Regulation of bi-color fluorescence changes of AIE supramolecular self-assembly gels by the interaction with Al$^{3+}$ and energy transfer

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Supramolecular fluorescent materials have attracted considerable attention in recent years since they endow specific and unique properties to materials. Nevertheless, the utilization of photo-responsive characteristics to modulate their fluorescence emission behaviors and functions are still rarely explored. Here a facile fabrication strategy for producing dual emissive materials based on the supramolecular gels was proposed. A bi-acylhydrazone supramolecular gelator BD was designed and synthesized by a Schiff base reaction. Interestingly, the gelator BD could self-assemble into stable supramolecular gel BDG with strong aggregation-induced emission (AIE) in DMF-H$_2$O binary solutions via π-π stacking interactions. On the one hand, the BDG could selectively identify Al$^{3+}$ in the gel state. Upon addition of Al$^{3+}$, the AIE BDG shows an obvious blue shift (85 nm, from yellow-green to sky-blue). On the other hand, artificial light-harvesting systems were successfully fabricated in gel environment based on the supramolecular strategy. In these systems, efficient energy transfer occurs between the BD assembly and the loaded acceptors. For instance, the transition from yellow-green to red light could be accomplished in BDG/SR 101 system. Based on these, the manipulation of bi-color fluorescence emission have been realized by the interaction with Al$^{3+}$ and energy transfer.

1. Introduction

The phenomenon and concept of aggregation-induced emission (AIE) of organic compounds, proposed by Tang and co-workers in 2001, has been attracting considerable research interest and shows an extensive application prospects in many filed including chemical sensing, fluorescent sensors, bioimaging and so on. In the AIE process, AIEgens exhibit strongly fluorescence emission in the aggregated state, which is different from the aggregation caused quenching (ACQ) effect. Supramolecular materials, where the component molecules are combined together through the non-covalent bond, has been attracting great interest. In these systems, the AIE can attribute much to provoke wholesale academic interest for innovative practical applications.

Supramolecular gels were constructed by single noncovalent interaction or the combination of multiple noncovalent interactions. By comparison, the dynamic and reversible properties of multiple noncovalent interactions endow supramolecular gels with excellent response to various external stimuli, such as heat, light, pH, metal cations and so forth. Meanwhile, the gel is a soft substance between a liquid state and a solid state, and a large amount of solvent molecules are fixed/wrapped by gelators, in which the solvent could contribute also. These characteristics will provide a broad scope for the fabrication of smart materials or devices.

Recognition and sensing of metal ions have become the focus of considerable attention in biological, chemical, material and environmental fields. Aluminum is the third most abundant of all the elements (after oxygen and silicon) in the earth's crust, accounting for 8.3% of total mineral components. High aluminium intake can damage the central nervous system and be involved in Alzheimer's disease, Parkinson's disease, bone softening, chronic renal failure and smoking-related diseases. Accordingly, the development of convenient and efficient testing methods for Al$^{3+}$ is of great significance for environmental protection and human health. In this way, developing a fluorescent chemosensor for the selective recognition and monitoring of Al$^{3+}$ in environmental or in living cells is essential.

Photosynthesis plays a vital role in the survival foundation for organisms, in which the large number of closely packed antenna pigments (ca. 200) around the reaction center is applied in the energy transfer and accumulation of sunlight. Several scaffolds have had extraordinary results in...
mimicking natural light-harvesting process by achieving efficient energy transfer from donors to acceptors through a Förster resonance energy transfer (FRET) process,19, 20 such as protein assemblies,21 dendrimers,22 metal complex polymers, and porphyrin assemblies. These artificial light-harvesting systems/materials are of significant importance for practical applications, which is still less emphasized in the gel state to date.23

