A hydrogen bonded complex could self-assemble into one-dimensional fibers in its gel phase. The fibrous film could be used as a sensor to detect and discriminate aromatic and aliphatic amines.

Detecting organic amines at the trace vapor level is very crucial for environmental pollution monitoring and control, food safety, and even medical diagnosis.9 To date, some methods, such as gas or liquid chromatography,2 electrochemical devices,3 and various chemical sensors,4 have been established for the detection of organic amines. Fluorescent sensors were developed because of the distinct advantages offered by fluorescence detection in terms of sensitivity, selectivity, response time, local observation, and remote sensing.5 Recently, some fluorescent sensors based on self-assembled fibrous films have been developed to detect organic amine vapors because of their high sensitivity. For instance, Zang, Liu, and Fang et al. reported several fluorescent nanofiber films of perylene bisimide derivatives as expedient sensors for detecting organic amines.6 Our group also developed fluorescence fibrous films of boron diketonate complexes for probing organic amines.7 The detection mechanism of these sensors is primarily based on the photoinduced electron transfer (PET) from amines to excited sensing molecules caused by the difference in the HOMO energy levels between organic amines and sensing molecules. Some fluorescence sensors can simultaneously respond to aromatic and aliphatic amines with similar emission quenching behaviors, implying poor selectivity, whereas some might selectively recognize aromatic amines. To selectively detect aliphatic amines, Takagai et al. employed “turn-on” fluorescent sensors.8 In the presence of amines, acid-base interaction deprotonates fluorescent probes consisting of carboxylic acid derivatives, thereby resulting in greater emission. Sensing arrays were developed to discriminate vapors of organic amines.9 However, the discrimination of aromatic and aliphatic amines using only one fluorescence sensor molecule is still a challenge.

In this communication, a new strategy for identifying the different responsive behaviors of a fibrous film sensor to aromatic and aliphatic amines and for detecting and discriminating the types of amine is presented. Such fibrous films were prepared using the gels of a two-component gelator (C12PhBPVB). This gelator is composed of two N-lauroyl phenylanilines (C12Ph) and one 1,4-bis(2-(pyridin-4-yl)vinyl)-benzene (BPVB) and is linked by two OH···N hydrogen bonds between the carboxylic acid groups and the pyridine units (Scheme 1).

Although C12Ph did not self-assemble to form a gel phase in cyclohexane,10 hot cyclohexane solutions of the C12PhBPVB complex can transform into gels at low concentrations under cooling conditions. The gelator (1 mg) can gelatinize 3 mL of cyclohexane (0.34 mM). This result suggests that the introduction of BPVB increases the gelation ability of C12Ph. The FT-IR spectrum of C12Ph in the solid state had an absorption peak at 1707 cm−1, indicating a dimer structure of carboxylic acid groups.11 The IR absorption peak of carboxylic acid in the cyclohexane xerogel of C12PhBPVB is located at 1730 cm−1 (Fig. S1, ESI†), suggesting that the dimer structure was damaged and a hydrogen-bonded complex instead of a hydrogen-bonded ion pair was formed.12 Moreover, the vibration absorption peaks of NH and amide I appeared at 3311 and 1643 cm−1, respectively, indicating the formation of hydrogen bonds between amide units in the gel.13

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![Scheme 1 Molecular structure of C12PhBPVB and the presentation for its low HOMO energy level and hydrogen bond.](c3cc42892c)
As shown in Fig. 1a, the maximal absorption peak of C12PhBPVB in hot cyclohexane (80 °C) was located at 345 nm. During gelation, this peak gradually decreased, and a new peak at 368 nm was observed (Fig. 1a). This finding suggests the formation of J-aggregates (head-to-tail packing) between BPVB during gelation and the presence of π–π interaction between BPVB. Moreover, the colorless cyclohexane solution of C12PhBPVB at 80 °C with blue-violet fluorescence can form a yellow gel with strong yellow-green fluorescence (λem = 544 nm, Fig. 1b), implying the apparent color change of emission during gelation because the intermolecular interaction alters the photophysical processes. As shown in the SEM image of the cyclohexane xerogel, 3D networks consisting of numerous intertwined nanoribbons with widths ranging from 150 nm to 1 μm were found (Fig. S2a, ESI†). Images acquired using a light microscope also suggest fibrous networks (Fig. S2b, ESI†). Generally, the long-range exciton migration intrinsic to the 1D molecular aggregates enables amplified fluorescence response by the adsorption of analytes on the surface as an energy or electron trap. Therefore, a low detection limit of fibrous film for aromatic amines can be expected.

A sensing film of approximately 740 nm thick was obtained by casting the solution (100 μL, 0.51 mM) on a glass slide (1.3 × 2.5 cm), followed by slow evaporation of the solvent. As shown in Fig. 2a, upon exposure to aniline vapor (329 ppm), the fluorescence of the xerogel film was reduced by almost 98%. Moreover, aniline vapor reduced the fluorescence of the xerogel film in as short as 0.8 s regardless of large sensing film thickness. The fast response time is mainly due to the 3D continuous, porous structure of the xerogel film, which allows expedient diffusion of the aniline molecules. The detection limit of our sensing film for aniline can be deduced using the plot of quenching efficiency versus aniline concentration. A good linear relationship between quenching efficiency and aniline concentration was observed when the latter was below 100 ppm (Fig. S3, ESI†).

