

Selectivity via insertion: Detection of dicarboxylic acids in water by a new film chemosensor with enhanced properties

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Abstract

A novel fluorescence film sensor was designed and prepared to improve the performance of the film sensors reported recently for dicarboxylic acids. The reported sensors suffered from slow response and low sensitivity to the analytes. Simple elongation of the spacer by using 1,4-diaminobutane instead of 1,2-diaminoethane or 1,3-diaminopropane improved the performances of the film sensors greatly. The response time was reduced from tens of minutes, or even hundreds of minutes to less than 10 min, and the sensitivity was improved from more than 10 mM to tens of micro-molars. Similar to the reported films, the new film also shows combined monomer and excimer emission of pyrene (Py) both in wet and dry states, and both the emissions in the monomer and excimer regions increases along with addition of dicarboxylic acids. The excimer formed in the present film, however, mainly adopts, especially in aqueous phase, sandwich-like structure. The differences in the photophysical behavior and the improvement in the sensing performance mentioned above have been attributed to the increase in the length of the spacer, which makes the spacer in the present film more flexible and gives the sensing molecule more chance to form perfect excimers. Furthermore, the response of the film to dicarboxylic acids is well reversible.

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Keywords: Fluorescence; Film sensor; Dicarboxylic acids; Pyrene

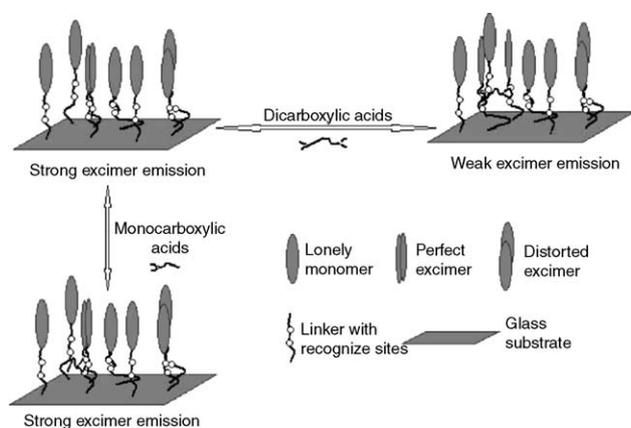
1. Introduction

Compared with molecular sensors used in solution, fluorescence film sensors have no contamination to the analyte systems, are easy to be made into devices and can be reused. Recently, these kinds of studies have attracted increasing attention. For example, Soumillion and co-workers [1] designed a film sensor for pH by chemical binding of anthracene onto a glass plate surface. Crego-Calama and Reinhoudt [2] prepared two film sensors for Pb^{2+} via immobilization of dansyl or coumarin onto a glass plate surface. van der Veen et al. [3] prepared a sensing film for Na^+ by chemical binding of Py and calix [4] arene onto a glass plate surface. Bandyopadhyay et al. [4] designed a fluorescent film sensor with high selectivity to K^+ . The selectivity is reached

by introduction of crown-ether, which functions as the host of the guest, on the substrate surface. Recently, two fluorescent sensing films for Cu^{2+} were reported by Leblanc and co-workers [5]. They synthesized two surfactant molecules with unique head structures, which can bind the cation selectively. The molecules were assembled into films by employing LB technique.

It is to be noted, however, that unlike metal ions, film sensors for organic compounds and anions are less well developed as a result of the difficulty in obtaining appropriate affinity and selectivity in aqueous phase [6]. As part of ongoing project directed toward preparation of fluorescent film sensors with pyrene as a sensing element, we postulated that introduction of a molecular recognition mechanism into the design of sensors can impart a higher affinity and a greater selectivity to a given sensor relating to a similar non-recognition system. The promise was initially verified using a film sensor that contains β -cyclodextrin as a host for

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Scheme 1. General film sensor for dicarboxylic acids design.

nitromethane [7]. More recently, we described a new design for sensing dicarboxylic acids, which are used as energy sources to fuel nitrogen fixation in nature. Dicarboxylic acids are commonly found in liquid fertilizers and water-soluble organic compounds (WSOC) in atmospheric aerosols [8,9]. Their identification and determination are commonly conducted by an esterification gas chromatography technique, which is quite complicated and time consuming [8,10].

