Electronic Supporting Information

A "self-shrinking" supramolecular hydrogel with a 3D shape memory performance from an unnatural amino acid derivative

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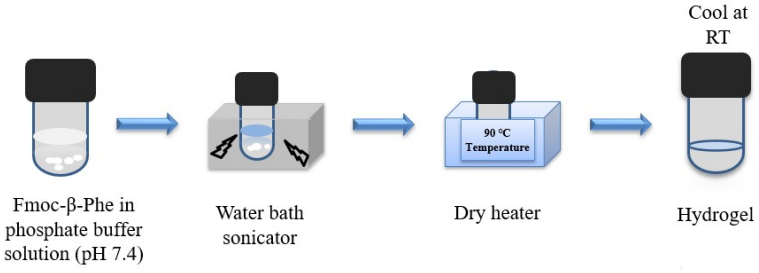
Experimental section

Materials

Fmoc-β-Phe and Rhodamine 6G were purchased from Sigma Aldrich. Brilliant blue was procured from Parchem. Congo red was procured from Tokyo chemical industry. Methylene blue, Indigo carmine and crystal violet were obtained from S D Fine-Chem limited, India. Alizarin red S was procured from Loba Chemie (India).

Supramolecular hydrogel preparation

Fmoc-β-Phe hydrogel was prepared using annealing approach. Fmoc-β-Phe (5 mg/ml) was dispersed in 50 mM phosphate buffer solution (pH 7.4) using ultrasonic bath for two to three minutes until it formed turbid solution. After that, the hydrogel solution was maintained at 90°C for 15 minutes in glass vial. Thenceforth, glass vial was kept at room temperature for the formation of a stable hydrogel. Different concentration of Fmoc-β-Phe was used for the assessment of the minimum gelation concentration (MGC). All Fmoc-β-Phe hydrogels were prepared several times to check for reproducibility and for other experiments. For shape



memory experiments, fluorescence (representation of square shape) and CD (representation of rectangular shape) quartz cell was used instead of conventional circular glass vial.

Thermal stability of the Hydrogel (Tgel):

Fmoc-β-Phe hydrogel was prepared using the procedure stated in hydrogel preparation. The prepared hydrogel vial was placed in a dry block heater. The temperature was raised from 30 ºC and equilibrated for 5 mins at each desired temperature (5ºC interval). The digital images were captured at the desired temperature by taking of the sample vail and immediately put back in the dry block heater. This monotonous course of action was repeated until hydrogel completely dissolved.

FT-IR measurements

FTIR spectra of normal and shrunken hydrogel of Fmoc-β-Phe were recorded using PerkinElmer 1000 spectrometer. Fmoc-β-Phe shrunken hydrogel was prepared before two days of analysis. The Fmoc-β-Phe fresh hydrogel was made on the day of the analysis. The concentration of gelator was 5 mg/ml. A small quantity of hydrogel was carefully taken using a spatula and air-dried on CaF_2 plates. The IR spectra were recorded within the range of 4000-400 cm^{-1} at 8 cm^{-1} spectral resolution.

Fluorescence measurements

Fluorescence experiments were carried out using Carry (eclipse) fluorescence spectrometer. Fmoc-β-Phe hydrogel solution was transferred from 90°C to directly into a 400 μL quartz cell and time-dependent fluorescence emission at 285 nm, associated with Fmoc-moiety, was initiated. Fluorescence emission spectra were collected at 25ºC. The emission and excitation slit width was 2.5 nm. The same method was followed for Fmoc-β-Phe shrunken hydrogel.

UV-Visible spectroscopic measurement

Preheated Fmoc-β-Phe solution in 50 mM phosphate buffer (pH 7.4) was transferred to quartz cell with 1mm pathlength. After 30 mins rest at room temperature (normal hydrogel), the UV-Visible spectrum was recorded on CARY-5000 (Agilent Technologies, Inc.) spectrophotometer at room temperature. The wavelength was scanned from 800 to 200 nm at a rate of 100nm/min. After 5 days, the experiment was repeated for shrunken Fmoc-β-Phe hydrogel

Dye removal study

To demonstrate the dye removal capability of Fmoc-β-Phe self-shrinking hydrogel, brilliant blue was used initially. Here, Fmoc-β-Phe hydrogel was prepared using 50 mM phosphate buffer (pH 7.4) containing 0.5M of brilliant blue and digital images were captured at different time intervals. For quantitative dye release study, methylene blue, crystal violet and rhodamine 6G as cationic dyes and congo red, indigo carmine and alizarin red S as anionic dyes were used. Fmoc-β-Phe gel was prepared using 50 mM phosphate buffer (pH 7.4) containing 0.5 M of dyes except alizarin red S where 0.1 M was used due to solubility limit. The same annealing method was performed to make hydrogel. After 24 hrs, 400 μL of liquid separated out from the shrunken hydrogel was diluted with phosphate buffer (pH 7.4) to get the final volume of 4 mL. The absorbance spectra for these solutions were measured in the visible region on SPECORD 200 PLUS (Analytik Jena Corp, India) spectrophotometer. For control, 400 μL of dye stock solution was diluted with buffer to get 4mL and absorption spectra were measured as stated before. The percentage of dye release was calculated by comparing the absorbance of test dye solutions with control dye solution at the wavelength maximum of 494nm, 612nm, 508nm, 667nm, 593nm and 530nm for congo red, indigo carmine, Alizarin red S, methylene blue, crystal violet and rhodamine 6G, respectively.

