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Fluorescent Films Based on Molecular-Gel Networks and Their Sensing Performances

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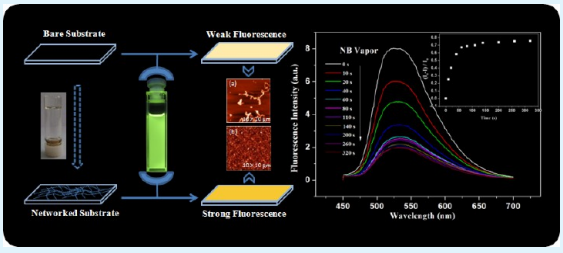
Supporting Information

ABSTRACT: A pyrene-capped terthiophene of cholesteryl derivative (CholG-3T-Py) was designed, synthesized, and utilized for the fabrication of a fluorescent film. Unlike the commonly adopted direct-coating method, the film was fabricated by the physical immobilization of the fluorophore, CholG-3T-Py, onto a glass plate surface via preformed low-molecular-mass gelator (LMMGs)-based molecular-gel networks. The photophysical behavior of the film as prepared and its sensing performances to nitrobenzene (NB) were conducted after activation with toluene. It was found that the film as prepared and activated is sensitive to the presence of NB, and the sensing process is fully reversible. Furthermore, the effects of commonly found interferents, including structural analogues, raw materials, which are commonly used for the production of NB, and other nitroaromatics (NACs), on the sensing process were also tested. It was shown that only aniline and phenol possess slight interference. The present work not only extends the applications of LMMGs-based molecular gels but also provides a new approach for preparation of micro- and nano-structure-based fluorescent sensing films.



KEYWORDS: *pyrene-capped terthiophene (Py-3T), low-molecular-mass gelator (LMMGs), fluorescence films, micro- and nanostructures, nitrobenzene*

1. INTRODUCTION

As typical photonic noses/tongues, fluorescent chemosensors have received increasing attention since their introduction in the early 1980s when fluorescent calcium indicators were first reported.[1,2] This is because this kind of sensor not only possesses the advantages of sensitivity, selectivity, abundant signals but also of requiring no reference for sensing. It is for these reasons that fluorescent chemosensors have been widely studied for their uses in environmental monitoring,[3,4] medical diagnosis,[5,6] biological analysis,[7,8] food safety monitoring,[9,10] and antiterrorism[11,12] during the last few decades. In terms of real-life applications, film sensors are superior to solution-based chemosensors because their reusability and convenience of use.[13]

There are a number of methods that can be used for preparing fluorescent film sensors. Among them, self-assembled monolayers (SAMs) and sol−gel methods have gained extensive interest because the films prepared by these approaches possess long-term stability and reusability and because of their ease for implementing and miniaturizing.[14,15] However, for the SAMs method, the quality control of a large-scale production is difficult to realize because of the complication of the fabrication process, even though the films fabricated via this route are much more robust and easier for analytes to reach the sensing sites within the fluorescent layer. As for the sol−gel methods, it is more suitable for developing fluorescent films with inorganic oxides as fluorophores rather than organic fluorophores.[15,16] Conjugated polymers and even the derivatives of commonly found low-molecular-mass fluorophores can be also used for fabricating fluorescent films via spin-coating, dipping coating, and other physical methods.[17,18] Generally speaking, the performance of the films developed by direct methods are dependent upon not only the nature of the fluorophores and the substrates adopted but also their micro- and nanostructures.[19] In addition, this method suffers from at least two shortcomings even though it is much easier to conduct. One shortcoming is that the regulation of the micro- and nanostructures of the film for a given fluorophore and substrate system is limited, and the other is that for quenching-based fluorescence sensing, the films developed by this method suffer from strong background fluorescence because the emission from the interior of the micro- and nanostructures is not easily quenched by the analytes tested because of difficulty in diffusion.[20,21] Therefore, the development of new strategies to integrate the advantages and minimize the weaknesses of known fabricating methods is of great importance both theoretically and practically.

Over the past decade, our group has focused on the development of environmentally sensitive materials and their applications, in particular, monolayer chemistry-based fluorescence sensing films and stimulus-responsive molecular gels.[22,23] On the basis of the motivation described above as well as the

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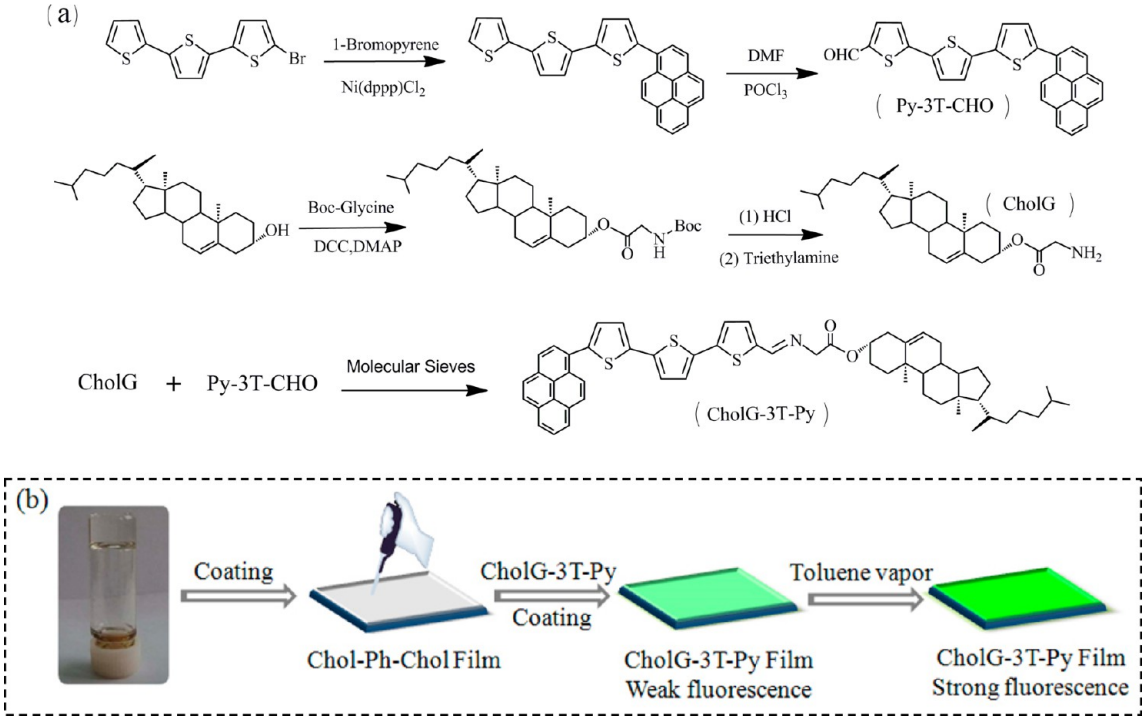
Scheme 1. Schematic Representation of the Synthetic Route of CholG-3T-Py(a) and Fabrication and Activation of a Molecular-Gel Networks-Based Fluorescent Film (b)



