Striking influence of SWNT-COOH in self-assembled gelation

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Electronic Supplementary Information (ESI)

Materials. All amino acids, palmitic acid, dicyclohexylcarbodiimide (DCC), 4-*N,N*-(dimethyl)aminopyridine (DMAP), 1-hydroxybenzotriazole (HOBT) and all the solvents were purchased from SRL India. 1,1′-carbonyl diimidazole (CDI), thionyl chloride, sodium hydroxide were purchased from Spectrochem, India. Single walled carbon nanotubes (SWNT, 1-2 nm diameter), acid functionalized single walled carbon nanotubes (SWNT-COOH, 1-2 nm diameter, functional content 2.73 wt%) were procured from Cheap Tubes. Inc. Purity of the sample is >90 wt% and ash <1.5 wt%. All deuteriated solvents for NMR experiments were obtained from Aldrich Chemical Co. Thin layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates. ^{1}H NMR spectra were recorded in AVANCE 300 MHz (Bruker) spectrometer. Mass spectrometric data were acquired by electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer (Micromass). Elemental analyses were performed on Perkin Elmer 2400 CHN analyzer.

Synthetic procedure. All the dipeptide based gelators were synthesized following the reaction conditions as reported by us previously.[1] Briefly, methyl ester protected L-amino acid was coupled with C-16 long chain acid chloride in dry chloroform and dry pyridine. The ester protected long chain amide was then purified through column chromatography using 60-120 mesh silica gel and ethyl acetate/hexane as eluent. The product was hydrolyzed using 1N NaOH (1.1 equivalent) in MeOH for 6h with stirring at room temperature. Solvents were

removed on a rotary evaporator, and the mixture was diluted with water and then washed with ether, followed by acidification by 1N HCl to get the corresponding carboxylic acid. This acid was then coupled with another methyl ester protected L-amino acid by using CDI (1 equivalent) in dry dichloromethane (DCM). The purified product was obtained by column chromatography using 60-120 mesh silica gel and ethyl acetate/toluene as eluent. The product was then subjected to hydrolysis by 1N NaOH (1.1 equivalent) in MeOH for 6h with stirring at 45-50 $^{\circ}$C to obtain amphiphilic dipeptides with free carboxylic acid end. DCC was used as coupling agent instead of CDI when one of the amino acid was L-tryptophan.

Characterization of amphiphilic gelators. Data for gelators **1-5** was reported earlier.[1]

Preparation of soft nanocomposites.

1 mg of *f*-SWNT was precisely weighed in a screw cap glass vial with internal diameter of 10 mm. To it 1 mL of gelator solution of required concentration in toluene was added and tip sonicated for 8 min at 30% power output. The sol was then kept at static condition for 15 min. Now the composite material with *f*-SWNT concentration 0.1% w/v formed nanohybrid gel which was stable to inversion of glass vials. The gel was then properly diluted with the same gelator solution to get nanocomposites with different *f*-SWNT concentration.

Determination of gel-to-sol transition temperature (T_{gel}) of the nanocomposites.

The gel-to-sol transition temperature (T_{gel}) was determined by placing the hybrid gel containing glass vial (i.d. 10 mm) in thermostatted oil bath and slowly the temperature was raised at a rate of 2 °C/min. The T_{gel} was defined as the temperature (± 0.5 °C) at which the gel melted and started to flow.

Differential scanning Calorimetry (DSC) Study. DSC was carried out on a Perkin-Elmer Diamond DSC. 30 mg of *f*-SWNT-gel composite in toluene was placed in a large volume capsule (LVC) and then it was sealed. The sample LVC pan was placed in the DSC apparatus together with an empty LVC pan as reference. The pans were cooled to 10 °C, and aged for

30 min at this temperature. Heating scans were then recorded from 20 °C to 90 °C at a scan rate of 1 °C/min.

UV-vis-NIR study. The nanohybrid gel in toluene obtained after the sonication was used for UV-vis-NIR experiment. In this case, a background correction was performed with the toluene solution of the respective amphiphiles and the spectroscopic study was monitored using Varian Cary 5000 spectrophotometer.

