Chapter 6: Synthesis and Self-assembly of Sugar Based Amphiphiles: Morphology Transition in the Helical Tubules Driven by Metal Ions

Abstract

The highlight of hierarchically organized supramolecular self-assembly is the reversibility of various types of noncovalent interactions resulted in the construction of smart nanostructures, duly responsible for various biological prospects. Our aim to access a particular chemical functionality on the helical tubules has been achieved by rational molecular design and synthesis of glucono-appended cardanol derivatives. The molecular geometry and interactions of the derived amphiphile afford the opportunity to generate tubules with $\alpha$-helicity. For the first time the chiral molecular packing was reported to form helical tubules and chiral symmetry breaking on exposure to $\text{Cu}^{2+}$ generated the final ordered structure through an in situ morphological transition without making any phase change. Notably, helical tubules on exposure to water lead to the spontaneous formation of unzipped helical tubules. The reported most promising bio-based scaffold demonstrates the creation of dynamic assembled structures with complex functions arising from the transition of ordered state.

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6.1 Introduction

The research in last few decades witnessed an incredible development of multifunctional soft-materials in turn derived from molecular self-assembly process.\textsuperscript{1} In this context, supramolecular gels based on low molecular weight gelator have attracted immense research interest.\textsuperscript{2} Most of the supramolecular gels possess ample applications in sensing, light harvesting, photovoltaics, oil spill recovery, medicine and biology.\textsuperscript{3} In recent past, researchers have focused on the elucidation of structural change in solution phase such as micelles or vesicles into helical ribbons and tubules.\textsuperscript{4} Even though twisting and wrapping of self-assembled sheet into a helical tube has been reported in literature,\textsuperscript{5} science behind the tubules continue to persist as mysterious system because they have involved in complex biological processes such as organization of intercellular structure, intercellular transport and stimuli responsive drug delivery.\textsuperscript{6,7} Under this circumstance, experimental\textsuperscript{8} and theoretical\textsuperscript{9} studies on the elucidation of mechanistic pathway for tubule formation has been addressed by several authors (Figure 6.1).\textsuperscript{8-15} Since carbohydrates are involved in various biological processes, detailed study on complex supramolecular architectures based on carbohydrates are niche area of research.\textsuperscript{11} Pfennermuller and Welte were the first to report the formation of helical structure by $n$-alkyl-D-gluconamides.\textsuperscript{12} Further, studies on the formation of helical tubules was extended to various $n$-alkyl-D-gluconamides having both saturated and unsaturated units.\textsuperscript{13} Shimizu and co-workers have demonstrated the use of cardanol for the construction of self-assembled tubules.\textsuperscript{14} Recently, John and co-workers have discussed the glimpses on cardanol derived functional amphiphiles and their ability to develop functional nanomaterials.\textsuperscript{15} However, to our knowledge, the reported systems not engaged in explaining the
morphological transition, tubular to fibrillar or unzipped tubules without phase change in response to Cu$^{2+}$ and water.

Figure 6.1. Nanotubes self-assembled from aldonamides.$^{10a,10b,13}$

The development of chemically functionalized tubules sensing cation is an interesting task. Especially an excess or deficit of heavy metal ions such as Fe$^{3+}$, Cu$^{2+}$ and Zn$^{2+}$, and intracellular ions including Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ in biological system leads to various disorder.$^{16}$ In this chapter, by rationally introducing a competitive binding site into a gelator derived from renewable resources, a supramolecular gel, formed by helical tubular network displaying gel-to-gel transition i.e. switching of ordered state in response to Cu$^{2+}$ and other cations was generated. As the observation of tubule formation and rearrangement into fibers and unzipped tubules on exposure to metal ion and water have not been reported in literature, this study provides a new insight into the morphological transition and their properties.
6.2 Results and Discussion

6.2.1 Synthesis of Sugar Based Amphiphiles 3a-c

2-Hydroxy-4-alkylbenzaldehydes 2b and 2c were prepared by following the procedure described in chapter 2. Reaction of gluconolactone 1 (1.0 mmol) with hydrazine hydrate (1.5 mmol) followed by the reaction of 2-hydroxy-4-alkylbenzaldehydes 2a-c (1.0 mmol) under reflux condition in one-pot afforded glucono-appended cardanol derivatives 3a-c in good yields (Scheme 6.1).

