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ARTICLE TYPE

A correlation study between hydrogen bonded network and gelation ability of three galactose derivatives

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Correlation study between gelling/non-gelling behaviour and presence (or absence) of one dimensional (1D) hydrogen bonded network in single crystal structures of three galactose derivatives (*p*-methoxyphenyl-β-D-galactopyranoside, **1**, *p*-methoxyphenyl-3,4-O-isopropylidene-β-D-galactopyranoside, **2** and *p*-methoxyphenyl-6-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranoside, **3**) is attempted. Structure-property correlation studies in literature suggest that the presence of 1D hydrogen-bonded network promotes efficient gelation in hydrogen-bond-based gelators. Unexpectedly, saccharide **1** having 2D hydrogen bonded network (HBN) showed efficient gelation ability in various solvents while saccharide **3** with 1D HBN failed to show gelation. Failure of the latter could be because of unsuitable surface compatibility of self-assembled fibrillar networks (SAFiNs) and solvent molecules. On the other hand, saccharide **2** with 2D HBN was found to be a non-gelator as expected. Importantly, saccharide **1,** which is a simple, small and eco-friendly LMWG and easily prepared from cheaply available D-galactose, is an efficient gelator for 1,2-dichlorobenzene with the critical gelation concentration of only 0.25% w/v. FT-IR spectroscopy showed the involvement of intermolecular hydrogen bonding in gelation process and rheological experimental results confirmed its true gel behaviour. SEM and AFM studies revealed the fibrous entanglement of the molecules in the gel state.

1. Introduction

Low-molecular-weight gelators (LMWGs)[1] are soft materials that have gained attention in recent years owing to their unique characteristics and wide range of potential applications in diverse fields.[2] LMWGs are a family of small molecules having molecular mass typically < 3000 that are capable of encapsulating solvents through molecular self-assembly and thus form three-dimensional (3D) structural architectures. Several non-covalent interactions such as π-stacking, van der Waals interactions or hydrogen bonding are responsible for the 3D structures formed by LMWGs. LMWGs can be classified into two groups: non-hydrogen-bond-based and hydrogen-bond-based gelators depending on the driving forces. The carbohydrate gels having free OH groups generally fall within the latter category. Recently, structural modification of carbohydrates has gained the attention of researchers to obtain smart LMWGs [3] because carbohydrate molecules are biocompatible and their gels can be prepared in large quantities from cheap starting materials using relatively simple and well established synthetic methodologies.

Most of the gelators reported in the literature correspond to serendipitous discoveries and it is still difficult to predict the gelation ability accurately. Shinkai and co-workers[4] by analyzing hydrogen bonding network (HBN) in single-crystal structures of some structurally isomeric sugar molecules proposed that the 1D HBN is the key for gelation behaviour. In their correlation study, the molecules having 1D network formed by two intermolecular H-bonds were only found to be good gelators but not the 2D, 3D or 0D HBN structures. It is quite reasonable to believe that strong and unidirectional HBN may facilitate the growth of the gel fibrils in one direction to form elongated gel fibrils and thus resulting gelation and that was the logic behind their proposal. Hanabusa *et al*.[5] and Esch and Ferringa[6] mentioned the importance of 1D self-assembly in gelation. Thereafter very few reports appeared in the literature[7] on that correlation hypothesis and in most of the cases compounds showing 1D HBN in the crystal structures were found to be good gelators. In 2008, Dastidar[8] has discussed the correlation phenomenon elaborately for a variety of different hydrogen bonded gelators in his review.

However, there are very limited number of reports of the crystal structures of gelator molecules owing to the difficulties in obtaining good quality single crystals of gelators and this is generally a limitation in this regard. Moreover, a molecule necessarily may not possess the similar structures in both the gel and crystal states. The, prerequisite for a molecule to self-assemble in one dimensional network in order to be a gelator is an important indicator rather than a sufficient criteria to ensure gelation. Although that working hypothesis has some exceptions

and limitations but it can be quite useful in designing efficient LMWGs. Therefore, more number of H-bonded gelators with their single crystal structures is important to establish a reliable structure-property correlation.

In our present study, we have synthesised three galactose derivatives through protecting group manipulations (Fig. 1). Among these galactosides, *p*-methoxyphenyl-β-D-galactopyranoside (**1**), which is simple, biodegradable and easy to synthesise in large quantities, serves as a low molecular weight thermo-reversible gelator. The self-aggregation behaviour of this organogelator was characterized using several commonly used techniques. Notably, we were able to obtain single crystals of all the three compounds and attempted to correlate the gelling/non-gelling behaviour with the hydrogen bonding networks in their single crystal structures. Unpredictably, galactoside **1** having 2D HBN exhibited efficient gelation while galactoside **3** with 1D HBN was not a gelator, contrary to the generally noticed one-dimensional hydrogen-bonded architecture in gelation. On the other hand, galactoside **2** forms 2D hydrogen bonding array and it does not act as a gelator, hence in line with the general hypothesis.

