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# Ultra-fast self-healing PVA organogels based on dynamic covalent chemistry for dye selective adsorption

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Ultra-fast self-healing organogels based on dynamic covalent chemistry for dye adsorption were prepared from polyvinyl alcohol (PVA), 4-formylphenylboronic acid (FPBA), and tartaric acid dihydrazide (TDH) by an effective situ reaction approach. The relative xerogels can adsorb methylene blue selectively with high efficiency. The boronate ester bonds and acylhydrazone bonds endow organogels a very fast self-healing property. What's more, the chirality can be transferred from TDH to the organogels. The organogels obtained from L-TDH and D-TDH hold opposite chirality according to circular dichroism spectra.

# Introduction

Gels based on dynamic covalent chemistry are different from classical covalent-linked or physical-linked gels. Dynamic covalent bonds, combining the stability of covalent bonds and the reversibility of non-covalent bonds, can break and reform reversibly under suitable conditions.<sup>1</sup> Thus, the networks constructed via dynamic covalent chemistry not only are more stable and have better mechanical properties than non-covalent cross-linking networks, but also can respond to external stimuli. Therefore, gels based on dynamic covalent chemistry have attracted much interest for their applications in pharmaceuticals,<sup>2-4</sup> biotechnology,<sup>5,6</sup> and intelligent materials.<sup>7,8</sup>

The dynamic covalent chemistry is a dynamic process, during which molecule exchange occurs at any time. Dynamic covalent chemistry, including the formation of boronate eater bonds,<sup>9</sup> disulfide bonds,<sup>10</sup> acylhydrazone bonds,<sup>11</sup> dials-alder reaction,<sup>12</sup> and imine bonds,<sup>13</sup> has been employed to construct smart materials. Boronic acid has been studied extensively due to its excellent ability to interact with diols to form boronate ester bonds reversibly, and the formation depends on pH, as well as the pKa of boric acid-ester pair.<sup>14</sup> The most common interaction with 1,2 or 1,3-diols occurs in basic media, forming five or six membered rings, respectively.<sup>15</sup> Boronate ester bonds can exchange reversibly at the interface of damage, making the gel self-healing.<sup>16</sup> Self-healing gels are a new kind of intelligent

59 60 materials which can identify and repair the damage immediately without any external force. There are a variety of self-healing gels which are stimulus-independent.<sup>17-20</sup> However, the main problem is the long self-healing time in application.<sup>21-23</sup> Hence, in this paper, polyvinyl alcohol (PVA) was employed, its excellent adhesion property can make the cut halves contact more sufficiently to reduce the time caused, which can also improve the mechanical property of the gels obtained.

The rapid development of industry and agriculture has resulted in considerable emissions of pollutants (particularly dyes) into the environment. Dyes have mutagenic and carcinogenic impacts on various living forms, and can cause detrimental health effects in humans and other organisms.<sup>24</sup> Among the various strategies, adsorption is one of the most sought-after techniques due to its simplicity, comparably low cost and high adaptability.<sup>25</sup> Adsorbents made from gels and polymer materials<sup>26</sup> are widely used to remove dyes, due to  $\pi$ - $\pi$ interaction, electrostatic interaction and hydrogen bond.

In many cases, the non-covalent interactions such as hydrogen bonding, electrostatic interactions, hydrophobic interactions or metal-ligand coordination between the chiral and achiral gelators make it easy to achieve transfer of chirality from monomers to assemblies.<sup>27,28</sup> Gels with chirality can also be obtained from chiral monomers by dynamic covalent chemistry, which provide many opportunities for developing chiral property involved intelligent materials.<sup>20</sup>

Herein, an ultra-fast self-healing organogel based on boronate ester bonds and acylhydrazone bonds was fabricated in situ by the reaction between PVA, 4-formylphenylboronic acid (FPBA), and chiral monomer tartaric acid dihydrazide (TDH). The chirality can be transferred from the chiral monomer to organogel. Additionally, due to the  $\pi$ - $\pi$  stacking interaction, hydrogen bonds and electrostatic interaction between adsorbents and dye molecules, the xerogels can also adsorb

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 <sup>&</sup>lt;sup>†</sup> Electronic Supplementary Information (ESI) available: synthesis route, <sup>1</sup>H NMR,

rheometer experiments and additional figures. See DOI: 10.1039/x0xx00000x.

