Electronic Supporting Information

Electrothermally Powered Synergistic Fluorescence-Colour/3D-Shape Changeable Polymer Gel Systems for Rewritable and Programmable Information Display

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Experimental Section

1. Material

Acrylic acid (AAc, 99%), Dimethyl sulfoxide (DMSO, 99.0%), ethyl alcohol (≥99.5%), acetic acid (99.0%), ethylene glycol (99.0%), 2,2-Dimethoxy-2-phenylacetephenenone (I651) and Zinc acetate dehydrate were obtained from Aladdin Chemistry Co. Ltd. N-(2-hydroxyethyl)acrylamide (HEAA, 98%), dithiosalicylic acid (DTSA, 98.0%), melamine (MA, 99.0%), and acetic acid (99.5%) were purchased from Shanghai Macklin Biochemical. Co. Ltd. The raw graphene, a slurry with a solid content of 5 wt%, was fabricated by Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, assisting with Ningbo Morsh Technology Co., Ltd. PDMS films (thickness of 100 μm, 150 μm and 200 μm) were purchased from Hangzhou Bald Advanced

Materials Co. Ltd. All materials were used without further purification.

2. Synthesis of CDs

CDs were synthesized according to the previously reported method[1]. Specifically, 0.2016 g MA and 0.544 g DTSA were dissolved in 40 mL acetic acid through ultrasonic treatment for 20 min, follow by being transferred into an 80 mL Teflon reactor to react at 180 °C for 10 h. After completing this reaction and cooling to room temperature, the obtained product was poured into 1 L boiling water and then filtrated for removing by-products. Finally, the collected solids were dried at 65 ^{o}C to get red CDs powders.

3. Synthesis of the PAHCDs gel

AAC (monomer, 2.1 g), HEAA (monomer, 0.9 g), I651 (photoinitiator, 30 mg), Zinc acetate dihydrate aqueous solution (1 mol/L, 200 μL) and ethylene glycol (1 mL) were fully dissolved. Then, 1 mL of the obtained solution was mixed with 5 mg (0.17 wt%), 10 mg (0.33%) or 15 mg (0.50 wt%) of CDs dissolved in 100 μL DMSO. The precursor solution was transferred into the molds with two quartz glass plates and a 0.5 mm thick silicon plate, followed by free radical copolymerization under 365 nm UV light (8 W) for 1 h to prepare the PAHCDs gels.

4. Synthesis of the PAHCDs gel actuator

HEFC actuator was prepared by interfacial assembly of PAHCDs gel layer and soft Graphene/PDMS electrothermal film. Firstly, the bonding strategy between PAHCDs gel and PDMS film was inspired by the previously published interfacial interpenetration method[2]. Typically, the PDMS film was firstly treated by plasma and then immersed into a mixed solution (V_{H2O}: V_{H2O2}: V_{HCl}, 5 :1 :1) for 3 h and further another mixed solution (V_{Water}: $V_{Ethanol}$, 1:1) containing 2 wt% 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) for 12 h. Then, the chemically modified PDMS film and a 0.2-mm thick silicon rubber were placed on the quartz glass in sequence. The precursor solution mentioned above was added into the mold with another quartz glass, followed by photopolymerization under 365 nm UV light for 1 h. During this polymerization process, the new formed PAHCDs gel polymer chains were interpenetrated with PDMS polymer chains, guaranteeing the firm adhesion of two layers. After that, the obtained PAHCDs gel/PDMS laminated film was conformally placed on a glass substrate. Meanwhile, the graphene film was prepared according to previously reported work. Specifically, the graphene flakes were dispersed in anhydrous ethanol through ultrasonication for 6 h to acquire a 1.5 mg mL^{-1} dispersion. Then, 30 mL of the as-prepared dispersion was sprayed onto the standing water surface by a spray bottle to form a uniform and thin graphene film on the water surface. Afterward, microporous sponges were inserted into water along the wall of the container to unbalance the surface tension, leading to the formation of a more compactly assembled graphene film. Finally, the obtained compact graphene film was transferred onto the surface of PDMS side of PAHCDs gel/PDMS laminated film to get HEFC actuator.

