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## PAPER

# Freezing-induced multi-colour emissions of AIE luminogen di(4-propoxyphenyl) dibenzofulvene

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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This work reports the freezing-induced emission change of di(4-propoxyphenyl) dibenzofulvene (DBF) molecules, which exhibits unusual aggregation-induced emission (AIE) and crystallization-induced emission enhancement (CIEE) effects. DBF powders in both amorphous (orange) and crystalline (yellow and green) states undergo rapid reversible shifts in their maximum emission wavelengths ( $\lambda_{em}$ ) during the freezing-thawing (F-T) process. When the acetonitrile/water DBF dispersions emitting orange or yellow colours are F-T treated, their emissions change to green. Moreover, the DBF dispersions containing poly(*N*-vinylpyrrolidone) (PVP) and acrylamide (AAm) undergo gradual and more significant blue-shift in  $\lambda_{em}$  with F-T cycles, further blue-shifts in  $\lambda_{em}$  are found when F-T treated dispersions are gelled or just kept for some times. The emission change of the DBF dispersions with the F-T process and the after-treatment is confirmed to be due to the change of their aggregation morphologies. DBF dispersions and hydrogels with different emission colours are obtained, and the luminescent hydrogels exhibit excellent mechanical properties. This study reveals a new freezing-induced emission change of AIE substances and provides a simple method for preparing hydrogels emitting different colours by using one luminogen.

## Introduction

Fluorescent materials emit either visible or invisible light when irradiated with a shorter wavelength, such as ultraviolet light and X-rays. Fluorescent materials, especially those with stimulus-responsive properties, have many practical applications, such as chemical sensors,<sup>1-7</sup> fluorescent labelling,<sup>8,9</sup> and biological detectors.<sup>10-13</sup>

Common organic fluorescent luminophores typically comprised of planar aromatic rings (*e.g.* perylene) show aggregation-caused quenching (ACQ) behaviour, which is harmful for many practical applications. Just exactly opposite to the ACQ effect, Tang and co-workers discovered the “aggregation-induced emission” (AIE) effect of 1-methyl-1,2,3,4,5-pentaphenylsilole, which is non-emissive in dilute solutions but becomes highly luminescent when the molecules are aggregated.<sup>14</sup> Based on the understanding that the restriction of intramolecular rotation (RIR) in the aggregates is a main cause for the AIE effect, a large variety of new propeller-shaped AIE luminogens have been developed.<sup>15-21</sup> AIE substances have potential applications as chemical sensors, biological probes, light-emitting devices.<sup>20-24</sup>

Some AIE substances also show crystallization-induced emission enhancement (CIEE) effect, and hence they exhibit multiple switchable colours corresponding to different aggregation morphologies.<sup>25-27</sup> For instance, di(4-propoxyphenyl)-dibenzofulvene (hereafter shortened as DBF, Fig. 1) emits orange (580 nm), yellow (547 nm) and green (500 nm) colours when the DBF aggregates in the amorphous and two crystalline structures, respectively. The crystalline structures of DBF differ in the torsion angles of the two phenyl rings, and that in the green single crystals is larger than that in the yellow single crystals, *i.e.* the DBF molecules in the green single crystals adopt a more twisted conformation than those in the yellow single crystals (Fig. 1).<sup>25</sup> The amorphous and crystalline structures are interchangeable upon thermal, solvent, and mechanical stimuli.

In our very recent work, we incorporated the AIE and CIEE luminogen DBF into hydrogels to prepare luminescent hydrogels emitting different colours. We observed that blue-emitting hydrogels can only be obtained when the DBF dispersions are treated with freezing-thawing (F-T) method.<sup>28</sup> To the best of our knowledge, the freezing-induced emission change of fluorescent materials has never been studied. In this

work, we studied the freezing-induced emission change of DBF powders and dispersions and the aggregation morphologies in detail.

Incorporating fluorescent materials into hydrogels broadens their practical applications.<sup>29-31</sup> However, the reported fluorescent hydrogels are usually mechanical very weak. In the last decade, several types of tough mechanical hydrogels have been developed,<sup>32,33</sup> including a series of tough hydrogels developed by our group based on the concept of polyfunctional initiating and crosslinking centers (PFICC).<sup>34-38</sup> Very recently we developed a novel tough hydrogel physically cross-linked by very strong cooperative hydrogen bonding, which is fabricated by *in situ* polymerization of acrylamide (AAM) in the presence of PVP without using any chemical initiators and cross-linking agents.<sup>39</sup> In this work, we incorporated DBF molecules into the tough hydrogel to obtain luminescent hydrogels with excellent mechanical properties.

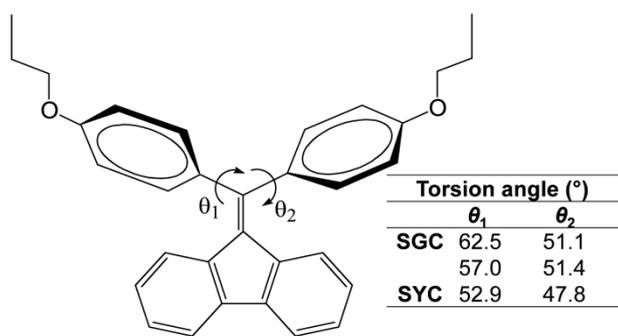


Fig. 1. Chemical structure of DBF and its torsion angles in single green crystals (SGC) and single yellow crystals (SYC). Adapted from literature [25].

