

A novel picric acid film sensor *via* combination of the surface enrichment effect of chitosan films and the aggregation-induced emission effect of siloles†

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A novel fluorescent film was fabricated by doping the aggregates of hexaphenylsilole (HPS) into a chitosan film. It was demonstrated that the fluorescence emission of the film is stable, sensitive and highly selective to the presence of picric acid (PA). The detection limit for PA is about 2.1×10^{-8} mol/L. Introduction of 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), nitrobenzene (NB), phenol, benzene, toluene, methanol, ethanol, and zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) had little effect upon the fluorescence emission of the film. The selectivity of the film was attributed to the specific electrostatic association effect of the protonated substrate film to picrate anion and the screening effect of the film to the interferents. The network structure of the substrate film is also favourable for the stabilization of the fluorescence emission of the hybrid film, by preventing the further aggregation of silole aggregates. Fluorescence lifetime measurements revealed that the quenching is static in nature. Furthermore, the quenching process is fully reversible. Considering the simplicity of the preparation and the outstanding performance of the hybrid film, it is anticipated that it could be developed into a real-life PA sensor.

Introduction

Picric acid, 2,4,6-trinitrophenol (PA), is a common reagent used in the leather, pharmaceutical, and dye industries, as well as in the manufacture of explosives and rocket fuels, but it is also a strong irritant and allergen.¹ The wide use of this compound has made it a significant environmental pollutant, and sensitive detection of it has recently attracted attention.² Various methods, including a membrane electrode method,³ gas chromatography,⁴ spectrophotometry⁵ and capillary electrophoresis,⁶ have been established for the detection of PA, but these methods, suffered from drawbacks such as the cumbersome pretreatment of samples, interference from other compounds, or sophisticated instrumentation. Fluorescence-based films are generally employed for the sensing of PA due to their sensitivity, selectivity, simplicity, and low cost in instrumentation.⁷ Yu and coworkers reported an optical fiber sensor for PA,⁸ designed on the basis of fluorescence energy transfer (anthracene as the donor, and porphyrin as the acceptor). This sensor was much more sensitive to PA than the sensors only containing the donor or the acceptor. To further improve the performance of the sensors for PA, the same group also employed 3-(*N*-methacryloyl)amino-9-ethylcarbazole as a sensing element, and chemically immobilized it on a surface-modified quartz glass plate. They demonstrated its superiority to other sensors, showing that it had better stability, faster response, and greater selectivity.⁹

Recently, our group reported a new kind of fluorescent PA sensor, which was fabricated by a single-layer chemistry approach employing pyrene as a sensing element. It was shown that the film is sensitive to PA both in vapor and aqueous medium.¹⁰

Compared with small molecules, conjugated polymers have been proven to be excellent sensing elements due to the so-called molecular wire effect,¹¹ and they have been successfully used for the detection of PA. For example, some Si-containing conjugated polymers prepared by Trogler and coworkers have shown high sensitivity to PA.¹² Similarly, Fujiki and coworkers reported a fluoroalkylated polysilane-based chemsensor, which shows remarkable sensitivity to the analyte.¹³ These sensing systems, however, suffered from interference from other electron-deficient compounds because of their electron-transfer mechanism. Therefore, searching for a sensitive and highly selective PA detection method is still a challenging task.

Siloles are a group of five-member silacycles, which possess unique low-lying LUMO level associated with the $\sigma^*-\pi^*$ conjugation arising from the interaction between the σ^* orbital of two exocyclic σ -bonds on the silicon atom and the π^* orbital of the butadiene moiety.¹⁴ Siloles exhibit high electron mobility and high photoluminescence quantum yields, and they are frequently employed to fabricate electroluminescence devices.¹⁵ Unlike organic compounds, silole and polysilole possess an exceptional aggregation-induced emission (AIE) property, and as a result, the aggregates of them exhibit stronger luminescence because the aggregates restrict molecular rotation.^{14a} In particular, the aggregates can be used as sensing elements for the buildup of new sensing systems with better performance. Trogler and coworkers¹⁶ prepared a new polysilole, and demonstrated that the aggregates (nanoparticles) of it show good selectivity and great sensitivity to PA and other nitro-aromatics. Aggregates of siloles or polysiloles therefore appear to be excellent fluorophores for sensing applications.