5. Characterization

The digital photos of fluorescence PAHCDs gel and corresponding colour changeable actuator were recorded under a UV lamp (ZF-5, 8 W, 365 nm) using a smartphone (IPHONE 13 pro). Temperature-dependent FT-IR spectra were performance using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a temperature control module. Steady-state fluorescence spectra and fluorescence decay curves were measured by a Hitachi F-4600 fluorescence spectrofluorometer equipped with a 150 W xenon lamp. The micro-morphology was characterized by a Hitachi S-4800 field-mission scanning electron microscope with a 5.0-KV accelerating voltage. The glass transition temperature of the dried polymer gel was obtained by DSC (DSC3, METTLER TOLEDO, Switzerland). The sample was heated from -100 to 180 °C at a rate of 10 °C/min under a nitrogen atmosphere.

Supplementary Figures:

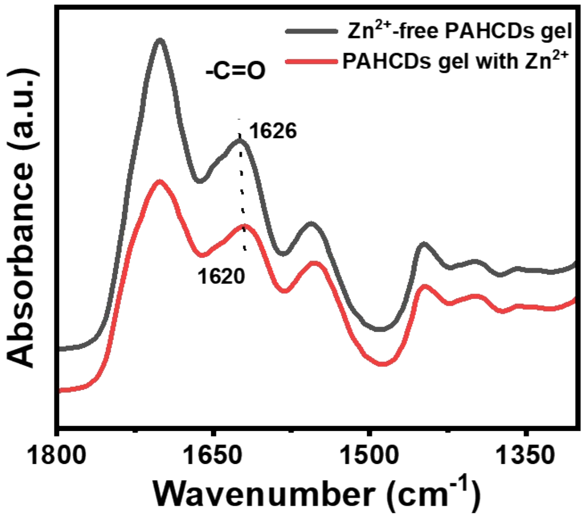

Figure S1. FT-IR spectra of PAHCDs-0.50 gel containing Zn^{2+} and Zn^{2+}-free PAHCDs-0.50 gel.

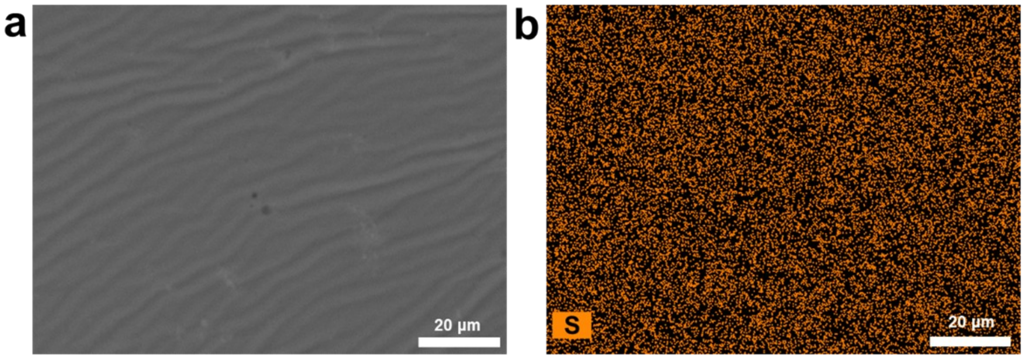

Figure S2. (a) SEM image of the PAHCDs-0.50 gel and (b) the EDS mapping of S element.