Scheme 6.1. One-pot synthesis of gelator 3a-c.

In \(^{1}H\) NMR spectra, compounds 3a-c, displayed singlet at \(\delta = 11.49\) ppm and 11.39 ppm corresponding to -OH and -NH protons respectively. Singlet observed at around \(\delta = 8.6\) ppm corresponding to -CH=N proton. The appearance of two signals for a single proton is due to the E-Z isomerization of N'-4-alkyl-2-hydroxybenzylidene-2,3,4,5,6-pentahydroxyhexanehydrazide in solution form. Exact molecular structure has also been confirmed using mass spectral studies.

6.2.2 Gelation Studies

The gelation abilities of compounds 3a-c were examined in a wide range of solvents by adopting “stable to inversion of a test tube” method.\(^{17}\) The list of solvents
used for the gel studies is summarized in Table 6.1. It is evident from Table 6.1 that compounds 3b and 3c showed an excellent gelation ability in a wide range of solvents such as olive oil, linseed oil, silicone oil, and 1,2-dichlorobenzene with low critical gelation concentration (CGC) whereas, compound 3a did not form gel in any of the tested solvents. The gelator 3b and 3c displayed CGCs of 1.0% and 0.5% in dichlorobenzene. This shows that the presence of hydrophobic part in compounds 3b and 3c was responsible for the gelation and compound 3a did not form gel in any of the tested solvents due to the lack of hydrophobic part (Figure 6.2). Further, gelation studies clearly show that compounds 3a-c do not form gel in lower alcohols, water, and DMSO whereas compound 3c displays an excellent gelation behavior in vegetable oils. The gelation ability of these amphiphiles 3a-c was found to increase with increase in hydrophobicity.

Figure 6.2. (a-d) Photographs of gel formed by (a) 3b in dichlorobenzene; (b) 3b in olive oil; (c) 3c in olive oil; (d) 3c in dichlorobenzene.
### Table 6.1. Gelation studies of compounds 3a-c in organic solvents and oils

<table>
<thead>
<tr>
<th>S.No</th>
<th>Solvents/Oils</th>
<th>3a</th>
<th>3b</th>
<th>3c</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Hazelnut oil</td>
<td>I</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>2</td>
<td>Sesame oil</td>
<td>I</td>
<td>S</td>
<td>G (1.0)</td>
</tr>
<tr>
<td>3</td>
<td>Jojoba oil</td>
<td>I</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>4</td>
<td>Olive oil</td>
<td>I</td>
<td>G (1.0)</td>
<td>G (0.5)</td>
</tr>
<tr>
<td>5</td>
<td>Soybean oil</td>
<td>I</td>
<td>S</td>
<td>G (0.8)</td>
</tr>
<tr>
<td>6</td>
<td>Linseed oil</td>
<td>I</td>
<td>G (1.0)</td>
<td>G (0.8)</td>
</tr>
<tr>
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<td>Light paraffin oil</td>
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<td>PG</td>
</tr>
<tr>
<td>9</td>
<td>Eucalyptus oil</td>
<td>I</td>
<td>S</td>
<td>PG</td>
</tr>
<tr>
<td>10</td>
<td>Neem oil</td>
<td>I</td>
<td>S</td>
<td>G (0.5)</td>
</tr>
<tr>
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<td>Castor oil</td>
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<td>P</td>
<td>G (0.8)</td>
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<td>G (1.0)</td>
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<td>I</td>
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</tr>
<tr>
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<td>Benzene</td>
<td>P</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>24</td>
<td>1,2-Dichlorobenzene</td>
<td>S</td>
<td>G (1.0)</td>
<td>G (0.5)</td>
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<tr>
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<td>P</td>
<td>P</td>
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<td>DMF</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>27</td>
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<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>28</td>
<td>Water</td>
<td>S</td>
<td>P</td>
<td>I</td>
</tr>
<tr>
<td>29</td>
<td>Acidic Buffer</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>30</td>
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<td>I</td>
<td>I</td>
</tr>
<tr>
<td>31</td>
<td>DMSO+Water</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
</tbody>
</table>