## Experimental section

### Materials

Poly(*N*-vinylpyrrolidone) (PVP,  $M_w=4.0 \times 10^4$ , high pure grade) and acrylamide (AAM, ultra pure grade) were purchased from Amresco Inc. (OH, USA). Acetonitrile (HPLC grade) was purchased from Kemiou Chemical Reagent Co. (Tianjin, China). Di(4-propoxyphenyl) dibenzofulvene was prepared by ourselves.<sup>25</sup>

### Preparation of DBF dispersions

DBF solution ( $1 \times 10^{-3}$  mol L<sup>-1</sup>) was firstly prepared using acetonitrile as the solvent, and then DBF dispersions ( $1 \times 10^{-4}$  mol L<sup>-1</sup>) with different water contents were prepared by adding different amounts of deionized water and acetonitrile in the solution. DBF dispersions with different concentrations of AAM ( $C_{AAM}$ ) and/or PVP ( $C_{PVP}$ ) were also prepared by adding AAM and PVP into the DBF water/acetonitrile dispersions.

### Freezing-thawing of DBF dispersions

The DBF dispersions with or without AAM and PVP were treated with the freezing-thawing method. They were immersed into liquid nitrogen or kept in a refrigerator until the solutions were frozen completely, and then the solutions were thawed at

room temperature. The freezing-thawing process was repeated for different times.

### Luminescent hydrogels synthesis

The DBF dispersions containing AAM and PVP were transferred into test tubes or molds made by placing a silicone spacer with a height of 2 or 4 mm between two glass plates. Dissolved oxygen in the solution was then removed by 3 cycles of vacuum evacuation and exchange with high-purity nitrogen. Finally, the solutions were kept at 50 °C for 36 h to form hydrogels.

### Photoluminescence and UV-visible spectroscopy

The photoluminescence spectra of the DBF powders, the dispersions and the hydrogels were measured with a Cary Eclipse fluorospectrophotometer (Varian Inc., Walnut Creek, CA, USA). The excitation wavelength ( $\lambda_{ex}$ ) was selected as 370 nm, and the slit width was 5 nm.

A thin layer of DBF powders was glued to one side of a quartz cuvette and then its photoluminescence spectrum was measured at room temperature. Next, the cuvette was frozen in liquid nitrogen for 2 min and then the cuvette was immediately put into the fluorospectrophotometer, the change of the photoluminescence spectra of the frozen DBF powders kept at room temperature with time was recorded after every one minute. The DBF dispersions and the gel samples with a thickness of 2 mm were put in a quartz cell to record their photoluminescence spectra.

The UV absorption spectra of the DBF dispersions were measured with a UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu spectrometer, Japan).

### Fluorescence microscopy

Fluorescent observations of the morphologies of DBF aggregates in the DBF dispersions were performed with an upright fluorescence microscope (ZEISS Imager M1, Germany) equipped with a shift-free EX G 365 excitation filter (excitation, 365 nm) using an EM LP 420 emission filter.

### Scanning electron microscope (SEM) investigations

The DBF dispersions were dropped on Si substrates. After the evaporation of solvents and sputtered with gold for 10 min, the morphologies of DBF aggregates were investigated with a HITACHI S-4800 scanning electron microscope (Tokyo, Japan) with an accelerating voltage of 10 kV.

### Mechanical tests

The as-prepared hydrogels were cut into dumbbell shaped specimens for tensile testing, according to DIN-53504 S3 size (inner width: 2 mm; gauge length: 10 mm, thickness: 2 mm), and then tested with an Instron 3366 electronic universal testing machine (Instron Corporation, MA, USA) at a cross-head speed of 100 mm min<sup>-1</sup>. The tensile stress  $\sigma_t$  was calculated as follows:  $\sigma_t = \text{Load}/tw$  ( $t$  and  $w$  were the initial thickness and width of the dumbbell shaped hydrogel sample, respectively). The tensile strain  $\varepsilon_t$  is defined as the change in the grip

separation relative to the initial length,  $\varepsilon_t = [\Delta l/l_0] \times 100\%$  ( $\Delta l$  is the grip displacement during testing and  $l_0$  is the length of the sample before tests). Tensile fracture stress or tensile strength ( $\sigma_b$ ) and the tensile fracture strain or elongation at break ( $\sigma_b$ ) are defined as the tensile stress and strain at which the specimen breaks, respectively. To obtain reliable values, at least three samples per experimental point were tested in all mechanical measurements and the gel samples were covered with a thin layer of silicon oil to prevent the evaporation of water before the tests.

## Results and Discussion

### DBF powders

We firstly noticed that DBF powders in both amorphous (orange) and crystalline (yellow and green) states undergo emission change during the freezing-thawing (F-T) process. Fig. 2 shows the photoluminescence (PL) spectra of the DBF powders emitting orange, yellow and green colours after being frozen with liquid nitrogen and then thawed at room temperature for different times. An obvious blue-shift in the maximum emission wavelength ( $\lambda_{em}$ ) is observed for the DBF powders after freezing, *i.e.* from 586 nm (orange) to 557 nm (yellow) (Fig. 2a), from 551 nm (yellow) to 505 nm (green) (Figure 2b), and from 508 nm (green) to 486 nm (sky blue) (Fig. 2c). Upon thawing at room temperature, the  $\lambda_{em}$  of the powders rapidly red-shifts to their original values. These results reveal that the DBF powders undergo rapid reversible photoluminescence change during the freezing-thawing process.

