Supplementary Information

Lanthanide-polyoxometalate-based self-erasing luminescent hydrogels with time-dependent and resilient properties for advanced information encryption

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Experimental section

Materials: Sodium tungstate dihydrate (≥ 99.5%), dysprosium nitrate pentahydrate (99.99%), acetic acid (99%), acrylamide (AAm, 99%), *N,N'*-methylenebis (acrylamide) (MBA, 99%), [2-(methacryloyloxy)ethyl] trimethyl ammonium chloride solution (DMC, 75%), potassium persulfate (KPS, 99.99%), tetramethylethylenediamine (TMEDA, 99%), urease (≥ 45 units/mg), and urea (≥ 99.5%) were provided by Shanghai Aladdin Reagent Co., Ltd.

Synthesis and characterization of DyW_{10}: $Na_2WO_4 \cdot 2H_2O$ (4.12 g) was dissolved in 10 mL deionized water and the solution was heated to 90 °C and adjusted the pH to about 6.7 using acetic acid. $Dy(NO_3)_3 \cdot 5H_2O$ (0.54 g) was dissolved in 1 mL deionized water. Then the $Dy(NO_3)_3$ solution was added into the Na_2WO_4 solution slowly under stirring at 90 °C. The crystals were acquired after cooling the solution to room temperature and were filtered and dried in the air.[1] As depicted in Fig. 1a, four characteristic peaks of DyW_{10} appeared at wavenumbers of 935 cm^{-1} was attributed to ν ($W{=}O_d$), 848 cm^{-1} was attributed to ν ($W\text{-}O_b\text{-}W$), 794 cm^{-1} and 709 cm^{-1} were attributed to ν ($W\text{-}O_c\text{-}W$), respectively.[2,3] The thermogravimetry analysis (TGA) showed that the weight loss was 6.4% when heated to ~ 338 °C, which was attributed to the loss of 11 water molecules, as shown in Fig. S1. The above results suggested that lanthanide-polyoxometalate $Na_9DyW_{10}O_{36} \cdot 11H_2O$ has been synthesized successfully.

Measurements: Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were tested by a PerkinElmer Frontier. The TGA curve was determined by a NETZSCH STA2500 analyzer. The storage modulus G' and loss modulus G" were measured by a HAAKE MARS60 rheometer. Scanning electron microscopy (SEM) image was obtained on a JEOL JSM-5600LV instrument. Optical transmittance spectra were performed on a PerkinElmer LAMBDA 750 spectrophotometer and the thickness of hydrogels were 2 mm. The tensile data was obtained from a ZQ-990LB device. Luminescence spectra were collected on a PerkinElmer FL6500 spectrometer. Luminescence lifetimes were carried out on a FLS 920 Edinburgh spectrophotometer. The number of water molecules q coordinated at the center of dysprosium was calculated according to the following equation:

$$q = 2.61 \times 10^{-2} \left(1/\tau H_2O - 1/\tau D_2O\right) \quad (1)$$

where τ are the reciprocal experimental lifetimes in H_2O and D_2O solutions in ms, respectively.[4]

Rheological test of hydrogel. The cylindrical hydrogel with 30 mm in diameter and 2 mm in height was applied for rheological test using a parallel plate. The storage modulus G' and loss modulus G" were measured at a constant strain of 1 % and the frequency range of 0.1 - 100 Hz.

Mechanical tests of hydrogels. The dumbbell hydrogels were applied for tensile tests, with a width of 13 mm, a thickness of 2 mm, the gauge length of 45 mm, and the tensile rate was 100 mm/min. Moreover, the similar method was applied for mechanical tests of the hydrogels after treatment with HCl-urea mixed solution for 1.5 min immediately.

Water loss tests of hydrogels. The water retention was determined by measuring the weight of hydrogel at different conditions. The water loss ratio of the hydrogel was calculated using the following equation:

$$\text{Water loss (\%)} = (W_0 - W_t)/W_0 \quad (2)$$

where W_0 is the mass of original hydrogel, and W_t is the mass of hydrogel at some time.[5]

The different humidity environment (68% and 98% relative humidity) were obtained by using saturated aqueous solutions of $CuCl_2$ and distilled water.[6]

Puncture resistance test of hydrogel. The square hydrogel (32 mm × 32 mm × 2 mm) was applied for puncture resistance test by using a sharp steel thorn.

Cutting resistance test of hydrogel. The semi-cylindrical hydrogel (8 mm in diameter and 5 mm in height) was applied for cutting resistance test using a knife and the cutting speed was 2 mm/s.

