

Monomolecular Layers of Pyrene as a Sensor to Dicarboxylic Acids

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A novel photoinduced luminescence film has been prepared by immobilizing pyrene on a quartz plate surface via a flexible long spacer. The film shows combined monomer and excimer emission of pyrene both in wet and dry states, and the excimer may be formed mainly by direct excitation of ground-state dimers and/or monomers in aggregates. Classical Birks' scheme plays a little role in the formation of the excimers. The emission of the film is sensitive to the presence of dicarboxylic acids, including ethanedioic acid, malonic acid, succinic acid, etc. The emission in the monomer and excimer region increases with addition of the acids. The time needed for the emission to reach equilibrium depends on the nature of the acids. It has been shown that the longer the chains of the acids, the more time is needed. This observation is explained by considering the conformational reorganization of the immobilized pyrene due to insertion of the dicarboxylic acids into the space between neighboring spacers. Experimental results from similar studies using formic acid and acetic acid are in support of this explanation. Furthermore, the response of the film to dicarboxylic acids is reversible.

Introduction

In recent years, monomolecular assemblies on solid surfaces have attracted growing attention due to their potential application in creation of novel electronic, photoelectronic, and sensing films.^{1–4} Chemical immobilization of small molecules onto the substrate surface is one of the important approaches to prepare monomolecular assemblies⁵ and provides a convenient way to produce surfaces with specific chemical functionalities that allow the precise turning of surface properties.^{5,6} The properties of the modified surfaces depend on a number of factors, including, at least, the nature of the small molecules, the properties of the substrate surface, the structure of the spacer, which links the small molecule and the substrate, and the density of the small molecules on the substrate surface. Clearly, a variety of functional films with ideal properties may be prepared by careful selection and combination of the small molecules, the substrate, and the spacer.

On the basis of this methodology, a number of functional films with pyrene (Py) as a fluorescence-active molecule have been prepared and studied as sensing materials in our laboratory.^{7–11} It has been demonstrated that the intensity and/or the profile of the fluorescence emission of the films are sensitive to the purity of water⁸ and the presence of nitrite in aqueous phase⁹ and nitromethane in methanol, ethanol, or water.¹⁰ Simple embedding of Py into a chitosan (CS) film results in a medium polarity sensitive film.⁷ It is to be noted that all the sensing films reported from our laboratory have been designed with a short or even no spacer, and the sensing principles of the films are based on the hydrophobic aggregation of the sensing element, Py, and its dependence on the presence of analytes. Therefore, it should be more practical to introduce recognition sites or structures on the substrate surface or into the monomolecular layer in terms of actual device implementation.

For selective sensing of dicarboxylic acids, imino units were intentionally introduced into a spacer, via which Py was immobilized on a substrate surface. Imino units were chosen due to their character to form hydrogen bonds with the carboxyhydroxy group.¹² Dicarboxylic acids are commonly found in liquid fertilizers and water-soluble organic compounds (WSOC) in atmospheric aerosols.^{13,14} Their identification and determination are commonly conducted by an esterification–gas chromatography technique, which is quite complicated and time consuming.^{13,15} It was expected that the specific interaction of the imino group with the carboxyhydroxy group would result in insertion of a dicarboxylic acid into the spacer layer, altering the spatial distribution of the sensing element, Py. This variation must be accompanied by a profile change in the fluorescence emission spectrum of the sensing element since the emission is characterized by both monomer emission and excimer emission, and the relative intensities of the two emissions are sensing element distribution dependent. On the basis of this consideration, the quartz plate was selected as a substrate due to its resistance to common solvents and ease to be functionalized. Py was chosen again due to similar reasons as described before,⁸ and a long, flexible spacer containing an imino structure was designed via combination of ethylenediamine and 3-glycidoxypropyltrimethoxysilane. It is expected that with this designation a novel film of selective responses to dicarboxylic acids may be obtained. This article reports the results.

Experimental Section

Reagents. Py (Acros, 96%) was recrystallized from an ethanolic solution and then extracted with Soxhlet extractor by ethanol. 3-Glycidoxypropyltrimethoxysilane (GPTS, Acros, 97%) was used directly without further purification. Ethylenediamine (EDA) was washed with KOH solution and then distilled. *N,N*-Dimethylformamide was freshly distilled from calcium hydride before use. Dichloromethane, trichloromethane, and toluene were washed with concentrated sulfuric acid and

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then distilled. Diethyl ether was washed with ferrous sulfate solution to remove peroxide and then distilled. Thionyl chloride was rectified three times in the presence of pure sulfur (sublimed grade). Other reagents were of analytical grade at least. Water used in this work was deionized and then double distilled.

Instrumentation. 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 Perkin-Elmer 2400 CHN elemental analyzer. Pressed KBr disks for all the powder samples were used for the transmission infrared spectroscopy measurements, and their FTIR spectra were obtained with a Bio-Rad FTIR spectrometer. The reflection-absorption infrared spectroscopy measurements of the films were conducted on a Nicolet Nexus 670 FTIR spectrometer, and their Raman spectra were recorded by using a Nicolet Almega laser scattering Raman spectrometer. A Bruker AM400 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.

