A Smart Gelator as a Chemosensor: Application to Integrated Logic Gates in Solution, Gel, and Film

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Abstract: A gelator that consisted of one benzimidazole moiety and four amide units was used as a chemosensor. We found that its absorption and emission spectra in solution were sensitive to two complementary chemical stimuli: protons and anions. Thus, YES and INH logic gates were obtained when absorbance was defined as an output. A combination gate of XNOR and AND with an emission output was also obtained. Moreover, wet gels in two solvents were used to construct two more-complicated three-input-three-output gates, owing to the existence of the gel phase as an additional output. Finally, in xerogel films that were formed from two kinds of wet gels, reversible changes in their emission spectra were observed when they were sequentially exposed to volatile acid and NH₃. Another combination two-input logic gate was obtained for xerogel films. Finally, three states of the gelator were used to construct not only basic logic gate, but also some combination gates because of their response to multiple chemical stimuli and their multiple output signals, in which one chemical input could erase the effect of another chemical input.

Keywords: chemosensors · gels · logic gates · self-assembly · thin films

Introduction

Molecular switches, which can be converted from one state into another by an external stimulus, such as light, electricity, magnetism, or ions, have recently received considerable attention.[1] If two states of these switches are defined as 0 and 1, respectively, these switches can be manipulated as molecular logic gates whose inputs and outputs don’t need to be confined to electrical signals.[2] Recently, smart gels formed by low-molecular-mass organogelators have been studied because of their excellent stimuli-responsive properties, not only to various external physical stimuli, but also to chemical stimuli.[3] Moreover, some organogels and hydrogels have been also developed as binary logic gates. For example, in 2009, Park and co-workers constructed a fluorescent organogel and achieved binary OR logic gates with optical and thermal inputs through the combination of an emission-enhanced organogelator and a photochromic compound.[4] In the same year, Hamachi and co-workers reported a phosphate-type hydrogelator, which exhibited macroscopic gel–sol behavior in response to four input stimuli: temperature, pH, Ca²⁺ ions, and light. As a result, four basic logic gates were realized in this one-component hydrogel.[5] However, these gel-based logic gates were only basic logic gates. Therefore, it is still a great challenge to realize more-complicated calculations in one-component gels. Moreover, only wet gels were used as responsive switches for logic gates and their solution- or film states were not taken into account, which limited the widespread application of gelator.

The benzimidazole moiety has been integrated into a variety of functional molecules to construct sensors for anions, metal ions, and protons, which were accompanied by significant changes in their absorption and fluorescence spectra.[6] One would expect the responsive properties of gelator 1 to be similar with these sensors.

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Scheme 1. Chemical structure of organogelator 1 and the expected binding sites.
gates from these systems and combination logic gates, such as INH (INHIBIT) and three-input-three-output logic gates, were also obtained in which anions could erase the influence of protons and vice versa; in other words, these systems did not need additional chemical inputs to recover the original state of the logic gate. Moreover, these results suggested that gelator 1 is a promising candidate for applications not only in its gel state, but also in its other phases.

Results and Discussion

Self-assembly characteristics: Compound 1 readily dissolved in DMSO on heating to form a yellow solution. When 20% water (v/v) was added, a gel was formed; compound 1 also gelatinized aromatic solvents, such as o-dichlorobenzene (ODCB), toluene, etc. In the FTIR spectrum of the wet DMSO/H2O gel, vibration peaks appeared at 1655 and 1634 cm⁻¹, which were ascribed to aromatic and aliphatic amide units, respectively (see the Supporting Information, Figure S1). In ODCB gel, these peaks appeared at 1655 and 1633 cm⁻¹, respectively, thereby indicating the formation of intermolecular hydrogen bonds between amide groups in two separate gels.[7] The UV/Vis spectra of compound 1 in DMSO/H2O and in ODCB showed obvious hypsochromic shifts during gelation, which were indicative of the strong π–π interactions between aromatic units and the formation of H-aggregates (Figure 1).[8] These results indicated that intermolecular hydrogen bonds and π–π interactions played important roles in the gel-formation.[9] SEM images of gel 1 in DMSO/H2O and ODCB revealed that compound 1 was able to aggregate into long, intertwining bundles of fibers, which were constructed in a 3D network and which promoted the formation of a gel phase (see the Supporting Information, Figure S2). We also observed drastic differences between the emission colors of compound 1 in the gel and sol states under UV irradiation. Fluorescence spectra of these materials are shown in Figure 1c,d. Strong blue–green fluorescence was observed in a hot solution of compound 1. During the cooling process, the gelator began to aggregate, with a gradual accompanying red shift in the emission spectrum and a decrease in the emission intensity owing to the delocalization of the exciton across the self-assembled aggregates.[3i,9c] Finally, the gel of compound 1 showed a green