achievements acquired by our group, a new strategy has been developed for creating novel fluorescent-sensing films. In the strategy, a low-molecular-mass gelator (LMMG) with abundant self-assembly properties was employed for the creation of a network thin film on a glass substrate surface, and then a fluorescence-active compound, of which a specific structure was introduced so that it can be physically but selectively adsorbed by the preformed thin film, was dip coated on the preformed thin film. In this way, a stable and fluorescent-active film with limited thickness can be created. Sensing performance studies demonstrated that the film developed via this strategy is superior to the one developed by the direct coating of the fluorescent-active compound onto a bare glass plate surface and it is also superior to the one prepared by the direct coating of the mixtures of this fluorescent-active compound and the LMMG used for the preparation of the preformed networks. This Article reports the details.

2. EXPERIMENTAL SECTION

2.1. Materials. Scheme S1 shows the structure of the LMMG, Chol-Ph-Chol, which was used for the creation of the substrate network (cf. Figure S1, Supporting Information). The details for the preparation of the compound were reported by us in a former publication.[24] The solvent, THF, was distilled over sodium in the presence of benzophenone under a N_2 atmosphere before use, and the other solvents were also pretreated with molecular sieves before use to remove trace water. The chemicals used in the interference test are aniline, phenol, benzoic acid, toluene, benzene, H_2SO_4, HNO_3, 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrophenol (PA), which were of analytical grade and were used directly without further purification. The water used throughout was doubly distilled.

2.2. Measurements and Characterization. The ^{1}H NMR data of the samples were collected on a Bruker AV 400 NMR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a KRATOS AXIS Ultra DLD photoelectron spectroscope. Melting points were determined on an X-5 Microscopic melting point meter (Beijing Tech Instrument). UV−vis absorption spectra were recorded on a spectrophotometer (Lambda 950, PerkinElmer). The high-resolution mass spectra (MS) were acquired in ESI positive mode using a Bruker maxi UHR-TOF mass spectrometer. Fluorescence measurements were performed at 16 °C on a time-correlated single-photon-counting fluorescence spectrometer (Edinburgh Instruments FLS 920). AFM measurements were conducted on a SOLVER P47 PRO system.

2.3. Synthesis of the Fluorescence-Active Compound. The fluorescence-active compound, CholG-3T-Py, was prepared using two formally reported compound as intermediates, 5″-(pyren-1-yl)-[2,2′:5′,2″-terthiophene]-5-carbaldehyde (Py-3T-CHO) and cholesteryl glycinate (CholG), which were synthesized and characterized in the same way as reported before (cf. Scheme 1a).[25,26] For the reaction of Py-3T-CHO with CholG, the procedure is as follows: CholG (2.66 g, 6.0 mmol) and 5 drops of glacial acetic acid were added to dry methanol (20 mL) under stirring and nitrogen purging. After that, a preprepared trichloromethane solution (50 mL) of Py-3T-CHO (1.43 g, 3.0 mmol) was added dropwise under stirring and a nitrogen atmosphere over 4 h followed by the addition of molecular sieves, and the system was then heated to reflux at 80 for 1 h. After the reaction, the solution became green under the illumination of UV light (365 nm). The reaction mixture was filtered, and the filtrate was evaporated to dryness. The solid obtained was washed with ethanol and dried under vacuum. In this way, CholG-3T-Py was obtained as a yellow powder (1.89 g, 71%). Melting point: 177.5−178.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.58−8.05 (m, 9H, pyrene), 7.34−7.30 (d, 3H, 3T), 7.21−7.16 (d, 3H, 3T), 5.38 (s, 1H, oxycyclohexyl), 4.69 (s, 1H, alkenyl), 4.35 (s, 2H, CH2CO), 3.50 (s, 1H, CHN), 2.37−0.68 (m, 46H, cholesteryl protons) (cf. Figure S2, Supporting Information). MS (ESI, m/z): $[M + H]^+$ calcd, 902.4099; found, 902.4085 (cf. Figure S3, Supporting Information).