Synthesis of *N*-1-Pyrenesulfonyl-ethylenediamine (PSE-DA). A literature method¹⁶ was employed for the preparation of pyrenesulfonyl chloride (PSC). The coarse PSC was purified by chromatography on silica gel with dichloromethane as eluent, $R_f = 0.85$. Anal. Calcd for PSC $\text{C}_{16}\text{H}_9\text{SO}_2\text{Cl}$: C, 63.89; H, 3.00. Found: C, 63.60; H, 2.99. Mp of the purified PSC is 172–174 °C (not corrected, literature value 172 °C¹⁶). ^1H NMR (CHCl_3 -*d*): δ (ppm) 9.1 (1H), 8.8 (1H), 8.1–8.5 (7H) (detailed ^1H NMR spectra are given in the Supporting Information). IR (cm^{-1}): 1364 (s), 1170 (s), 845 (s), 819 (m), 753 (m). PSEDA was prepared by adopting a modified literature method.¹⁶ Here, CHCl_3 was employed as a solvent to replace CH_2Cl_2 in order to increase the successive reaction temperature. The resulting solution was kept as a PSEDA solution and used directly in the following surface reactions.

For characterization, PSEDA was isolated from the above solution in its salt form by acidification of the solution with 0.1 M HCl in diethyl ether. The fine white precipitate was filtered and dried at room temperature. Anal. Calcd for the salt of PSEDA $\text{C}_{18}\text{H}_{17}\text{N}_2\text{SO}_2\text{Cl}$: C, 59.92; H, 4.72; N, 7.77. Found: C, 59.22; H, 4.74; N, 7.42. ^1H NMR ($\text{DMSO}-d_6$): δ (ppm) 9.0 (1H), 8.2–8.6 (8H), 3.0 (2H), 2.7 (2H). IR (cm^{-1}): 3043 (m), 1590 (m), 1497 (m), 1326 (s), 1160 (s), 851 (s), 758 (m), 716 (m).

Activation and Silanization of the Quartz Plate Surface. A clean quartz plate ($\sim 0.9\text{ cm} \times 2.5\text{ cm}$) was treated in a “piranha solution”¹⁷ (7/3, 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 quartz plate was immersed in a warm (50 °C) toluene solution of GPTS (0.6%, V/V), containing a trace of water, for 12 h. The plate was washed with toluene and trichloromethane for tens of times, respectively, to ensure that it was free of unbound GPTS on the plate surface.

Chemical Coupling of Py on the Plate Surface. The trialkoxysilane-treated quartz plate was macerated into a PSEDA solution in CHCl_3 (cf. synthesis of *N*-1-pyrenesulfonyl-ethylenediamine) at 61 °C for 12 h. To remove unreacted PSEDA, the plate was rinsed with plenty of CHCl_3 and then extracted with CH_2Cl_2 in a Soxhlex extractor for 5 h. The plate was further rinsed with CH_2Cl_2 , acetone, and water, respectively, after the extraction.

TABLE 1: Advancing Contact Angles (θ) of Various Quartz Plate Surfaces and Water

quartz plates ^a	1	2	3	4
θ (deg)	41.4 ± 1.2	21.1 ± 1.4	55.3 ± 1.6	56.8 ± 1.1

^a (1) stands for the original clean quartz plate, (2) the activated quartz plate with hydroxyl surface, (3) the quartz plate with expoxide surface, and (4) the plate with pyrene surface.

Results and Discussion

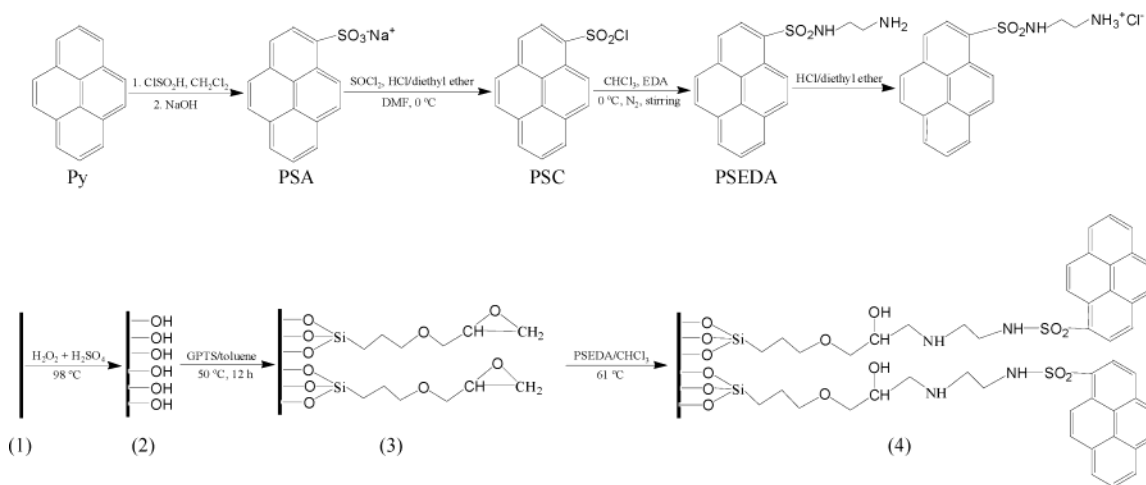
Functionalization of the Quartz Plate Surface. In the early 1980s, Sagiv and co-workers successfully assembled a highly ordered and tightly organized monomolecular layer on glass surface by employing long-chain alkyl trichlorosilane.¹⁸ Since then, various organic silicon derivatives have been developed and widely used to build monomolecular layers on glass surfaces in order to alter its surface properties and introduce some reactive groups.^{19–22} To introduce an expoxide group on the plate, GPTS was employed to react with the substrate, a quartz plate. It is expected that the expoxide group will react with the amino group of PSEDA, and form an imino structure within the spacer.

