Transient cucurbit[7]uril-mediated host-guest complexes for time-dependent fluorescence and information self-erasing hydrogel

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Experimental Section

Instrumentation:

Chemicals were weighed on analytical balances METTLER-TOLEDO, ME204T/02. Flash column chromatography was measured using silica gel (Greagent, 200-300 mesh) to purified crude products. The ^{1}H and ^{13}C NMR spectra were acquired on a Brüker AV-400 and AV-600 spectrometer at 298 K using tetramethylsilane to be the internal standard. The ESI-MS was experimented on a LCT Premier XE mass spectrometer. The UV-Vis absorption spectra data were documented by a Shimadzu UV-2600 UV-Vis spectrophotometer and the fluorescence spectra were acquired by a Shimadzu RF6000 spectrofluorophotometer. The absolute fluorescence quantum yield was detected by a Hamamatsu Quantaurus-QY C11347-11 absolute quantum efficiency analysis system.

Materials:

Chemicals were purchased from TCI, Adamas-beta, Macklin and Sigma-Aldrich used without any further purification: 1-bromopyrene, 4-pyridineboronic acid pinacol ester, 4-bromomethylbenzoic acid, acrylamide (AAm), Sodium acrylate (AAcNa), N,N'-methylenebisacrylamide (MBAA), Potassium persulfate ($K_2S_2O_8$), N,N,N',N'-Tetramethylethylenediamine (TMEDA), urea, urease, hydrochloric acid (HCl), CF_3COOH, Cucurbit[7]uril (CB[7]), Sodium hydroxide (NaOH). Deionized water (DI water) was obtained from a Milli-Q Integral Water Purification System.

Preparation of Fluorescent Hydrogel:

380 mg acrylamide, 994 mg sodium acrylate, 2 mg N, N'-methylenebisacrylamide, 5 mL compound PPC aqueous solution (0.1 mM, pH = 12), 2 mL CB[7] aqueous solution (0.5 mM, pH = 12), 0.2 mg $K_2S_2O_4$, 100 μL N,N,N',N'-Tetramethylethylenediamine and 10 mg urease were dissolved in 10 mL NaOH aqueous solution (pH = 12). After ultrasonication for 10 min, the obtained pre-gel solution was sealed and purged with nitrogen for 30 min. Next, it was transferred into a white PTFE mold of 5 cm × 5 cm, and sealed with a transparent glass, before being heated at 60°C for 30 min. The obtained hydrogel was removed from the PTFE mold and then cut into the required shape.

Preparation of the information encryption systems:

Star shaped paper soaked in an aqueous solution containing urea and HCl. Then the paper was attached to the hydrogel surface for 1 min. After removing the paper, the hydrogel exhibited green fluorescence and gradually disappeared over time. A new one was allowed to encode again following the above steps.

Fluorescence spectroscopic titration experiments:

With reference the pervious literature [1], the following equation was used to determine the binding affinities in the case of 1:1 binding at any given wavelength:

$$y = \frac{I - I_0}{I_F - I_0} = \frac{1 + aK + xK - \sqrt{-4axK^2 + (-1 - aK - xK)^2}}{2K} \times E$$

where $(I–I_0)/(I_F–I_0)$ (normalized change in emission intensity) is the y variable; x is the concentration of the added host; a is the initial concentration of the guest (kept constant over the course of titration); E is a coefficient (the derivation of this value from basic photophysical constants is omitted for clarity); K_a is the binding affinity.

Synthetic procedure of compound PPC:

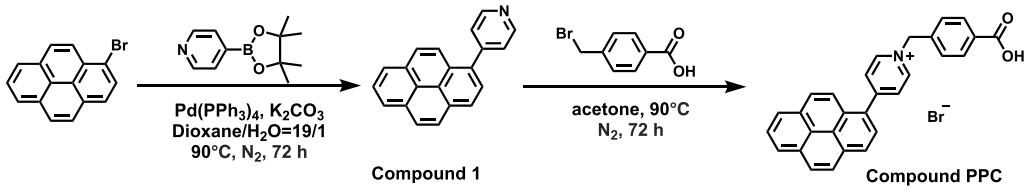

Figure S1 Synthesis of compound **PPC**.

Compound **1** was synthesized according to previous report [2].

Compound **1** (50 mg, 0.18 mmol), 4-bromomethylbenzoic acid (230 mg, 1.07 mmol) were mixed with acetone (20 mL) and refluxed for 72 hours under stirring in nitrogen gas atmosphere. Then the reaction mixture was cooling down to room temperature. The crude products were separated by filtration and wished by acetone (3 mL×6). Drying in vacuum oven gave 74 mg of yellow solid in 83% yield. ^{1}H NMR (400 MHz, DMSO) δ = 13.19 (s, 1H), 9.41 (d, J = 6.7 Hz, 2H), 8.56 (d, J = 6.7 Hz, 2H), 8.51 (d, J = 8.0 Hz, 1H), 8.45 (d, J = 6.0 Hz, 1H), 8.44 (d, J = 5.5 Hz, 1H), 8.37 (m, 2H), 8.32 (d, J = 9.0 Hz, 1H), 8.24 (d, J = 8.6 Hz, 2H), 8.19 (t, J = 7.6 Hz, 1H), 8.08 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 6.10 (s, 2H).^{13}C NMR (101 MHz, DMSO) δ 166.81, 157.01, 144.79, 138.92, 132.41, 131.56, 130.79, 130.52, 130.20, 130.08, 129.58, 129.45, 129.28, 129.06, 127.88, 127.69, 127.23, 127.00, 126.58, 126.11, 125.21, 123.93, 123.57, 123.25, 62.18. HRMS (ESI) (m/z): $[M-Br]^+$ calcd. for $C_{29}H_{20}NO_2^+$, 414.1489; found, 414.1493.

