Supplementary Material (ESI) for Chemical Communications

A Supramolecular Hydrogel that Responds to Biologically Relevant Stimuli

Dibyendu Khatua[1], Rabindranath Maiti[2], and Joykrishna Dey[1*]

[1]Department of Chemistry, [2]Central Research Facility

Indian Institute of Technology, Kharagpur-721 302

India

Supporting Information:

Materials. Glycine, L-alanine, L-valine, D,L-valine, dodecylamine, and octylamine were purchased from SRL and were used without further purification. Sodium hydroxide (S.D. fine, Mumbai, India), sodium chloride (Qualigens, Mumbai, India) and hydrochloric acid from Ranbaxy (New Delhi, India) were used as received. Acryloyl chloride, warfarin, coumarin-1, and sodium dodecyl benzene sulphonate were used as obtained from Aldrich. Sodium dodecyl sulphate was purchased from SRL and was used after three times recrystallization from acetone. All solvents used were of good quality commercially available and whenever necessary purified, dried and distilled fresh before use. Double distilled water was used for all the experiments.

The amphiphiles employed in this study were synthesized according to the procedure reported earlier by us.[1] Briefly, N-acryloyl-L-valine was obtained from the reaction of L-valine and acryloyl chloride in aqueous ethanol in the presence of a base. Sodium N-acryloyl-L-valinate was prepared by stirring equimolar mixtures of sodium methoxide and N-acryloyl-L-valine in dry methanol for 4 hours at 0-5 ^{o}C. The salt was obtained after evaporation of the solvent. It was recrystallized from ethanol-acetone mixture. Sodium N-(n-dodecyl-2-aminoethanoyl)-L-valinate was synthesized by Michael

addition reaction of n-dodecylamine with one mole equivalent of sodium N-acryloyl-L-valinate. The other amphiphiles sodium N-(n-dodecyl-2-aminoethanoyl)-L-glycinate, sodium N-(n-dodecyl-2-aminoethanoyl)-L-alaninate, sodium N-(n-dodecyl-2-amino-ethanoyl)-DL-valinate, sodium N-(n-octyl-2-aminoethanoyl)-L-valinate were prepared in the same way as described above.

Gelation test of water. Stock solutions of the amphiphiles (**1**-**5**) were made in methanol. Appropriate volumes of the stock solutions of the amphiphiles were mixed in a 4-mL glass vial and the solvent was evaporated to dryness either by passing N_2 gas or by heating in water bath. A known volume of water was then added. The solid was dispersed either by gentle hand shaking or by heating at 70 ^{o}C. Although gelation does not require heating but it becomes slower when left at room temperature. The gelation test was performed with samples containing different [amphiphile]/[SDS] ratios in the range 0.2 to 1.0. The gelation was confirmed by inversion test of the vial.

Determination of gel melting temperature. The gel-sol transition temperature (T_m) was determined by measuring turbidity at 450 nm at different temperature. The turbidity was observed to increase with temperature. The temperature at which the turbidity increased strongly was recorded as T_m.

Small angle X-ray diffraction (SA-XRD). For SA-XRD measurements were performed using cast films of the gel. Spreading a few drops of the dispersion on a glass slide and slowly drying in atmosphere at room temperature prepared the films. The SA-

XRD patterns of the cast films were measured on a PAN alytical (PW 3040/60), X' pert PRO. (Holland) diffractometer using Co-Kα (178.9 pm) radiation (40 kV, 30 mA). The spectrum was measured at room temperature between 1^{o} and 40^{o} in the 2θ scan mode in steps of 0.01^{o} in 2θ. .

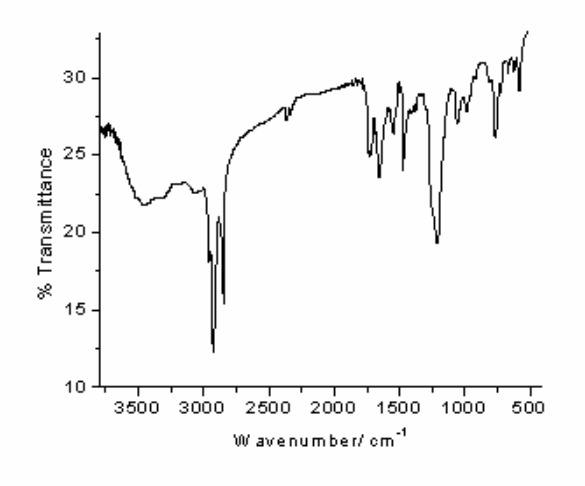

Fig. S1 FTIR spectra of xerogel of **1**.

FT-IR spectra. The FT-IR spectra were measured with a Perkin-Elmer 1760X FT-IR spectrometer. The dry gel film was ground carefully with KBr and pellete was made. The spectrum was average of 32 scans. The spectrum can be seen in Fig. S1.

Fluorescence spectra. Steady-state fluorescence spectra were recorded with a Perkin Elmer LS-55 luminescence spectrometer equipped with filter polarizers that uses the L-format configuration using a 1-cm^2 quartz cuvette. Aqueous solutions of warfarin, WF (2x 10^{-5} M), and coumarin-1, C-1 (1x 10^{-5} M) were used for sample preparation. The samples containing C-1 and WF were excited at 380 nm and 300 nm, respectively. The

excitation slit width was kept fixed at 2.5 nm for all measurements. All spectra were blank subtracted. Figure 6S shows the plot of relative fluorescence intensity (F/F_o) at the emission maximum of C-1. The inflection point corresponds to the T_m value determined by turbidity measurement (Fig. S2).

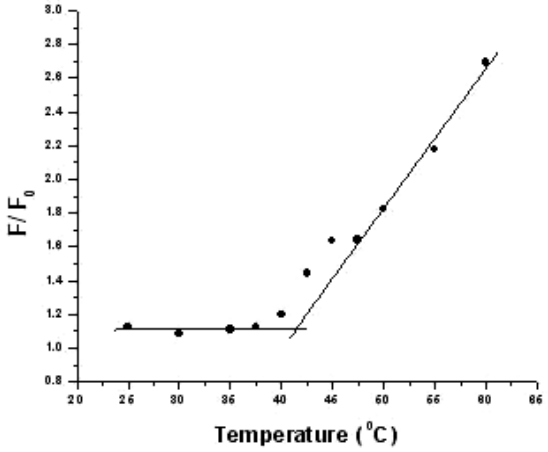

Fig. S2 Plot of relative fluorescence intensity **(**F/F_o) of C-1 against temperature.

Circular dichroism (CD) spectra. CD spectra of the samples were recorded with a Jasco-810 spectropolarimeter using 10 mm pathlength rectangular quartz quvette. The spectrum is an average of 4 scans. The spectrum was corrected by the spectrum of the corresponding reference blank.

Scanning electron microscopy (SEM). For SEM measurements a thin layer of the gel was cast on a thoroughly cleaned aluminium foil and dried in air. A layer of gold was spluttered on the sample. The specimen was analyzed on a scanning electron microscope, JEOL model JSM-5800 (Japan)

References.

1 D. Khatua, J. Dey, *Langmuir*, 2005, **21**, 109.