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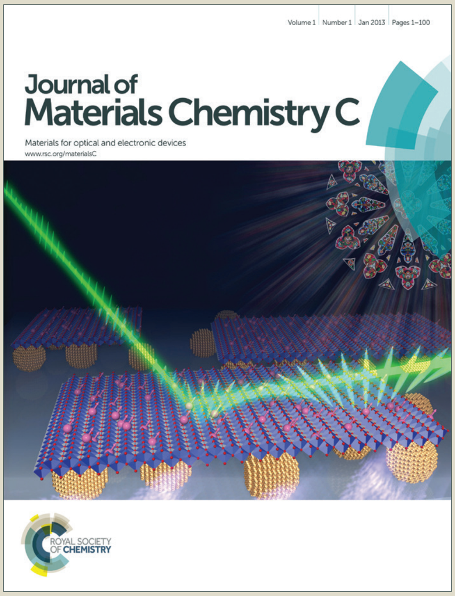

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ARTICLE TYPE

Luminescent hydrogels based on di(4-propoxyphenyl)-dibenzofulvene exhibiting four emission colours and organic solvents/thermal dual responsive properties

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This work reports the fabrication of intelligent luminescent hydrogels by physically incorporating a propeller-shaped di(4-propoxyphenyl)-dibenzofulvene molecule, which shows unusual aggregation-induced emission (AIE) and crystallization-induced emission enhancement (CIEE) effects, into a hydrogel matrix. Hydrogels with orange, yellow and green emissions are obtained by adjusting the water contents of the dispersions of di(4-propoxyphenyl)-dibenzofulvene for hydrogel syntheses, and more interestingly, blue emission of di(4-propoxyphenyl)-dibenzofulvene is observed for the first time when its dispersions are frozen and thawed, and the thereafter prepared hydrogels also emit blue colour. The emissions of these luminescent hydrogels can be switched between different colours by fuming with organic solvent vapours or heating/cooling process and some of the switches are reversible.

1. Introduction

Hydrogels are three-dimensional polymeric networks that cannot be dissolved in water, instead absorb a large amount of water and keep their shapes. As a kind of soft and wet material, hydrogels are usually with good biocompatibility and stimuli-responsive properties, which impart them a wide variety of applications, such as sensors, tissue engineering, drug delivery systems, immunoassay, biomedicine, *etc*.[1-5] Luminescent hydrogels, which emit light under the irradiation of ultra-violet (UV) or visible light, have attracted much attention due to their potential uses in sensing imaging,[6] luminescent probes,[7,8] optical switches,[9,10] and so on.[11-15]

The most common strategy for preparing luminescent hydrogels is to physically or chemically incorporate luminescent substances into a hydrogel matrix, and semiconductor quantum dots (QDs),[16-18] organic fluorescent dyes,[19-21] and metal complex[22-24] are the mostly commonly employed luminescent substances. Unfortunately, the intrinsic drawbacks of these luminescent substances have strongly impeded practical applications of luminescent hydrogels. For example, the toxicity of QDs impedes their medical and biological applications.[25-28] The aggregation-caused quenching (ACQ) nature of traditional organic fluorescent dyes makes it difficult to prepare luminescent hydrogels with high fluorescent intensity. In addition, these luminescent hydrogels generally exhibit single-colour emission, and hence their responsiveness to external stimuli can only be measured through the change in emission intensity. There are only very few examples of luminescent hydrogels with multicolour emissions, which are usually prepared by using different kinds of luminescent substances[7,16] or the same kind of QDs with different sizes[29,30].

Therefore, fabricating luminescent hydrogels which can overcome the drawbacks of current luminescent hydrogels and exhibit different, switchable colours under environmental stimuli is a challenging and fascinating problem. To obtain novel luminescent hydrogels with these advantageous properties, one of the key problems is to find novel luminescent substances. Tang and co-workers found that a propeller-shaped organic molecule 1-methyl-1,2,3,4,5-pentaphenylsilole exhibits a fascinating aggregation-induced emission (AIE) effect,[31] *i.e.* it is non-emissive in dilute solutions but highly luminescent when it is in concentrated solutions or casted into solid films. Up to now, a series of AIE luminophores with emission colours covering the entire visible spectral region have been synthesized. More interestingly, some AIE luminophores can exhibit different colours and the colours are switchable, as it is found that the emissions are dependent on aggregation morphologies which are changeable.[32-39] Recently, a series of derivatives of diphenyldibenzofulvene have been reported to show AIE and crystallization-induced emission enhancement (CIEE) effects, which afford their thermochromic and mechanochromic fluorescence. For example, two kinds of crystals and one amorphous solid of di(4-propoxyphenyl)-dibenzofulvene (hereafter shortened as **DBF**) emit green (500 nm), yellow (547 nm) and orange (580 nm) light when excited, respectively. The emission of DBF can be switched among three colours upon