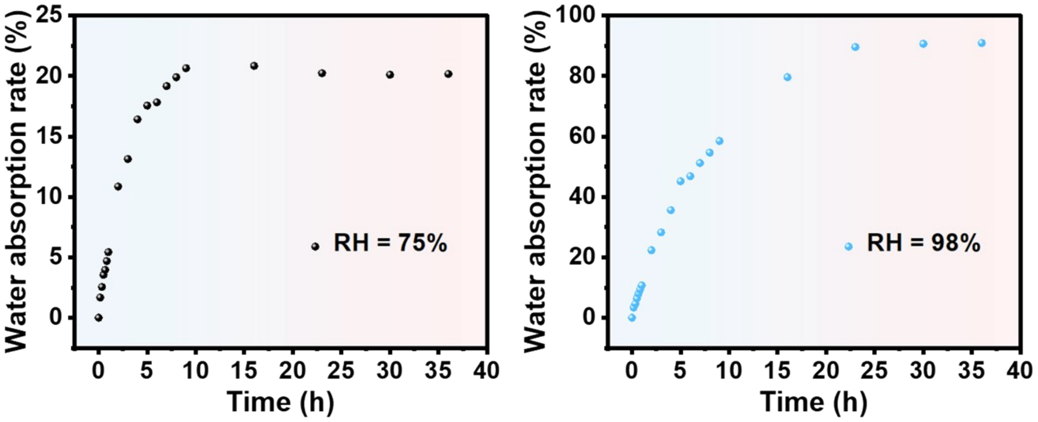

Figure S3. The time-dependent water absorption rate of the PAHCDs-0.50 gel in both normal (75% RH) and extreme (98% RH) conditions.

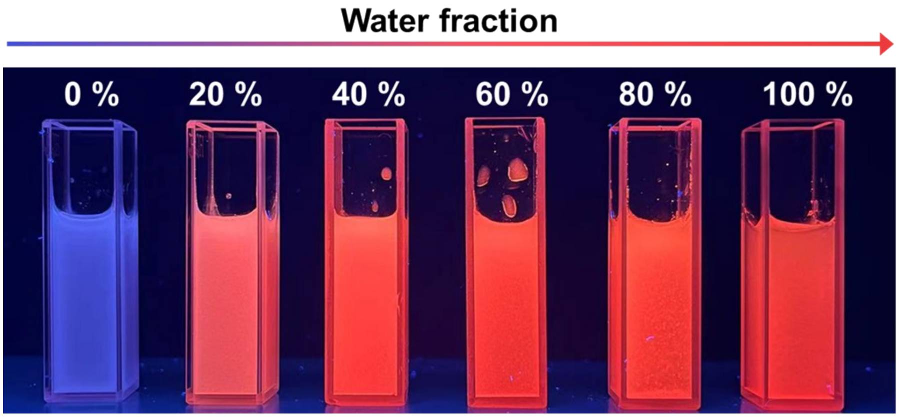

Figure S4. Photos of the CDs with increasing water fraction from 0% to 100% in glycol/water mixed solvent. Photos taken under 365 nm UV light.

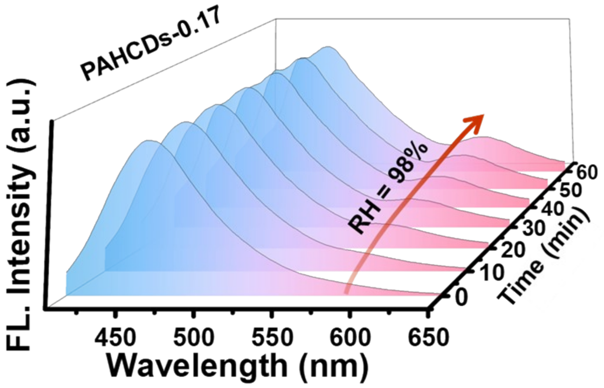

Figure S5. The fluorescence spectra of PAHCDs-0.17 gel that were recorded at different time intervals after being imposed under RH of 98% (λ_{ex} = 365 nm).

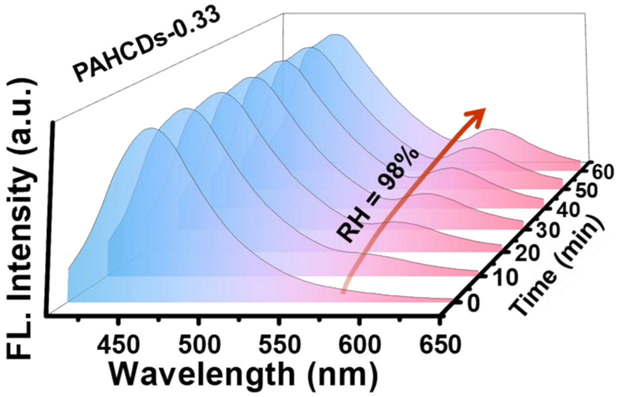

Figure S6. The fluorescence spectra of PAHCDs-0.33 gel that were recorded at different time intervals after being imposed under RH of 98% (λ_{ex} = 365 nm).