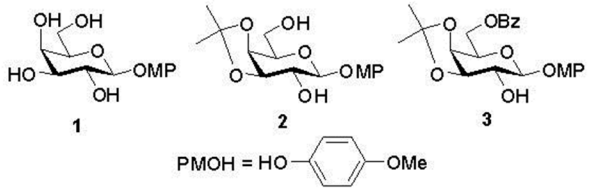

Fig. 1. Chemical structures of the compounds used in this study.

2. Experimental

2.1. Materials:

D-galactose and other reagents were purchased from Sigma-Aldrich. Commercially available solvents were used as received without further purification.

2.2 Chemical synthesis:

Three galactose derivatives (*p*-methoxyphenyl-β-D galactopyranoside (**1**)[9], *p*-methoxyphenyl-3,4-O-isopropylidene-β-D-galactopyranoside (**2**)[10], *p*-methoxyphenyl-6-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranoside (**3**)[11] are reported in the literature and they were synthesized and purified by following the reported methods. NMR (^{1}H and ^{13}C) and Mass spectrometry were used for their characterization and their spectra were matched with previously reported data.

2.3. NMR:

^{1}H and ^{13}C nuclear magnetic resonance (NMR) analyses of compounds **1**, **2** and **3** were performed on a Bruker 500 MHz NMR at 298 K. CD_3OD was used as NMR solvent for compound **1** whereas $CDCl_3$ was used for **2** and **3**.

2.4. Mass Spectrometry:

Mass spectra were recorded on a Q-TOF Micro YA263 high-resolution (Waters Corporation) mass spectrometer by positive-mode electrospray ionization.

2.5. Gelation and Gel Characterization:

Required amount of the gelator and measured volume of selected pure solvent were placed in a screw-capped vial with internal diameter (i.d) of 10 mm and slowly heated until the solid was completely dissolved. Then the solution was cooled to room temperature in air to form the gels. The vials were inverted to observe formation of the gels. Minimum gelation concentration (MGC) was determined by finding the minimum amount of gelator required for gel formation at room temperature. All of the gels were found to be thermally reversible. Upon heating above their gel dissociation temperature they transformed to solution state and returned to their original gel state upon cooling.

2.6. Determination of gel-sol transition temperature (T_{gel}):

The gel-to-sol transition temperature (T*gel*) was determined by dropping ball method. A small glass ball (210 mg) was placed on a 1 mL gel in a standard 15 mm vial. Then the vial was heated slowly in a thermostated oil bath while observing the temperature. The temperature at which the ball dropped to the bottom of the gel was recorded as T*gel*.

2.7. FT-IR Spectroscopy:

FT-IR spectra of the galactoside **1** in its solid state and xerogel state were obtained using a Fourier-transform infrared spectrometer (PerkinElmer 502). KBr samples (2 mg in 20 mg of KBr) were prepared and 10 scans were collected at 4 cm^{-1} resolution for each sample. The spectra were measured at room temperature over the range of 4000-500 cm^{-1}.

2.8. Atomic Force Microscopy (AFM):

The morphology of the dried gels was studied by using AFM (NTMDT instrument, model AP0100) in semi-contact mode. A small portion of gel sample was placed on a freshly cleaved mica sheet and dried for a few hours under vacuum before imaging.

2.9. Field Emission Scanning Electron Microscopy (FE-SEM):

FE-SEM was performed using JEOL-6700F microscope. A small piece of gel sample was placed on a clean microscope cover glass and dried first in air and then in vacuum. Then, the sample was coated with platinum and dried in vacuum before imaging.

2.10. Rheological study (frequency sweep) of gel:

Rheological measurement was done using a stress-controlled rheometer (TA Instruments, ARG2) equipped with steel parallel-plate geometry (40 mm diameter). The gap distance was fixed at 750 μm. A solvent-trapping device was placed above the plate to avoid evaporation. All measurements were made at 15 °C. The frequency sweep was obtained from 0.62 to 628.3 rad s^{-1} at a constant stress of 4000.0 Pa.

2.11. Single crystal preparation:

For X-ray investigation, crystals of the three galactose derivatives (galactoside **1**, **2** and **3**) were obtained. Crystals of galactoside **1** were obtained by the slow evaporation from acetone solution. Needle type colourless crystals in pure form

appeared in two days. In case of galactoside **2** colourless needle type crystals were obtained after ten days from the hexane/ethyl acetate solution (1:2) while the galactoside **3** crystals (colourless needles) appeared after eight days by slow evaporation method from toluene solution.

2.12. Crystallography:

Crystals of the three galactose derivatives were individually mounted on a glass pip. Intensity data were collected on a Brukar's KAPPA APEX II CCD Duo system with graphite-monochromatic Mo *K*α radiation (λ = 0.71073 Å). The data were collected at 298 K temperature for all the crystals. Data reduction was performed using Bruker SAINT software.[12] Crystal structures were solved by direct methods using SHELXL-97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELXL-97.[13] Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. Hydrogen atoms associated with oxygen atoms were included in the located positions. Structure graphics shown in the figures were created using the X-Seed software package version 2.0 and mercury software package version 2.4.