Microscopic study. Field emission scanning electron microscopy (FESEM) images were obtained on a JEOL-6700F microscope. A drop of native gel (at MGC) and gel composite was placed on a piece of cover slip and dried for few hours under vacuum before imaging. The morphology of the dried gel was also studied by using transmission electron microscopy (TFM) on a JEOL JEM 2010 high resolution microscope operated at an accelerated voltage 200 kV. For TEM images a drop of the nanocomposites gel was placed on a 300-mesh Cu-coated TEM grid and dried under vacuum for 4 h before taking the image. For 0.3 % w/v gelator solution 3 mg of amphiphile was dissolved in 1 mL of toluene by heating and kept undisturbed for 1h at room temperature. Then one drop of that solution was placed either on a piece of cover slip or a 300-mesh Cu-coated grid for SEM/TEM study.

Rheology. The rheological experiments were carried out in cone and plate geometry (diameter was 40 mm) on the rheometer plate using an Advanced Rheometer AR 2000 (TA Instruments, USA). The native gel **1** and the CNT-gel composite of gelator **1** and **5** were scooped on the rheometer plate so that there was no air gap with the cone. Frequency sweep experiment was performed as a function of angular frequency (0.1-200 rad/s) at fixed strain of 0.01% at 25 ºC and the storage modulus ($G^{/}$) and the loss modulus ($G^{//}$) was plotted against angular frequency.

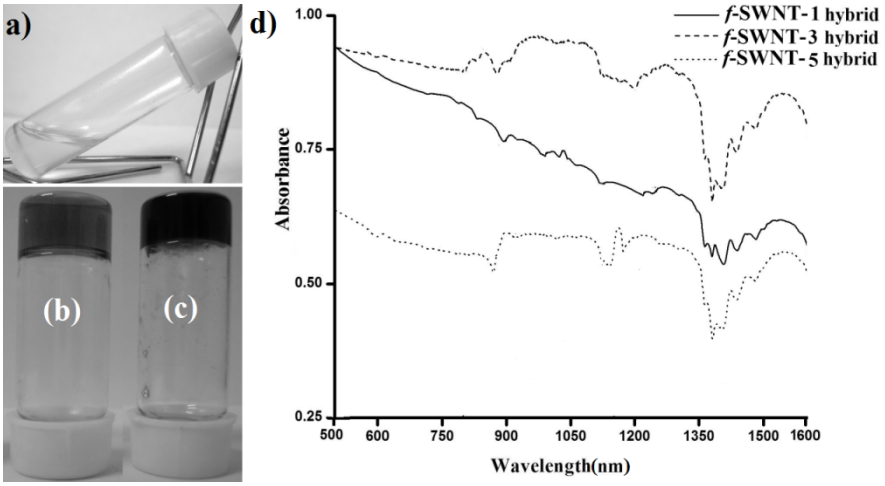

Fig. S1 Photograph of (a) the solution of **1** in toluene (0.3% w/v), (b) nanohybrid gel of **1** (0.5% w/v) with *f*-SWNT (0.01% w/v), (c) nanohybrid gel of **1** (0.3% w/v) with *f*-SWNT (0.1% w/v), (d) UV-vis-NIR spectra of *f*-SWNT-**1**, *f*-SWNT-**3**, *f*-SWNT-**5** hybrid in toluene.

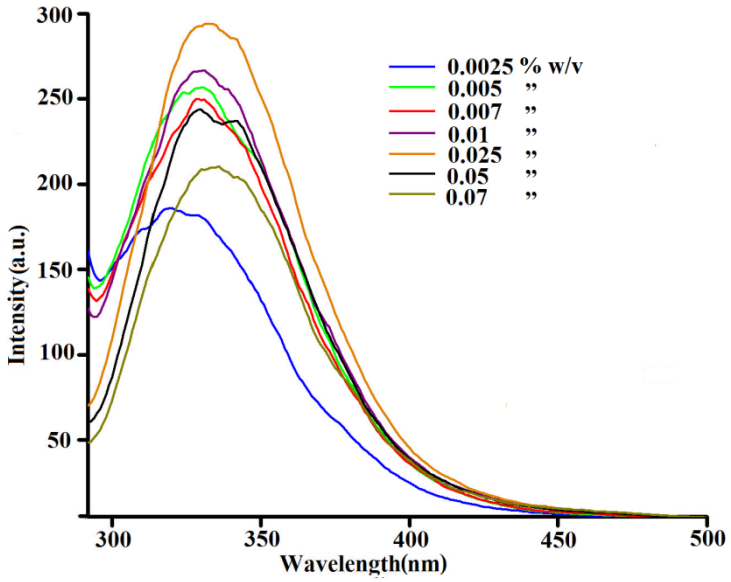

Fig. S2 Fluorescence spectra of *f*-SWNT-**1** nanocomposite in toluene at fixed *f*-SWNT concentration (0.0025% w/v) with variable gelator concentration.