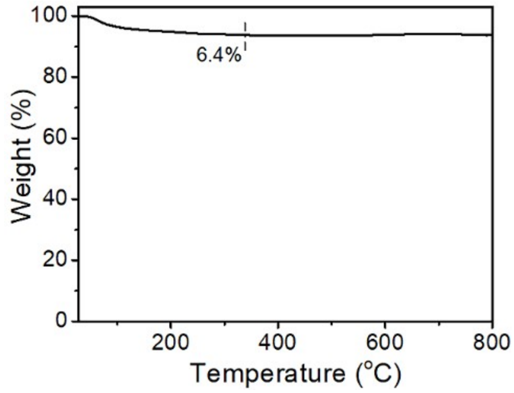

Fig. S1 TGA curve of DyW_{10}.

Table S1 Recipes of PAAm/DyW_{10}/urease hydrogels with different contents of AAm, DMC, DyW_{10} and urease.

Samples	H_2O (mL)	AAm (mmol)	MBA (mmol)	DMC (mmol)	KPS (mmol)	DyW_{10} (mmol)	urease (mg mL^{-1})	TMEDA (mmol)
$PAAm_8/(DyW_{10})_{0.02}/urease_5$	6	8	0.012	0.180	0.06	0.020	5	0.06
$PAAm_{12}/(DyW_{10})_{0.02}/urease_5$	6	12	0.012	0.180	0.06	0.020	5	0.06
$PAAm_{16}/(DyW_{10})_{0.02}/urease_5$	6	16	0.012	0.180	0.06	0.020	5	0.06
$PAAm_{16}/(DyW_{10})_{0.01}/urease_5$	6	16	0.012	0.090	0.06	0.010	5	0.06
$PAAm_{16}/(DyW_{10})_{0.005}/urease_5$	6	16	0.012	0.045	0.06	0.005	5	0.06
$PAAm_{16}/(DyW_{10})_{0.02}/urease_3$	6	16	0.012	0.180	0.06	0.020	3	0.06
$PAAm_{16}/(DyW_{10})_{0.02}/urease_1$	6	16	0.012	0.180	0.06	0.020	1	0.06
$PAAm_{16}/urease_5$	6	16	0.012	0.180	0.06	0	5	0.06
$PAAm_{16}/(DyW_{10})_{0.02}$	6	16	0.012	0.180	0.06	0.020	0	0.06

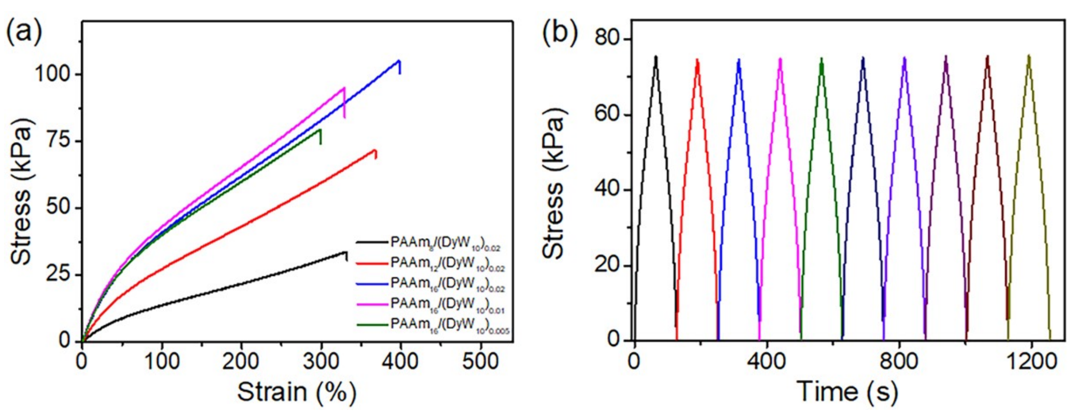

Fig. S2 (a) The representative tensile stress-strain curves of PAAm/DyW_{10}/$urease_5$ hydrogels with different contents of AAm and DyW_{10}, respectively. (b) Antifatigue test curve of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel.

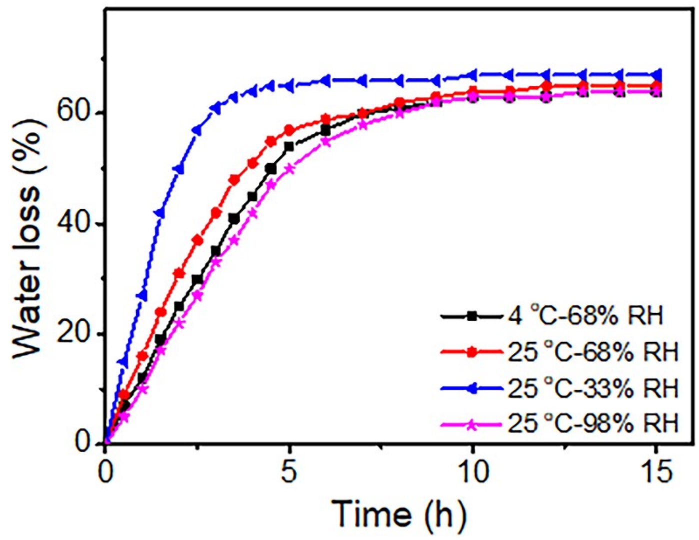

Fig. S3 Water loss ratio of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different temperatures and relative humidity.