Fluorophores with aggregation-induced emission properties are good candidates for the construction of fluorescent supramolecular systems. However, supramolecular gels with tunable emission have been rarely reported, although some progress has recently been made on the construction of discrete fluorescent supramolecular assemblies.24 Traditionally, more than one kind of fluorophores should be incorporated to construct this kind of gel, thus resulting in the complexity of the designed systems. Besides this method, the emission behavior could also be tuned by the introduction of interactions with ions, host-guest interactions or other forms of interaction,9-10, 23 resulting in the change in the emission wavelength. Herein, we reported a bi-acylhydrazone compound, which was found to exhibit competitive guest stimuli responsiveness in the gel state and AIE properties. The stable organogel (BDG) shows selective and sensitive stimuli-response for Al^{3+} but the BD in solution could not detect Al^{3+} in the fluorescence analysis experiment. Moreover, efficient light-harvesting systems (LHSs) are successfully fabricated using organogel BDG as an energy donor, and a series of dyes such as sulforhodamine 101, acridine red, rhodamine B and rhodamine 6G as energy acceptor, respectively. Additionally, the fluorescence color and emission spectrum of BD can be effectively tuned by metal ion coordination or fabricating light-harvesting systems. As far as we know, this is the first report that connects self-assembly, AIE activity, light-harvesting and ion recognition through a multifunction bi-acylhydrazone derivative (Scheme 1).

![Scheme 1. Schematic representation for bi-color fluorescence changes of a bi-acylhydrazone compound](image)

2. Experimental

2.1. Materials and general methods

2 - (2 - hexyl - 1 H - benzimidazole - 1 - yl ) Acetohydrazide, terephthalaldehyde, organic solvent and metal salt were commercially available and were used without further purification. Deionized water was used for the whole experiment process. The measurements of steady-state luminescence were performed with a Shimadzu RF-5301PC spectrometer and spectrofluorophotometer (F-4500, Japan). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-1750 spectrometer. The infrared spectra were recorded on a Thermo Scientific Nicolet iSS FT-IR spectrophotometer. Fluorescence micrographs (FOM) of the samples were performed with Olympus IX 71. The 1H and 13C NMR spectra were recorded on a Bruker 400 MHz spectrometer. The internal standard was TMS and the solvents were dimethyl sulfoxide (DMSO-d<6>). Time-resolved photoluminescence decay measurements were carried out using a time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, FLS 980). Mass spectra were carried out by a Bruker solanX 70 FT-MS mass spectrometer equipped with ESI interface and ion trap analyzer. The morphologies of the as-synthesized samples were characterized with a SM-74190UEC SEM using an accelerating voltage of 10kV. The quantum yield was measured on a FLS980 fluorescence spectrometer. X-ray diffraction patterns (XRD) were determined with a X’ Pert PRO diffractometer using Cu-Kα radiation over the 2θ range of 5-90°.

2.2. Synthesis of compounds

As shown in Scheme 2, 2-(2-hexyl-1H-benzimidazole-1-yl) Acetohydrazide (6.855 g, 25 mmol) and terephthalaldehyde (1.341 g, 10 mmol) with a molar ratio of 2.5:1 were dissolved
in DMF (100 mL). The mixture was stirred under reflux at 80 °C for 8 h at acetic acid (2 - 3 drops). After reaction was finished and cooling to room temperature, the precipitate was collected by filtration, washed three times with hot absolute ethanol, and then dried in vacuum; giving a faint yellow powder compound BD (5.030 g, yield: 61%). 1H NMR (400 MHz, DMSO-d6, Fig. S1) (ppm): 11.88 (d, 2H, N=H), 8.31-8.11 (d, 2H, N=CH), 7.94-7.15 (m, 12H, ArH), 5.49-5.03 (d, 1H). ESI-MS: m/z 647.4 ([C38H30N30]+ H+). Scheme2. Synthesis of gelator BD

and various nitrate solutions containing Na⁺, K⁺, Mn²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Cu²⁺, Cr³⁺, Fe³⁺, Hg²⁺, Cd²⁺, Co²⁺, Mg²⁺, and Al³⁺ of 1 mol·L⁻¹ were used for testing the fluorescence performance of the gel BDG towards metal ions. All the fluorescence spectra experiments were implemented in DMF-H₂O (1 : 4, v/v) binary system. Any fluorescence changes of compounds were recorded on the addition of nitrate salt, while gelation concentration of the supramolecular gel was 0.5% in all experiments. To further study the sensitivity of the gel BDG for Al³⁺ detection, the gelator BD in DMF and various concentrations of Al³⁺ aqueous solution were mixed intensively before measurement.