2.13. Melting Point:

Melting points of three crystals were measured using a digital melting point apparatus, SECOR INDIA. Melting points for crystals **1**, **2** and **3** were found as 160°C, 135°C and 155°C respectively.

3. Results and discussion

The gelation behaviour of compounds **1**, **2** and **3** have been tested from different solvents and the results are summarized in Table 1. The compound **1** showed impressive gelation capability from 1,2-dichlorobenzene, chlorobenzene, bromobenzene etc. with the range of minimum gelation concentration of 0.25 to 2% w/v. The very low CGCs in 1,2-dichlorobenzene and chlorobenzene elevate it to the category of super-gelator. The gelation process was reversible, such that it can be turned to solution by heating and be reformed upon cooling. Repetition of the cycle was done many times and gelation ability was found to be unchanged, showing the thermoreversible nature of the gel. The gels were stable at room temperature and no noticeable changes occurred after storing in a closed container for 2 months, indicating their temporal stability. The effect on gel to sol transition temperature (*T*gel) with increasing gelator concentration in case of 1,2-dichlorobenzene gel is shown in Fig. S1 (ESI†). T*gel* values increased to 403 K with an increase of gelator concentration upto 4% w/v and then (4%-8% w/v) it reached a plateau where nearly no dependence of the phase transition on concentration was observed.

3.1 FT-IR study of the hydrogen bond network:

Various noncovalent interactions are generally responsible for self-assembly in the gel state. Among them, hydrogen bonding is one of the major driving forces for the formation of a supramolecular architecture in LMWGs. The Fourier transform infrared (FT-IR) study is very useful for the detection and characterization of hydrogen bonding in self assembled state. Fig. 3 shows the FT-IR spectra of the crystalline (a) and xerogel (b) state of **1**. The theoretical calculation predicts the O–H stretching modes in FT-IR spectra to be at 3640 cm^{-1}, 3566 cm^{-1}, 3592 cm^{-1} and 3660 cm^{-1}, as shown in Fig. S2 (ESI†). Such bands are not present in the experimental spectra and in both the states no bands are observed at 3600 cm^{-1} (free OH stretching vibration), indicating that all the O-H groups are hydrogen bonded. In the FT-IR spectra, crystalline state exhibits O–H stretching vibrations at 3568 cm^{-1}, 3468 cm^{-1}, 3353 cm^{-1} and 3252 cm^{-1}.

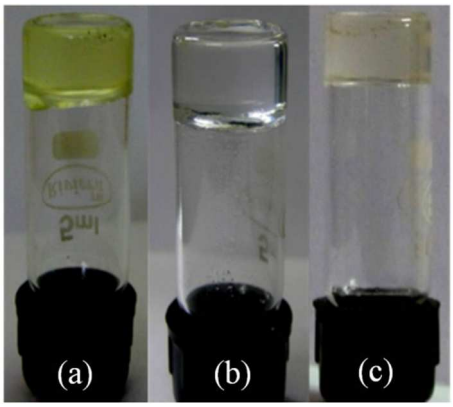

Fig. 2. Photographs to show the gels of compound **1** in different solvents: (a) nitrobenzene, (b) 1,2-dichlorobenzene and (c) bromobenzene.

Table 1 Gelation ability of the compound **1** in various solvents[a]

Liquids	**1**	**2**	**3**
	MGC (% w/v)	MGC (% w/v)	MGC (% w/v)
1,2-Dichlorobenzene	0.25 (T.G)	PS	PS
Toluene	I	P	crystal
Xylene	I	P	S
Mesitylene	I	PS	S
Benzene	2 (T.G)	P	P
Nitrobenzene	1 (O.G)	PS	PS
Bromobenzene	0.9 (O.G)	P	P
Acetone	crystal	S	S
Butanol	crystal	S	PS
Methanol	S	crystal	P
Water	I	I	I
CCl_4	PS	P	I
Flurobenzene	1.7 (O.G)	P	P
Chlorobenzene	0.4 (O.G)	P	P

[a]TG = transparent gel; OG = opaque gel; S = soluble; I = insoluble, P = precipitate, PS = partially soluble

On the other hand, in the xerogel state all the four bands merge

and result in a single broad band centering at 3370 cm^{-1}. This suggests that in xerogel state O–H group frequencies are not resolved. However, in both the states compound **1** reveals hydrogen bonded O–H signals and on the basis of the experimental results it can be concluded that intermolecular hydrogen bonding acts as one of the major driving forces for self-assembly of the gelator in both the gel and solid states.