### DBF acetonitrile/water dispersions

DBF is in an amorphous state and hence nonluminescent when dissolved in its good solvents, such as acetonitrile and acetone. However, when a large amount of a poor solvent (*e.g.* water) is added, it aggregates to form crystalline structures which emit different colours depending on the volume ratios of the good and poor solvents. For instance, DBF emits green, yellow and orange colours when the water contents are 60%, 70% and 90% in acetonitrile/water mixed solvents, respectively.<sup>25</sup>

We tried to freeze the DBF dispersions with different acetonitrile/water ratios in liquid nitrogen (-196 °C) for 2 min or in a refrigerator (-20 °C) for 24 h and then thaw them at room temperature, and found that in both cases the emission colours of DBF in these dispersions are changed to green (Fig. 3 and Fig. S1). For the dispersions with 70% (Fig. 3a) and 80% (Fig. S1a, b) water, their emission colours change from yellow or orange to green after only one F-T treatment, respectively. For the dispersion with 90% water, its emission colour changes from orange to green after freezing at -20 °C for 24 h (Fig. S1c). When it is frozen at -196 °C for 2 min, its emission colour changes from orange to yellow after one F-T cycle and further to green after two cycles (Fig. 3b). No further emission colour change can be found when more F-T treatments are carried out.

In the later work, the freezing was carried out in liquid nitrogen (-196 °C) for 2 min if not otherwise stated. The

concentration of DBF in the dispersions was fixed to  $1 \times 10^{-4}$  mol L<sup>-1</sup>, and the excitation wavelength ( $\lambda_{ex}$ ) was always 370 nm. To simplify the expression, the F-T treatments are referred as F-T- $x$ , where  $x$  is the number of F-T cycles.

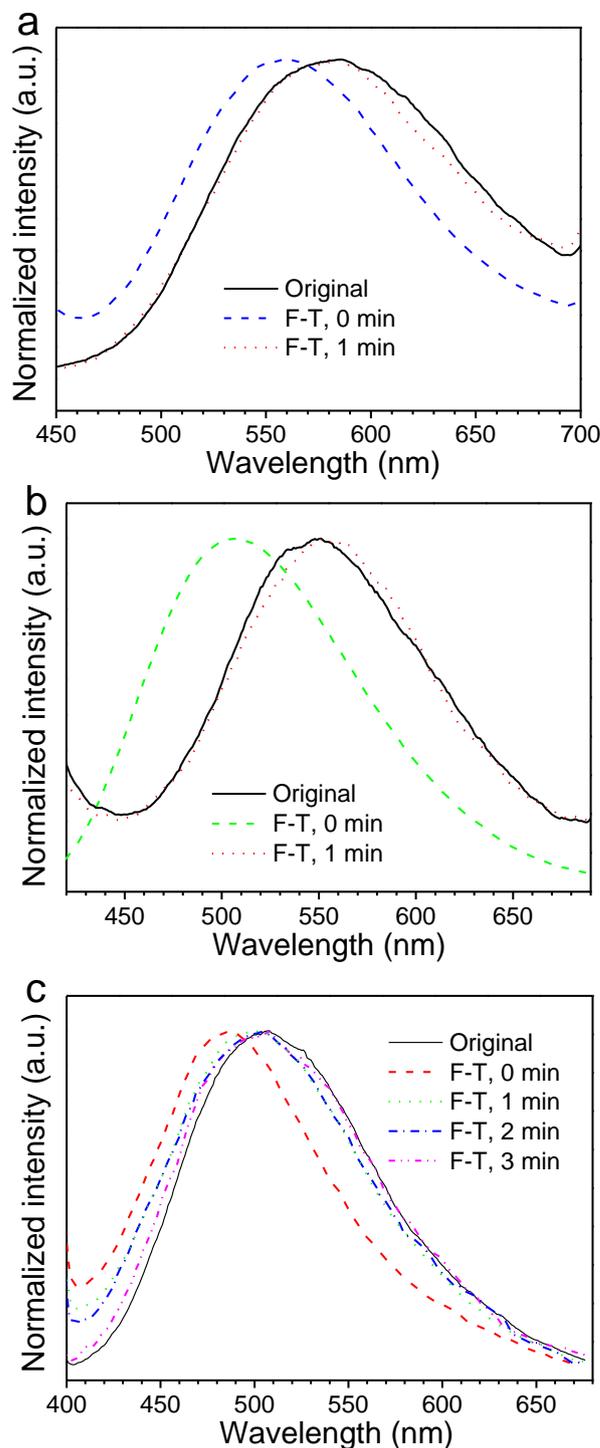
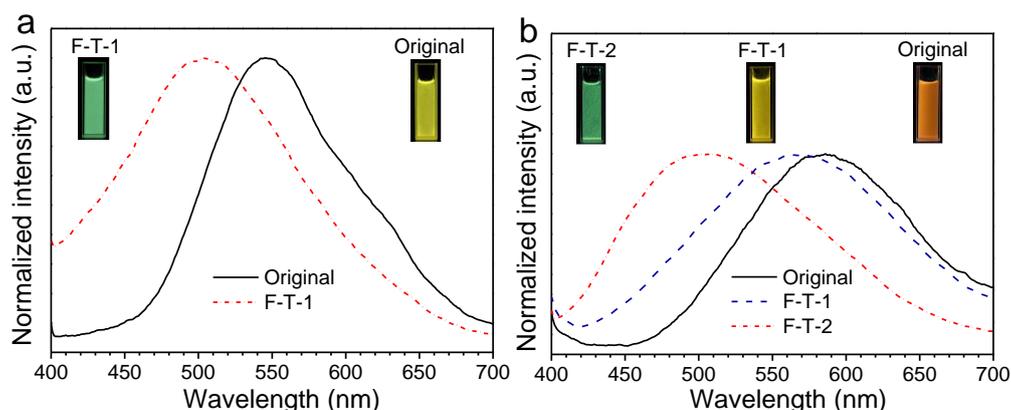


Fig. 2. F-T induced reversible photoluminescence change of orange (a), yellow (b) and green (c) emitting DBF powders.