Table 1 shows the advancing contact angle data of the surface and water at 18 °C. Reference to the Table, it is revealed that the contact angle decreased significantly from 41 to 21° after treatment with the “piranha solution”. Further treatment of the surface with GPTS resulted in a sharp increase in the data (from 21 to 55), indicating the surface becoming less hydrophilic. The angle slightly increased further after treatment with PSEDA. These results are consistent with the expectation from the chemical composition of the surface, of which the composition changed from a less hydroxyl group, more hydroxyl group, expoxide group, and Py along with the treatment (cf. Scheme 1).

The stability of Py on the plate surface was examined by monitoring the fluorescence emissions of the systems and the medium, within which the plate had been immersed, as a function of time at 380 nm with 340 nm as the excitation wavelength. It was demonstrated that the emission intensities and emission profile of the film, the control, and the medium hardly changed with time, suggesting clearly that leaking of Py from the plate surface was negligible and should not affect the follow-up measurements. Actually, the emission of the film was stable within several days when it was kept in aqueous phase. Moreover, 3 months, at least, preservation of the film in a dry and clean place has little effect upon its behavior in aqueous medium.

Successful chemical coupling of Py on the plate surface is further confirmed by FTIR and Raman spectroscopy studies (cf. parts a and b of Figure 1). The ultrastrong absorption of the Si–O bond near 1000 cm^{-1} makes the absorptions of other bonds much weaker, and thereby it is difficult to recognize the modification by IR absorptions of the relative bonds, except Si–O, of which the absorption shifted from 1011.1 to 1026.9 after surface modification with GPTS, a strong evidence of chemical binding of the reagent to the plate surface. Further treatment of the GPTS-modified quartz plate surface with PSEDA, however, did not alter the peak position significantly (less than 3 cm^{-1}). This observation is not difficult to understand considering that the reaction occurs a number of bonds away from the Si–O bond. Chemical coupling of Py on the plate surface was directly confirmed by Raman spectroscopy measurements. Reference Figure 1b reveals that modification of the activated quartz plate surface with GPTS does not cause any significant change in the profile of the Raman spectrum.

SCHEME 1. Synthesis and Immobilization of 2-Pyrenesulfonylethylenediamine onto the Quartz Plate Surface



Reaction of PSEDA, however, with the GPTS modified quartz plate surface produces two significant bands at 1617.9 and 1939.3 cm^{-1} , respectively. The band at 1617.9 cm^{-1} is just within the double-bond stretching region between 1500 and 1700 cm^{-1} and may be assigned to the vibrational motion of the carbon–carbon stretching of the fused rings of Py.²³ The origin of the band at 1939.3 cm^{-1} is not clear. It is probably an overtone or a combination band.

Photophysical Behavior of Py Immobilized on the Plate Surface. As revealed by Karpovich and Blanchard,²⁴ the translational and rotational motions of a fluorophore immobilized on a substrate surface should be very different from those of the fluorophore in free state due to restrictions from the surrounding structures and the substrate. This difference may result in different photophysical behavior of the fluorophore in immobilized state to that of it in free state. Figure 2 depicts the steady-state fluorescence excitation and emission spectra of the functional plate in aqueous medium as functions of excitation and emission wavelengths. Examination of the figure reveals that the emission is composed of two sharp peaks and one broad band. The peaks and the band may be attributed to Py monomer emission and excimer emission, respectively. Compared with the results reported in the literature,^{22,25,26} a perfect “sandwich-like” structure may be adopted by the excimer due to its emission centering around 490 nm. Furthermore, the right-hand side of the excitation spectrum is broadened and redshifted along with the analysis wavelength shifting to longer wavelength, suggesting that some of the immobilized Py may exist in associated states.^{27–28} This tentative conclusion is further supported by time-resolved (fluorescence) emission spectroscopy (TRES) studies.

Figure 3a shows the TRES measurement results of the film in aqueous medium with time gates being set at 0–2, 2–4, 4–6, 6–8, 10–30, and 120–200 ns, respectively. Time 0 corresponds to the time at which the excitation pulse reached its maximum intensity. Interrogation of the Py excimer formation via TRES reveals that for the film, contribution from monomer emission to the spectrum decreases dramatically and the maximum emission shifts gradually to longer wavelength along with the time-gate moves away from the excitation pulse. Domination of monomer emission in the early time-gate spectrum and that of excimer emission in the middle and late time-gate spectra indicates that some immobilized Pys are in their lonely monomer state and that the excimer is mainly dynamic in nature (dynamic excimer).²⁵ Careful examination of the early time-gate (0–2 ns) spectrum reveals that excimer emissions centering around

430 and 490 nm (cf. the time-gate 0–2 spectrum), respectively, are also important contributors of the TRES results, indicating that some excimer may originate from direct excitation of the ground-state dimers (static excimer),²⁵ and some static excimers may be distorted due to difficulties in reorientation of the fluorophore.

