Terthiophene Derivatives of Cholesterol-Based Molecular Gels and Their Sensing Applications

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ABSTRACT: Three novel terthiophene derivatives of cholesterol (TtGC, TtLPC, TtDPC), of which the two building blocks are linked by a structure of glycine, t-phenylalanine, or l-phenylalanine, respectively, were designed and prepared, and their gelation behaviors in 26 liquids were tested. It was demonstrated that the compounds show different gelation abilities with the variation of the linker structures even though the variation is small. FTIR, 1H NMR, and UV–vis measurements revealed that intermolecular hydrogen bonding and van der Waals interaction are the main driving forces for the gel formation. As for TtDPC, CD and AFM measurements revealed that it aggregated into chiral structures of left-helical feature in benzene. Importantly, the morphologies of the gel networks could be subtly adjusted via alteration of the gelator concentration. Considering the brightness in fluorescence and the unique micro/nanostructures of the gel networks, a fluorescent film (film 1) was fabricated by simple dip-coating of TtDPC/benzene solution (before gelation) onto a glass plate surface. Fluorescent studies demonstrated that the film is photochemically unstable. Two hours UV irradiation of the film results in film 2, which is almost fluorescent silence. However, the presence of HAc vapor or the vapors of some other volatile organic liquids induces new fluorescence emission, laying the foundation for creating a turn-on type fluorescent sensor of the organic vapors. Furthermore, as a new type of low-molecular-mass gelators (LMMGs), of which oligothiophene was employed as a building block, the present study has provided a possibility to explore the photo-/electronic applications of oligothiophenes via a molecular gel strategy.

INTRODUCTION

Gels, as a known kind of soft matter, have received increasing attention during the past few decades due to their potential applications such as purification,1 controlled release,2 new mediums for preparation,3 and mild separation,4 etc. However, ribbons, or other morphologies.5 molecules of a gelator could self-assemble into ent from others. This is because among these gels, the low-molecular-mass compound-based molecular gels are di
ergistics and even the high-tech applications.10,11 As we know, the supramolecular organization of organic molecules with functional properties is promising for application in nanoscience and nanotechnology. For example, introduction of a π-conjugated system into the gel networks resulted in utilization of them in the fabrication of optoelectronic nanodevices,12,13 which may be functioning as light-emitting diodes (LEDs),14 field-effect transistors (FETs),15 solar cells,15 or fluorescent sensors16 etc. Fluorescence chemosensors have experienced a rapid development during the past several decades because of their high sensitivity and great selectivity.16,17 Generally speaking, the fabrication methods of fluorescent film such as self-assembled monolayers (SAMs),17 dipping coating or spin-coating through solution,18–20 and template method21 have been focused on for many years. Unlike routine chemosensors reported, however, fluorescence chemosensors based on self-assembled structures of fluorescence compounds are superior because the sensors as prepared possess structures with not only great surface area but also ideal porosity, which is favorable for target molecules to diffuse within them.16,22,23 Recently, Ajayaghosh and co-workers reported a molecular gel based explosive fluorescent chemosensor, which demonstrates unprecedented attogram detection sensitivity.24 Similarly, Bhalla and colleagues demonstrated a super-sensitive picric acid fluorescent chemosensor, which was also taking advantage of the unique molecular packing of an organogelator and the associated photophysical properties.25

As mentioned already, for molecular gels based fluorescent chemosensors, the low-molecular-mass gelators (LMMGs) employed must be fluorescence active. In other words, the LMMGs must contain a fluorescent structure. In the present

Received: December 5, 2013
Revised: January 19, 2014
Published: January 20, 2014
work, terthiophene, a typical oligothiophene, was chosen. This is because (1) oligothiophenes possess unique optical and electronic properties and have been widely exploited in preparation for FETs, LEDs, and solar cells due to their superior performances in electron conduction among molecules, the so-called molecular wire effect, and electron migration crossing molecular chains; (2) compared to polythiophenes, oligothiophenes are easier to be modified and synthesized; and (3) fluorescent chemosensors based on LMMGs with oligothiophenes as building blocks have not been reported until now. Accordingly, three terthiophene derivatives of cholesterol (TtGC, TtLPC, TtDPC) with glycine, L-phenylalanine, or D-phenylalanine as the main component of the linkers were designed and synthesized, of which cholesterol was chosen due to its superior ability to form LMMGs. The gelation behaviors of the compounds in 26 liquids were tested, and the relevant gelling mechanisms such as evolution of the gel networks and the molecular interactions which are responsible for driving the gel network formation were systematically examined. It was found that TtDPC gels benzene efficiently and forms unique but variable aggregates in the solvent. Based on TtDPC/benzene gel, a turn-on type fluorescent chemosensor for HAc and other volatile organic liquids was developed. This paper reports the details.

