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.Supplementary Information

A pH-Controlled Bidirectionally Pure DNA Hydrogel: Reversible Self-Assembly and Fluorescence Monitoring

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Materials and Apparatus

β-Morpholinoethanesulfonic acid (MES) was purchased from Sigma-Aldrich (USA), and all other reagents were of analytical grade. Ultrapure water (18.25 MΩ.cm) was used throughout all of the experiments. All synthetic DNA oligonucleotides were obtained from Sangon Biotechnology Co. Ltd. (Shanghai, China), and the sequences are listed in Table S1. Atomic force microscopy (AFM) images were obtained using the tapping mode in air with a Dimension Icon SPM (Bruker, Germany). Fluorescence measurements were carried out using an F-4600 fluorescence spectrophotometer (Hitachi) and all of the optical images were taken with a digital camera.

Self-Assembly of DNA Modules

Using the process for module (a) as an example, we first mixed equivalent amounts of the three single DNA strands (1-1, 1-2 and 1-3) that composed module (a) and then performed an annealing process. In brief, the mixture was rapidly heated to 95°C, where it was maintained for 5 minutes, followed by slow cooling to room temperature within two hours. All of the other DNA modules except (d) underwent a similar annealing process to complete the self-assembly.

Formation of Hydrogels and the pH-Activated Transitions between Hydrogel and Fluid States[1]

Using the process for hydrogel (I) as an example, stoichiometric amounts of modules (a) and (b) were mixed in a 50 mM MES buffer (pH = 7.0; with 50 mM NaCl), with a final concentration of 0.5 mM for each module. The mixture quickly transformed to the hydrogel state. However, when 0.5 μL HCl (6 M) was added into 60 μL hydrogel (I) to adjust the pH to 5.0, the hydrogel transformed to the fluid state. Then, 0.5 μL NaOH (6M) was added to recover the hydrogel state. Hydrogel (II) and hydrogel (III) were also formed and tested with this method.

Native-Polyacrylamide Gel Electrophoresis Experiment[2]

Prepared samples were applied to native polyacrylamide gels and then run at 4 °C in 1×TBE buffer for 60 minutes or longer (100 V). The native-gels were stained with silver ions to visualize the position of the DNA strands. Images were then obtained directly with a commercial scanner.

Fluorescence Test

To facilitate the fluorescence test, we diluted three microliters from each sample to the liquid state before taking the fluorescence measurement.

Table S1. The DNA sequences used in this paper.

1	(FAM-)CCTCCCCTCCGTTTCCCTCCCCTCCATTTGGAGGGGAGGATCTAGTAAATCTTATATCATACTGGCA(-FAM)
2	TTCTTTTCTTTTCTTTTCTTACATGACGATTGACAAGATTTACTAGAT
3	CGAACGTAATAGCAGATAATTGCCAGTATGATATGTCAATCGTCATGT
1--1/1	(FAM-)CCTCCCCTCCGTTTCCCTCCCCTCCATTTGGAGGGGAGGATCTAGTAAATCTTATATCATACTGGCA
1--2	(FAM-)CCTCCCCTCCGTTTCCCTCCCCTCCATTTGGAGGGGAGGACATGACGATTGACAAGATTTACTAGAT
1--3	(FAM-)CCTCCCCTCCGTTTCCCTCCCCTCCATTTGGAGGGGAGGTGCCAGTATGATATGTCAATCGTCATGT
1'- 1	CGGAGGGGAGGACGCTGTCCTAACCATGACCGTCGAAG(-BHQ1)
1'- 2	CGGAGGGGAGGTTCGACGGTCATGTACTAGATCAGAGG(-BHQ1)
1'- 3	CGGAGGGGAGGCTCTGATCTAGTAGTTAGGACAGCGTG(-BHQ1)
2'	(BHQ1-)AAGAAAAGAAAAGAAAAGAA(-BHQ1)
2''- 1	TTCTTTTCTTTTCTTTTCTTACATGACGATTGACAAGATTTACTAGAT(-FAM)
2''- 2	TTCTTTTCTTTTCTTTTCTTATCTAGTAAATCTTATATCATACTGGCA(-FAM)
2''-3	TTCTTTTCTTTTCTTTTCTTTGCCAGTATGATATGTCAATCGTCATGT(-FAM)
3'- 1	ATTATCTGCTATTACGTTCGTGGATCCGCATGACATTCGCCGTAAG
3'- 2	ATTATCTGCTATTACGTTCGCTTACGGCGAATGACCGAATCAGCCT
3'- 3	ATTATCTGCTATTACGTTCGAGGCTGATTCGGTTCATGCGGATCCA
1--1/1#	CTCATGCCTCCCCTCCCCTCCGTTTCCCTCCCCTCCCCTCCATTTGGAGGGGAGGGGAGGATCTAGTAAATCTTATATCATACTGGCA
1--2#	CTCATGCCTCCCCTCCCCTCCGTTTCCCTCCCCTCCCCTCCATTTGGAGGGGAGGGGAGGACATGACGATTGACAAGATTTACTAGAT
1--3#	CTCATGCCTCCCCTCCCCTCCGTTTCCCTCCCCTCCCCTCCATTTGGAGGGGAGGGGAGGTGCCAGTATGATATGTCAATCGTCATGT
1'- 1#	GGGAGGCATGAGCACGCTGTCCTAACCATGACCGTCGAAG
1'- 2#	GGGAGGCATGAGCTTCGACGGTCATGTACTAGATCAGAGG
1'- 3#	GGGAGGCATGAGCCTCTGATCTAGTAGTTAGGACAGCGTG