3.2 Microscopy studies:

To get a visual insight into the morphology of organogels, the microstructure was inspected by AFM and FE-SEM. Fig. 4 (a, b and c) show AFM images of the xerogels of compound **1** in 1,2-dichlorobenzene and nitrobenzene respectively. 1,2-Dichlorobenzene gel shows the three dimensional networks formed by cross linking of self-assembled fibrillar networks (SAFiNs)[1h], approximately 80-120 nm in diameter and several micrometers in length and which probably indicate the entrapment of the solvent molecules into the spaces in the 3D network. In case of nitrobenzene gel, spiral fibrous type of morphology was observed with approximately 50-70 nm in diameter and several micrometer long fibres. FE-SEM image in Fig. 4 (d) of the 1,2-dichlorobenzene gel shows cross linked nano-fibrous morphology and these are approximately 70-120 nm in diameter.

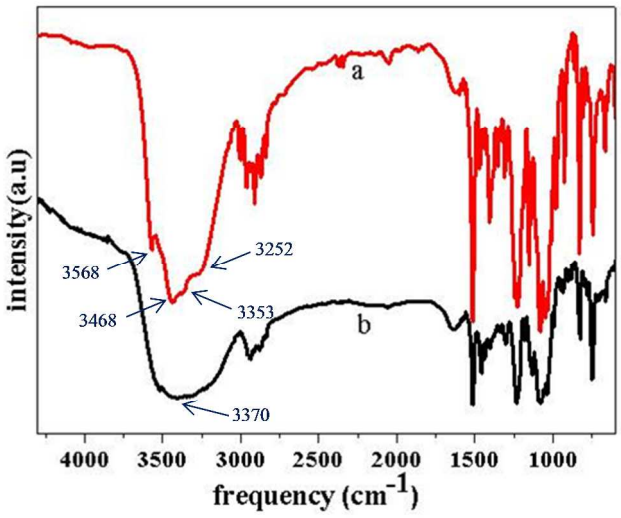

Fig. 3. (a) FT-IR Spectra of compound **1** in (a) crystalline state and (b) xerogel state (0.25% w/v in 1,2-dichlorobenzene).

3.3. Rheological study (frequency sweep) of gel:

In rheological measurements, frequency sweep is often used to record the tolerance power of a material to external forces. The frequency sweep rheometry measurement of the gelator was carried out using 1,2-dichlorobenzene gel (1.0%, wt/v) at a low shear stress. As shown in Fig. 5, storage modulus (G') was higher than loss modulus (G") and no crossover is observed over the whole frequency range, showing a typical gel behaviour with a good tolerance performance to external forces. In addition, storage modulus (G') was found in the order of 10^4, indicating the significant mechanical strength of the gel.

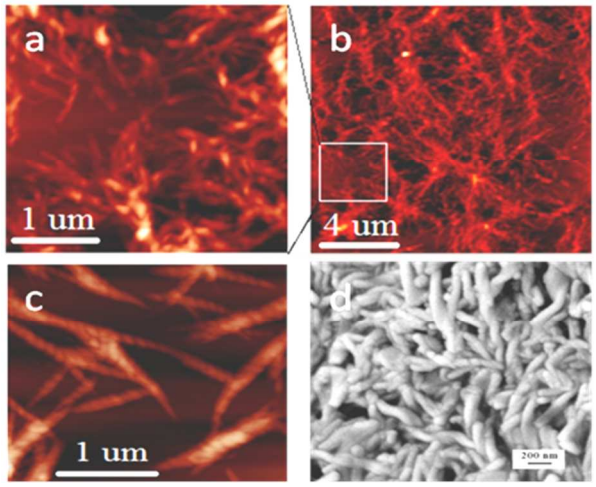

Fig. 4. AFM images of the gels of **1** from (a,b) 1,2-dichlorobenzene and (c) nitrobenzene. (d) FE-SEM image of the gel of **1** from 1,2-dichlorobenzene at their CGCs.

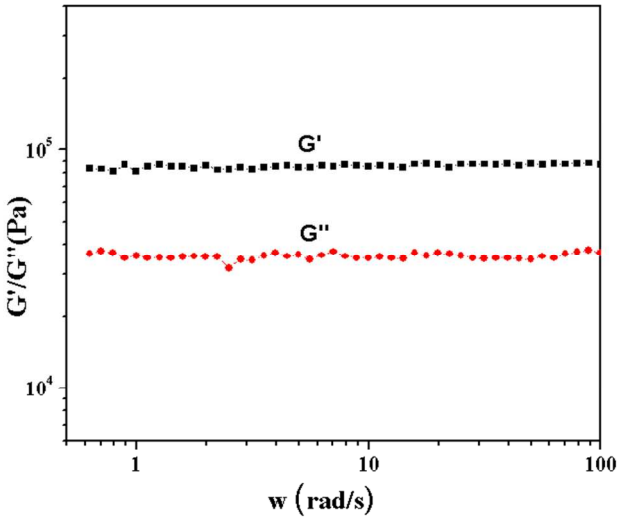

Fig. 5. Dynamic rheology of the organogel containing 1.0% w/v gelator **1** in 1,2-dichlorobenzene as a function of angular frequency (rad s^{-1}) at 15 °C

3.4. Single Crystal X-Ray Diffraction studies:

For X-ray diffraction investigation, crystals of the three galactose derivatives (**1**, **2** and **3)** were obtained. The experimental data and structure refinement parameters are given in Table S1 (ESI†). Selected bond lengths and angles are given in Table S2-S4 (ESI†). Crystal structure analysis indicates that in all the sugar compounds, pyranose ring remain in the typical $^4C_1$ conformation.

