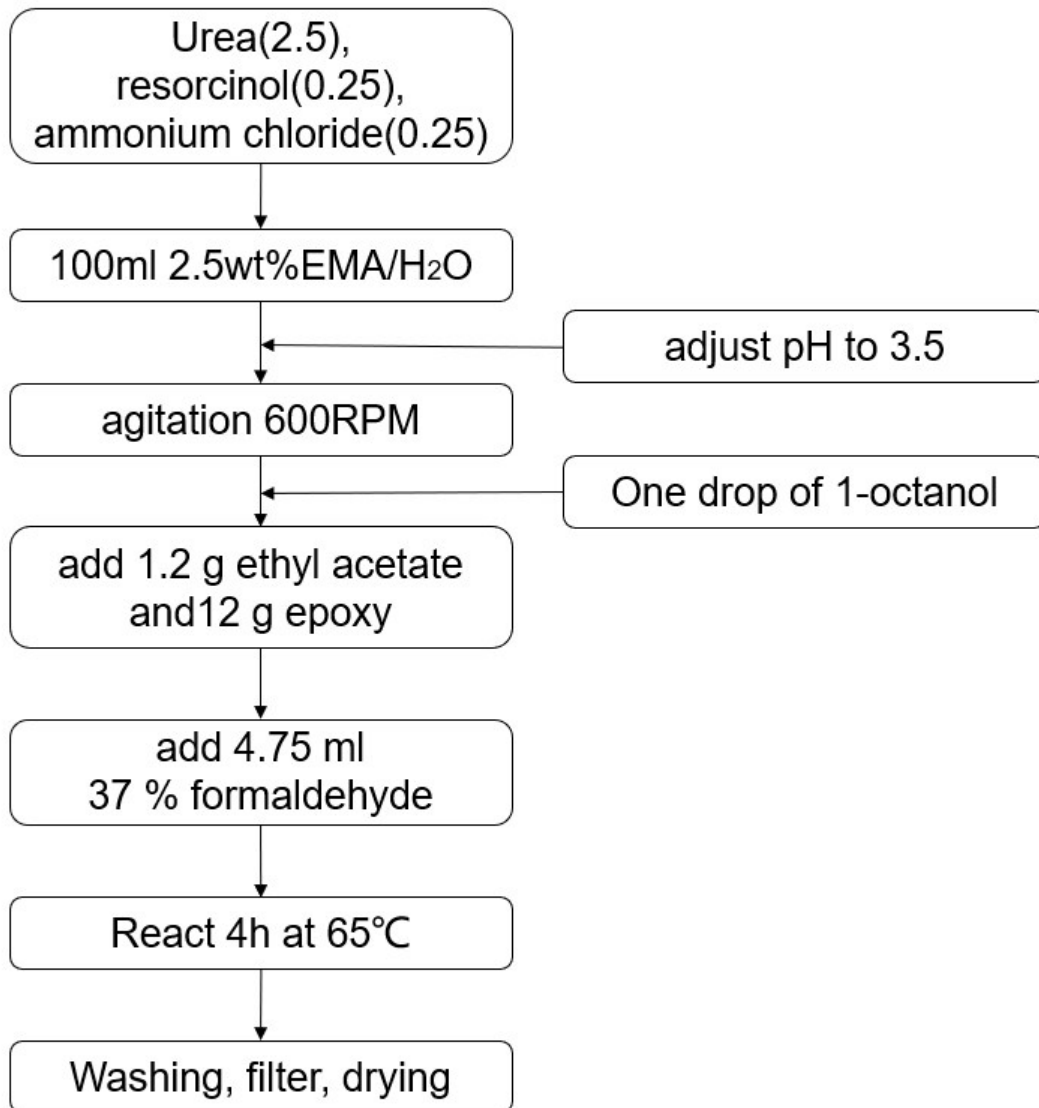


Supporting Information

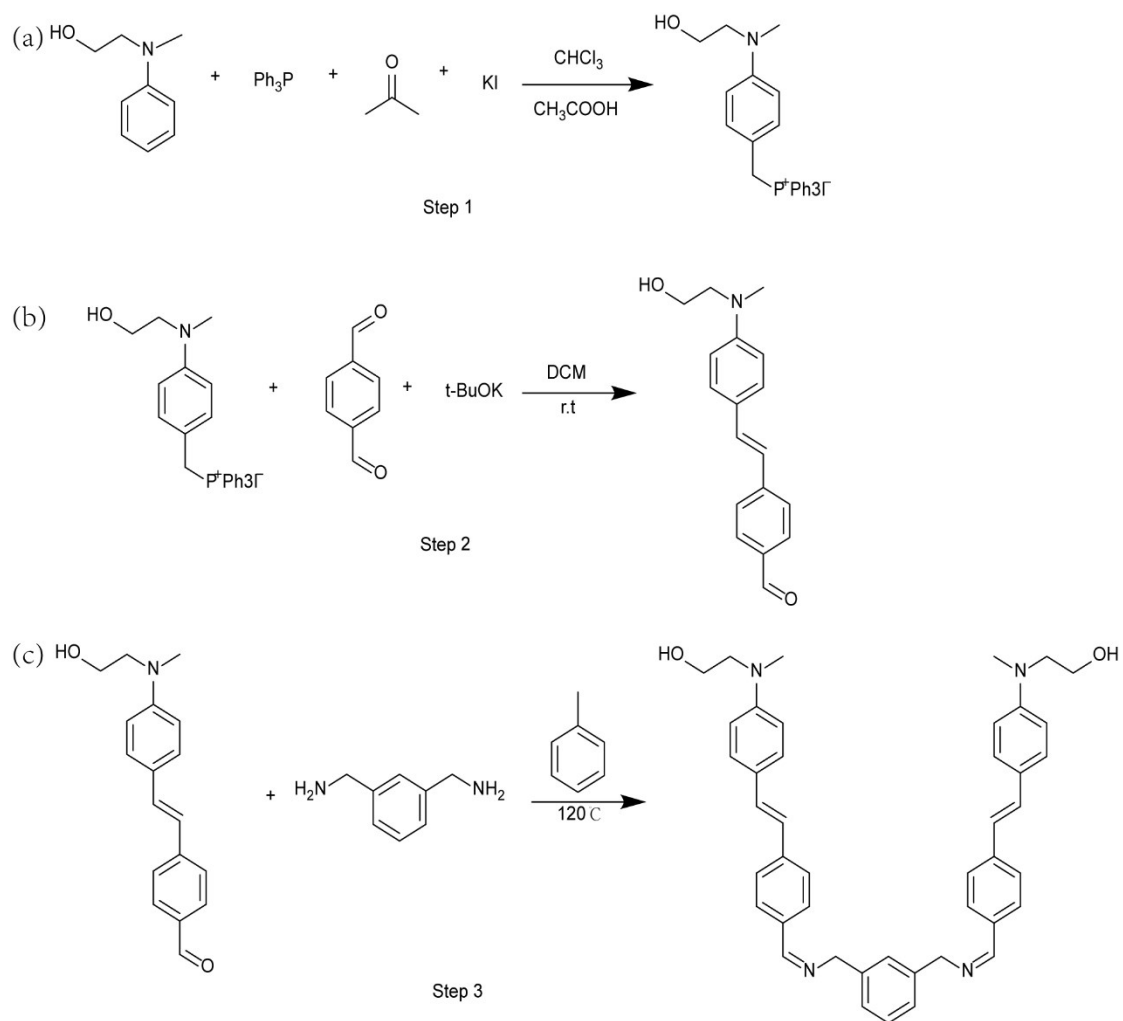
Fabrication of Microcapsule-type Composites with the Capability to Underwater Self-healing and Damage Visualization