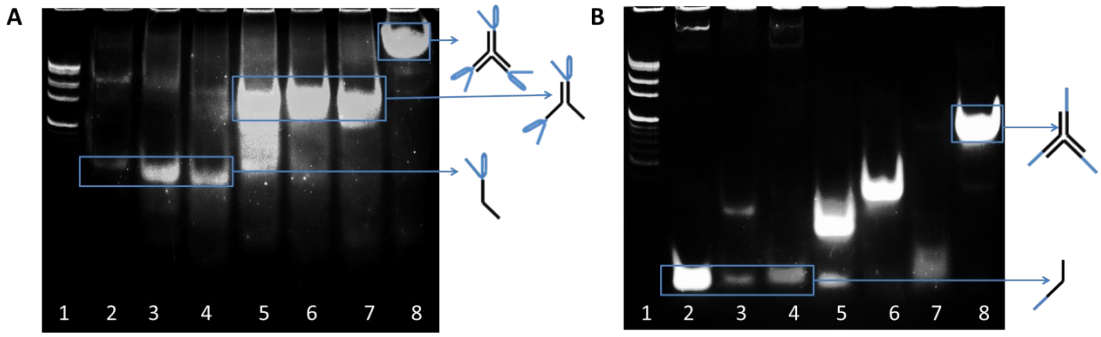

Fig. S1 (A) Characterization of the formation of DNA module (a) by 10% Native-PAGE. (1) 20bp DNA Marker; (2) 1-1; (3) 1-2; (4) 1-3; (5) 1-1 + 1-2; (6) 1-1 + 1-3; (7) 1-2 + 1-3; (8) 1-1 + 1-2 + 1-3. (B) Characterization of the formation of DNA module (b) by 10% Native-PAGE. (1) 20bp DNA Marker; (2) 1'-1; (3) 1'-2; (4) 1'-3; (5) 1'-1 + 1'-2; (6) 1'-1 + 1'-3; (7) 1'-2 + 1'-3; (8) 1'-1 + 1'-2 + 1'-3.

