

Electronic Supplementary Information for

Bioinspired Simultaneous Regulation in Fluorescence of AIEgen- embedded Hydrogels

Li-Li Zhang,^a Yu Zhao,^a Ke-Xin Li,^a Sheng-Sheng Yu,^a Rui-Zhi Dong,^a Shuanhong Ma,^c Hui Liu,^{*a,b}
Ling-Bao Xing^{*a} and Feng Zhou^b

^aSchool of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255000,
P. R. China.

^bState Key Laboratory of Solid Lubrication Lanzhou Institute of Chemical Physics Chinese
Academy of Sciences, Lanzhou 730000, P. R. China.

^cShandong Laboratory of Yantai Advanced Materials and Green Manufacture, Yantai 264006, P. R.
China.

*Corresponding author: Tel. /fax: +86 533 2781664. E-mail: liuhui@sdut.edu.cn;
lbxing@sdut.edu.cn.

Experimental

Materials: 4,4'-Dihydroxybenzophenone (98%), zinc (Zn, AR), titanium tetrachloride (TiCl₄, 99%), tetrahydrofuran (THF, AR), 2-bromo-2-methylpropionyl bromide (98%), triethylamine (Et₃N, AR), 3-sulfopropyl methacrylate potassium salt (SPMA, 95%), 2,2'-bipyridine (bipy, AR), copper(I) bromide (CuBr, 99%), 4-vinylpyridine (VP, 95%) tetrabutylammonium bromide (TBAB, AR), dodecyltrimethylammonium bromide (DTAB, AR) and cetyltrimethylammonium bromide (CTAB, AR) were purchased from Aldrich. Tetrahydrofuran and triethylamine were used after purification by distillation, and copper(I) bromide was purified by refluxing in ethanol. Other general reagents and solvents were used as specified.

Characterizations: ¹H NMR spectra is recorded on a Bruker Advance 400 spectrometer (400 MHz) at 298 K. Fourier-transform infrared spectrometer (FT-IR) (PerkinElmer, Massachusetts) is employed to analyze the chemical composition of the samples. UV-vis spectra are obtained on a Shimadzu UV-1601PC spectrophotometer in a quartz cell (light path 10 mm) at 298 K. Steady-state fluorescence measurements are carried out using a Hitachi 4500 spectrophotometer. Dynamic light scattering and zeta potential are characterized on Malvern Zetasizer Nano ZS90. The morphology of samples is obtained on a scanning electron microscope (SEM, JSM-5600LV at an accelerating voltage of 20 kV) by the freeze-drying technique. Characterization of mechanical properties is conducted upon an electrical universal material testing machine with a 500 N load cell (EZ-Test, SHIMADZU). The crosshead velocity is kept at 100 mm min⁻¹ for tensile tests. Three parallel tests are performed to obtain the average value. All the specimens are coated in silicone oil during the tests.

Synthesis of 1,1,2,2-tetra(4-hydroxyphenyl)ethylene (TPE-4OH): A mixture solution of 4,4'-Dihydroxybenzophenone (6.0 g, 0.028 mol), zinc powder (7.32 g, 0.11 mol) and dry tetrahydrofuran (THF, 100 mL) in a round-bottom flask is reacted in an ice water bath under N₂ atmosphere for 0.5 h. Then TiCl₄ (6 mL, 0.05 mol) is added by syringe injection and the reaction is continued in an ice water bath for 0.5 h. After that, the suspension is heated to reflux for 24 h. In the end, the reaction mixture is cooled to

room temperature, poured into 10% aqueous K_2CO_3 (60 mL), and the organic phase is collected using dichloromethane as extractant. The combined organic fractions are evaporated and the crude product is purified by silica gel column with petroleum ether-ethyl acetate (3:2, v/v) as the eluent. TPE-4OH is obtained as a light-yellow powder in 30% yield (1.67 g). 1H NMR (400 MHz, $DMSO-d_6$) δ 9.26 (d, $J = 2.0$ Hz, 4H), 6.76 – 6.66 (m, 8H), 6.49 (dd, $J = 8.6, 2.1$ Hz, 8H).