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Chitosan (CS), which has chemical composition poly[β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose], is produced by partial deacetylation of chitin, which is a typical biopolymer and is abundant in shells of crustaceans. The monomer units of CS are glucosamine and *N*-acetylglucosamine.¹⁷ Good film-forming ability and ease of modification make CS an ideal substrate for the preparation of various functional films.¹⁸ As for the preparation of fluorescent films, fluorophores can be introduced by either chemical immobilization *via* the amino groups on the CS films or simple doping into the substrate films.¹⁹ Our group fabricated a fluorescent CS film with dansyl as a fluorophore which is sensitive to the polarity of the medium.²⁰ Similarly, pyrene and β -CD have been chemically immobilized onto CS films coated on a quartz plate, and it was shown that the film is very sensitive to (and selective for) the presence of nitromethane. The sensitivity and selectivity were attributed to the host-guest interaction between pyrene and β -CD.²¹

In this paper, we report a new fluorescent film based on hexaphenylsilole (HPS) aggregates and CS networks, and describe the fluorescence behavior of the film and its sensing properties for PA.

Experimental section

Materials

High-purity lithium (Acros), diphenylacetylene (Alfa) and dichloro(diphenyl)silane (Alfa) were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under nitrogen prior to use. Other reagents were of analytical grade or higher. Water used in this work was de-ionized and then double-distilled. CS was prepared and purified by a method described before.²² The degree of deacetylation was determined to be 100% by FTIR and pH titration, and the viscosity-average molecular weight was 7.82×10^5 .

Instrumentation

Melting points were determined on a Beijing Tech instrument X-5 instrument. Fluorescence measurements were performed at room temperature on a time-correlated single photon counting Edinburgh FLS 920 fluorescence spectrometer with a front-face method. The fabricated film was inserted into a quartz cell with its surface facing the excitation light source. The cell was fixed in the solid sample holder of the instrument, and the position of the film was kept constant during each set of measurements. ¹H NMR spectra were obtained on a Bruker AV 300 NMR spectrometer. Analysis of C, H and N was conducted on a Perkin-Elmer 2400 CHN elemental analyzer. Pressed KBr disks for the powder

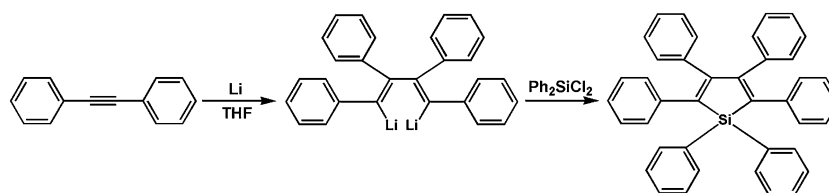
samples were used for the transmission infrared spectroscopy measurements, and the FTIR spectra were obtained with a Bio-Rad FTIR spectrometer. Transmission electron microscopy (TEM) was performed on a Hitachi H-600 instrument.

Synthesis of HPS

HPS was synthesized by employing a slightly modified literature method.^{23,18a} Clean lithium shavings (111 mg, 16 mmol) were added to a solution of diphenylacetylene (3 g, 16.8 mmol) in dry THF (20 mL). The reaction mixture was stirred at room temperature for 12 h in a dry argon atmosphere. Then the mixture was diluted with 100 mL THF, followed by the addition of 1.8 g (7.2 mmol) of dichloro(diphenyl)silane. After refluxing for 5 h, the reaction mixture was cooled and filtered. The filtrate was washed with water, and the organic layer was extracted with diethyl ether and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography over silica gel using hexane-chloroform (2:1) as eluent. Re-crystallization from ethanol gave faintly greenish-yellow crystals in 60% yield (2.3 g) (see Scheme 1). Mp = 186–187 °C (uncalibrated thermometer). ¹H NMR (300 MHz, CDCl₃): δ 7.71 (m, 4H), 7.44 (m, 6H), 7.18 – 6.90 (m, 20H). FTIR (KBr): 3058, 2923, 1627, 1490, 1432, 1384, 1297, 1108, 1068, 995, 792, 744, 709, 703, 511 cm⁻¹. Anal. Calcd for C₃₀H₂₆Si: C, 86.91; H, 6.32. Found: C, 86.50; H, 6.42.