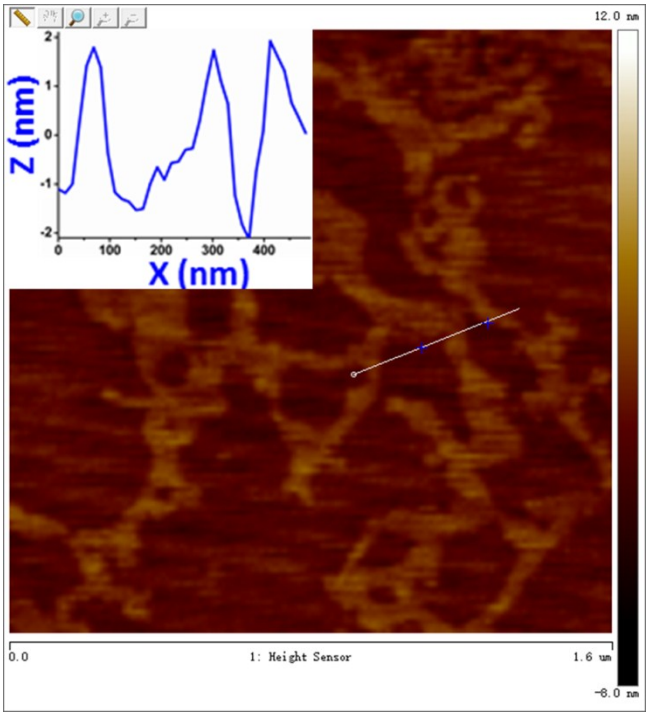

Fig. S2 The AFM image of hydrogel (Ⅰ) and its cross-section analysis of different positions.

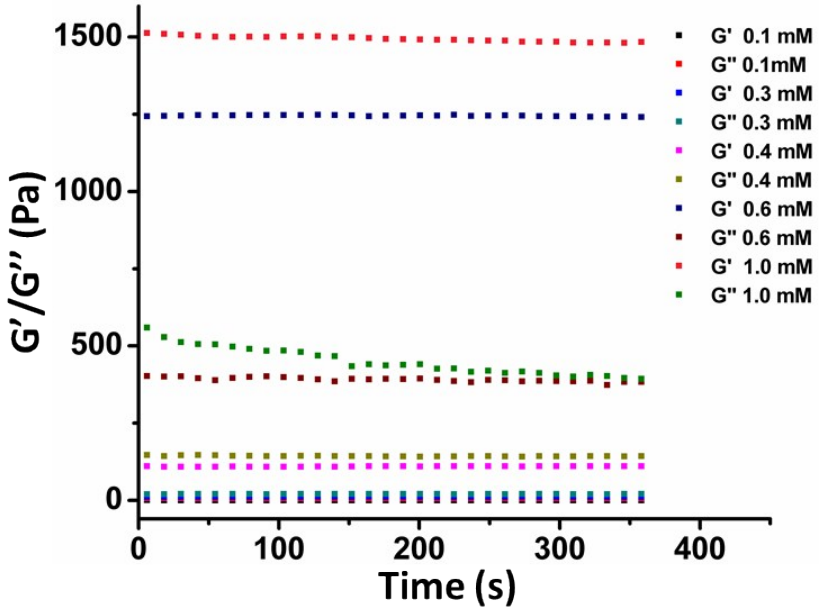

Fig. S3 Rheometric characterization of hydrogel (Ⅰ) with different concentration of units at pH 7.0.

