List of Figures

Contents	Pages
----------	-------

Chapter 1: General Introduction

Figure 1:	Kakoli plant.	2
Figure 2:	Jeevaka plant.	3
Figure 3:	Vriddhi plants and its dried tuber.	4
Figure 4:	Dried tuber roots of Mahameda.	4
Figure 5:	Self-assembly of amphiphiles into different architectures.	11
Figure 6:	Schematic representation of formation of gel via self-assembly	
	of LMOG's(Low molecular weight gelators).	12

Figure 7: LMOG's yielding vesicles in aqueous binary liquid mixtures via selfassembly, mechanism of the formation of bilayer vesicular and tubular self-assembly and gel (the inverted vial with a leaf of *Terminalia arjuna* in the background contains a supramolecular gel of arjunolic acid in ethanol-water. 13

Figure 8: LMOG's yielding flowers, petals and fibrillar networks. Schematic representation for 1D growth, fibrillar network and gel. The inverted vial with the leaf of *Ziziphus jujuba* in the background contains a gel of betulinic acid in o-dichlorobenzene.

Chapter 2: Chemical Investigation on Astavarga Plants and Study of their Antioxidant Property

Figure 1:	Astavarga plants.	22
Figure 2:	Different part of kakoli (a) whole plant (b) flower (c) root.	26
Figure 3:	Kakoli plants in Himalayan.	26
Figure 4:	Schematic representation of the extraction of stigmasterol from	
	kakoli leaves.	27

- Figure 5:Image of different part of kakoli plant.28Figure 6:Chemical structure and Energy minimized structure of stigmasterol 30Figure 7:jeevak plant and pseudobulb of jeevak.35Figure 8:Schematic representation of the extraction of erucic acid from pseudobulb of jeevak.36
- Figure 9: Image of jeevak. 37
- Figure 10: Antioxidant activity studies of the tuber extract of Vrddhi: (i) UV-visible spectra of (a) DPPH, (b -e) DPPH + with ethanol extract of tuber 30, 60, 90, 120 µgmL-1., Inset: photographs of the vials containing the respective solutions; (ii) reaction scheme showing quenching of DPPH radical by the antioxidant (A-H); (iii) plot of % DPPH radical scavenging by the ethanol extract of tuber.
- Figure 11: (a) Scavenging property of jeevak(b)Comparison of radical scavenging activity of pseudobulb extract with naturally occuring Ascorbic acid standard 43
- Figure 12: (A) Antioxidant activity studies of the rhizome extract of Kakoli: (i) UV-visible spectra of (a) Extract, (b) DPPH, (c) DPPH + ethanol extract, Inset: photographs of the vials containing the respective solutions; (ii) reaction scheme showing quenching of DPPH by the antioxidant (A-H); (iii) plot of % DPPH readical scavenging by the methanol extract of rhizome (20 120 µg/mL) and its comparison with ascorbic acid (120 □g/mL, brown); (iv) and (v) UV-visible spectrum of DPPH with increasing concentration of the methanol extract of rhizome (RE). 44

Chapter 3: Self-assembly study of Stigmasterol in organic liquids

- Figure 1:Schematic representation of self-assembly of stigmasterol 1 in organicliquids forming supramolecular gel yielding fibrillar network.50
- Figure 2: Energy minimized structure of stigmasterol 1 obtained by (a) DFT calculation using Gaussian 09 software, the molecular length is 1.73 nm and (b) MMX force field as implemented in PC MODEL version 9.2 (Serena Software), the molecular length is 1.73 nm.