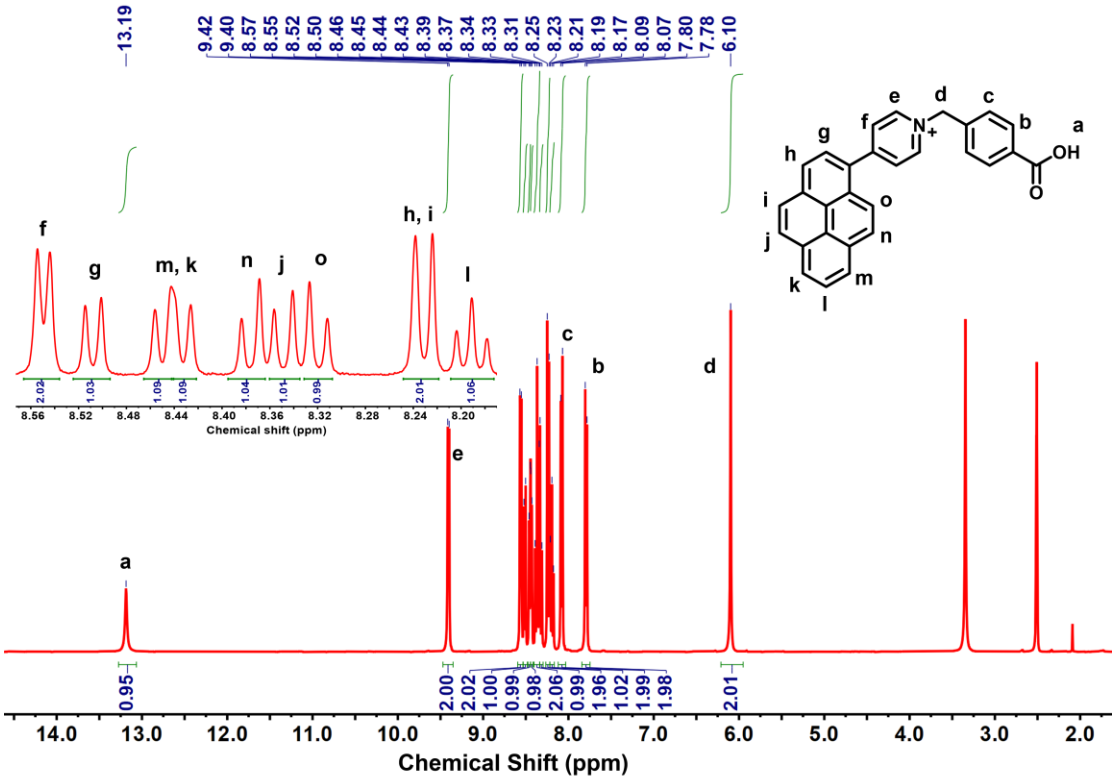

Figure S2 ^{1}H NMR spectrum of compound **PPC**.