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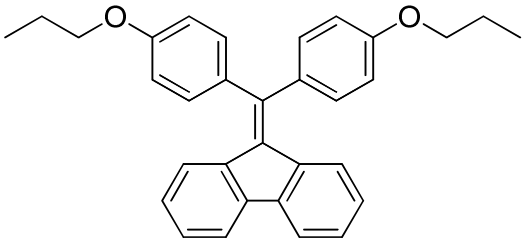
thermal, solvent, and mechanical stimuli due to the transformation among the three aggregation states.[40]



Scheme 1 Chemical structure of di(4-propoxyphenyl)-dibenzofulvene (DBF).

In this work, we fabricated luminescent hydrogels by physically incorporating DBF as the luminophore into a hydrogel matrix. Luminescent hydrogels exhibiting four emission colours were obtained, and the stimuli-responsive properties of DBF in hydrogels to organic solvents and temperature were investigated.

2. Experimental Section

2.1. Materials

Acrylamide (AAm, ultra pure, Amresco Inc., Beijing, China) was used without further purification, potassium persulfate (KPS, chemical pure, Shanghai Chemical Reagent Company, shanghai, China), *N,N,N',N'*-tetramethylethylenediamine (TEMED, ultra pure, InnoChem Science & Technology Co. Ltd., Beijing, China), *N-N'*-methylenebisacrylamide (BIS, analytical pure, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), acetonitrile (HPLC grade, Xinhua Special Reagent Factory, Tianjin, China). Di(4-propoxyphenyl)-dibenzofulvene was prepared by ourselves.[40]

2.2. Preparation of DBF dispersions

DBF solution (1×10^{-3} mol/L) using acetonitrile as the solvent was prepared, and then different amounts of deionized water and acetonitrile were added to get the DBF dispersions (1×10^{-4} mol/L) with different water contents.

2.3. Preparation of luminescent hydrogels

Given amounts of AAm, BIS (0.1 wt% of the monomer) and TEMED (0.04 v/v‰ of the mixture) were dissolved in a DBF dispersion thoroughly, then the mixture was bubbled with nitrogen to remove dissolved oxygen, and then KPS (equimolar to TEMED) was added quickly. To prevent the undesirable polymerization, the mixture was prepared and bubbled in an ice-water bath. Finally the mixture was put into a 26°C water bath for 36 h to form hydrogel.

Another method was also employed to synthesize hydrogels. AAm was dissolved in a DBF dispersion firstly, the mixture was immersed into liquid nitrogen, and then it was thawed at room temperature. Finally, after adding BIS, KPS and TEMED (the amounts are the same as above-mentioned) hydrogels were synthesized by the same method stated above. All photographs of the luminescent hydrogels in this paper were taken under UV illumination.

2.4. Photoluminescence spectroscopy

The photoluminescence (PL) spectra of the hydrogels were obtained on a Cary Eclipse fluorospectrophotometer (Varian Inc., Walnut Creek, CA, USA) using a quartz cell. The samples were cut into slides with a thickness of 2 mm. The excitation wavelength (λ_{ex}) was selected as 370 nm if not otherwise stated, and the slit width was 10 nm.

To observe the response of the hydrogels to organic solvents, the hydrogels were kept in a Petri-dish set saturated with acetonitrile or acetone vapour for 30 min, and then the emissions of the gels were observed with the fluorospectrophotometer. To observe the temperature-response of the hydrogels, the hydrogels were firstly dried at 50°C to constant weights and then heated at 148°C for 10 min, after being cooled at room temperature the PL spectra of the gels were measured. And for some green emission hydrogels, the as-prepared samples were heated at a temperature in the range of 50-90°C and then measured immediately, after being cooled down they were measured again.

2.5. Fluorescence microscopy observation

Upright fluorescence microscope (ZEISS Imager M1, Germany) equipped with a shift free EX G 365 excitation filter (excitation, 365 nm) and an EM LP 420 emission filter was used to observe the distribution of DBF aggregates in hydrogels.

