Aliphatic amine responsive organogel system based on a simple naphthalimide derivative†

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A new gelator 1 based on a simple naphthalimide derivative was synthesized and fully characterized. It was found that the organogel 1 was formed only in a mixed solvent of methanol and H2O (1/1, v/v). The organogel was thoroughly characterized by using various microscopic techniques including field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and UV-vis, fluorescence and Fourier transform infrared (FTIR) spectroscopy. Hydrogen bonds were the main driving force for the organogel formation. Interestingly, the organogel 1 exhibited the ability to distinguish aliphatic amines from aromatic amines. The gel state and fluorescence emission intensity were both changed after two minutes after the addition of aliphatic amines. This organogel system could be applied in the detection of aliphatic amine pollutants.

Introduction

A novel class of self-assembled materials, low molecular weight gelators (LMWGs) with well-defined molecular structures, have recently gained considerable attention for their potential applications such as in materials science, tissue engineering, separation technologies, catalysis, regenerative medicine, drug delivery, light harvesting systems and environmental science, among others.1 The low molecular weight gels can be formed and created with three-dimensional networks capable of entrapping solvents through noncovalent interactions including hydrogen bonds, hydrophobic–hydrophobic interactions, π–π interactions, van der Waals forces, etc.2 In addition, multifarious anisotropic nanoarchitectures can be prepared in the sol-gel transition process, such as fibres, ribbons, platelets, tubular structures or cylinders.3 There are a wide range of known supramolecular gelators, such as amide ureas, carbohydrates, steroids, nucleobases, and long chain alkanes.4

Naphthalimide is a classical and very useful fluorescent dye which has been widely applied in the fields of fluorescent chemosensors and optical-electronic devices.5 The spectroscopic properties of naphthalimide can be tuned from red to blue with a high fluorescence quantum yield by modifying the C-4 substituent.6 Naphthalimide has also been introduced into a supramolecular self-assembly system which could provide intermolecular π–π interactions and a facile tool to study molecular aggregation.7 We have previously studied a class of naphthalimide derivative gels with tunable R-G-B fluorescence on the basis of intermolecular energy transfer.8 We have reported a white light-emitting organogel from controlled donor self-assembly and energy transfer by addition of an iridium complex. This two-component organogel can work as a luminescence and colorimetric test kit for cysteine detection.9

Organic amines are widely used in fine chemical engineering and the pharmaceuticals industry. However, organic amine pollution does not gain enough attention because of the lack of understanding of its jeopardy to human health. For example, triethylamine can irritate respiratory passages. When triethylamine is inhaled, it can cause pulmonary edema and even death. If triethylamine is taken orally, the mouth, esophagus and stomach will be corroded. Therefore it is necessary that a smart material with the capability of response to organic amine stimuli is developed. Herein, a simple organogelator 1 (Scheme 1) was

†Electronic supplementary information (ESI) available: Details of XRD experiments, scheme of synthesis of 1 and partial absorption spectra. See DOI: 10.1039/c4ob00728j
The above crude product was dissolved in anhydrous dichloromethane (100 mL), and boron tribromide (5.59 g, 22.3 mmol) was added to the solution dropwise at 0 °C. The mixture was stirred overnight, and monitored by TLC. After the reaction was over, the solution was washed with saturated sodium carbonate solution three times. The organic phase was dried using anhydrous sodium sulphate. The solvent was removed under vacuum. The crude product was further purified by column chromatography (CHCl₃-MeOH = 20/1, v/v) on silica gel to give 1 as a pale yellow solid. Total yield 67.6%; ¹H NMR (400 MHz, d⁶-DMSO in Fig. S1): δ 12.018 (s, 1H), 8.479 (d, J = 6.8 Hz, 1H), 8.450 (d, J = 6.0 Hz, 1H), 8.409 (d, J = 6.8 Hz, 1H), 7.771 (t, J = 6.0 Hz, 1H), 7.283 (d, J = 6.8 Hz, 1H), 4.117 (s, 3H), 3.993 (t, J = 6.0 Hz, 2H), 2.223 (t, J = 6.0 Hz, 2H), 1.617 (m, 2H), 1.556 (m, 2H), 1.346 (m, 2H); ¹³C NMR (100 MHz, d⁶-DMSO): δ 174.96, 163.96, 163.32, 160.73, 133.66, 131.42, 128.94, 128.63, 126.77, 123.16, 122.30, 114.65, 106.67, 57.06, 34.01, 27.77, 26.52, 24.70. HRMS (ESI⁺) calcd for C₁₉H₂₀NO₅ [M + H⁺]: 342.1341; found: 342.1338.