Distorted excimer emission originating from partially overlapped Pys has been reported by a number of groups.^{26,28–30} It is to be noted that the position of the excimer emission of the film in aqueous medium is around 490 nm (cf. Figure 2), a wavelength corresponding to a perfect “sandwichlike” structure, an indication of quite even distribution of Py on the plate surface. This argument is also supported by steady-state and TRES studies of the emission of the film in the dry state (Figures 4 and 3b). Compared with that of the film in the wet state, the excimer emission in the dry state is much broader and blueshifted. In addition, by careful examination of the emission in the dry state, it can be noted that there is a small defect around 450 nm, an indication of coappearance of the distorted and perfect Py excimer emissions. Focusing our attention to the monomer emissions of the film at both wet and dry states (Figures 2 and 4), it is observed that the ratio of the relative intensities of the two sharp peaks (I_{400}/I_{380}) of the monomer emission is greater than 1 for the film at the dry state. For the film at the wet state, however, the ratio is less than 1. These observations may be rationalized by considering the appearance of the partially overlapped excimer, which is ironically confirmed by TRES measurement (cf. Figure 3b). By interrogation of the TRES spectra, it should not be difficult to conclude that both excimers are main contributors for the middle time-gate spectra (2–4 and 4–10 ns) and that the distorted excimer is short-lived and the main contributor for the early time-gate spectrum (0–2 ns). The dramatic appearance of the partially overlapped Py excimer in the dry state may be a result of the collapse of the long flexible spacer due to lack of extension condition, such as miscible solvent. It should not be difficult to imagine that collapse of the spacer makes the motion and reorientation of the immobilized Py more difficult, and thereby opportunity for formation of perfect excimer decreases. On the basis of these discussions and inspiration by literature studies, a model for the photophysical processes occurring at the plate surface is proposed, and shown in Scheme 2.

The model, even though a little bit oversimplified, is also supported by the results from fluorescence lifetime measurements. Table 2 lists the decay data of the film, at various analysis

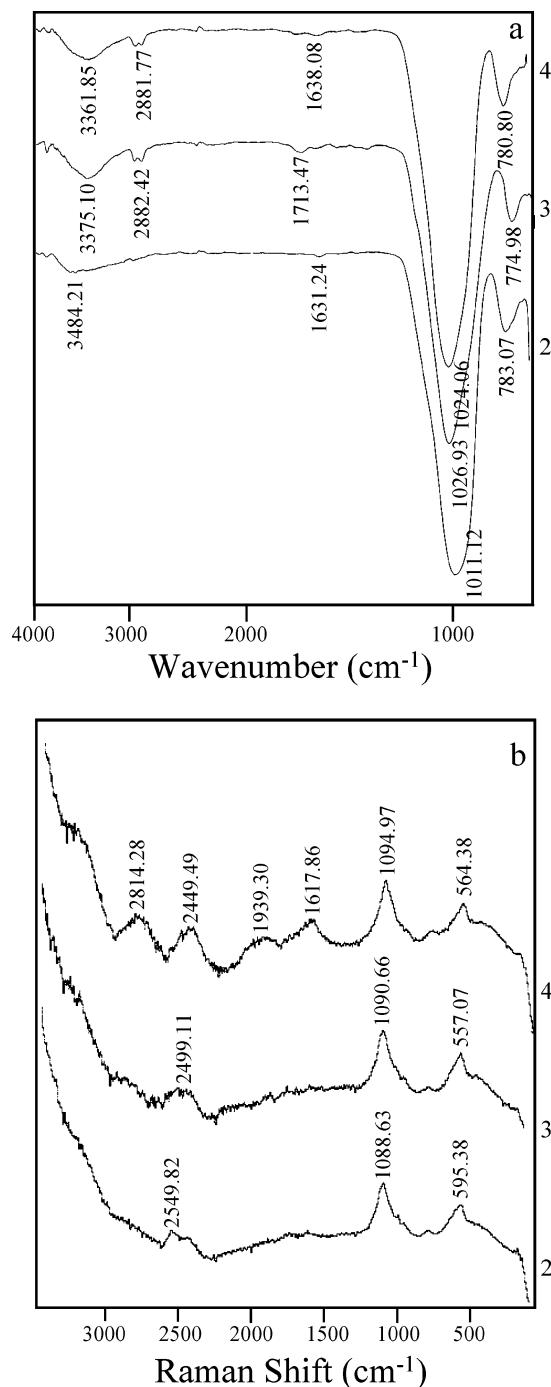


Figure 1. (a) IR and (b) Raman spectra of the quartz plates of various surface structures.

wavelengths, resultant upon four exponential analysis of the general form

$$i(t) = A + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) + A_4 \exp(-t/\tau_4) \quad (1)$$

