitroaromatics like nitrobenzene, 4-nitrotoluene, 3,5-dinitrotoluene, and 2,4,6-trinitrotoluene, etc were found to strongly quench the fluorescence emission of the film while some other commonly-used quenchers like nitromethane, KI, acrylamide, etc showed no or slight quenching effect on the emission. The quenching mechanism was examined through fluorescence lifetime measurements and it was proved that the quenching is static in nature and may be caused by electron transfer from the fluorophore to the nitroaromatics. The presence of other aromatics like benzene, toluene, etc had little effect upon the sensing performance of the film to nitroaromatics. Solvent effect studies revealed that the conformations adopted by the spacer connecting the fluorophore and the substrate played a crucial role in the performance of the film sensor. Furthermore, the response of the film to nitroaromatics is fast and reversible.

1. Introduction

The identification and quantification of traces of nitroaromatic explosives have attracted great attention during the last few years due to their extensive security and pollution problems for humans and ecosystems [1]. Consequently, a great variety of analytical methods have been developed for monitoring these compounds both in solution and in air, for example, mass spectrometry [2], ion mobility spectrometry [3], electrochemical methods [4], fluorescence [5], chemiluminescence [6], etc. Compared with other analytical techniques, fluorescence is more attractive because of its high sensitivity, high selectivity, and multiple choices in signals or parameters like emission intensity, maximum wavelength, the profile of an emission spectrum, anisotropy, lifetime and even excimer or exciplex formation [7]. Actually, a number of homogeneous fluorescent sensors and fluorescent film sensors for nitroaromatics have

been designed and prepared during the last few years [8–11]. Although the homogeneous sensors are rapid, simple, and show promise for near real-time evaluation of nitroaromatic contamination in environmental samples, from the viewpoint of practical use, film sensors have a number of advantages like re-usability and ease of being made into devices. Therefore, the design and preparation of fluorescent film sensors for nitroaromatics have become the focus of research.

From the chemical composition of the films, fluorescent film sensors can be fluorophore modified or doped polymeric or oxide films, and fluorescent conjugated polymeric films. With the unique property of 'molecular wire effect' or 'one point contact, and multipoint response' [12, 13], fluorescent active conjugated polymers have become the first choice for building up fluorescent film sensors for nitroaromatics. Swager and co-workers [14–17] have developed a number of novel conjugated polymers, and on the basis of these polymers, several fluorescent film sensors for TNT and its analogues have been successfully prepared. It is interesting to note the report

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that the performance of these film sensors depends strongly on a number of factors including, at least, the permeability of the analytes in the polymeric films and the strength of the interaction between the analytes and the conjugated polymers [18]. To overcome these weaknesses, various bulk groups have been introduced as side chains or side groups to the conjugated backbones of the polymers and thereby formed the so-called ‘molecular tunnels’ in the polymeric films in order to achieve faster and larger amplitude responses [19, 20]. As an alternative, Whitten and co-workers [21] doped a surfactant into a conjugated polymeric film and found that the response of the film to TNT and DNT had significantly improved. However, contamination of the analytical system is hard to avoid due to leaking of the chemicals from these polymeric films when they are used in solutions.

On the basis of the considerations mentioned above and the previous work conducted in our lab, it might be an even better way to solve the problems by immobilizing a fluorescent electron-rich fluorophore, like dansyl, onto a solid substrate through a self-assembled monolayer (SAM) terminated with suitable reactive groups. This is because, firstly, the films produced in this way can avoid, at least in principle, the leaking problem which is usually an obstacle in the practical use of fluorescent film sensors [22]; secondly, the permeability problem may be solved automatically due to direct exposure of the fluorophore to the bulk medium, and thirdly, binding of TNT and other nitroaromatics by the fluorophore is natural due to electron transfer between them. Recently, a dansyl-modified film designed by our group was found to have a selective response to nitrobenzene when compared with some other common quenchers like nitromethane, KI, acrylamide, etc [23]. It is to be noted, however, that the work was focused on the photophysical properties of the fluorophore of which the motion is partially restricted. Inspired by this work, and the spacer length effect studies of other films of similar structures [24, 25], a new dansyl-modified film was developed by employing an even longer spacer. The sensing performance of the film to a series of nitroaromatics in aqueous medium has been examined and a possible quenching mechanism was proposed.