*S* = soluble; *I* = insoluble; *P* = precipitate; *G* = gel and *PG* = partial gel.
6.2.3 Morphological Analysis

The representative optical micrographs of gel formed by 3b and 3c in 1,2-dichlorobenzene are shown in Figure 6.3. Well defined densely packed fibrillar morphology was observed for gel formed by compound 3b, whereas tubular morphology was observed in case of 3c. This behavior has been further confirmed by HRTEM analysis. In order to generate helical tubules by chiral molecular packing and chiral symmetry breaking in response to biologically important cations via ordered phase, further studies have been carried out on organogel formed by compound 3c, Glucono-Appended-N-Pentadecylphenol (GAP).

![Optical micrographs of gel formed by compounds (a) 3b; (b) 3c in 1,2-dichlorobenzene.](image)

6.2.4 FT-IR Studies

ATR-FTIR is used as a tool to investigate the molecular interaction in tubule assembly. GAP in powder form, the stretching vibration of -OH, secondary amide and carbonyl group appeared at 3351, 3318 and 1690 cm\(^{-1}\) respectively, while in helical tubules formed by chiral molecular packing, owing to the formation of intermolecular hydrogen bonding between the hydroxyl groups, and -C=O with -NH group of amide,
the -OH, -NH and carbonyl stretching peak of amide has shifted to 3306, 3232 and 1629 cm\(^{-1}\) (Figure 6.4).

![Figure 6.4. ATR-FTIR spectra of GAP in powder and helical tubular form.](image)

### 6.2.5 X-ray Diffraction Studies

To obtain the further insight into the hierarchically assembled structure of GAP, small angle X-ray diffraction study was performed on the film prepared by the evaporation of solvent from gel. The diffraction pattern shows periodic peaks at \(2\theta = 2.47^\circ, 5.05^\circ, 10.12^\circ, 15.20^\circ\) and \(20.32^\circ\) corresponding \(d\)-spacing, calculated according to Bragg’s equation were 3.57, 1.75, 0.87, 0.58 and 0.44 suggesting the J-type molecular assembly (Figure 6.5).\(^{18}\)
To understand the formation mechanism of tubules, HRTEM experiment in more dilute condition was performed. HRTEM images show the tubule formation by coiling the individual ribbon in a helical fashion (Figures 6.6a and 6.6b). Tubules were characterized by their pitch angle ($\psi$) and diameter as described by Raghavan and co-workers. Figure 6.6b demonstrates that most of the tubules have diameter in the range of 300-400 nm and having pitch angle of 15º (±5º). Formation mechanism for self-assembled helical tubules from glycolipids has been extensively reviewed by Matisons and co-workers. Though few reports are available on the nanotube template directed synthesis of nanoparticles, there is no report on chiral molecular packing and metal ion enabled chiral symmetry breaking i.e. morphological transition of self-assembled tubules without phase transition, which is considered as a crucial process in biology. In order to demonstrate the influence of ions on tubules, a known concentration (1x10^{-3} M) of Cu(OAc)$_2$ solution on gel was introduced and observed their intrinsic morphological transition. In fact, 1,2-dichlorobenzene trapped in densely packed microtubules displayed translucent gel.
The addition of Cu(OAc)$_2$ dissolved in major proportion of hydrophobic solvent (1:9 ratio of ethanol-1,2-dichlorobenzene) on gel leads to the formation of green translucent gel (Figure 6.7a), whereas the aqueous Cu(OAc)$_2$ solution displayed opaque gel (Figure 6.7b). In the first case Cu$^{2+}$ ion present in hydrophobic solvent percolate in the gel network void as well as tubules, further interaction with the ion binding site resulted in the formation of a translucent green gel. In latter case, Cu$^{2+}$ ion in hydrophilic solvent can able to penetrate only in tubules, not over the network void resulted in the formation of opaque gel, which can be attributed to the poor miscibility of water in 1,2-dichlorobenzene (0.01%). This simple experiment demonstrated the hydrophilic nature of tubular cavities and hydrophobic nature of the outer layer without the need of more expensive modern analytical tools (Figure 6.8).
Figure 6.7. Response of gel formed by GAP in 1,2-dichlorobenzene after the addition of (a) Cu(OAc)$_2$ dissolved in water; (b) Cu(OAc)$_2$ dissolved in ethanol:1,2-dichlorobenzene (1:9 ratio); (c) double distilled water.