2.4. Preparation of Chol-Ph-Chol-Based Network Films. For the present study, glass slides (0.9 × 2.5 cm^2) were chosen as the substrate because of their inertness to fluorescence emission. Before the preparation of the substrate networks, the glass wafers were thoroughly washed with ethanol and then treated with the piranha solution (30% H_2O_2/98% H_2SO_4, 3:7, v/v), which was adopted because of its strong oxidation property (*Caution: this solution must be handled with extreme*

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care). At the same time, a trichloromethane solution of the Chol-Ph-Chol (0.5%, g/mL) was prepared by heating in a dust-free container and was then slowly cooled to room temperature. A 30 μL sample of the Chol-Ph-Chol solution was dipped onto the pretreated glass-slide surface at room temperature, and the slide was then spun slowly and horizontally. Finally, the films as prepared were dried at room temperature in a dust-free oven for 1 h (Film 2).

2.5. Fabrications of Fluorescent Films. CholG-3T-Py was dissolved in acetone (100 μg/mL), and a defined amount (30 μL) of the solution was then dipped onto Film 2 prepared under slow spinning. The films as prepared were dried at room temperature in a dust-free oven for 1 h (Film 3). To be clear, the fabrication process is schematically shown in Scheme 1b. Furthermore, as a control, Film 1 was also prepared in which the fluorescence-active compound was directly coated on a clean glass-slide surface.

2.6. Sensing Performance Test. As an important industrial chemical, nitrobenzene (NB) has been widely used as a solvent as well as in the production of dye and medical intermediates, such as aniline and its relevant compounds.[27−29] At the same time, NB is also a hazardous compound because of its carcinogenicity and explosibility.[28,30,31] Moreover, NB also affects the central nervous systems of humans and animals via skin absorption and vapor inhalation, and it may produce fatigue, headache, vertigo, vomiting, general weakness, unconsciousness, coma, and so forth.[32] Therefore, the development of sensitive and selective NB sensors is of importance. This is why there have been so many papers published during the last few years that are relevant to the determination of NB in both the gaseous phase and solution state.[33,34] Considering the electron-rich property and the conjugated structure of the fluorophore, CholG-3T-Py, employed in the development of the present fluorescent films, the fluorescence-quenching effect of NB on the emission of the films tested was examined. The test was conducted in the way as described below. First, a film being tested was adhered to one inner-side of a quartz cell, the fluorescence emission spectrum of the film was recorded in the absence of NB, and the film was then inserted into a sealed vial, which was prefilled with NB vapor, for a period of time. Finally, the fluorescence emission of the film after the treatment was recorded again. This operation was repeated several times to obtain the fluorescence emission spectra at different exposure times. It should be noted that filter paper was preinserted into the vial to avoid the direct contact of the film with the liquid.

3. RESULTS AND DISCUSSION

3.1. Fluorescent Behaviors of CholG-3T-Py. The fluorescent spectra of CholG-3T-Py and relevant fluorescence-active compounds are shown in Figure 1. Their photophysical parameters are summarized in Table 1. Note that the parameters of 3T, Py-3T, and Py-3T-CHO are adopted from ref 25, which is a publication from our group. Compared with 3T, for the derivatives, the positions of the maximum excitations and emissions are all shifted to longer wavelengths, the Stoke's shifts of are all larger, and, furthermore, their fluorescence quantum yields are also significantly greater. These results may be attributed to the enlarged degree of conjugation, as discussed already in the ref 25. The introduction of a cholesteryl unit reversed the photophysical properties of its mother compound, Py-3T-CHO, to those of the original compound, Py-3T, as indicated by the data shown in Table and the phenomenon observed, which showed that the dichloromethane solution of the compound possesses a bright-green color when it is illuminated by ultraviolet light, a color strongly resembling that of Py-3T. Moreover, the fluorescence quantum yield is also reversed to that of Py-3T, a result attributable to the reduction of the aldehyde group of Py-3T-CHO.

3.2. Morphologies of the Substrate-Supported Films. As a typical low-molecular-mass gelator (LMMG), Chol-Ph-Chol was specifically chosen because it possesses the ability to gel a number of organic solvents and forms well-organized and uniform gel networks at room temperature.[24] For this reason, it is believed that the compound is suitable for building network films that can be used to support fluorescent-active compounds and to assist them in distributing smoothly on the substrate surface, which is a prerequisite for fabricating high-quality fluorescent films. Acetone was chosen as a solvent for CholG-3T-Py because of its ability to dissolve the fluorophore but not the LMMG, Chol-Ph-Chol, as well as its ease to evaporate. For these reasons, it is believed that this approach allows the morphologies of the substrate networks to be maximally maintained.

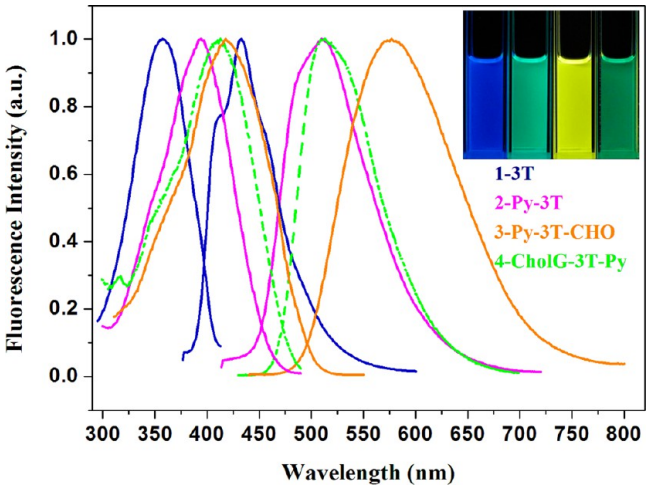

Figure 1. Normalized fluorescence excitation and emission spectra of the dichloromethane solutions of 3T, Py-3T, Py-3T-CHO, and CholG-3T-Py. The inset shows pictures of the solutions of the four compounds under UV light (λ = 365 nm).