The film sensors were designed by covalent binding of Py on a glass plate surface via a spacer containing 1,2-diaminoethane or 1,3-diaminopropane in order to introduce imino group into the spacer [11,12]. It was anticipated that introduction of the functional group and the hydroxyl group next to the imino group would make the film recognize dicarboxylic acids via hydrogen bonding. Insertion of dicarboxylic acids into the space between neighboring spacers would alter the distribution of the fluorophore on the surface and thereby changing the profiles and intensities of the fluorescence emission of the films (Scheme 1).

Study of the sensing properties of the films showed that the fluorescence emission of the films are, as that expected, sensitive to the presence of dicarboxylic acids, such as ethanedioic acid, malonic acid, succinic acid, etc. Existence of monocarboxylic acids has little effect upon the sensing properties of the film to dicarboxylic acids. The response of the films, however, to dicarboxylic acids is too slow, and the time needed for establishment of a new equilibrium after each measurement is too long, restricting the applicability of films. As for the films reported, the time needed for establishment of a new equilibrium after each addition of ethanedioic acid, malonic acid and succinic acid, are 80, 210 and 540 min, respectively, for the film with spacer containing 1,2-diaminoethane [11] and 50, 160 and 240 min, respectively, for the film with spacer containing 1,3-diaminopropane [12]. These results revealed that the length of the spacer is crucial for the sensing behavior of the films. Accordingly, 1,4-diaminobutane was employed to immobilize Py on a glass plate surface via a similar method as that reported earlier.

2. Experimental

2.1. Reagents and instruments

Pysulfonyl chloride (PSC) was synthesized in our lab by adopting a literature method [13]. 1,4-Diaminobutane (DAB, Acros, 99%) and 3-glycidoxypropyltrimethoxysilthoxysilane (GPTS, Acros, 97%) were used directly without further purification. Dichloromethane, chloroform and toluene were washed with concentrated sulfuric acid and then distilled. Diethyl ether was washed with ferrous sulfate solution to remove peroxide and then distilled. Other reagents were of analytical grade at least. Water used in this work was de-ionized and then double distilled.

Fluorescence measurements were performed at room temperature on a Perkin-Elmer LS-50B fluorescence/phosphorescence/luminescence spectrometer and a time-correlated single photon counting Edinburgh FLS 920 fluorescence spectrometer with a front-face method. Analyses of C, H and N were conducted on a GmbH VarioEL CHN elemental analyzer. Pressed KBr disks for the powder samples were used for the transmission infrared spectroscopy measurements, and their spectra were obtained with a Bruker Equinox 55 FTIR spectrometer. A Bruker AV300 NMR spectrometer was used to measure the ^1H NMR spectra of the samples. The advancing contact angles of the films were measured by using a JY-82 contact angle goniometer.

2.2. Synthesis of *N*-1-pysulfonyl-diaminobutane (PSDAB)

The previously reported PSC was used as the starting material for the synthesis of PSDAB. Under a N_2 atmosphere, PSC (0.15 g, 5×10^{-4} mol) was dissolved in 50 ml CHCl_3 and added drop-wise to 50 ml CHCl_3 dissolved 0.65 ml DAB (5×10^{-3} mol) with stirring at 0°C . The system was further stirred for another 1 h after addition of the PSC solution. The final light yellow solution was washed with 150 ml water and 100 ml 5% NaCl solution for two times, respectively. The CHCl_3 layer was separated and dried by filtering through a pad of anhydrous MgSO_4 . The resulting PSDAB solution was kept and used directly in the following surface reactions.