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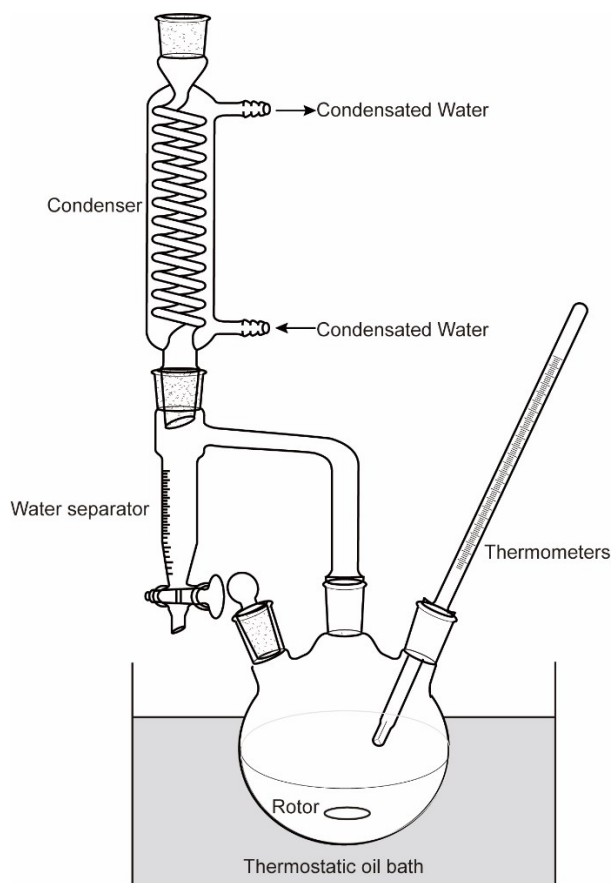
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Supplementary Fig. 1. Synthetic processes of microcapsule



Supplementary Fig. 2. (a) Synthesis of fluorescent dye precursor; (b) Synthesis of fluorescent dye; (c) Synthetic processes of FLCA



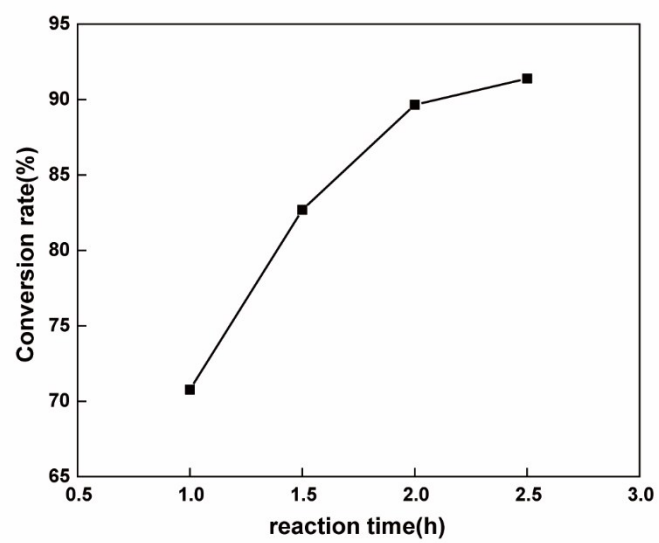
Supplementary Fig. 3. The reaction device for the synthesis of FLCA

In principle, MXDA with fluorescent reaction molar ratio of 1:2, this experiment adopts azeotropic water to the preparation of FLCA (as show in the supplementary Fig. 3), and MXDA with fluorescent dyes of mole ratio of 1:2.5. Because the boiling point of toluene is close to it of water, thus toluene can be used for dehydrant, when toluene and water azeotrope back into the water separator after condenser cooling, and the discharged water sinks to the bottom of the water separator. The toluene on top can be recycled back into the reaction.

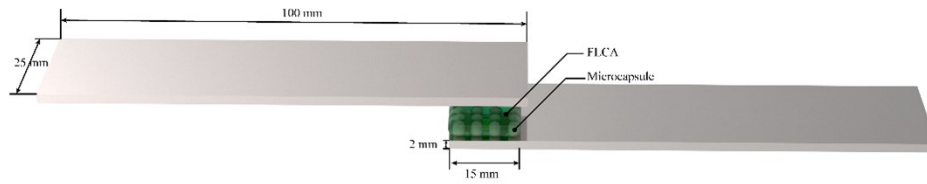
The synthesis of FLCA is a reversible process. With the increase of conversion rate, the reaction becomes more and more difficult, and the later reaction rate becomes slower. As shown in supplementary Table 1, the conversion rate of FLCA was determined by weighing the separated water content. By calculation, the effect of reaction time on conversion rate is shown in supplementary Fig. 4.