## EXPERIMENTAL SECTION

**Gelation Test.** A known weight (0.025 g) of a given gelator and a measured volume (1 mL) of a given liquid were put in a sealed test tube, and the system was placed at room temperature. The state was evaluated by the “stable to inversion of a test tube” method. Gels obtained after placement at room temperature were referred to as “G”*; some were transparent (TG)*. If the result was negative, the test tube was heated until the solid was dissolved completely, and then the solution was cooled slowly to room temperature in air and left for 12 h at the ambient conditions. After that, the test tube was inverted to observe the state. A gel, which represented a positive test if the flow test was negative, was denoted as “G”. “TG” was related with a transparent gel. In some cases, a mixture of gel and solution was referred to as “PG” (partial gel). Some systems in which only solution remained until the end of the tests were denoted as “S” (solution). For systems, in which heating resulted in dissolution but cooling was accompanied by precipitation, they were referred to as “P” (precipitation). Systems in which the gelator could not be dissolved even at the boiling point of a liquid were denoted as “F” (insoluble). In a few cases, some systems looked like turbid solutions, and they were referred to as “Tus”.

**Scanning Electron Microscopy (SEM) Measurements.** SEM images of xerogels were taken on a Quanta 200 scanning electron microscopy spectrometer (Philips-FEI). The accelerating voltage was 20 kV, and the emission current was 10 mA. Xerogels for the measurement were prepared by freezing gels in liquid nitrogen and then dried at ambient condition. After that, the glass plate surface, and AFM measurements were conducted on a SCD 005 cool sputter coater (Bal-Tec) at 30 mA and 20 kV, and the emission current was 10 mA. Xerogels for the measurement were prepared by freezing gels in liquid nitrogen and then dried at ambient condition. After that, the test sample was prepared by placing a freeze-dried gel of TtDPC or powder directly onto a glass sample holder.

**Fluorescence Measurements.** 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.

**Preparation of Three Novel Gelators.** Details of the synthesis and characterization of the three terthiophene derivatives of cholesterol are described in the Supporting Information.

## RESULTS AND DISCUSSION

**Gelation Properties of the Compounds.** The gelation properties of the terthiophene derivatives of cholesterol, TtGC, TtLPC, and TtDPC (Scheme 1) in 26 different liquids have been evaluated at a standard concentration of 2.5% (w/v), and the results are summarized in Table 1. With reference to the table, it is seen that there are 25 gels among 78 combinations. In the 25 gels, the contribution of TtGC is only 4; the corresponding liquids are n-decanol, benzene, acetone, and acetic acid. Compared with TtGC, TtLPC and TtDPC are more effective gelators, which gel 11 and 10 of the tested liquids, respectively. Moreover, they gel most alcohol liquids under test, but TtGC gels only one alcohol liquid that is
decanol. Clearly, the structure of the linkers connecting the cholesteryl moiety and the terthiophene unit in the LMMGs as prepared is crucial for determining the gelation properties of the final compounds, and furthermore, introduction of an aromatic structure seems favorable for enhancing the gelation abilities of the compounds.

Further reference to Table 1 reveals that TtLPC and TtDPC are versatile gelators because they gel not only benzene-like nonpolar liquids but also alcohol-like polar liquids. However, the gelation behavior of TtLPC is different from that of TtDPC. In particular, TtLPC gels xylene at room temperature without the need of heating and cooling treatment. As for the gelation rate, gels with TtDPC as a gelator form more quickly, and these gels are more stable than the corresponding gels with TtLPC as a gelator. Therefore, it is clearly demonstrated that a subtle change or vibration in the structure of the linker alters the gelling abilities of the terthiophene derivatives of cholesterol significantly.