Figure 6.8. Pictorial representation of morphological transition triggered by Cu$^{2+}$ and water.

To corroborate the morphological transition and chiral symmetry breaking within the gel, HRTEM experiments were performed on the xerogel prepared by diluting a green gel in a suitable solvent followed by fast evaporation. HRTEM images showed that the interaction of Cu$^{2+}$ ions in chemically functionalized tubules experiences a morphological transition to randomly twisted fibers without affecting the gel phase (Figure 6.6c). It was believed that the binding of Cu$^{2+}$ ions to the coordinating unit present in GAP is responsible for morphological transition (Figures 6.6d and 6.6e). To prove further, the importance of metal ion in such transition, a
control experiment was performed, in which double distilled water was added on gel formed by tubular network, and observed their morphological and phase transition. On addition of water, translucent gel slowly attained the opaque character (Figure 6.7c), and morphological transition associated was investigated using HRTEM. HRTEM micrographs revealed the formation of unzipped tubules (Figure 6.6f and 6.6g). Water triggered unzipping of tubules substantially reduces the size to 100-200 nm, which is exclusively different from uncoiling of helical tubules. In general, uncoiling of helical tubules leads to the formation of either helical/twisted or lamellar fibers.\(^{13}\)

### 6.2.6 Circular Dichroism (CD) Spectral Analysis

In order to confirm the chiral molecular packing, origin of chirality in helical tubules and Cu\(^{2+}\) induced randomly twisted fibers, CD spectra in 1,2-dichlorobenzene was measured. The examination of helical tubules showed CD signals with positive and negative Cotton effects having dominant peaks at 268, 287 and 341 nm, which is consistent with the UV-vis absorption spectra (Figure 6.9).

![Graph](image)

**Figure 6.9.** UV absorption spectra of gelator 3c in 1,2-dichlorobenzene.
The CD spectral pattern indicates that there must be a formation of α-helical chiral structure over a period of chiral molecular packing (Figure 6.10). Remarkably, the addition of Cu$^{2+}$ ions triggers a significant morphological transition in gel network. Upon addition of Cu$^{2+}$ ions, CD spectra showed a substantial Cotton effect in the spectral region of the aromatic segment, in contrast to that solution before Cu$^{2+}$ addition. In the aromatic segment, a negative first Cotton effect and a positive second Cotton effect indicating the randomly coiled morphology (Figure 6.10).

![Figure 6.10. CD spectra of helical tubules (red line) and randomly twisted fiber formation triggered by Cu$^{2+}$ (blue line). CD spectra was recorded in 1,2-dichlorobenzene at 25 °C.](image)

