

## Supporting Information

### **Water-sensitive fluorescent microgel inks to produce verifiable information for highly secured anti-counterfeiting**

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## Experimental

**Materials for preparing microgels:** N-isopropylacrylamide (NIPAM,  $\geq 98\%$ ) were purchased from TCI (shanghai) reagent Co. Ltd. Acrylic acid (AAc, 98%), N,N'-Methylene bis (acrylamide) (BIS,  $\geq 98\%$ ), 2,2'-azobis-2-methyl-propanimidamide (AAPH), rhodamine B (Rh B), 5-aminofluorescein (FITC), Sodium dodecyl sulfonate (SDS) and sodium hydroxide (NaOH, 96.0%) were commercially provided by Aladdin reagent Co. Ltd. Hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Co. Ltd. Anthracen-9-yl acrylate (9-ANA) was synthesis by the reported work[40]. All reagents were used without any treatment or purification.

**Synthesis and characterization of MG:** First, different mass of 9-ANA (0.0025 g, 0.005 g and 0.01 g), 0.5 g SDS were added into a three-necked round-bottom flask with 200 mL deionized water and stirring at room temperature for the dissolution of 9-ANA. Then, the three-necked round-bottom flask was bubbled with N<sub>2</sub> gas for 20 min to remove the dissolved oxygen. Subsequently, NIPAM (2.263 g), AAc (305  $\mu$ L), and 0.387 g of BIS were added to the water and stirred with a magnetic bar at 70 °C for 1 h. The flask was sealed, and the N<sub>2</sub> gas was blown into the flask below the liquid level. Next, 0.15 g of AAPH was added to the solution. The polymerization was performed for 2 h at 70 °C, with a stirring of about 450 r.p.m. The microgels dispersion was immediately cooled in an ice-water bath for terminating the reaction, and NaOH was added for deprotonation. The obtained product was dialyzed for two weeks. Microgel particles were freeze-dried (DGJ-10C, Shanghai Boden) for subsequent use.

## Preparation and characterization of MG-FITC, MG-Rh B and MG-1F1R

**Microgels:** Firstly, FITC was prepared into an aqueous solution with a concentration of  $1 \times 10^{-4}$ , and the pH of the solution was adjusted to 5.5 in order to protonate FITC. Rh B was also prepared into the same concentration. Then, 0.02 mL solution (0.02 mL of FITC, or 0.02 mL of Rh B, or 0.01 mL of FITC and 0.01 mL of Rh B) was taken and 1 mg of MG was added, respectively. Finally, the MG-FITC, MG-Rh B and MG-1F1R

microgels were obtained. As for fluorescent ink, configuring the corresponding concentration according to the requirements.