Compound **1** crystallizes in the monoclinic $P2_1$ space group with two molecules in the asymmetric unit (Z = 2). The *p*-methoxyphenyl ring of the molecule in the asymmetric unit is not

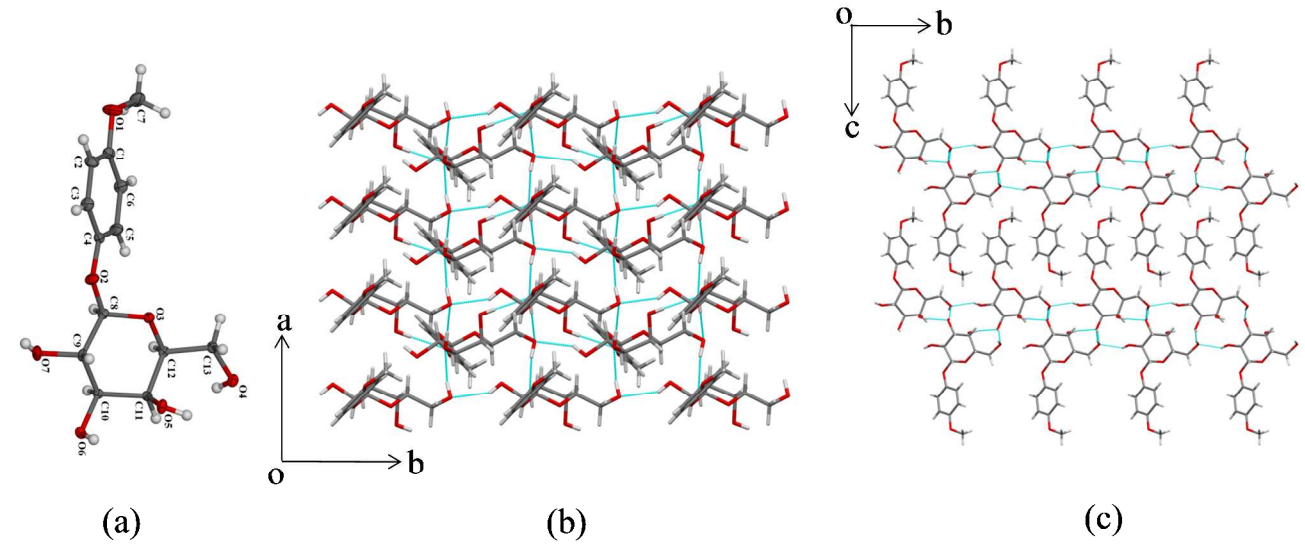

Fig. 6. (a) Crystal structure of compound **1**. ORTEP representation of the molecule. Thermal ellipsoids are drawn at the 50% probability level. (b) Molecular packing showing 2D HBN in the crystal structure (c) Formation of double sided comb-like 2D sheets via strong intermolecular O–H...O hydrogen bonds. Notice the interlocking of methoxyphenyl groups from the planar molecular packing, in the *ab*-plane.