Preparation of HPS nanoparticles

The HPS nanoparticles were prepared in THF–water mixture solvents with different compositions. As a typical preparation, 0.0269 g of HPS was dissolved into 1 mL of THF. Then 24 mL of water was added rapidly with stirring. The resulting suspension was kept at room temperature and used for fluorescence measurements and TEM observation. As revealed by Tang and others,¹⁴ all siloles are practically non-emissive when they are fully dissolved in common solvents at room temperature. However, emission occurs when a poor solvent is introduced, and this phenomenon is called aggregation-induced emission (AIE). A similar phenomenon was observed in our experiment. A THF solution of HPS (1.00 g/L) was specially prepared and its fluorescence emission was found to be enhanced dramatically by the addition of water to the system. Further experiment reveals that the increase depends upon the ratio of the final mixed solvent (see Fig. 1). It is to be noted, however, the stability of the mixtures (suspensions) also depends upon, but not linearly, the ratios of the mixed solvents. For example, phase separation occurs for systems with approximately 60–70% (v/v) water and those with more than 99% (v/v). Systems with other compositions are stable (see ESI†).



Scheme 1 Synthesis of hexaphenylsilole (HPS).

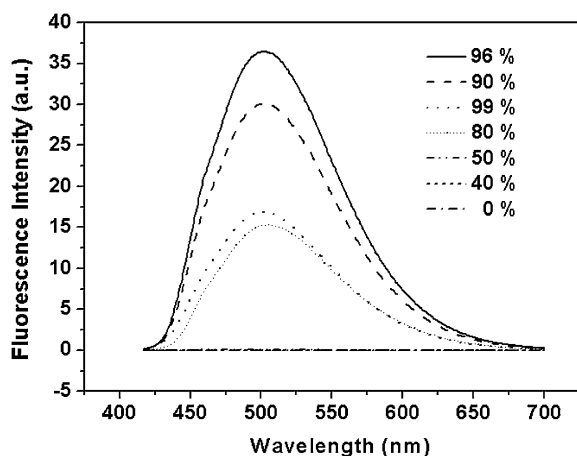
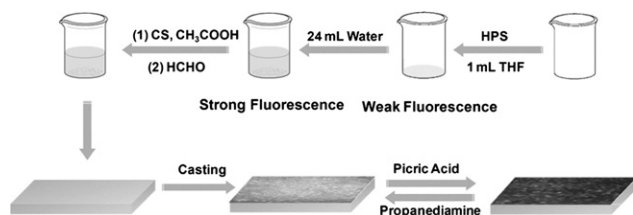


Fig. 1 Fluorescence emission spectra of HPS-NP in THF-H₂O suspension with water content, from top, of 96, 90, 99, 80, 50, 40, and 0% (v/v).

Preparation of CS film doped with HPS nanoparticles

Based upon the experimental results presented in Fig. 1 and the considerations described above, the suspension with 96% (v/v) water was employed for the preparation of the composite film. To the suspension, 0.5 g of purified CS and 500 μ L of acetic acid (2 mol/L) were added under stirring. After the addition, the mixture was further stirred for another 20 min to ensure complete dissolution of CS. Then, the mixture was thoroughly degassed by air-pumping, and then mixed with 200 μ L of formaldehyde solution (37–40%). The mixture thus prepared was kept at room temperature in a dust-free container for film preparation. At the same time, a clean glass plate (0.9 cm \times 2.5 cm) was treated with “piranha solution”²⁴ (7:3, v/v, 30% H₂O₂–98% H₂SO₄) (**Warning: Piranha solution should be handled with extreme caution because it can react violently with organic matter.**) at 98 $^{\circ}$ C for 1 h, then rinsed thoroughly with plenty of water, and finally dried at 100 $^{\circ}$ C for 1 h. A quantitative amount (15 μ L) of the CS-HPS suspension as prepared was added onto the activated glass plate surface, and a homogeneous film was formed about 1 h later. Then, the plate with the film was gently transferred to a dust-free oven, and left there for 24 h at room temperature. The plate was then dried in the oven at 50 $^{\circ}$ C for 24 h. After drying, the film was taken out off the oven, submerged in NaOH solution (0.1 mol/L) for 10 min, rinsed thoroughly with plenty of water, and finally dried again in the oven. The film fabrication process is shown in Scheme 2.



Scheme 2 Schematic representation of the fabrication and sensing performance of the sensing film.

Results and discussion

Characterization of the HPS aggregates

The boiling point of THF is significantly lower than that of water, and therefore as the mixed solvent evaporates from the film layer, the ratio of THF to water will decrease, resulting in further aggregation of the HPS nanoparticles. Accordingly, it is important to characterize the change of the HPS aggregates before and after film preparation before conducting further studies of the film behavior. Fig. 2a shows the TEM images of the HPS aggregates in THF–water mixtures. It is clear that the HPS molecules aggregate into uniform spheres with an average diameter of about 130 nm. Direct observation of the HPS aggregates trapped within the substrate film demonstrated that introduction of CS, fabrication into films, and drying in an oven had little effect upon the sizes of the aggregates, as evidenced by the results shown in Fig. 2b. The fact revealed by the two TEM images may be understood by considering that 96% is already a very high content of water in the THF–water mixture, the space for further increase in water content is limited, and therefore faster evaporation of THF has little effect upon the sizes of the aggregates. Another way to understand the result is to consider the possible compartment effect of the substrate networks to prevent further aggregation of the HPS nanoparticles.