As expected, with the utilization of the LMMG a uniform film with a rich network of structures was obtained, as evidenced by the AFM images shown in Figure 2b,b′. In Figure 2c,c′, it can be clearly seen that immobilization of CholG-3T-Py produces numerous nanoparticles on the substrate surface. Furthermore, it can be also seen that immobilization of the fluorophore does not significantly change the morphology of the Chol-Ph-Chol-based substrate networks. On the contrary, the morphology of Film 1, which is a control for Film 3, is characterized by randomly distributed aggregates with different sizes and shapes of the fluorescent compound (cf. Figure 2a,a′). These results confirm that introduction of the LMMG-based gel network as a substrate film does help the fluorescent compound distribute on the glass-slide surface equally and smoothly, which lays, no doubt, the foundation for improving their sensing performance. The equal distribution of the fluorophore on the substrate surface may be attributed to the specific interaction between the molecules of the substrate films and those of the fluorescent compound because both of them possess a cholesteryl structure, which is recognized as a typical supramolecular building block because of van der Walls interactions among the molecules.[35] It is this interaction that may inhibit the diffusion of the molecules of CholG-3T-Py on the substrate network surface when they are adsorbed. For the film (Film 1) with the bare glass slide as the substrate, the situation will be different. In this case, the van der Walls interaction among the molecules of CholG-3T-Py makes them aggregate, and, as a result, there appear various aggregates of different morphologies and sizes on the substrate surface (cf. Figure 2a,a′).

3.3. Fluorescence Behaviors of Film 3 in Toluene Vapor. Figure 3 shows the fluorescence emission spectra of Film

Table 1. Optical Properties of the Dichloromethane Solutions of 3T, Py-3T, Py-3T-CHO, and CholG-3T-Py

compounds	excitation (nm)	emission (nm)	Stokes' shift (nm)	abs (nm)	ε (L/mol·cm)	φ_F
3T	357	433	76	354	21 600	0.22−0.26
Py-3T	394	510	116	394	28 100	0.59−0.62
Py-3T-CHO	419	578	159	422	24 100	0.28−0.30
CholG-3T-Py	410	522	112	415	19 900	0.52−0.58

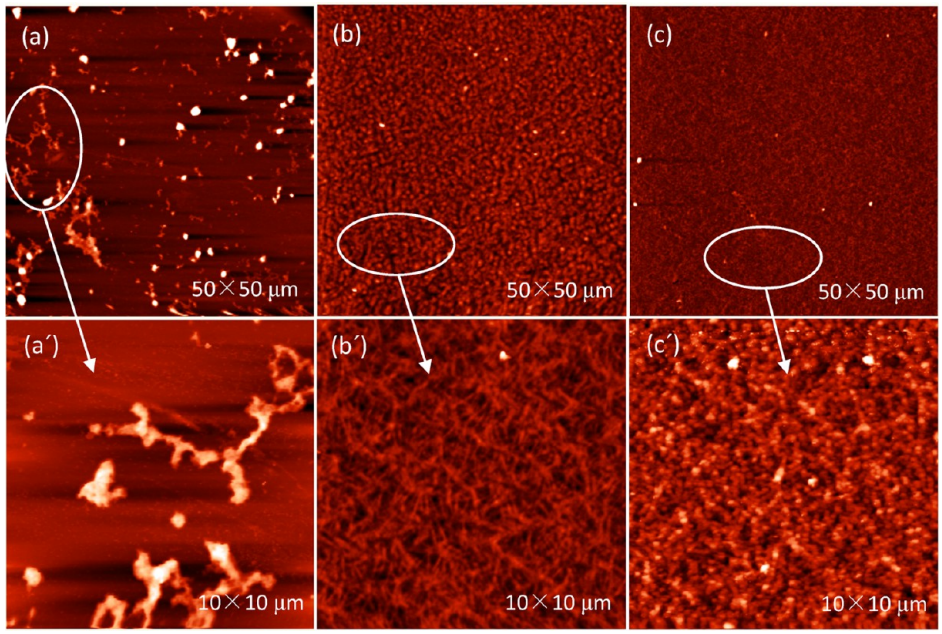

Figure 2. AFM images of Film 1 (a), Film 2 (b), and Film 3 (c) as well as their corresponding magnified images.

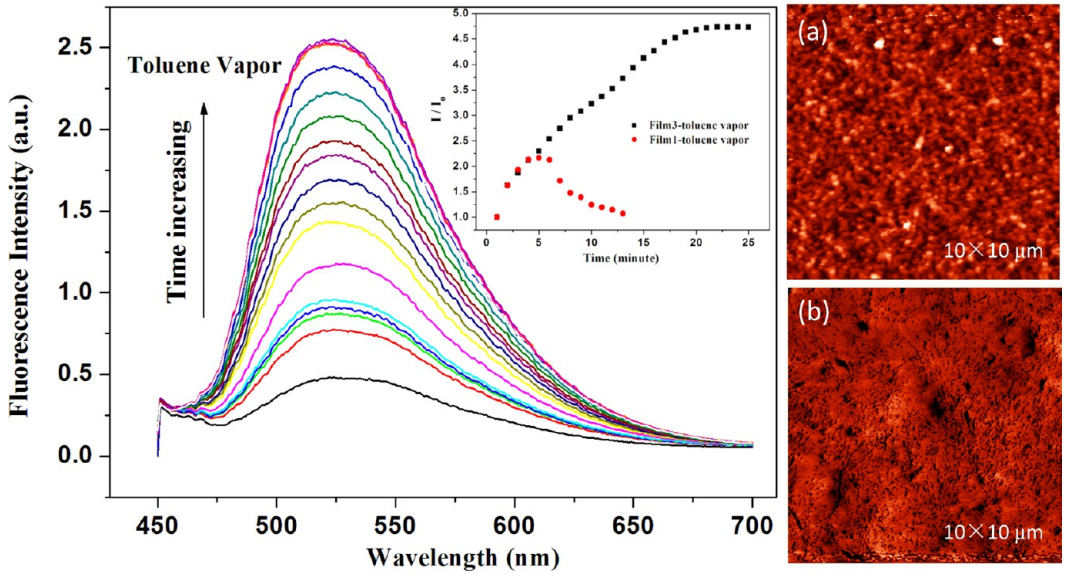

Figure 3. Fluorescence emission spectra of Film 3 recorded at different exposure times in toluene vapor. The inset shows the plots of Film 1 and Film 3 upon exposure in toluene vapor, respectively. AFM images of the original Film 3 (a) and the film after toluene treatment (Film 4; b).