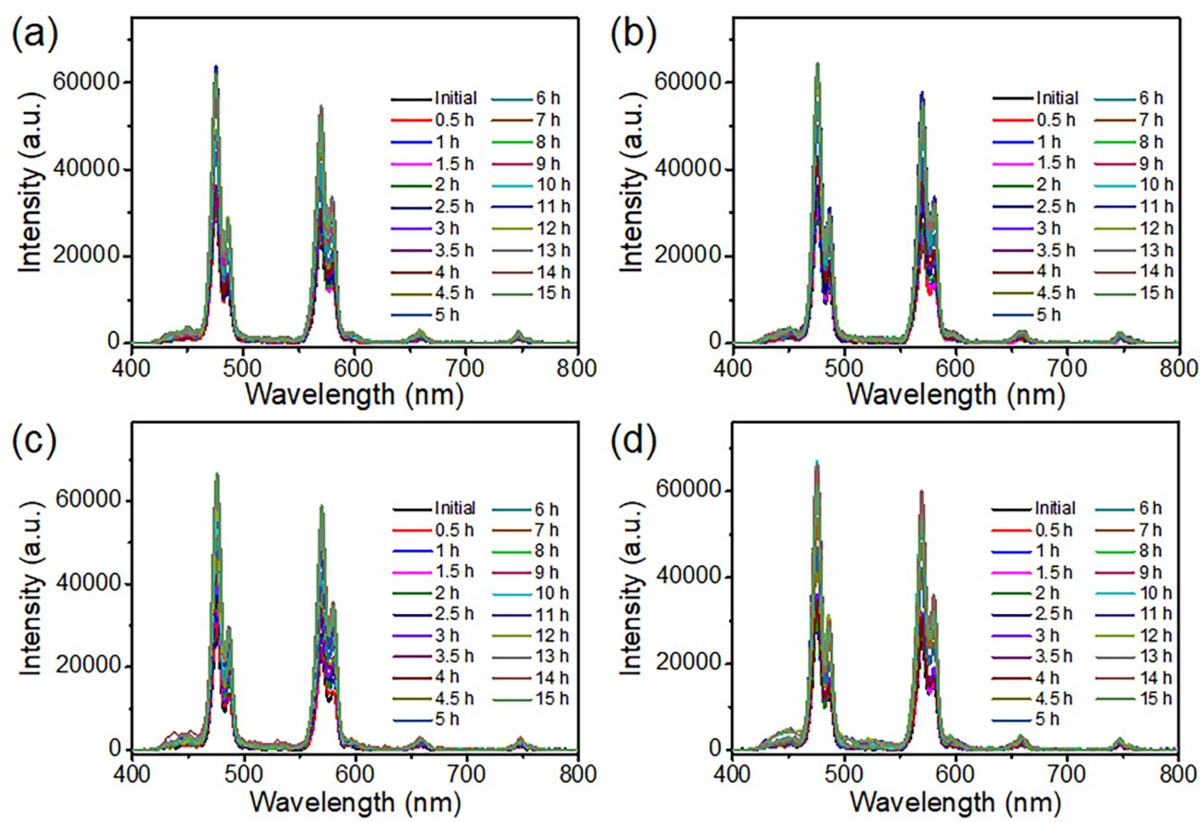

Fig. S4 Time-dependent emission spectra of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different temperatures and relative humidity (λ_{ex} = 286 nm). (a) 4 °C, 68% RH. (b) 25 °C, 68% RH. (c) Ambient condition: 25 °C, 33% RH. (d) 25 °C, 98% RH.