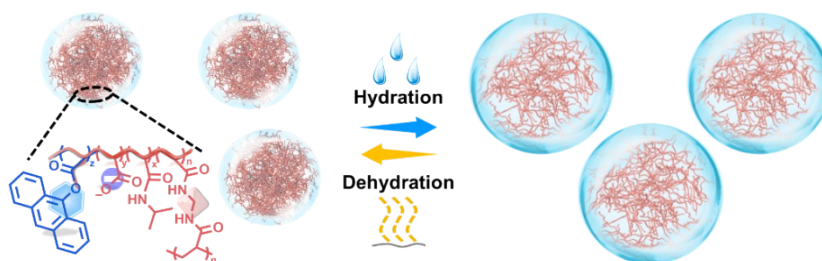
### **Measurements**

<sup>1</sup>H NMR spectra were obtained from a Bruker Avance III 400 MHz spectrometer in D<sub>2</sub>O. UV-Vis absorption and transmittance spectra were measured on an UV-Vis spectrophotometer (TU-1810, Purkinje General Instrument Co. Ltd.). ATR-FTIR spectra was recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. The digital photos of the polymeric films were taken under a UV lamp (ZF-5, 5 W, 254 nm). All fluorescent photographs were taken using the same UV lamp. Steady-state fluorescence measurements, fluorescence lifetime of microgels with different water content were obtained from a HPRIBA FL3-111 fluorescence spectrofluorometer at room temperature with a 500 W Xenon lamp. Quantum efficiency of MG-derived systems with different water content were obtained from quantum efficiency tester (Otsuka Photol Electronics QE-2100). The excitation wavelength was 254 nm. The morphology of microgels were performed by a field-emission scanning electron microscopy (SEM, S-4800, Hitachi) with an accelerating voltage of 4.0 kV. The laser confocal pattern was conducted on a Biotype laser confocal microscope (LEICA) machine. The hydrodynamic diameters of the microgels in water at different temperatures and Zeta potential were measured by dynamic light scattering (Zetasizer Nano ZS, Malvern).

### **Simulation calculation method**

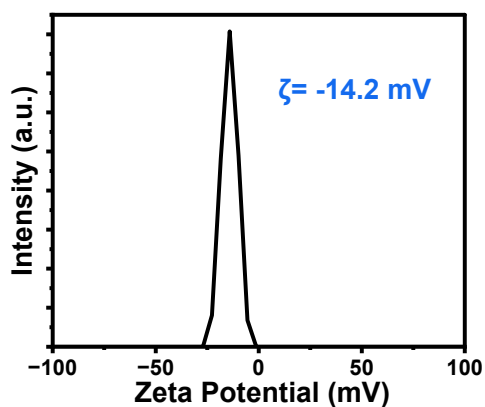
The DMol3 module in Materials Studio software was used to calculate the electron orbital changes of single fluorescent monomer systems, 9-ANA, FITC and Rh B.<sup>[1-3]</sup> To obtain the most stable conformations and its energies of single 9-ANA, FITC and Rh B, the DFT calculation (GGA-PW91, VWN) were used. Firstly, multiple times of structural optimization were performed. In the process of structural optimization, Perdew -Wang 91 (PW 91), a function of generalized-gradient approximation (GGA) was applied, and Core treatment as “All Electron”. “Spin unrestricted” was chosen for

optimizing the structure. After calculating the energy of optimized structure, the localized orbitals can be predicted.

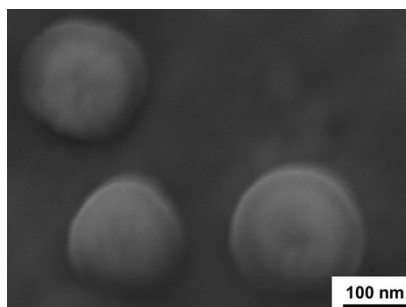


**Figure S1.** The composition of MG and their swelling-deswelling performance.

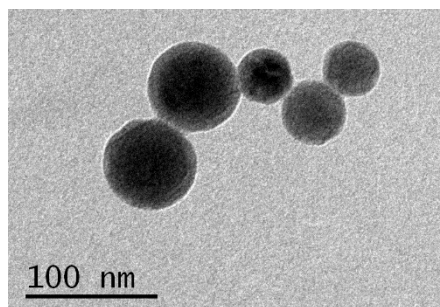
$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  7.70 (s, 14H), 4.19 (s, 1H), 3.82 (s, 22H), 2.48 (s, 1H), 1.98 (s, 35H), 1.07 (s, 193H).



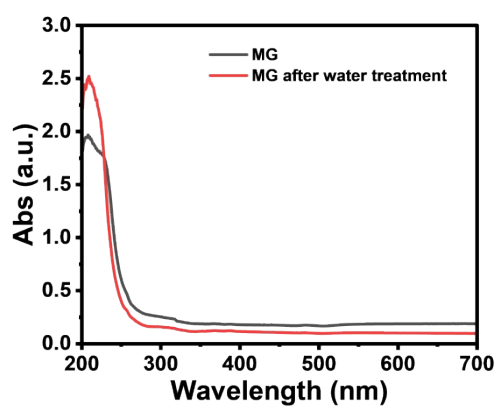
**Figure S2.** Zeta potential spectra of MG in aqueous solution.