Steady-state fluorescence behavior of the hybrid film

Fig. 3 shows both the excitation and emission spectra of the hybrid film determined in aqueous phase and those of the suspension employed to prepare the hybrid film. It can be seen that the profiles of the spectra of the film and the suspension are almost the same, indicating that further aggregation of the HPS nanoparticles was significantly prohibited, as expected. This stabilization effect can be attributed to the network structures of the substrate film, because the aggregates of HPS might be isolated by the substrate networks (see Fig. 2). Further investigation revealed that the intensity of the fluorescence emission does not depend on the scanning time, and furthermore, the fluorescence emission of the remaining aqueous medium is almost undetectable, indicating that release of the HPS aggregates into the medium is negligible.

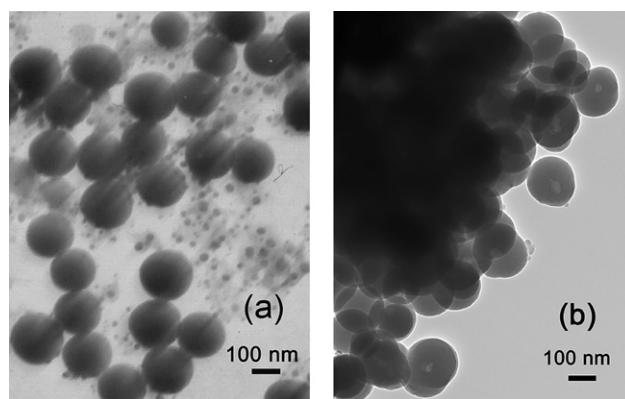


Fig. 2 TEM images of hexaphenylsilole (HPS) nanoparticles in (a) THF–H₂O (96%) and (b) in the sensing film in the dry state.

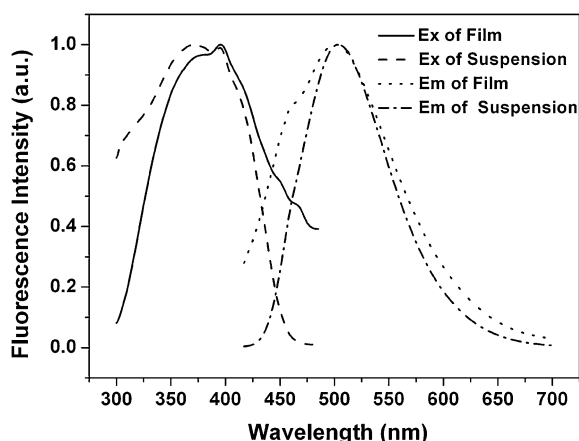


Fig. 3 Excitation and emission spectra of the sensing film and HPS-NP in aqueous medium ($\lambda_{\text{ex}} = 397$ nm, $\lambda_{\text{em}} = 505$ nm).

Fluorescence lifetimes of the film and the HPS aggregates

The fluorescence lifetimes of the hybrid film in both the wet and dry states and its corresponding HPS aggregates in THF–water were measured. The decay profiles are shown in Fig. 4. Double-exponential fitting is sufficient to get a satisfying result ($\chi^2 = 1.0\text{--}1.4$), and the residuals of the fittings are randomly distributed. The average lifetimes for the HPS nanoparticles in suspension, in wet film and in dry film are 7.11, 3.53 and 3.02, respectively. This is not a surprising result considering that the lifetime of a fluorophore depends not only upon its own chemical nature, but also is affected by its micro-environment. Therefore, the difference may be a result of the effect of changes in its physical environment.

Response of the fluorescent film to PA

Fig. 5 depicts the fluorescence emission spectra of the film at various PA concentrations in an aqueous medium. It can be seen that the fluorescence emission is almost completely quenched when the concentration of PA reaches 0.24 mmol/L.