**Morphology Studies.** The network structures of the gelators in the gels were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements. To make a comparison of the aggregation behaviors of TtGC, TtLPC, and TtDPC, their benzene gels (2.5%, w/v) were taken as examples. The SEM pictures of them are shown in Figure 1a–c. As expected, the microstructures of the xerogels from them are very different from each other, indicating directly that the linker structure and spatial configuration shows great effect to the aggregation of the compounds even though their main building blocks are the same. Further reference to the pictures reveals that the morphologies of TtGC and TtLPC xerogels are similar to each other, and they both display beehive-like structures even though the one from TtLPC is more complete. Moreover, the xerogel from TtDPC takes a prism-like structure, which is obviously different from the microstructures from TtGC or TtLPC.

Furthermore, the self-assembling formation process of the gel networks was also explored through the studies of the AFM or SEM images of the corresponding xerogels, in which TtDPC/benzene was chosen as an example system, and the gelator concentrations varied from 0.1% to 2.5% (w/v, Figures 1d,e,f,c). It is clearly seen that with increasing the concentration of the gelator in the gels, the morphology of the gel networks varies from fibers with some sheets, to sheets with some fibers, to a homogenous gel.

### Table 1. Gelation Properties of the Three Compounds in 26 Liquids (2.5%, w/v)

<table>
<thead>
<tr>
<th>solvents</th>
<th>TtGC</th>
<th>TtLPC</th>
<th>TtDPC</th>
<th>solvents</th>
<th>TtGC</th>
<th>TtLPC</th>
<th>TtDPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>octane</td>
<td>I</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>ethanol</td>
<td>I</td>
<td>I</td>
<td>nonane</td>
<td>I</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>n-propanol</td>
<td>I</td>
<td>G (1.40)</td>
<td>I</td>
<td>decane</td>
<td>I</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>n-butanol</td>
<td>P</td>
<td>G (1.45)</td>
<td>I</td>
<td>kerosene</td>
<td>PG</td>
<td>PG</td>
<td>P</td>
</tr>
<tr>
<td>n-pentanol</td>
<td>P</td>
<td>G (1.44)</td>
<td>G (1.59)</td>
<td>benzene</td>
<td>TG (2.31)</td>
<td>PG</td>
<td>G (2.22)</td>
</tr>
<tr>
<td>n-hexanol</td>
<td>P</td>
<td>G (1.47)</td>
<td>G (1.66)</td>
<td>toluene</td>
<td>P</td>
<td>TG (2.15)</td>
<td>PG</td>
</tr>
<tr>
<td>n-heptanol</td>
<td>P</td>
<td>G (1.43)</td>
<td>G (1.64)</td>
<td>xylene</td>
<td>P</td>
<td>TG* (2.17)</td>
<td>TuS</td>
</tr>
<tr>
<td>n-octanol</td>
<td>P</td>
<td>G (1.46)</td>
<td>G (1.67)</td>
<td>CCl₄</td>
<td>P</td>
<td>TG (--)</td>
<td>P</td>
</tr>
<tr>
<td>n-nonanol</td>
<td>P</td>
<td>G (1.45)</td>
<td>G (1.65)</td>
<td>ethyl acetate</td>
<td>P</td>
<td>P</td>
<td>G</td>
</tr>
<tr>
<td>n-decanol</td>
<td>G (2.01)</td>
<td>G (1.42)</td>
<td>G (1.64)</td>
<td>acetone</td>
<td>G (--)</td>
<td>P</td>
<td>TG (--)</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>I</td>
<td>I</td>
<td>TG (--)</td>
<td>DMSO</td>
<td>P</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>heptane</td>
<td>I</td>
<td>I</td>
<td>TG (--)</td>
<td>DMF</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>hexane</td>
<td>I</td>
<td>I</td>
<td>acetic acid</td>
<td>G (--)</td>
<td>TuS</td>
<td>I</td>
<td></td>
</tr>
</tbody>
</table>

*a*Concentration of gelator: 2.5% (w/v). G: gel (G*: gel forming at ambient without heating); TG: transparent gel; PG: partial gel; TuS: turbid solution; P: precipitation; S: solution; I: insoluble when heated. The number in parentheses is the CGC of the system (%, w/v).
and then to sheets with tendons inside, and finally to rod-like structures. Further studies with even lower concentration of the gelator (0.05%, w/v) as an example sample showed that the fiber-like structures shown in Figure 1d comes from even smaller aggregates with discontinuous, short and twisted structures (Figure 2). The uniqueness in structure, the insolubility in water, and the activity in fluorescence emission of the TtDPC networks from its benzene gel may lay the foundation for finding its uses in sensing. However, before any attempt in application was initiated, the detailed structures of the gel networks need to be clarified.