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 were recorded with a Bruker Equinox 55 FTIR spectrometer. The $^1\text{H-NMR}$ 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 $\text{Mg K}\alpha$ x-ray source. The contact angles of the glass surfaces were measured using a JY-82 contact angle goniometer.

Dansyl chloride (99%) and silane coupling agent (SCA), 3-glycidoxypropyltrimethoxysilane (GPTS, 97%), were purchased from Acros and used directly without further purification. 1,3-Diaminopropane was purchased

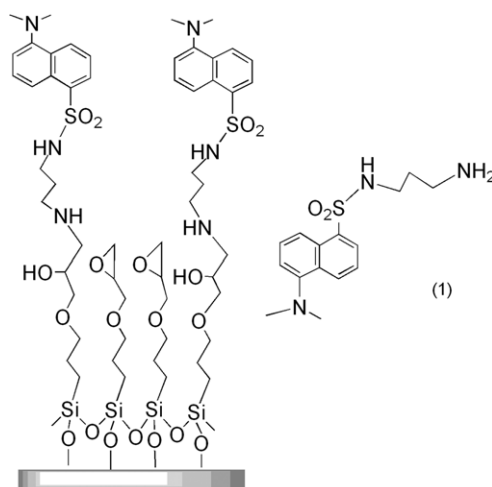


Figure 1. Schematic representation of the structure of the dansyl-modified glass slide.

from Fluka Chemicals and used directly without further purification. 2,4,6-trinitrotoluene (TNT), m-dinitrobenzene (m-DNB), 2,4-dinitrotoluene (DNT), nitrobenzene (NB), 4-nitrotoluene (NT), 4-Cl-nitrobenzene (CNB) were of at least analytical grade. Water used throughout was de-ionized and then double distilled.

An amino derivative of dansyl, N-(3-aminopropyl)-5-(dimethylamino)-naphthalene sulfonamide (1) (shown in figure 1), was obtained by reacting 1,3-diaminopropane with dansyl chloride according to a similar method for synthesizing a 1,2-diaminoethylene derivative of dansyl [23, 26]. The product, a kind of light-green needle, was characterized by various techniques, and the results are listed below: m.p. 100–102 °C. IR (KBr): 3419 cm^{-1} , 3074 cm^{-1} , 2937 cm^{-1} , 2784 cm^{-1} , 1653 cm^{-1} , 1612 cm^{-1} , 1536 cm^{-1} , 1450 cm^{-1} , 1310 cm^{-1} , 1130 cm^{-1} , 1094 cm^{-1} , 948 cm^{-1} , 791 cm^{-1} , 625 cm^{-1} and 571 cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.14 (d, 1H, ArH); δ 8.50 (d, 1H, ArH); δ 8.31 (d, 1H, ArH); δ 8.22 (d, 1H, ArH); δ 7.49 (m, 2H, ArH); δ 2.94 (m, 10H, $\text{N}(\text{CH}_3)_2$, SO_2NHCH_2 and CH_2NH_2); δ 1.57 (m, 2H, $\text{CH}_2\text{CH}_2\text{NH}_2$).

2.2. Immobilization of dansyl onto a glass slide surface

Glass slides were selected as solid substrates because they do not quench fluorescence of fluorophores attached on them [27, 28]. During the modification, the slides ($\sim 0.9 \text{ cm} \times 2.5 \text{ cm}$) were first cleaned with ‘piranha solution’ (98% $\text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2$ 70:30 V/V) at 98 °C for 1 h, then rinsed thoroughly with double-distilled water after it had been cooled and dried at 100 °C in a dust-free oven for 1 h. The slides were then immersed at 50 °C in a toluene solution of GPTS (0.6%, V/V), containing trace amount of water, for at least 12 h. (Caution: ‘piranha solution’ is a very strong oxidant and should be handled very carefully.) After treatment with the coupling agent, the slides were washed successively with fresh toluene and dichloromethane (CH_2Cl_2) for several times to remove any physically adsorbed GPTS. Finally, the epoxide-terminated glass slides were put into the solution of (1) in CH_2Cl_2 at room temperature for 48 h. After the treatment, the slides were washed with plenty of CH_2Cl_2 and then rinsed with acetone and water successively. The possible structure

Table 1. Advancing water contact angles (θ) for glass slide surfaces with different structures.