For characterization, PSDAB was isolated from the above solution in its salt form by acidification of the solution with 0.1 mol l^{-1} HCl in diethyl ether. The light yellow precipitate was filtered and extracted with dichloromethane in a Soxhlet extractor for several hours, and then vacuum-dried at room temperature. Anal. Calcd. for the salt of PSDAB $\text{C}_{20}\text{H}_{21}\text{N}_2\text{SO}_2\text{Cl}$ (%): C, 61.77; H, 5.40; N, 7.21. Found: C, 61.94; H, 5.67; N, 7.50. ^1H NMR (DMSO-*d*): δ (ppm) 9.0 (1H), 8.2–8.6 (8H), 3.0 (4H), 1.7 (4H). IR (cm^{-1}): 2943 (m), 1587 (m), 1483 (m), 1293 (s), 1069 (s), 847 (s), 757 (m), 715 (m).

2.3. Preparation of the film sensor

A clean glass plate ($\sim 0.9 \text{ cm} \times 2.5 \text{ cm}$) was treated in a “piranha solution” (3:7, v/v, 30% H_2O_2 :98% H_2SO_4) at 98°C for 1 h, then rinsed thoroughly with plenty of water, and finally dried at 100°C in a dust-free oven for 1 h. The activated glass plate was immersed in a warm (50°C) toluene solution of GPTS (0.6%, v/v), containing a trace amount of water, for 12 h. The plate was respectively washed with toluene and trichloromethane for tens of times to ensure that it was free of unbound GPTS. The trialkoxysilane-treated glass plate was put into the PSDAB solution in CHCl_3 at 61°C for 8 h. To remove unreacted PSDAB, the plate was rinsed with plenty of CHCl_3 , then extracted with CH_2Cl_2 in a Soxhlex extractor for 5 h and finally it was rinsed with CH_2Cl_2 , acetone and water, respectively. The reaction scheme is similar to that reported earlier [11,12].

3. Results and discussion

3.1. Functionalization of the glass plate surface

The value of the advancing contact angle of a surface and water directly reflects how hydrophilic or hydrophobic of the surface is. It is no doubt that modification of a substrate surface must alter its property more or less, and thereby changing the character value of the surface. Based upon this consideration, the contact angle of the present glass plate was measured after each modification. The results are shown in Table 1. It can be seen that the contact angle decreased from 26° to 18° after activation with the “piranha solution”, increased from 18° to 50° after treatment with GPTS, and further increased to 52° after final reaction with PSDAB. These results are in consistent with the expectation from the chemical composition of the surface, of which the composition changed from less hydroxyl group, more hydroxyl group, epoxide group and Py along with the treatment [11,12].

Successful coupling of Py on the plate surface is further confirmed by FTIR spectroscopy. Reference to Fig. 1, it can be seen that the ultra-strong absorption of the Si–O bond near 1000 cm^{-1} in the FTIR spectrum of the glass plate (Fig. 1, bottom) makes the absorptions of other bonds much weaker. Treatment of the surface with GPTS made the absorption both red shifted (from 976 to 1037 cm^{-1}) and relatively weakened

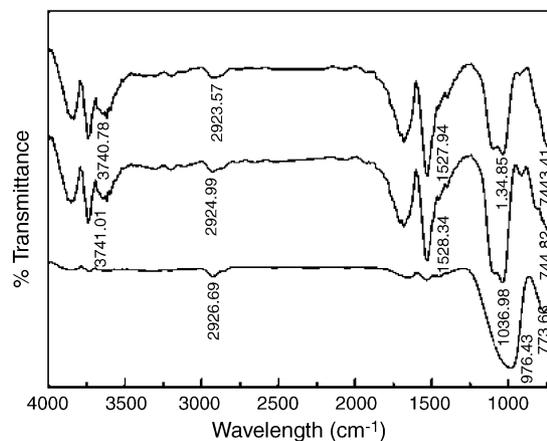


Fig. 1. FTIR spectra of the glass plates of various surface compositions. Bottom: the activated glass plate with hydroxyl surface; middle: the plate with epoxide surface; top: the plate with Py surface.

(Fig. 1, middle). Reaction of the plate of epoxide functionality with PSDAB decreased the relative intensity of the absorption of the Si–O bond even further (Fig. 1, top), and in fact made its intensity even weaker than the neighboring absorptions. Leaking of Py from the plate surface in aqueous medium was monitored by measuring the fluorescence emission of the plate in water and that of the medium as functions of time at 380 with 350 nm as an excitation wavelength. It was demonstrated that the emission intensity and emission profile of the plate, the control and the medium hardly changed with time, indicating that the sensing element had been successfully coupled on the substrate surface via chemical bonding.

