Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Self-assembly of monohydroxy Terpenoid Lupeol yielding nano-Fibers, Sheet and Gel: Environmental and drug Delivery application

Saikat Kumar Panja, Soumen Patra, Braja Gopal Bag*

Department of Chemistry and Chemical Technology

Vidyasagar University

Midnapore, 721102, West Bengal, India

Email: brajagb@gmail.com

Table of contant **Pages**

1. Energy minimized structure of lupeol

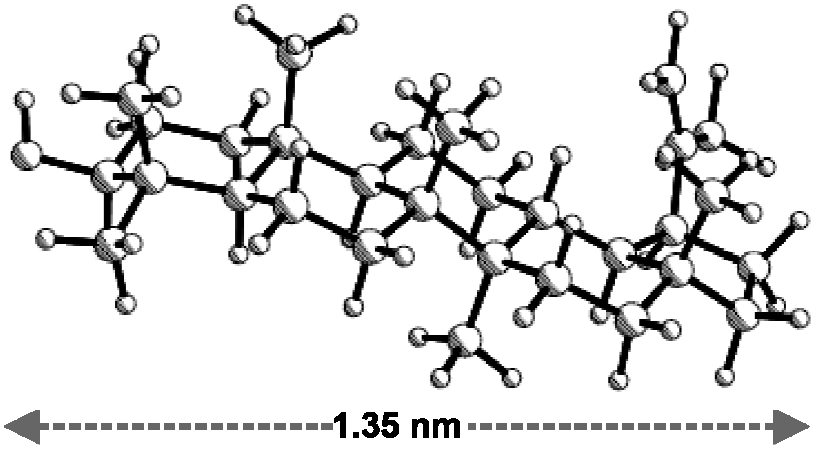


Figure S1: Energy minimized structure of Lupeol 1 using MMX force field as implemented in PCMODEL version 9.2 (Serena software)®.

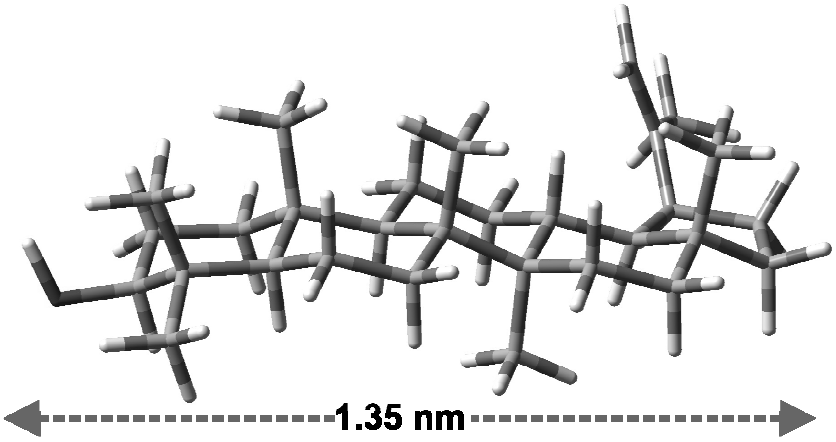


Figure S2: Energy minimized structure of Lupeol 1 obtained from DFT using (Gaussian 09 software)®.

2. T_{gel} vs. Concentration Plots:

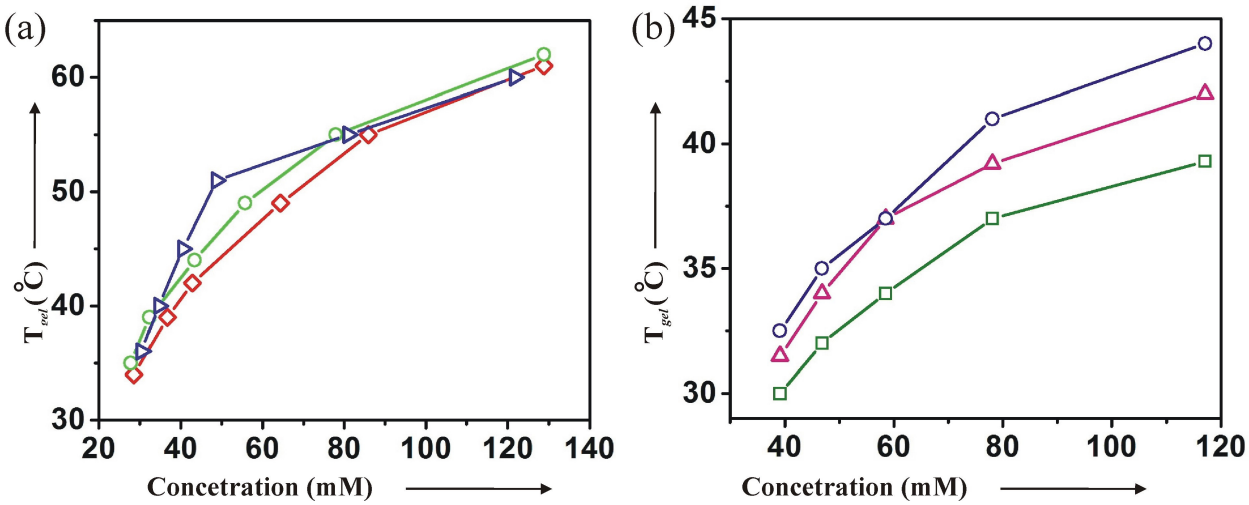


Figure S3: Tgel vs. concentration plots in (a) DMSO-water (3:2), DMF-water (2:1), DMF-water (3:2), (b) n-hexane, n-heptane, n-octane respectively.