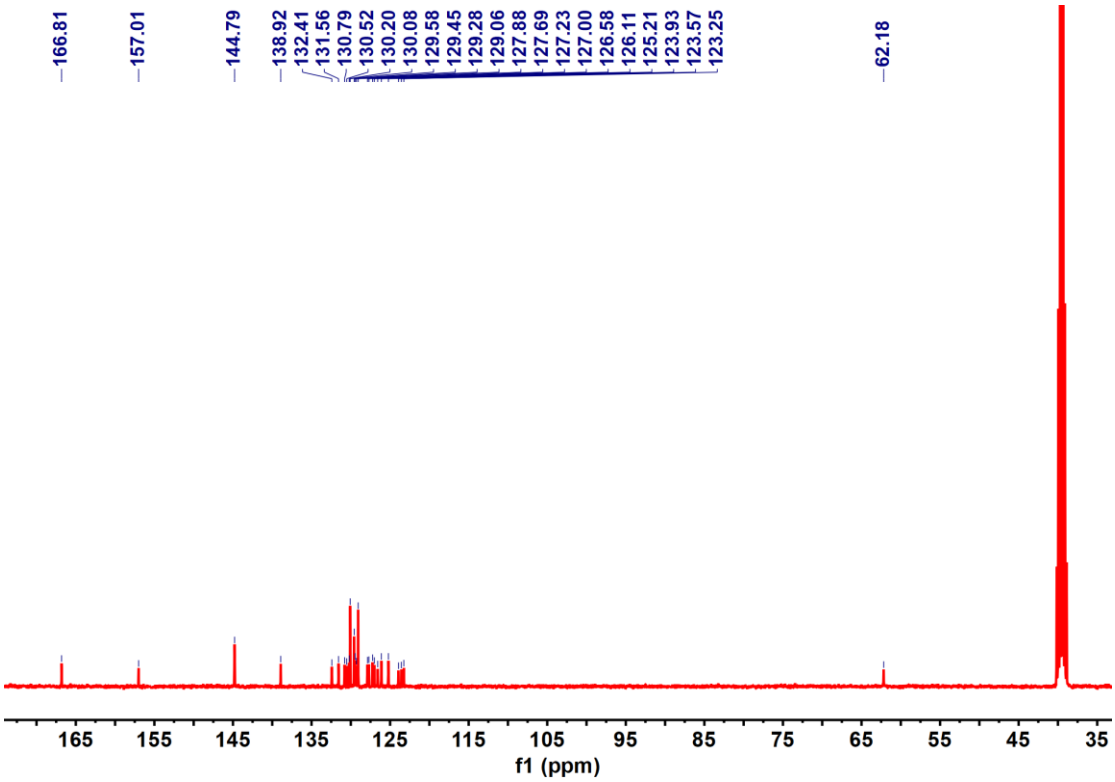

Figure S3 ^{13}C NMR spectrum of compound **PPC**.

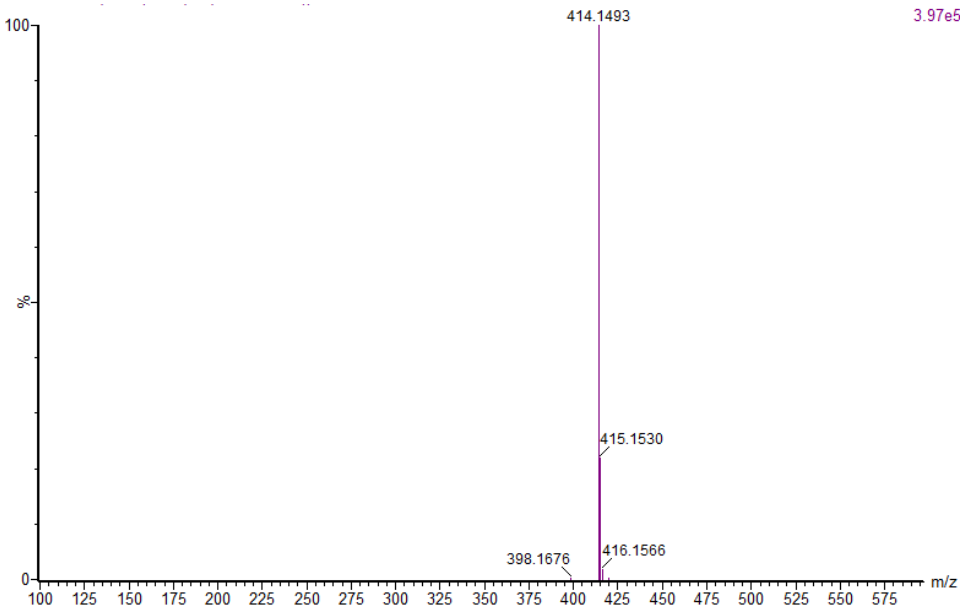

Figure S4 Mass spectrum of compound **PPC**.