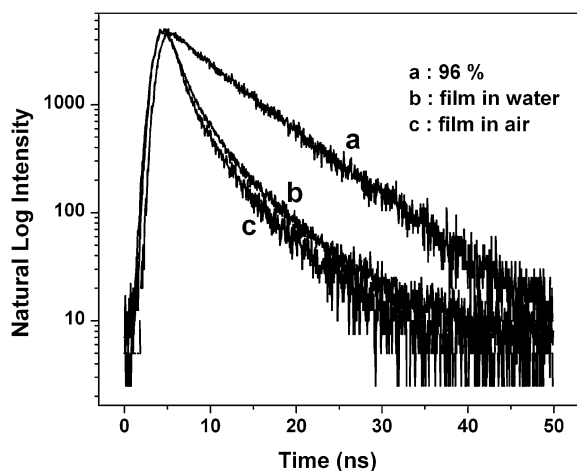


Fig. 4 Semilog plots of fluorescence decay *versus* time for HPS-NP in (a) THF–H₂O (96%), (b) film in water, (c) film in air ($\lambda_{\text{ex}} = 397$ nm, $\lambda_{\text{em}} = 505$ nm).

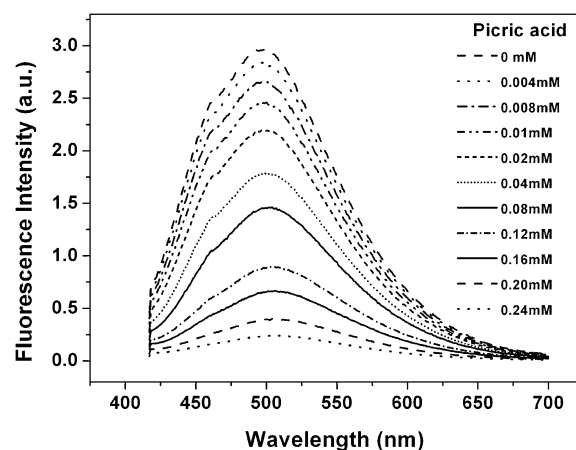


Fig. 5 Fluorescence emission spectra of the sensing film in the presence of different concentrations of PA (from top to bottom, 0, 0.004, 0.008, 0.01, 0.02, 0.04, 0.08, 0.12, 0.16, 0.2 and 0.24 mM) in an aqueous medium ($\lambda_{\text{ex}} = 397$ nm).

The fluorescence quenching results can be also treated with the Stern–Volmer equation, $I_0/I = 1 + K_{\text{sv}}[\text{PA}]$, where I_0 and I are the fluorescence intensity of the film in the absence and presence of PA, respectively, and K_{sv} is the Stern–Volmer constant. A linear Stern–Volmer relationship may be observed if either a static or dynamic quenching process is dominant. In this case, however, the Stern–Volmer plots curve up, which could be a result of combination of dynamic quenching and static quenching.²⁵ But for our system, the main reason for this phenomenon is that the local concentration of PA near the HPS aggregates within the substrate film is significantly greater than that in the bulk aqueous phase because of the surface enrichment effect of substrate film to the quencher (see discussion on the selectivity of the film to PA).

Selectivity of the hybrid film to PA

Fig. 6 shows the histograms of $(I_0/I) - 1$ to the concentrations of PA and its common interferences. It was found that TNT, DNT, NB, Zn(NO₃)₂, phenol, methanol, ethanol, benzene, and other

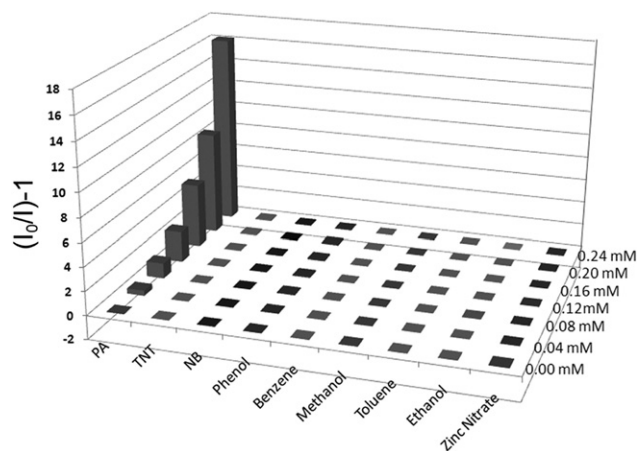


Fig. 6 Quenching efficiencies of PA and common interferences to the emission of the film at different concentrations.