3. Calculation the thermodynamic parameter:

Calculation:

The thermo-reversibility of a gel melting can be expressed as:

$$\text{Gel} \rightarrow \text{sol}$$

The equilibrium constant (K_{eqm}) for gel to sol transition:

$$K_{eqm} = [\text{Gelator}]/ [\text{Gel}]$$

Assuming unit activity of the gel, the equilibrium constant can be expressed as:

$$K_{eqm} = [\text{Gelator}]$$

The Gibbs free energy (ΔG°) change during gel melting can be expressed as:

$\Delta G^\circ = - RT\ln K_{eqm} = \Delta H^\circ - T\Delta S^\circ$, Hence, $\ln K_{eqm} = -\Delta^\circ/R.\ (1/T) + \Delta S^\circ/R$

The gel melting temperature (T_{gel}) increases with increasing concentration of the "solutes". A plot of lnK vs 1/T allowed us to calculate the thermodynamic parameters.

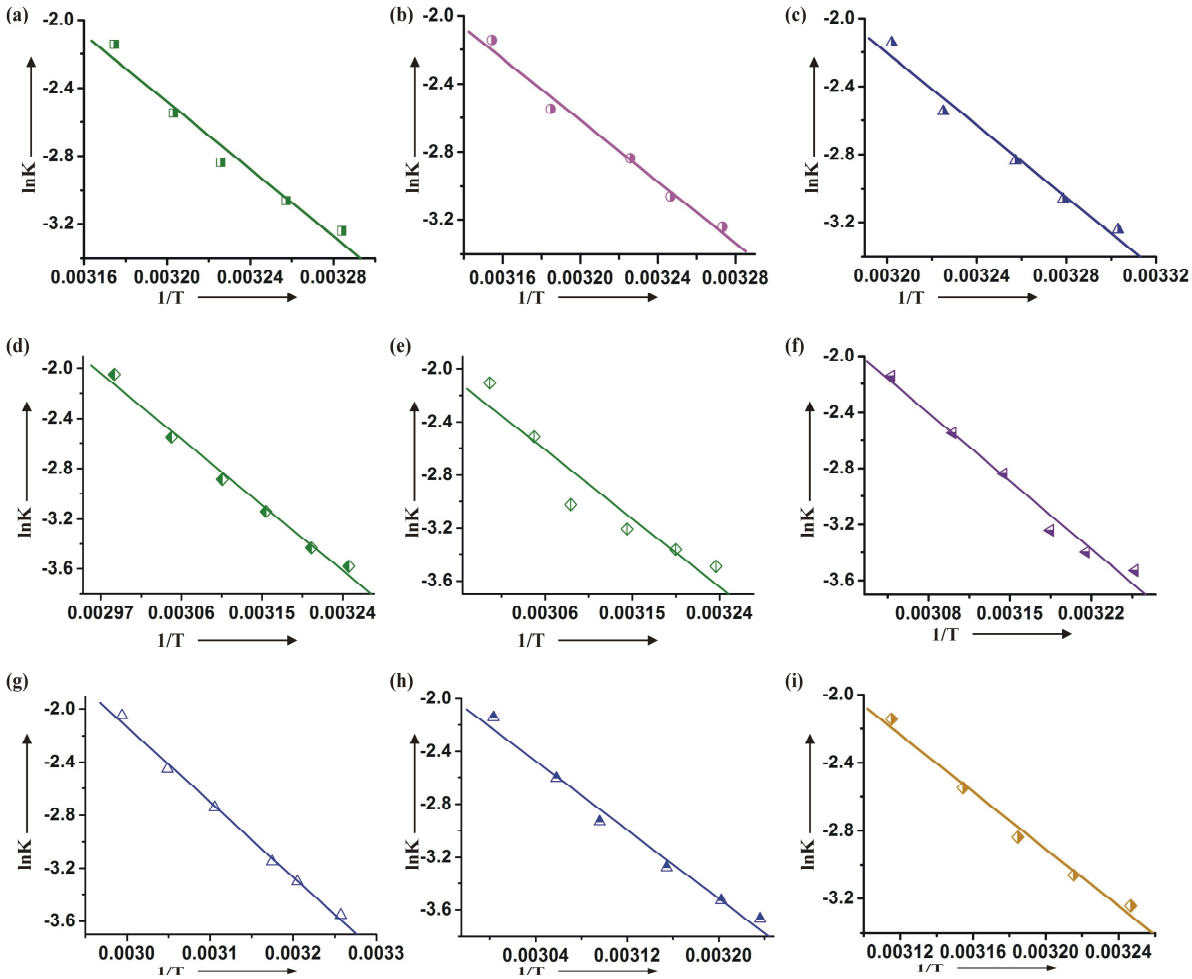


Figure S4: lnK vs. 1/T plots in (a) n-hexane, (b) n-heptane, (c) n-octane, (d) DMSO, (e) DMF, (f) DMSO-water (2:1), (g) DMSO-water (3:2), (h) DMF-water (2:1), (i) DMF-water (3:2)