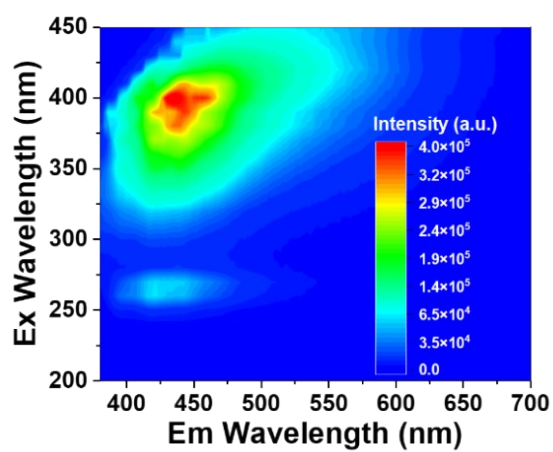
**Figure S3.** SEM images of freeze-dried MG.



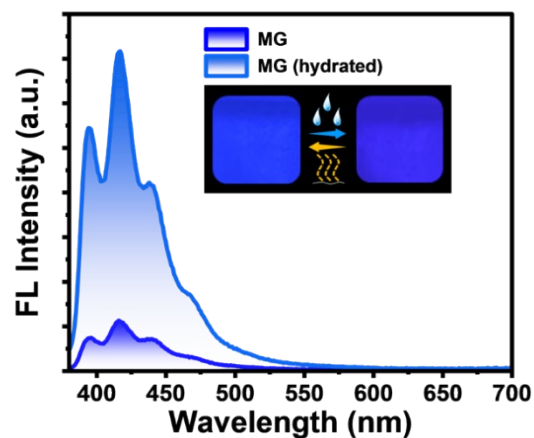
**Figure S4.** TEM images of MG.



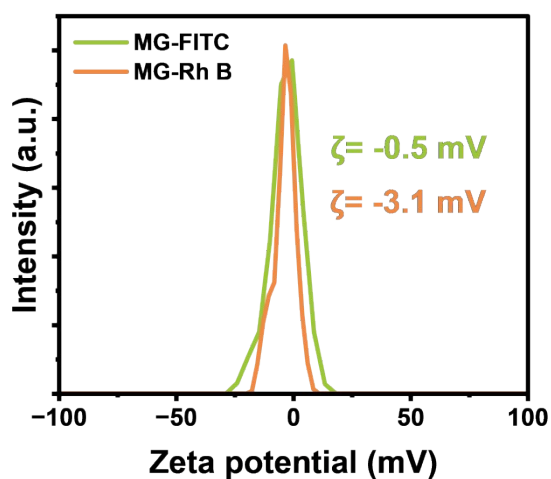
**Figure S5.** UV-Vis absorption spectra of MG before and after water treatment.



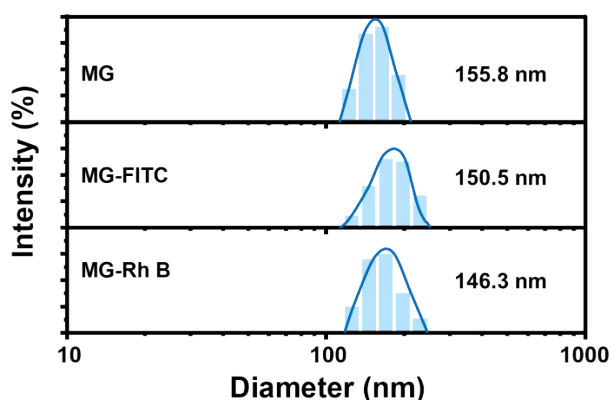
**Figure S6.** PL mapping spectra of MG powder at room temperature.