**Experimental section**

**Reagents and solvents**

The organic solvents, i.e. DMF, DMSO, and CH₂Cl₂ were HPLC grade and were obtained from Sinopharm Chemical Reagent Co. Ltd. 6-Aminohexanoic acid (99%), 4-bromo-1,8-naphthalic-anhydride (95%) and boron tribromide were supplied by Aladdin Reagent (Shanghai) Co., Ltd.

**Techniques and instrumentation**

The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Mercury Plus-Varian instrument. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). HRMS was carried out on a LTQ-Orbitrap mass spectrometer (ThermoFisher, San Jose, CA). SEM images were obtained using a FE-SEM S-4800 (Hitachi) instrument. Samples were prepared with KBr pellets. Original spectra were baseline-corrected using Omnic 5.1 software.

The gelation tests

The gelation tests on compound 1 were carried out with various single solvents and mixed solvents using a test tube inversion method; the results are shown in Table 1. Compound 1 had one hydroxyl group, and was a polar compound. It was insoluble in petroleum ether. A precipitate was obtained in toluene and acetonitrile even if compound 1 was heated in them to dissolve. Polar solvents were used for the gelation ability tests for compound 1. Compound 1 could not form a gel, but was soluble, in ethyl acetate, 1,4-dioxane, ethanol, N,N-dimethyl formamide, methanol etc. Therefore mixtures of polar solvent and H₂O (1/1, v/v) were tried. Fortunately, compound 1 could form a gel in a mixed solvent of methanol and H₂O. Photos of gel were shown in Fig. 1. Gel 1 could be stable for at least two months as shown in Fig. 1a. Gel 1 could emit blue light under irradiation by 365 nm light as shown in Fig. 1b.

<table>
<thead>
<tr>
<th>Solvent Product 1</th>
<th>Solvent Product 1</th>
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<tbody>
<tr>
<td>Petroleum ether P</td>
<td>N,N-Dimethyl formamide S</td>
</tr>
<tr>
<td>Toluene P</td>
<td>N,N-Dimethyl formamide-H₂O (1/1, v/v) S</td>
</tr>
<tr>
<td>Acetonitrile P</td>
<td>Methanol S</td>
</tr>
<tr>
<td>Ethyl acetate S</td>
<td>Methanol–H₂O (1/1, v/v) G(25)</td>
</tr>
<tr>
<td>1,4-Dioxane S</td>
<td>Tetrahydrofuran S</td>
</tr>
<tr>
<td>1,4-Dioxane–H₂O</td>
<td>Tetrahydrofuran–H₂O (1/1, v/v) S</td>
</tr>
<tr>
<td>1,4-Dioxane–H₂O</td>
<td>Dimethyl sulfoxide S</td>
</tr>
<tr>
<td>Ethanol S</td>
<td>Ethanol–H₂O (1/1, v/v) PG</td>
</tr>
</tbody>
</table>

S = soluble; P = precipitate; G = gel; I = insoluble; PG = partial gel; the value in the brackets denotes the critical gel concentration (CGC) (25 mg mL⁻¹).
Organogel structure

All kinds of morphologies can be obtained in the sol–gel transition process through intermolecular noncovalent interactions. The structure of gel in a mixed solvent of methanol and H2O (1/1, v/v) was investigated using field emission scanning electron microscopy (FESEM). As shown in Fig. 2a, a framework of fibers with a diameter of about 50 nm and length of several micrometers was observed in xerogel. The fibers were intertwined and formed a three-dimensional network structure (Fig. 2b).

Absorption and emission spectra

The absorption spectra of compound 1 in the solution and gel states are shown in Fig. 3a. Compound 1 in a mixed solvent of methanol and H2O (1/1, v/v) at a concentration of 10⁻⁴ M has two absorption bands at 243 and 372 nm which are related to π-π* and n-π* transition bands, respectively. When compound 1 was in the gel state, the corresponding absorption bands also showed hypochromatic-shifts from 243 and 372 nm to 237 and 356 nm. Simultaneously, the two absorption bands of organogel 1 were broadened to a certain extent. This result shows that the “H-aggregate” mode was employed in the gel state. Fluorescence emission spectra of compound 1 in the solution and gel states were also studied as shown in Fig. 3b. The maximum emission of compound 1 in a solution of methanol and H2O at a concentration of 10⁻⁴ M was located at 454 nm. The maximum emission of gel 1 was also at 454 nm. This result indicates that intermolecular π-π stacking was not obviously occurring in the gel state.