4. OPM images of the self-assemblies

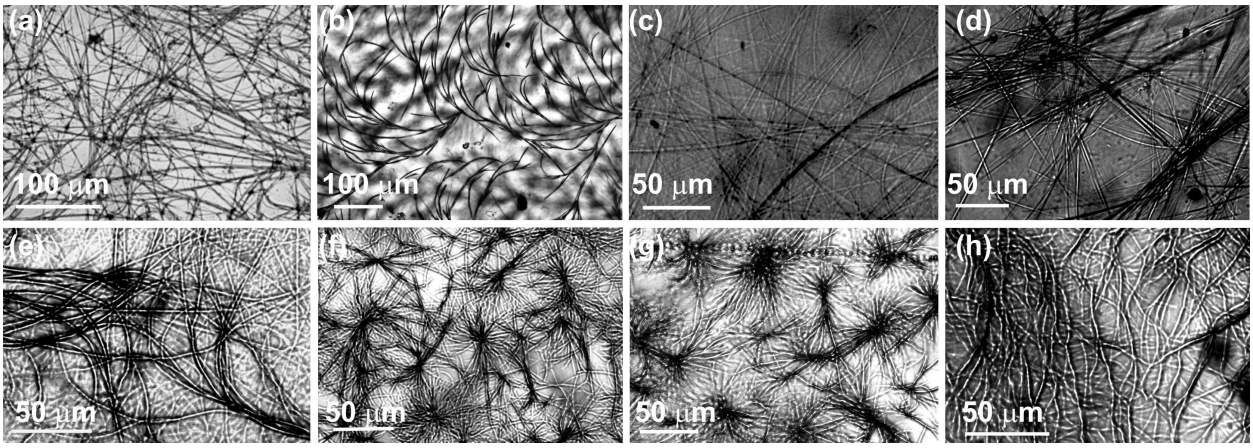


Figure S5: OPM images of self-assemblies of 1: (a,b) THF (1.5% w/v, 35.2 mM), (c) cyclohexane (1.5 % w/v, 35.2 mM), (d) DMF-H_2O (1:1, 2.0 % w/v, 46.9 mM), (e,f) n-hexane (1.5 %w/v, 35.2 mM), (g,h) n-heptane (1.5 %w/v, 35.2 mM)

5. AFM images of the self-assemblies

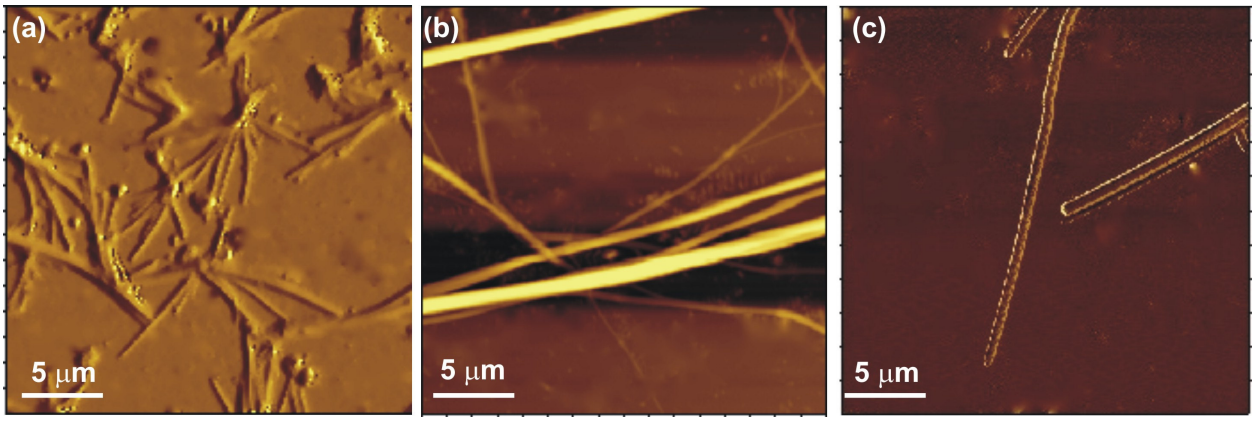


Figure S6: AFM micrographs of dried self-assemblies of 1 : (a) n-heptane (0.12%w/v), (b) o-dichlorobenzene(0.15 %w/v), (c) DMF-H_2O (1:1, 0.12 % w/v)