3.2. Photophysical behavior of Py immobilized on the substrate surface

Fig. 2a and b show the excitation and emission spectra of the functional film in wet state (aqueous medium) and at dry state, respectively. Similar to those of the film sensors reported earlier, the emission spectra of the present film in aqueous phase (Fig. 2a) are also characterized by two sharp peaks and one broad structure-less band. The two sharp peaks (380 and 400 nm) could be attributed to the monomer emission, and the broad one (500 nm) was recognized as the excimer emission of the fluorophore. It may be interesting to note that unlike the emission of Py in solution, the monomer emission of it in immobilized state lacks fine structures, upon which “Pyrene Scale” [14,15] is based. The differences in the profile of the monomer emission may be originated from the different motion behavior of Py in the two states. In immobilized state, the orientation, rotation and other motions of Py must be relatively restricted if compared with those in solution state. Similar observations have been reported in references [16,17]. Immobilization, however, has little effect upon excimer emission of Py. Further examination of the figure, it can be found that the monomer emission and the excimer emission are well resolved and the excimer emission situates at 490 nm and is quite symmetrical, indicating

Table 1
Advancing contact angles (θ) of various glass plate surfaces and water

Glass plates ^a	θ ($^\circ$)
(1)	25.8 ± 1.4
(2)	18.0 ± 0.1
(3)	49.8 ± 2.1
(4)	52.2 ± 1.1

^a (1) stands for the original clean glass plate, (2) the activated glass plate with hydroxyl surface, (3) the glass plate with epoxide surface and (4) the plate with Py surface.

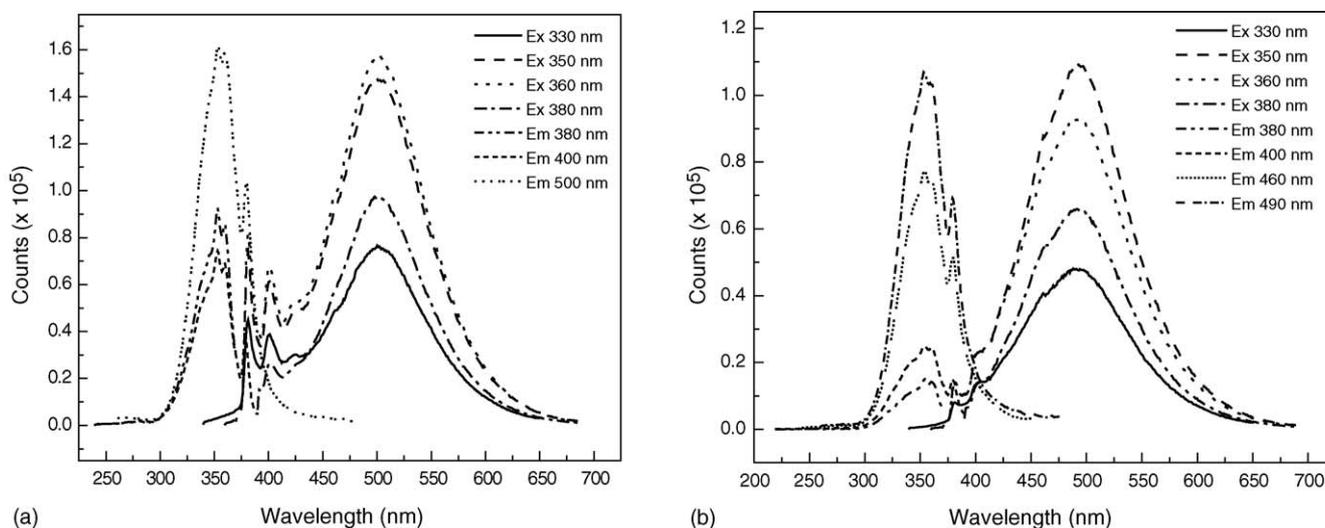


Fig. 2. Excitation and emission spectra of the functionalized film in aqueous medium (a) and at dry state (b).