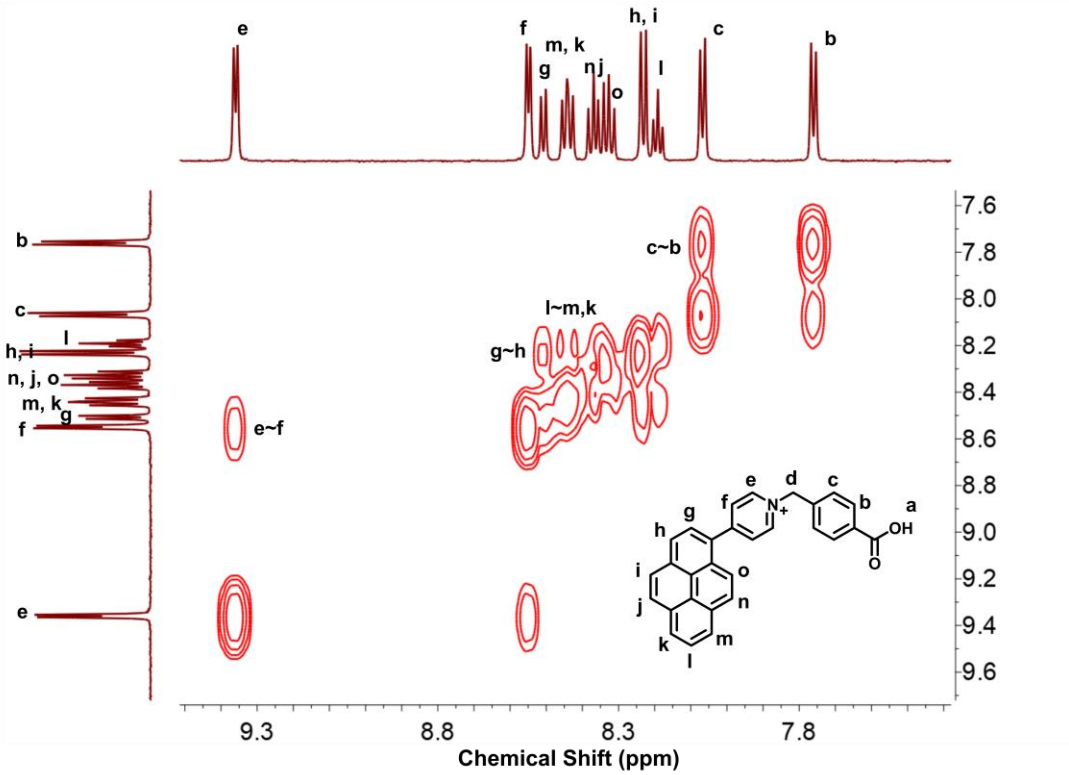

Figure S5 ^{1}H-^{1}H COSY of compound **PPC** in DMSO at 298 K.

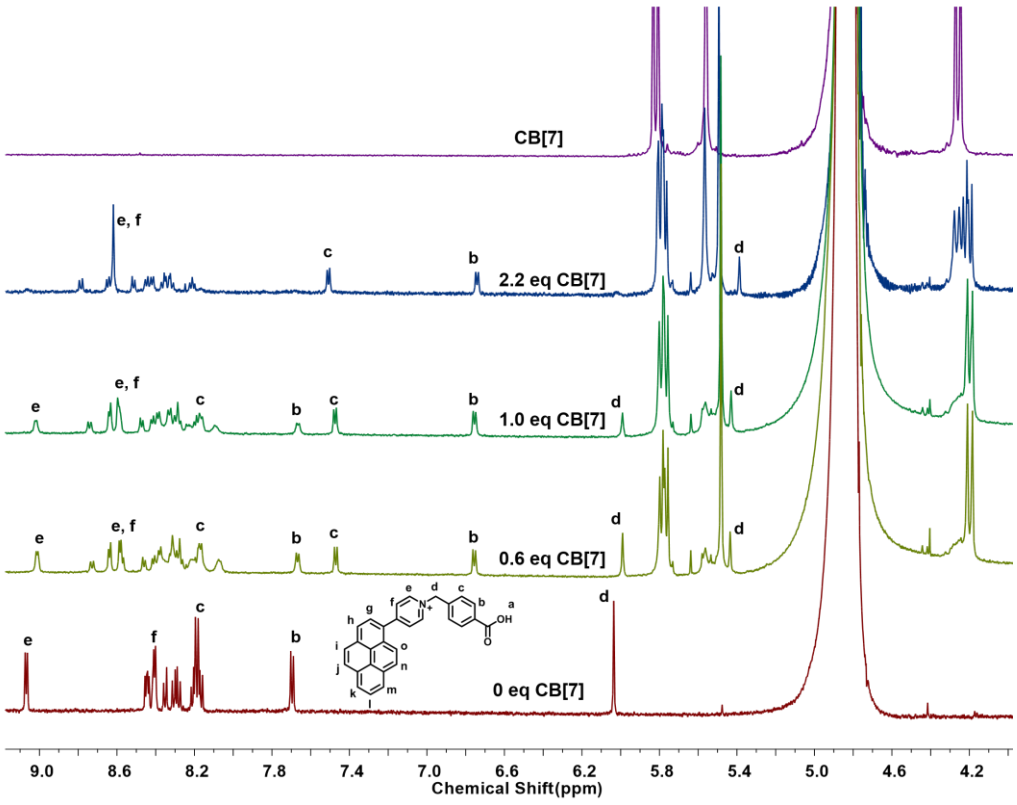

Figure S6 ^{1}H NMR spectra of compound **PPC** with an increasing concentration of CB[7] (PPC: 0.1 mM, CB[7]: 0-2.2 equivalent, pH=1).