Rheology

The normal and shrunken Fmoc-β-Phe hydrogels were subjected to strain and frequency sweep experiments on a Anton Paar MCR-502 rheometer at room temperature. Rheometer was operated in oscillatory mode with a 25 mm parallel plate geometry with a gap of 1mm between lower and upper plate. The strain sweep was carried out from 0.1 to 100 % at a fixed frequency of 1 rad/s. Frequency sweep measurement was done in the range of 0.1 – 100 rad/s at a constant strain (0.5 %).

FE SEM

A small amount of normal and shrunken Fmoc-β-Phe hydrogels were placed on the glass plate and dried at room temperature. The dried samples were gold sputter before scanning. High resolution SEM images were captured on a FEI quanta FEG 200 FE SEM (FEI, Netherland) at an accelerating voltage of 10 keV with the magnification of 20kx and 100kx.

Figure S1 Digital image showing the Fmoc-β-Phe hydrogel sticking on the top of the vial after inversion.

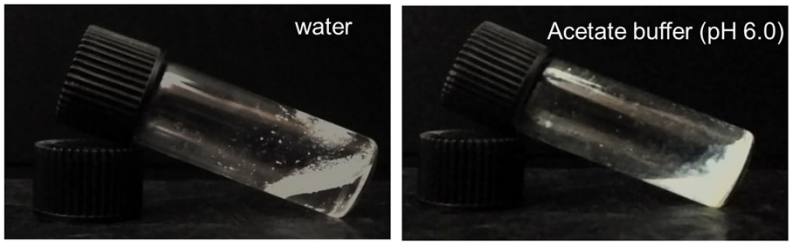


Figure S2 Digital image of Fmoc-β-Phe in water and acetate buffer (pH 6.0)

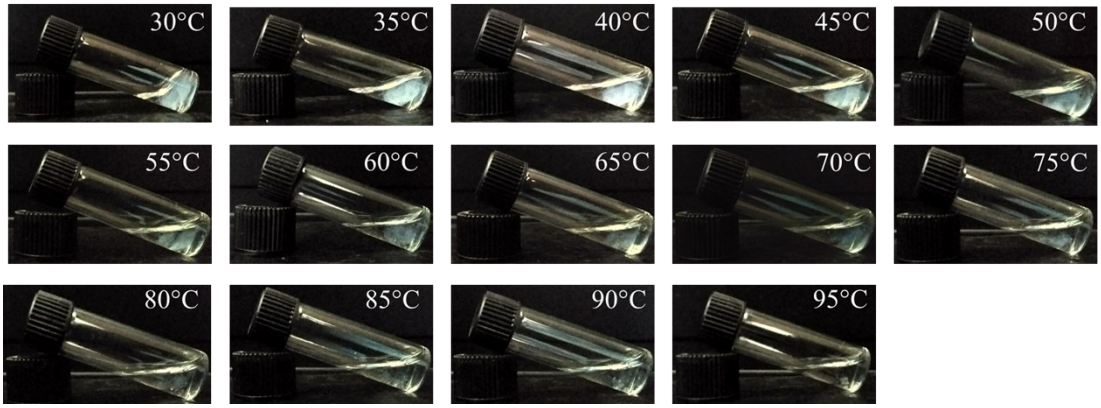


Figure S3 Digital images of Fmoc-β-Phe hydrogel at different temperatures.

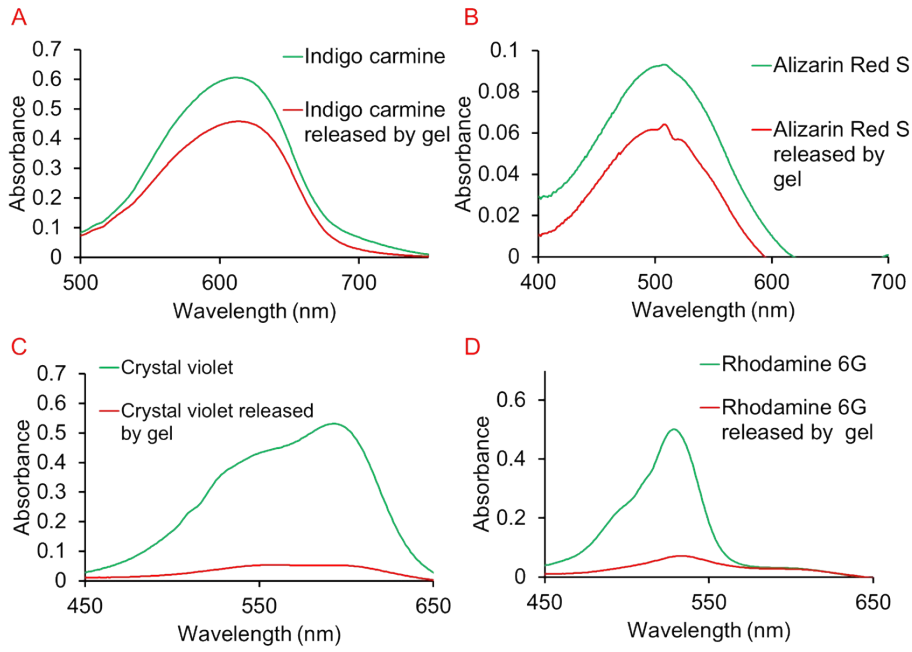


Figure S4 Visible spectra of anionic dyes, namely Indigo carmine (A) and Alizarin Red S (B), and cationic dyes, namely Crystal violet and Rhodamine 6G, alone and after their release from the Fmoc-β-Phe hydrogel after shrinking.