Thus, considering that a well-calibrated photodetector can detect intensity changes as low as 0.1%, the detection limit for aniline vapor was calculated to be as low as 1.8 ppb using the linear function. The low detection limit may be associated with the large surface area of the fibrous film and the enhanced exciton diffusion along the long axis of the nanofiber. In addition, we found that the fluorescence quenched by aniline can be recovered by blowing with a gas blower for 2 min. Such a process can be repeated multiple times, indicating excellent reversibility (Fig. S4, ESI†).

The responsive behaviors of the xerogel film toward different aliphatic amines were also investigated. Interestingly, the yellow xerogel film transformed into a colorless film, and its fluorescence changed from yellow-green to blue upon exposure to aliphatic amines (Fig. 2 and Fig. S5, ESI†). Upon exposure to the saturated vapor of n-butylamine, the yellow-green emission peak at 544 nm disappeared, and a new blue emission band with two peak maxima at 440 and 460 nm emerged. Moreover, the colorless sensing film did not transform into the yellow film, and its fluorescence remained blue after blowing with a gas blower for 10 min. This finding indicates an irreversible response to aliphatic amines. To further elucidate the difference, the UV-vis absorption and IR spectra of the xerogel film before and after exposure to n-butylamine and aniline were recorded. The absorption peak of the xerogel film showed no significant change after exposure to aniline vapor. However, n-butylamine induced the disappearance of the original absorption band and the appearance of a new blue-shifted band with a maximum at 320 nm (Fig. S6, ESI†). Similarly, aniline did not induce a change in the IR absorption peak of the xerogel film. By contrast, upon exposure to n-butylamine vapor, the peak at 1730 cm⁻¹ ascribed to the carboxylic acid group disappeared. Simultaneously, a new peak at 1590 cm⁻¹ was observed (Fig. S7b, ESI†), which can be associated to the vibration peak of the carboxylate group. The results suggest that aniline was absorbed physically on the surface of nanofibers and that n-butylamine destroyed the hydrogen-bonded complex (C12PhBPVB) and released free BPVB by deprotonating carboxylic acid. Therefore, the emission of the sensing film quenched by aniline can be recovered through aniline desorption, and the response to aliphatic amines is irreversible.

The differences in the HOMO energy level and basicities of aromatic and aliphatic amines may account for the diverse responses of xerogel film. Electrochemical experiments showed that the formation of hydrogen bonds between carboxylic acid and the pyridine terminal unit reduced the HOMO energy level of BPVB from −5.62 eV to −5.73 eV. Theoretical calculation also implied a decrease in the energy level (Table S1, ESI†). The HOMO energy level is low enough to allow PET from aromatic amines to excited C12PhBPVB. Furthermore, aromatic amines possessed relatively weak basicities (larger pKₐ, Table S2, ESI†); therefore, they cannot deprotonate the carboxylic acid moiety of C12Ph to decompose the hydrogen bonded complex (Fig. 3). The aromatic amines were physically absorbed on the surface of C12PhBPVB nanofibers and then quenched the fluorescence of the sensing film through electron transfer from aromatic amines to sensing molecules. Conversely, low pKₐ renders aliphatic amines as stronger bases. When aliphatic amines were absorbed on the sensing film, they first gained protons from carboxylic acid moieties to form ammonium salts, which cannot quench the fluorescence of C12PhBPVB due to a lower LUMO energy level. In addition, the...
released free BPVB had an elevated energy level, which prohibited the electron transfer from aliphatic amines to excited BPVB (Fig. S8, ESI†). Thus, the sensing film emitted blue fluorescence of BPVB. Consequently, the sensing film responded to aromatic and aliphatic amines in different ways.

When a 740 nm thick xerogel film was selected as the sensing film to evaluate the relationship between quenching yield and n-butylamine vapor concentration, a high detection limit of 1400 ppm was observed (Fig. S9, ESI†). This observation is due to the fact that aliphatic amines quench the emission of the xerogel film without enhancing the quenching efficiency. To decrease the detection limit for aliphatic amines, a thin xerogel film was considered. The detection limit for n-butylamine dropped to 1.16 ppm using a 76 nm thick film (Fig. S10a, ESI†). This finding implies the continuous deprotonation of C12PhBPVB. Overall, the quantitative detection of low concentrations of aliphatic amine vapor was realized using a thin xerogel film.

Some common solvents were used as interference reagents to study the selectivity of our xerogel film. No appreciable fluorescence quenching (less than 3%) of xerogel film was observed upon exposure to common organic solvents (ethanol, CH2Cl2, ethyl acetate, hexane, and acetone), with the exception of toluene (Fig. S11, ESI†). Upon exposure to aniline and n-butylamine, the gel possessed excellent selectivity for organic amines.

In summary, we designed a two-component hydrogen-bonded gelator and studied its self-assembly properties. Nanofibers in the gel phase were used to prepare sensing fibrous film for detecting and discriminating aromatic and aliphatic amines. The fibrous sensing film exhibited different responsive behaviors to aromatic and aliphatic amines based on their different HOMO energy levels and basicities. Moreover, our sensing film exhibited rapid response time and a low detection limit for organic amines. Consequently, a new strategy using a hydrogen-bonded complex for detecting and discriminating aliphatic and aromatic amines was successfully established. Therefore, this work contributes to the expansion of the design concept of sensory materials for detecting organic amines.

This work was financially supported by the National Natural Science Foundation of China (21103067, 91127005, 20874034, and 51073068), the 973 Program (2009CB939701), the NSFC-JSPS Scientific Cooperation Program (21011140069), and the Open Project of the State Key Laboratory of Supramolecular Structure and Materials (SKLSSM201203).

Notes and references