![Figure 1](image-url)

Figure 1. UV/Vis and fluorescence spectra of gels of compound 1 during cooling from 90°C and 120°C to RT in DMSO/H2O (a,c) and in o-dichlorobenzene (b,d), respectively. ε = 0.05 wt/vol %, λex = 400 nm.
emission. These results further confirmed the existence of H-aggregates in the gel phase.\[8e\]

**Response properties in the sol state:** As shown in Scheme 1, gelator 1 had two kinds of binding sites: to anions and protons. Therefore, the response properties of compound 1 to chemical stimuli in DMSO solution were examined first. Thus, the anion-response properties of compound 1 toward a number of selected anions, including OH\(^-\), F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), AcO\(^-\), H\(_2\)PO\(_4\)\(^-\), and HSO\(_4\)\(^-\) ions as their tetrabutylammonium (TBA) salts were examined in DMSO. In neat DMSO solution, the maximum absorption of compound 1 occurred at 396 nm, which changed greatly upon the addition of ten equivalents of TBAF and TBAOH, with shifts to 445 and 472 nm, respectively. No significant changes were observed upon the addition of other anions, thus suggesting a highly selective responsive to F\(^-\) and OH\(^-\) ions (see the Supporting Information, Figure S3). As shown in Figure 2a, the peak at 396 nm gradually decreased when the concentration of TBAF increased, and the new peak at 445 nm gradually became more intense and reached saturation after five equivalents of TBAF had been added, thereby indicating a good affinity of compound 1 for fluoride because of the existence of five binding sites for fluoride in compound 1.\[10\]

Meanwhile, the color of the solution changed from yellow to red (Figure 3), thus showing a vivid color change that was visible to naked eyes. Similarly, when TBAOH was added to the yellow solution of compound 1 a red solution was formed. However, the absorbance of the mixture reached a saturated value with a maximum absorption at 472 nm when

Figure 2. Absorption of compound 1 (0.5 mM) in DMSO upon the addition of a) TBAF, b) TBAOH, and c) TFA; d) truth tables of “YES” and “INH”.

Figure 3. Photographs of compound 1 in neat DMSO and in DMSO solutions mixed with TFA, TBAF, and TBAOH under natural light and illumination at 365 nm.
the concentration of TBAOH was only twice as large as that of compound 1 (Figure 2b).

To understand the difference between TBAOH and TBAF and the nature of these new absorption peaks, $^1$H NMR titration experiments of OH$^-$ and F$^-$ ions in [D$_6$]DMSO were performed (Figure 4; also see the Supporting Information, Figure S4). For the TBAF system, the signals for all of the protons on the aromatic group showed a distinct upfield shift after the addition of OH$^-$ ions (Figure 4b), thereby suggesting the deprotonation of the NH groups on the imidazole ring and the aromatic amide moiety. Moreover, the signals corresponding to the phenyl protons adjacent to the aromatic amide moiety and the protons in benzimidazole showed no further shift after the addition of two equivalents of OH$^-$ ions. Furthermore, the signals corresponding to the protons adjacent to the three alkyl amide units showed a visible upfield shift until the amount of OH$^-$ ions exceeded two equivalents, thus indicating the deprotonation of these alkyl amides at that point. Because aqueous TBAOH (25%) was used in the NMR titration experiment, there was an amount of water present in the solution, which decreased the activity of the OH$^-$ ions. As a result, almost all of the OH$^-$ ions were concerned with deprotonation of the NH proton on the aromatic ring, and none or only a small amount of OH$^-$ ions interacted with the aliphatic amide, thus resulting in the need for only two equivalents of OH$^-$ ions to complete the color change. If the input (I) was OH$^-$ or F$^-$ ions, and the gate output (O) was determined by measuring the absorbance at 500 nm, a YES logic gate could be operated (Figure 2).