6. FESEM images of the self-assemblies

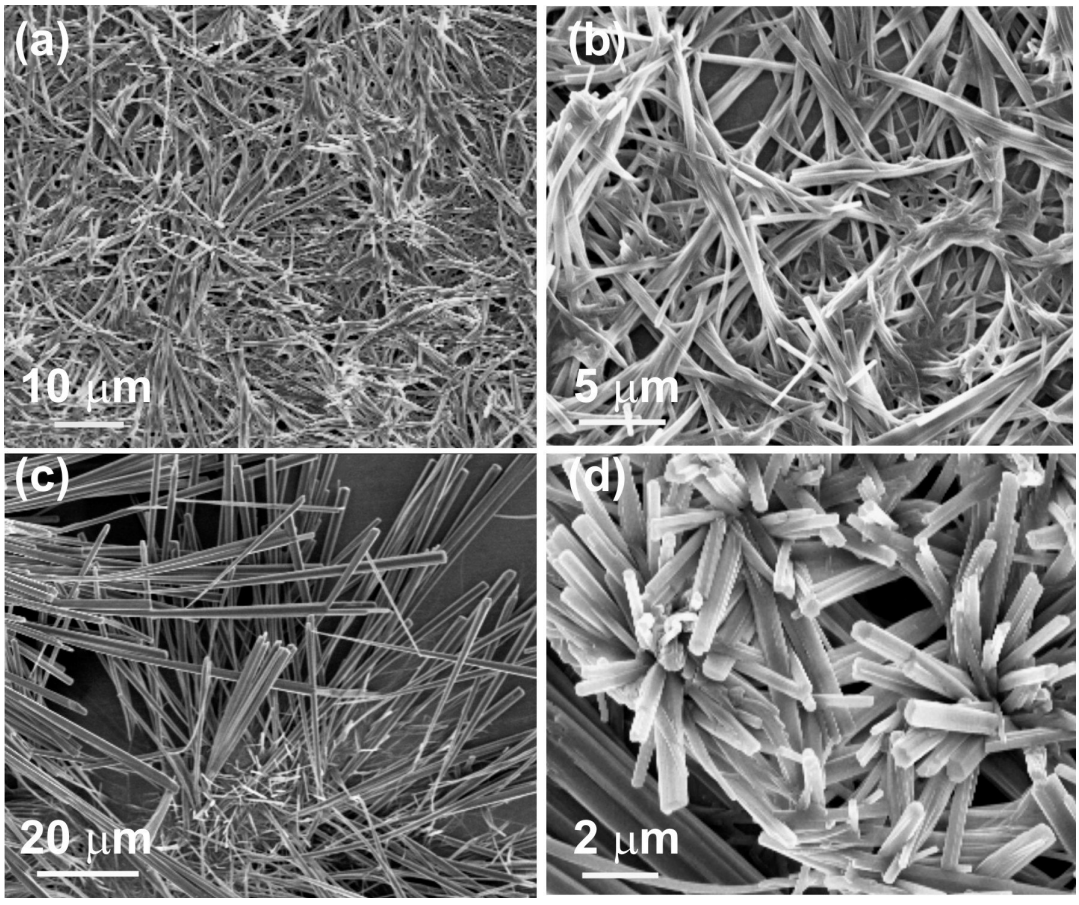


Figure S7: FESEM images of self-assemblies of 1: (a,b) DMF (1.5 %w/v), (c,d) EtOH (1.25 %w/v).

7. HRTEM images of the self-assembled twisted fibers

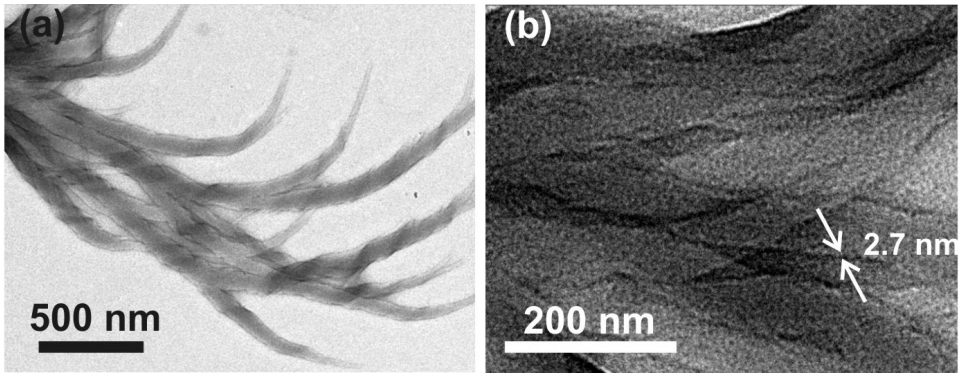


Figure S8: HRTEM images of self-assemblies of 1: (a,b) n-heptane DMF (0.8 %w/v).