Synthesis of tetraphenylethylene-2-bromo-2-methylpropionate (TPE-Br): A solution including TPE-4OH (1.67 g, 0.0042 mol), triethylamine (2.8 mL, 0.02 mol) and dry THF (150 mL) is prepared. Then 2-bromo-2-methylpropionyl bromide (6.0 mL, 0.02 mol) is added to the mixture solution. The resultant solution is stirred at room temperature for 6 h and filtered. The filtrate is concentrated and the crude product is purified by silica gel column using petroleum ether-ethyl acetate (6:1, v/v) as eluent to give a white powder (2.5 g) in 60% yield. 1H NMR (400 MHz, Chloroform- d) δ 7.05 (dd, $J = 8.5, 2.3$ Hz, 8H), 6.92 (dd, $J = 8.6, 2.3$ Hz, 8H), 2.04 (s, 24H).

Synthesis of TPE-PSPMA: SPMA (6.0 g, 0.024 mol) is dissolved in water/methanol (12 mL, v/v=2:1) at room temperature and degas with dry N_2 for 30 min under stirring conditions. Then, bipy (0.08 g, 0.5 mmol), CuBr (0.035 g, 0.24 mmol) and TPE-Br (0.05 g, 0.05 mmol) are added successively to above solution, and then the mixture is further stirred and degassed with dry N_2 and react at room temperature for 6 h. Finally, the reaction mixture is diluted with ethanol (50 mL) and collect by centrifugation. The product (3.5 g) is obtained after purifying by three repeated cycles of water and ethanol (1:5, v/v). 1H NMR (400 MHz, Deuterium Oxide) δ 4.39 – 3.66 (m, 2H), 2.89 (s, 2H), 1.92 (d, $J = 70.0$ Hz, 3H), 0.98 – 0.74 (m, 2H).

Synthesis of P(AAm-VP) hydrogel doped with TPE-PSPMA: The P(AAm-VP) hydrogel with TPE-PSPMA is synthesized by hybrid covalently cross-linked network and physical doping. The general procedures are described in the following: a homogeneous solution, containing various monomers of AAm (1.4216 g, 0.02 mol), the proper amount of VP (0.2695 mL, 0.001 mol), TPE-SPMA (0.1 g, 0.5 mg/mL), cross-linking BIS (0.1908 g, 0.0012 mol) and initiator APS (1 wt%) is prepared in 20 mL of

deionized water. Then the mixture solution, after degassing for 10 min with N₂, is sandwiched between two flat glass plates with 1.0 mm interval to synthesize covalently crosslinked P(AAm-VP) hydrogel with TPE-PSPMA at 60°C for 2 h. Afterward, the as-prepared hydrogels are immersed into deionized water to remove unreacted monomers.