that the excimer adopts a perfect sandwich-like structure. In contrast, the emission of the film at dry state is dominated by excimer emission. The profile of this emission, however, is very similar to that of the film in wet state, suggesting that most of the excimers in dry state adopt also nearly perfect sandwich-like structure. This finding is quite different from those observed in the emissions of the former films with spacers containing 1,2-diaminoethane or 1,3-diaminopropane, of which the excimer emissions are distorted, and situate at shorter wavelengths [11,12]. The differences may be understood by considering the different flexibility of the spacer in the three films. It is not difficult to imagine that the spacer containing 1,4-diaminobutane is a little bit longer and more flexible than those containing 1,2-diaminoethane or 1,3-diaminopropane, and thereby, the motion of Pys on the present film is less restricted, and should have more chance to form perfect excimers. As for the difference between the profiles of the emission spectrum of the film in wet state and that in dry state, the hydrophilic nature of the long flexible spacer makes the sensing element, Py, relatively free when the film is immersed in water, and thereby form “standard excimer” easily. On the contrary, however, the sensing element, Py, is hard to motion when the film is left at dry state, and would form more excimer structures due to association between aromatic rings and claps of the spacers. It is natural to expect that more distorted excimer structures may be formed at this case. Compared with that of the emission of “standard excimer”, the emission of excimer with distorted structure should blue shift. In fact, compared with the profile of the excimer emission of the film in wet state, the excimer emission of the film at dry state is a little bit broader in its left hand side. The dependence of excimer emission on the regularity of its structure was also reported by a number of groups in the studies of Py-labeled macromolecular systems [17–19].

Examination of Fig. 2a and b, it can be revealed that change in the excitation wavelength or analysis wavelength has little effect upon the position and profile of fluorescence emis-

sion and excitation spectra of the film, indicating that Pys immobilized on the substrate surface are almost uniformly distributed. This tentative conclusion is further supported by time-resolved emission spectroscopy (TRES) measurements.

The profiles of the TRES spectra of the film in aqueous medium and at dry state with time-gates being set at 0–5, 6–10, 11–15, 16–35, 41–81 and 101–200 ns, respectively, are shown in Fig. 3a and b, respectively. Time 0 corresponds to the time at which the excitation pulse reached its maximum intensity. Interrogation of the excimer formation of Pys immobilized on the glass plate surface via TRES measurement reveals that for the film in aqueous medium, contribution from the monomer emission to the spectrum decreases dramatically and the emission is gradually dominated by the excimer emission along with the time-gate moves away from the excitation pulse, indicating that most Pys immobilized on the substrate are in their lonely monomer state and that the excimer is mainly dynamic in nature (dynamic excimer) [19]. Although it is not as significant as those found in the TRES results for the films with spacers containing 1,2-diaminoethane or 1,3-diaminopropane, contribution of excimer emission to the early time-gate spectrum of the present film is still obvious, suggesting that some excimers may originate from direct excitation of the ground-state dimer (static excimer) [19]. It might be worthwhile to mention that the position of the excimer emission of the present film in wet state does not change very much along with the time-gate moving to longer time. This observation reveals that the Pys on the present film are more mobile than those on the previous films and have more chance to form perfect excimers. This is in support of the tentative conclusion from steady-state fluorescence studies.

The difference between the profiles shown in Fig. 3a and b is obvious. In the latter case (dry state), the profile of the early time-gate spectrum is dominated by a broad structureless band, which may be attributed to the emission of partially overlapped excimer [20]. Further interrogation of the TRES