8. Epifluorescence microscopy of dye entraped gel

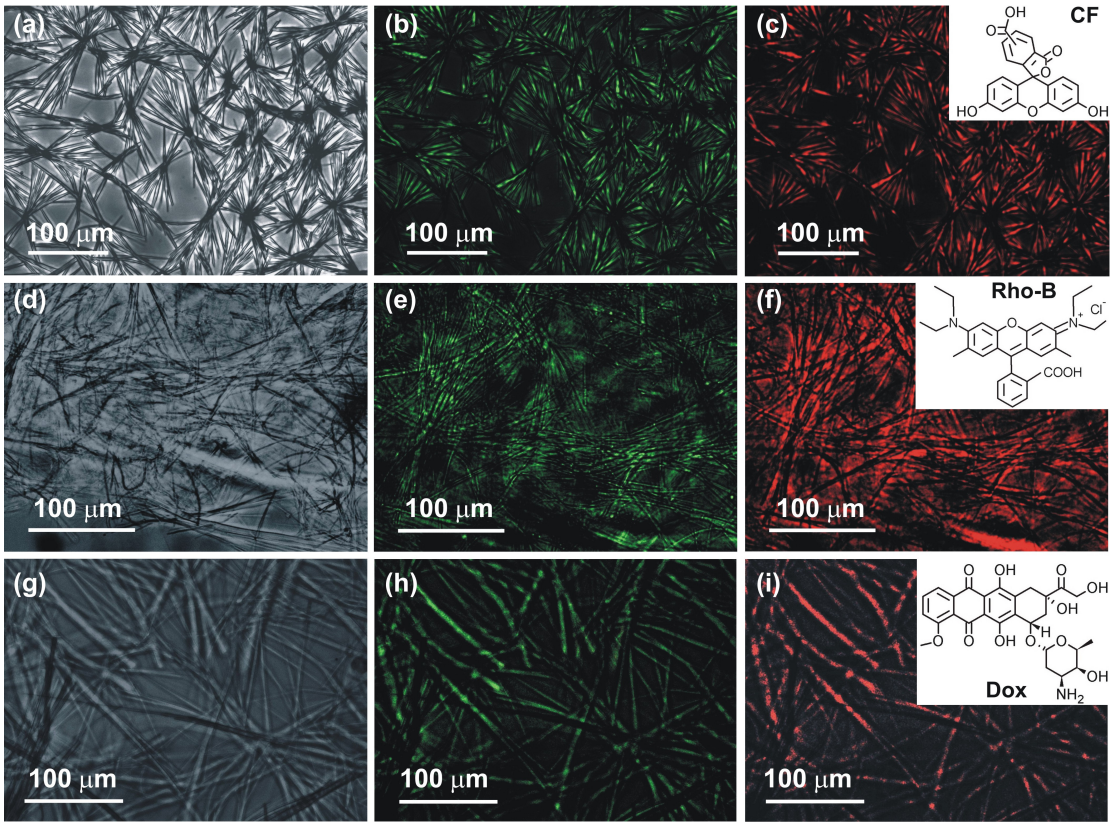


Figure S9: Epifluorescence microscopy images of the adsorbed fluorophores by the gels of **1** in DMSO-water (2:1): (a-c) adsorbed rhodamine-B (0.2 mM), (d-f) adsorbed CF (0.2 mM), (g-i) adsorbed doxorubicin (0.15 mM) after release respectively. Grey, green and red images are under normal, blue, green lights respectively.

9. Rheology of gels

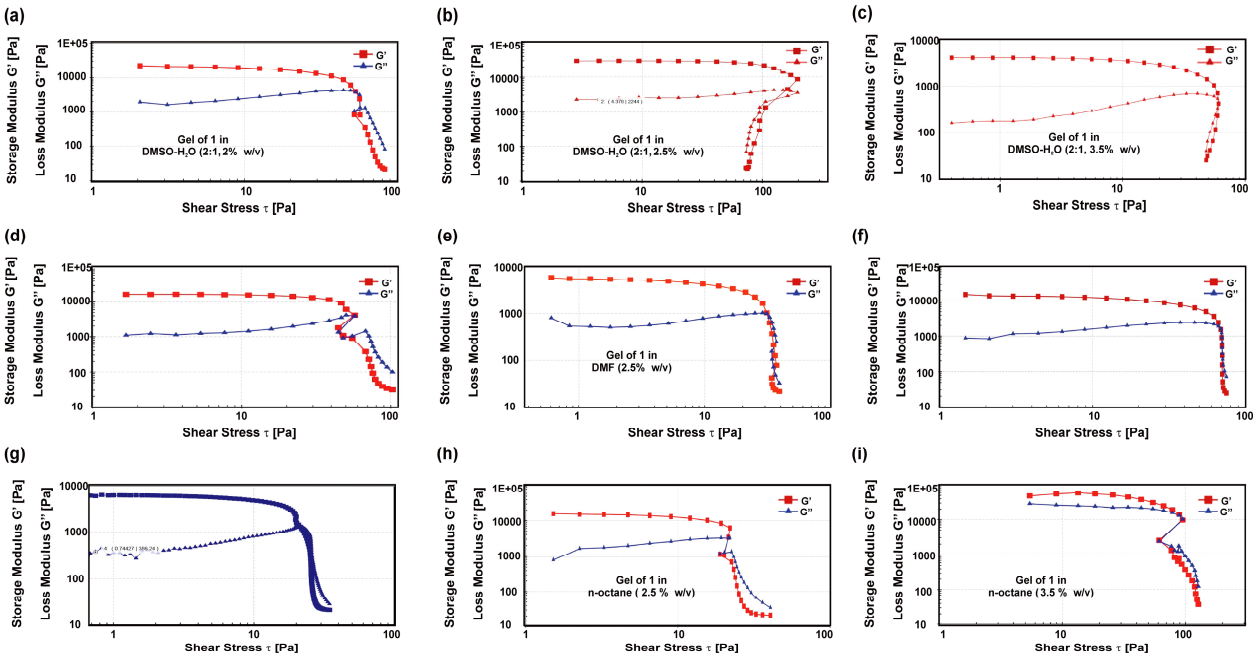


Figure S10 : Rheological amplitude stress Sweep experiments of the gels of 1 (a-c) in DMSO-H_2O (2:1 v/v), (d-f) in DMF 2.5 %w/v, (g-i) in n -octane at concentration 2.0 % w/v, 2.5 %w/v, 3.5 % w/v, respectively.