3. Results and Discussion

3.1. Preparation of luminescent hydrogels with four emission colours

DBF is nonluminescent when dissolved in its good solvent, such as acetonitrile, but when a large amount of deionized water (a poor solvent) is added, the emission of DBF turns on as different aggregation morphologies are formed.[40] When the water volume ratios in water/acetonitrile mixed solvents were 90%, 70% and 60%, the emission colours of the DBF dispersions were orange, yellow and green, corresponding to the maximum emission wavelengths (λ_{em}) of 505 nm, 545 nm and 580 nm, respectively. When acrylamide (AAm) was added into the DBF dispersions, the colours of the dispersions were nearly of no change (Table 1).

Table 1 Key reaction conditions and the maximum emission wavelength (λ_{em}) of the dispersions with monomer and the corresponding luminescent hydrogels.

Sample	C_{AAm}/mol/L	Water content/%	λ_{em}/nm, dispersion	λ_{em}/nm, gel
1	1	90	583	576
2	2	90	577	581
3	1	70	542	547
4	2	70	545	549
5	1	60	505	504
6	2	60	508	503

When the monomer-containing dispersions were polymerized, luminescent hydrogels were obtained. Table 1 shows the key reaction conditions and the λ_{em} of the luminescent hydrogels. Similar to the case of DBF dispersions in water/acetonitrile mixed solvents, the water content is the key factor affecting the emission colour of the prepared luminescent hydrogels. The hydrogels emitted orange, yellow and green colours when the water contents of DBF dispersions were 90%, 70% and 60%, respectively (Fig. 1a-c). The photoluminescence (PL) spectra of

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the hydrogels are shown in Fig. 1e. These results suggest that aggregation morphologies of DBF formed in the dispersions can be well preserved during the polymerization process and hence in the prepared hydrogel network.

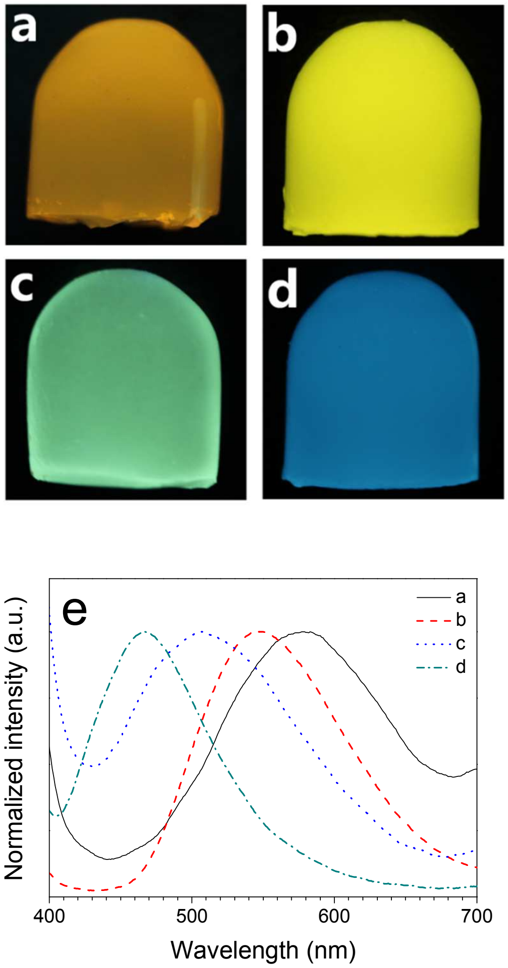

Fig. 1 (a-d): Photographs of the hydrogels emitting orange (a), yellow (b), green (c) and blue (d) colours, and normalized PL spectra (e) of the hydrogels emitting different colours.

Interestingly, we found that when the DBF dispersions containing AAm and 60-90% water content were frozen in liquid nitrogen and then thawed at room temperature, the dispersions emitted blue colour (λ_{em} = 466 nm) (Fig. S1). Correspondingly, the thereafter prepared hydrogel also emitted blue colour (Fig. 1d). This is the first report on the blue emission of DBF. It is worth noting that the DBF dispersions without AAm did not emit blue colour after the freezing-thawing process (Fig. S1).

3.2. Stimuli response of the luminescent hydrogels

The stimuli-responsive properties of DBF in hydrogels to organic solvents and temperature were investigated.