**1H NMR and FTIR Studies.** It is well-known that physical gels are based on noncovalent interactions which usually lead to reversible gel-to-sol phase transition. Intermolecular hydrogen bonding is one of various noncovalent interactions and may play a crucial role in the formation of our gel systems considering the structures of our gelators. 1H NMR spectroscopy is an effective approach to confirm the hydrogen-bonding formation during the gelation process. Accordingly, temperature-dependent 1H NMR studies of the TtDPC/C6D6 gel system (1%, w/v) were conducted, and the results are presented in Figure 3a. It is clearly seen that the 1H NMR signal of the amide proton shifted from 6.67 to 6.60 ppm and then to 6.57 ppm with the temperature increasing from 298 to 308 K and then to 318 K, indicating clearly that hydrogen-bonding interaction definitely exists. To make sure if the hydrogen bonding originated intermolecularly or intramolecularly, concentration-dependent 1H NMR spectroscopy measurements were also conducted, and the results are shown in Figure 3b. Referring to the spectra shown in the figure, it is seen that the N–H proton signal shifted from 6.55 to 6.59 ppm and then to 6.64 ppm with the concentration of the gelator increasing from 0.5% to 1.0% and then to 1.5% (w/v) at 298 K. This concentration-dependent variation indicates that the hydrogen bonding originates from intermolecular interactions. Similar phenomena could be found in TtGC and TtLPC gels, which are shown in Figures S1 and S2.

FTIR spectroscopy studies can also provide useful information for hydrogen-bonding formation. Accordingly, the FTIR spectra of the xerogel of TtDPC/benzene and the true solution of TtDPC in CDCl3 were recorded, and the results are shown in Figure S3A. As shown in the FTIR spectrum of TtDPC from its CDCl3 solution, it shows a broad band around 3390 cm$^{-1}$ and a sharp band at 1644 cm$^{-1}$ which can be assigned to the stretching and the bending vibrations of the N–H bond, respectively, and furthermore, the stretching vibration of the C=O double bond appeared at 1732 cm$^{-1}$. After gelation, however, the bands shifted to 3377, 1636, and 1729 cm$^{-1}$, respectively, further evidence to support that hydrogen bonding is one of the driving forces in the formation of the gel networks. Studies of other gel systems demonstrated similar results (Figure S3B,C).

**UV–vis and CD Spectroscopic Studies.** The existence of π-conjugated structures in the gelators may induce intermolecular π–π stacking which may be also helpful for the formation of the gel networks. UV–vis spectroscopy study is a useful technique to elucidate the interaction and even can be used to distinguish the interaction type, the aggregation mode (H- or J-type aggregate). Accordingly, concentration-dependent absorption spectra of the benzene solution of TtDBC were recorded, and the results are shown Figure S4a. It is seen from the spectra shown in the figure that the position of the maximum absorption does not change along with increasing the gelator concentration even though the absorption intensity changes. This is a result rather different from those reported in the literature,$^{33–35}$ indicating that there is no obvious π–π
interaction in the systems, at least within the concentration range studied. Studies of the systems with TtGC or TtLPC as gelators showed similar results (see Figure S4a,b). Without \( \pi-\pi \) interaction in the gel systems may be rationalized by considering that the van der Waals force between the cholesteryl units of the gelator and the intermolecular hydrogen bonding are dominating forces to maintain the gel networks, which may suppress the intermolecular \( \pi-\pi \) interactions between the thiophene structures and/or the phenyl rings of the gelator.

CD is a technique which can be used to study not only molecular chirality but also the chirality of supramolecular architectures. Therefore, the concentration-dependent CD spectra of the benzene solution of TtDPC were recorded in order to obtain additional information on the self-assembled structures of the gel networks. The results are presented in Figure 4a. It is obvious that the CD signal is silent in lowest concentration corresponding to the solution phase whereas in higher concentration the CD signal appears. These findings revealed that the molecules of the gelator aggregate into chiral structures in the self-assembling process. Upon further examination of the CD spectra shown in the figure, a strong negative Cotton effect is found at the position of the \( \pi-\pi^* \) band and the wavelength of zero-crossing (\( \theta = 0 \)) near to the absorption maximum (\( \lambda_{\text{max}} = 376 \) nm), suggesting that in gel phase cholesteryl moieties assembled in a chiral direction which enforces the oligothiophene, the chromophore, unit of TtDPC to arrange in an asymmetric manner, often helical.\(^{29-32,36}\) This assumption is consistent with the result from AFM studies (Figure 2) which shows that the aggregates took a left-hand helical structure. The conclusion was further verified through temperature-dependent CD measurements as those shown in Figure 4b.