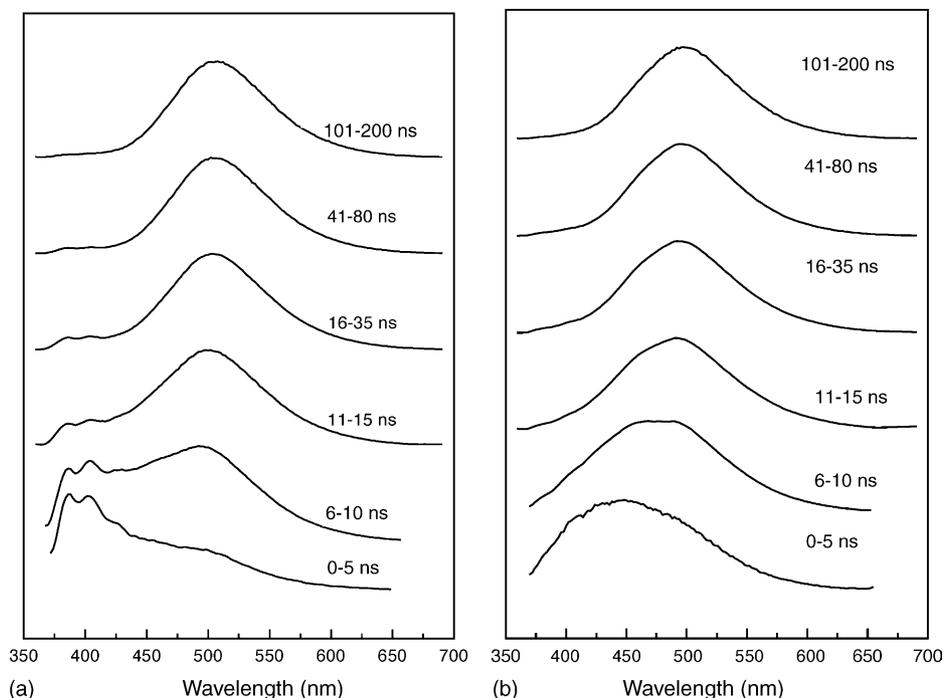
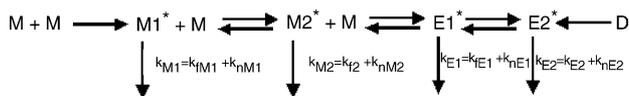


Fig. 3. Time-resolved emission spectra of the functional film in aqueous (a) medium and at dry (b) state. The time-gates are shown in the figure.

spectra shown in Fig. 3b, it should have no difficulty to conclude that the partially overlapped excimer has shorter lifetime and it is one of the main contributors for the middle time-gate spectra (6–10, 11–15 and 16–35 ns). The dramatic appearance of the partially overlapped excimer in dry state may be a result of collapse of the long flexible spacer due to lack of extension condition, such as miscible solvent. It can be imaged that collapse of the spacer restricts the motion and reorientation of the immobilized Py, and thereby the fluorophore has less chance to form perfect excimers. Based upon these discussions and inspiration by literature studies, a model proposed earlier [11,12] can be employed to describe the photophysical processes occurring at the substrate surface of the present film (Scheme 2).

The model is further supported by the results from fluorescence lifetime measurements. Table 2 lists the decay data of the film, at various analysis wavelengths, resultant upon exponential analysis of the general form:

$$i(t) = A + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) + A_4 \exp\left(-\frac{t}{\tau_4}\right) \quad (1)$$



Scheme 2. A proposed model describing the photophysical processes occurring on the functionalized glass plate surface.

where t is the time after a light pulse, $i(t)$ the intensity of the emission at time t and τ the lifetime of the corresponding species. The lifetimes from the fit are 0.7, 6.0, 23.9 and 59.0 ns, respectively, which have been tentatively attributed to, according to the model and the TRES and steady-state emission studies, a quenched excited monomer (M_1^*), an excited monomer (M_2^*), a distorted excimer (E_1^*) and a perfect excimer (E_2^*), respectively. References to the table, it can be found that in most of the cases, four-exponential function is inadequate for fitting the decays (greater χ^2 values). This is not surprising because only a limited number of possible fluorophore situations have been taken into account in the evaluation of the time-resolved kinetics. For example, for partially overlapped excimers, a distribution of overlap conformations might be present and even for excimers with specific conformation, their microenvironments might be different. Similarly, for isolated monomers, they could either be surrounded by a hydrophobic microenvironment or exposed to a hydrophilic microenvironment because some of the sensing molecules may exist on the surface of spacer layer, and