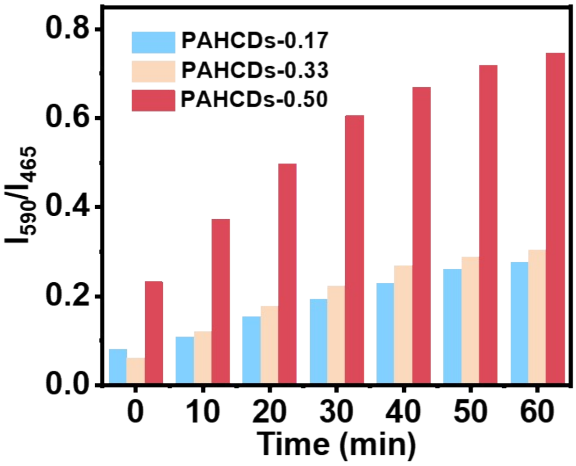

Figure S7. Fluorescence intensity ratio (I_{590}/I_{465}) of PAHCDs gels with different dosage of CDs as the function of the exposure time under 98% RH (λ_{ex} = 365 nm).

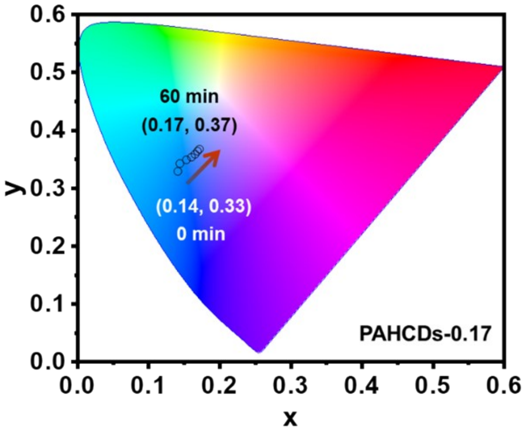

Figure S8. Fluorescence color change of PAHCDs-0.17 gel before and after being under RH of 98% for 60 min at a CIE (1978) chromaticity diagram.

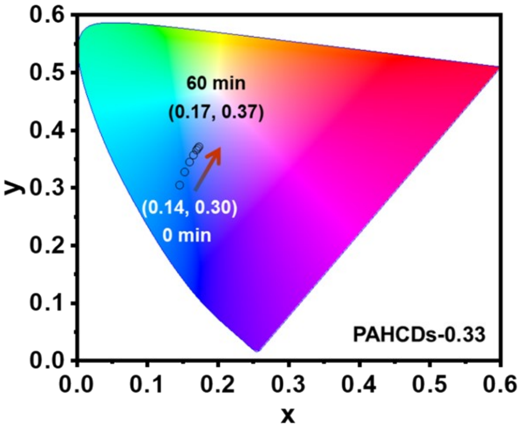

Figure S9. Fluorescence color change of PAHCD-0.33 gel before and after being under RH of 98% for 60 min at a CIE (1978) chromaticity diagram.

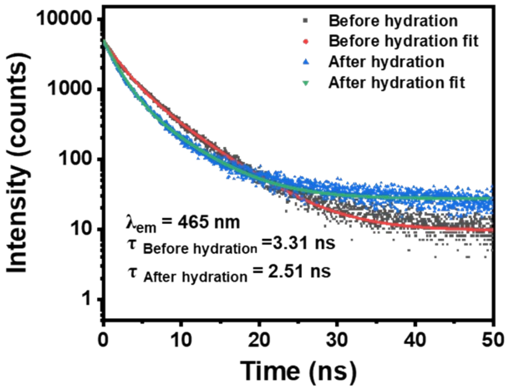

Figure S10. Fluorescence decay curves of PAHCDs-0.50 gels before and after being hydrated under the excitation wavelength of 320 nm