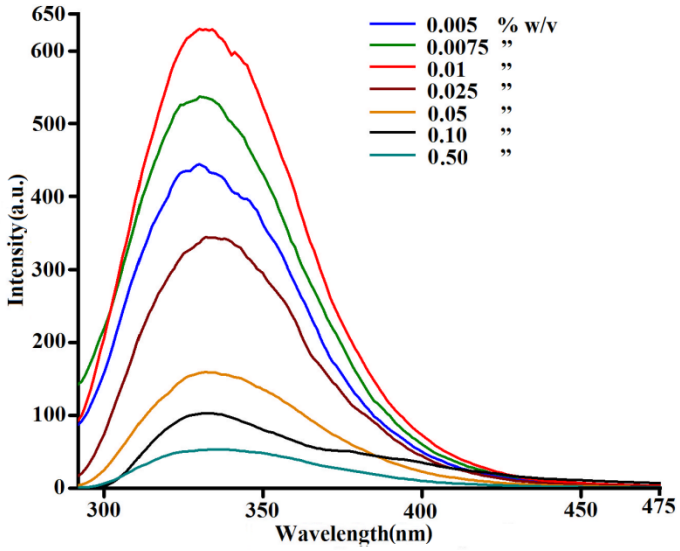

Fig. S3 Fluorescence spectra of *f*-SWNT-**5** nanocomposite in toluene at fixed *f*-SWNT concentration (0.005% w/v) with variable gelator concentration.

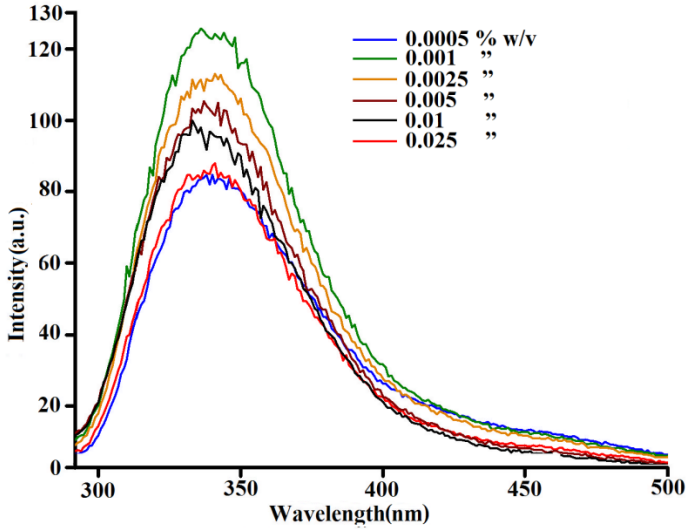

Fig. S4 Fluorescence spectra of *f*-SWNT-**1** nanocomposite in toluene at fixed gelator concentration (0.3% w/v) with variable *f*-SWNT concentration.

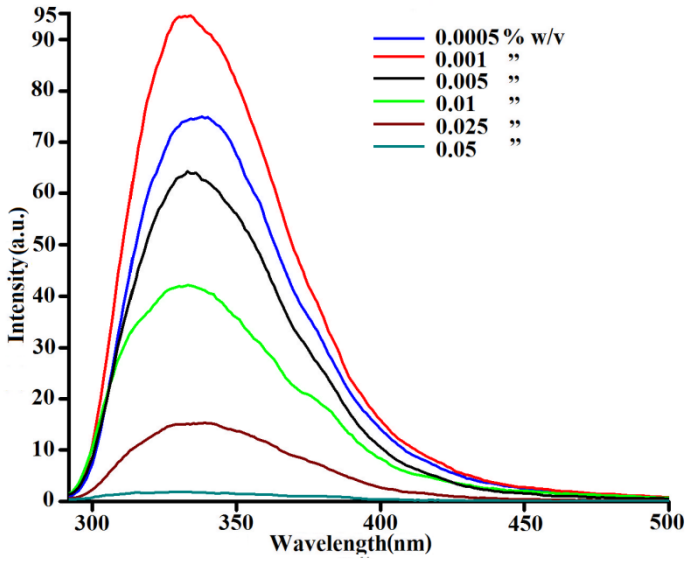

Fig. S5 Fluorescence spectra of *f*-SWNT-**5** nanocomposite in toluene at fixed gelator concentration (0.1% w/v) with variable *f*-SWNT concentration.