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organic dye from aqueous solution. We expect this work can provide a possibility in practical applications.

## Experimental Section

#### Materials

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Poly(vinyl alcohol) (PVA, degree of hydrolysis 99%), 4formylphenylboronic acid (FPBA, 97%), hydrazine hydrate (98%), L-tartaric acid dimethyl ester (99%), and D-tartaric acid dimethyl ester (99%) were purchased from J&K Scientific Ltd. NaOH, methanol, dimethyl sulfoxide (DMSO), rhodamine B (99%), methylene blue (98.5%), and methyl orange (AR) were obtained from Sinopharm Chemical Reagent Co. Ltd. All materials above were used without further purification.

#### Synthesis of tartaric acid dihydrazide (TDH)<sup>29</sup>

The cross-linker tartaric acid dihydrazide (TDH) was synthesized as shown in Scheme S1. L-tartaric acid dimethyl ester or D-tartaric acid dimethyl ester (2 g, 11.23 mmol) was dissolved in methanol (30 mL), and hydrazine hydrate (1.38 g, 28.08 mmol) was added. Firstly, the reaction was stirred at room temperature for 2 h. Then, the reaction was refluxed at 60 °C under a nitrogen atmosphere for 12 h. The resulting product was removed by filtration, and washed by cold methanol (2×10 mL) and diethyl ether (2×10 mL), giving to a white solid. The purity was characterized by <sup>1</sup>H NMR, as shown in Figure S1 in the Supporting Information. The <sup>1</sup>H NMR (300 MHz, DMSO-d6) of TDH:  $\delta$ H / ppm 8.77 (s, 1H), 5.33 (d, 1H), 4.26 (s, 1H), 4.24 (s, 3H).

#### **Gel Preparation**

The synthesis of the organogel is a dynamic process. PVA and FPBA were dissolved in DMSO (0.4 g) in a sealed vial (water bath at 90 °C for 30 min) to get a homogeneous solution. TDH dissolved in a small amount of DMSO was added. (Figure 1). The previous work demonstrated that the reaction of boric acid and diols occurred at pH values above the pKa of boric acid, and the pKa of FPBA is 7.6.<sup>14</sup> So the pH of the mixture obtained was adjusted to 8 by NaOH solution (pH = 13). TDH served as a cross-





-linker to form acylhydrazone bonds between FPBA and TDH, giving rise to a three dimensional network101Aimg9PVAPand FPBA at alkaline condition, or mixing the three monomers together at acid condition, only sol can be acquired (Figure S2). The obtained organogel was called gel<sub>xyz</sub>, where x corresponds to the concentration of PVA (w/w), and y and z are the ratio of FPBA to TDH. During the experiments, the amount of FPBA was fixed, and the mole ratio of FPBA to TDH was altered by changing the weight of TDH. Taking the preparation of gel<sub>331</sub> as an example, PVA (0.0150 g) and FPBA (0.0038 g) was dissolved in DMSO (0.4 g), and a small amount of DMSO solution of TDH (0.0015 g) was added into the solution obtained above. Upon cooling to room temperature, we observed a transparent organogel that can hold its own weight upon vial inversion.

#### Preparation of xerogels

DMSO, the solvent used, was difficult to be removed completely by freeze-drying. So the organogel was washed by ultrapure water to place the DMSO trapped in the gel to get a hydrogel, and then the hydrogel was freeze-dried for 12 hours to obtain a xerogel. Xerogels were used in SEM, FT-IR spectra, and dye adsorption tests, and hydrogels obtained after washing were employed directly in circular dichroism (CD) experiments.

#### Characterization

<sup>1</sup>H NMR measurements. The purity of TDH was detected on a Bruker Advance 300 MHz NMR. The instrument was operated at a frequency of 300 MHz at  $25 \pm 0.1$  °C, with deuterated DMSO as a solvent.

**FT-IR spectra.** Infrared spectra were collected on a Thermo Nicolet is 10 FT-IR spectrometer equipped with a single bounce diamond stage attenuated total reflectance (ATR) accessory. The resolution was 4 cm<sup>-1</sup> with the range of 4000-600 cm<sup>-1</sup>, and per sample was scanned for 16 times.