6.2.7 X-ray Photoelectron Spectroscopic Studies

In tubules, the segment which is responsible for the Cu$^{2+}$ interaction should be investigated. In order to identify the mode of interaction between Cu$^{2+}$ and tubules, and chemical state of copper, X-ray photoelectron spectrum (XPS) was recorded for helical tubules and copper triggered randomly twisted fibers. The peaks for C 1s, N 1s and O 1s are observed for helical tubules (Figure 6.11).
Figure 6.11. (a-g) XPS spectra of helical tubules and randomly twisted fiber formation triggered by Cu$^{2+}$ fitted using Gaussian-Lorentzian peak: (a) C 1s, (c) N 1s and (e) O 1s spectra of helical tubules; (b) C 1s, (d) N 1s, (f) O 1s, (g) Cu 2p spectra of randomly twisted fiber formation triggered by Cu$^{2+}$; (h) XPS spectra of helical tubules (red line) and randomly twisted fiber formation triggered by Cu$^{2+}$ (blue line).
Deconvolution of C 1s signal in helical tubules shows the presence of -C=C-/C=C- (285.2 eV), -C-O/-C-N- (285.5 eV) and C=N (286.5 eV). The absence of signal corresponding to -C=O (287-289 eV) confirms the involvement of carbonyl group in H-bonding (Figure 6.11). Peak for N 1s on deconvolution resulted in six signals, which corresponds to inter- and intramolecularly hydrogen bonded -NH, =N- and -N(C=O)- respectively. Similarly, deconvolution of O 1s into 3 signal shows the presence of -N-C=O* (532.6 eV), aliphatic -OH (533.1 eV, H-bonded) and aromatic -OH (533.7). After morphological transition induced by Cu$^{2+}$, XPS spectrum of randomly twisted fibers showed three peaks at 933.2, 934.9, and 954.7 eV along with satellite peaks, which were attributed to -Cu-N, Cu 2P$_{3/2}$ and Cu 2P$_{1/2}$ respectively. Figure 6.8 shows the mode of binding of metal ion in the tubule structure.

**6.2.8 Emission Studies**

Considering the presence of receptor unit in helical tubules formed by chiral molecular packing of GAP, the addition of Cu$^{2+}$ trigger the morphological transition via chiral symmetry breaking, which could also be visualized by measuring photophysical properties. Fluorescence spectra of helical tubules in 1,2-dichlorobenzene displayed a prominent peak at 515 nm for the excitation at 315 nm. Figure 6.12a shows the temperature dependent fluorescence spectra of helical tubules. It is clearly evident that the fluorescence intensity of peak observed at 515 nm decreases with increase in temperature, whereas the peak observed at 615 nm for 1,2-dichlorobenzene remain unchanged. Owing to the increasing temperature the inception of breaking of chiral molecular packing occurs, thereby the emission intensity decreases sharply. In addition, there is a bathochromic shift of the emission peak in assembled state than the solution form supporting the J-type of molecular assembly (Figure 6.12a). A gradual decrease in emission intensity in response to
increasing temperature proposes the involvement of aggregation induced emission (AIE) (Figure 6.12b).²¹

**Figure 6.12.** (a and b) Temperature and Cu²⁺ dependence of emission profile of GAP in 1,2-dichlorobenzene.

It should be noted that the intensity of fluorescence signal decreased almost linearly with the increasing Cu²⁺ concentration corroborate the morphological transition from helical tubules to randomly twisted fibers (Figure 6.12b). *In situ* morphological transition via chiral symmetry breaking of helical tubules on exposure to biologically significant ions with or without making any phase change can be directly inferred from visual inspection and emission studies (Table 6.2).

The above studies revealed that the change in emission intensity and wavelength can be attributed to the morphological change. The phase change in gel system can be keyed out by visual inspection. The addition of Ca²⁺ and Mg²⁺ did not affect both the phase and morphology of helical fibers, whereas Zn²⁺ and Al³⁺ induces morphological transition without affecting the phase (Figure 6.13). Helical tubules on exposure to Fe³⁺ induces phase change (gel to sol) and morphological transition
The phase transition of gel formed by GAP in 1,2-dichlorobenzene in response to various metal ion is shown in Figure 6.14.