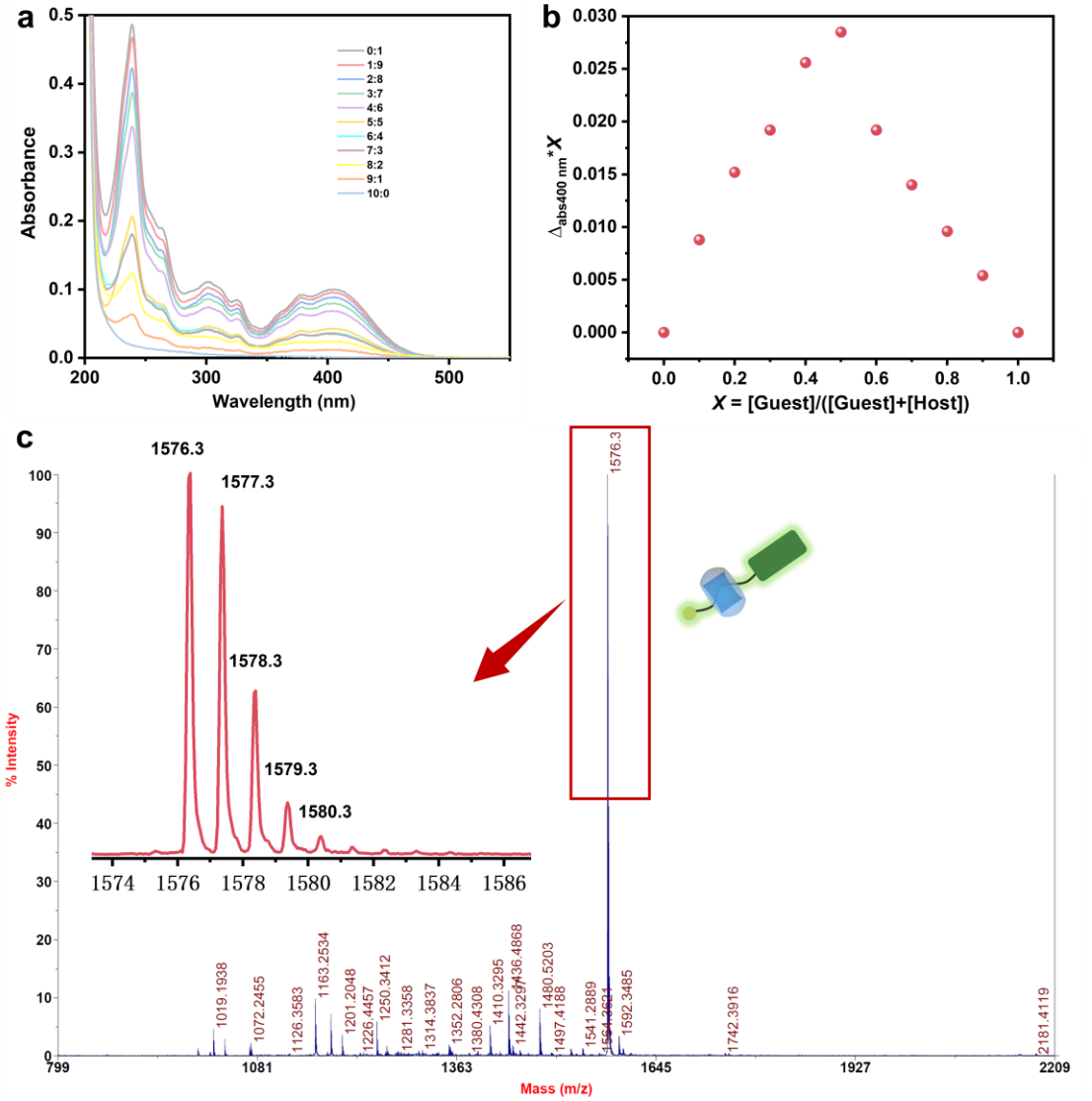

Figure S7 (a) UV–vis absorption and (b) Job's plot of the complexation of PPC with CB[7] in water. (PPD + [CB[7]] =0.01 mM) (c) MALDI-TOF-MS of complexes **PPC**@CB [7]. The peak exhibited at m/z = 1576.3 corresponded to [**PPC** + CB [7]-Br]$^{-}$. The schematic representation inset showed the assembly mode of **PPC**@CB [7].

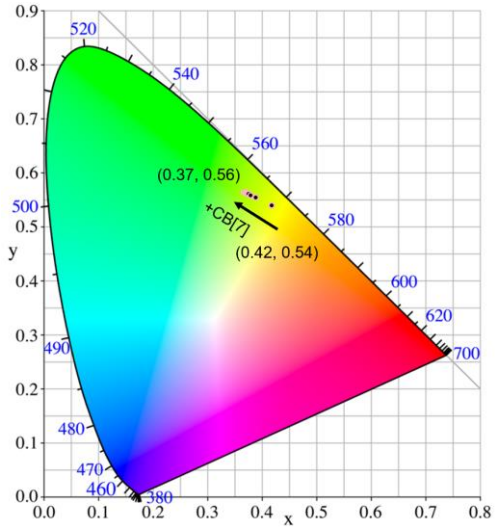

Figure S8 Changes in the 1931 CIE chromaticity coordinate with the addition 0–2 eq. of the CB[7] host to an aqueous solution of compound **PPC**.

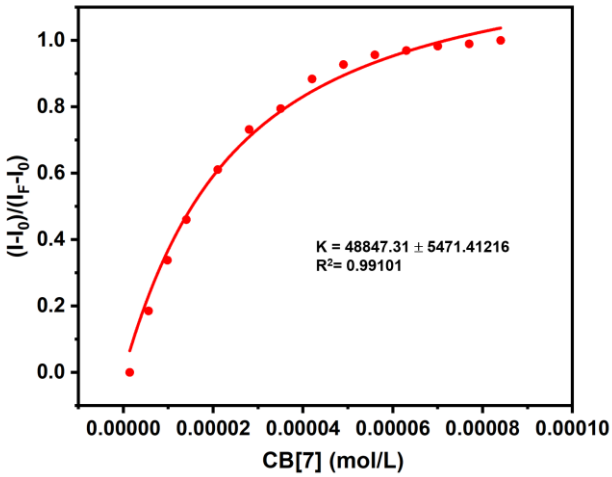

Figure S9 Least-squares nonlinear fitting of the normalized change in fluorescence at 545 nm obtained as a function of the concentration of CB[7].