Slides ^a	(a)	(b)	(c)	(d)
θ (°)	16.8 ± 3.2	1.5 ± 1.0	25.4 ± 0.6	27.2 ± 3.8

^a Stands for (a) original glass slide, (b) surface cleaned by 'piranha solution', (c) surface coupled with SCAs, and (d) surface coupled with dansyl moieties.

of dansyl-functionalized glass slide is schematically shown in figure 1.

3. Results and discussion

3.1. Characterization of the dansyl-modified glass slide

Contact angle measurement can provide useful information about the structure and compositions of a surface by examining the wettability of the surface. The advancing contact angles with water for the glass slides at different coupling stages are shown in table 1. It can be seen that the contact angle decreased from 16.8° to 1.5° after the surface was cleaned with 'piranha solution', indicating that more hydroxyl groups had been formed on the slide surface during the treatment [23]. The treatment with the silane coupling agents increased the contact angle from 1.5° to 25.4° , in agreement with the presence of the relatively hydrophobic monolayer of GPTS. Finally, the introduction of dansyl moieties to the surface further increased the contact angle to an even higher value. These results are consistent with the expectation from the chemical compositions of the glass slide surfaces treated in different steps.

The results of XPS studies further confirmed that the fluorophore is successfully attached on the slide surface. The x-ray photoelectron spectra of the glass slide with different surface structures are presented in figure 2. The C1s (284.6 eV) signal in the spectrum of surface c is much stronger than that in the spectrum of surface b, which should have originated from the introduction of GPTS. In addition to that, N1s (400.8 eV) and S2p (170.1 eV) signals appeared in the XPS spectrum of surface d, indicating successful coupling of dansyl on the slide surface.

3.2. Steady-state fluorescence of the dansyl-modified glass slide

The steady-state fluorescence excitation and emission spectra of the film in aqueous phase were recorded at different analysis and excitation wavelengths, and it was found that the profiles of all the excitation spectra obtained have almost no difference (figure 3). Similarly, all the emission spectra also look similar to each other, indicating that each of the immobilized dansyl moieties has similar microenvironment according to Kasha's rule [7]. Possible leaking of the fluorophore moieties from the functional film had been examined by monitoring the fluorescence emission of water, within which the functional film had been immersed, as a function of time. No significant emission from the solvent was found, indicating again that the fluorophore was chemically coupled on the substrate surface rather than physically adsorbed.