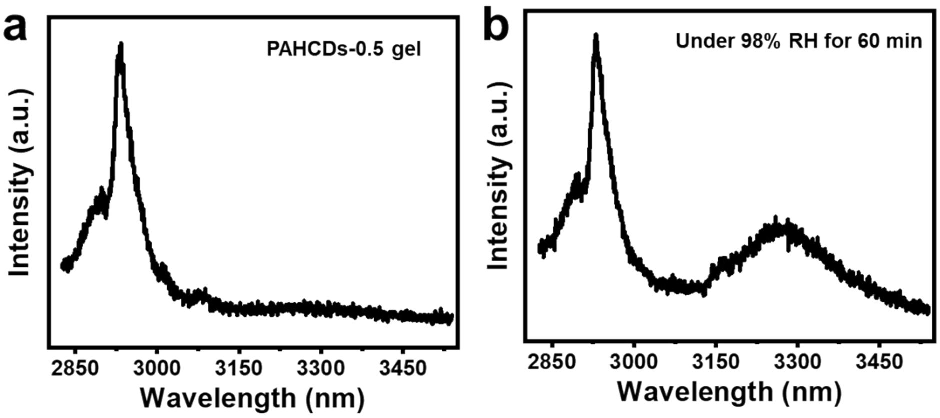

Figure S11. Raman spectra of PAHCDs-0.50 gel before (a) and after (b) being under RH of 98% for 60 min.

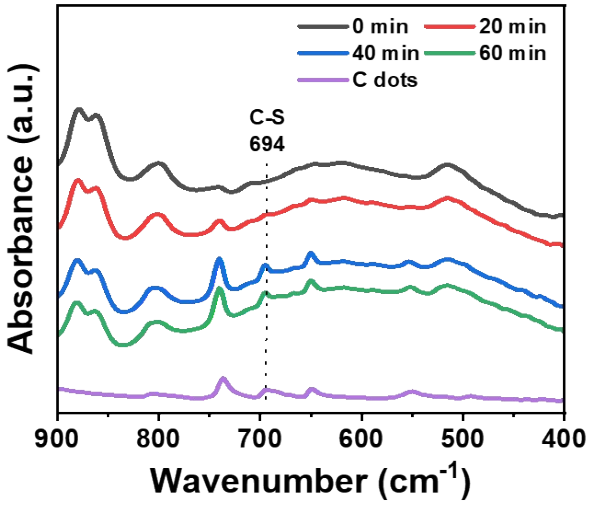

Figure S12. FT-IR spectra of CDs and PAHCDs-0.50 gel that was exposed to 98% RH for different time.

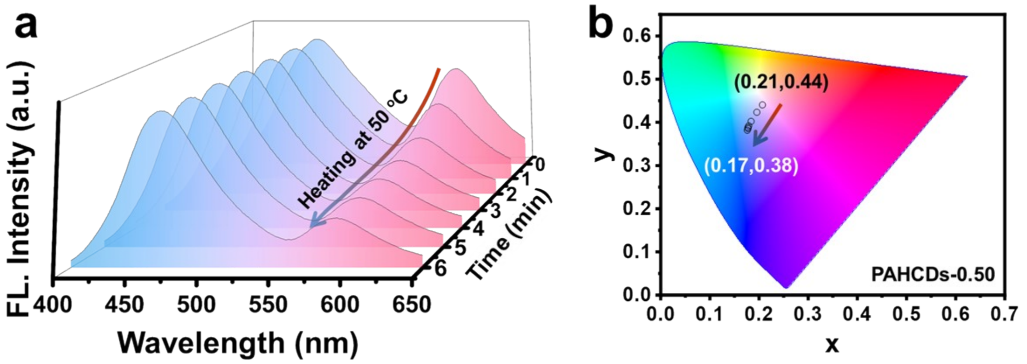

Figure S13. The fluorescence spectra (a) and corresponding CIE (1978) chromaticity diagram of PAHCDs-0.50 gel that was recorded at different time intervals after being heated at 50 °C.