10. FTIR spectrum of Lupeol

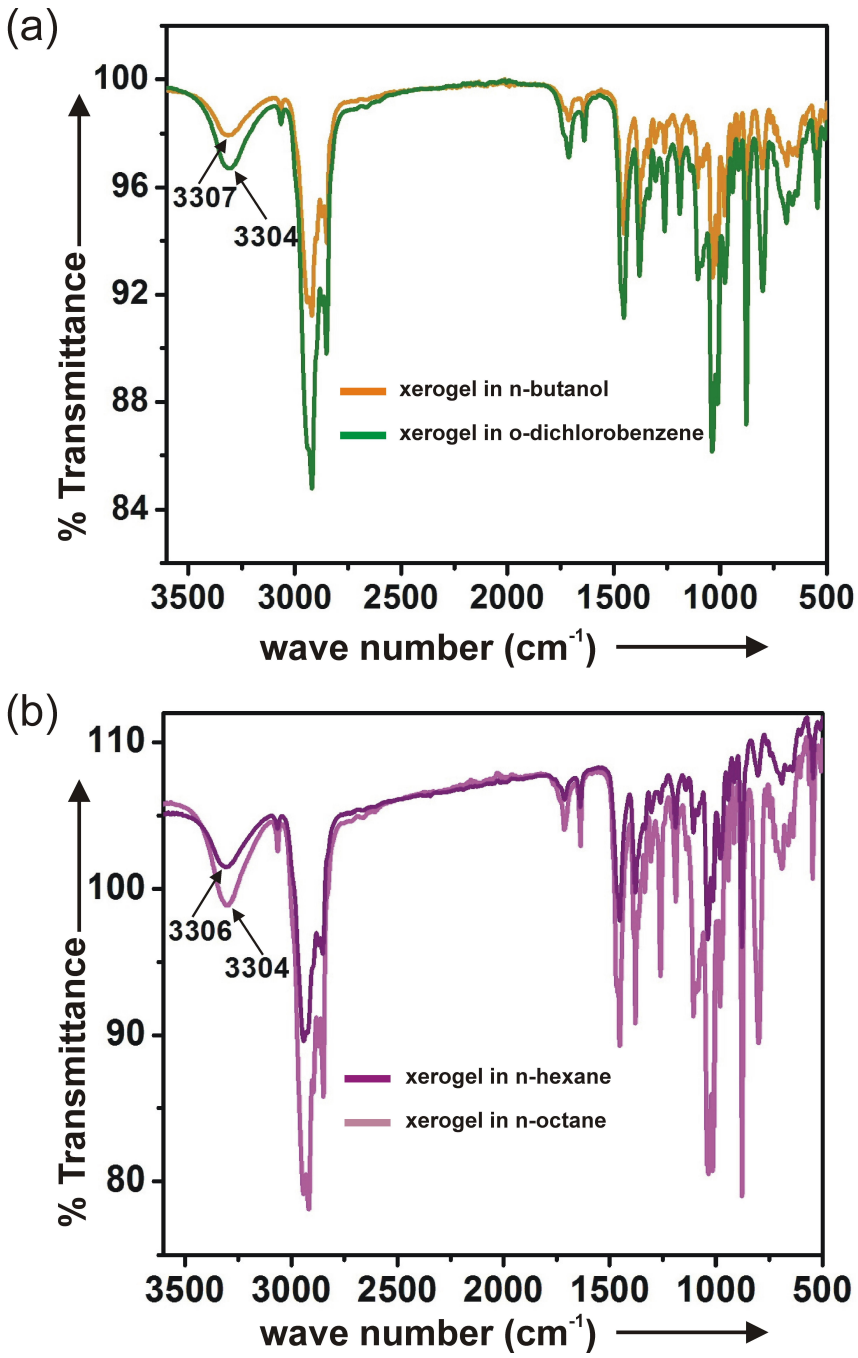


Figure S11: FTIR spectra of xerogel of 1 (a) butanol (5 % w/v) and o-dichlorobenze (4 % w/v), (b) n-hexane (1.7 % w/v) and n-octane (2 % w/v) respectively

11. Various possible modes of assembly of lupeol

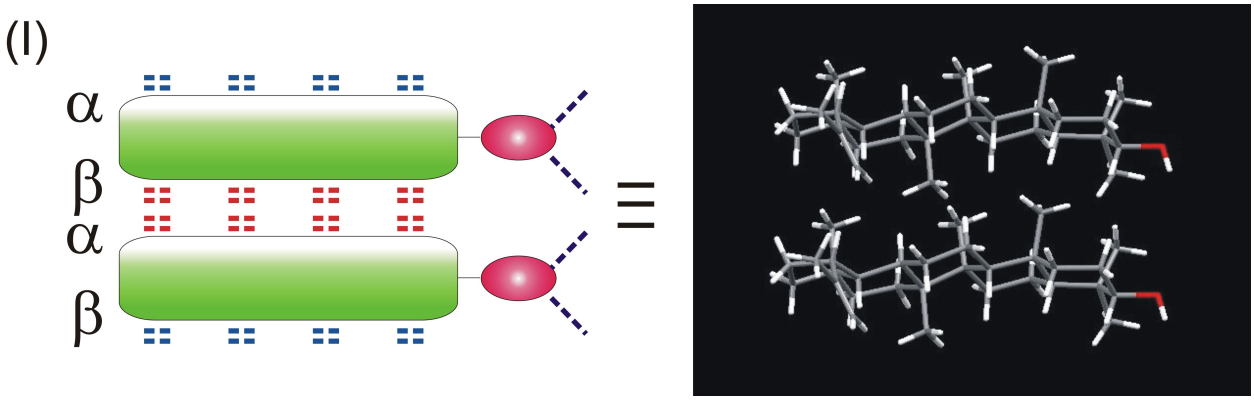


Fig. S12: Schematic representation of two interacting lupeol molecules within van der Waals contact and facing opposite (α–β) to each other