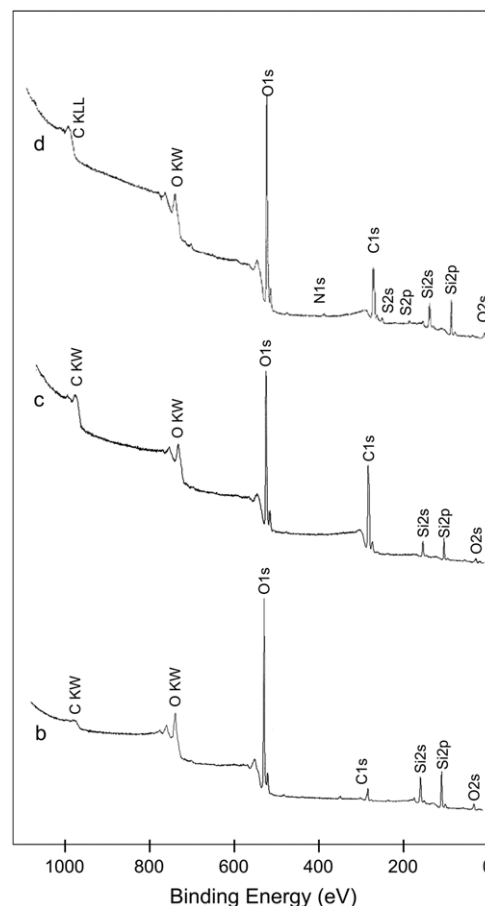


Figure 2. XPS spectra of the glass slide surfaces at different stages. Note: b, c and d refer to the same surfaces as those shown in table 1.

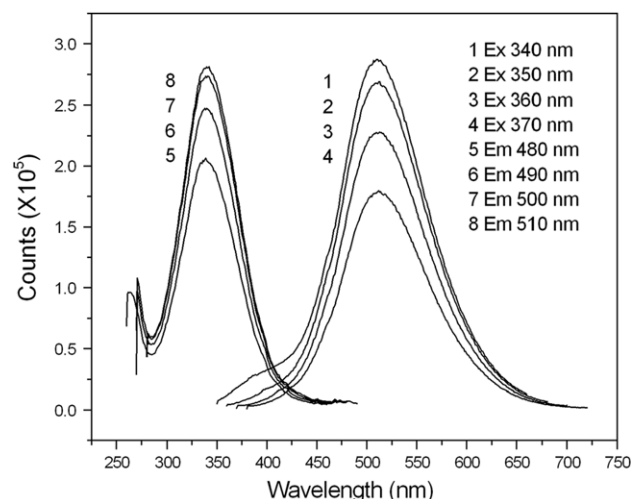


Figure 3. The steady-state fluorescence excitation and emission spectra of the dansyl-modified film in water.

3.3. Effect of nitroaromatics on the fluorescence emission of the functional film

Fluorescence quenching has proved an effective approach in chemical sensing and surface studies [7]. For example, Chen and Frank [29] examined the quenching effect of nitromethane on the fluorescence emission of pyrene-modified SAM film

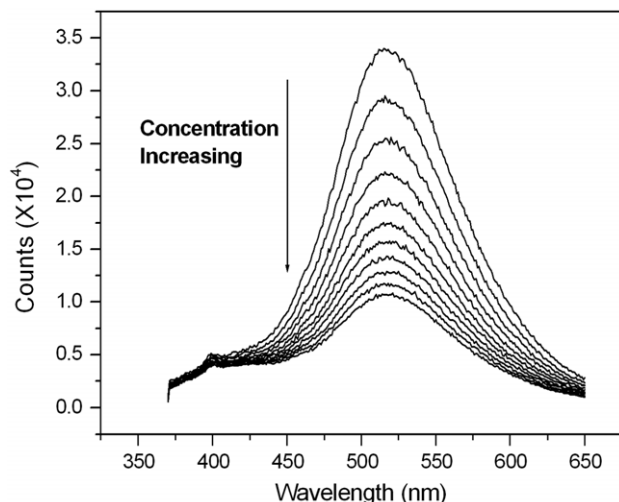


Figure 4. Fluorescence spectra of the dansyl-modified film in the presence of different concentrations of m-DNB.

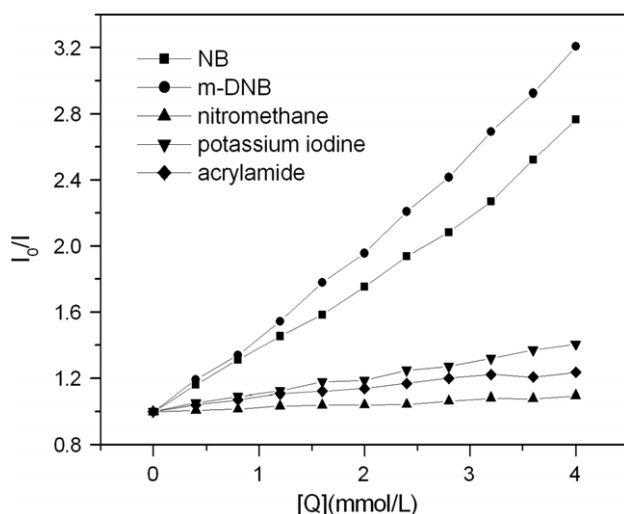


Figure 5. Responses of the dansyl-modified film to various quenchers in aqueous solutions.