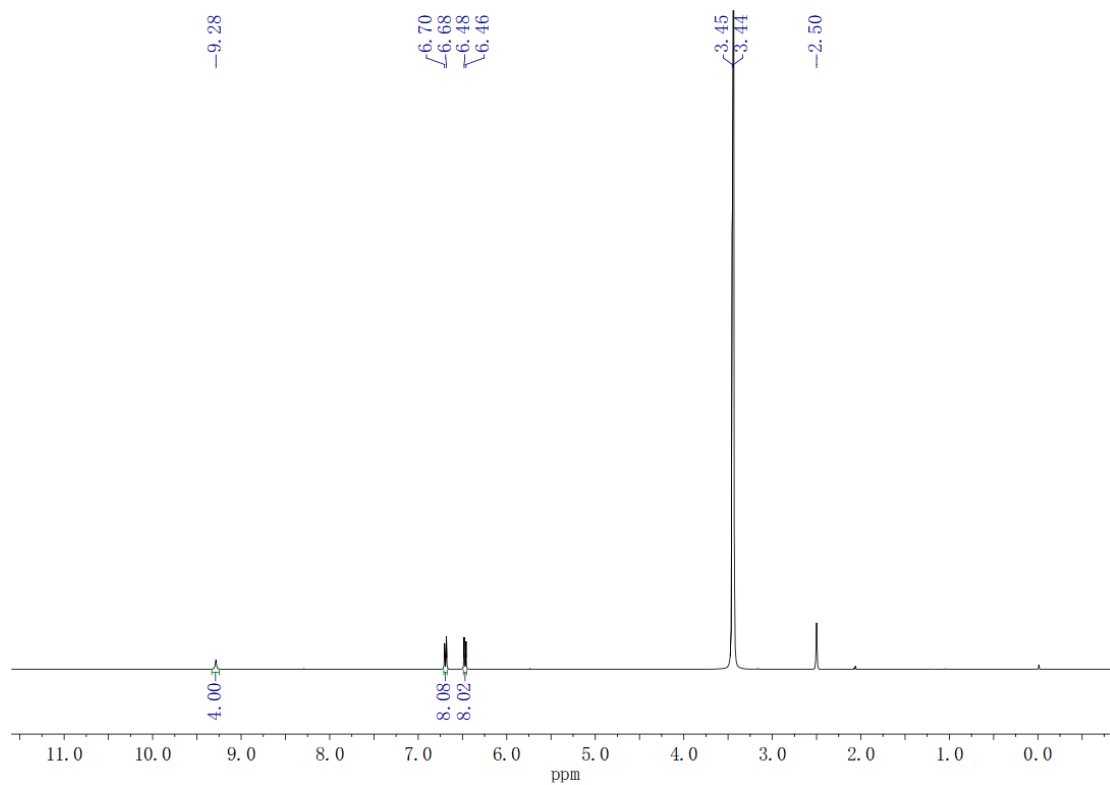


Fig. S1 ^1H NMR spectra of TPE-4OH measured in $\text{DMSO-}d_6$ at room temperature.