3.2.1. Reversible orange-yellow switches

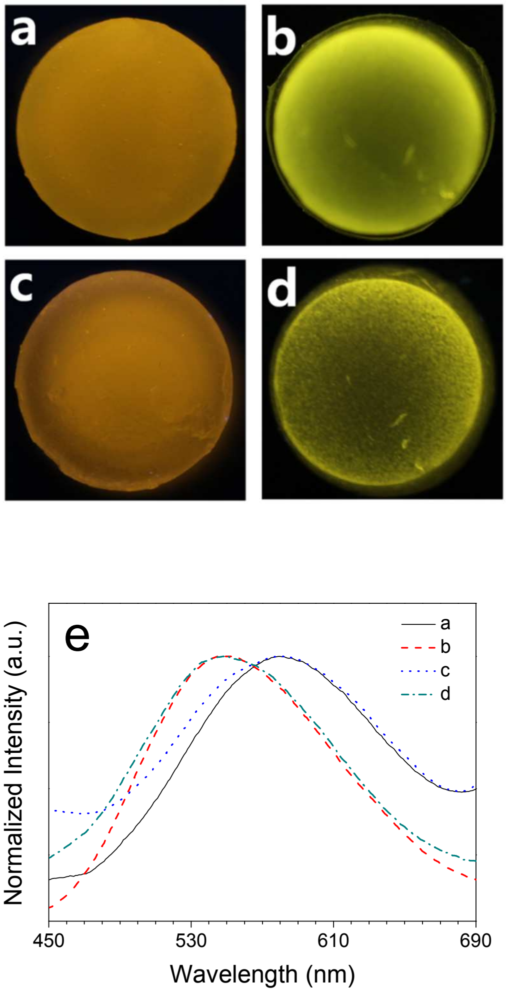

Fig. 2 The reversible orange-yellow switches of the hydrogel with orange emission. Photographs of the as-prepared hydrogel (a), and the hydrogel after different treatments (b-d): fuming with acetonitrile (b), heating and then swelling (c), fuming with acetonitrile again (d); and the corresponding PL spectra of the hydrogels (e).

When the hydrogel with orange emission was fumed with acetonitrile vapour, its emission shifted from orange (λ_{em}=579 nm) to yellow (λ_{em}=549 nm) (Fig. 2a, b), and when the yellow-emitting hydrogel was heated at 148°C, the emission shifted from yellow to orange again. Moreover, the dried hydrogel could easily swell in water, and the swollen hydrogel also emitted orange (λ_{em}=581 nm) (Fig. 2c). When this orange-emitting hydrogel was kept in a saturated acetonitrile vapour again, its emission was switched to yellow (λ_{em}=548 nm) again (Fig. 2d). A similar phenomenon was also observed when acetone was used as the fuming agent (Fig. S2). These results suggest that the orange-yellow luminescent switches are completely reversible.

3.2.2. Reversible yellow- orange switches

The as-prepared hydrogel emitting yellow colour (λ_{em}=545 nm) could be switched to orange (λ_{em}=581 nm) in the dried state upon heating at 148°C. When the dried orange hydrogel was swollen in water and then fumed with acetonitrile vapour, it changed to yellow emission (λ_{em}=545 nm) again (Fig. 3).

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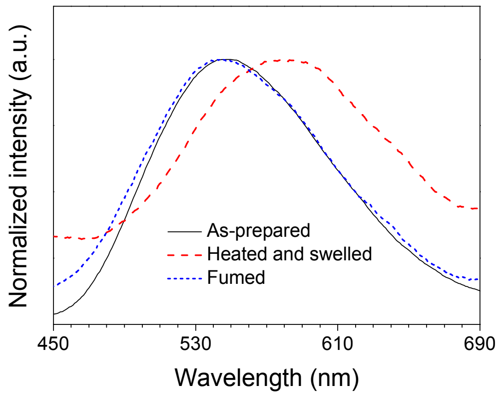

Fig. 3 Normalized PL spectra of the as-prepared hydrogel emitting yellow colour, and the hydrogel after being heated and swelled as well as the hydrogel after being fumed with acetonitrile.