Figure 6.13. (a-e) Emission spectra of helical tubules in 1,2-dichlorobenzene and its response to metal ions (a) Ca$^{2+}$; (b) Mg$^{2+}$; (c) Zn$^{2+}$; (d) Al$^{3+}$; (e) Fe$^{3+}$. In titration experiments, direction of arrow shows the response of emission intensity with piecemeal addition of 100 µL of corresponding M$^{n+}$ solution. 2 mL of initial volume of solution (1x10$^{-5}$M) was taken for titration experiments.
Figure 6.14. Phase transition of gel formed by GAP in 1,2-dichlorobenzene in response to (a) Cu$^{2+}$; (b) Zn$^{2+}$; (c) Ca$^{2+}$ (d) Mg$^{2+}$ and (e) Al$^{3+}$.

### Table 6.2. Metal ion induced phase and morphological transition of gel formed by GAP in 1,2-dichlorobenzene

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Emission Intensity</th>
<th>Phase Transition</th>
<th>Morphological Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>Decrease</td>
<td>No (gel)</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>No effect</td>
<td>No (gel)</td>
<td>No</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>No effect</td>
<td>No (gel)</td>
<td>No</td>
</tr>
<tr>
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<td>Increase</td>
<td>No (gel)</td>
<td>Yes</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
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<td>Yes</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>Decrease</td>
<td>Yes (sol)</td>
<td>Yes</td>
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</tbody>
</table>

### 6.2.9 Rheological Studies

Rheological studies show that the morphological transition is accompanied with change in viscoelastic character (Figures 6.15a and 6.15b). In the entire range of frequency sweep, the value of the storage modulus ($G'$) was found to be much higher than that of the loss modulus ($G''$) indicating that the gel exhibit good tolerance to external forces (Figure 6.15b). The critical strain ($\gamma_c$) values for GAP and after the addition of Cu$^{2+}$ are 4.29 ($G' = G'' = 7313.79$ Pa) and 15.77 ($G' = G'' = 1390.77$ Pa).
Figure 6.15. (a) Strain amplitude dependence; (b) Dynamic frequency sweep of gel derived from GAP-red line, and after addition of Cu$^{2+}$-blue line.

Continuous temperature ramp up and ramp down experiments was used to analyze the thermo-responsive behavior these gels (Figures 6.16a and 6.16b). These results clearly depict the structural and mechanical integrity of gels.

Figure 6.16. (a-d) Time course change of storage ($G'$) and loss ($G''$) modulus in (a and b) temperature ramp experiment; (c and d) step strain experiment of gel formed by (a and c) GAP in 1,2-dichlorobenzene; (b and d) after the addition of Cu$^{2+}$ solution on gel formed by GAP in 1,2-dichlorobenzene, respectively.
The thixotropic behavior of these gels was identified by performing step strain experiments of $G'$ and $G''$ (Figures 6.16c and 6.16d). When high magnitude of strain (100%) was applied, decline of $G'$ and $G''$ occurs due to the broken network structure and quick recovery of $G'$ and $G''$ was observed by the simultaneous decrease in strain to 0.1%. These results suggest that there is no significant loss in mechanical behavior.

6.3 Experimental Section

Materials and methods has been discussed in the section 2.3.1 of chapter 2.

6.3.1 Characterization Methods

The detailed discussion of the characterization methods involving NMR and mass spectral analysis is given in the section 2.3.2 of chapter 2. Electrospray ionization mass spectra (ESI-MS) were carried out in positive mode with a Thermo Fisher LCQ Advantage Max. instrument by dissolving the solid sample in methanol. FT-IR spectra of GAP in powder and helical tube form were recorded as xerogel in an attenuated total reflectance (ATR) mode using Perkin Elmer 100 FTIR Spectrometer in the spectral range of 4000 to 500 cm$^{-1}$.