- Figure 3: A gel of stigmasterol in (a) DMSO (b) n-hexane and (c) n-heptane; (d)
 Plots of Tgel versus concentration for 1 in DMSO (-▲-); n-hexane (-●-);
 n-heptane(-■-). 55
- Figure 4: ln K vs 1/T (K) plot of stigmasterol in (a) DMSO; (b) n-heptane and (c) n-hexane 56
- Figure 5: Polarizing Optical microscopy images of **1** in (a) and (b) m-xylene (67.87 mM)(c) and (d) o-xylene(67.87 mM). 57
- Figure 6:Optical microscopy images of 1 in (a) and (b) n-hexane (17 mM) (c) n-
heptane(17 mM) and (d) cyclohexane (37.69 mM).58
- Figure 7: (a–d) Scanning electron micrographs of the dried selfassemblies of Stigmasterol prepared from dilute solution in n-heptane (25.92 mM). 59
- Figure 8: Scanning electron micrographs of the dried self-assemblies of stigmasterol prepared from dilute solution in (a–b) nitrobenzene (1.07 % w/v), (c-d) in n-hexane (1.10% w/v).
- Figure 9: HRTEM (unstained) of self-assembled stigmasterol in n-heptane (2.5 mM).
- Figure 10: AFM images (a and c) 2D, (b and d) 3D of the self-assemblies of Stigmasterol in (a -b) n-heptane (6.057 mM) (c and d) cyclohexane (6.06 mM).
- Figure 11: Rheology of gel of 1 in DMSO (49 mM). 63
- Figure 12: FTIR spectra of stigmasterol (powder) and its gels in cyclohexane, nhexane and nitrobemzene. 64

Figure 13: X-Ray diffractogram have been recorded at room temperature (25 ° C) using Cu-K α filament (λ = 1.54 Å). (a) Neat powder of 1 in n-hexane. 65

- Figure 14. Energy-minimized structure of stigmasterol: The length of the molecule is 1.73 nm. Two molecules are formed dimeric structure by H-bonding and the length of the dimer is 3.47 nm. 65
- Figure 15: The computer generated X-ray powder diffraction peaks obtained from the X-ray crystal structure. (Mercury 4.2.0 (Build 257471); http:// www.ccdc.cam.ac.uk/ mercury). 66

- Figure 16. Schematic representation of various modes of self-assembly of stigmasterol. The OH groups can take part in H-bonding and the lipophilic surface of steroid can take part in van der Waals interaction. The α and β face of the steroid leads to two types of assembly formation of the type I V. 67
- Figure 17: Schematic representation of two interacting stigmasterol molecules within van der Waals contact having steroid α-face facing each other (0.5H2O present as solvent of crystallization is not shown for clarity).

67

Figure 18: Schematic representation of two interacting stigmasterol molecules within van der Waals contact having steroid β-face facing each other (0.5H2O present as solvent of crystallization is not shown for clarity).

68

- Figure 19: Schematic representation of two interacting stigmasterol molecules within H-bonding (0.5H2O present as solvent of crystallization is not shown for clarity). 68
- Figure 20: Schematic representation of interacting stigmasterol molecules forming 1D, 2D and 3D architecture (a) within van der Waals contact (b) with OH participating in H-bonding (0.5H2O present as solvent of crystallization is not shown for clarity).
- Figure 21. Schematic representation of interacting stigmasterol molecules forming 1D, 2D and 3D architecture within van der Waals contact and OH participating in H-bonding (0.5H2O present as solvent of crystallization is not shown for clarity).
- Figure 22. Inverted vials containing gels of 1 in DMSO (I and VI). Rho-B loaded gel of 1 in DMSO (II under normal light and III under 366 nm UV light). CF loaded gel of 1 in DMSO (V under normal light and VI under 366 nm UV light). Release of the fluorophores Rho-B (VII), CF (VIII) and the anticancer drug Doxorubicin (IX) from Rho-B (1.5 mM), CF (1.5 mM) and Doxorubicin (2.0 mM) loaded gels of stigmasterol (40 mM) in DMSO (300 µL) respectively into aqueous media (900 µL): overlay of the UV-visible spectra of released Rho-B (VII), CF (VIII) and DOX (IX) into aqueous media at various time intervals. Inset in VII, VIII and IX

are the plots of % of release of fluorophore/drug vs time for the respective experiments. 72