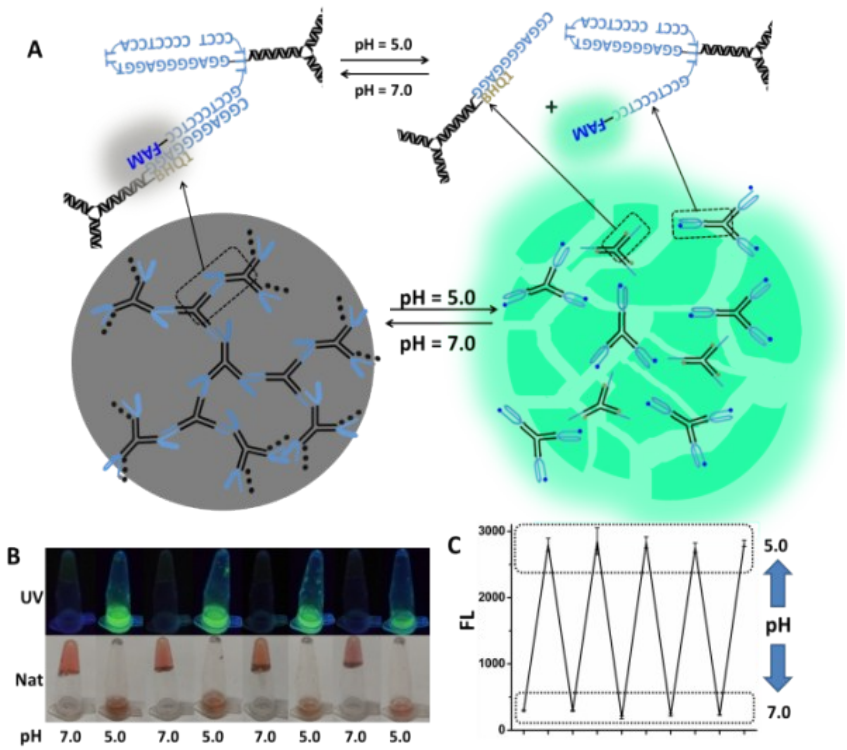

Fig. S4 (A) Schematic diagram of the principle of fluorescent hydrogel (I) association and dissociation. (B) Images corresponding to the pH-activated reversible formation and dissociation of fluorescent hydrogel (I). (C) The changes of fluorescence intensity when the pH values changed between 7.0 and 5.0.

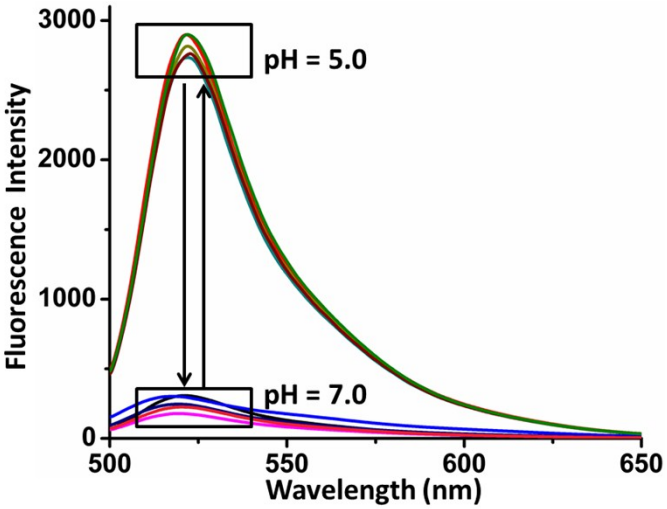

Fig. S5 Fluorescence emission spectra of fluorescent hydrogel (Ⅰ) when the pH values changed between 7.0 and 5.0.