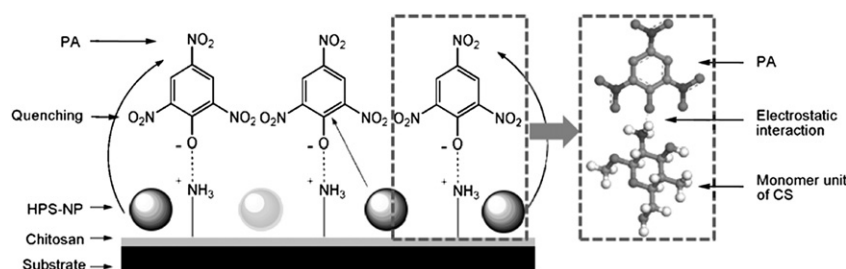


Fig. 7 Schematic representation of the selective sensing and the simulation result of the electrostatic interaction between PA and the monomer unit of CS.

common solvents have little effect upon the fluorescence emission of the film, indicating that the film is highly selective to PA. This is very different from those obtained from the sensing performance studies of other fluorescent films. Like other electron-deficient nitro-aromatics (NACs), PA should quench the fluorescence emission of the films *via* a donor–acceptor interaction mechanism because the sensing fluorophore employed in the hybrid film is also an electron-rich compound. For the present study, however, the situation is much more complex because the substrate is not inert; it should have some interactions with the quenchers. In fact, the special selectivity of the film to PA may be only understood by considering this interaction. It is well known that PA behaves as a strong acid because of the three nitro-groups affixed on the benzene ring. In contrast, the CS film is rich in amino groups, which have a strong tendency to attract protons, and thereby proton transfer will occur with insertion of the film into the aqueous solution of PA. It is the electrostatic association that makes PA have a special affinity to the substrate. This might be the reason why PA is so efficient at quenching the fluorescence emission of the film. These considerations can be visualized by the schematic cartoon shown in Fig. 7.

This cartoon also explains the observation that other NACs showed little effect upon the fluorescence emission of the hybrid film. Other NACs such as TNT, DNT and NB have no hydroxyl groups (as PA does), and therefore they have no tendency to be enriched on the film surface. Furthermore, the substrate is a hydrophilic film, but the NACs are hydrophobic in nature. Therefore, it can be expected that the compatibility of the substrate film to these NACs will be poor, and the substrate will screen the approach of the quencher molecules to the fluorescence-active HPS nanoparticles, resulting in lower quenching efficiencies.

The role of the amino groups of the substrate film in the selectivity and sensitivity of the hybrid film to PA was proved by an additional experiment. Considering the chelating effect of CS to Zn(II), the film was intentionally immersed in a $\text{Zn}(\text{NO}_3)_2$ solution for several minutes, and then the film was removed from the solution and washed with distilled water several times. It was found that the intensity of the fluorescence emission of the film did not change very much after the salt treatment, indicating that $\text{Zn}(\text{NO}_3)_2$ is not an efficient quencher for the fluorescence emission of the hybrid film (see Fig. 6). Furthermore, we believe that the amino groups of the substrate film should bond to the metal ions, and the binding ability of the film to PA should be decreased, resulting in lower quenching efficiency. Fig. 8 shows the Stern–Volmer plots of both the original film and the

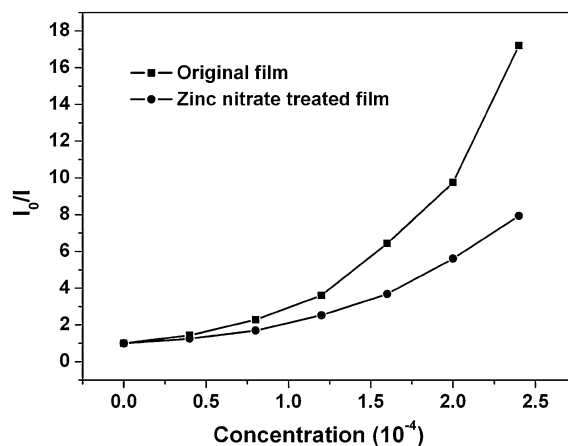


Fig. 8 Quenching efficiencies of the original sensing film and the $\text{Zn}(\text{NO}_3)_2$ -treated film in the presence of different concentrations of PA.

$\text{Zn}(\text{NO}_3)_2$ -treated film. It is clear that the treatment does decrease the quenching efficiency, a result in support of the hypothesis that the amino groups of the substrate play an important rule in the highly selective and sensitive sensing of PA.