Supplementary Table 1 The amount of water discharged during the reaction

Time	1h	1.5h	2h	2.5h
quality	0.184g	0.215g	0.233g	0.238g



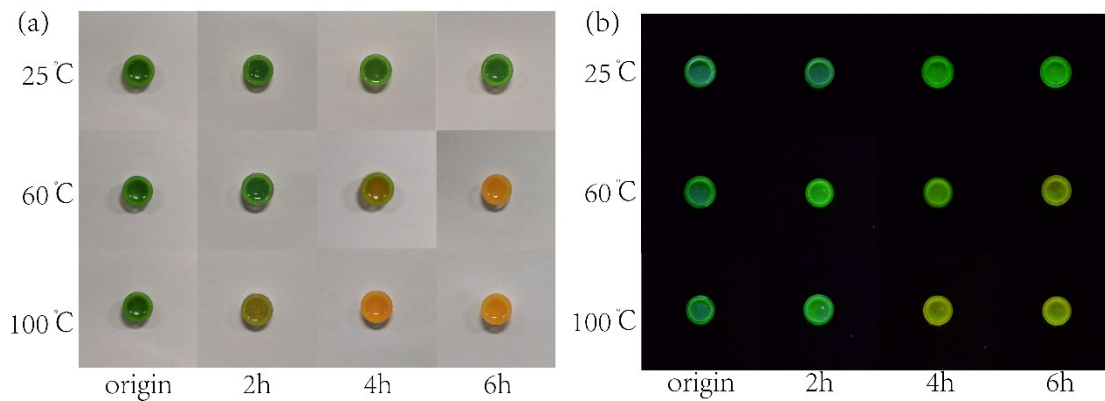
Supplementary Fig. 4. Effect of reaction time on conversion rate



Supplementary Fig. 5 Sample size of lap-shear tests

Supplementary Table 2 Shear strength of microcapsule and FLCA

	Sample 1	Sample 2	Sample 3	Average
Shear strength	10.43 MPa	7.52 MPa	11.46 MPa	9.80 MPa

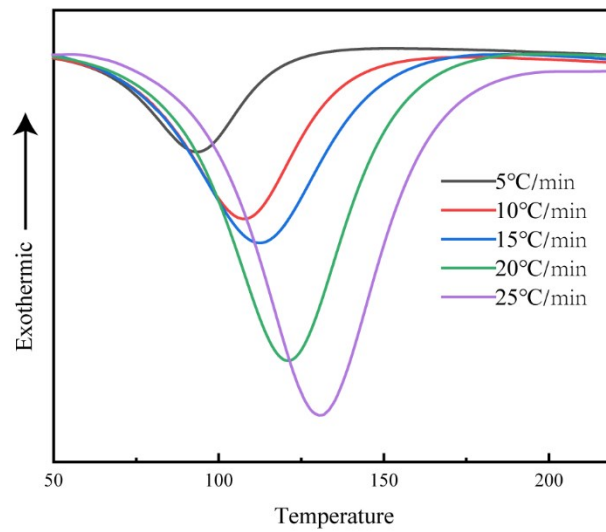


Supplementary Fig. 6. (a) The color changes of mixture which consisted of ethyl acetate, epoxy, FLCA with a mass ratio of 7:2:1 in visible light; (b) The fluorescent color changes of mixture which consisted of ethyl acetate, epoxy, FLCA with a mass ratio of 70:20:10 in ultraviolet light

The non-isothermal curing behavior of epoxy resin was studied with the assistance of a differential scanning calorimeter (Netzsch, Germany), the samples were heated from 30 °C to 250 °C at varying heating rates (5, 10, 15, 20 and 25 °C/min) under nitrogen atmosphere. Subsequently, all the samples were cooled down from the melting temperature to 30 °C at the rate of 10 °C/min. In order to ensure the reliability of measurement results, all the specimens were measured three times for each variety of composites. The DSC instrument was calibrated with sodium and zinc at each cooling

rate used herein.