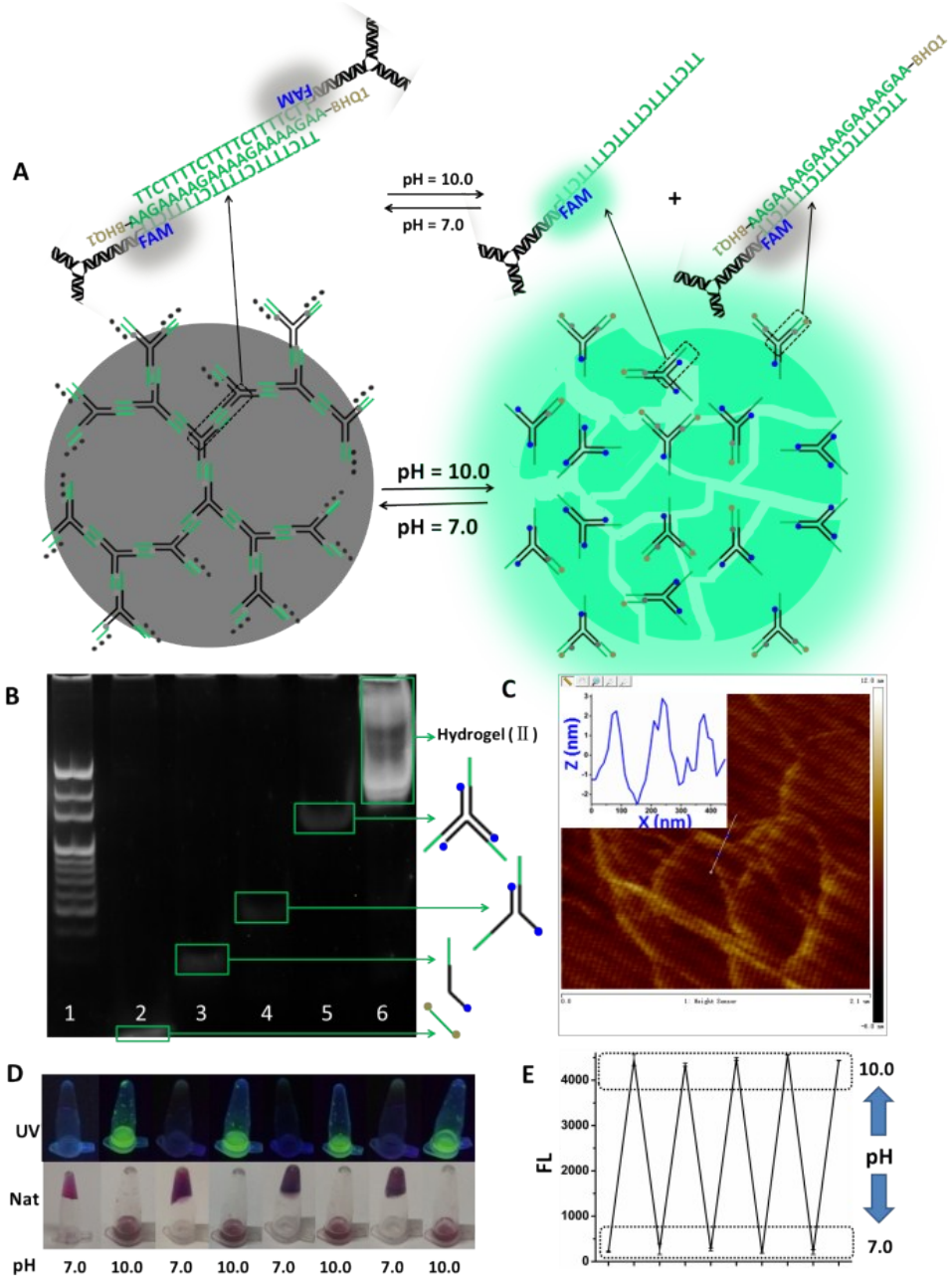

Fig. S6 (A) Schematic diagram of the principle of fluorescent hydrogel (II) association and dissociation. (B) Characterization of the formation of fluorescent hydrogel (II) by 10% Native-PAGE. (1) 20bp DNA Marker; (2) 2'; (3) 2''-1; (4) 2''-1 + 2''-2; (5) 2''-1 + 2''-2 + 2''-3; (6) (2) + (5). (C) The AFM image of fluorescent Hydrogel (II) and its cross-section analysis of different positions. (D) Images corresponding to the pH-activated reversible association and dissociation of fluorescent hydrogel (II) in the UV or natural light irradiation. (E) The changes of fluorescence intensity when the pH values changed between 7.0 and 10.0.

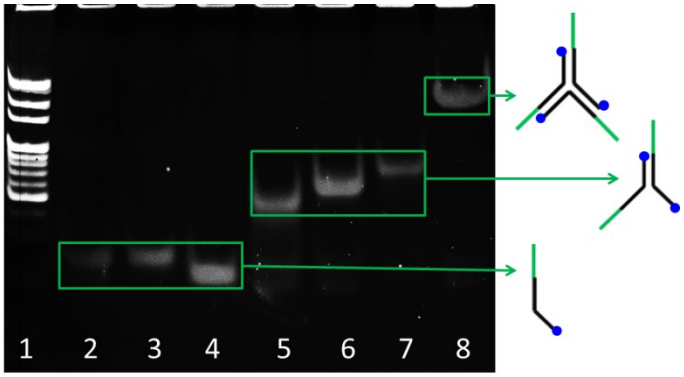

Fig. S7 Characterization of the formation of fluorescent DNA module (c) by 10% Native-PAGE. (1) 20bp DNA Marker; (2) 2’’-1; (3) 2’’-2; (4) 2’’-3; (5) 2’’-1 + 2’’-2; (6) 2’’-1 + 2’’-3; (7) 2’’-2 + 2’’-3; (8) 2’’-1 + 2’’-2 + 2’’-3.