To confirm the electrostatic interaction between the picrate anion and the protonated CS film, a specially designed experiment was conducted. In the experiment, a given amount of NaNO_3 solution was intentionally introduced into a sensing system containing some PA, and it was found that introduction of the salt resulted in partial recovery of the fluorescence which had been quenched by the quencher, PA (see Fig. 9). As was expected, the extent of the recovery depended upon the concentration of the salt. This result can be explained by considering the salt screening effect. It has been demonstrated that electrostatic association is the main reason for the film to enrich PA on its surface, which explains why the film is so sensitive and selective to the presence of the analyte. Introduction of a salt, like NaNO_3 , must screen the association due to electrostatic reasons. This electrostatic screening effect could be very prominent, particularly when the concentration of the salt is significantly greater than that of the analyte. Elimination of the analyte from the film surface must result in lower quenching efficiency, and thereby the emission of the film is recovered.

pH effect

With reference to the cartoon shown in Fig. 7, it is reasonable to expect that the sensing performance of the hybrid film to PA

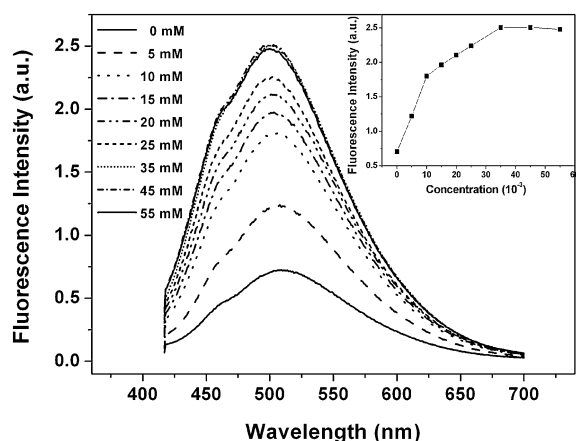


Fig. 9 Fluorescence emission spectra of the quenched sensing film in the presence of different concentrations of NaNO_3 (from bottom to top, 0, 5, 10, 15, 20, 25, 35, 45, 55 mM) in an aqueous medium ($\lambda_{\text{ex}} = 397 \text{ nm}$).

should be highly sensitive to the changes in pH of the medium. Accordingly, a pH effect upon the sensing performance of the fluorescent film to PA was studied. A solution containing 0.05 mM PA and 4 mM NaCl was taken as a reference sensing system. NaCl was introduced for the screening of the possible ionic effect resulted from the neutralization of PA during the adjustment of the pH of the system. To the solution, NaOH solution (0.01 M) was added carefully to adjust the pH of the solution. The dependence of the quenching efficiency upon the pH of the system is shown in Fig. 10. It is clear from the figure that there is a very sharp decrease in the quenching efficiency with increasing pH from about 4.58 to 5.53. But at other pH values, a change in pH has little effect upon the quenching efficiency. This result can be also understood by considering the principles shown in the cartoon (see Fig. 7).

Response time

The response time of the film to the analyte, PA, was studied by monitoring the fluorescence intensity of the film as a function of time at different concentrations of the analyte. The results are depicted in Fig. 11. It can be seen that the response of the film to

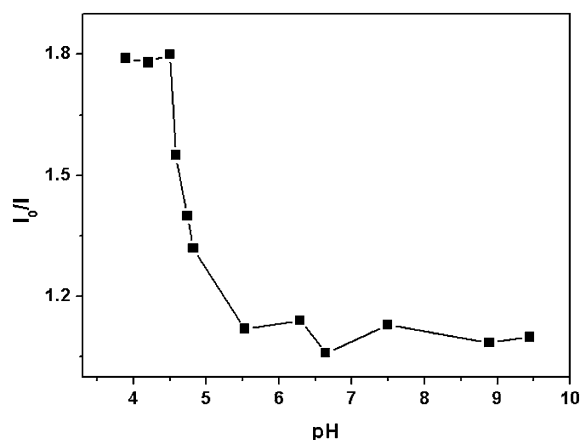


Fig. 10 Effect of pH upon the sensing performance of the film to PA.

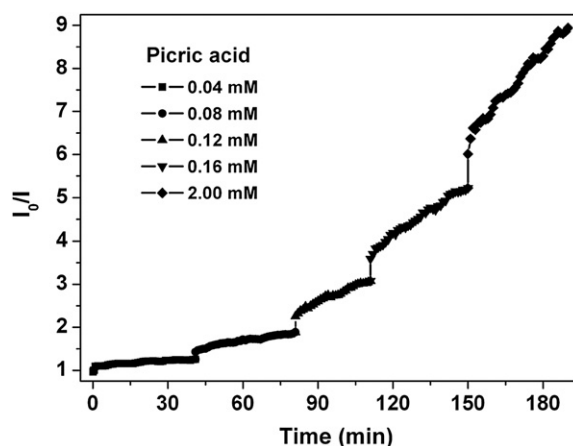


Fig. 11 The time-dependent quenching efficiency of the film immersed in different concentrations of PA.