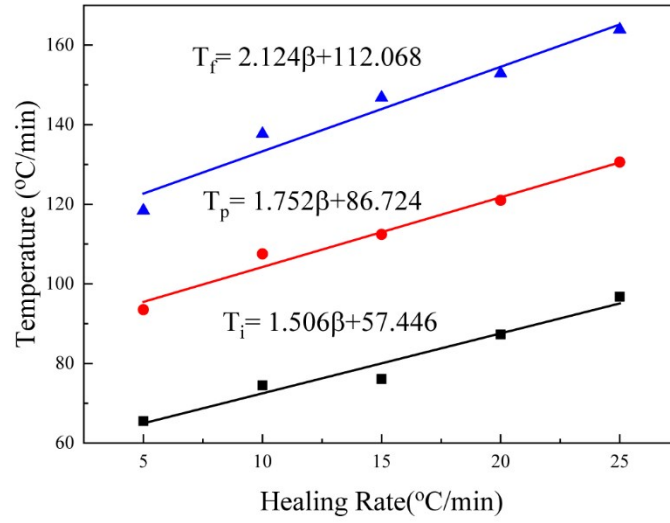
The single exothermic peaks for epoxy resin at varying healing rate (5 to 25 °C/min) are shown in Fig... and heating rate had a great influence on the shape of the exothermic curves. The curing onset (T_s), peak (T_p) temperature and curing enthalpy (ΔH) of epoxy resin are indicated in supplementary Table 2. As shown in supplementary Fig.5., it's indicated that the gel initial temperature is 57.4 °C, the curing temperature is 86.7 and the post-curing temperature is 112.1 °C, respectively. On the basic of Table 2, T_s and T_p of curing process for epoxy resin are increased with the increase of healing rate, while the curing enthalpy are decreased.



Supplementary Fig. 7 DSC curves of non-isothermal curing behavior of epoxy at various healing rate

Supplementary Table 3 Non-isothermal curing kinetic parameters of epoxy

Heating Rate °C/min	T_i °C	T_p °C	T_f °C	ΔH J/g
5	65.53	93.51	118.40	476.53
10	74.48	107.52	137.68	460.69
15	76.09	112.41	146.77	436.04
20	87.32	120.98	152.86	428.66
25	96.76	130.57	163.90	414.65



Supplementary Fig 8 Fitting line of epoxy resin non-isothermal curing temperature versus heating rate

The curing process of a thermosetting polymer is commonly described by a single step kinetic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E\alpha}{RT}\right) f(\alpha)$$

where α represents the curing degree of the polymer, t is the time, $k(T)$ is usually assumed to follow the Arrhenius equation, which depends on temperature T , T stands for absolute temperature, A is the apparent pre-exponential factor, E_{α} is the curing activation energy, R is the universal gas constant and $f(\alpha)$ is the kinetic model functions.

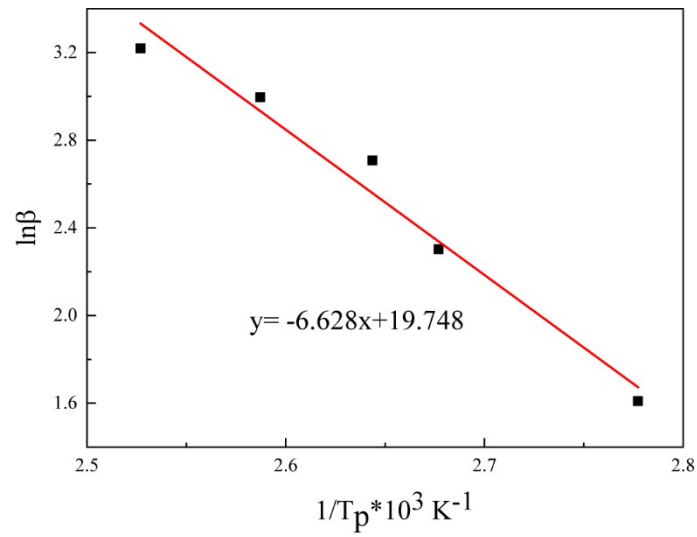
Based on the DSC method, Kissinger and Flynn-Wall-Ozawa are generally used to calculate the non-isothermal curing reaction kinetic parameters.