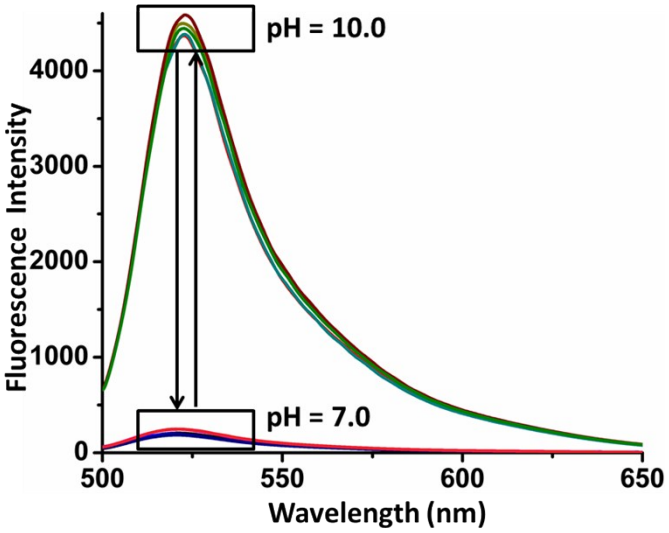

Fig. S8 Fluorescence emission spectra of fluorescent hydrogel (Ⅱ) when the pH values changed between 7.0 and 10.0

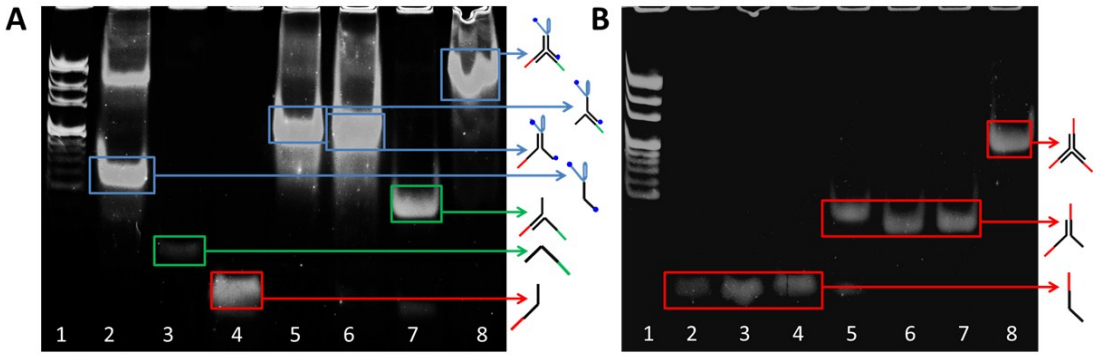

Fig. S9 (A) Characterization of the formation of fluorescent DNA module (e) by 10% Native-PAGE. (1) 20bp DNA Marker; (2) 1; (3) 2; (4) 3; (5) 1+2; (6) 1+3; (7) 2+3; (8) 1+2+3. (B) Characterization of the formation of fluorescent DNA module (f) by 8% Native-PAGE. (1) 20bp DNA Marker; (2) 3'-1; (3) 3'-2; (4) 3'-3; (5) 3'-1+3'-2; (6) 3'-1+3'-3; (7) 3'-2+3'-3; (8) 3'-1+3'-2+3'-3.

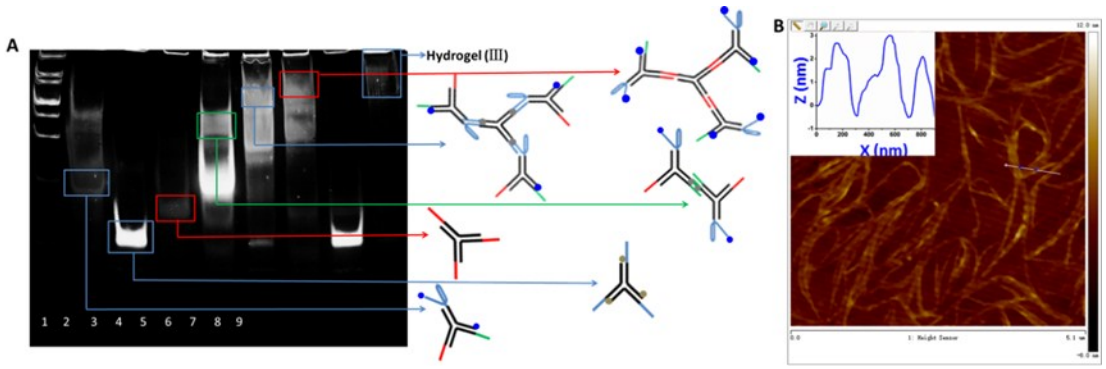

Fig. S10 (A) Characterization of the formation of fluorescent hydrogel (Ⅲ) by 6% Native-PAGE. (1) 100bp DNA Marker; (2) e; (3) b; (4) f; (5) e + d; (6) e + b; (7) e + f; (8) b + f; (9) e + b + d + f. (C) The AFM image of fluorescent Hydrogel (Ⅲ) and its cross-section analysis of different positions.