Because benzimidazole can be easily protonated, compound 1 was expected to show a response to protons. When ten equivalents of trifluoroacetic acid (TFA) was added to a solution of compound 1 in DMSO, the color of the solution became darker (Figure 3). In the absorption spectrum, the addition of TFA led to a slight increase at the edge of the absorption spectrum and a small decrease in the peak at 399 nm, as shown in Figure 2c. Interestingly, red solutions of compound 1 in DMSO that contained OH$^-$ or F$^-$ ions could be changed into yellow solutions, similar to that of a solution of compound 1 in neat DMSO, by the addition of equimolar amounts of TFA to the concentrations of OH$^-$ or F$^-$ ions. Moreover, this reversible color change could be repeated many times. If the OH$^-$ or F$^-$ ions were one input and protons were defined as another input of a logic gate, and the gate output was determined by measuring the absorbance at 500 nm, a combination logic gate (INH) would be constructed. In this logic gate, only in the presence of input 1 (OH$^-$ or F$^-$) would afford the output = 1, and one input could erase the influence of the other stimulus.

Considering the intrinsic quality of the fluorophore of compound 1, it was reasonable to assume that the fluorescence of compound 1 was also sensitive to anions and protons, which could then act as another output of a logic gate to construct more-complex logic gates. As shown in Figure 5a, the addition of TBAF gradually quenched the fluorescence of compound 1 and led to a red shift of the emission band. When five equivalents of TBAF was added in a

Figure 4. Partial $^1$H NMR spectra of compound 1 (5.3 m in [D$_6$]DMSO in the absence and the presence of a) TBAF and b) TBAOH.
solution of compound 1 in DMSO, the system emitted a weak red fluorescence with a maximum at 634 nm ($\lambda_{\text{ex}} = 400$ nm). Similarly, the addition of two equivalents of TBAOH quenched the fluorescence of compound 1, whereby a mixed solution with a peak maximum at 616 nm was obtained. Moreover, the fluorescence spectrum of compound 1 was sensitive to protons. The emission band gradually decreased and exhibited a large red-shift from 498 to 560 nm on addition of TFA (Figure 5c). Furthermore, the fluorescence of the mixture of compound 1 and OH$^-$ or F$^-$ ions in DMSO was restored to a state similar to the neat solution of compound 1 if equimolar amounts of TFA to the anions were present, and vice versa. If the emission intensity of compound 1 at 470 nm is defined as an output, and two equivalents of H$^+$ and OH$^-$ ions (or F$^-$) and 400 nm light are In1, In2, and In3, respectively, a three-input gate could be constructed (Figure 5d). In this logic gate, H$^+$ and OH$^-$ ions (or F$^-$) constitute a two-input XNOR gate, which is only activated in the presence of the third input (400 nm light), and can be represented by an XNOR gate feeding into an AND gate. In other words, only when the values of inputs In1 and In2 are the same and In3 is true, is the emission intensity at 470 nm high or the output is 1. Thus, a solution of compound 1 in DMSO can be used not only as a basic logic gate with one input but also as a combination logic gate to bring about more-complex functional smart systems.