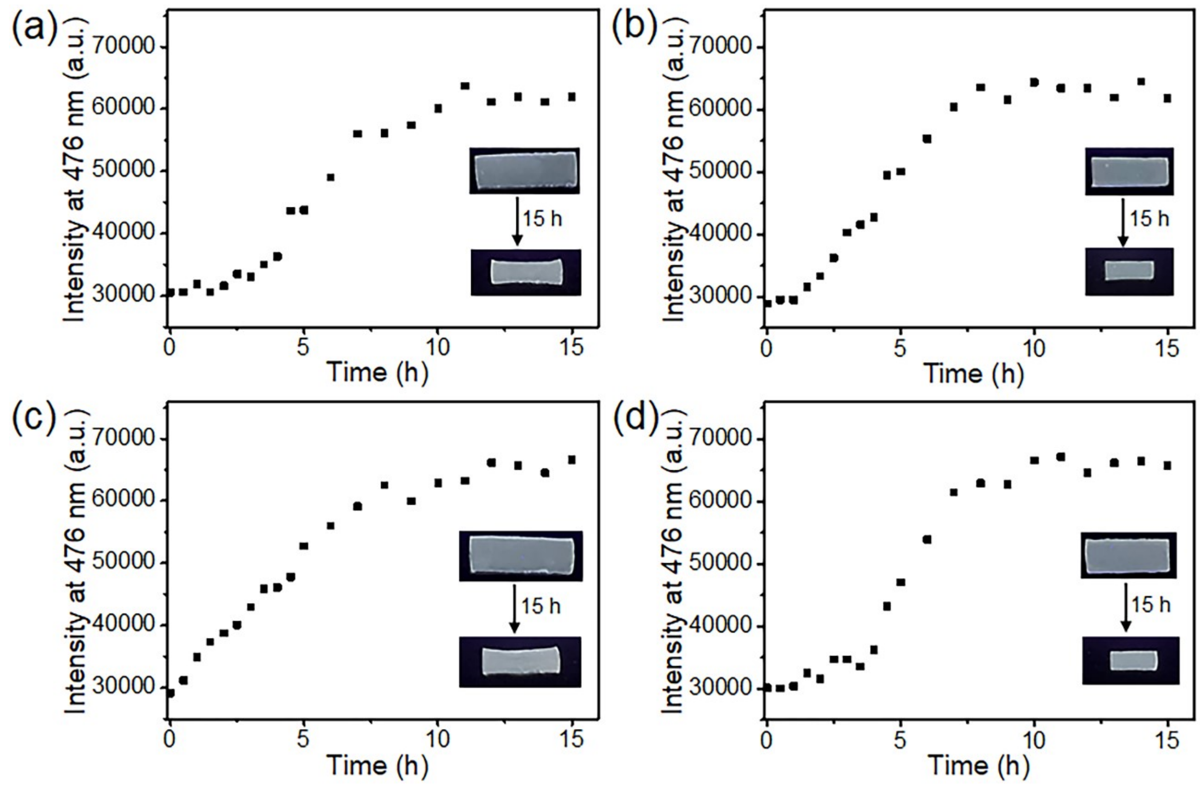

Fig. S5 Time-dependent luminescence intensity and photographs of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different temperatures and relative humidity. (a) 4 °C, 68% RH. (b) 25 °C, 68% RH. (c) Ambient condition: 25 °C, 33% RH. (d) 25 °C, 98% RH.

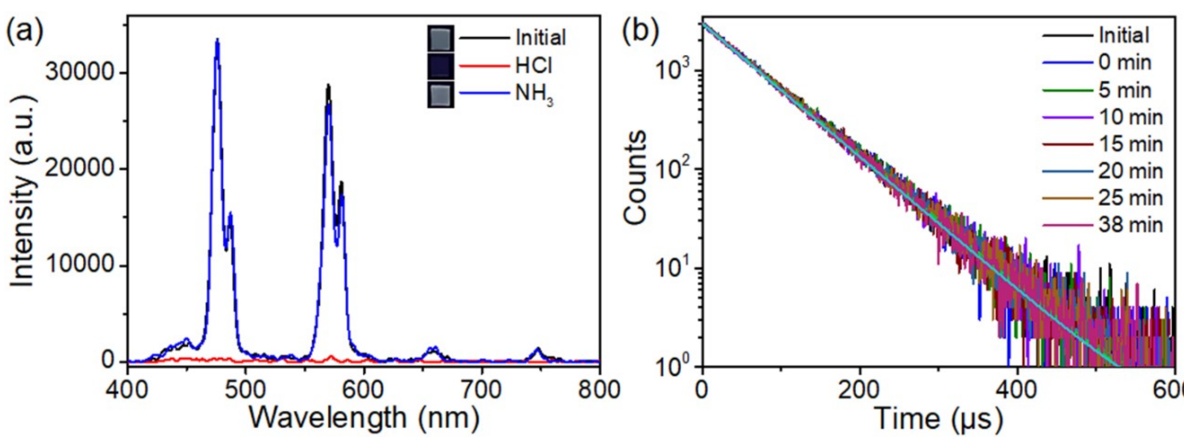

Fig. S6 (a) Emission spectra of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel treated with HCl aqueous solution and NH_3 aqueous solution, and photographs were taken under UV light at 254 nm. (b) Time-dependent luminescence decay curves of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel (λ_{ex} = 286 nm, λ_{em} = 476 nm) after treatment with the HCl-urea mixed solution (c_{HCl}: 0.02 M and c_{urea}: 15 M).

Table S2 Summary of time-dependent luminescence lifetimes of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel after treatment with the HCl-urea mixed solution (c_{HCl}: 0.02 M, c_{urea}: 15 M).