The gelation ability of the compound were systematically studied in different organic solvents and oils by adopting the procedure given in the section 2.3.3 of chapter 2. Morphology of self-assembled structure formed by $\text{3c}$ and its corresponding $\text{Cu}^{2+}$ induced morphological transition was studied by following the procedure discussed in the section 2.3.5 chapter 2. The mechanical properties of gel were investigated using rheometer by following the procedure discussed in the section 2.3.8 of chapter 2.
6.3.2 UV-visible and Circular Dichroism (CD) Spectral Analysis

UV-vis spectra were recorded on Thermo Scientific Evolution 220 UV/visible spectrophotometer. The spectra were recorded in the continuous mode between 200 and 700 nm, with a wavelength increment of 1 nm and a bandwidth of 1 nm. CD spectra were obtained using JASCO J-815 CD spectrometer. The samples were loaded in a quartz cuvette of 0.1 cm path length.

6.3.3 X-ray Photoelectron Spectral Analysis (XPS)

XPS spectra of helical tubules and randomly twisted fiber formation triggered by Cu$^{2+}$ were recorded using Thermofisher scientific, UK, K-Alpha surface analysis model using Al. X-ray in a wide range of 0-1350 eV.

6.3.4 Emission Studies

Emission spectra were measured on a JASCO spectrofluorometer FP-8200, by fixing the excitation value at 310 nm for 1,2-dichlorobenzene solvent. Samples for absorption and emission measurements were contained in quartz cuvette. Fluorescence was also recorded at 25 °C and upto 75 °C for every 5 °C increment.

6.3.5 Synthetic Procedure and Characterization Data

6.3.5.1 General Procedure for the Synthesis of Sugar Based Amphiphiles 3a-c

To gluconolactone (1.0 mmol) in ethanol (15 mL), hydrazine hydrate (1.5 mmol) was added and refluxed for 30 min and 2-hydroxy-4-alkylbenzaldehydes 2a-c (1.0 mmol) was added and further refluxed for 90 min. The progress of the reaction was monitored by performing TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the precipitated solid was filtered and dried.
**Compound 3a**

Appearance : White solid

Yield : 96%

Mp : 200-202 °C

$^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta = 11.49$ (s, 1H, Ar-OH), 11.39 (s, 1H, -NH), 8.60 (s, 1H, -CH=N), 7.43 (dd, $J = 8.1, 1.8$ Hz, 1H, Ar-H), 7.29 (t, $J = 8.1$ Hz 1H, Ar-H), 6.90 (dd, $J = 8.1, 6.0$ Hz, 2H, Ar-H), 5.64 (d, $J = 5.1$ Hz, 1H, Sac-H), 4.62 - 4.54 (m, 3H, Sac-H), 4.39 (t, $J = 5.4$ Hz, 1H, Sac-H), 4.21 (t, $J = 4.5$ Hz, 1H, Sac-H), 4.02-3.95 (m, 1H, Sac-H), 3.62-3.58 (m, 1H, Sac-H), 3.52–3.49 (m, 2H, Sac-H)

$^{13}$C NMR (DMSO-$d_6$, 75 MHz) $\delta = 170.67, 169.00, 157.38, 148.55, 131.26, 129.78, 119.30, 118.40, 116.35, 73.37, 71.86, 71.45, 70.41, 63.23$

HRMS (ESI+) $m/z$ calculated: for C$_{13}$H$_{18}$N$_2$O$_7$ [M+H]$^+$: 314.1114. Found: 315.4376.

**Compound 3b**

Appearance : Pale white solid

Yield : 92%

Mp : 192-194 °C

$^1$H NMR (DMSO-$d_6$, 300 MHz) $\delta = 11.43$

(s, Ar-OH), 11.38 (s, -NH), 10.16 (s, Ar-OH), 8.55 (s, -CH=N), 7.58 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.29 (d, $J = 7.8$ Hz, 1H, Ar-H),
6.80-6.72 (m, 2H, Ar-H), 5.62 (d, J = 5.1 Hz, 1H, Sac-H),
5.34–5.30 (m, 2H, -CH=CH₂), 4.60-4.53 (m, 3H, Sac-H),
4.37 (t, J = 5.7 Hz, 2H, Sac-H), 4.20 (t, J = 4.5 Hz, 1H,
Sac-H), 3.99 (s, 1H, Sac-H), 3.58–3.40 (m, 3H, Sac-H),
2.59-2.53 (m, 2H), 2.0-1.97 (m, 4H), 1.56-1.53 (m, 4H),
1.35-1.25 (m, 14H), 0.88-0.83 (m, 3H)