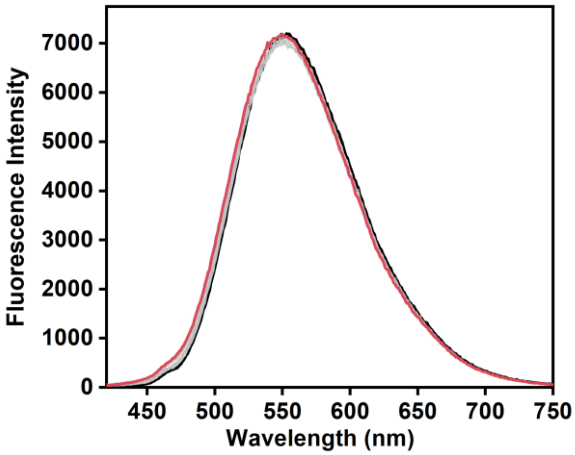

Figure S10 Fluorescence spectrum of compound **PPC** aqueous solution upon titration of CB [7] (0–2 equivalent) in pH=12.

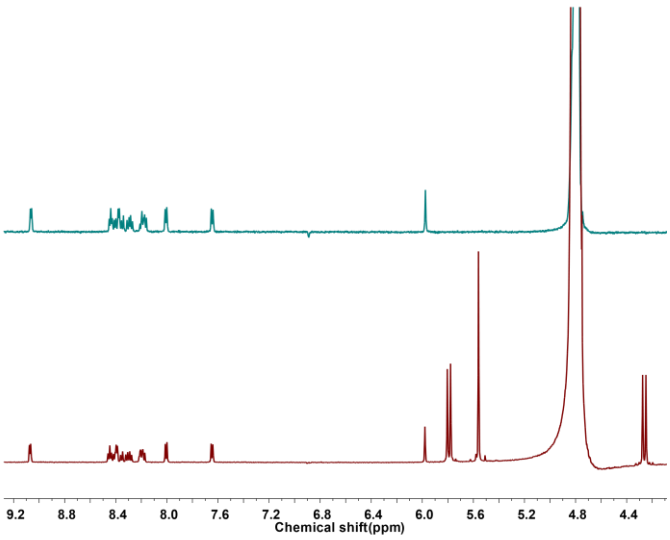

Figure S11 ^{1}H NMR (D_2O) spectra of compound **PPC** (0.1 mM) prior (green line) and after (red line) addition of 2.2 eq. of CB[7] (pH=12).

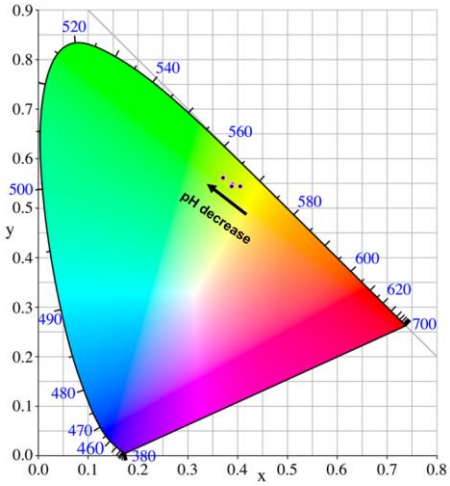

Figure S12 CIE chromaticity coordinate of the host-guest complex in different pH.

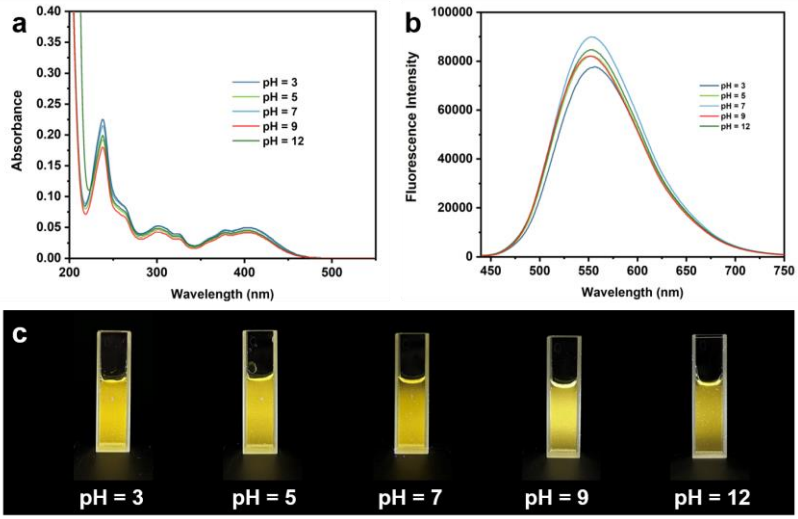

Figure S13 (a) UV–vis absorption, (b) fluorescence spectrum and (c) fluorescence photograph of compound **PPC** aqueous solutions in different pH.