**UV-Vis spectroscopy.** The gel formation characterization and dye adsorption experiments were performed on a UV-4100 spectrophotometer. As to gel formation characterization, the samples tested were water solutions of PVA, FPBA, TDH, and their mixture, because DMSO has adsorption at around 200 nm. The amount of each monomer in the mixture solution is trace, but the ratio between different monomers is the same as that for the as-prepared organogel. The path length of quartz cell was 10 mm. A 1 mm path length quartz cell was used for dye adsorption test. The water was used as a blank solvent.

**Circular dichroism (CD).** The CD spectra was performed on a JASCO-815 spectrometer using a 0.1 mm quartz cell. The TDH (D and L) solution  $(1.0 \times 10^{-3} \text{ mol/L})$  was measured directly, while the organogels made from L-TDH or D-TDH before tested were washed by water to remove DMSO, because DMSO has strong adsorption at around 200 nm, covering the CD signal of gels.

**Field-emission scanning electron microscopy (FE-SEM).** The morphology was observed on a Hitachi S-4800 FE-SEM microscope. A small volume of xerogels were cast onto single-crystal silica plates and then Pt coated.

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Figure 2 Dynamic frequency sweep of organogels with different concentrations.

**Rheological measurements.** Rheological experiments were carried out using a HAAKE RS75 Rheometer at  $25 \pm 0.1$  °C with a cone-plate system (C35/1° Ti L07116, diameter: 35 mm, cone angle: 11). The temperature was controlled with a Circulator HAAKE DC10 cyclic water bath (Karlsruhe, Germany).

**Self-healing test.** The organogels were cut to halves, and then the two separate gels were placed together. There was no other outside stimulus applied during the self-healing process. After self-healing, the tensile and rheology tests were carried out, and optical microscope was employed to observe the change of damage in real time.

**Tensile test.** Texture Analyzer (TMS-PRO) equipped with a twoway stretch fixture and a 5 N load cell was used to test the fracture tensile stress of the original and healed organogel to characterize the self-healing capacity. The tested sample was prepared in a mold (25 mm×10 mm×5 mm). The stretching speed was 50 mm/min.

**Dye adsorption experiment.** The preliminary adsorption ability was tested as follows: Xerogel (20 mg) was soaked in 1 mL dye solution (50 mg/L) at room temperature. Then, the residual dyes in solution were detected with UV–Vis spectrophotometer. The samples employed for all the characterization mentioned above were organogels made from L-TDH except chiral characterization.

# **Results and discussion**

# Rheological experiments of the PVA organogel

We initially characterized the mechanical property of the obtained PVA organogels with different concentrations (Figure 2). For all samples, the values of the storage modulus (G') are higher than those of the loss modulus (G") over the test frequency range, indicating that all the obtained organogels are elastic. Besides, the storage modulus is PVA concentration dependent. The higher the PVA concentration, the larger the values of G'. The PVA is the skeleton of the organogel, so that the greater the concentration of PVA, the better the elasticity of the organogel. As to the organogels with the same PVA



Figure 3 (a) FT-IR spectra of FPBA, TDH, PVA, and  $gel_{333}$ ; (b) UV-Vis spectra of solution of TDH, FPBA, and the mixture of PVA, TDH, and FPBA.

concentration, the larger the molar ratio of FPBA to TDH, the less the amount of TDH, making the degree cross-linking of gel<sub>331</sub> lower than that of gel<sub>321</sub>. As a result, the values of G' of gel<sub>331</sub> is smaller than gel<sub>321</sub>, and its elastic deformation is easier to occur, which made gel<sub>331</sub> more suitable for self-healing test followed.

### The organogel formation via dynamic covalent chemistry

The formation of the organogel was verified by FT-IR and UV-Vis spectroscopy. As shown in the FT-IR spectra of gel<sub>331</sub> (Figure 3a), the characteristic adsorption peaks assigned to stretching vibration of the aldehyde groups (C-H, 2844 cm<sup>-1</sup> and C=O, 1666 cm<sup>-1</sup>) and the stretching vibration of the primary amine (-NH<sub>2</sub>, 3308 cm<sup>-1</sup> and 3285 cm<sup>-1</sup>) disappear. Compared to the curve of PVA, there is a new peak at 1666 cm<sup>-1</sup> for gel<sub>331</sub>, which is the combination of C=O and C=N of acylhydrazone bond.<sup>30</sup> The wide adsorption band corresponding to hydroxyl groups (-OH, 3250 cm<sup>-1</sup>) is weaker than that of pure PVA, indicating that hydroxyl groups were reacted.