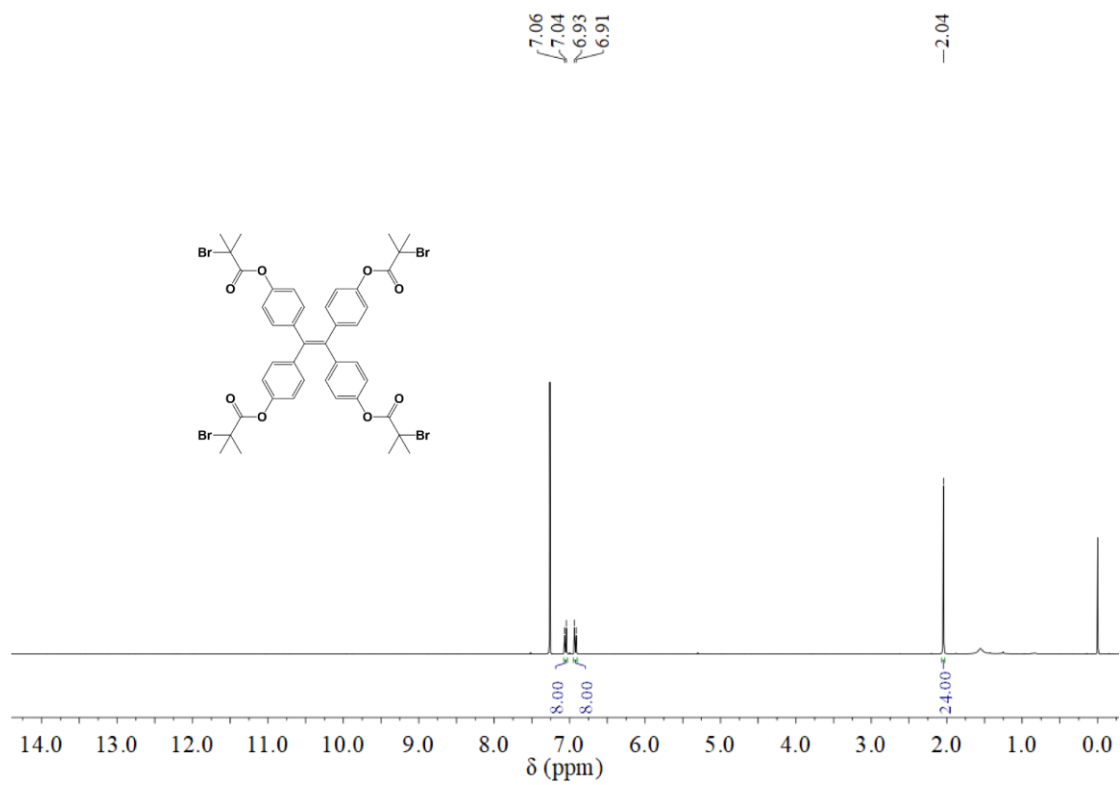


Fig. S2 ^1H NMR spectra of TPE-Br measured in CDCl_3 at room temperature.

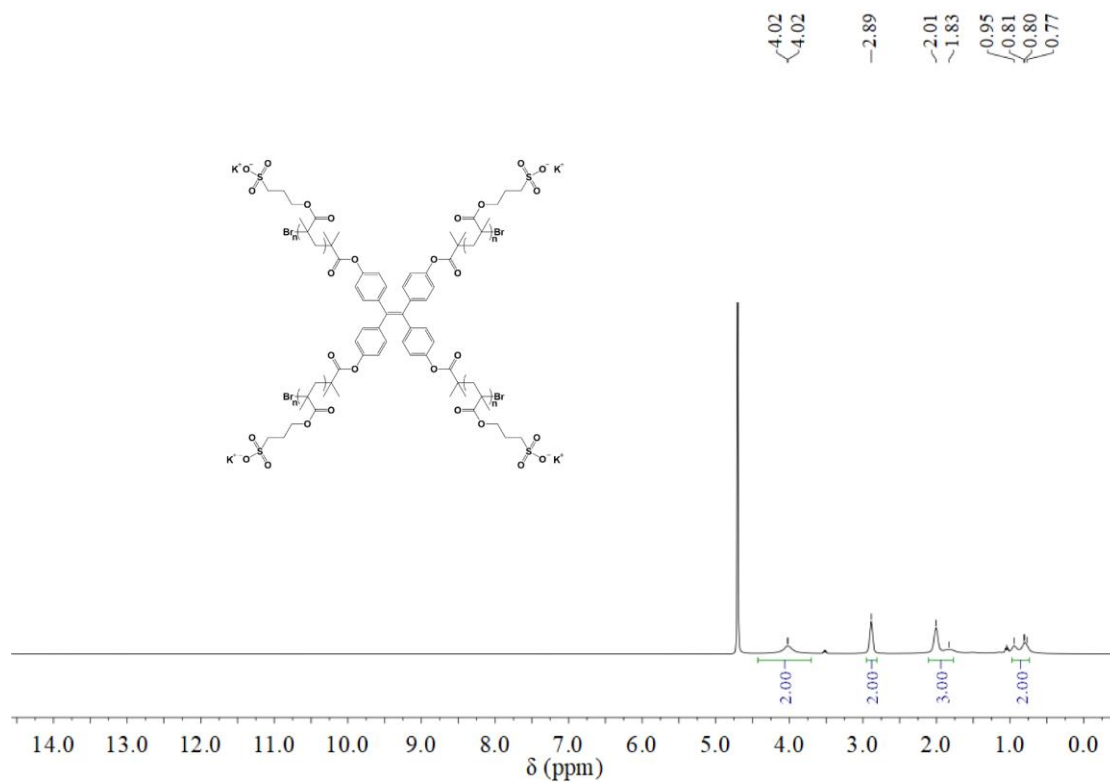


Fig. S3 ^1H NMR spectra of TPE-PSPMA.