**XRD Studies.** In order to elucidate the detailed packing mode of the gelator in gel networks at a molecular level, XRD measurements of the TtDPC powder and its xerogel from benzene were performed. The results are shown in Figure 5. It is seen that the XRD pattern is characterized by a group of reflection peaks, indicating that the tested samples are mixed crystals. This is because that from the XRD trace of the xerogel, it is found that the main peaks \( d \) values are 1.92, 1.44, 1.07, 0.93, 0.82, 0.70, 0.66, and 0.63 nm. Further analyzing the data, the \( d \) values can be classified into two groups. The \( d \) values of one group are 1.92, 1.44, 0.93, 0.82, 0.66, and 0.63 nm, respectively, corresponding to the ratio of 1: (1/\( \sqrt{2} \)): (1/2):(1/

\( \sqrt{3} \)):(1/\( \sqrt{8} \)):(1/3), and those of another group are 1.92, 1.07, 0.93, 0.70, and 0.63 nm, respectively, corresponding to the ratio of 1:(1/\( \sqrt{3} \)):(1/2):(1/\( \sqrt{7} \)):(1/3). The TtDPC powder also shows similar results. The findings indicate that TtDPC in gel state mainly assembled into both a cubic and a hexagonal phase.\(^{37,38}\) 1.92 nm is the basic distance which is close to half of the length of TtDPC dimer calculated from molecular dynamics simulation, of which two molecules are connected via hydrogen-bonding interaction.

On the basis of the results obtained via \(^1\)H NMR, FTIR, CD, UV–vis, SEM, AFM, and XRD measurements, a plausible gel formation process of TtDPC in benzene is proposed and illustrated in Scheme 2.

**Fluorescent Films and Their Sensing Applications.** Morphology studies confirmed that the molecular gels formed by the LMMGs as created originated from network formation of them via self-assembling pathway in suitable liquids. Considering the unique micro/nanostructures and the brightness in fluorescence emission, the TtDPC/benzene gel system with a gelator concentration of 0.15% (w/v) was chosen to fabricate a fluorescent film on a glass plate surface. Simple dipping of the gel system before gel forms results in a fluorescent film (film 1) possessing porous structures as revealed by AFM observation (Figure 6).

The fluorescence excitation and emission spectra of film 1 in air were recorded, and the normalized spectra are presented in

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**Figure 4.** Concentration dependence of the CD spectrum of TtDPC in benzene (concentration range 0.26–2.5 mM). Arrows indicate the direction of change with increasing concentration (a) and the temperature dependence of the CD spectrum of TtDPC in benzene (2.0 mM). Arrows indicate the direction of change with decreasing temperature (b).

**Figure 5.** XRD pattern of the xerogel from benzene and the powders of TtDPC. dx.doi.org/10.1021/la4046836 | Langmuir 2014, 30, 1257–1265
Figure 7a. It is clearly seen that the maximum excitation and emission wavelengths appear at 372 and 488 nm, respectively. It is to be noted, however, that the emission decreases along with increasing the scan number in air (Figure 7b), a phenomenon similar to that observed in oligothiophene functionalized fluorescent films, of which the single-layer chemistry approach was adopted.39 The observation can be ascribed to photochemical oxidation of the terthiophene moieties with oxygen as the oxidizer.39−41 This result was verified by XPS shown in Figures S5 and S6. Reference to the traces reveals that before irradiation the binding energies of S2p appear at 163.21 and 164.26 eV, respectively. After irradiation with UV light, however, the intensities of these signals decrease, and new peaks at 168.01 and 169.16 eV appear, which may be ascribed to oxidized sulfur as those shown in the inset of the figure. In conjunction with the observation, a new peak (288.76 eV) corresponding to C=O occurs at the same time, another evidence for the oxidation of the terthiophene structure. It seems that the photochemical instability of the film may block its direct use in fluorescence sensing or others relevant to

Figure 6. AFM images of the TtDPC film from the gel.