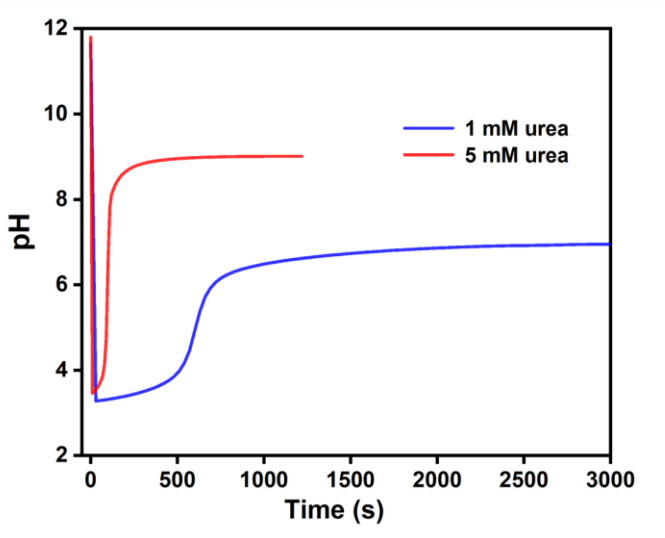

Figure S14 The change in pH with time for different urea concentrations.

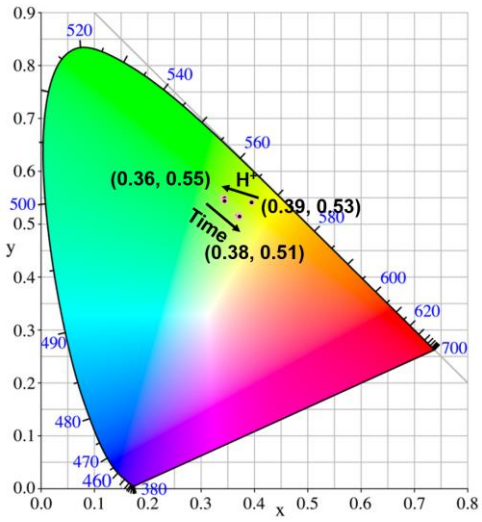

Figure S15 Time-dependent CIE coordinate diagram after treatment with acid/urea.

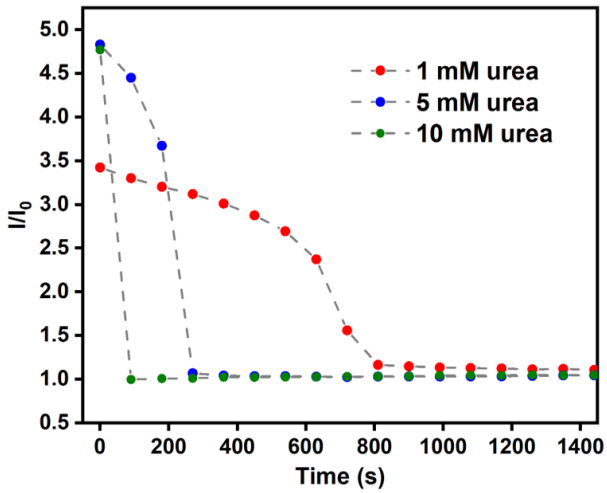

Figure S16 The influence of urea concentrations (urease: 0.1 mg/mL).

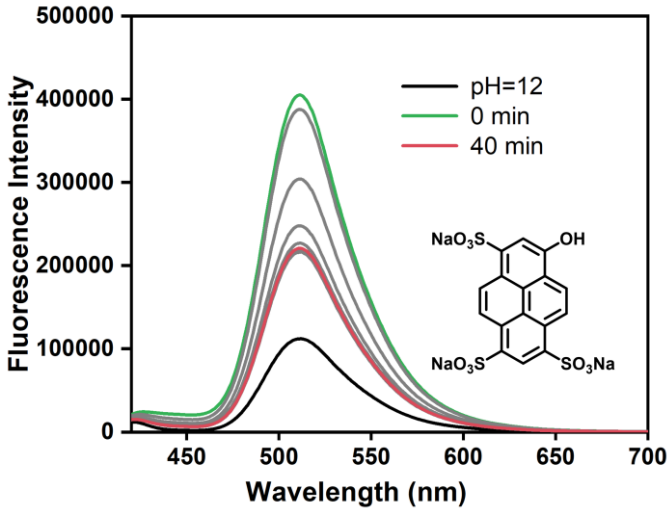

Figure S17 Time-dependent fluorescence spectra of compound HPTS (10 μM) in aqueous solutions after introducing trifluoroacetic acid/urea (urea: 1 mM, urease: 0.05 mg/mL). 0 min (green line) and 40 min (red line) after the addition of acid/urea.

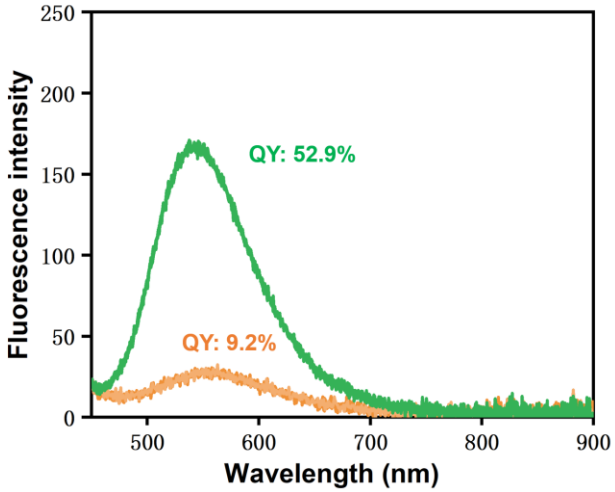

Figure S18 The absolute solid fluorescence quantum yield of hydrogel in acid (green line) and alkaline (yellow line) conditions.