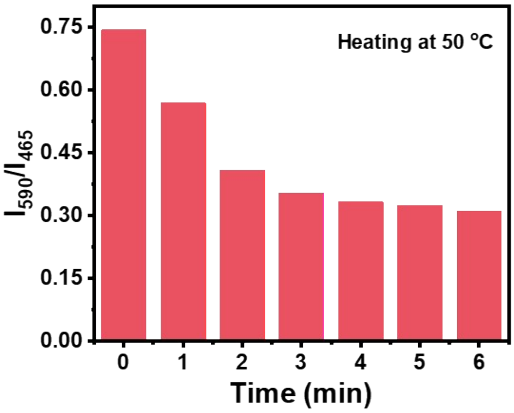

Figure S14. Fluorescence intensity ratio (I_{590}/I_{465}) of PAHCDs-0.50 gel as the function of the heating time at 50 °C (λ_{ex} = 365 nm).

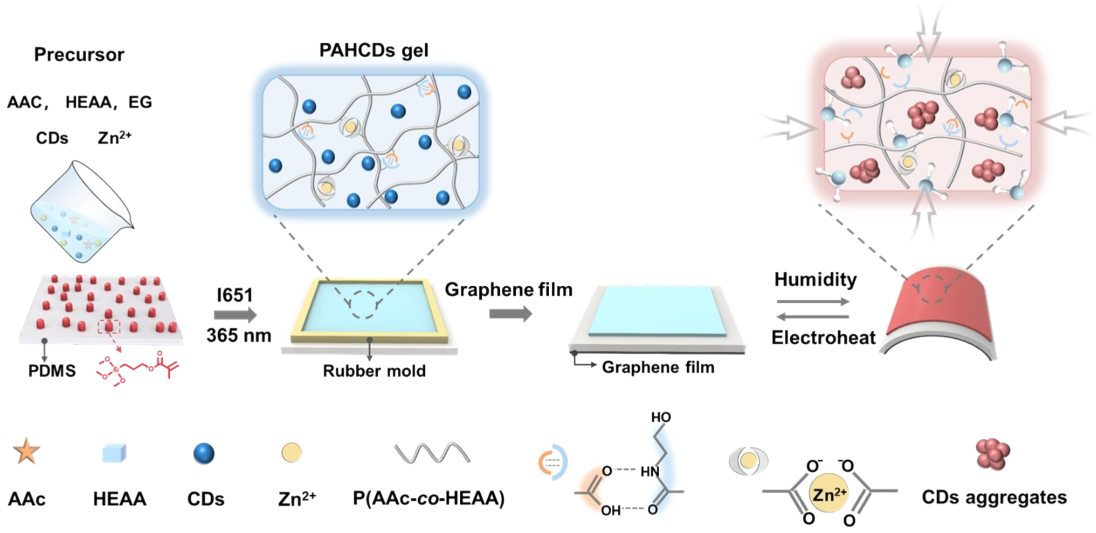

Figure S15. Illustration showing the preparation process of HEFC actuator.

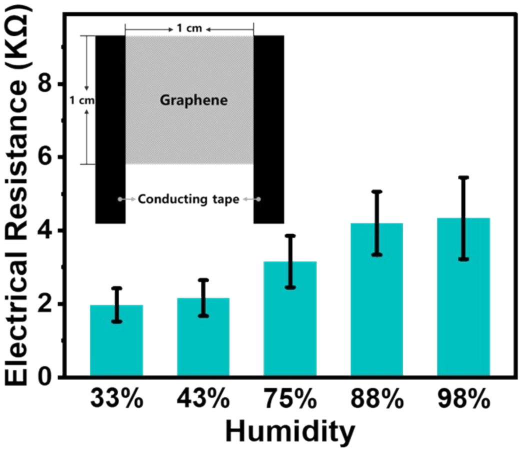

Figure S16. The electrical resistance of graphene film under different environmental humidity.