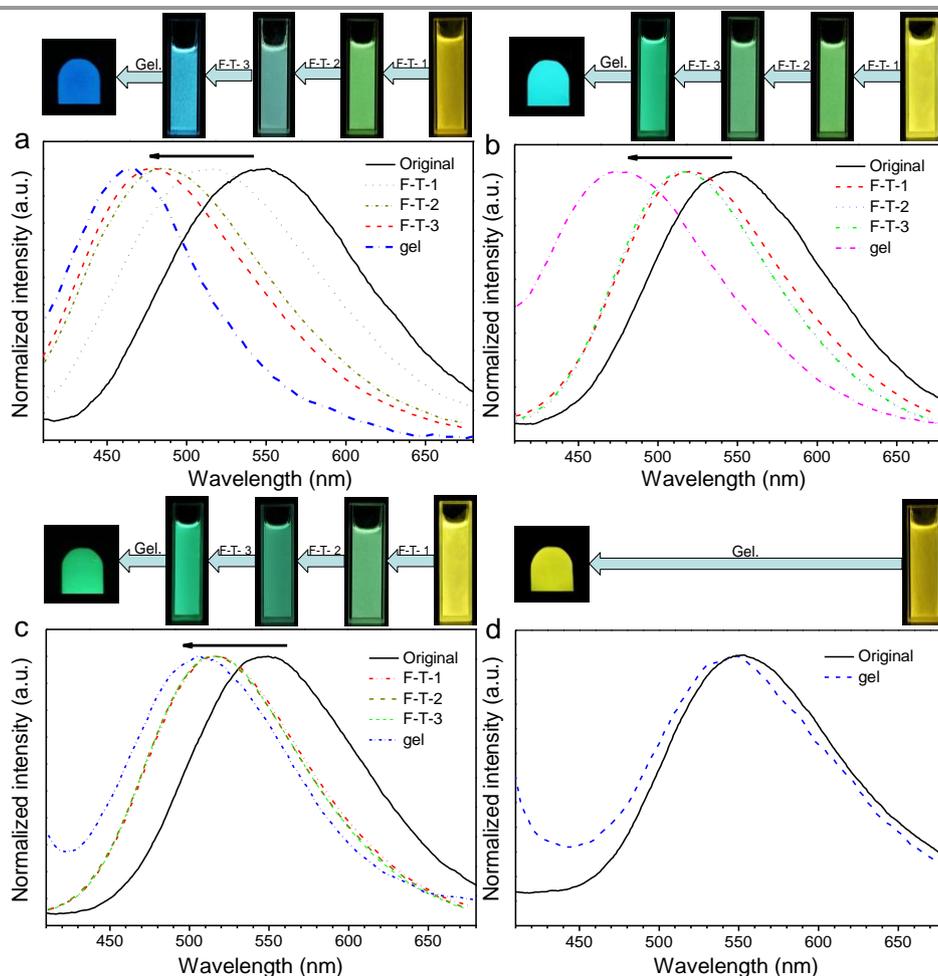


**Fig. 3.** Normalized PL spectra and photos of the DBF water/acetonitrile dispersions with 70% (a) and 90% (b) water before (original) and after one or two F-T treatment(s) (F-T-1 and F-T-2).

### DBF acetonitrile/water dispersions containing AAm and PVP

As mentioned in the introduction part, our very recent work shows that blue-emitting hydrogels containing DBF can be obtained when the solutions were treated with F-T method.<sup>25</sup> In

this work, we tried to incorporate DBF into a tough hydrogel physically cross-linked by very strong cooperative hydrogen bonding between the pre-existing PVP chains and *in situ* polymerized polyacrylamide (PAAm) chains.<sup>39</sup>



**Fig. 4.** PL spectra and photographs of the DBF dispersions with 80% water content but different  $C_{AAm}$  and with (a-c) or without (d) F-T treatments and gelation.  $C_{AAm} = 3.0 \text{ mol L}^{-1}$  (a),  $5.0 \text{ mol L}^{-1}$  (b), and  $6.0 \text{ mol L}^{-1}$  (c, d); and  $C_{PVP} = 0.017 \text{ g mL}^{-1}$ .

**Table 1.** The  $\lambda_{em}$  of the DBF dispersions (originally 80% water) with different AAm concentrations before and after different F-T cycles as well as after treatment.

$C_{AAm}$ /mol L <sup>-1</sup>	$C_{PVP}$ /g mL <sup>-1</sup>	$\lambda_{em}$ /nm				
		Original	F-T-1	F-T-2	F-T-3	After treatment
3	0.017	550	518	485	476	465 <sup>a</sup>
4	0.017	548	520	515	511	462 <sup>a</sup>
5	0.017	545	520	518	513	483 <sup>a</sup>
6	0.017	547	513	515	516	504 <sup>a</sup>
3	—	587	500	486	481	465 <sup>b</sup>
4	—	573	511	510	495	465 <sup>b</sup>
5	—	565	512	510	510	468 <sup>b</sup>
6	—	557	541	532	513	501 <sup>b</sup>

<sup>a</sup>: Keeping at 50 °C for 36 h, gelation.

<sup>b</sup>: Keeping at 50 °C for 36 h, no gelation.

PVP and AAm were added into the DBF dispersions with different acetonitrile/water ratios. We found that when the water contents are 60% and 70% the DBF dispersions containing PVP and AAm form opaque and nonluminescent hydrogels after gelation. Therefore, only the dispersions with water contents of 80% and 90% were used in this work.