Figure 7. Excitation and emission spectra of film 1 (a) and the fluorescence emission spectra of the TtDPC film recorded in air and at different scan numbers (b).
for other tested vapors, the responses are much weaker. The gelation properties in 26 liquids were tested. It was seen that CHCl₃, HCl, and HNO₃ also enhance the fluorescence emission. Inspired by the work conducted by our group a few years ago, film 1 was specially treated under UV light for 2 h to see if anything happens. As expected, almost no emission is left after the irradiation. The film as obtained is called film 2.

It is interesting to find that treatment of film 2 with HAc vapor results in fluorescence emission similar to that observed in film 1. Figure 8a shows the emission spectra of film 2 recorded at different exposure times in the presence of saturated HAc vapor. Clearly, with the exposure, the emission around 503 nm increased, and in contrast the one near 400 nm decreased instantly and greatly, which might be originating from scattering. The reason for the fluorescence turn-on might be unmasking of the photochemically undamaged TtDPC molecules, which emit at the same position and in the same way as that revealed in the studies of film 1. The unmasking of the TtDPC molecules in the film or the peeling off of the oxidized TtDPC molecules on the film surface was evidenced by the changes of the AFM image of the film after HAc treatment (cf. Figure 8b).

For real-life uses, the reversibility of a sensing film is crucial, and thereby, studies on the reversibility of the sensing process were performed. In the studies, first the fluorescence emission of film 2 in air was recorded; next the film was exposed to saturated HAc vapor for a given time at room temperature, then the fluorescence emission measurement was repeated again, and finally the film was purged with hot air for 2 min and its emission was measured again. The process was repeated four times, and the result is depicted in Figure 8b. Clearly, the sensing process of the film to HAc vapor is fully reversible.

The selectivity of film 2 for HAc vapor was also evaluated in the same way as that used for detecting HAc vapor through examining its responses to common interfering vapors, such as CH₂Cl₂, CHCl₃, toluene, n-hexane, cyclohexane, H₂O, HCl, HBr, HNO₃, and H₂SO₄. The results are shown in Figure 9. It is seen that CHCl₃, HCl, and HNO₃ also enhance the fluorescence emission of the film, but with less efficiencies. As for other tested vapors, the responses are much weaker.

**CONCLUSION**

In summary, three terthiophene derivatives of cholesterol (TtGC, TtLPC, TtDPC) with glycine, L-phenylalanine, or D-phenylalanine structure in the linkers were prepared, and their gelation properties in 26 liquids were tested. It was demonstrated that the compounds as created, in particular TtLPC and TtDPC, are efficient gelators. At a concentration of 2.5% (w/v), the first one gels 4 of the 26 liquids, two gels 11 of them, and three 10 of them. SEM measurements revealed the evolution process of the morphology of the gel network formed in the TtDPC/benzene system, which began with fibers with some sheets, then sheets with some fibers, and then sheets with tendons inside and finally rod-like structures. FTIR, ¹H NMR, and UV–vis measurements revealed that intermolecular hydrogen bonding and van der Waals interaction are the main driving forces for the gel formation. As for the system of TtDPC/benzene, CD and AFM analyses demonstrated that the molecules of the gelator aggregated into chiral structures with left-hand helical feature. XRD study indicates that TtDPC in gel state mainly assembled in both a cubic and hexagonal modes. Importantly, a fluorescent film (film 1) fabricated by dip-coating TtDPC/benzene onto a glass plate surface is photochemically unstable, and it experiences photobleaching under UV light in air. However, this UV treated film (film 2) can be used as turn-on fluorescent sensor for HAc vapor and some other volatile organic liquids. The sensing of the film to HAc vapor is fully reversible.

**ASSOCIATED CONTENT**

Supporting Information

Synthesis and characterization of TtGC, TtLPC, and TtDPC, ¹H NMR spectra, FTIR spectra, UV–vis pictures, XPS data, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 8. Fluorescence emission spectra of film 2 recorded after treatment with HAc vapor for different times (a) and the reversibility of the sensing performance of the film in the presence of HAc vapor (b) ($\lambda_{ex} = 370 \text{ nm}; \lambda_{em} = 498 \text{ nm}$).

Figure 9. Sensing performances of film 2 for different vapors ($\lambda_{ex} = 370 \text{ nm}; \lambda_{em} = 498 \text{ nm}$).
We thank the Natural Science Foundation of China (91027017, 91227314, and 21206089) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1070). This work was also supported by the Fundamental Research Funds of Shaanxi Normal University (GK201301006) and Research Funds of Shaanxi Normal University (X2012YB02).

REFERENCES