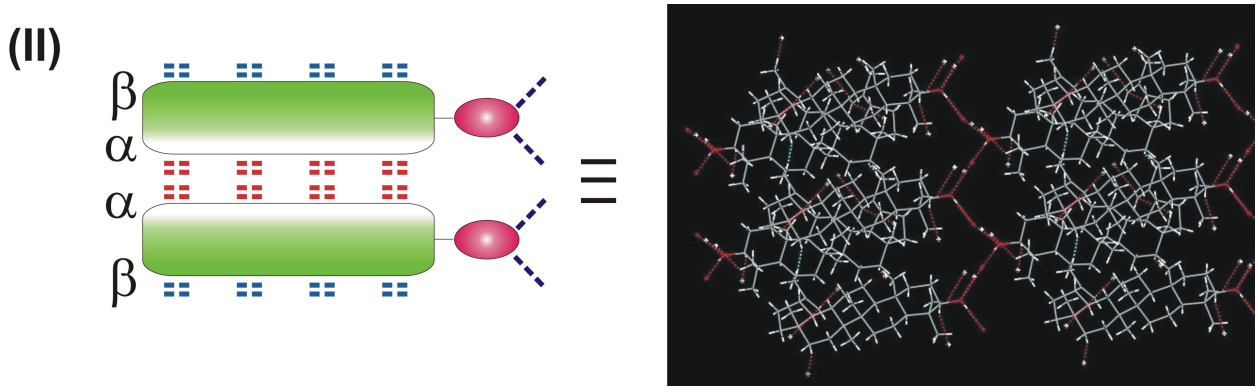


Fig. S13: Schematic presentation of two interacting lupeol molecules within van der Waals contact and facing (α–α) to each other

(III)

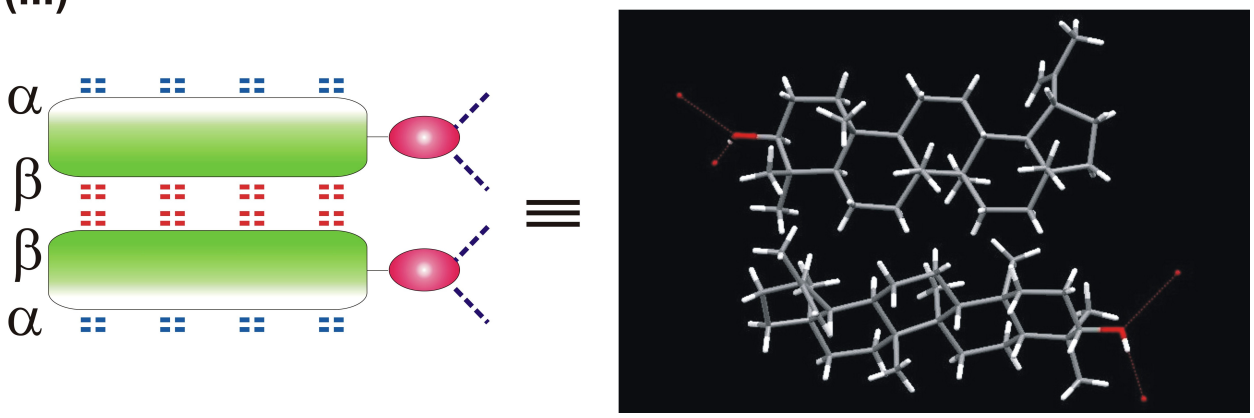
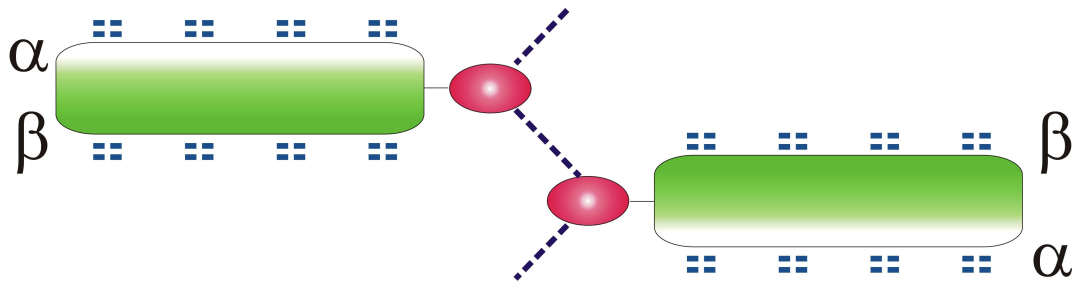


Fig. S14: Schematic representation of two interacting lupeol molecules within van der Waals contact shown as terpenoid β-face facing each other