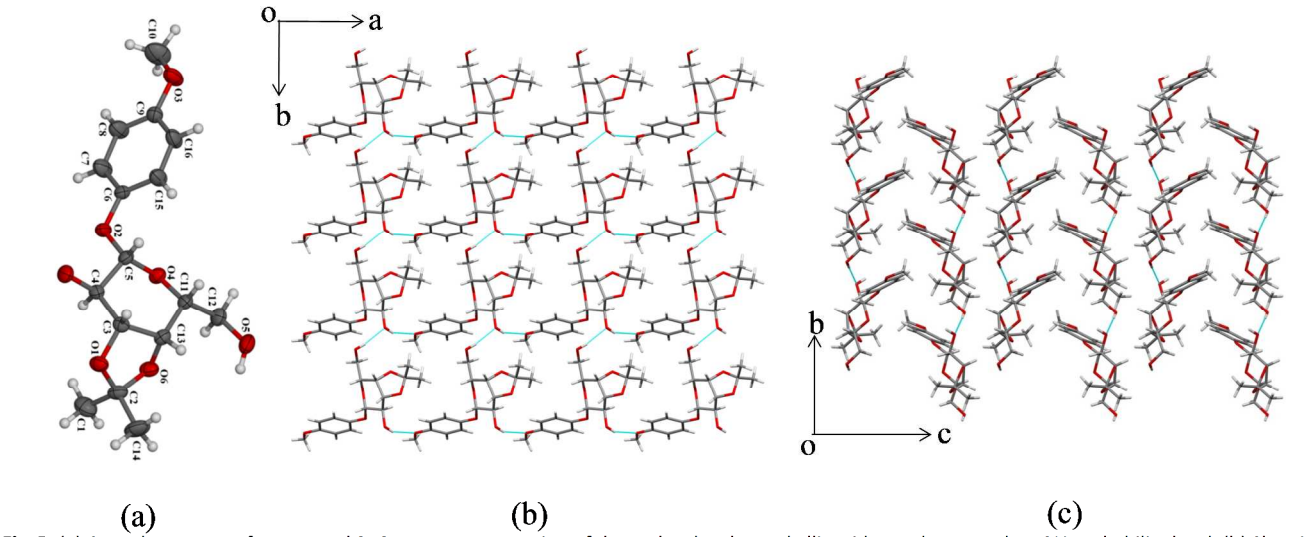

Fig. 7. (a) Crystal structure of compound **2**. ORTEP representation of the molecule. Thermal ellipsoids are drawn at the 50% probability level. (*b*) Showing the formation of 2D-square grid network via the strong O–H···O hydrogen bonds. (c) Molecular packing viewed along *a*-axis and the molecules are connected via O–H···O interactions.

coplanar with galactoside moiety. The torsional angles of the *p*-methoxyphenyl ring and galactoside moieties are -164.6(2)º (C4-O2-C8-C9) and 179.7(3)º (C8-O2-C4-C3), which indicate that there is no planarity in the molecule. The molecule contains four free hydroxyl groups which form multiple intermolecular hydrogen bonds. The galactoside moieties of adjacent molecules are connected via multiple O–H···O hydrogen bonding interactions in the crystal structure and extended in 2D HBN as shown in Fig. 6b. As a result, the molecules form a thick two sided comb-like 2D sheets running along *b*-axis. Furthermore, the adjacent 2D sheets are interlocked by close packing of *p*-methoxyphenyl groups in space filling manner and thus form 2D layer structure with intralayer π-stacking interactions (Fig. 6c).

Compound **2** crystallizes in the monoclinic $P2_1$ space group with two molecules in the asymmetric unit (Z = 2). The molecule contains two free hydroxyl functional groups which form two O–H···O (O3–H3A···O1: 2.857(3) Å, 156°; O5–H5A···O3: 2.833(3) Å, 168°) hydrogen bonds and thus forms 2D HBN in single crystal structure. These intermolecular hydrogen bonding interactions lead to the formation of a 2D square grid network parallel to (001) plane (Fig. 7b). These layers are stacked along the *c*-axis to further stabilize the structure by multiple weak C–H···O interactions (C3–H3···O7: 3.275(4) Å, 139°; C12–H12···O5: 3.335(3) Å, 133 °) (Fig. 7c).

Compound **3** crystallizes in the monoclinic *C*2 space group with four molecules in the asymmetric unit (Z = 4). The *p*-

methoxyphenyl ring and benzoyl ester of the molecule in the asymmetric unit are not coplanar with galactoside moiety. The molecule contains only one free hydroxyl functional group which forms O–H···O (O4- H5...O5; 2.777(5) Å, 159°) hydrogen bond with O-atom of the five membered ring of **3**. This leads to formation of a zig-zag linear 1D tape parallel to *b*-axis and thus exhibits 1D HBN (Fig. 8b).

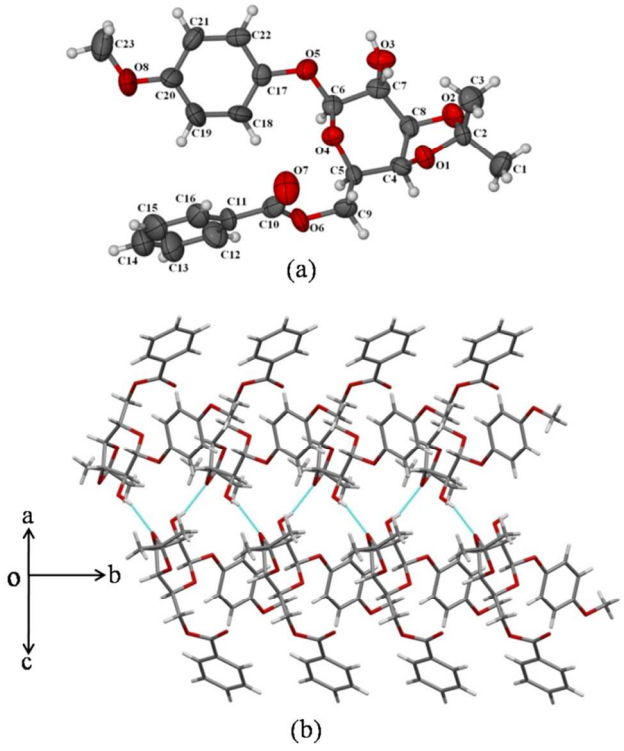

Fig. 8. (a) Crystal structure of compound **3**. ORTEP representation of the molecule. Thermal ellipsoids are drawn at the 50% probability level. (b) Showing the formation of 1D tapes via O4–H5...O5 hydrogen bonds.