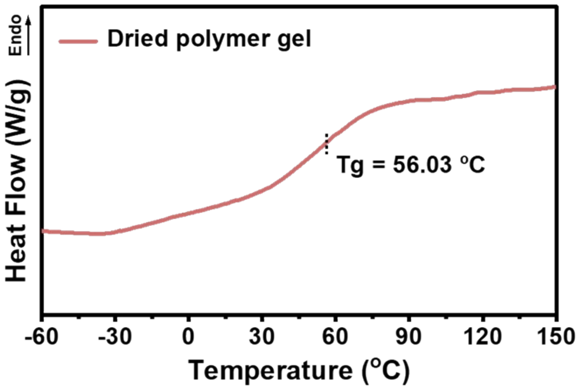

Figure S17. Differential scanning calorimetry (DSC) curve of dried polymer gel.

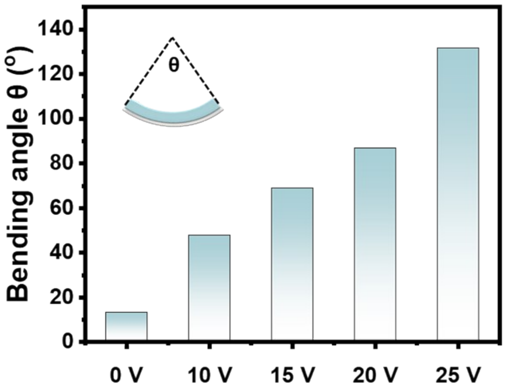

Figure S18. The bending angel of HEFC actuator under different voltage.

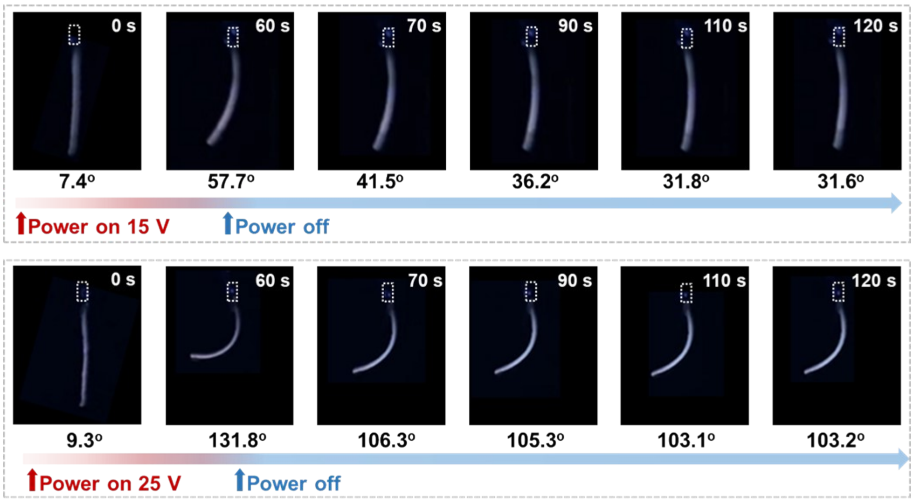

Figure S19. Fluorescent photos showing the actuation behavior of HEFC actuator after 15 V and 25 V voltage were turned off, respectively.

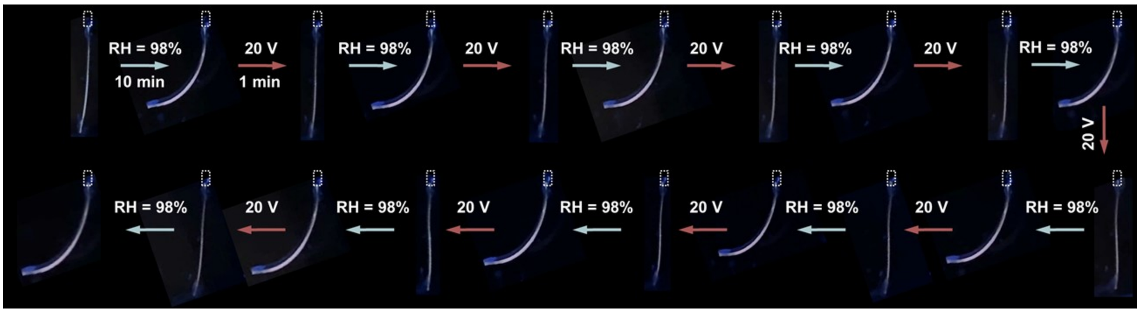

Figure S18. Fluorescent photos showing the humidity/electroheat-triggered reversible actuation behavior of HEFC actuator.