3 that were recorded at different exposure times of the film to toluene vapor as well as the AFM images of the original film and the film after the treatment. It can be seen that Film 3 is sensitive to the presence of toluene, where it responds by increasing its fluorescent emission. However, the emission cannot be reversed after removing the solvent absorbed. The reason for this unreversible response can be attributed to the change of the film structure, as shown in their AFM images (cf. AFM images a and b of Figure 3). As for the sensitization of the fluorescence emission of the original film, the observation might be rationalized by considering the commonly encountered phenomenon that is the aggregation-induced (fluorescence) quenching (AIQ) effect.[36,37] As revealed in the AFM measurements, the molecules of CholG-3T-Py aggregated into nanoparticles on the substrate network surface, which may explain why the film emits weakly, a reflection of AIQ effect.[38,39] Upon

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absorption of a good solvent such as toluene, the particles might be slightly swelled, which makes the molecules inside go far away from each other and more widely distribute on the substrate network surface, resulting in partial blocking of the AIQ effect that rationalizes why the emission increases along with absorption of the solvent vapor. It is to be noted that in this case the molecules of Chol-Ph-Chol within the substrate networks may function as "solvent" molecules, assisting the uniform distribution of the fluorescent molecules, which is a benefit to enhancing the fluorescence emission. The rationalization raised above was confirmed by other solvent-effect studies. The results are provided in Figure S4 (Supporting Information). These results reveal that the solvents that enhance the fluorescence emission of the film are good solvents of the fluorescent compound, but others are poor solvents of the fluorescent compound.

For comparison, a similar activation experiment was also conducted for Film 1, and the result is shown in the inset of Figure 3. It can be seen that, different from that of Film 3, the fluorescence emission of this film cannot be significantly enhanced even though the exposure does induce enhancing at the beginning. Furthermore, the enhanced emission is not stable, and longer exposure makes the emission decrease rather than become further enhanced or stabilized as was seen for Film 3 (cf. the inset of Figure 3). For an additional comparison, the fluorescence excitation and emission spectra of Film 1, Film 2, Film 3, and Film 4 are collectively depicted in Figure 4. The inset

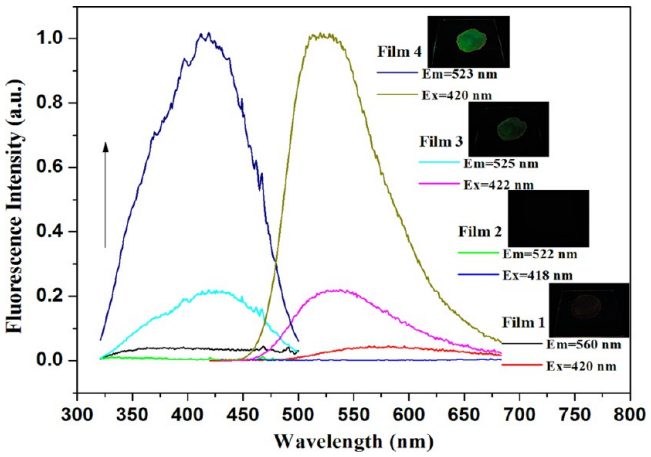

Figure 4. Fluorescence excitation and emission spectra of Film 1, Film 2, Film 3, and Film 4. The inset shows the pictures of the four films under UV light (λ = 365 nm).

shows the images of the three films under UV light illumination. Clearly, the introduction of the supporting networks and the subsequent solvent treatment significantly enhanced the fluorescence emission of the CholG-3T-Py-functionalized film, laying the foundation for its sensing applications.

3.4. Nitrobenzene Sensing in Vapor Phase. NB is a well-known electron-deficient compound and thereby it is usually used as an effective quencher of the fluorescence emission of most aromatic fluorophores.[40] Because the fluorescence emission of CholG-3T-Py comes from the 3T-Py unit within it and because this structure is a simple extension of the conjugated structure of Py, the response of Film 4 to NB in the vapor phase was systematically examined. It was found that NB exhibits a significant quenching effect on the emission of the film. The results are shown in Figure 5. The data reveal that a 60 s exposure

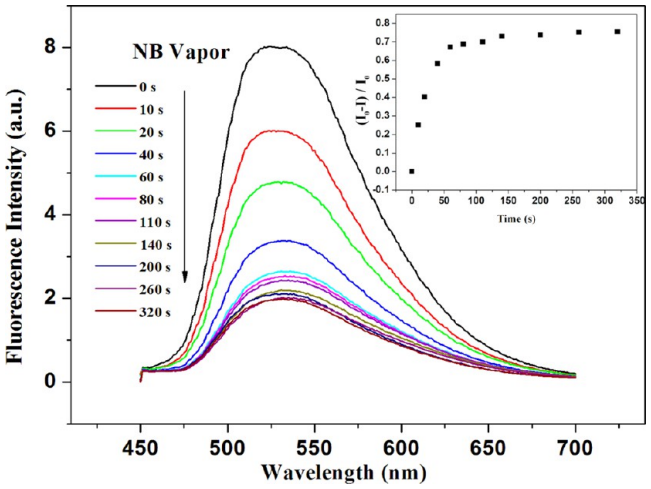

Figure 5. Time-dependent fluorescence emission spectra of the sensing film upon exposure to NB vapor (16°C) (from top to bottom: 0, 10, 20, 40, 60, 80, 110, 140, 200, 260, 320 s) and the plot of the fluorescence quenching efficiency (%) against time (inset).

resulted in a 70% reduction of the emission. However, further exposure has little effect on the fluorescence emission of the film. To be clear, a plot of the emission intensity at the maximum emission wavelength of the film against the exposure time is provided as an inset in Figure 5.