Table 2
Four exponential fits to the decay of the functionalized glass plate in aqueous medium monitored at various emission wavelengths with an excitation wavelength of 350 nm

λ_{em} (nm)	A_1 (%)	A_2 (%)	A_3 (%)	A_4 (%)	χ^2
380	61.57	25.02	12.79	0.62	2.05
460	11.73	29.65	43.60	15.02	2.16
500	4.09	20.29	55.68	19.95	1.68
540	3.03	18.68	58.02	20.27	1.81
600	2.10	22.92	57.61	17.37	1.08

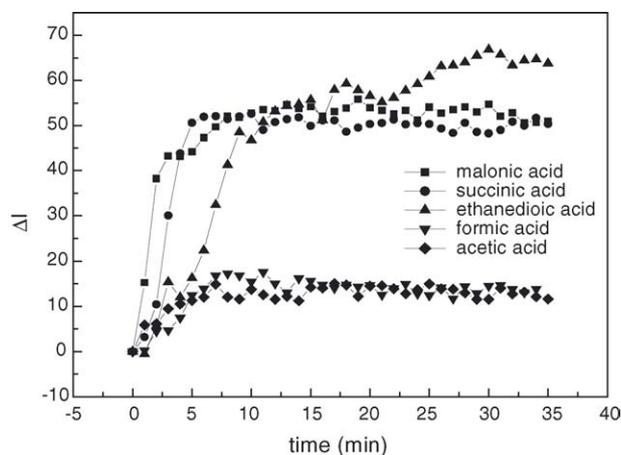


Fig. 4. Excimer emission as a function of time in the presence of dicarboxylic acids or mono-carboxylic acids. ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 350/500$ nm).

some of them may exist within the layer as revealed by Monte Carlo simulations [21,22]. In summary, analysis of the lifetime data revealed that the existing states of the sensing molecules immobilized on the plate surface are much more complex than that described by the model. Even so, however, this result is in support of the conclusion that the Pys on the present film are quite mobile and have more chance to form perfect excimers.

3.3. Sensing properties to dicarboxylic acids

As expected, the fluorescence emission of present film is sensitive to the presence of dicarboxylic acids, and both the monomer emission and the excimer emission increase along with increasing the concentration of the tested dicarboxylic acids. Explanation of the observation may be obtained by considering that insertion of dicarboxylic acid between a ground state dimer and/or excited state dimer (excimer) would increase the surface density of the monomer, and thereby increase the monomer emission. However, insertion of the acid into the aggregated fluorophores would also decrease the number of Py “clusters” on the film surface, and make its distribution more homogeneous. In this way, “self-quenching” or “inner-filtering” effect [23,24] may be diminished and results in increase in the excimer emission. This explanation is further supported by the results from studies of mono-carboxylic acid effect upon the emission of the film (cf. Fig. 4). From the figure, it can be seen that introduction of formic acid or acetic acid has much smaller effect upon the excimer emission of the film, even though the sensitization is significant. This result demonstrates that insertion of the dicarboxylic acids into the space between neighboring spacers is the main factor affecting the distribution of the sensing molecules on the film surface.

It is a rather surprising result that a small increase in the length of the chain of di-amine causes a very sharp

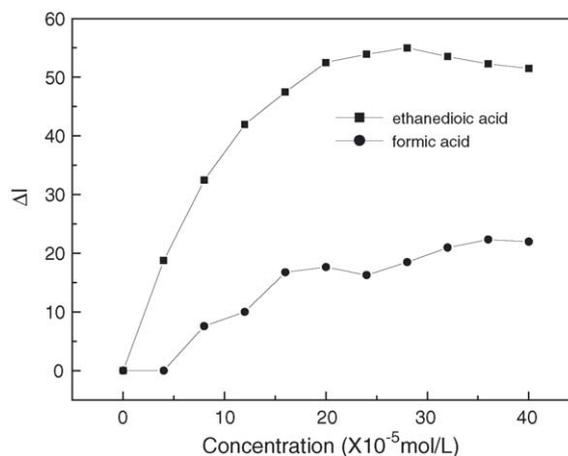


Fig. 5. Plot of excimer emission intensity of the film sensor in aqueous medium as a function of each acid concentration. ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 350/500$ nm).