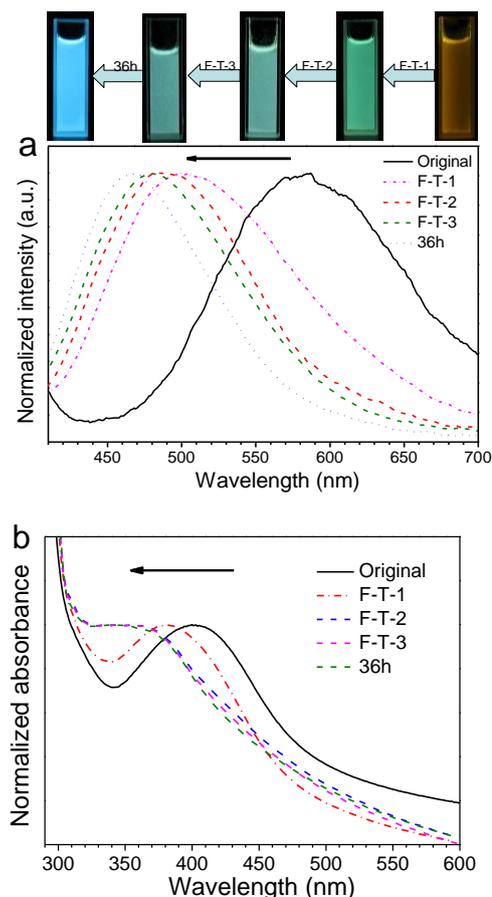
Interestingly, when the DBF dispersions containing PVP and AAm are treated with the F-T method, a gradual blue-shift in  $\lambda_{em}$  with F-T times is observed. For example, when the DBF dispersion (originally 80% water) containing 3.0 mol L<sup>-1</sup> AAm ( $C_{AAm}=3.0$  mol L<sup>-1</sup>), the emission colour changes from yellow ( $\lambda_{em} = 550$  nm) to green ( $\lambda_{em} = 518$  nm) after F-T-1 treatment, and sky blue ( $\lambda_{em} = 485$  nm) and blue ( $\lambda_{em} = 476$  nm) after F-T-2 and F-T-3 treatments, respectively (Fig. 4a). No further change in emission is observed after more F-T cycles. Similarly, a blue-shift in  $\lambda_{em}$  with F-T times is also observed for the DBF dispersions with higher  $C_{AAm}$  (4.0, 5.0 and 6.0 mol L<sup>-1</sup>). However, the emission colour can only be changed to green with the  $\lambda_{em}$  of about 510 nm (Fig. 4b, c). The  $\lambda_{em}$  of the DBF dispersions before and after F-T treatment are summarized in Table 1. In addition, the DBF dispersions originally with 90% water content and with different  $C_{AAm}$  also change from yellow to green after F-T treatment (Table S1).

For the DBF dispersions with 80% water content, a further blue-shift in  $\lambda_{em}$  is observed when the F-T treated DBF dispersions containing AAm and PVP are gelled. The obtained hydrogels exhibit dark blue ( $\lambda_{em} = 465$  nm), sky blue ( $\lambda_{em} = 483$  nm) and green ( $\lambda_{em} = 504$  nm) colours at the AAm concentration of 3.0, 5.0 and 6.0 mol L<sup>-1</sup>, respectively (Fig. 4a-c). For the DBF dispersions with 90% water content, there is no further blue-shift after gelation (Table S1). It is necessary to mention that, when the dispersions are not F-T treated, the hydrogels

emit only yellow colour (with  $\lambda_{em}$  around 550 nm) and their emission does not change with AAm concentration (Fig. 4d).

### DBF dispersions containing only AAm or PVP

To understand the functions of AAm and PVP on the photoluminescence change of DBF during F-T treatment, we studied the photoluminescence of the DBF acetonitrile/water dispersions containing only AAm or PVP.



**Fig. 5.** Normalized PL spectra and photographs (a) and the corresponding UV spectra (b) of the DBF dispersion containing 3.0 mol L<sup>-1</sup> AAm after different F-T cycles and then keeping at 50 °C for 36 h.

The original DBF dispersions with only AAm show higher  $\lambda_{em}$  than the corresponding dispersions with both PVP and AAm, and the  $\lambda_{em}$  decreases with the increase of AAm concentration. The original DBF dispersions with only PVP also show higher  $\lambda_{em}$  than the DBF dispersions with both AAm and PVP. A decrease in  $\lambda_{em}$  with the increase of  $C_{PVP}$  is also found, from 580 nm at  $C_{PVP} = 0.005$  g mL<sup>-1</sup> to 541 nm at  $C_{PVP} = 0.100$  g mL<sup>-1</sup> (Table S2). These results indicate that both AAm and PVP lead to blue-shifts in the emissions of the original DBF dispersions. Adding AAm or PVP into a DBF dispersion with a fixed acetonitrile water ratio leads to the decrease of water content in the final dispersion, therefore its emission is blue-shifted to a lower wavelength, similar to that of the DBF dispersions with lower water contents. When PVP and AAm are both used, the original DBF dispersions exhibit lower  $\lambda_{em}$

due to the synergistic effect of them. It is interesting to note that all original dispersions with both AAm and PVP show very similar emissions with the  $\lambda_{em}$  close to 550 nm (Table 1). This suggests that AAm and PVP cannot lead to further decrease in  $\lambda_{em}$ , very possibly due to their hydrophilic nature.