Response properties in the gel state: As described above, compound 1 can gelate some solvents and is responsive to anions, protons, and light in the solution state; therefore, we postulated that such gels of compound 1 may also respond to these inputs. Moreover, the state of the system itself (gel or sol) can be defined as additional output, so a more-complex gate was expected. The absorption spectra of gels of compound 1 in DMSO/H$_2$O (v/v = 4:1) before and after the addition of TBAF were almost identical, and the presence of TBAF only induced small enhancements in the emission intensity without a peak shift (see the Supporting Information, Figure S5), which suggested the existence of no or weak interactions between F$^-$ ions and the gelator. This result may have been due to the presence of a large amount of more-acidic water, which would decrease the activity of fluoride. On the other hand, the addition of two equivalents of TBAOH resulted in a phase-transformation from a yellow gel into an orange solution (Figure 7), thereby inducing a vanishing of the peak at 360 nm in the gel and the appearance of a peak at 424 nm (Figure 6a). In the emission spectra, an emission band of the gel at 540 nm shifted to 623 nm upon the addition of OH$^-$ ions. More importantly,
we found that this orange solution could change back into a yellow gel upon the addition of one equivalent of TFA relative to OH⁻/C₀ ions (Figure 7), and that the reformed gel exhibited absorption and fluorescence spectra that were similar to those of the neat gel. When more TFA was added, the gel phase was not destroyed, and the emission band of the gel gradually shifted to 570 nm, although a slight change in absorption spectra was observed (Figure 6c; also see the Supporting Information, Figure S6). Interestingly, such an emission band was again shifted to 540 nm when additional TBAOH was added to consume the TFA. This reversible change could be repeated many times (Figure 7).

Based on these results, a more-complex logic gate with three inputs and three outputs was afforded (Figure 6d). Two equivalents of OH⁻/C₀ ions, two equivalents of H⁺ ions, and light (400 nm) are In₁, In₂, and In₃, respectively. Emission intensity at 650 nm and absorbance at 450 nm are Out₁ and Out₂, respectively. A high value is 1, a low value is 0. For Out₁, In₁ and In₂ first afforded an XOR gate, which was activated by In₃. Thus, Out₁ is only true when In₁ or In₂ and In₃ are applied. Moreover, In₁, In₂, and optical Out₂ built an INH logic gate. However, In₁, In₂, and optical Out₃ created an exclusive INH logic gate, which gave a reverse signal to an INH logic gate.

Because of the phase separation of the TBAOH aqueous solution and ODCB, TBAOH was not considered as an anion source for the ODCB gel system. Anions (Cl⁻, Br⁻, ...
I−, AcO−, HSO4−, and H2PO4−) did not change the phase state and the absorption spectrum of ODCB gel (see the Supporting Information, Figure S7). Fortunately, the addition of two equivalents of TBAF prohibited the formation of the yellow gel of compound 1; rather, a dense yellow solution was formed (see the Supporting Information, Figure S8). The corresponding absorption spectrum exhibited an obvious bathochromic shift from 357 (gel) to 385 nm (solution). When more TBAF was added, a corresponding red shift was observed. The absorption spectra reached a saturated value with a maximum absorption at 409 nm when the amount of TBAF was more than five equivalents (Figure 8a). The small red shift of 18 nm in the absorption spectrum relative to neat ODCB solution (391 nm) indicated the formation of hydrogen-bonding interactions between the F− ions and the aromatic NH units, rather than deprotonation of the NH proton,[14] which induced a larger red shift of about 50 nm in DMSO. In the emission spectrum, an obvious enhanced and red-shifted emission was observed when more than five equivalents of TBAF were added. The response behavior of ODCB gel to TFA (less than 5 equiv) was similar to that in DMSO (Figure 8b). Moreover, TFA...
could also induce the ODCB solution of compound 1 and TBAF to reform the gel phase, with a corresponding restoration of the absorption and emission spectra of compound 1 to match those of the neat gel. Therefore, we can operate a three-input and three-output logic gate in an ODCB system similar to that in DMSO/H2O (Figure 8).