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. As expected, the decay behavior of Py immobilized on the plate is complex, and employment of a four-exponential decay model, at least, in describing the decay behavior of the film is necessary (even so, in some cases, the “goodness of fitting”, χ^2 , is still larger than 1.3, cf. Table 2). As an example, parts a and b of Figure 5 show triple and four-exponential fits

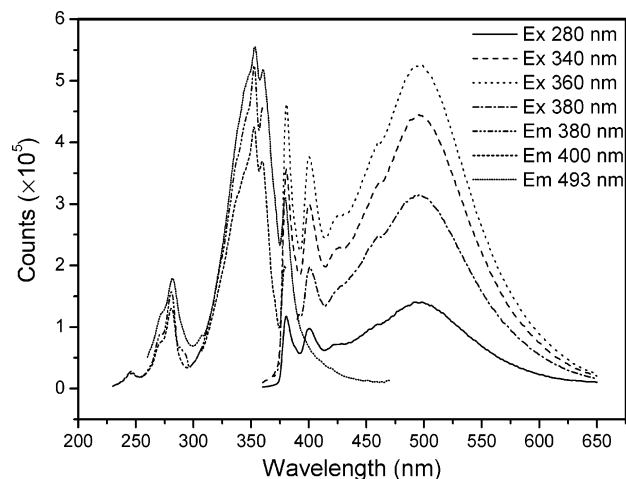


Figure 2. Excitation and emission spectra of the functionalized quartz plate in aqueous medium.

SCHEME 2. A Proposed Model Describing the Photophysical Processes Occurring on the Functionalized Quartz Plate Surface

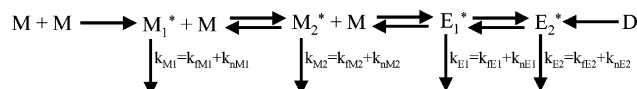


TABLE 2: Four Exponential Fits to the Decay of the Functionalized Quartz Plate in Aqueous Medium Monitored at Various Emission Wavelengths with an Excitation Wavelength of 353 nm

λ_{em} (nm)	A_1 (%)	A_2 (%)	A_3 (%)	A_4 (%)	χ^2
380	49.2	42.0	5.8	3.0	1.49
400	45.6	43.4	6.7	4.3	1.62
450	17.4	39.8	28.1	14.8	1.49
500	6.1	18.5	45.4	30.0	2.49
550	4.6	15.2	48.1	32.1	2.98

to the decay of the film measured at 450 nm at the wet state. Clearly, a substantial improvement in the “goodness of fitting” is apparent (as evidenced by the reduction in χ^2). The lifetimes from the fit are 0.9, 3.4, 12.3, and 42.1 ns, respectively, which have been tentatively attributed, according to the model and the TRES and steady-state emission studies, to a quenched excited monomer (M^*), an excited monomer (M_2^*), a distorted excimer (E_1^*), and a perfect excimer (E_2^*), respectively. Reference to the Table, it can be found that in most of the cases, the four-exponential function is inadequate for fitting the decays. 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. The real situation might be much more complicated. For example, for distorted excimers, a distribution of overlap conformations might be present. Similarly, for isolated monomers, they could either be surrounded by a hydrophobic microenvironment or exposed to a hydrophilic microenvironment. By further examination of the data shown in the Table, it was also found that all the pre-exponential coefficients are positive for the decays analyzed at wavelengths beyond 400 nm, indicating that either all but a very small fraction of the excimers are formed by direct excitation of the ground-state dimers or excitation of one of the monomers, which may be surrounded by a number of Py as its neighbors, in the aggregates. Therefore, diffusion of the fluorophore within the lifetime of the excited state of a fluorophore and/or energy migration to an excimer-forming site (cf. Birks’ scheme)³¹ may be negligible and the rising stage in the excimer decays, which should originate from the diffusion or migration, may be absent.

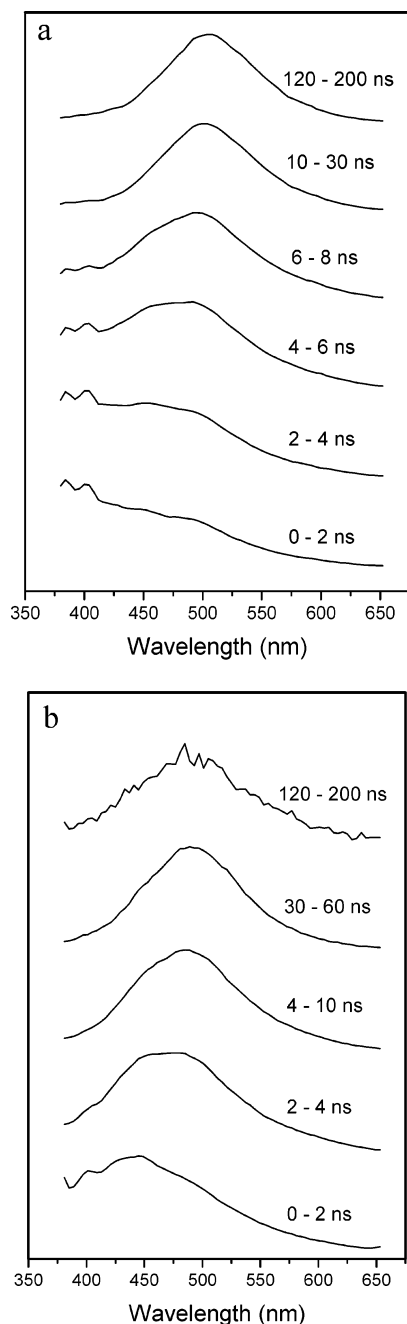


Figure 3. Time-resolved emission spectra of the functionalized quartz plate in (a) aqueous medium and (b) at dry state. The time gates are shown in the figure.