	Initial	0 min	5 min	10 min	15 min	20 min	25 min	38 min
τ (μs)	66.27	65.64	66.60	65.67	64.92	65.48	65.47	64.36

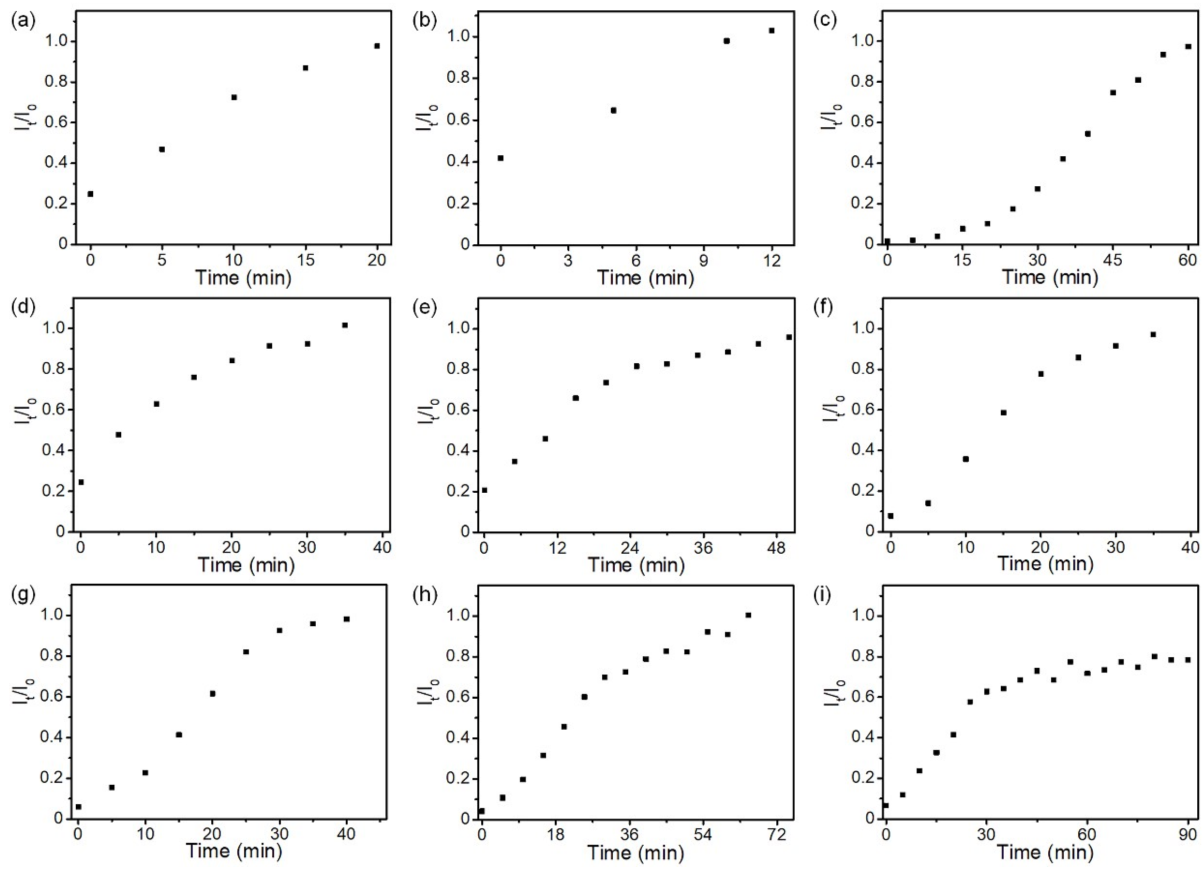

Fig. S7 Time-dependent luminescence intensity ratio at 476 nm of the hydrogels with different urease concentrations after treatment with different concentrations of HCl-urea mixed solution (I_0: initial luminescence intensity, I_t: luminescence intensity at different time). (a) c_{HCl}: 0.02 M, c_{urea}: 15 M, and urease: 5 mg mL^{-1}. (b) c_{HCl}: 0.01 M, c_{urea}: 15 M, and urease: 5 mg mL^{-1}. (c) c_{HCl}: 0.1 M, c_{urea}: 15 M, and urease: 5 mg mL^{-1}. (d) c_{HCl}: 0.02 M, c_{urea}: 15 M, and urease: 3 mg mL^{-1}. (e) c_{HCl}: 0.02 M, c_{urea}: 15 M, and urease: 1 mg mL^{-1}. (f) c_{HCl}: 0.02 M, c_{urea}: 1 M, and urease: 5 mg mL^{-1}. (g) c_{HCl}: 0.02 M, c_{urea}: 0.1 M, and urease: 5 mg mL^{-1}. (h) c_{HCl}: 0.02 M, c_{urea}: 0.05 M, and urease: 5 mg mL^{-1}. (i) c_{HCl}: 0.02 M, c_{urea}: 0.01 M, and urease: 5 mg mL^{-1}.