3.5. Selectivity of the NB Sensing. To examine the selectivity of the response of Film 4 to NB, three categories of commonly found chemicals were adopted to conduct the test. The first series included aniline, phenol, benzoic acid, and toluene, which are also monosubstituted benzene derivatives, the second series included the compounds that are used in the production of NB, such as benzene, H_2SO_4 (65%), HNO_3 (5%), and water, and the third series included TNT, DNT, and PA, which are the byproducts of NB. The interfering test was conducted in the same way as that for the examination of the response of the film to NB vapor. Interestingly, no significant change in the fluorescence emission of the film was observed upon exposing the film to the vapor of any of the aforementioned compounds. The results are shown in Figure 6. On the basis of these results, it may be concluded that the sensing of the film to NB is selective. The selectivity may be understood by considering the differences in the vapor pressure of these compounds as well as the binding ability of the film to them. It is known that as a quencher the vapor pressure of NB is significantly greater than those of the other organic quenchers tested such as TNT, DNT,

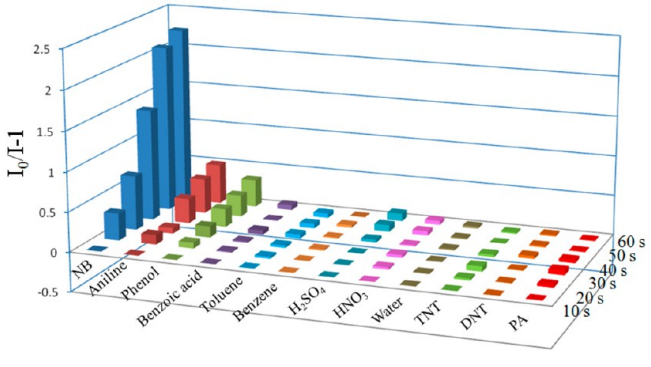

Figure 6. Sensing performances of Film 4 to different chemicals in the vapor phase at different exposure times ($\lambda_{ex}/\lambda_{em}$ = 422/525 nm).

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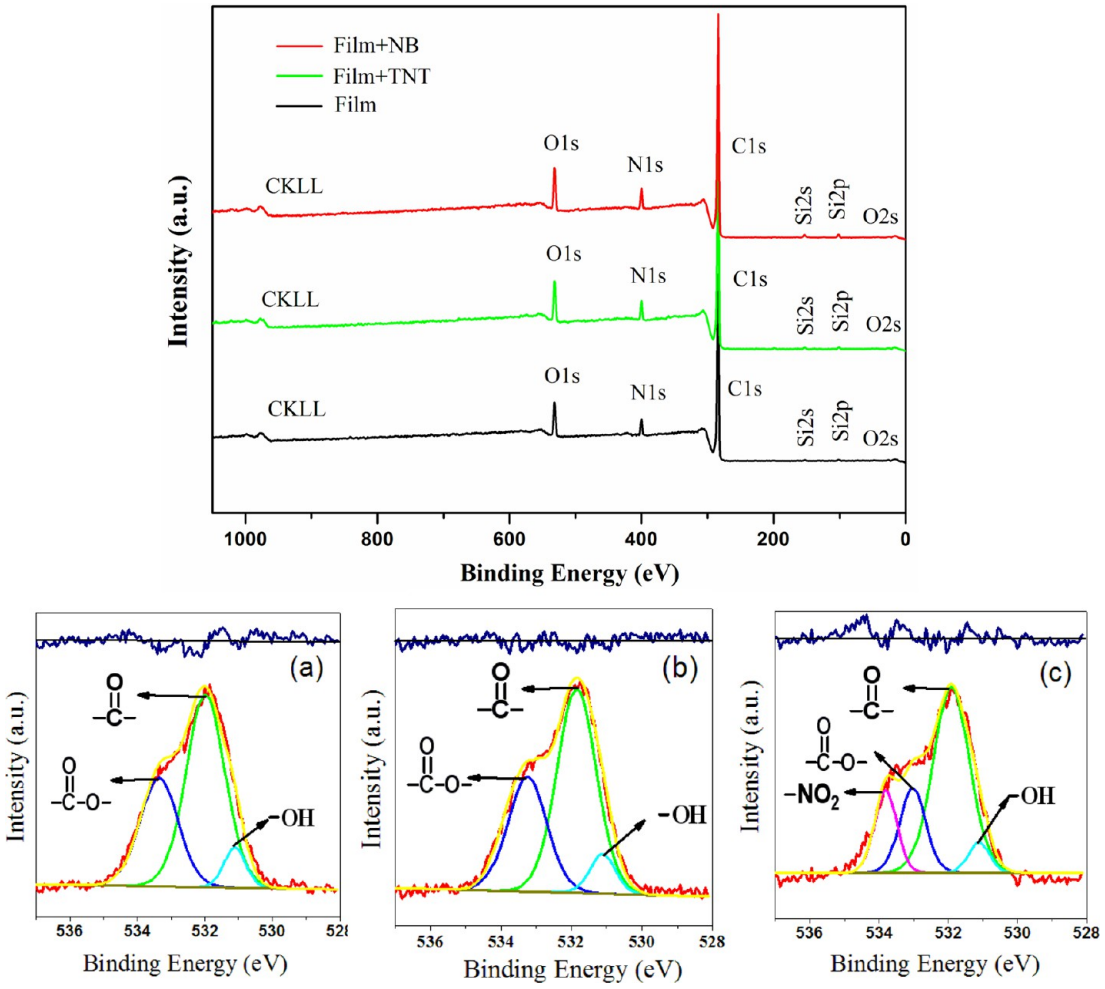

Figure 7. XPS trace of Film 4 with and without treatment with TNT or NB. O 1s signal and ACM simulation results of Film 4 (a) untreated and pretreated with (b) TNT and (c) NB.