Similar spectra data were also observed for pyrene carboxylic acids in Langmuir–Blodgett (LB) monolayer films consisting of stearic acid and small amounts of 16-(1-pyrenyl) hexadecanoic acid^{32,33} and for pyrenyl carboxylic acids and anthracene carboxylic acids in mixed LB films of ω -arylalkanoic acids and fatty acids.^{34,35}

Sensing Properties to Dicarboxylic Acids. As expected, the fluorescence emission of the film is sensitive to the presence of dicarboxylic acids, such as ethanedioic acid, malonic acid, and succinic acid. The intensity of the monomer emission (380 nm) increases along with increasing the dicarboxylic acid concentration (cf. Figure 6a). A similar phenomenon was also observed for the excimer emission (480 nm) (cf. Figure 6b). Upon further interrogation of the figures, it is revealed that, unlike the effect to monomer emission, introduction of ethanedioic acid had little effect upon the excimer emission of the

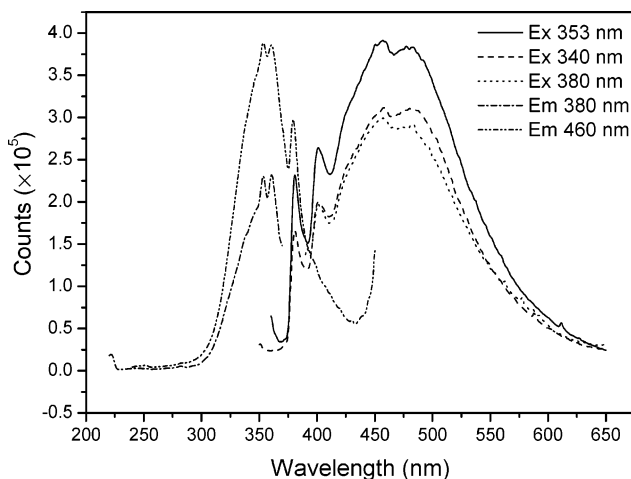
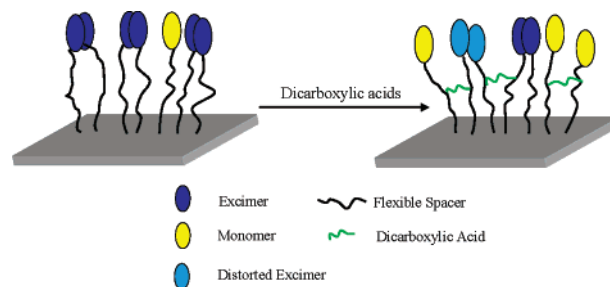


Figure 4. Excitation and emission spectra of the functionalized quartz plate at dry state.

SCHEME 3. Schematic Representation of the Physical State of Pyrene Immobilized on the Quartz Plate Surface



film. The effect of malonic acid to the excimer emission is similar to that of ethanedioic acid before its concentration exceeds 14 mM. The effect of succinic acid, however, is much greater than those of either ethanedioic acid or malonic acid, and the addition starts to affect the emission at a significant smaller concentration (cf. Figure 6b). These observations may be rationalized by considering that (1) the introduced dicarboxylic acid might insert into the space between the neighboring spacers on the substrate surface (cf. Scheme 3), and thereby alter the distribution of the sensing element and (2) the effect should be chain-length dependence because the longer the chain length, the greater the disturbing effect. Clearly, change in spatial distribution of the sensing element must result in change in the profile and intensity of the fluorescence emission of the film. It might be interesting to note that both the monomer emission and the excimer emission increase along with introduction of dicarboxylic acids. This observation might be accounted for by considering that insertion of a dicarboxylic acid between a ground-state dimer would increase the number of isolated monomers and thereby increase the monomer emission (cf. Scheme 3). However, for the sensing molecules in the aggregated state, insertion of the acid would decrease the number of them, and deduct the “self-quenching” or “inner-filtering” effect, thereby enhancing excimer emission.^{36–38} The explanation is further supported by the results from studies of the effect of monocarboxylic acids on the emission behavior of the film.

Reference to parts a and b of Figure 6, it can be observed that introduction of formic acid or acetic acid had little effect upon the emission behavior (both the profile and intensity of the emission) of the film, indicating that alteration to the emission behavior of the film caused by addition of dicarboxylic acids may not be results of pH variation but results of alteration in surface distribution of the sensing element.