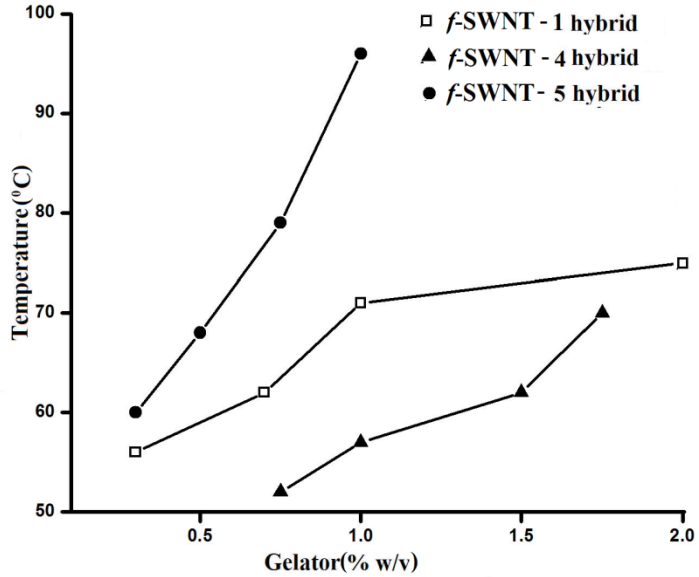

Fig. S6 Plot of gel-to-sol transition temperature (T_{gel}) with gelator concentration at fixed *f*-SWNT (0.1% w/v).

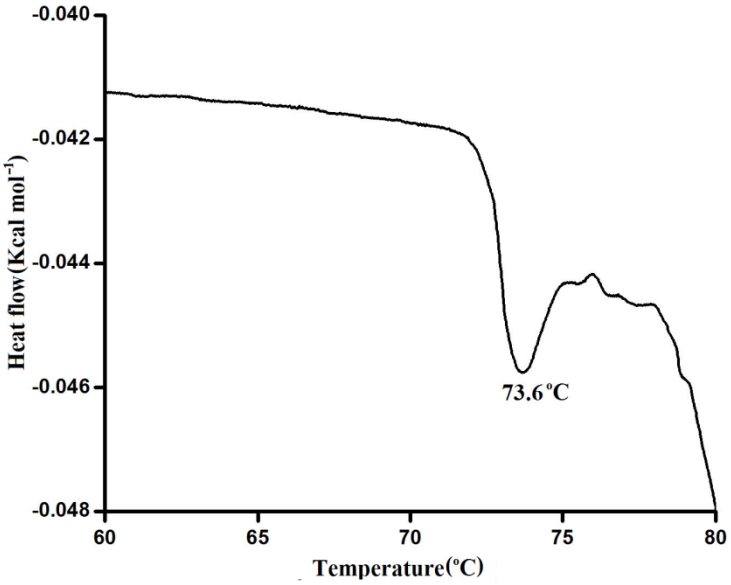

Fig. S7 DSC thermogram (endothermic) of *f*-SWNT-**1** nanocomposite with 1.0% w/v gelator concentration and 0.1% w/v *f*-SWNT concentration.