3.5. Powder X-ray diffraction (PXRD):

PXRD is a very useful technique to determine the molecular packing in different states. Weiss and co-workers[14] for the first time proposed a structure-property correlation by comparing the PXRD patterns of the native gel state with simulated PXRD patterns obtained from single-crystal data. Typically it is difficult to obtain good quality PXRD patterns from gel samples owing to their poor diffraction. Xerogel samples may be regarded as logically representative, although one cannot throw away the possibility of formation of other morphs, solvates, and so on. In our studies, PXRD patterns of compound **1** in xerogel state were compared with that of the bulk solid and simulated PXRD patterns obtained from single-crystal data. All the three patterns were found nearly superimposable as shown in Figure 9a. Therefore, it can be concluded that the nature of crystal packing in single-crystal, bulk solid and the xerogel state is similar. Figure 9b shows the comparison of PXRD patterns for compound **2** in simulated, bulk solid and precipitate states. Interestingly, the bulk solid pattern, which is very similar to the precipitate, shows some additional peaks that are not present in the simulated pattern obtained from single-crystal data, indicating the presence of some other crystalline phases in the bulk solid forms. In case of compound **3**, the PXRD patterns of simulated, bulk solid and precipitate from benzene show a good agreement, suggesting the presence of similar crystal packing in the three samples (Fig. 9c).

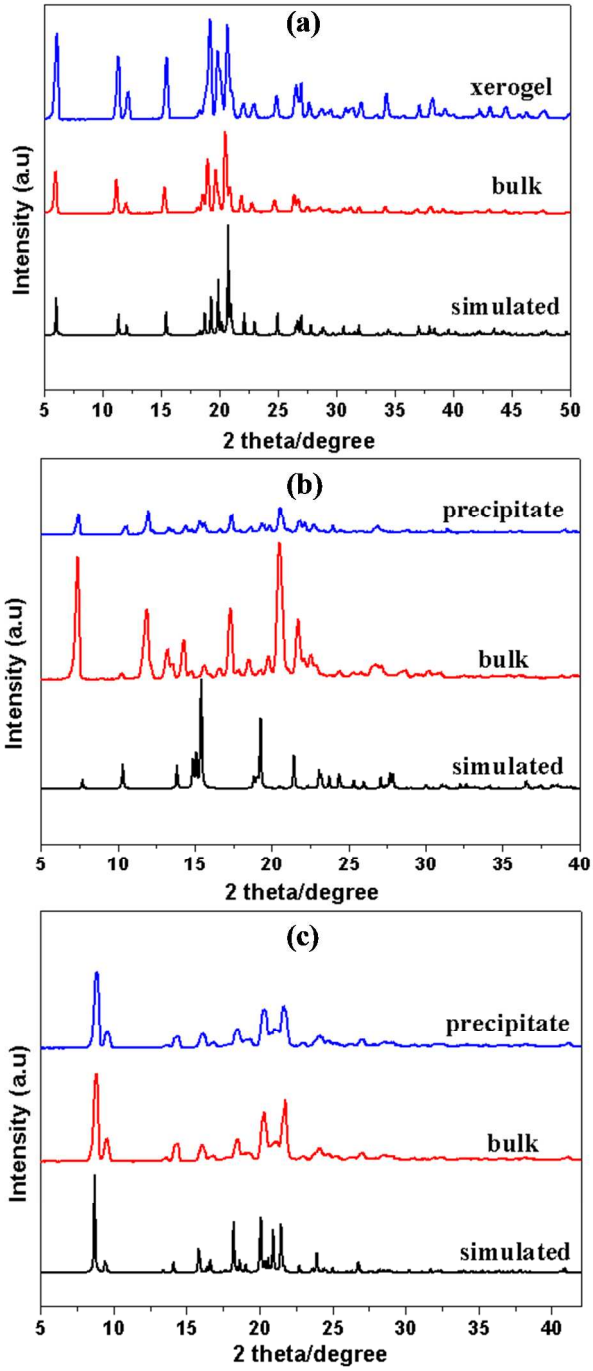

Fig. 9. PXRD patterns of compound **1** (a), **2** (b) and **3** (c) from various states; the xerogel of **1** was prepared from 1,2- dichlorobenzene and precipitates of **2** and **3** were prepared from benzene.