2.3. Fluorescence measurements

Various nitrate solutions containing Na⁺, K⁺, Mn²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Cu²⁺, Cr³⁺, Fe³⁺, Hg²⁺, Cd²⁺, Co²⁺, Mg²⁺, and Al³⁺ of 1 mol·L⁻¹ were used for testing the fluorescence performance of the gel BDG towards metal ions. All the fluorescence spectra experiments were implemented in DMF-H₂O (1 : 4, v/v) binary system. Any fluorescence changes of compounds were recorded on the addition of nitrate salt, while gelation concentration of the supramolecular gel was 0.5% in all experiments. To further study the sensitivity of the gel BDG for Al³⁺ detection, the gelator BD in DMF and various concentrations of Al³⁺ aqueous solution were mixed intensively before measurement.

3. Results and discussions

3.1 Form of the gel BDG

First of all, to exam the assembly ability and gelation properties of the gelator BD, we configured BD in a variety of polar, non-polar organic and component solvents (organic solvents-H₂O), respectively into the proportion of 5% and heated it completely. After cooled to room temperature, we found that BD could self-assemble into a stable gel only in DMF, DMF-H₂O binary solution, DMSO and DMSO-H₂O binary solution. The successful preparation of the gel BDG was verified via a “stabilized reverse tube” method and the results were summarized in Tables S1. As a general procedure, the compound BD (0.015 mmol) were completely dissolved in DMF (0.4 mL), then H₂O (1.6 mL) was added, dissolved completely by mixing a hot solution, and finally the mixture was cooled to ambient temperature. As a vital parameter of supramolecular gel, we investigated the effect of different water content on the assembly ability of gel (Fig. S4), which plays an important role when we were choosing the solvent composition of BD gel. In DMF-H₂O binary system, with the water content less than 67.5%, the gel of BD cannot be obtained. And meanwhile, we also conducted partial tests for DMSO (Tables S1, Fig. S6 and S7). By comparison, BD dissolves more quickly in DMF than in DMSO. The lowest critical gelation concentration (CGC) in DMF is 2.5% (w/v %, 10 mg·mL⁻¹ = 1.0%) and the gel-sol transition temperature (Tgel) in DMF is 74 °C. More interestingly, The CGC of the BD in DMF-H₂O (1 : 4, v/v) is 0.5% and the Tgel is 95 °C in DMF-H₂O (1 : 4, v/v). Hence, the DMF-H₂O (1 : 4, v/v) binary system is optimal for the formation of the gel BDG. As shown in Fig. 1a, the morphology structure of the BDG is further investigated by scanning electron microscopy (SEM), which is observed in homogeneous uniform state. We can find that large fibres exhibit some fine structure and appear to be multi-layered. 3D entangled network structures comprised of fibers with high aspect ratios were obtained, revealing well-ordered molecular packing properties. The fibres lacking of twisting and regular shape exist in the form of widths of 200-500 nm and lengths of dozens of micrometers. As the FOM (fluorescent optical microscopy) images show, the morphology of BDG are formed of dense aggregated bundles of fibres (Fig. 1b). Interestingly, a significantly yellow-green light can be achieved in the BDG.

Fig. 1 (a) FE-SEM micrographs of the xerogel of BD. The gel was two days old before the images were taken. (b) FOM images of the BDG (0.5%, V_{DMF} : V_{water} =1 : 4)
Fig. 2  Temperature-dependent fluorescent spectra of BDG ($V_{DMF} : V_{water} = 1 : 4$, 0.5%) during gelation process ($\lambda_{ex} = 372$ nm)