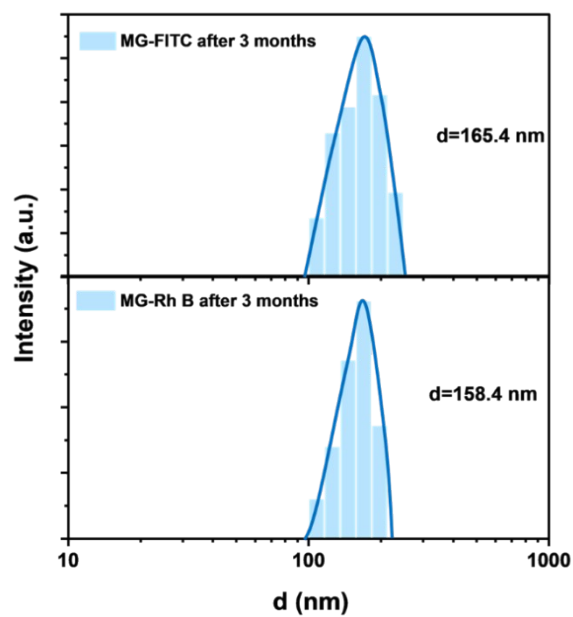
**Figure S7.** Fluorescence spectra of MG before and after water treatment at room temperature. Inset: Photographs of the corresponding MG taken before and after water treatment under UV lamp.



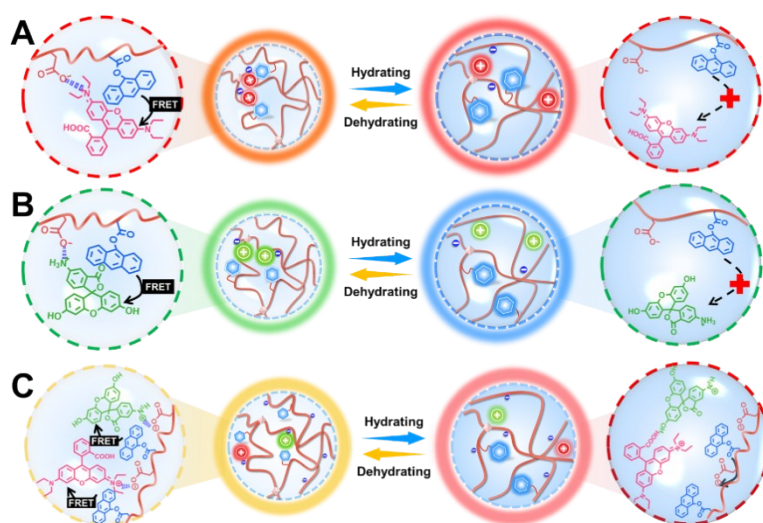
**Figure S8.** Zeta potential spectra of MG-derived particles binding cationic dyes in aqueous solution.



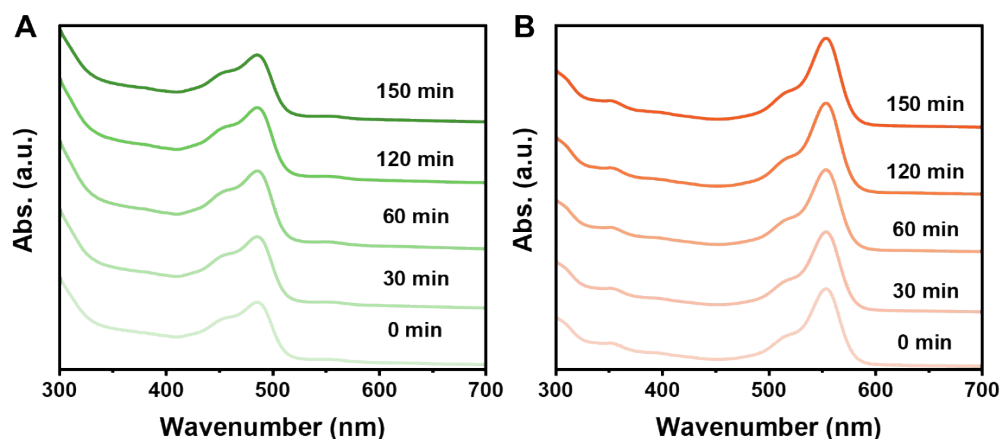
**Figure S9.** The particle size distribution diagram of MG and its derived particles binding cationic dye in aqueous solutions.