More interestingly, excess TFA, such as 20 equivalents, could decompose the ODCB gel into solution (see the Supporting Information, Figure S9), with a maximum absorption peak at 395 nm, which was indicative of a red shift of 4 nm relative to that of the monomeric state (391 nm). The corresponding emission spectrum exhibited a strong green fluorescence with a maximum of 515 nm (Figure 9b). If the addition of 20 equivalents of protons, 20 equivalents of fluoride anions, and light irradiation (400 nm) were regarded as inputs of a logic gate, a new three-input-three-output gate, different from the DMSO/H2O system, could be obtained (Figure 9c). The inputs of H+ ions, F- ions, and 400 nm light, and the output of fluorescence intensity at 600 nm were built a combination logic gate of NOR and AND gates. Two inputs of H+ and F- ions afforded a XNOR gate, which incorporated the absorbance at 400 nm as another output (Out2), and created a NOR with third output (Out3; gel phase = 1, sol = 0).

**Logic gate of xerogel films**: The response properties of xerogel films were also examined. Xerogel films synthesized from DMSO/H2O and ODCB emitted strong yellow fluorescence, with red shifts of the emission bands relative to those of the wet gels.[15] For example, the maximum emission peak of the wet DMSO/H2O gel was located at 540 nm, whereas the corresponding xerogel film possessed an emission peak at 552 nm. The emission peak for the xerogel film from ODCB also showed a red-shifted emission peak, with a maximum at 562 nm. Moreover, both xerogel films showed responses to the vapor of some volatile acids, such as TFA and hydrochloric acid. Upon exposure to the saturated vapor of TFA, the fluorescence of the films was quenched and their emission bands exhibited a clear red shift (Figure 10). The

![Figure 9](image1.png)

**Figure 9.** a) Absorption and b) fluorescence spectra of compound 1 in ODCB (0.5 mM) in the presence of TBAF and TFA; c) representation and truth table of a combination logic gate.

![Figure 10](image2.png)

**Figure 10.** Emission spectra of xerogel films exposed to TFA gas and the saturated vapor of ammonia water (25%) in a) DMSO/H2O and b) ODCB. Insets: emission quenching of xerogel films by TFA gas over time. The detectable wavelength was 550 nm. Inset images: corresponding photographs of films under illumination at 365 nm. c) Representation and truth table of a combination logic gate.
fluorescence color of the films was observed to change from yellow to orange by the naked eye. Furthermore, the xerogel films of compound 1 provided fast responses to the vapor of TFA: 1.3 s for DMSO/H₂O xerogel film and 3.0 s for the ODCB xerogel film. More importantly, the fluorescence of films exposed to TFA vapor could be recovered quickly by exposure to ammonia vapor (see the Supporting Information, Figure S10). Such a reversible fluorescence change could be repeated many times. Thus, these film systems provided a new combination logic gate with three inputs and two outputs (Figure 10c). The emission intensity at 520 nm (Out1) gave a high value (1) when only the exclusive INH gate of TFA (In1) and NH₃ (In2), was activated by irradiation of 400 nm light as In3. If the naked eye acted as additional output, yellow fluorescence = 0, and red fluorescence = 1, the system only gave a true terminal output (1) when only the signals of the INH gate of TFA (In1) and NH₃ (In2) was activated by In3.

Conclusion

We have examined the responsive properties of a gelator, which contained five amide moieties and one benzimidazole group, to anions, protons, and optical inputs in its solution, gel, and film states, and applied them to construct a logic gate. The results indicated that these three states of the gelator could not only construct a basic logic gate, but also some combination gates because of their response to multiple chemical stimuli and multiple output signals. We believe that these switchable systems may have a variety of applications. Moreover, these results suggest that the gelator can act as a promising candidate for applications not only in the gel state, but in its other phases.

Experimental Section

Instruments: IR spectra (KBr disks) were measured using a Nicolet-360 FTIR spectrometer. UV/Vis spectra were obtained on a Perkin-Elmer 240C elemental analyzer. Photoluminescence measurements were taken on a Shimadzu RF-5301 Luminescence Spectrometer. 1H NMR spectra were recorded on Mercury plus 500 MHz. SEM images were carried by a scanning electron microscope. The samples were prepared by a casting-film method.

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