Flynn-Wall-Ozawa equation:

$$\frac{d(\ln\beta)}{d(1/T_p)} = \frac{1.052E_{\alpha}}{R}$$

Flynn-Wall-Ozawa integral method:

$$\lg\beta = \lg\frac{AE}{RG(\alpha)} - 2.135 - 0.4567\frac{E}{RT}$$



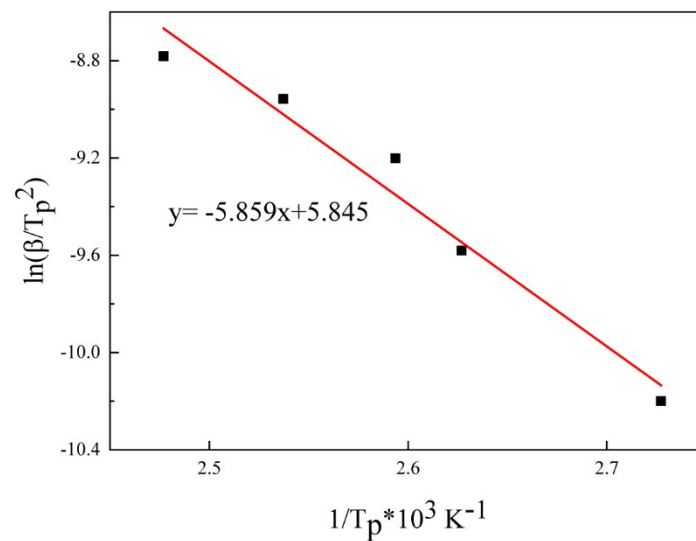
Supplementary Fig 9 The fitting plot of $\ln\beta$ vs. $1/T_p \cdot 10^3 \text{ K}^{-1}$ according to Ozawa's method

Kissinger equation:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_\alpha}{RT_p} - \ln\left(\frac{AR}{E_\alpha}\right)$$

Kissinger differential method:

$$\ln\frac{\beta}{T_p^2} = \ln\frac{AR}{E_\alpha} + \ln\left(-\frac{df(\alpha)}{d\alpha}\right) - \frac{E_\alpha}{RT_p}$$

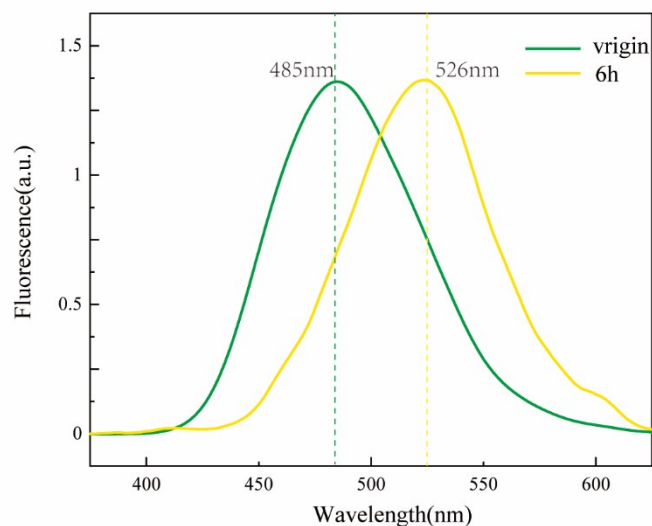


Supplementary Fig 10. The fitting plot of $\ln(\beta/Tp^2)$ vs. $1/TP*103K-1$ according to

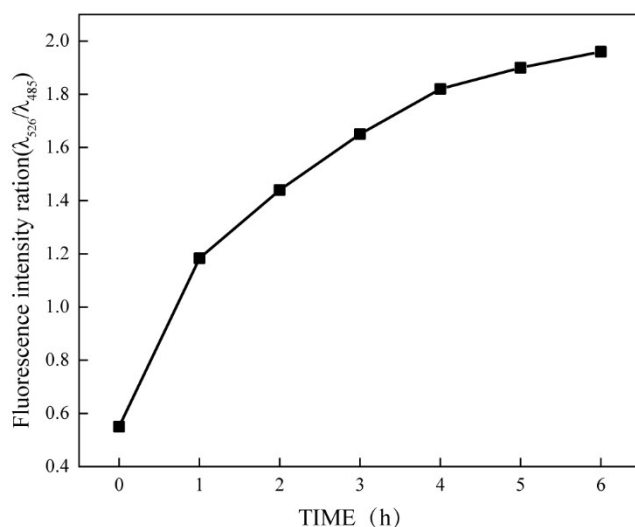
Kissinger's method

The linear fitting plots of epoxy according to Kissinger's and Ozawa's methods are exhibited in Supplementary Fig.8, and the values of the E_a are obtained are 48 and 52 kJ/mol, respectively. The values of reaction activation energy calculated by the two methods are similar, indicating the calculated result is credible. What's more, the smaller activation energy proves that the resin shows higher reactivity.