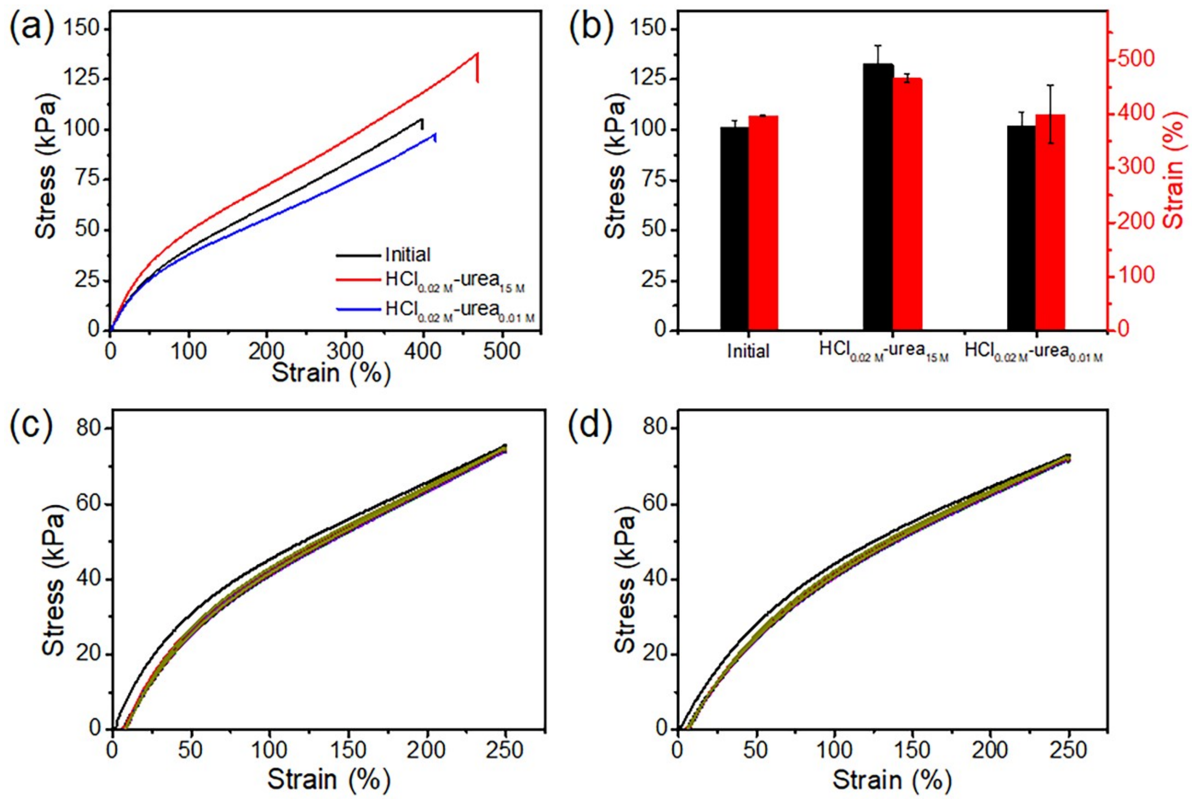

Fig. S8 (a) The representative tensile stress-strain curves of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel after treatment with different concentrations of HCl-urea mixed solution. (b) The maximum stress and maximum strain of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel after treatment with different concentrations of HCl-urea mixed solution. Cyclic tensile curves of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel after treatment with different concentrations of HCl-urea mixed solution. (c) c_{HCl}: 0.02 M and c_{urea}: 15 M. (d) c_{HCl}: 0.02 M and c_{urea}: 0.01 M.

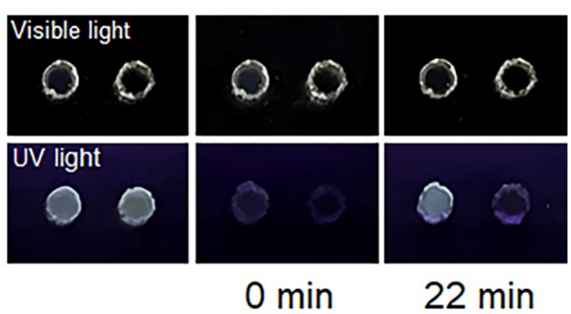

Fig. S9 The real information can only be recognized at a specific time with the help of a Morse code.

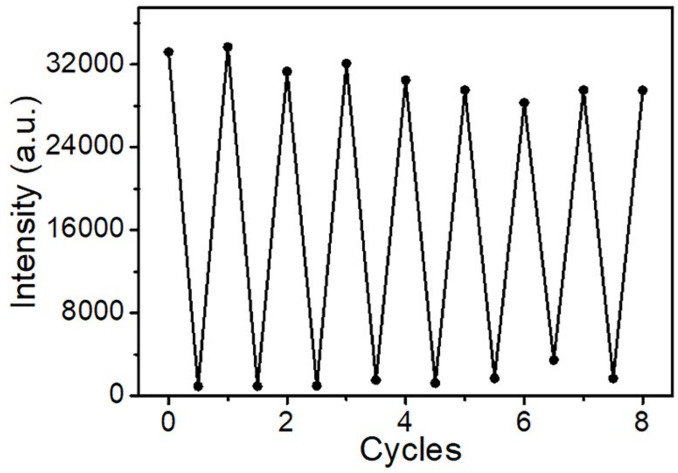

Fig. S10 Cyclic luminescence switching process of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel (c_{HCl}: 0.02 M and c_{urea}: 0.05 M).