3.2 AIE behaviours

As shown in Fig. 2, the solution of BD had inappreciable fluorescence. Whereas, the emission intensity emerged rapidly, and reached a steady state finally at $\lambda = 520$ nm in the process of the temperature of heated DMF/water solution declined under the $T_{gel}$ ($T < T_{gel}$) of BDG, which indicated that the fluorescence of supramolecular gel BDG was aggregation induced emission (AIE), accompanied by yellow-green fluorescence. In order to indicate that it wasn’t a pure thermal effect, we did another experiment as a supplementary proof of AIE properties of the BD gel (Fig. S8). From the experiment, we can see that BD powder (25 °C) has a yellow-green light under UV light, which corresponds to the description in Fig. 2. However, this phenomenon does not exist in BD powder (25 °C) under daylight or BD in DMF (1 × 10⁻⁴ M, 25 °C) under UV light. That means the molecule BD presents the interesting aggregation-induced emission phenomenon. BD was insoluble in water, and the fluorescence of BD in aggregation state was also studied in a DMF/water mixtures with different water fractions to investigate its solvent-dependent aggregation behavior (Fig. S9). The emission peak at 430 nm of BD (3 × 10⁻⁴ M) was very weak in DMF and almost kept constant until the water fraction reached 30%. The fluorescence intensity of BDG were investigated in the gel state (Fig. S12). When the concentration of Al³⁺ is further increased, a blue shift of 85 nm emerges; meanwhile the original peak disappears. Then the fluorescence intensity of BDG at 435 nm enhances gradually with the continuing increase of Al³⁺ concentration. The fluorescent selectivity of BDG towards Al³⁺ may be attributed to the smaller ionic radius (0.5 Å), which allowed a suitable coordination geometry with BD and higher charge density that made Al³⁺ coordinate to BD strongly.²⁶ In the presence of the Al³⁺ ion, the carbonyl O and acylhydrazone N can coordinate with the Al³⁺ center atom, which increased the energies of the n–p* transitions compared to the corresponding p–p* transitions, and finally the PET process was interrupted, and the fluorescence changes from yellow-green to blue emission. As the Job’s plot experiments showed, we can see an obvious peak at 3 : 7 of BDG–Al³⁺, assignable to the best composition ratio of BDG–Al³⁺ (1 : 2) (Fig. 4a). In terms of the performance of identifying Al³⁺, for example, Fig. 4b shows an investigation...
total concentration of BD and Al$^{3+}$ is $1 \times 10^{-3}$ mol/L. (b) Fluorescence responses of the BD-gel based sensor array to the presence of various cations under UV at 365 nm. In gels, the concentration of BD in the sample is 0.5 wt%.

![Figure 5](image)

**Fig. 5** Partial $^1$H NMR spectra (400 Hz, 298 K) of BD ($2.0 \times 10^{-2}$ M) in DMSO-$d_6$ with increasing amounts of Al$^{3+}$ (0.1 M, DMSO-$d_6$ (a) free BD; (b) 1.0; (c) 2.0; (d) 5.0 equiv.

in which various metal cations (including Na$^+$, K$^+$, Mn$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Mg$^{2+}$ and Al$^{3+}$) are put into dot arrays of BD-gel, but only Al$^{3+}$ gave BDG bright sky-blue color under UV light at 365 nm.

In addition, the response mechanism of the BDG for Al$^{3+}$ was further investigated by $^1$H NMR titration, IR, and XRD. In the $^1$H NMR titrations of Al$^{3+}$ for BD (Fig. 5) with the increasing concentration of Al$^{3+}$, the N–H (H$^\delta$) signals show a downfield shift. When adding proper Al$^{3+}$, the weakness of the N–H(H$^\delta$) signal at $6.11$ ppm indicated that the deprotonation process occurred. In the meanwhile, the hydrogen bond existing in the acylhydrazone group was destroyed during the coordination of Al$^{3+}$ with the carboxyl group of BD. Additionally, at low concentration of BD, $=\text{CH}$ (H$^\delta$) on BD appeared and its signals show a downfield shift with the increasing concentration of Al$^{3+}$. Therefore, the possible sensing mechanism based on deprotonation was proposed as given in Fig. S13. The XRD patterns of free BDG and BDG-Al (Fig. S14) showed $d$-spacings of 3.52 Å and 11.45 Å at $2\theta = 25.23^\circ$ and 7.71$^\circ$ supporting the presence of π–π stacking and hydrophobic interaction in the BD. At the meantime, $d$-spacings of 3.51 Å and 3.80 Å at $2\theta = 25.37^\circ$ and 23.34$^\circ$ suggested that the $\pi$–$\pi$ stacking remained in metallogel BDG-Al. FT-IR spectra of the powder gelator BD and the xerogel BDG-Al were measured to deeply understand the coordination of Al$^{3+}$ with the gelator BD (Fig. S15). The bands at 1695 and 1596 cm$^{-1}$ corresponding to $\nu$ (C=O) and $\nu$ (C=N) are present in the IR spectrum of the gelator BD. However, with the addition of 2.0 equiv. of Al$^{3+}$ and the formation of Al$^{3+}$ coordinated metallogel BDG-Al, the $\nu$ (C=N) band shifts to lower wavenumber (1562 cm$^{-1}$), respectively, due to coordination with the metal centre.