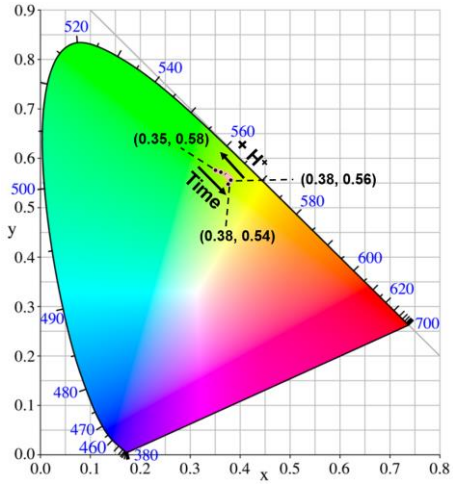

Figure S19 Time-dependent CIE coordinate diagram of the hydrogel after treatment with acid/urea.

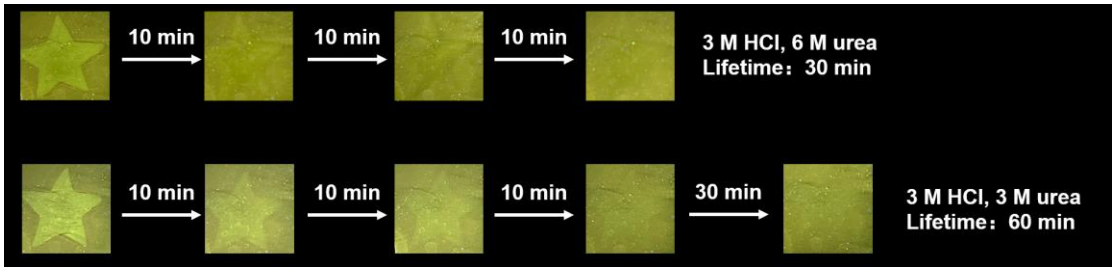

Figure S20 Image of the fluorescent pattern self-erasing process with different urea and urease concentrations.

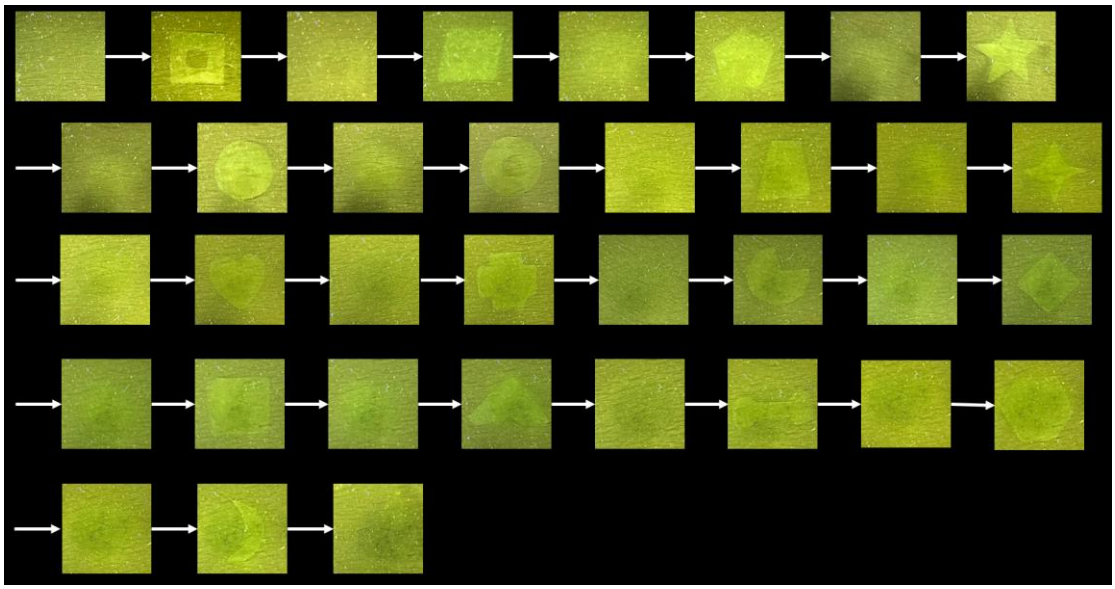

Figure S21 Illustrations of 17 repeating cycles of the fluorescent hydrogel.

Reference

[1] W. Chen, C. Guo, Q. He, X. Chi, V. M. Lynch, Z. Zhang, J. Su, H. Tian, J. L. Sessler, *J. Am. Chem. Soc.* 2019, **141**, 14798-14806.

[2] Q. Lu, G. K. Kole, A. Friedrich, K. Müller-Buschbaum, Z. Liu, X. Yu, T. B. Marder, *J. Org. Chem.*, 2020, **85**, 4256-4266.