UV-Vis spectroscopy was further employed to confirm the reaction between PVA, FPBA, and TDH. As can be seen from Figure 3b, the absorption bands of aldehyde group of FPBA (n  $\rightarrow \pi^*$  transition, 201 nm, and  $\pi \rightarrow \pi^*$  transition, 290 nm) disappear. Compared with the UV absorption of the FPBA and TDH solutions alone, new peaks appear at around 220 and 310 nm after mixing the three monomers with the same ratio of gel<sub>331</sub>. The new adsorption peaks are assigned to the n  $\rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transitions of C=N of the acylhydrazone bond (-CH=N-NH-CO-), thus proving the formation of acylhydrazone bonds.<sup>31</sup> Besides, compared with the curves of FPBA, the adsorption band of benzene ring of the curve of mixture shows obvious bathochromic shift (from 256 to 288 nm), which is probably caused by the enhanced conjugation after the formation of acylhydrazone bonds.

Given these results, we confirmed that the organogel was synthesized in situ by boronate ester bonds and acylhydrazone bonds.

# Self-healing capability of the PVA organogels

Owing to the reversibility of dynamic covalent chemistry, the organogels can spontaneously repair themselves after mechanical damage.<sup>32,33</sup> Cut/heal tests were carried out to assess the self-healing behavior (Figure 4). Firstly, two gel<sub>331</sub> stained with rhodamine B (RhB) and methylene blue (MB) were



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Figure 4 Photographs of the self-healing test. (a) gel<sub>331</sub> was cut into two pieces; (b) the two pieces were put together; (c) the organogel can hold its weight; (d) the healed organogel was stretched.



Figure 5 Optical microscope images of the self-healing process of the gel<sub>331</sub>. Images of the cut surfaces with self-healing time of (a) 0, (b) 1, (c) 5, (d) 15, (e) 25, and (f) 30 min; (g) rheological curves of the original and the self-healed gel. The bar is 100  $\mu\text{m}.$ 

cut into two pieces, respectively. Then, the blue and red pieces were placed in contact (the diameter is 1.5 cm), allowing for self-healing at room temperature. The cut pieces automatically merged into a single one within 30 s, which can support its own weight easily. After 5 min, it can be stretched to 6 cm, 4 times the length of its original state (Figure 4d). Self-healing mechanism is shown in scheme 1. The Dynamic covalent chemistry is a dynamic process, and the complexation and dissociation of boronate ester bonds or acylhydrazone bonds are in dynamic equilibrium.<sup>34</sup> When the two pieces of organogel were put together after cut into two halves, the unassociated groups and the groups after dissociation at the cut surface can react with each other to form new boronate ester bonds and acylhydrazone bonds to make the two halves a whole one. In addition, PVA is an adhesive polymer, which can make the two halves contact sufficiently enough to form new dynamic covalent



Scheme 1 Proposed mechanism of self-healing process, (a) damaged, and (b) self-healed.



Figure 6 Curves of tensile stress of original and healed organogels after different time.

bonds at the interface. As a result, the organogel possesses a faster self-healing property than other gels reported 18,35-37

The disappearance of the crack between the two pieces was monitored by optical microscopy, showing that the scar shallows and almost no gap can be observed in the healed region after 30 min (Figure 5f). Meanwhile, the storage modulus (G') and loss modulus (G") of the healed gel<sub>331</sub> are almost identical to those of its original state. Furthermore, tensile experiment was employed to characterize the self-healing capacity of organogel. The tensile strength of the original and healed organogel after different time is shown in Figure 6. The maximum tensile strength (5.44 kPa) of the original state was at 248% strain. The fracture tensile stress of the healed organogel is relatively lower than that of the original state, and is almost self-healed after 10 min (up to 5.09 kPa, 93.6% of the original state). These results suggested the restoration of the inner structure of the organogel after self-healing.