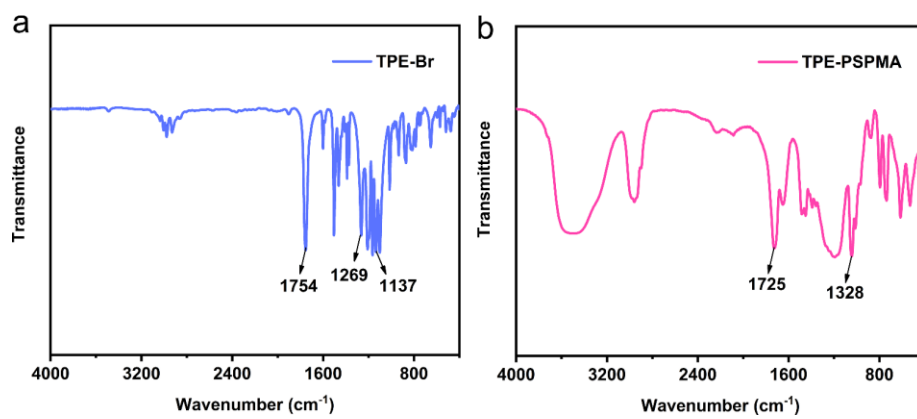


Fig. S4 FT-IR spectra of TPE-Br (a) and TPE-PSPMA (b).

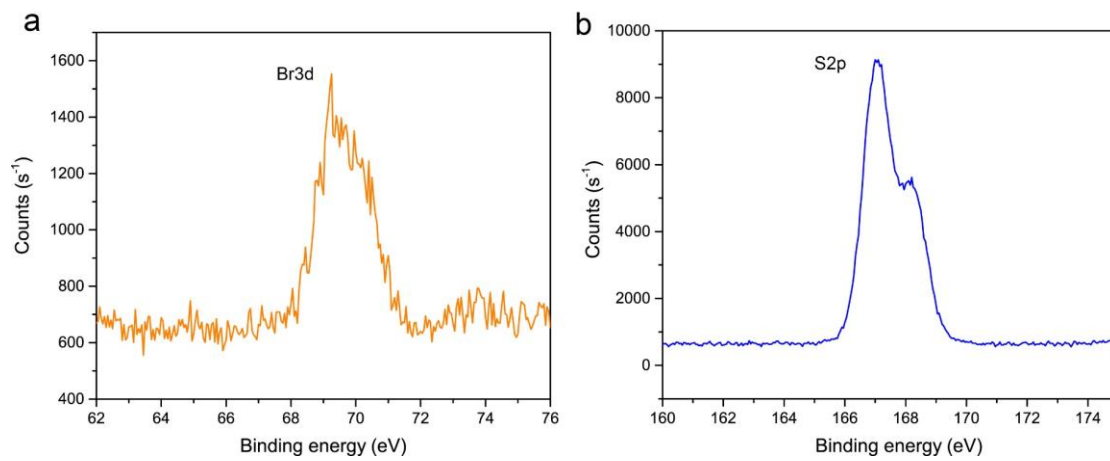


Fig. S5 XPS spectra of TPE-PSPMA.