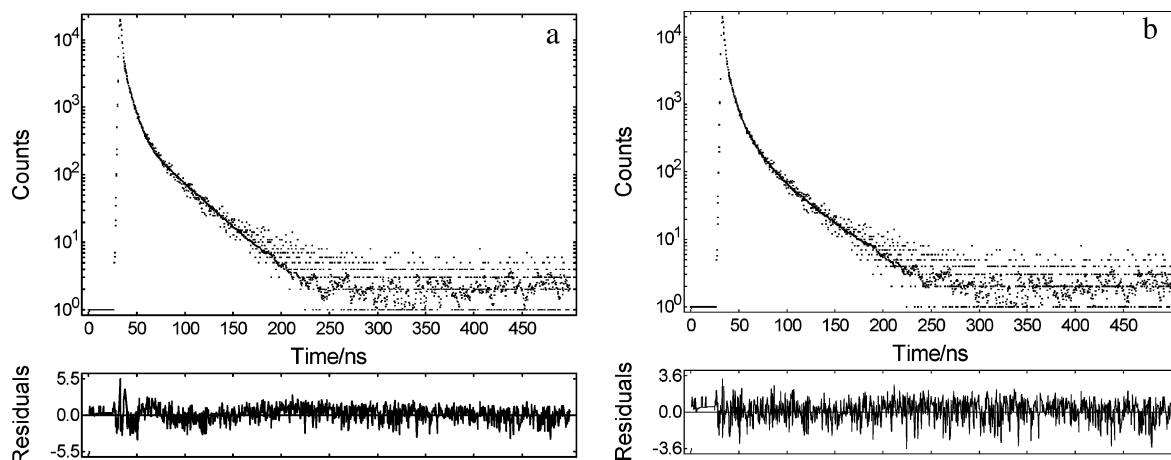


Figure 5. (a) Triple exponential and (b) four exponential fits to the fluorescence decay of the functionalized quartz plate in aqueous medium monitored at an emission wavelength of 450 nm with an excitation wavelength of 353 nm.

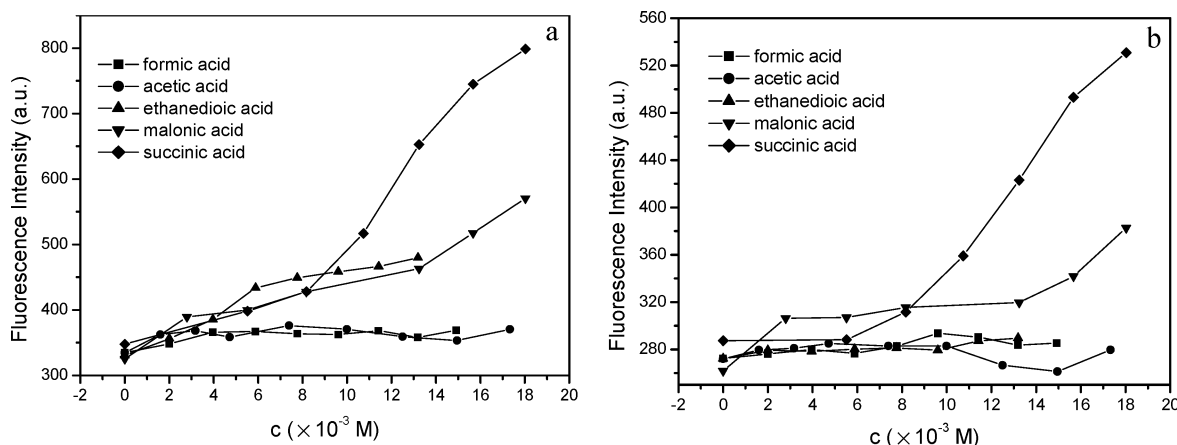


Figure 6. Plots of the (a) monomer (380 nm) and (b) excimer (480 nm) emission intensities of the functionalized quartz plate in aqueous medium as functions of acid concentrations (excitation wavelength 353 nm).

It was also found that the time needed for establishment of a new equilibrium after each addition of the acids is the chain length of an acid dependence. In fact, the longer the chain length of the acid, the more time is needed. For formic acid, acetic acid, ethanedioic acid, malonic acid, and succinic acid, the times are <1, <1, 80, 210, and 540 min, respectively, in support of the statement that dicarboxylic acids function via insertion into the space of the neighboring spacers.

It might be worth well to mention that response of the film to dicarboxylic acid is reversible because both the monomer emission and the excimer emission of the film could be fully restored by washing the film with pure water after each measurement. The sensitive response, the stability, and the reversibility of the film may guarantee it as potential sensing materials for common dicarboxylic acids.

Conclusions

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 the excimer emission of the fluorophore. However, the excimer emission is complicated due to presence of both "sandwichlike" structures and partially overlapped structures. Fluorescence lifetime measurement and TRES studies reveal that the excimer may be formed mainly by direct excitation of the ground-state dimers or excitation of one of the monomers in the aggregates. Moreover, both the monomer emission and

the excimer emission are sensitized by introduction of some dicarboxylic acids. This phenomenon has been attributed to the insertion of dicarboxylic acids into the space between the neighboring spacers. In contrast, introduction of monocarboxylic acids, such as formic acid and acetic acid, has little effect upon the emission of the functional film. In addition, response of the film to dicarboxylic acids is reversible, and the film is stable within a number of months if it is properly preserved. These characteristics guarantee the film as a potential sensing material for common dicarboxylic acids.