#### Dye adsorption performance of the xerogels

Water pollution is a very serious environment problem, which is hazardous to the health of people and animals.<sup>38</sup> Adsorption is one of the most effective ways to solve the problem. In order to verify the dye adsorption capacity of the organogels, the xerogels made from L-TDH were used as adsorbents to adsorb different kinds of toxic dyes, MB, RhB, and MO (the chemical structures are shown in Figure S3 in ESI). UV-Vis spectroscopy was employed to record the dye adsorption of xerogels at different time. As shown in Figure 7, the concentration of MB decreases rapidly with the xerogels soaked into dye solutions,



Figure 7 Temporal evolution of UV-Vis absorption spectra of dye solutions (a) MB, (b) MO, and (c) RhB. The photographs show the color of solutions before and after adsorption.

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Figure 8 Photographs of mixture solutions of (a) MB/RhB and (b) MB/MO before and after adsorption for 20 min. The UV-Vis spectra of mixture solutions of (c) MB/RhB and (d) MB/MO before and after adsorption.

and MB cannot be detected after 20 min, while the adsorption peaks of RhB and MO are still relatively strong after 50 min. In addition, the removal efficiency of MB is 95.89%, higher than those of MO and RhB (Table 1). In order to further reveal the selective adsorption of MB, dye mixture solutions of MB/MO and MB/RhB were chosen (Figure 8). When the xerogels were soaked in mixture solutions of MB/RhB or MB/MO, the colour changed significantly from purple to pink or from green to yellow, which was the colour of RhB or MO, respectively. In other words, the xerogels are able to absorb MB selectively. The selective adsorption process can also be observed by UV-Vis spectroscopy. For both of the mixtures, two obvious adsorption peaks can be observed before adsorption. After 20 min, the peak at 664 nm corresponding to MB cannot be detected, while strong adsorption bands can still be seen for RhB and MO. The xerogel prepared from D-TDH can also adsorb MB selectively.

Table 1 Removal efficiency of different dyes.				
Adsorbate	Fitted equation	Concentratio n before adsorption (mg/L)	Concentratio n after adsorption (mg/L)	Removal efficiency (%)
MB	A=0.0072 2C	50.00	2.06	95.89
RhB	A=0.0371 5C	50.00	12.41	75.18
МО	A=0.0095 9C	50.00	21.32	57.36

Where A is adsorption, and C is the concentration of dye solution.

As shown in scheme 2, owing to the benzene ring and surface charge properties of dyes, the xerogels are able to adsorb dyes through  $\pi$ - $\pi$  stacking interaction, hydrogen bond and electrostatic interaction.<sup>39</sup> MB and RhB can be adsorbed preferentially owing to the stronger  $\pi$ - $\pi$  interactions with the adsorbent. More importantly, the boric acid group of FPBA can associate with OH<sup>-</sup> under basic condition to be negatively charged. In addition to the prominent  $\pi$ - $\pi$  stacking and electrostatic interaction, the  $\pi$ -cation interaction could also occur with the positively charged centre of the dye, so the removal efficiency of negatively charged dye (MO) is lower than that of positively charged dyes (MB and RhB). Moreover, the



Scheme 2 Proposed mechanism of adsorption. (a) MB, (b) RhB and (c) MO.

molecular structure of RhB is larger than that of MB. The steric hindrance will hinder adsorption. As a result, the adsorbent can adsorb MB more efficiently.

#### **Chirality characterization**

Chirality can be transferred from small chiral molecule gelators to gels.<sup>40</sup> Since the chiral small molecule TDH is involved in the formation of acylhydrazone bonds, we expect that chirality can be transferred to organogels via acylhydrazone bonds. CD spectrum was employed to measure the chirality of L-TDH, D-TDH, L-gel<sub>331</sub>, and D-gel<sub>331</sub> (Figure 9). L-TDH and D-TDH solutions have opposite Cotton effects at around 200 nm, corresponding to the UV absorption of the  $\pi \rightarrow \pi^*$  electronic transition of amide (R-NH-CO-). Compared with the CD spectrum of monomers, the signal at 200 nm is obviously weakened, while new peaks appear at 210 – 290 nm and 320 nm, which are consistent with the adsorption of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transitions of C=N of the acylhydrazone bond (-CH=N-NH-CO-).<sup>41</sup> What's more, the organogels obtained from L-TDH and D-TDH showed opposite Cotton effects, which indicates that the chirality is transferred from small molecule to the organogels through the acylhydrazone bond.