PA, and so forth.[25] Therefore, it is easier for NB to reach the organic layer of the film. Furthermore, the hydrophobic nature of NB and that of the sensing layer of the film that may allow the film to possess a specific affinity for NB, something like the enrichment effect, which was proposed and discussed by us before.[14,41] This explanation was partially supported by the results from X-ray photoelectron spectroscopy (XPS) measurements. Figure 7 depicts the XPS trace of Film 4 and those of the same film pre-treated with TNT or NB as well as the simulation results by using a computational multipeak resolution method (ACM). Careful study of the high-resolution XPS traces suggests that the intensities of the O 1s signal (Figure 7a–c) are dependent on the nature of the compounds that were employed for the treatment of the film. It can be clearly seen that the signal of the oxygen atom in the nitro group was observed after treatment with NB and that the contribution to the signal of O 1s reaches 13%. In contrast, for the film treated with TNT no significant contribution of the O 1s signal from the nitro group was observed, which is all the more striking because of the fact that the number of nitro groups in TNT is three times greater than that of NB. This may explain why NB is much more efficient at quenching the fluorescence emission of the film than the other compounds. Additional fluorescence lifetime measurements also support the tentative conclusion of the static binding of the film to NB, as shown in Figure S5. The results demonstrate clearly that absorption of NB does not significantly change the fluorescence lifetime of CholG-3T-Py that was adsorbed on the substrate network surface, which is evidence to support the static quenching of NB on the fluorescence emission of the film. In other words, the molecules of NB were statically bound by the fluorophore molecules immobilized on the substrate surface.

3.6. Reversibility of the Sensing Process. Reversibility is another crucial criterion for the practical use of a sensing film. Herein, the reversibility of the film to NB was examined in the following way. The film in an airtight cell was put in the sample holder of a fluorometer, the fluorescence emission of the film was measured, 1 mL of NB vapor was injected at room temperature, and the fluorescence emission was then recorded again. This process was repeated three times so that 4 mL of the NB vapor was injected in total. After these measurements, the cell was purged with air for 5 min, and the fluorescence emission of the system was then measured again. The entire quenching and recovery process was repeated at least six times. The results are shown in Figure 8. It is clear that the response of the film to NB vapor is fully reversible after the first cycle of the test.

CONCLUSIONS

As an example of LMMGs, Chol-Ph-Chol was used for the first time to build, via a molecular-gel strategy, networked micro- and nanostructures on a glass-slide surface. The networks prepared were employed to support a specifically designed fluorophore, CholG-3T-Py, to create fluorescent films that may possess the

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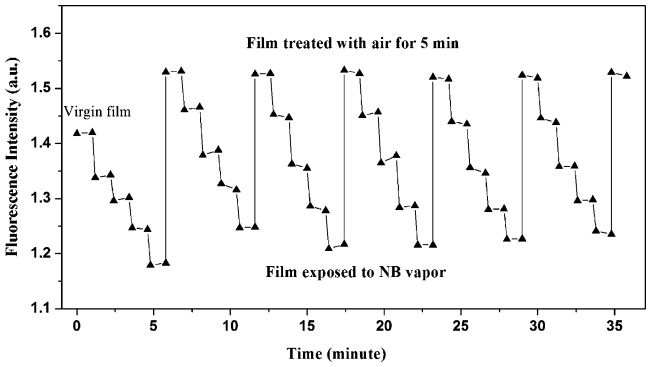

Figure 8. Reversibility of the response of Film 4 to the presence of NB vapor (0, 1, 2, 3, and 4 mL, respectively) ($\lambda_{ex}/\lambda_{em}$ = 422/525 nm).