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Supporting Information Available: ^1H NMR spectra of PSC and PSEDA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Wei, T. X.; Huang, C. H.; Xie, P. H.; Hou, Y. J.; Zhang, B. W.; Liu, F. Q.; Ibrahim, K.; Qian, H. J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1333.
- (2) Taton, T. A.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **2000**, *122*, 6305.
- (3) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 42.

- (4) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.
- (5) Ulman, A. *Chem. Rev.* **1996**, 96, 1533.
- (6) Crego-Calama, M.; Reinhoudt, D. N. *Adv. Mater.* **2001**, 13, 1171.
- (7) Ning, G. H.; Lü, J. R.; Fang, Y.; Hu, D. D. *Chem. J. Chin. Univ.* **2000**, 21, 1196.
- (8) Fang, Y.; Ning, G. H.; Hu, D. D.; Lü, J. R. *J. Photochem. Photobiol., A* **2000**, 135, 141.
- (9) Wang, H.; Fang, Y.; Cui, Y. L.; Hu, D. D.; Gao, G. L. *Mater. Chem. Phys.* **2002**, 77, 185.
- (10) Wang, H.; Fang, Y.; Ding, L. P.; Gao, L. N.; Hu, D. D. *Thin Solid Films* **2003**, 440, 255.
- (11) Zhang, S. J.; Fang, Y.; Hu, D. D.; Gao, G. L. *Chin. J. Chem.* **2003**, 21, 249.
- (12) Liu, L.; Tong A. *Spectrosc. Spectral Anal.* **2002**, 22, 273.
- (13) Rogge, W. F.; Mazurek, M. A.; Hildemann, L. M.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ.* **1993**, 27A, 1309.
- (14) Limbeck, A.; Puxbaum, P. *Atmos. Environ.* **1999**, 33, 1847.
- (15) Xu, S.; Hu, M.; Zeng, L. *Environ. Chem.* **2002**, 21, 83.
- (16) Ezzell, S. A.; McCormick, C. L. In *Water-Soluble Polymers*; Shalaby, S. W., McCormick, C. L., Butler, G. B., Eds.; ACS Symposium Series 467; American Chemical Society: Washington, DC, 1991; Chapter 8.
- (17) Kurth, D. G.; Bein, T. *Langmuir* **1993**, 9, 2963.
- (18) Sagiv, J. *J. Am. Chem. Soc.* **1980**, 102, 92.
- (19) Pilloud, D. L.; Moser, C. C.; Reddy, K. S.; Dutton, P. L. *Langmuir* **1998**, 14, 4809.
- (20) Flink, S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Chem. Commun.* **1999**, 2229.
- (21) McCallien, D. W. J.; Burn, P. L.; Anderson, L. J. *Chem. Soc., Perkin Trans. 1* **1997**, 2581.
- (22) Van der Veen, N. J.; Flink, S.; Deij, M. A.; Egberink, R. J. M.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2000**, 122, 6112.
- (23) Bell, A. F.; He, X.; Wachter, R. M.; Tonge, P. J. *Biochemistry* **2000**, 39, 4423.
- (24) Karpovich, D. S.; Blanchard, G. L. *Langmuir* **1996**, 12, 5522.
- (25) Winnik, F. M. *Chem. Rev.* **1993**, 93, 587.
- (26) Matsui, J.; Mitsuishi, M.; Miyashita, T. *J. Phys. Chem. B* **2002**, 106, 2468.
- (27) Fang, Y. *Fluorescence Techniques in Colloid and Polymer Science*; Shaanxi Normal University Press: Xi'an, 2002; p 79.
- (28) Winnik, F. M.; Tamai, N.; Yonezawa, J.; Nishimura, Y.; Yamazaki, I. *J. Phys. Chem.* **1992**, 96, 1967.
- (29) Taniguchi, Y.; Mitsuya, M.; Tamai, N.; Yamazaki, I.; Masuhara, H. *Chem. Phys. Lett.* **1986**, 132, 516.
- (30) Tsuchida, A.; Ikawa, T.; Yamamoto, M. *Polymer* **1995**, 36, 3103.
- (31) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970.
- (32) Yamazaki, I.; Tamai, N.; Yamazaki, T. *J. Phys. Chem.* **1987**, 91, 3572.
- (33) Milosavljevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1988**, 92, 2997.
- (34) Biesmans, G.; Verbeek, G.; Verschuere, B.; Van der Auweraer, M.; De Schryver, F. C. *Thin Solid Films* **1989**, 168, 127.
- (35) Verschuere, B.; Van der Auweraer M.; De Schryver, F. C. *Thin Solid Films* **1994**, 244, 995.
- (36) Itoh, Y.; Webber, S. E.; Rodgers, M. A. J. *Macromolecules* **1989**, 22, 2766.
- (37) Itoh, Y.; Satoh, H.; Yasue, T.; Hachimori, A.; Satozono, H.; Suzuki, S.; Webber, S. E. *Macromolecules* **1994**, 27, 1434.
- (38) Soutar, I. *Polym. Int.* **1991**, 26, 35.