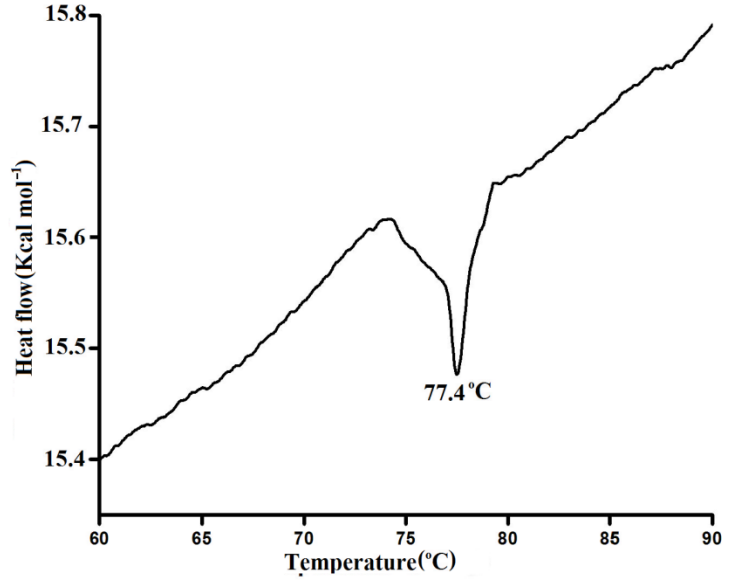

Fig. S8 DSC thermogram (endothermic) of *f*-SWNT-**5** nanocomposite with 0.75% w/v gelator concentration and 0.1% w/v *f*-SWNT concentration.

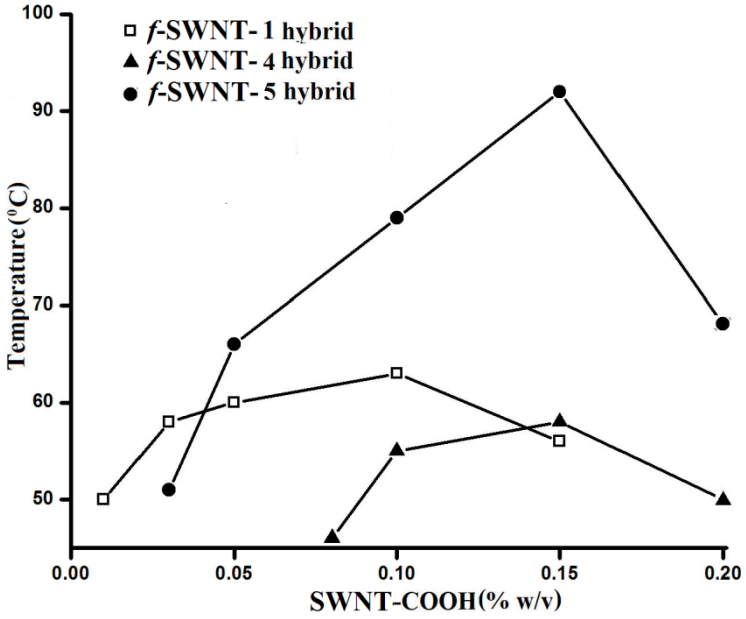

Fig. S9 Plot of gel-to-sol transition temperature (T_{gel}) with *f*-SWNT concentration at fixed gelator concentration (0.7% w/v).

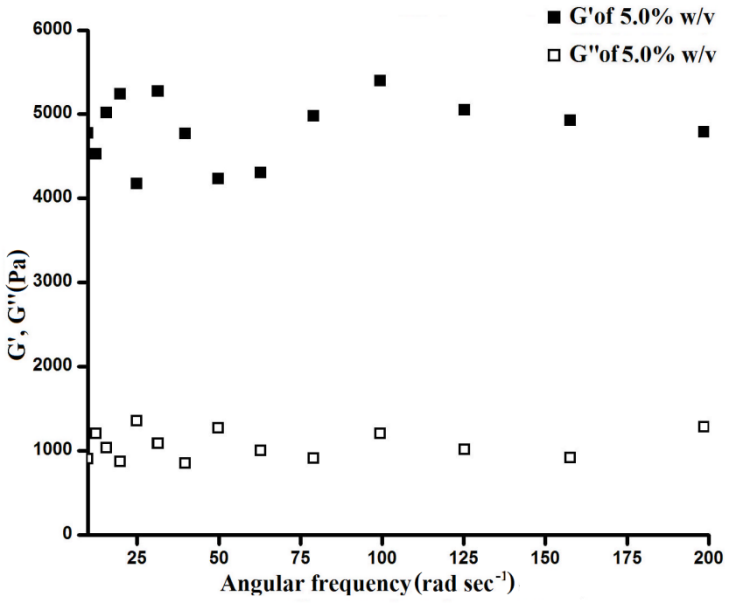

Fig. S10 Plot of storage modulus ($G^{/}$) and loss modulus ($G^{//}$) of gelator **1** in toluene at 5% w/v.