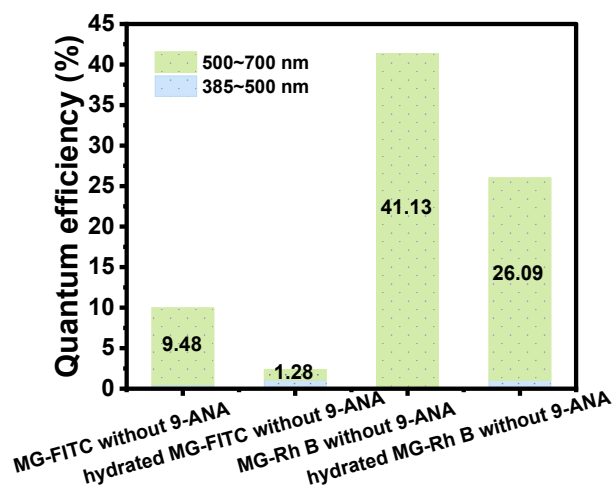
**Figure S10.** The particle size distribution diagram of MG-FITC and MG-Rh B after three months.



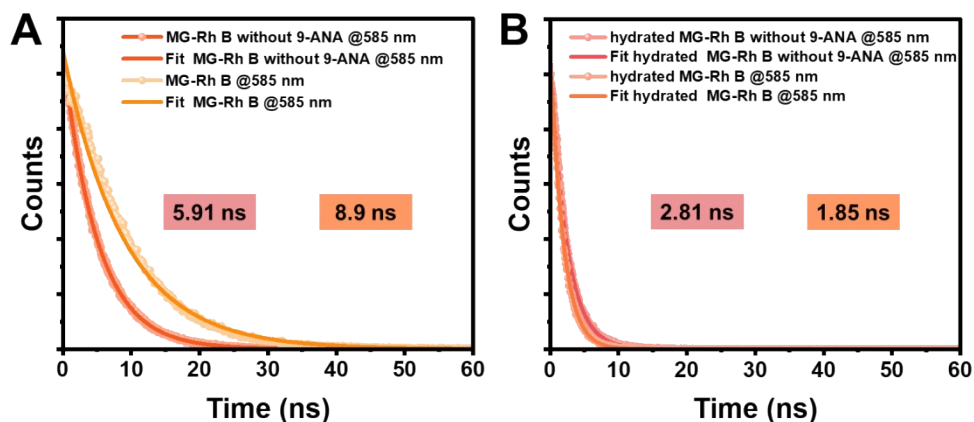
**Figure S11.** The mechanism of fluorescence color transition of the multicolor microgel system MG-FITC, MG-RHB, and MG-1F1R under hydration and dehydration conditions.



**Figure S12.** UV absorption spectra of MG-FITC A) and MG-Rh B B) before and after different durations of UV irradiation.