SEM was carried out to observe the morphologies of the transparent organogels obtained. Figure S4 presents the images of gel<sub>331</sub> consisting of D-TDH or L-TDH. The organogels exhibit fibrous structures, and the fibers twin into a network. Since one

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of the monomer is PVA, which is sticky and easy to for membrane, making it difficult to distinguish the spiral of the fibers.



Figure 9 CD spectra of water solution of FPBA, PVA, D-TDH, and L-TDH. (b) CD spectra of D-gel<sub>331</sub> and L-gel<sub>331</sub>.

#### Conclusion

In summary, ultra-fast self-healing and dye adsorption organogels based on dynamic covalent chemistry were prepared through a flexible and in situ method. Due to the reversible break and reform of boronate ester bonds and acylhydrazone bonds, the organogel had an ultra-fast self-healing capacity without a catalyst or external stimulus. The  $\pi$ - $\pi$  stacking interaction and electrostatic interaction endow the xerogel selective adsorption capability for organic dye MB. The ultra-fast self-healing organogel provides a new pathway for constructing smart materials for applications in experimental research and industrial production.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### Notes and references

- 1 T. Maeda, H. Otsuka and A. Takahara, Prog. Polym. Sci., 2009, 34, 581.
- 2 F. Plourde, A. Motulsky, A. Couffin-Hoarau, D. Hoarau. H. Ong and J. Leroux, J. Control. Release, 2005, 108, 433.
- 3 S. S. Sagiri, B. Behera, R. R. Rafanan, C. Bhattacharya, K. Pal, I. Banerjee and D. Rousseau, Soft Matter, 2013, 12, 47.
- 4 C. L. Esposito, P. Kirilov and V. G. Roullin, J. Control. Release, 2018, 271, 1.
- 5 T. R. Jenta, G. Batts, G. D. Rees and B. H. Robinson, Biotechnol. Bioeng., 2015, 53, 121.
- 6 F. Karimi, J. Collins, D. E. Heath and L. A. Connal, Bioconjugate Chem., 2017, 28, 2235.
- 7 T. Wang, X. D. Yu, Y. J. Li, J. J. Ren and X. L. Zhen, Acs Appl. Mater. Inter., 2017, 9, 13666.
- 8 W. Lu, X. X. Le, J. W. Zhang, Y. J. Huang and T. Chen, Chem. Soc. Rev., 2017, 46, 1284.
- 9 V. Yesilyurt, M. J. Webber, E. A. Appel, C. Godwin, R. Langer and D. G. Anderson, Adv. Mater., 2016, 28, 86.
  - e., (inderson), (av. (indee), 2010),
  - 6 | J. Name., 2012, 00, 1-3