Chapter 4: Vesicular Self-Assembly of Crotocembraneic Acid

- Figure 1: Schematic representation of self-assembly of crotocembraneic acid **1** extractable from Croton oblongifolius Roxb yielding vesicular selfassemblies and its use in drug entrapment studies (centre: energy minimized structure of **1**). 80
- Figure 2: Energy minimized structure of Crotocembraneic acid (1) (PCWin,® Serena Software, version 9.2). The amphiphilic nature of the molecule with the polar carboxyl 'head' group and macrocyclic 'lypophilic' backbone is depicted. 84
- Figure 3: (a-c) Optical micrographs of Crotocembraneic acid 1 in (a) ethanol-water (2% w/v) (b) DMSO-water (2% w/v) (c) DMF-water (2% w/v);
 (d) SEM of 1 (0.28% w/v) in DMSO-water (2:1 v/v). 86
- Figure 4: Polarizing optical micrographs (recorded in NIKON ECLIPSE LV100POL instrument) of Crotocembraneic acid in (a) Ethanol-water (2%w/v) (b) DMSO-Water (2%w/v) (c) DMF-Water (2%w/v) (d) histogram.
- Figure 5: SEM images of a dry sample prepared from crotocembraneic acid 1 in DMSO-water (2:1, v/v) (0.28% w/v) (a) Spheres (diameter = 780 nm);
 b) histogram.
- Figure 6: (a,b) FESEM of dried self-assemblies of 1 (0.28% w/v) prepared from its colloidal suspension in DMSO-water (2:1 v/v), (c) HRTEM of dried self-assemblies of 1 prepared from its colloidal suspension in ethanol-water (2:1 v/v), (d) schematic representation of the formation of bilayer membrane yielding vesicular self-assembly of 1.
- Figure 7: a) schematic representation of fusion of two vesicles forming a bigger vesicle, (b) HRTEM image showing fused vesicle. 89

- Figure 8: (a,b) AFM images (2D and 3D respectively) of spherical self-assemblies formed from **1** (0.28% w/v) in DMSO-water (2:1 v/v). 90
- Figure 9: AFM images of soft vesicles formed from **1** (46.32 mM) in DMSOwater (2:1 v/v). 90
- Figure 10: X-ray diffraction studies of the self-assemblies of **1** (1% w/v) in DMSOwater (2:1 v/v). 91
- Figure 11. Overlay of the FTIR spectra of compound **1** (recorded in ATR mode).
- Figure 12. DLS studies of self-assembled **1** in ethanol-water (2:1, v/v): (a) 1.6% (b) 1.8% (c) 2.2%. 93
- Figure 13: Variation of I1/I3 in the emission spectra of pyrene (fixed concentration = 10-6 M) encapsulated in 1 solutions of varying concentration, inset: emission spectra of pyrene in aqueous binary solvent mixture in presence of various concentration of 1.
- Figure 14: Epifluorescence microscopy images of self- assembled crotocembraneic acid 1 (46.32 mM) in DMSO-water (2:1 v/v) (a,b) containing crystal violet (0.463 mM), (c,d) containing rhodamine B (0.463 mM) (a,c) bright-field images, (b,d) fluorescent images.
- Figure 15: Epifluorescent microscopy images of (a,b) self-assembled 1 (26.0 mM) in DMSO-water (2:1 v/v) containing CF (0.26 mM); (c,d) self-assembled 1 (46.32 mM) in DMSO-water (2:1 v/v) containing doxorubicin (0.46 mM). (a,c) Fluorescent images, (b,d) bright-field image.
- Figure 16: Optical microscopy images of (a) rhodamine B (0.46 mM) entrapped vesicles via self-assembly of crotocembraneic acid 1 (46.30 mM) and (b) after 20 min. of the addition of Triton-X-100 (0.46 mM) into the rhodamine B entrapped vesicular self-assembly of crotocembraneic acid 1 (a,b) under fluorescence light.
- Figure 17: Fluorescence emission spectra ($\lambda ex = 510$ nm) of Rho-B under different experimental conditions showing the effect of entrapment by vesicular self-assemblies and partial release by sonication. 98