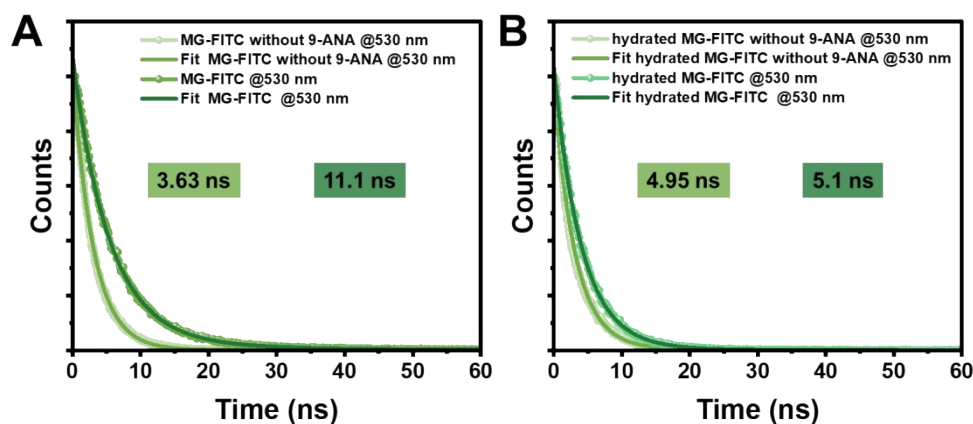


**Figure S13.** The quantum efficiency of MG-FITC without 9-ANA, MG-Rh B without 9-ANA before and after water treatment in the 385~500 nm range and 500~700 nm range, respectively.

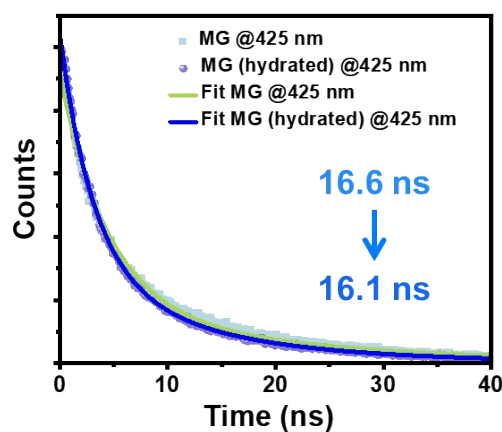


**Figure S14.** Time-resolved fluorescence decay curves and fitting curves of MG-Rh B with or without 9-ANA before and after water treatment.

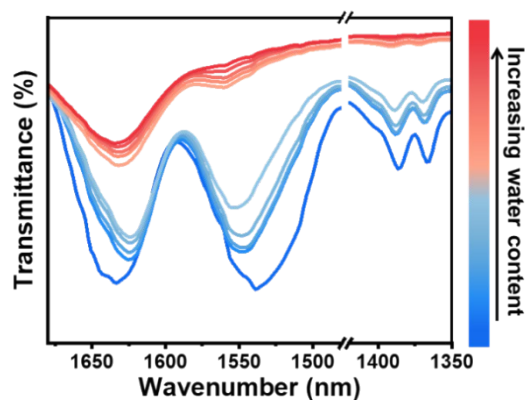




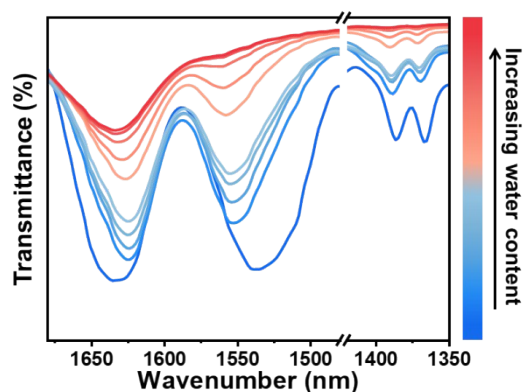
**Figure S15.** Time-resolved fluorescence decay curves and fitting curves of MG-FITC with or without 9-ANA before and after water treatment.