3.2.3. Reversible shift in λ_{em} for luminescent hydrogels with green emission

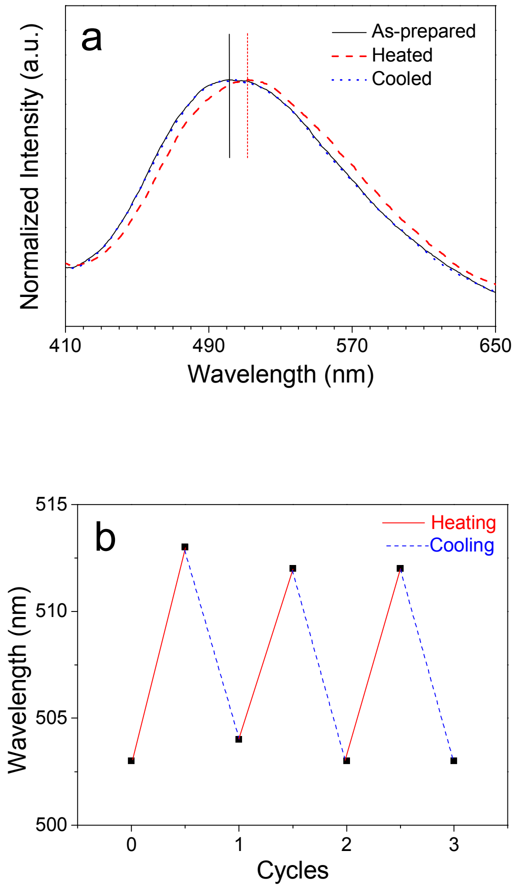

Fig. 4 (a): Normalized PL spectra of the as-prepared hydrogel emitting green colour, the hydrogel after being heated at 70°C, and then being cooled at room temperature; and (b): the change in λ_{em} of the hydrogel during the heating-cooling cycles between 50°C and room temperature.

When the as-prepared green luminescent hydrogel was heated at certain temperature (50-90°C), its λ_{em} red-shifted about 10 nm, and when the heated hydrogel was cooled at room temperature the λ_{em} blue-shifted to its original value (Fig. 4a), suggesting a reversible shift in λ_{em} during the heating-cooling cycle. Repeated experiments proved that the shift in λ_{em} was reversible for many times (Fig. 4b). It is necessary to mention that the yellow and orange luminescent hydrogels did not show the shift in λ_{em} during the heating-cooling cycles (Fig. S3).

3.2.4. Irreversible blue to orange and green to orange switches

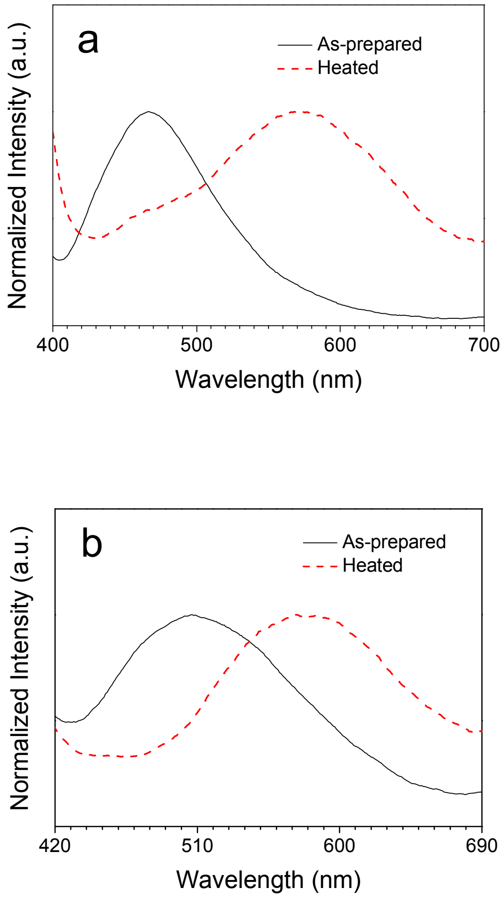

Fig. 5 Normalized PL spectra of the blue (a) and green (b) luminescent hydrogels before and after being heated at 148°C.

When the blue luminescent hydrogel was heated at 148°C and then cooled, its emission changed to orange, accompanying a dramatic change in the λ_{em}, from 467 nm to 574 nm (Fig. 5a). Similar change was found for the green luminescent hydrogels, accompanying a change in the λ_{em}, from 506 nm to 572 nm (Fig. 5b). Unfortunately, the blue to orange and green to orange switches were irreversible.