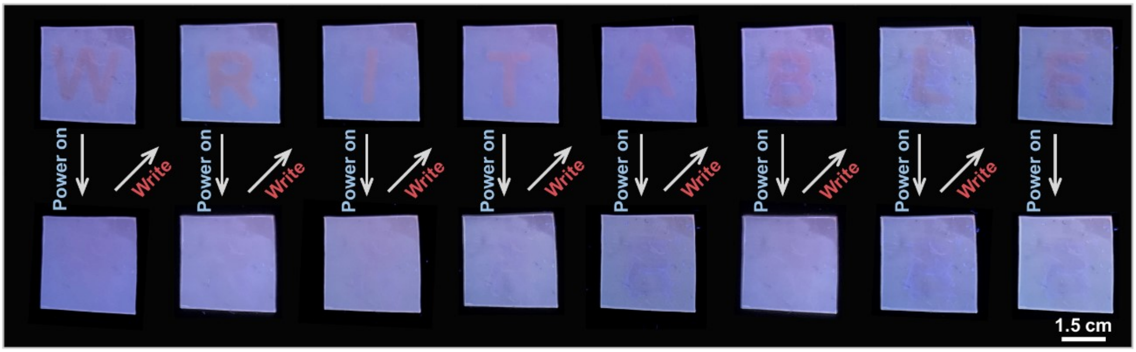

Figure S20. Fluorescent photos showing the writing-erasing-rewriting ability of our rewritable system. These letters were written by water ink and erased by applying 15 V voltage. All photos were taken under a 365 nm UV lamp.

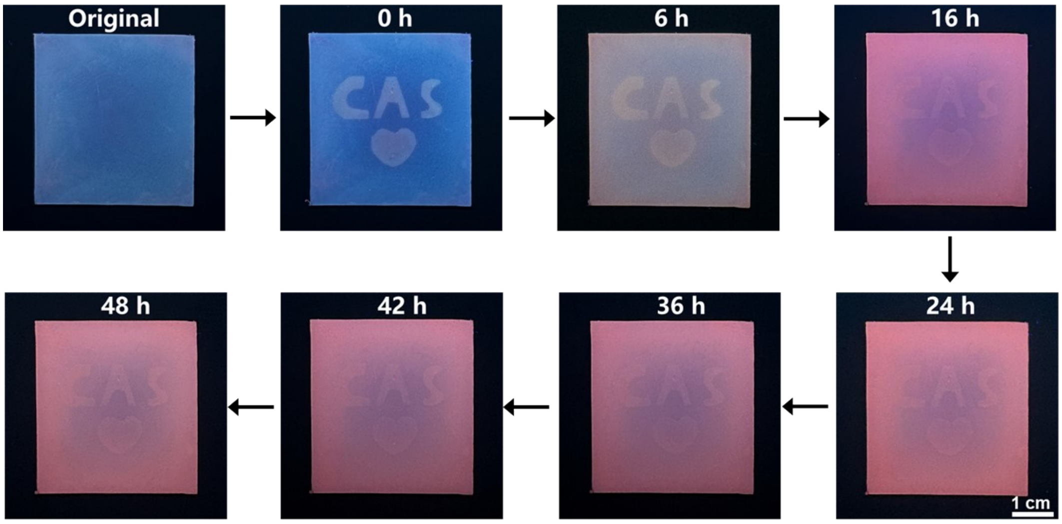

Figure S21. Fluorescent photos showing the information duration time of the water-written "CAS" letters and heart-shaped figure at ambient conditions (26 °C, 60~70% RH).

Reference

[1] S. Wu, H. Shi, W. Lu, S. Wei, H. Shang, H. Liu, M. Si, X. Le, G. Yin, P. Theato, T. Chen, *Angew. Chem. Int. Ed.* 2021, **60**, 21890.

[2] H. Lin, S. Ma, B. Yu, X. Pei, M. Cai, Z. Zheng, F. Zhou, W. Liu, *Chem. Mater.* 2019, **31**, 9504.