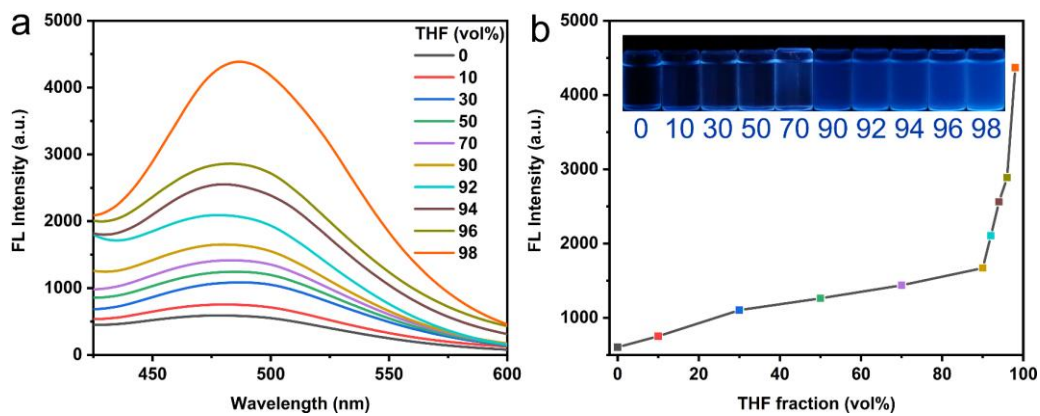


Fig. S6 (a) Fluorescence emission spectra of TPE-PSPMA (0.5 mg/mL) in different THF fractions. (b) The plot of fluorescence intensity changes of TPE-PSPMA against varied THF fractions from 0 to 98% and images under UV light (365 nm) in a THF/H₂O system.

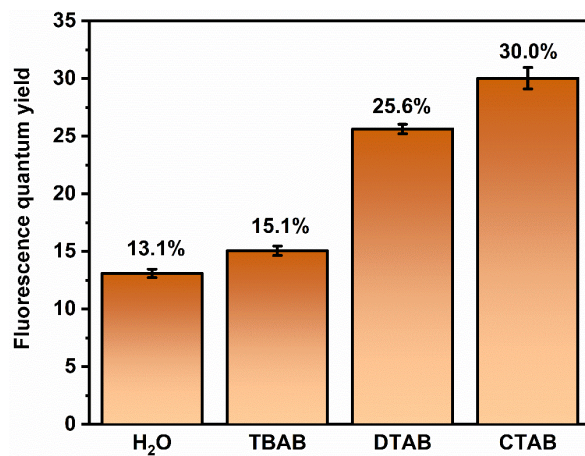


Fig. S7 Fluorescence quantum yield of TPE-PSPMA with the addition of different cations (TBAB, DTAB, CTAB).

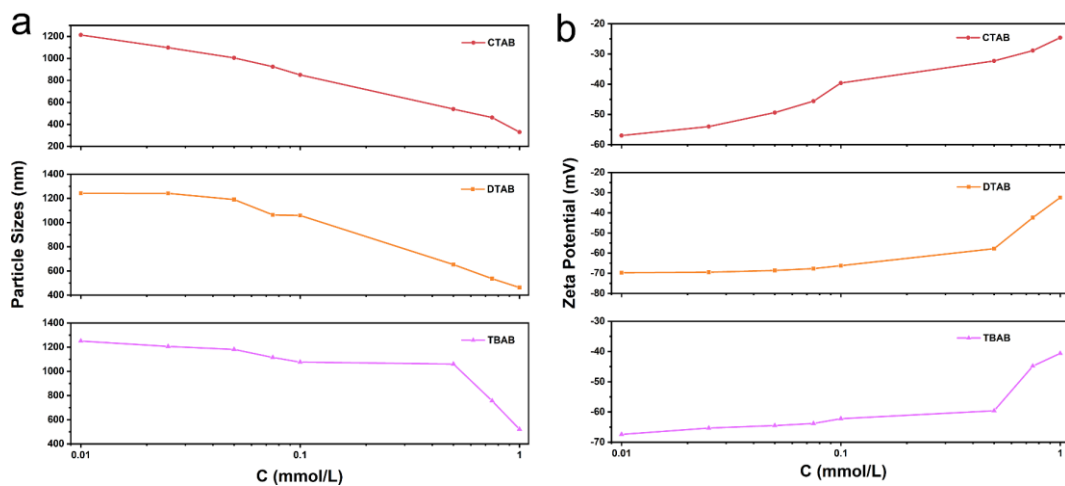


Fig. S8 Particle sizes (a) and zeta potential (b) changes of TPE-PSPMA along with the concentration of CTAB, DTAB and TBAB from 0.01 to 1 mmol L⁻¹, respectively.