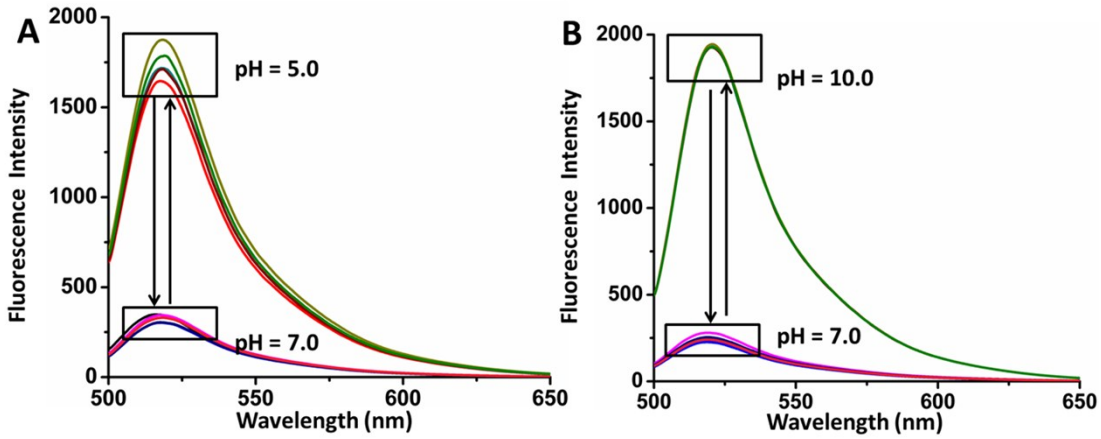

Fig. S11 Fluorescence emission spectra of fluorescent hydrogel (Ⅲ) when the pH values changed between 7.0 and 5.0 (A) or 10.0 (B).

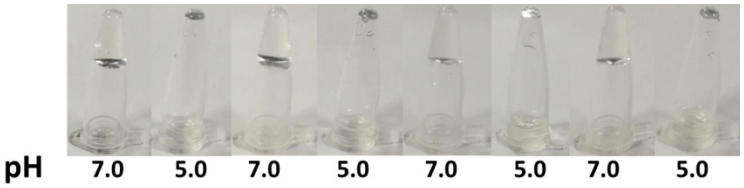

Fig. S12 Images corresponding to the pH-activated reversible association and dissociation of hydrogel (Ⅰ) [#].

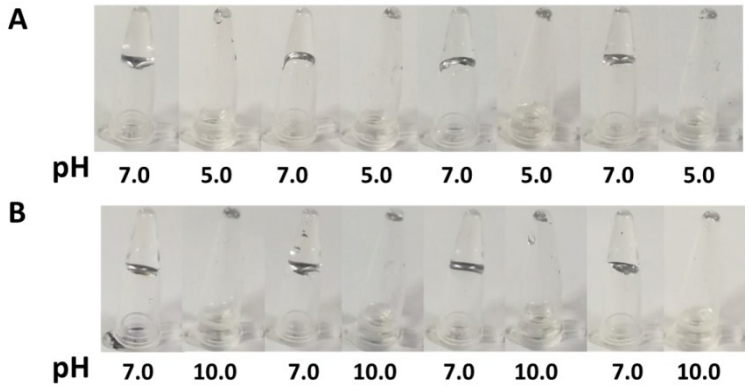

Fig. S13 Images corresponding to the pH-activated reversible association and dissociation of hydrogel (Ⅲ) [#] in faintly acidity (A) and faintly basicity (B) circumstances.

References

1 E. Cheng, Y. Xing, P. Chen, Y. Yang, Y. Sun, D. Zhou, L. Xu, Q. Fan, D. Liu, *Angew. Chem. Int. Ed.* 2009, **48**, 7660-7663.

2 S. Lu, T. Hu, S. Wang, J. Sun, X. Yang, *ACS Appl. Mater. Interfaces* 2017, **9**, 167-175.