3.3. Discussion

Our work shows that hydrogels with orange, yellow, green and blue emissions can be obtained by physically incorporating di(4-propoxyphenyl)-dibenzofulvene into a hydrogel matrix. In addition, the emissions of these luminescent hydrogels can be

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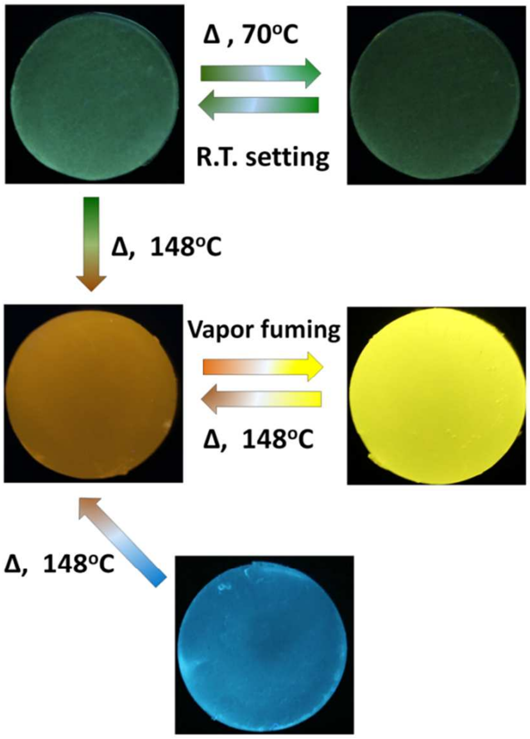
switched between different colours. Scheme 2 summarizes the four emission colours of the luminescent hydrogels and their switches upon temperature and organic solvent stimuli.



Scheme 2 The diagram of the emission colours of the luminescent hydrogels and their switches upon external stimuli.

DBF is a special kind of luminescent substance showing unusual AIE and CIEE effects, and it is reported to be able of emitting orange, yellow and green colours. The emission of DBF in acetonitrile/water mixed solvents can be tuned by adjusting the volume ratio of the two solvents. The emission of DBF is dependent on the aggregation morphology of DBF. Dong and Tang *et al*. has confirmed that the orange emission of DBF corresponds to an amorphous structure and the yellow and green emissions are attributed to two crystalline structures.[40]

Similar to the DBF dispersions in water/acetonitrile mixed solvents, luminescent hydrogels with orange, yellow and green emissions are obtained by simply adjusting the water content of the dispersions for hydrogel syntheses. Therefore, it is reasonable to conclude that the physical incorporation of DBF into the hydrogel matrix does not significantly affect the aggregation morphology of DBF.

A new blue emission of DBF is observed for the first time in the frozen-thawed DBF dispersions containing AAm and the thereafter prepared hydrogel. The freezing process induces the crystallization of the solvents and the monomer, and hence might lead to different aggregation morphology of DBF. We found that the DBF dispersions without AAm do not exhibit blue emission after freezing-thawing. So, very possibly, the crystallization of AAm in the freezing process is the main reason for the formation of a new type of aggregation morphology of DBF.

We empolyed fluorescence microscopy to investigate the aggregation morphologies of DBF in the luminescent hydrogels, and the typical images of the hydrogels are shown in Fig. 6. For the orange-emitting hydrogel, no obvious brighter regions can be found. While for the other hydrogels, many tiny bright particles are present, which correspond to the crystalline structures of DBF. The micron-sized crystals are needle-like for the yellow and blue luminescent hydrogels, and cubic for the green luminescent hydrogel. The blue-emitting particles of DBF should correspond to a new type of crystalline structure. Unfortunately, the crystalline structure of the blue-emitting particles of DBF could not be analyzed as the amount of DBF in the dispersions or hydrogels was too small and it could not be separated without the change of its crystalline structure.

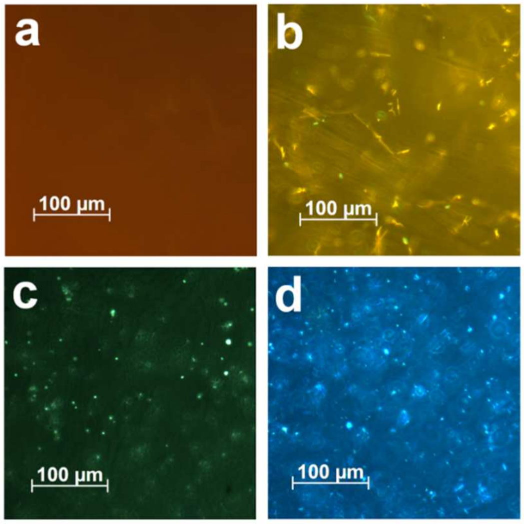


Fig. 6 Fluorescence microscopy images of hydrogels emitting orange (a), yellow (b), green (c), and blue (d) colours.