to obtain information about the possible position of pyrene in the film. Reinhoudt and coworkers [30, 31] reported the sensing properties of several fluorophore-modified SAM films to metal ions by examining the quenching efficiencies of the films to different ions. Similarly, several dansyl-modified LB films were found sensitive to copper ions through fluorescence quenching studies [32]. In the present work, fluorescence quenching was expected to occur due to possible electron transfer from surface-bound dansyl to nitroaromatics. Figure 4 depicts the fluorescence emission spectra of the film as a function of the concentration of m-DNB. It shows clearly that the fluorescence emission of the film decreased significantly with increasing m-DNB concentration. Figure 5 shows the plots of the ratios of I_0/I against the concentration of each quencher, where I_0 and I stand for the fluorescence intensities of the film in the absence and presence of the quenchers, respectively. Referring to the plots in the figure, it can be seen that the quenching efficiencies of NB and m-DNB are much greater than those of other common quenchers, including

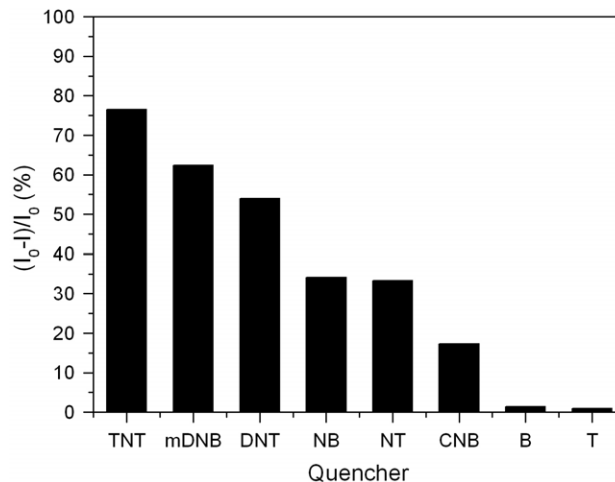


Figure 6. Responses of the dansyl-modified film to various nitroaromatics at the same concentration (2 mmol L^{-1}).

nitromethane, KI and acrylamide. This is quite similar to the findings in our previous work, where the dansyl-modified film responded selectively to nitrobenzene [23], indicating again that in the present work an intermediate phase may also be formed between the bulk solution and the solid substrate by the longer spacer, the fluorophore moieties and the solvent molecules within the spacer layer. Compared with nitromethane, KI and acrylamide, nitroaromatics are more compatible with the spacer layer due to similar hydrophobicity, and thereby they have more chances of entering the layer, staying in it and quenching the emission of the fluorophore located in it.

In order to examine the role of electron transfer in the quenching process of nitroaromatics to the fluorescence film, the response of the film to a series of nitroaromatics like TNT, m-DNB, DNT, NB, NT and CNB were investigated and as controls, the effects of some other non-nitroaromatics like benzene (B) and toluene (T) were also studied. The results are listed in figure 6. Referring to the figure, it can be seen that among the aromatics tested, (1) nitroaromatics exhibit much greater quenching efficiencies in the emission of the films than those of the aromatics with no electron-withdrawing groups; (2) generally speaking, the more the number of nitro-groups in the benzene ring of a nitroaromatic compound, the greater the quenching efficiency and (3) B and T did not quench the emission of the films at all. The results may be understood by considering the degree of the electron deficiency of the aromatics. And this is quite in agreement with the assumption that the quenching is believed to originate from electron transfer from the fluorophore to the aromatics. No doubt, more nitro-groups in the benzene ring of a nitroaromatic compound must make it have stronger affinity to the electron from the fluorophore moieties, and thereby shows greater quenching efficiency. This is also why TNT shows the highest quenching efficiency in the emission of the films. As for B and T, it is not surprising to find that the two compounds showed barely quenching effects in the emission of the films since both B and T are electron-rich compounds rather than electron-poor compounds, and there should be no electron transfer from the fluorophore, dansyl, to the compounds. Therefore, the electron transfer does play a crucial role in the quenching process.