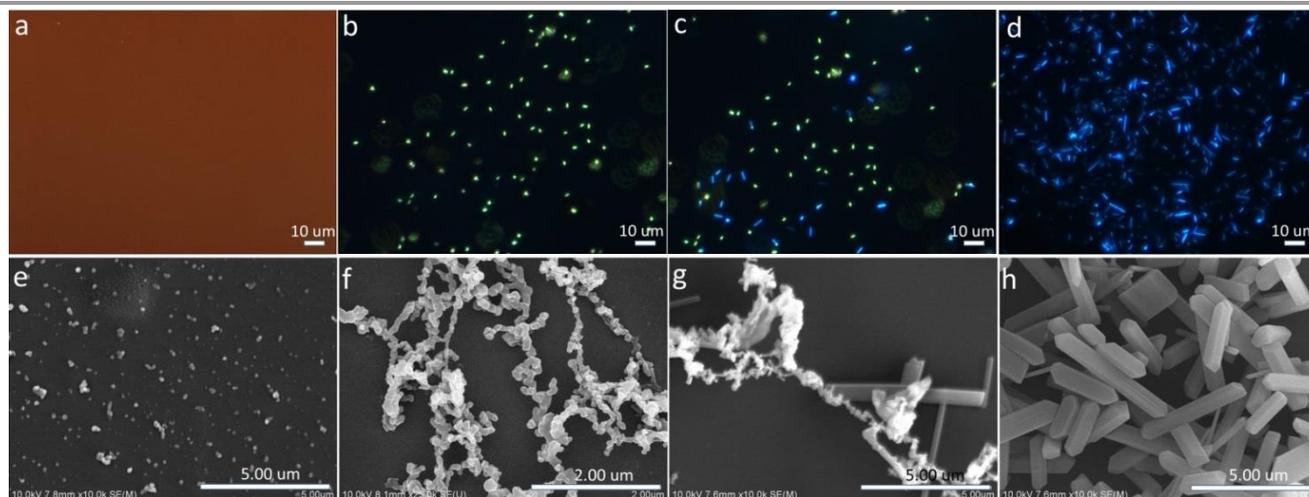
The DBF dispersions with only AAm shows similar blue-shift in  $\lambda_{em}$  with F-T times as that for the dispersions with AAm and PVP, suggesting that the F-T process is the critical factor leading to the emission change of DBF. However, some minor differences exist in the dispersions with different compositions. For the dispersions with only PVP, their  $\lambda_{em}$  keeps almost constant at about 500 nm after F-T-1 treatment, without further change with the increase of F-T cycles (Table S2). While for the dispersions with only AAm, there is a tendency of increasing  $\lambda_{em}$  with AAm concentration (Table 1).

Fig. 5a shows the PL spectra and corresponding photographs of the DBF dispersions containing 3.0 mol L<sup>-1</sup> AAm after different F-T cycles. The emission colour changes from orange ( $\lambda_{em} = 587$  nm) to sky blue ( $\lambda_{em} = 481$  nm) after F-T-3 treatments. Similar blue-shift in  $\lambda_{em}$  with F-T times is also observed for the DBF dispersions with higher  $C_{AAm}$  (4.0, 5.0 and 6.0 mol L<sup>-1</sup>) (Table 1 and Fig. S2), but they can only change to green colour after F-T-3 treatments. Fig. 5b shows the corresponding UV-Vis spectra of the the DBF dispersions after different F-T cycles. The maximum absorption wavelength ( $\lambda_{max}$ ) of the original DBF dispersion is at 400 nm, while it is blue-shifted to 380 nm after F-T-3 treatments and then to 340 nm after keeping at 50 °C for 36 h, in good agreement with the change of  $\lambda_{em}$ .

Although the dispersions containing only AAm or PVP cannot transform into hydrogels even under heating, we also observed a further blue-shift in  $\lambda_{em}$  when the F-T treated DBF dispersions are kept at 50 °C for 36 h. The dispersions exhibit blue ( $\lambda_{em}$  around 465 nm) colour at  $C_{AAm} = 3.0, 4.0$  and 5.0 mol L<sup>-1</sup>, and green colour ( $\lambda_{em} = 501$  nm) only at the  $C_{AAm} = 6.0$  mol L<sup>-1</sup> (Table 1).

### Microstructures of DBF aggregates

The microstructures of DBF aggregates with different emission colours have been characterized in previous work.<sup>25,28</sup> In this work, we studied the F-T process induced change of the microstructures of DBF aggregates with both fluorescence microscopy and SEM. The original dispersion emits homogeneous orange colour (Fig. 6a), and it forms some separated particles when freeze-dried (Fig. 6e). When the dispersion is F-T-1 treated, many green-emitting particles appear (Fig. 6b), and the particles with irregular shapes aggregate to form necklace-like morphology (Fig. 6f). With further F-T treatments, some needles emitting blue colour appear (Fig. 6c, g). Finally, after being kept at 50 °C for 36 h, only micro-sized hexagonal needles emitting blue colour can be found (Fig. 6d, h). These results suggest that the change of the emission colour of the DBF dispersion with the F-T process and the after-treatment is due to the change of the aggregation morphologies.



**Fig. 6.** Fluorescence microscopy images (a-d) and the corresponding SEM images (e-h) of the original DBF dispersion (80% water,  $C_{AAm} = 3.0$  mol L<sup>-1</sup>) (a, e), after F-T-1 (b, f) and F-T-2 treatments (c, g) and then being kept at 50 °C for 36 h (d, h).