\( ^{13}\text{C NMR} \) (DMSO-\( d_6 \), 75 MHz) \( \delta = 190.13, 168.94, 167.20, 159.12, 
155.86, 150.51, 147.13, 144.67, 139.82, 128.11, 118.51,
118.33, 114.88, 114.39, 71.79, 70.29, 69.88, 68.79, 61.65,
33.72, 33.47, 29.46, 28.52, 27.41, 27.32, 26.99, 26.89,
26.61, 24.92, 23.55, 20.41, 19.49, 12.24

HRMS (ESI+) \( m/z \) calculated for \( \text{C}_{28}\text{H}_{46}\text{N}_2\text{O}_7 \)[M+H]\(^{+}\): 522.3305. Found:
523.5875.

Note: Because of the possible E-Z isomerization of compound 3b, two different
signals for proton and carbon were observed.

**Compound 3c**

**Appearance**: White solid

**Yield**: 95%

**Mp**: 196-198 °C

\( ^1\text{H NMR} \) (DMSO-\( d_6 \), 300 MHz) \( \delta = 11.43 \) (s, 1H), 11.38 (s, 1H), 8.55 (s, 1H, 
-\( \text{CH}=\text{N} \)), 7.29 (d, \( J = 8.1 \) Hz 1H, Ar-H), 6.80-6.71 (m, 2H,
Ar-H), 5.62 (d, \( J = 5.1 \) Hz, 1H, Sac-H), 5.48 (d, \( J = 5.4 
\) Hz, 1H, Sac-H), 4.61-4.54 (m, 3H, Sac-H), 4.41–4.33 (m,
2H, Sac-H), 4.20-4.15 (m, 2H, Sac-H), 3.54–3.48 (m, 2H,
175

Sac-H), 2.59-2.53 (m, 2H), 1.59–1.54 (m, 2H), 1.35-1.25
(m, 24H), 0.88-0.83 (m, 3H)

^{13}_{C}\,NMR\quad (DMSO-d_6,\,75\,MHz) \quad \delta = 170.68,\,168.90,\,157.57,\,148.85,
146.40,\,129.91,\,119.59,\,116.10,\,72.97,\,71.65,\,71.54,
70.45,\,63.46,\,35.18,\,31.35,\,30.54,\,29.07,\,28.78,\,22.15,
13.97

HRMS (ESI+) \quad m/z\,calculated\,C_{28}H_{48}N_{2}O_{7}\,[M+H]^+:\,524.3462.\,Found:\,525.6153.

Note: Because of the possible E-Z isomerization of compound 3c, two different
signals for proton and carbon were observed.

6.4 Conclusion

In conclusion, by rational molecular design and synthesis of glucono-
appendedd cardanol derivatives, it was shown the chiral molecular packing forms
helical tubules and chiral symmetry breaking on exposure to Cu^{2+} ions generated the
final ordered structure through an in situ morphological transition without change in
phase. In addition, helical tubules on exposure to water lead to spontaneous formation
of unzipped helical tubules. The hydrophilic nature of tubule pores and hydrophobic
nature of tubule walls in gel form using a simple visual inspection was demonstrated.
Morphological and phase transition of gel formed by helical tubular network on
exposure to various biologically significant cations was established by emission
studies. Viscoelastic and thixotropic behavior of gel associated with the above
discussed transition was investigated by rheological measurements. The bio-based
scaffold reported in this communication explains the creation of dynamic assembled
structures, which is crucial in biological processes performing complex functions.
This hypothesis may lead to a new pathway molecular assembly studies in variety of research fields where morphological and phase transition were introduced.

6.5 References