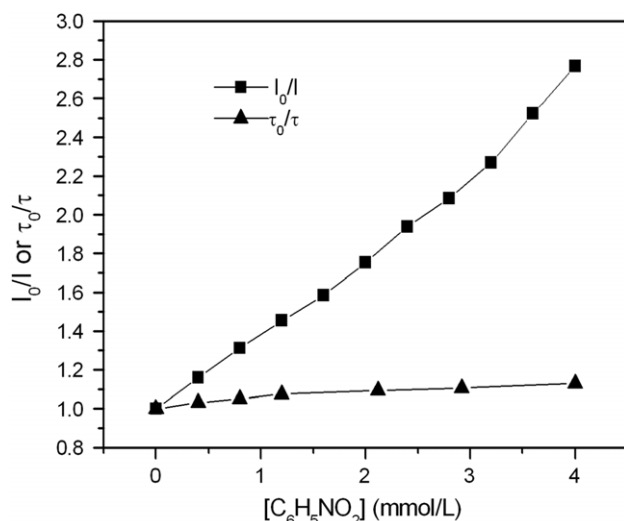


Figure 7. Quenching plots of the fluorescence intensity and fluorescence lifetime of the film in aqueous medium at room temperature.

Actually, the sensing of the film to nitroaromatics in aqueous phase is not only selective, but also sensitive. The detection limit of the film to TNT can be as low as 10^{-6} mol L⁻¹, which is a much better result than those reported in the literature for other fluorescent film sensors in solution [10, 11].

3.4. Fluorescence lifetime studies

The fluorescence lifetime studies were conducted to examine the quenching mechanism of the nitroaromatics to the film. As shown in figure 7, the lifetime ratio, τ_0/τ , is almost independent of the quencher concentration and nearly equals 1, where τ_0 and τ stand for the fluorescence lifetimes of the fluorophore in the absence and presence, respectively, of the quencher. This result indicates that the quenching process is static in nature, and reveals that a non-fluorescent complex is formed between the quencher and the surface-bound fluorophore. This is in support of the hypothesis that an electron-transfer process occurred from the electron-rich fluorophore, dansyl, to the electron-poor compounds, nitroaromatics, resulting in quenching the fluorescence emission of the dansyl-modified film.

3.5. Solvent effect studies

As discussed earlier, the low quenching efficiencies of those non-nitroaromatics tested in the film may be understood by considering the difficulties of molecular contact of the compounds with the surface-bound fluorophores. This is because of the poor compatibilities of these compounds with the spacer layer, within which the spacer may adopt relatively compact conformation in aqueous phase due to its hydrophobic nature as found in our previous work [23, 25]. This explanation is further supported by the results from solvent effect studies (cf figure 8). Referring to the figure, it is revealed that nitromethane, a common quencher, has greater quenching efficiency in the emission of the film in a more hydrophobic solvent, in support of the expectation that the spacer should adopt a relatively stretch conformation in a hydrophobic

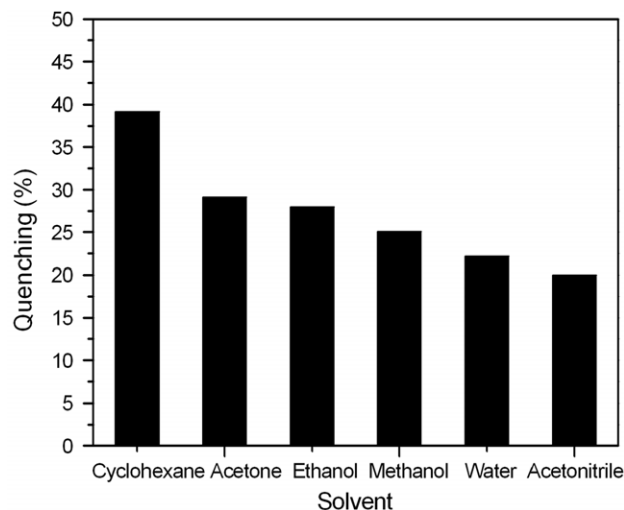


Figure 8. The quenching efficiency of nitromethane to the dansyl-modified film in different solvents.