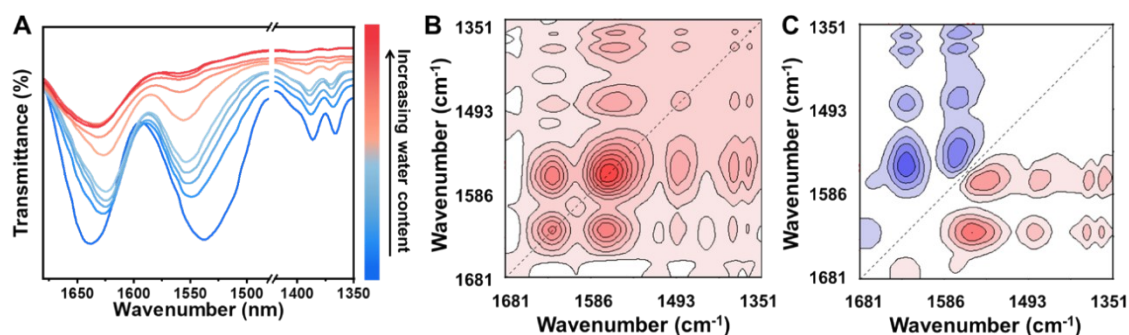
**Figure S16.** Time-resolved fluorescence decay curves and fitting curves of MG before and after water treatment.



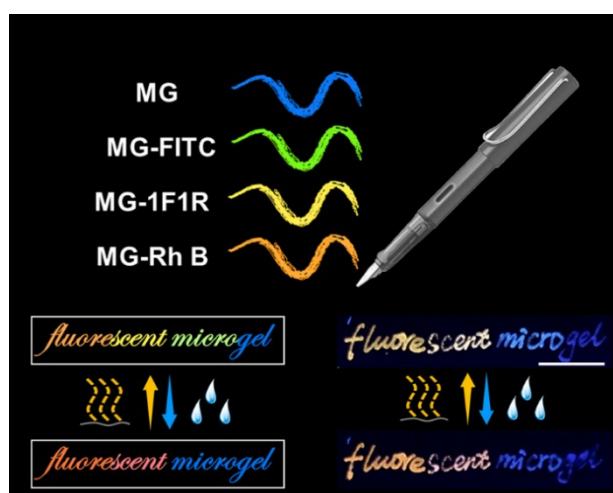
**Figure S17.** FTIR spectra of MG-FITC as water content increases.



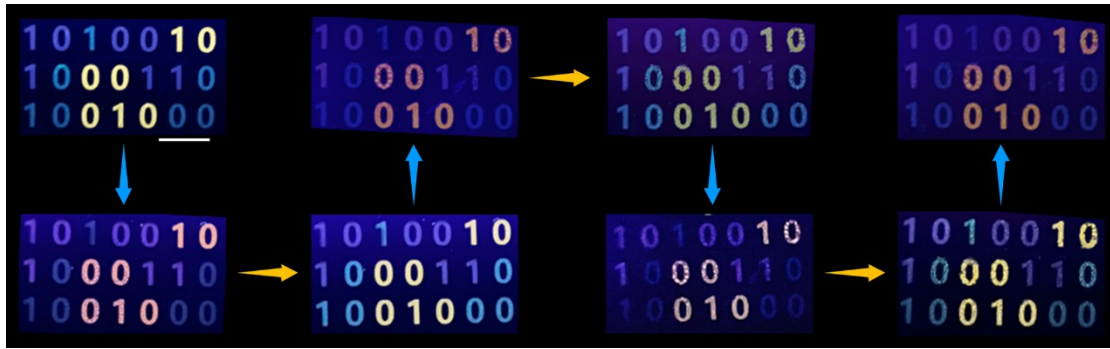
**Figure S18.** FTIR spectra of MG-Rh B as water content increases.