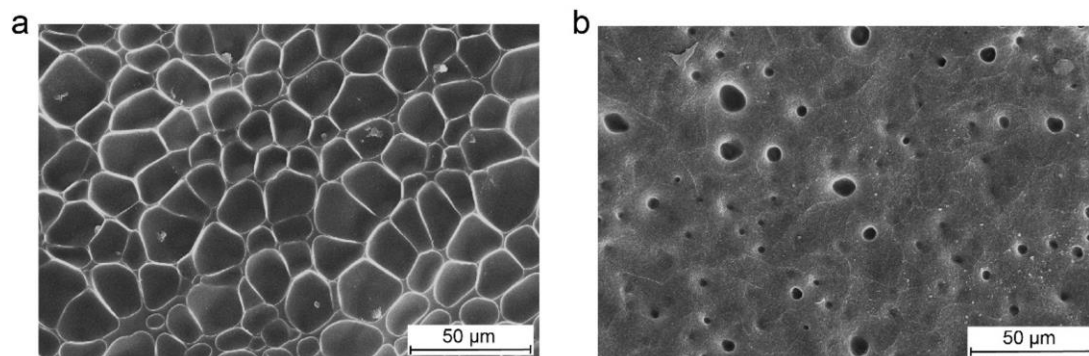


Fig. S9 SEM images of AIE-based P(AAm-VP) hydrogel before (a) and after (b) tuning with cation of CTAB.

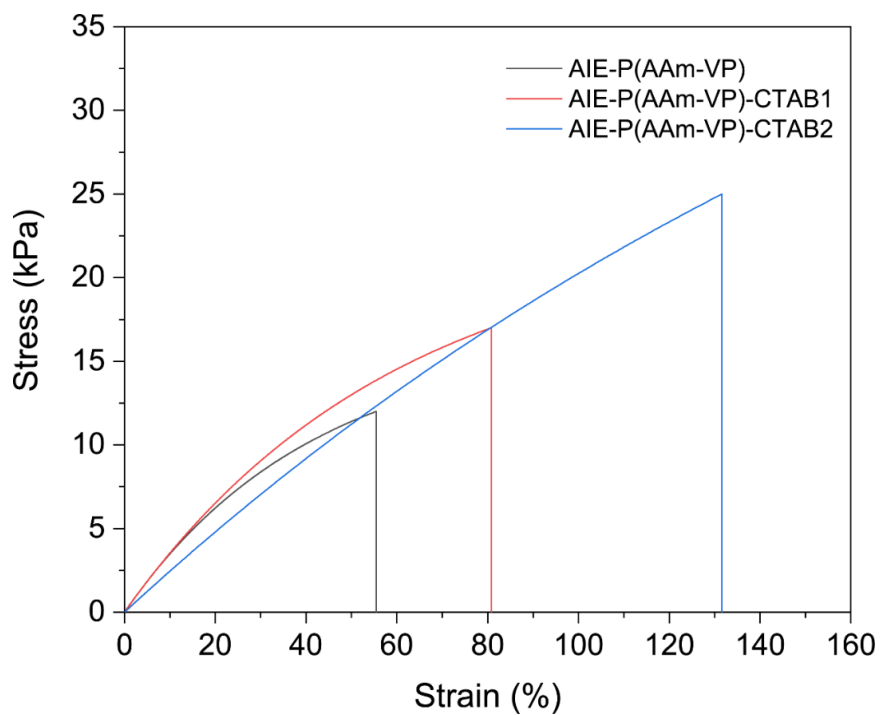


Fig. S10 The stress-strain curves of AIE-based P(AAm-VP) hydrogels treated with deionized water and CTAB solutions with concentrations of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ (red line) and $1.0 \times 10^{-2} \text{ mol L}^{-1}$ (blue line) for 6 h, respectively.