solvent. As a result, this stretch conformation provided nitromethane more chances to collide with the fluorophore moieties, resulting in greater quenching efficiency in more hydrophobic solvents. Therefore, it may be concluded that the conformation adopted by the spacer also plays a crucial role in the performance of the sensing films.

3.6. Reversibility of the film to nitroaromatics

To be a good sensor, or to be used practically, the response of a sensor to a given analyte must be reversible [32]. Therefore, m-DNB was chosen as a test analyte to examine the reversibility of the response of the present film to it in aqueous phase. The fluorescence intensity of the film in water was recorded and then a proper amount of m-DNB solution in ethanol was added. Three minutes later, the fluorescence intensity of the film was measured and thereafter every three minutes for five times. After the measurements, the film was washed with ethanol several times and then with pure water. Then, the process was repeated for another three cycles, but with different m-DNB concentrations. In this way, the results shown in figure 9 were obtained. Clearly, the response of the film to the quencher at a higher concentration can also be reversible and promises the film reversible detecting nitroaromatics at even lower concentration. In addition, the response is also fast, and a quenching equilibrium can be reached within five minutes at room temperature.

It is to be noted that proper preservation of the film in ethanol at room temperature for half a year has little effect upon the performance of the film. The high selectivity, reversibility, relatively short response time, and long stability may make this film a proper candidate for determining nitroaromatics in aqueous environment.

4. Conclusion

A novel fluorescent sensing film for nitroaromatics was developed by covalently attaching a small fluorophore, dansyl, onto glass slide surface via a relatively long, flexible spacer. Fluorescence quenching studies showed that the film is

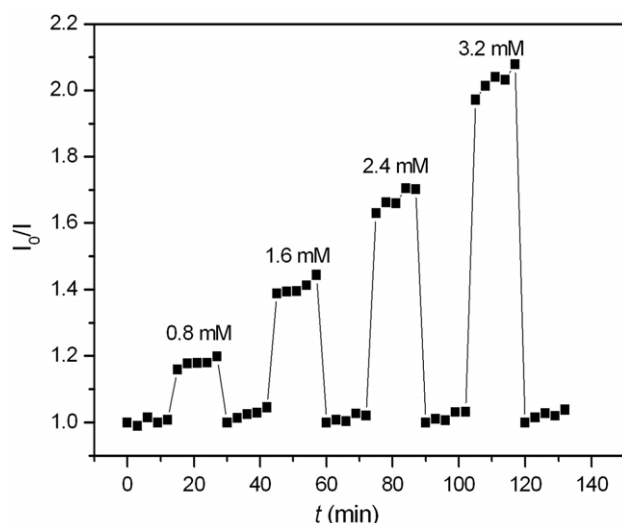


Figure 9. Reversibility of the dansyl-modified film responding to m-DNB in water.

sensitive and selective to the presence of nitroaromatics due to their strong electron-withdrawing ability. The presence of B,T, nitromethane, acrylamide and KI had little effect upon the emission of the film when it was tested in aqueous solution. It has been revealed that the structure and properties of the spacer connecting the sensing fluorophore and the substrate play a crucial rule, *via* the spacer layer screening effect, in the performance of the sensing film. Therefore, it may be expected that even better sensing films can be developed in the future by simply varying the structure, the property and the density of the spacer. Furthermore, alteration of the structures and properties of the microenvironment of a sensing fluorophore chemically immobilized on a substrate surface may also affect the performance of the film greatly. The relevant studies are in progress.

Acknowledgments

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