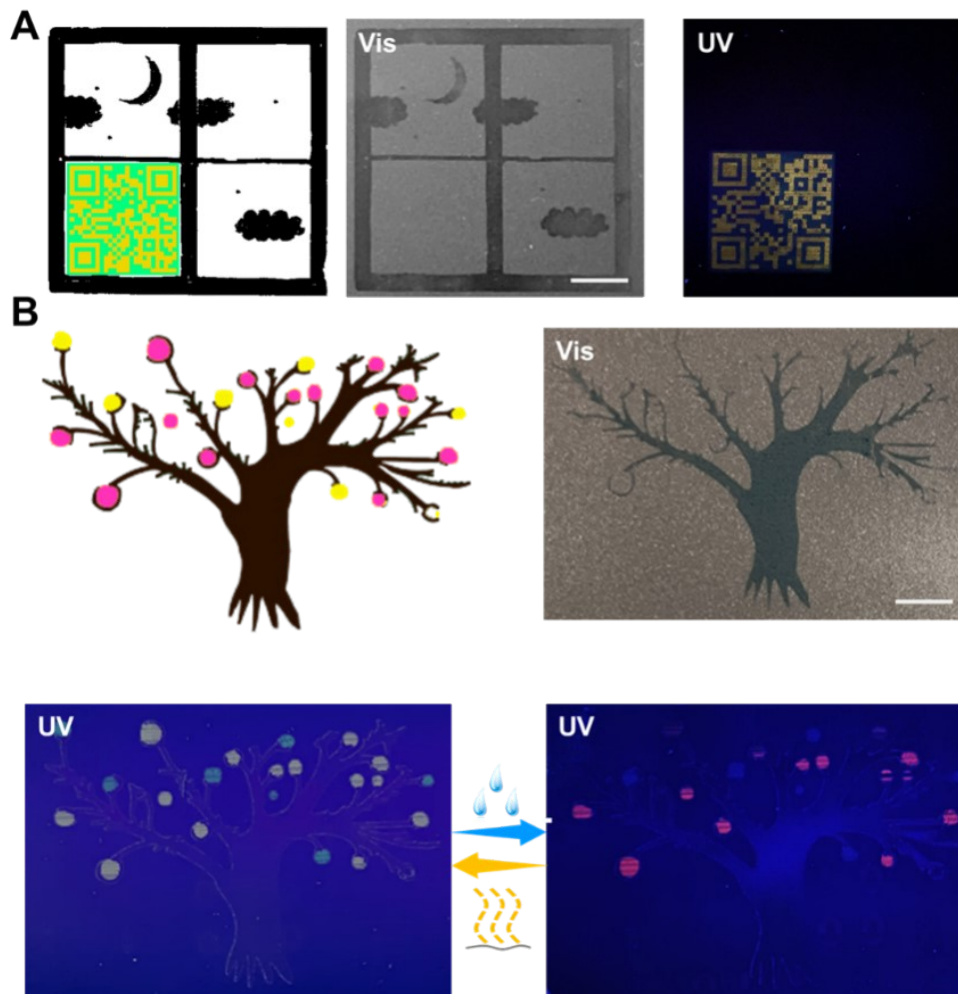
**Figure S19.** A) FTIR spectra of MG as water content increases. Two-dimensional COS synchronous spectra B) and asynchronous spectra C) generated from MG with different water content wherein red and blue colors are defined as positive and negative intensity, respectively.



**Figure S20.** A pen infused with fluorescent microgel inks (MG, MG-FITC, MG-1F1R, MG-Rh B) was used to write information “fluorescent microgel”, which can change color under the stimulation of water, scale bar :1 cm.



**Figure S21.** Photographs of binary codes during the process of cyclic encryption-decryption caused by water stimulation, scale bar :1 cm.



**Figure S22.** The schematic diagrams and photographs of the images printed by using a combination of commercial ink and fluorescent microgels, scale bar :1 cm.



**Figure S23.** The photograph taken under visible light.



**Figure S24.** Fluorescent images of the printed QR code before and after storage for one year (Scale bar: 1 cm).

#### Reference

- [1] S. Kwon, Y. Lee, Y. Jung, J. H. Kim, B. Baek, B. Lim, J. Lee, I. Kim, J. Lee, *Eur. J. Med. Chem.* **2018**, 148, 116.
- [2] H. Shan, D. Cai, X. Zhang, Q. Zhu, P. Qin, J. Baeyens, *Chem. Eng. J.* **2022**, 432, 134288.
- [3] K.-R. Wee, W.-S. Han, J.-E. Kim, A.-L. Kim, S. Kwon, S. O. Kang, *J. Mater. Chem.* **2011**, 21, 1115.