decrease in the response time of the films to dicarboxylic acids. Fig. 4 shows the changes of the excimer emission of the film as functions of time in the presence of various organic acids. Compared with the response times of the previous films with similar design, it can be seen that for the dicarboxylic acid systems, the excimer emission reached equilibrium within 10 min, indicating that the response of the functional films to the analytes are greatly improved. The sensitivity of the film to the analytes is also improved significantly. It has been reported that for the film with spacers containing 1,2-diaminoethane, its emission increases only when the concentration of ethanedioic acid exceeds 14 mmol l^{-1} . As far as the new film is concerned, however, as little as 0.05 mmol l^{-1} of ethanedioic acid can cause a significant increase in the excimer emission (cf. Fig. 5).

It has been demonstrated that the intensity of the excimer emission of the film depends upon the concentration of a dicarboxylic acid, indicating that the film might be used as a sensing material for the analytes provided the response is reversible. To verify the reversibility, the film was immersed in super-pure water, and the emission intensity at 500 nm was measured as a function of time. After the measurements, a proper amount of ethanedioic acid was added (final concentration, 0.2 mmol l^{-1}), and the emission was measured as a function of time again. Both the monomer emission and excimer emission of the film could be fully restored by washing the film with super-pure water after measurement of acid solution. The whole measurements were repeated for seven times, and the results are shown in Fig. 6. It can be seen that the response of the film to dicarboxylic acid is reversible, especially after three cycles. Furthermore, the film is stable either at dry state or in an aqueous phase (immersed in pure water). It must be, however, activated before use if it is kept at dry state. The activation can be conducted by simply immersing the film in super-pure water for more than 24 h.

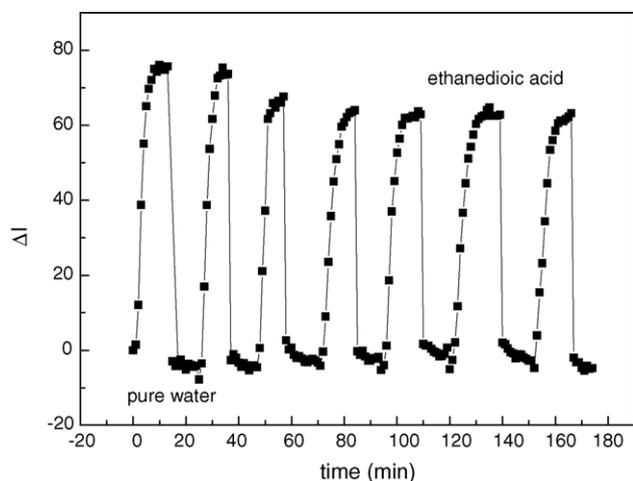


Fig. 6. Reversibility of the sensing property of the film to ethanedioic acid ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 353/500 \text{ nm}$).

4. Conclusions

In the present work, we designed and fabricated a new film sensor with enhanced sensing properties to dicarboxylic acids. Steady-state and time-resolved fluorescence studies demonstrated that the emission of the Py functionalized film in both dry and wet state are characterized by the monomer emission and excimer emission of the fluorophore. However, the excimer emission is complicated due to presence of both “sandwich-like” structures and partially overlapped structures. In this paper, we compare the photophysical behaviors and sensing properties of the new film sensor with those of the reported dicarboxylic acids sensors. Similar sensing behaviors were obtained, the intensity of the monomer and excimer emission increase along with introduction of dicarboxylic acids. As anticipated, the time needed for establishment of a new equilibrium after adding dicarboxylic acids has decreased significantly, and the sensitivity has been improved. Comparing with the performances of the films with similar structures reported earlier, it is concluded that increases in the length and flexibility of the spacer are responsible for the enhanced performance of the present film. In addition, sensing of the film to dicarboxylic acids is reversible.

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