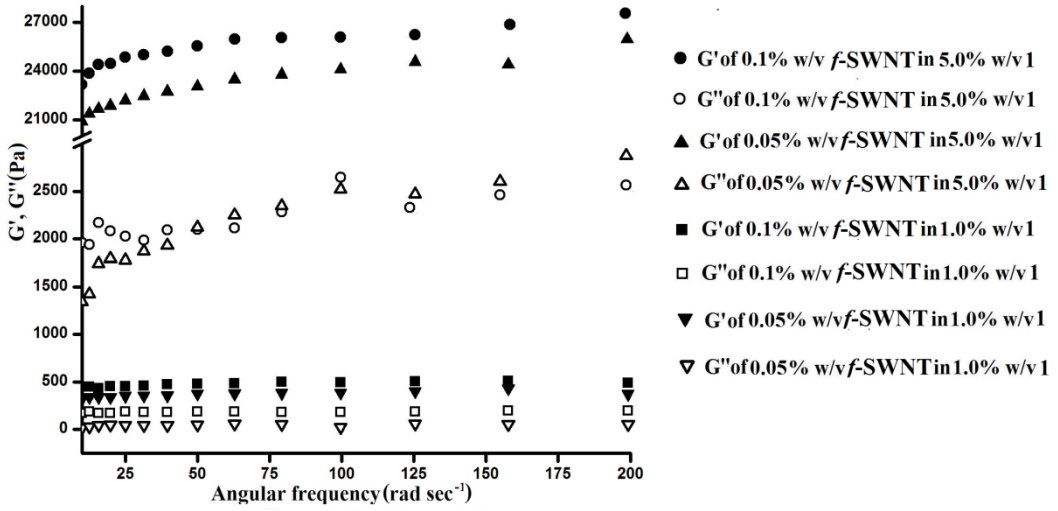

Fig. S11 Plot of storage modulus ($G^{/}$) and loss modulus ($G^{//}$) of *f*-SWNT-**1** composite gel as a function of angular frequency at 0.01% at different gelator (1% and 5% w/v).and *f*-SWNT concentration (0.05% and 0.1% w/v).

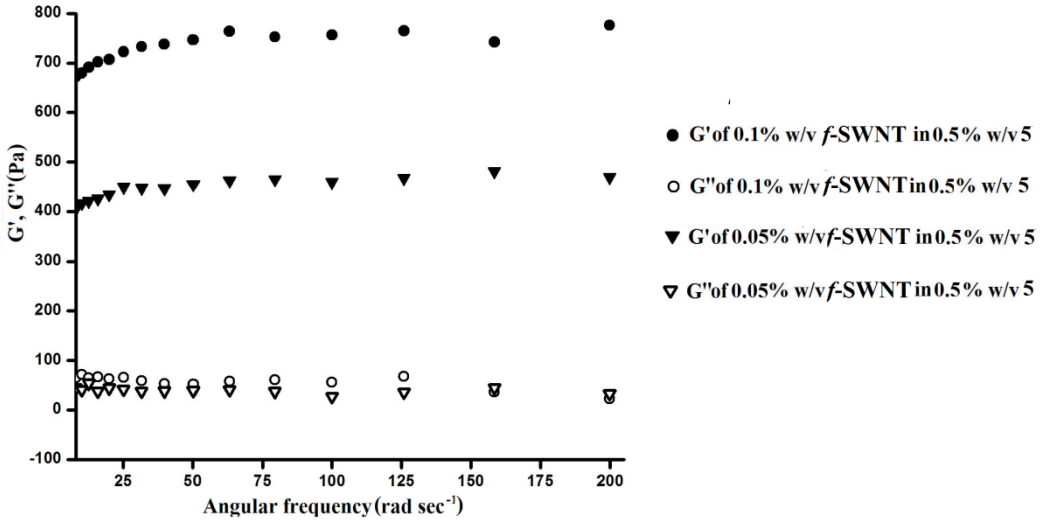

Fig. S12 Plot of storage modulus ($G^{/}$) and loss modulus ($G^{//}$) of *f*-SWNT-**5** composite gel as a function of angular frequency at 0.01% at different *f*-SWNT concentration (0.05% and 0.1% w/v).

References:

1. T. Kar, S. Debnath, D. Das, A. Shome, P. K. Das, *Langmuir*, **2009**, *25*, 8639.