combined advantages of routine coating-based physical films and those of SAMs-based chemical films. As demonstrated, the gel networks provide not only a support to assist the equal distribution of the fluorophore on the substrate surface but also generate the enrichment effect to accumulate the analyte, such as NB, onto the sensing layer. It is believed that the present effort has created a new strategy to design and fabricate novel fluorescent films with superior performance and has broadened the application of LMMGs-based molecular gels.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and MS of CholG-3T-Py, molecular structure of the LMMG, fluorescence emission spectra of film 3 in different solvent's vapor, and fluorescence decay of the films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Grynkiewicz, G.; Poenie, M.; Tsien, R. Y. *J. Biol. Chem.* **1985**, *260*, 3440−3450.
(2) Tsien, R. Y. *Biochemistry* **1980**, *19*, 2396−2404.
(3) Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Lett.* **2003**, *5*, 4065−4068.
(4) Malashikhin, S. A.; Baldridge, K. K.; Finney, N. S. *Org. Lett.* **2010**, *12*, 940−943.
(5) Li, X.; Qian, S.; He, Q.; Yang, B.; Li, J.; Hu, Y. *Org. Biomol. Chem.* **2010**, *8*, 3627−3630.
(6) Yu, F. B.; Li, P.; Song, P.; Wang, B. S.; Zhao, J. Z.; Han, K. L. *Chem. Commun.* **2012**, *48*, 2852−2854.
(7) Kim, S. K.; Lee, D. H.; Hog, J.; Yoon, J. *Acc. Chem. Res.* **2009**, *42*, 23−31.
(8) Regueiro-Figueroa, M.; Djanashvili, K.; Esteban-Gomez, D.; Chauvin, T.; Tóth, É.; de Blas, A.; Rodríguez-Blas, T.; Platas-Iglesias, C. *Inorg. Chem.* **2010**, *49*, 4212−4223.
(9) Aragay, G.; Pino, F.; Merkoci, A. *Chem. Rev.* **2012**, *112*, 5317−5338.
(10) Zhang, K.; Mei, Q.; Guan, G.; Liu, B.; Wang, S.; Zhang, Z. *Anal. Chem.* **2010**, *82*, 9579−9586.
(11) Freeman, R.; Willner, I. *Nano Lett.* **2009**, *9*, 322−326.
(12) He, G.; Zhang, G. F.; Lü, F. T.; Fang, Y. *Chem. Mater.* **2009**, *21*, 1494−1499.
(13) Zheng, Y.; Orbulescu, J.; Ji, X.; Andreopoulos, F. M.; Pham, S. M.; Leblanc, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 2680−2686.
(14) Ding, L. P.; Fang, Y. *Chem. Soc. Rev.* **2010**, *39*, 4258−4273.
(15) Basabe-Desmonts, L.; Reinhoudt, D. N.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 993−1017.
(16) Rudzinski, M.; Young, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 1723−1727.
(17) He, G.; Yan, N.; Yang, J. Y.; Wang, H. Y.; Ding, L. P.; Yin, S. W.; Fang, Y. *Macromolecules* **2011**, *44*, 4759−4766.
(18) Liu, Y.; Mills, R. C.; Boncella, J. M.; Schanze, K. S. *Langmuir* **2001**, *17*, 7452−7455.
(19) Kartha, K. K.; Babu, S. S.; Srinivasan, S.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2012**, *134*, 4834−4841.
(20) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864−1187.
(21) Yang, Y. F.; Wang, H. M.; Su, K.; Long, Y.Y.; Peng, Z.; Li, N.; Liu, F. *J. Mater. Chem.* **2011**, *21*, 11895−11900.
(22) Salinas, Y.; Martínez-Máñez, R.; Marcos, M. D.; Sancenón, F.; Costero, A. M.; Parra, M.; Gil, S. *Chem. Soc. Rev.* **2012**, *41*, 1261−1296.
(23) Svobodová, H.; Noponen, V.; Kolehmainen, E.; Sievänen, E. *RSC Adv.* **2012**, *2*, 4985−5007.
(24) Xue, M.; Gao, D.; Liu, K. Q.; Peng, J. X.; Fang, Y. *Tetrahedron* **2009**, *65*, 3369−3377.
(25) Liu, T. H.; Ding, L. P.; Zhao, K. R.; Wang, W. L.; Fang, Y. *J. Mater. Chem.* **2012**, *22*, 1069−1077.
(26) Li, Y. G.; Liu, K. Q.; Liu, J.; Peng, J. X.; Feng, X. L.; Fang, Y. *Langmuir* **2006**, *22*, 7016−7020.
(27) Rodriguez, M.; Timokhin, V.; Michl, F.; Contreras, S.; Gimenez, J.; Esplugas, S. *Catal. Today* **2002**, *76*, 291−300.
(28) Li, Y. P.; Cao, H. B.; Liu, C. M.; Zhang, Y. *J. Hazard. Mater.* **2007**, *148*, 158−163.
(29) Contreras, S.; Rodriguez, M.; Chamarro, E.; Esplugas, S. *J. Photochem. Photobiol., A* **2001**, *142*, 79−83.
(30) Wang, A. J.; Cheng, H. Y.; Liang, B.; Ren, N. Q.; Cui, D.; Lin, N.; Kim, B. H.; Rabaey, K. *Environ. Sci. Technol.* **2011**, *45*, 10186−10193.
(31) Li, H. L.; Cheng, Y.; Wang, H. F.; Sun, H. F.; Liu, Y. F.; Liu, K. X.; Peng, S. X. *Appl. Radiat. Isot.* **2003**, *58*, 291−298.
(32) Bhatkhande, D. S.; Pangarkar, V. G.; Beenackers, A. A. C. M. *Water Res.* **2003**, *37*, 1223−1230.
(33) Wang, H.; Xu, X. H.; Kojtari, A.; Ji, H. F. *J. Phys. Chem. C* **2011**, *115*, 20091−20096.
(34) Zhang, Y.; He, G.; Liu, T. H.; Yang, M. N.; Ding, L. P.; Fang, Y. *Sens. Lett.* **2009**, *7*, 1141−1146.
(35) Murata, K.; Aoki, M.; Suzuki, T.; Hanada, T.; Kawabata, H.; Komori, T.; Oseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664−6674.
(36) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 756−768.
(37) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121−128.
(38) Luo, J. D.; Xie, Z. L.; Lam, W. Y. J.; Cheng, L.; Chen, H.Y.; Qiu, C. F.; Kwok, H. S.; Zhan, X. W.; Liu, Y. Q.; Zhu, D. B.; Tang, B. Z. *Chem. Commun.* **2001**, 1740−1741.
(39) Yuan, W. Z.; Lu, P.; Chen, S. M.; Lam, J. W. Y.; Wang, Z. M.; Liu, Y.; Kwok, H. S.; Ma, Y. G.; Tang, B. Z. *Adv. Mater.* **2010**, *22*, 2159−2163.
(40) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339−1386.
(41) Lü, F.T.; Gao, L.N.; Ding, L.P.; Jiang, L.L.; Fang, Y. *Langmuir* **2006**, *22*, 841−845.