the analyte is almost instantaneous, even though the equilibrium is relatively slow. Further examination of Fig. 11 shows that it takes more than 40 min to reach equilibrium at low concentrations of PA, and that the time required for the equilibration gets longer and longer with increasing concentration of the analyte. The fast response could be a result of the specific affinity of PA to the film substrate, CS. The slowness in reaching equilibrium, however, can be understood by considering the structure of the HPS nanoparticles. A requirement for fluorescence quenching is contact of the quencher molecule with the fluorescent molecule. This is difficult in the present film due both to slow diffusion of PA within the HPS aggregates and physical association of PA on the CS networks, which further hinders the diffusion.

Quenching mechanism

The quenching mechanism of the sensing was studied by comparing the quenching results from static measurement and those from fluorescence lifetime measurement. Upon examination of the plots shown in Fig. 12, it is clear that the lifetime of the sensing film is almost independent of the concentration of the quencher, PA, indicating that the quenching process is static in

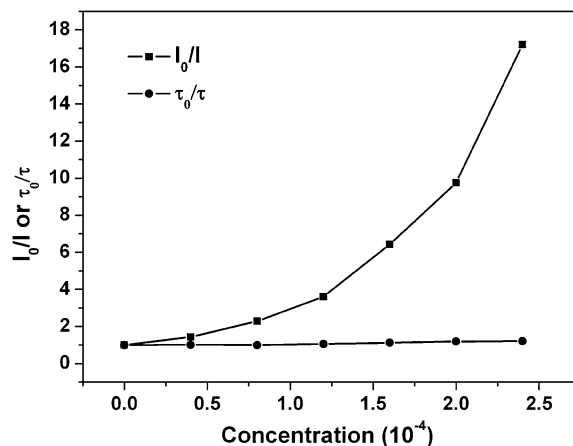


Fig. 12 Plots of I_0/I and τ_0/τ of the fluorescent film against the concentration of PA.

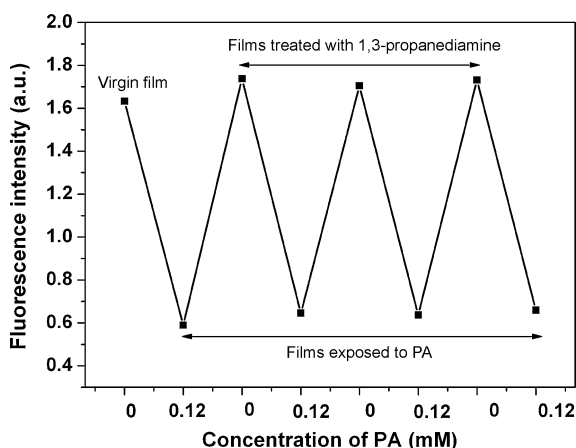


Fig. 13 Reversibility of the response of the fluorescent film to PA.

nature, and occurs *via* formation of a non-fluorescent complex. However, the film will be a useful sensor only if the sensing process is reversible, and so this was examined next.

Reversibility of the quenching process

The procedures adopted for examination of the reversibility of the sensing process are as follows: firstly, the film was inserted into a cell with 2.5 mL of distilled water, and the fluorescence emission of the film was recorded. Secondly, 30 μ L PA solution (0.01 mol/L) was added, and after 10 min equilibration the fluorescence emission of the film was recorded again. Thirdly, after the measurement the film was taken out of the cell, and immersed in an aqueous solution of 1,3-propanediamine (0.01 mol/L) for 10 min and then washed with distilled water several times. The film was re-used after the treatment, and the whole process was repeated several times. The results are shown in Fig. 13. It is clear that the response of the film to PA is fully reversible, and furthermore, the film is stable for at least six months provided it is properly preserved.

Conclusions

A very stable and bright fluorescent film was fabricated by the combination of the surface enrichment effect of a CS film and the AIE effect of siloles. Sensing performance studies demonstrated that the fluorescence emission of the film is sensitive and highly selective to the presence of PA, an important nitro-aromatic compound, with the detection limit being as low as 2.1×10^{-8} mol/L. Common interferents such as TNT, DNT, NB, benzene, methanol and ethanol had little effect upon the fluorescence emission of the film in the aqueous phase. This unexpected result was rationalized by considering the substrate screening effect and the specific electrostatic association effect of the substrate polymer to PA. Fluorescence lifetime measurements revealed that the quenching is static in nature; furthermore, the quenching process is fully reversible.

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