FLCA was tested by fluorescence spectroscopy and the excitation wavelength was 320nm. In order to clearly reflecting in the hydrolysis of the FLCA, the change of fluorescence intensity ratio during hydrolysis was compared to determine the degree of hydrolysis of FLCA. A comparison of the fluorescence spectra of a dilute ($c = 1 \times 10^{-5}$ mol/L) tetrahydrofuran solution of FLCA (which features maxima at 485 nm) and the fluorescence obtained after adding water (with maxima at 526) showcases the significant bathochromic shift that occurs upon hydrolysis.



Supplementary Fig 11 Fluorescence spectra of FLCA (1×10^{-5} mol/L) in THF-H₂O (volume ratio 4:1)



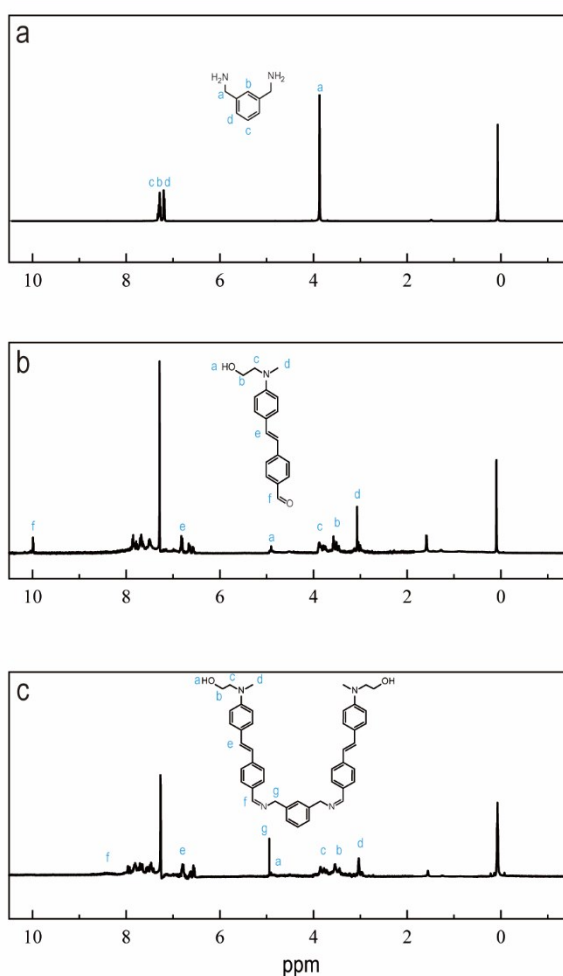
Supplementary Fig 12 Plot of the ratio of the fluorescence intensity at 526 nm and 485.

Supporting Molecular Characterization

H NMR spectrum of MXDA (400 MHz, CDCl_3) 7.29 (3 H, dd, J 16.7, 7.7), 7.19 (2 H, d, J 7.4), 3.87 (4 H, s).

H NMR spectrum of fluorescent dye (400 MHz, CDCl_3) 9.99 (1 H, s), 7.86 (1 H, d, J 8.3), 7.69 (3 H, d, J 10.5), 7.50 (2 H, d, J 7.7), 6.82 (2 H, s), 6.65 (2 H, d, J 8.6), 4.52 (1 H, s), 3.92 – 3.71 (2 H, m), 3.59 – 3.43 (2 H, m), 3.07 (3 H, s).

H NMR spectrum of FLCA (400 MHz, CDCl_3) 8.44 (2 H, s), 7.87 – 7.76 (4 H, m), 7.68 (4 H, dd, J 11.8, 7.4), 7.54 (1 H, dd, J 13.1, 5.4), 7.48 (2 H, d, J 8.3), 7.42 (1 H, s), 6.80 (4 H, s), 6.55 (4 H, d, J 8.5), 4.88 (2 H, s), 3.92 – 3.63 (4 H, m), 3.61 – 3.36 (4 H, m), 3.03 (6 H, s).



Supplementary Fig 13 (a) ^1H NMR spectrum of MXDA; (b) ^1H NMR spectrum of fluorescent dye; (c) ^1H NMR spectrum of FLCA