FTIR spectra and XRD study

Fourier transform infrared (FTIR) spectroscopy was the main method used for understanding the process of the self-assembly through intermolecular noncovalent interactions. Herein, FTIR spectroscopy of compound 1 in the powder and gel states was carried out and is shown in Fig. 4. The O–H stretching band (νOH) of powder 1 was present at 3460 cm⁻¹ at room temperature. However, this νOH band moved from 3460 cm⁻¹ to 3435 cm⁻¹ for gel 1. The blue shift of 25 cm⁻¹ in the gel state illustrated that intermolecular H-bonds were formed in gel 1. At the same time, the XRD experiment also demonstrated that intermolecular H-bonding existed in gel 1, as shown in Fig. S2. The peak corresponding to 4.1 Å was related to the hydrogen bonding distance between hydroxyls.
Fig. 4 FTIR spectra of compound 1 in powder state and as gel in mixed solvent of methanol and H₂O (1/1, v/v) at a concentration of 25 mg mL⁻¹ at room temperature.

The XRD data was consistent with the FTIR experimental result.

Aliphatic amine response properties study

Low molecular weight organogels have received considerable attention in materials science since they were prepared as a new class of smart materials sensitive to external stimuli, such as light, ultrasound, chemical species and so on. Therefore the behaviour of organogel of 1 in a mixed solvent of methanol and H₂O (1/1, v/v) towards the addition of different kinds of organic amine was investigated. Aliphatic amines or aromatic amines were added onto the gel carefully by pipette after the formation of the gel. The gel changed into a solution without any further treatment after five minutes after addition of aliphatic amines. Interestingly, only the addition of an aliphatic amine led to transformation of the gel into a solution. For example the gel could exhibit a rapid transformation from gel into solution after 5 min after 5.0 μL of triethylamine or ethanediamine was added (Fig. 5e). The minimum amount of aliphatic amine required for the transformation from gel to solution was then tested. The gel at a concentration of 5 mg mL⁻¹ could respond to a minimum amount of 0.5 μL of triethylamine. The transformation from gel to solution after addition of 0.5 μL of triethylamine was monitored by taking photos at fixed time intervals as shown in Fig. S3.† The gel gradually transformed into a solution over time after addition of 0.5 μL of triethylamine. When the time reached five minutes, the gel had almost changed into a solution. The fluorescence emission intensity of solution 1 from gel 1 with the addition of 5.0 μL of triethylamine was obviously weakened as shown in Fig. 5f. When aromatic amines, such as phenylamine and N,N-dimethylaniline, were used, organogel 1 remained stable for more than one month (Fig. 5a and 5c). Gel 1 retained its fluorescence emission intensity after the addition of the aromatic amines (Fig. 5b and 5d). It is possible that the aromatic amines were not soluble in the mixed solvent of methanol and H₂O (1/1, v/v), and the basicity of the aromatic amines was weaker than that of the aliphatic amines.

In order to verify the response differences of gel 1 to aromatic and aliphatic amines, the solubilities of the aromatic and aliphatic amines in the mixed solution of methanol and H₂O (1/1, v/v) was investigated. After 5.0 μL of phenylamine or triethylamine was added to 200 μL of a mixed solution of methanol and H₂O (1/1, v/v), a difference was seen between the two centrifuge tubes as shown in Fig. S4.† The centrifuge tube with addition of phenylamine had a liquid drop of yellow phenylamine in the bottom. However, the centrifuge tube with addition of triethylamine contained a clear solution. The aliphatic amine had a better solubility than the aromatic amine for the mixed solution of methanol and H₂O (1/1, v/v), which was confirmed by the above results to some extent. The lone pair electrons of the nitrogen-atom in the aromatic amine are delocalized over the benzene ring to some extent. In contrast, the aliphatic amine has no delocalization. So, the basicity of the aliphatic amine is stronger than that of the aromatic amine.