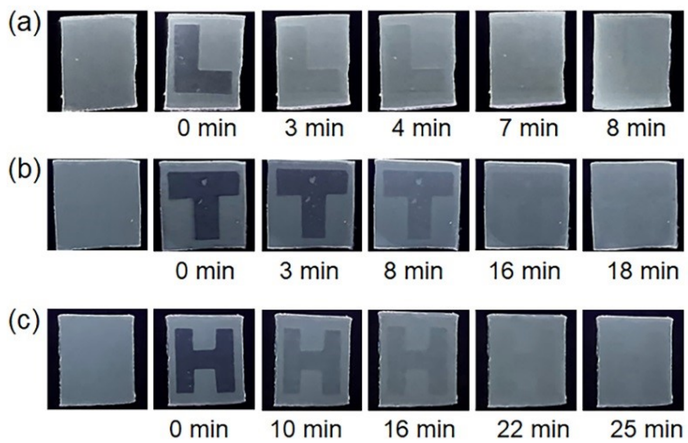

Fig. S11 The self-erasing process of information at different temperatures and photographs were taken under UV light at 254 nm. (a) 40 ^{o}C, (b) 25 ^{o}C, (c) 4 ^{o}C.

Table S3 pH of different concentrations of HCl-urea mixed solution.

$c_{HCl\ (M)}$	$c_{urea\ (M)}$	pH
0.5	15	1.6
0.1	15	2.4
0.02	15	3.2
0.01	15	3.4
0.005	15	3.8
0.02	0.01	2.0
0.02	0.05	2.0
0.02	0.1	2.1
0.02	1	2.2

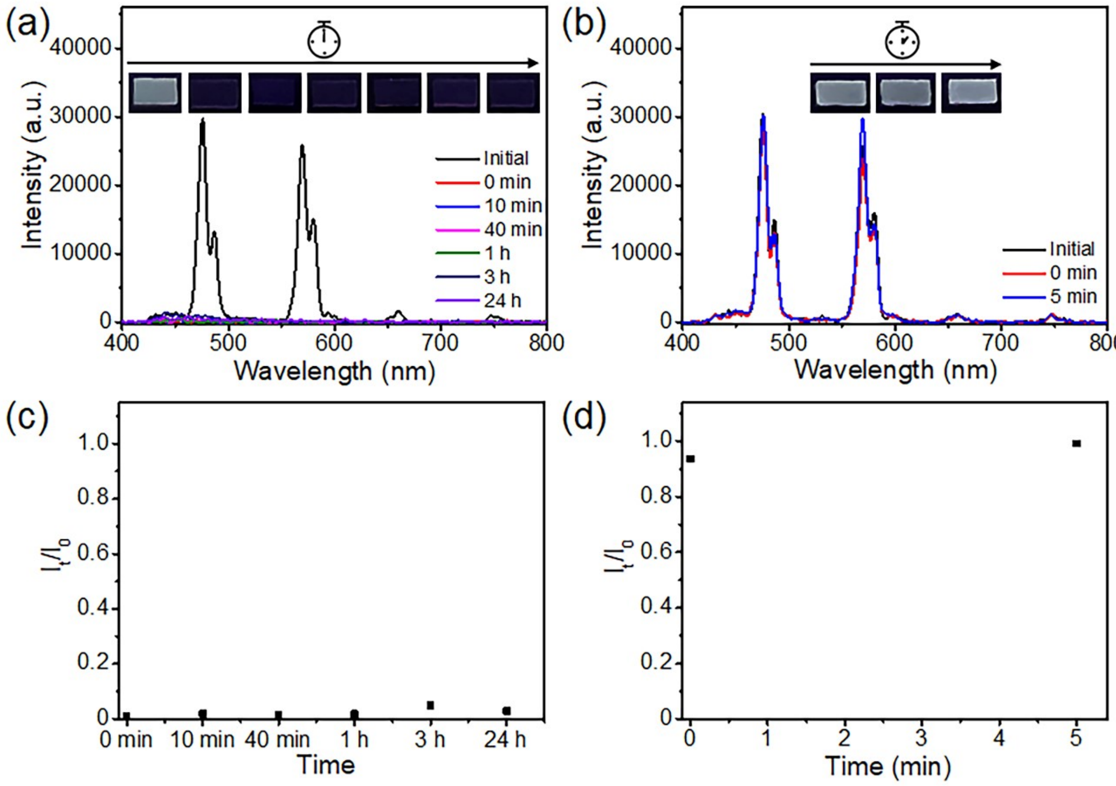

Fig. S12 Time-dependent emission spectra of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different pH of HCl-urea mixed solution and photographs were taken under UV light at 254 nm. (a) pH = 1.6. (b) pH = 3.8. Time-dependent luminescence intensity ratio of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different pH of HCl-urea mixed solution (I_0: initial luminescence intensity, I_t: luminescence intensity at different time). (c) pH = 1.6. (d) pH = 3.8.