The emission colours of the hydrogels did not change even when the gels have been swollen in water for 30 days (Fig. S4), suggesting that the DBF aggregates are stable in the polymeric network of the hydrogels containing a large amount of water, which is a non-solvent for DBF.

Our results also show that the emissions of these luminescent hydrogels can be switched between different colours by fuming with organic solvents or heating/cooling process and some of the switches are reversible. The mechanism for the switches is the changes of the aggregation morphology of DBF in the hydrogels upon external stimuli.

For the orange-yellow switch of the hydrogels, there should be a transition from amorphous to crystalline morphology of DBF in them. When the orange-emitting hydrogel with amorphous aggregates of DBF is fumed with acetonitrile (or acetone) vapour, which is a good solvent for DBF, acetonitrile (or acetone) molecules can diffuse into the hydrogel and hence leads to the decrease of water ratio, consequently the aggregation morphology of DBF is changed to the crystalline structures emitting yellow colour. Actually, the luminescent changes occurred from the surface to the whole internal structure of the hydrogels during the process of vapour stimulating, since the luminescent change is controlled by the diffusion of acetonitrile (or acetone) vapour, which occurs gradually from the surface to the inner part of the hydrogel (Fig. S5). However, the yellow emission hydrogel cannot be switched to green by further fuming with acetonitrile or

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acetone, the very possible reason is that the crystalline structures are relatively stable and hence they cannot transform easily once they are formed.

The yellow-emitting hydrogel can go back to orange upon heating at 148°C, the melting point of the crystalline structures of yellow-emitting DBF, and then being cooled at room temperature. During this process, the crystalline structures of DBF melt upon heating and the molecules may pack in a random way to form amorphous particles during cooling. This dried orange-emitting hydrogel can easily swell in water and the swollen sample is still orange emitting. In addition, the orange emitting hydrogel is fumed with acetonitrile or acetone vapor, its emission can be switched to yellow again. Therefore, the orange-yellow switches are totally reversible.

Interesting reversible shift in λ_{em} is found for green luminescent hydrogels by cyclic heating at 50-70°C and cooling at room temperature. The actual reason for this shift is unknown yet, possibly due to the change of the packing patterns of DBF molecules caused by the expanding or shrinking of the hydrogel network.

4. Conclusions

We successfully prepared luminescent hydrogels by physically incorporating di(4-propoxyphenyl)-dibenzofulvene (DBF), which shows unusual AIE and CIEE effects, into a hydrogel matrix for the first time. Orange, yellow, green and blue-emitting hydrogels are prepared by adjusting the reaction conditions and preparation methods. Moreover, these hydrogels show emission colour switches to external stimuli, such as organic solvents and temperature, in particular, some of the switches are reversible. With comparison to previous work on DBF in the solid state and in the dispersions of solvents, we obtained a new blue emission of DBF and observed an interesting shift in the maximum emission wavelength of green-emitting hydrogels unpon heating and cooling process. The different emissions of DBF in hydrogels and the switches among them are attributed to the aggregate morphologies of DBF and their transitions.

This work proves that the incorporation of molecules exhibiting AIE and CIEE effects into hydrogel matrix is a convenient and effective way to prepare luminescent hydrogels with different emission colours and stimuli-responsive properties. Using DBF as the luminophore overcomes the drawbacks of commonly used luminescent substances, for example, it has lower toxicity than QDs and it does not show ACQ effect. In addition, luminescent hydrogels with multiple emissions can be prepared by using the same luminophore (DBF) but adjusting preparation conditions. The stimuli-responsive luminescent hydrogels are expected to find applications in a variety of fields.

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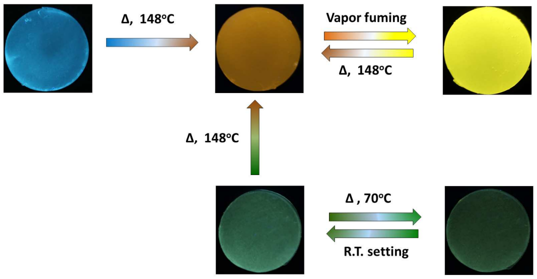
Luminescent hydrogels exhibit orange, yellow, green and blue emissions and reversible or irreversible organic solvents/thermal dual responsive properties.



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