### 3.3 Light-harvesting

Due to the unique AIE effect, compound BD in the aggregated form can exhibit broad emission at 520 nm, which enables BD act as a remarkable donor in gel. The potential of fluorescence resonance energy transfer (FRET) between AIE (BDG) and acceptors were investigated herein. Sulforhodamine 101 (SR 101), acridine red, rhodamine 6G (Rh 6G) and rhodamine B (Rh B) was selected as energy acceptor, respectively, since they show strong absorption in the visible region and overlap with the emission from BDG. As shown in Fig. 6a, Fig. S16a, S16c and S16e, the absorption band of these dye molecules overlapped well with the fluorescence emission of the BD assembly. On the other hand, a key parameter in facilitating efficient energy transfer process is the spatially well-organized chromophores. This can be realized in between the BD assembly and the dyes. As shown in Figure 6b, with the gradual addition of dye SR 101, the fluorescence intensity of BDG decreased significantly, while the fluorescence emission band of SR 101 appeared and increased when excited at 372 nm, accompanying with a change of emission color from green/yellow to red under a UV lamp.

The fluorescence quantum yield of BDG/SR 101 system was estimated to be 13.28% (Fig. S17a). According to fluorescence titration spectrum, the energy transfer efficiency was calculated to be 80% (Fig. S18a) at a donor/acceptor ratio of 200:1. Upon gradual addition of acridine red, Rh 6G and Rh B as acceptors to the BD assembly, respectively, the emission...
peak of BDG begin to decay while the emissive intensity of acceptors kept increasing (Fig. S16b, S16d and S16f). According to fluorescence titration spectrum, the energy transfer efficiency ($\Phi_{ET}$) of acridine red, Rh 6G and Rh B as acceptors are calculated to be 98%, 99%, and 98% (Fig. S18b, S18c and S18d). The fluorescence quantum yield of acridine red, Rh 6G and Rh B system was estimated to be 14.99%, 11.88% and 7.51% (Fig. S17b, S17c and S17d).

Furthermore, to clearly show the energy transfer (ET) from BDG to acceptors during the gelation process, we measured the fluorescence spectra of gelation in energy transfer systems (Fig. S19). In view of rapid gelation of BD, we performed the experiment at lower concentrations. Primarily, when adding SR 101 into BDG (molar ratio of BDG: SR 101 is 3000 : 1) in DMF/H$_2$O solution, fluorescence spectrum of BDG/SR 101 showed a continuous significant increase at 610 nm during the gelation process (Fig. S19a). In addition, compared with the emission spectrum of BDG (Fig. S20) at the same concentration, fluorescence intensity of BDG/SR 101 at 515 nm after 10 minutes is only half as much as intensity of BDG. Finally, the morphologies of BDG/SR 101, BDG/acridine red, BDG/Rh 6G and BDG/Rh B were investigated by scanning electron microscopy (SEM) (Fig. S21). The SEM images of the light-harvesting systems showed a number of micron rodlike structure. The transformation from network structures into stick structures indicated that dye molecules could create a interaction with BDG to change the previous intramolecular interactions, thereby the formation of rod-like supramolecular structure was observed. Subsequently, the fluorescent optical microscopy (FOM) images further truly reflected the morphology and luminescence phenomenon of the light-harvesting systems (Fig. S22).

4. Conclusion
In conclusion, we have designed a novel organogelator BD which can be self-assembled into organogel BDG with strong AIE. The supramolecular gel BDG can serve both as a selective fluorescence sensing system for Al$^{3+}$ and light-harvesting energy donor with several kinds of dyes through FRET mechanism. Notably, the supramolecular coordination complexes BDG-Al$^{3+}$ formed by the metal-coordination-driven self-assembly emit from yellow-green to sky-blue as the concentration of Al$^{3+}$ increases. The fluorescence emission from yellow-green to red was also obtained via the host–guest interactions in artificial light-harvesting systems. This simple bi-acylhydrazone demonstrates an example as a multi-function light-emitting material including AIE activity, light-harvesting, sensing properties and so on.

Conflicts of interest
There are no conflicts to declare.

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