(IV)



III

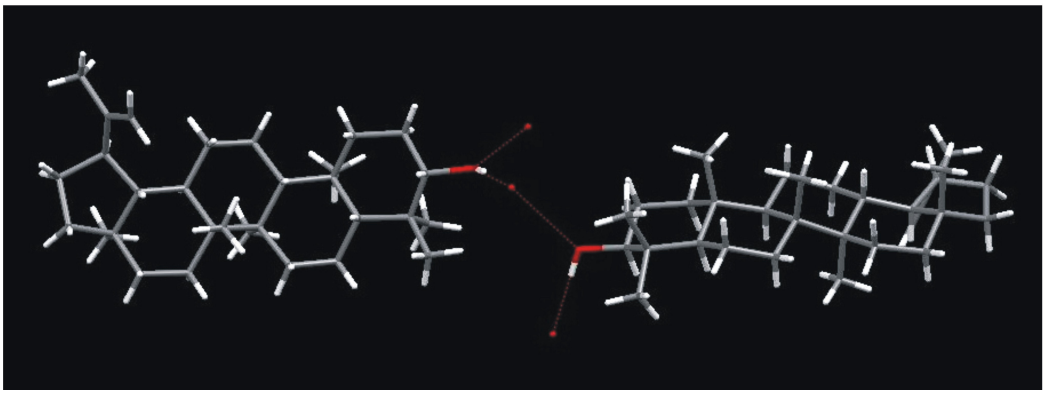


Fig. S15: Schematic representation of two interacting lupeol molecules within H-bonding

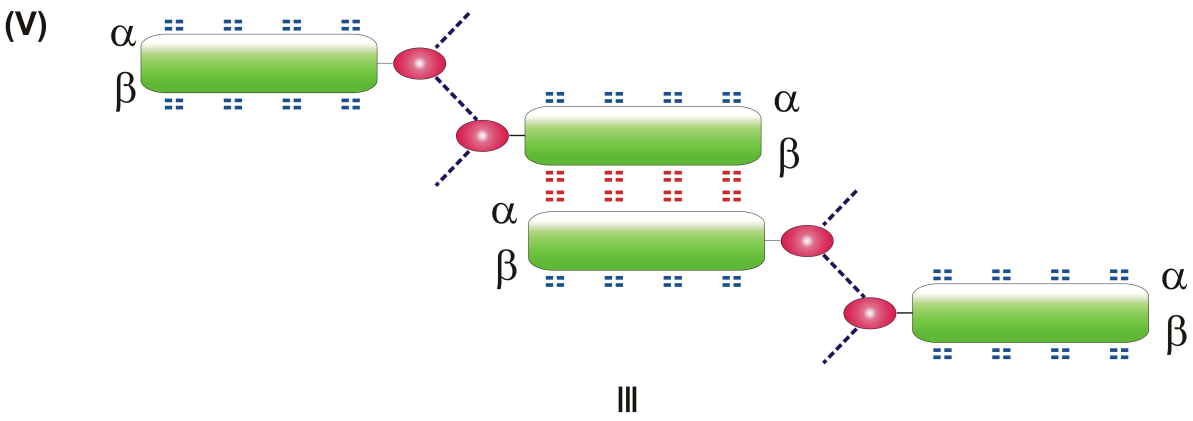


Fig. 16 Schematic representation of interacting lupeol molecules forming self-assembled architecture via within van der Waals interaction and contact and H-bonding

12. Experimental

12.1 Materials.

All solvents used for purification purposes were commercial grade and were distilled before use. The liquids used for gelation studies were laboratory-grade reagents and dried using standard literature methods and distilled before use.

12.2 Method of Sample Preparation and Characterization.

For self-assembly studies, 2−5 mg of compound 1 contained in a vial (1 cm id) was heated with a liquid with continuous magnetic stirring over a hot plate until a clear solution was obtained. The solution was then allowed to cool at room temperature (24−25 °C). When the material did not flow as observed by turning the vial upside down we called it a gel. The selfassemblies have been characterized by various spectroscopic and microscopic techniques. Scanning electron microscopy samples were prepared by placing a dilute solution of the sample on a aluminium foil and then allowing it to dry initially in air for 24 h and then under reduced pressure for 12 h and then sputter coated with Au before use for 120 s and studied using a Zeiss field-emission scanning electron microscope (FESEM). For optical microscopy, an aliquot of sample was taken on a glass plate and covered with a coverslip and observed both under normal and polarized light using a Nikon LV100 POL microscope. TEM images of the self-assemblies were recorded on dilute solution samples placed on 300 mesh carbon coated copper grids and dried at ambient temperatures in the air for 24 h and then under reduced pressure for 24 h and studied using JEOL transmission electron microscopy. For wide-angle X-ray scattering (WAXS) experiment, a thin layer of self-assemblies was placed on a glass plate and the volatiles were removed initially in air and then under reduced pressure and the diffractions were recorded in a Bruker X-ray diffractometer at 25 °C using Co−Kα filament (λ = 1.789 Å). For the measurement of diffraction pattern of a powder sample, it was taken directly in the diffractometer cell and measured. For FTIR spectra of the neat powder and self-assemblies were analyzed by using a PerkinElmer Spectrum.