- 10 Y. Dong, W. L. Chen and J. H. Hu, J. Phys. Chem. <u>9, 2014</u>, 118 12311. DOI: 10.1039/C9NJ00891H
- 11 G. H. Deng, C. M. Tang, F. Y. Li, H. F. Jiang and Y. M. Chen, Macromolecules, 2010, 43, 1191.
- 12 J. R. Davidson, G. A. Appuhamillage, C. M. Thompson, W. Voit and R. A. Smaldone, Acs Appl. Mater. Inter., 2016, 8, 16961.
- 13 Y. S. Xu, Y. S. Li, Q. M. Chen, L. H. Fu, T. Lei and Y. Wei, Int. J. Mol. Sci., 2018, 19, 2198.
- 14 J. Yan, G. Springsteen, S. Deeter and B. Wang, Tetrahedron, 2004, 60, 11205.
- 15 A. Pettignano, S. Grijalvo, M. Häring, R. Eritja, N. Tanchoux, F. Quignard and D. D. Díaz, Chem. Commun., 2017, 53, 3350.
- 16 R. W. Guo, Q. Su, J. W. Zhang, A. J. Dong, C. J. Lin and J. H. Zhang, Biomacromolecules, 2017, 18, 1356.
- 17 C. C. Deng, W. L. A. Brooks, K. A. Abboud and B. S. Sumerlin, Acs Macro Lett., 2015, 4, 220.
- 18 J. J. Cash, T. Kubo, A. P. Bapat and B. S. Sumerlin, Macromolecules, 2015, 48, 2098.
- 19 G. H. Deng, Q. Ma, H. X. Yu, Y. F. Zhang, Z. C. Yan, F. Y. Liu, C. Y. Liu, H. F. Jiang and Y. M. Chen, Acs Macro Lett., 2015, 4, 467.
- 20 A. Biswas, S. Malferrari, D. M. Kalaskar and A. K. Das, Chem. Commun., 2018, 54, 1778.
- 21 M. Nakahata, Y. Takashima, H. Yamaguchi and A. Harada, Nat. Commun., 2011, 2, 511.
- 22 R. Boris, Acs Nano, 2011, 5, 6791.
- 23 T. Kakuta, Y. Takashima, M. Nakahata, M. Otsubo, H.
- Yamaguchi and A. Harada, Adv. Mater. 2013, 25, 2849. 24 E. N. Zare, A. Motahari and M. Sillanpää, Environ. Res., 2018,
- 162, 173.
  25 L. Yu, L. Wang, W. C. Xu, L. M. Chen, M. L. Fu, J. L. Wu and D. Q. Ye, J. Environ. Sci.-China, 2018, 67, 171.
- 26 X. M. Li, M. J. Zhou, J. X. Jia and Q. Jia, React. Funct. Polym., 2018, 126, 20.
- 27 K. Lv, L. Qin, X. F. Wang, L. Zhang and M. H. Liu, Phys. Chem. Chem. Phys., 2013, 15, 20197.
- 28 G. F. Liu, X. Li, J. H. Sheng, P. H. Li, W. K. Ong, S. Phua, H. Ågren,
   L. L. Zhu and Y. L. Zhao, Acs Nano, 2016, 11, 11880.
- 29 G. Y. Ishmuratov, M. P. Yakovleva, G. R. Mingaleeva, M. A. Shutova, R. R. Muslukhov, E. M. Vyrypaev and A. G. Tolstikov, Chem. Nat. Compd., 2013, 49, 691.
- 30 Y. Tian, Y. W. Cao, Y. Wang, W. L. Yang and J. C. Feng, Adv. Mater., 2013, 25, 2980.
- 31 D. Janeliunas, P. Van Rijn, J. Boekhoven, C. B. Minkenberg, J. H. van Esch and R. Eelkema, Angew. Chem., Int. Ed., 2013, 52, 1998.
- 32 R. K. Schultz and R. R. Myers, Macromolecules, 1969, 2, 281.
- 33 S. W. Sinton, Macromolecules, 1987, 20, 2430.
- 34 L. He, D. E. Fullenkamp, J. G. Rivera and P. B. Messersmith, Chem. Commun., 2011, 47, 7497.
- 35 F. Tao, L. M. Qin, Z. K. Wang and Q. M. Pan, Acs Appl. Mater. Inter., 2017, 9, 15541.
- 36 N. N. Xia, M. Z. Rong and M. Q. Zhang, J. Mater. Chem. A, 2016, 4, 14122.
- 37 J. K. Chen, Q. Su, R. W. Guo, J. W. Zhang, A. J. Dong, C. G. Lin and J. H. Zhang, Macromol. Chem. Phys., 2017, 218, 1700166.
- 38 Y. Z. Niu, R. J. Qu, H. Chen, L. Mu, X. G. Liu, T. Wang, Y. Zhang and C. M. Sun, J. Hazard. Mater., 2014, 278, 267.
- 39 K. Gupta, D. Gupta and O. P. Khatri, Appl. Surf. Sci., 2019, 476, 647.
- 40 Y. G. Li, T. Y. Wang and M. H. Liu, Soft Matter, 2007, 3, 1312.
- 41 L. Gao, J. B. Fei, J. Zhao, W. Cui, Y. Cui and J. B. Li, Chem. Eur. J., 2012, 18, 3185.



The organogel can repair the damage rapidly, and the relative xerogels can adsorb methylene blue with high efficiency.

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