The detailed response process of organogel 1 to the stimulus of an aliphatic amine was studied though fluorescence emission and UV-vis absorption spectroscopy. The fluorescence emission spectra of compound 1 in solution at a concentration of 10⁻⁴ M were measured with different added quantities of triethylamine as shown in Fig. 6a. With the addition of triethylamine, the emission intensity at 454 nm gradually decreased. With the addition of 80 μL of triethylamine, the compound 1 solution exhibited a distinct fluorescence quenching of more than 93%. When the solution of 1 with 80 μL of triethylamine had glacial acetic acid gradually added, the fluorescence emission intensity was regained little by little. The fluorescence emission intensity of solution 1 was not restored to the original fluorescence intensity of 91% until the added amount of glacial acetic acid was 24 μL (Fig. 6b). Gel 1 turned into a solution and the fluorescence emission inten-
sity of gel $\text{1}$ was obviously weakened to about 15% of the origin-

al fluorescence intensity after 5 $\mu$L of triethylamine was

added. When an equimolar amount of glacial acetic acid was

added to the above solution, the fluorescence emission intensity

was restored to the original gel $\text{1}$ fluorescence intensity of 95%

(Fig. 6c). This result was in accord with the solution. The

absorption spectra change of solution $\text{1}$ in a mixed solvent of

methanol and H$_2$O (1/1, v/v) at a concentration of 10$^{-4}$ M after

addition of 80 $\mu$L of triethylamine during the titration with glacial acetic acid ($\lambda_{ex} = 372$ nm). (d) The absorption spectra change of solution $\text{1}$ in mixed solvent of methanol and H$_2$O (1/1, v/v) at a concentration of 10$^{-4}$ M during the titration of triethylamine.

Response mechanism

On the basis of the above experimental results, hydrogen

bonds were the main driving force for organogel $\text{1}$ formation.

The hydrogen bonds were formed between two hydroxyl

groups of molecule $\text{1}$. It was particularly important that the

hydroxyl group had a certain intensity of acidity due to the

electron-withdrawing inductive effects of naphthalimide.$^{16}$

After an aliphatic amine was added to organogel $\text{1}$, a quatern-

ary ammonium salt was possibly formed between the aliphatic

amine and molecule $\text{1}$. Then the intermolecular hydrogen

bonding was destroyed and organogel $\text{1}$ was turned into a solu-

tion. To some degree, the quaternary ammonium salt had elec-

tron-withdrawing inductive effects which had some effect on the

fluorescence emission intensity. At the same time, the formation

of the quaternary ammonium salt was in favour of the photo-

induced electron transfer between the excited state of molecule

$\text{1}$ and the amine molecules, which was the main driving force

for fluorescence quenching.$^{17}$ Therefore, the fluorescence emis-

sion intensity of compound $\text{1}$ in the solution and gel states was

weakened after addition of triethylamine. When an equimolar

amount of glacial acetic acid was added, the fluorescence emis-

sion intensity could almost be restored. Unfortunately, organo-

gel $\text{1}$ could not be formed again after addition of an equimolar

amount of glacial acetic acid. It is possible that this is because

of the presence of quaternary ammonium salt from triethyl-

amine and glacial acetic acid (Fig. 7).$^{18,19}$

Fig. 6  (a) The fluorescence emission spectra change of solution $\text{1}$ in mixed solvent of methanol and H$_2$O (1/1, v/v) at a concentration of 10$^{-4}$ M during the titration with triethylamine ($\lambda_{ex} = 372$ nm). (b) The fluorescence emission spectra change of solution $\text{1}$ in mixed solvent of methanol and H$_2$O (1/1, v/v) at a concentration of 10$^{-4}$ M after addition of 80 $\mu$L of triethylamine during the titration with glacial acetic acid ($\lambda_{ex} = 372$ nm). (c) The fluorescence emission spectra change of gel $\text{1}$ before and after addition of 5 $\mu$L of triethylamine, then addition of equimolar glacial acetic acid (the gel concentration = 25 mg mL$^{-1}$, $\lambda_{ex} = 372$ nm). (d) The absorption spectra change of solution $\text{1}$ in mixed solvent of methanol and H$_2$O (1/1, v/v) at a concentration of 10$^{-4}$ M during the titration of triethylamine.
Conclusion

The present results showed that an organogel could be formed by a new and simple gelator containing naphthalimide only in a mixed solvent of methanol and H_2O (1/1, v/v). The organogel from the mixed solvent was characterized by FESEM, XRD, and UV-vis, fluorescence and FTIR spectroscopy. The results indicated that the organogel in mixed solvent was responsive to aliphatic amines. This organogel system could sensitively distinguish aliphatic amines from aromatic amines. The XRD and FTIR experiments showed that hydrogen bonding was the main driving force for the gel formation. This soft material with the ability to sensitively distinguish organic amines and detect aliphatic amines provides potential for applications in detection of aliphatic amine pollutants.

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Notes and references