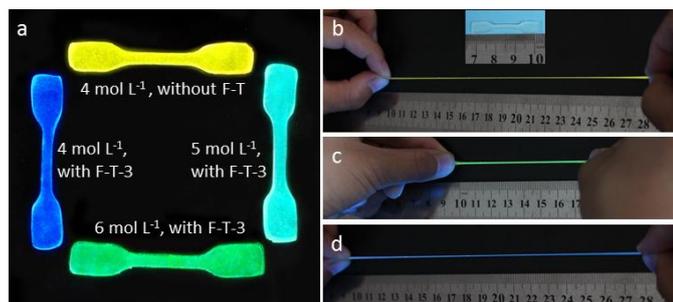
### Mechanical properties of the luminescent hydrogels

Luminescent hydrogels with yellow, green, sky blue and dark blue colours were obtained when the original and F-T treated DBF dispersions containing PVP and AAm were deaerated and then heated (Fig. 7a). The same as our previous work, the emissions of these luminescent hydrogels can be easily

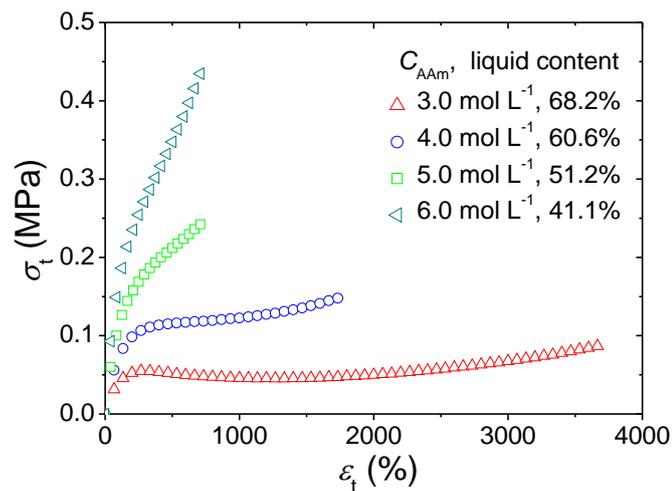
switched between different colours by fuming with organic solvent vapours or heating/cooling process.<sup>28</sup>

The obtained hydrogels exhibit very good tensile properties. They can be elongated to several times or more of their original length (Fig. 7b-d). Fig. 8 shows the tensile stress-strain ( $\sigma_t$ - $\epsilon_t$ ) curves of the luminescent hydrogels prepared with the DBF dispersions (originally 80% water) containing different  $C_{AAm}$ . The liquid contents of the hydrogels, which is the total amount

of water and acetonitrile and it varies with the AAm concentration, are specified in the figure. The fracture tensile stress ( $\sigma_t$ ) of the gels increases with increasing  $C_{AAm}$ , from 0.087 MPa at  $C_{AAm} = 3.0 \text{ mol L}^{-1}$  to 0.449 MPa at  $C_{AAm} = 6.0 \text{ mol L}^{-1}$ . Meanwhile, the elongation of the hydrogels decreases with increasing  $C_{AAm}$ . The highest elongation obtained at  $C_{AAm} = 3.0 \text{ mol L}^{-1}$  is about 3700%. Similar tensile properties are found for the hydrogels synthesized with the DBF dispersions containing an original water content of 90%.



**Fig. 7.** Dumbbell shaped original (a) and the elongated (b-d) hydrogel specimens emitting different colours under UV light at 365 nm, the inset in (b) shows an original specimen under visible light.  $C_{PVP} = 0.017 \text{ g mL}^{-1}$ , and the other hydrogel synthesis conditions are specified in (a).



**Fig. 8.** Tensile stress-strain ( $\sigma_t$ - $\epsilon_t$ ) curves of the luminescent hydrogels prepared with the DBF dispersions (originally 80% water content) containing different  $C_{AAm}$ .

## Discussion

Significant blue-shifts in the emissions of DBF powders in the solid state are observed when the orange, yellow and green DBF powders are frozen in liquid nitrogen ( $-196 \text{ }^\circ\text{C}$ ), and they undergo emission changes from orange to yellow, yellow to green and green to blue, respectively. The temperature-dependent shift in the fluorescence spectra of small molecular weight compounds has been well studied, and the  $\lambda_{em}$  generally blue-shifts with decreasing temperature due to the suppression of vibrational relaxation in excited state.<sup>40</sup> At room temperature, the relaxation of DBF molecules is complete prior to the emission, thus luminescence at room temperature is from the relaxed state. However, the relaxation rate of dye molecules

decreases with temperature, thus, emission at lower temperature should be from an unrelaxed or partly relaxed state, which affords the blue-shifted emission. Hence the emission of DBF powder could be switched between varied emission colour through repeated freezing and thawing process.

With comparison to the DBF powders, the DBF dispersions undergo more diverse and more significant freezing-induced emission changes. The  $\lambda_{em}$  of the dispersions vary in a very wide range from about 590 nm to 465 nm, corresponding to a colour spectrum from orange to dark blue (Table 1). In addition, the emission change is irreversible during the freezing-thawing process, suggesting that stable crystalline structures are formed during the freezing process. The major difference between the freezing of the DBF powders and the DBF dispersions is that the solvents (and in some cases the monomers) in the dispersions crystallize. Therefore, we can refer that the differences in the freezing-induced emission changes between the DBF powders and the DBF dispersions are caused by the crystallization of the solvents and the monomers.