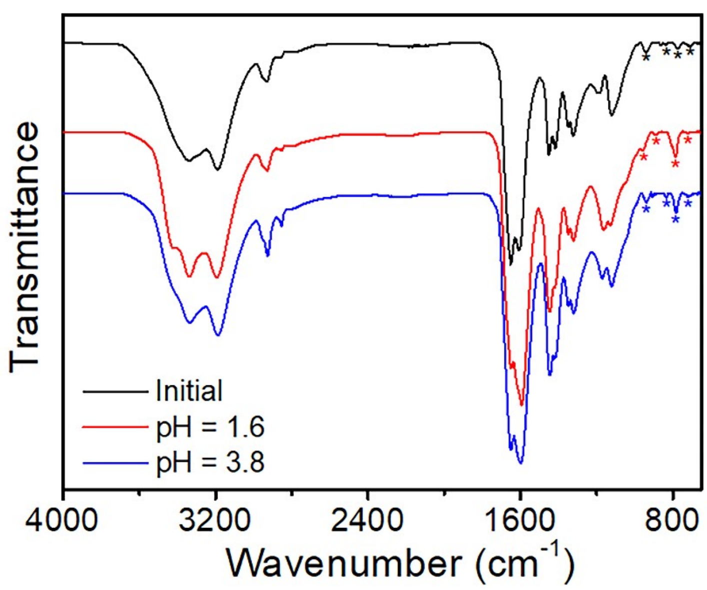

Fig. S13 ATR FT-IR spectra of dried $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel, and dried $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different pH of HCl-urea mixed solution.

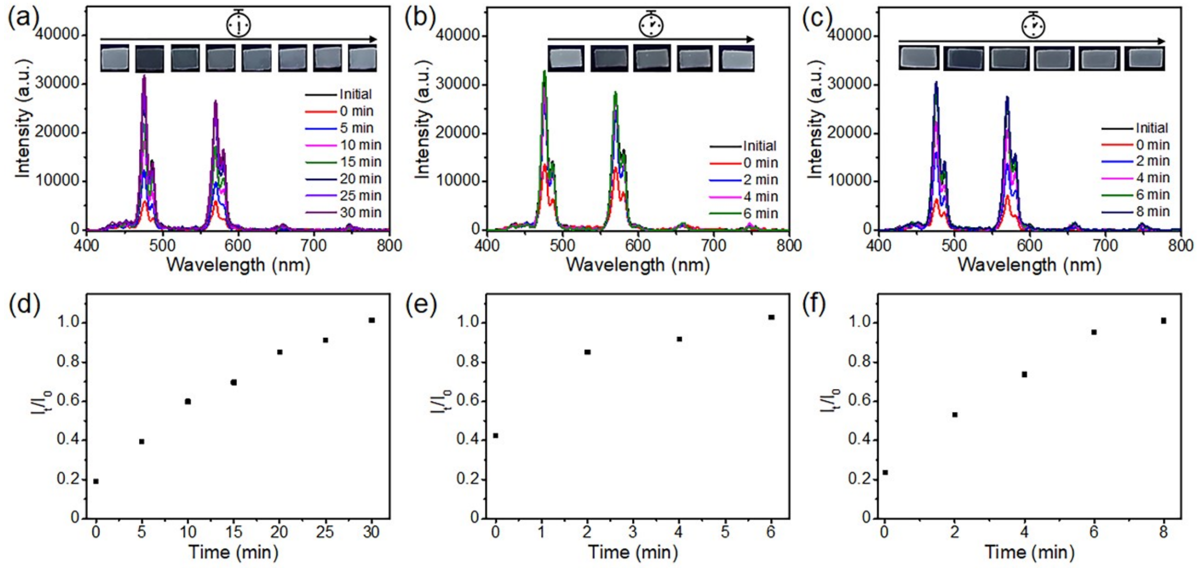

Fig. S14 Time-dependent emission spectra of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different temperatures and photographs were taken under UV light at 254 nm. (a) 0 °C. (b) 60 °C. (c) 80 °C. Time-dependent luminescence intensity ratio of $PAAm_{16}/(DyW_{10})_{0.02}/urease_5$ hydrogel at different temperatures (I_0: initial luminescence intensity, I_t: luminescence intensity at different time). (d) 0 °C. (e) 60 °C. (f) 80 °C.

Notes and references

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