We observed that DBF water/acetonitrile dispersions with different acetonitrile/water ratios undergo emission changes from orange or yellow to green when they are frozen in liquid nitrogen ( $-196 \text{ }^\circ\text{C}$ ) for 2 min or in a refrigerator ( $-20 \text{ }^\circ\text{C}$ ) for 24 h. Water has a higher melting point ( $0 \text{ }^\circ\text{C}$ ) than acetonitrile ( $-45 \text{ }^\circ\text{C}$ ), so when the DBF water/acetonitrile dispersions are frozen in a refrigerator, water crystallizes while acetonitrile does not. The crystallization of water leads to the high volume ratio of acetonitrile (a good solvent) around the DBF molecules, so they undergo morphologic change as that in the water/acetonitrile mixed solvent with a higher water content to that with a lower water content. When the dispersions are frozen in liquid nitrogen, both water and acetonitrile crystallize very rapidly. The crystallization of the solvents especially water, whose volume increases after freezing (*i.e.* forming ice), leads to the phase separation and the aggregation of DBF molecules. The force exerted on the DBF aggregates by the solvent crystals might enable the DBF molecules adopt a more twisted conformation, leading to the emission changes of DBF molecules. The twisted conformation of the DBF molecules is stabilized in the DBF aggregates which are stable even when the solvent crystals are thawed at room temperature, leading to the irreversible emission changes during the F-T process. With further F-T treatments, the crystallization of the solvents leads to further phase separation and the aggregation of small DBF aggregates into larger crystalline morphologies corresponding to more blue-shifted emissions (Fig. 6).

Most of the DBF dispersions can only be adjusted to green-emitting by F-T treatments, while the emission colour of the DBF water/acetonitrile dispersions at  $C_{AAm} = 3.0 \text{ mol L}^{-1}$  and with or without PVP can be tuned to blue after three F-T cycles. During the freezing process, with the crystallization of water and acetonitrile, the AAm molecules dissolved in the solvents separate out and form crystals, which also exert an extra force on the DBF aggregates and hence the DBF molecules can adopt a more twisted conformation, leading to a blue-shift in the emission of DBF. While for the DBF water/acetonitrile

dispersions containing only PVP, an amorphous polymer, their emission colours can only be tuned to green, and the possible reason is that the separated amorphous PVP cannot provide the extra force for the torsion of the two phenyl rings in DBF molecules. The emission colours of the DBF water/acetonitrile dispersions containing higher concentrations of AAm can only be tuned to green after three F-T cycles and there is a tendency of increasing  $\lambda_{em}$  with the increase of  $C_{AAm}$  (Table 1). The reason is the increase of  $C_{AAm}$  leads to the decrease of water content in the dispersions, and hence the force exerted on the DBF aggregates by ice crystals is lowered.

When the F-T treated DBF dispersions are kept at 50 °C for 36 h, further blue-shift in  $\lambda_{em}$  is observed in the dispersions gelled or not. This phenomenon suggests that the formation of the more twisted conformation of DBF molecules in the aggregates is a relatively slow process, which cannot be finished during the fast freezing process and hence more time is required for the completion of conformation change and the formation of a more stable crystalline structure. Unfortunately, we cannot obtain the torsion angles of the two phenyl rings of DBF molecules in the blue-emitting crystals as they are not big enough for single-crystal X-ray diffraction analysis.

Luminescent hydrogels with different emission colours are obtained when the original and F-T treated DBF dispersions containing PVP and AAm are gelled. These gels exhibit very good mechanical properties, as indicated by their high tensile strengths and high elongations. However, it is necessary to mention that the mechanical properties of the luminescent hydrogels are not as good as those of the hydrogels fabricated from the aqueous solutions without acetonitrile and DBF molecules. The very possible reason is the presence of acetonitrile diminishes the cooperative hydrogen bonding between PVP and the *in-situ* formed polyacrylamide chains.<sup>39</sup>

## Conclusions

Our work demonstrates that di(4-propoxyphenyl) dibenzofulvene (DBF) powders in both amorphous (orange) and crystalline (yellow and green) states can undergo reversible emission changes during the freezing-thawing process. Moreover, DBF molecules in the dispersions of acetonitrile/water mixed solvents with or without poly(*N*-vinylpyrrolidone) (PVP) and acrylamide (AAm) all undergo more diverse and more significant freezing-induced emission changes, but the changes are irreversible. The emission colours of the dispersions blue-shift gradually with the F-T cycles, and the DBF dispersions containing a low concentration of AAm become blue-emitting after three F-T cycles. The crystallization of the solvents and AAm leads to the phase separation and the aggregation of DBF molecules. The freezing-induced torsion of the two phenyl rings in DBF molecules and the force exerted on the DBF aggregates by the solvent crystals enable the DBF molecules adopt a more twisted conformation, leading to the morphologic changes. Further blue-shift in  $\lambda_{em}$  is observed in the F-T treated DBF dispersions when they are kept for some times. Furthermore, luminescent hydrogels with different

emission colours are obtained when the original and F-T treated DBF dispersions containing PVP and AAm are gelled. The hydrogels show very good mechanical properties.

This work demonstrates a novel stimuli-responsive property of DBF, which exhibits AIE and CIEE effects, *i.e.* freezing-induced emission colour changes. DBF dispersions with different emission colours can be obtained from the dispersion with a fixed acetonitrile/water ratio by simple adjusting the F-T times and after-treatment. Very possibly, the emissions of some other AIE fluorescent substances can also be adjusted by the very simple F-T method. The luminescent hydrogels with different emission colours and very good mechanical properties might find applications in a variety of fields.

## Acknowledgements

We appreciate the financial support of the National Science Foundation of China (No. 21274013), the Fundamental Research Funds for the Central Universities and the Beijing Municipal Commission of Education.

## Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Freezing-induced significant blue-shifted emission is observed for AIE luminogens for the first time, and tough luminescent multi-colour hydrogels are prepared.

**Keywords:** luminescent, hydrogels, freezing-thawing, tensile properties, aggregation-induced emission

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**Freezing-induced multi-colour emissions of AIE luminogen di(4-propoxyphenyl) dibenzofulvene**

TOC figure