3.6. Correlation between single crystals and gelling/non-gelling behaviour:

The molecular self-assembly need not necessarily be similar in both gel and the crystalline states. Recently, noteworthy similarities were found between gel fiber structure and crystal structure for hydrogen bond based gelators.[15,16] Generally, gel fibrils are not as long and thin like crystals. It is reasonable to believe that strong self-complementary and unidirectional noncovalent interactions are needed to drive one-dimensional growth of gel fibrils to form such elongated fibrils. Strong and one dimensional hydrogen bonding network may facilitate the growth along fibril axis to form 1D elongated fiber and thus resulting gelation. From this point of view 1D HBN is very important for gelation in case of hydrogen bond based compounds and this is the basis of the correlation hypothesis.[4,8] Therefore, according to this hypothesis molecules with 1D hydrogen bonding network in single crystal structure can results efficient gelation while 2D, 3D or 0D HBN may result poor gelation.

In our study, we attempted to correlate single crystal structures of **1**, **2** and **3** (intermolecular hydrogen bonded systems) with their gelation ability. Among these three, only galactoside **1** shows effective gelation in various solvents, while **2** and **3** do not act as gelators. Galactoside **1** exhibits 2D HBN which is supported by multiple O–H···O hydrogen bonding interactions (Fig. 6b), thus is not expected to display gelation ability. However, it shows efficient gelation ability and thus deviates from Shinkai's hypothesis. PXRD studies for compound **1** in single-crystal and xerogel states suggest the presence of similar nature of crystal packing (Fig. 9a). Therefore, it is not clear to us why compound **1,** with 2D HBN instead of the favoured 1D HBN for forming SAFiNs, shows efficient gelation. At the same time, in addition to HBN, we should also consider some other unknown factors (such as rolling of 2D sheets into 1D SAFiNs) that may play a crucial role in the gelation. Indeed, many factors regarding gelation process are yet to be fully understood. Galactoside **2** shows 2D HBN (Fig. 7b), so resulting in a nongelator as expected from the general hypothesis. Although, galactoside **3** forms 1D hydrogen bonding array (Fig. 8b) but it is not a gelator. Although, 1D HBN ensures 1D growth of the fibers but not necessarily the gel formation. If 1D HBN is the only criterion, any gelator would have gelled all the solvents available. In reality, it is not the case. In gelation, solvent molecules are immobilized due to the capillary force within complicated three-dimensional (3D) self-assembled fibrillar networks (SAFiNs). Therefore, the gel would form only when there exists suitable surface compatibility of the SAFiNs and the solvent molecules under consideration.[8] Thus, galactoside **3**, inspite of producing 1D fibre owing to the lack of suitable surface compatibility of the SAFiNs and the solvent molecules failed to show gelation. In this study, galactoside **1** and **3** are not in agreement with the proposed HBN correlation hypothesis, whereas galactoside **2** fits well.

4. Conclusion:

In summary, we have attempted to demonstrate a correlation between hydrogen bonded network in single crystal structures and the gelation abilities of three simple galactose derivatives, **1**-**3**. Among the three compounds, *p*-methoxyphenyl-β-D galactopyranoside (**1**) having 2D HBN in crystal structure was found to act as a simple, eco-friendly low molecular mass gelator which forms stable oraganogels towards organic solvents with CGCs approaching 0.25% w/v and we have characterized its gelation behaviour using several techniques. On the other hand, compound **2** and **3** having 2D and 1D hydrogen bonding networks in crystal packing, respectively, were found to be nongelators. In this study, compound **1** and **3** deviate from the Shinkai's hypothesis while **2** is in agreement. Gelling behaviour of **1** was unexpected and this deviation might be dependent on some other factors rather than only HBN, indicating the complexity of the correlation hypothesis. On the other hand, in case of compound **3**, the unsuitable surface compatibility of the SAFiNs and the solvent molecules under consideration might be the reason for its failure. Therefore, **1** and **3** deviate from this structure based hypothesis. From our study these deviations are not fully explained, but reveal the complexity of this approach. 1D HBN is important but not the only decisive factor for gelation. In fact, this logic may not be applicable in all cases and also factors other than HBN can play a role in gelation which is yet to be fully understood. On the other hand, molecular level understanding of gelation process is still not very well established owing to the lack of understanding of the parameters that trigger gelation process. Some main issues related to the nucleation of fibers, formation of SAFiNs, interactions between the SAFiNs with solvent molecules in 3D network etc. need to be addressed in order to design LMWGs. Therefore, more efforts are needed to establish the molecular level understanding between gel network and solvent molecules for formulating a more generalized hypothesis suitable for designing promising gelators.

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Notes and references

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†Electronic supplementary information (ESI) available: Synthetic scheme, experimental part of PXRD studies, NMR characterization, ^{1}H and ^{13}C NMR spectra and mass spectra for three compounds; X-ray crystallographic data, structure refinement parameters and hydrogen bond parameters of three crystals; gel to solution temperature (*T*gel) graph for **1**; vibrational transitions for **1**. CCDC 865730-865732. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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TOC:

Hydrogen bonding network in the crystals of three saccharides was correlated with their gelling ability or inability and unexpectedly, a 2D hydrogen bonded system was found to show efficient gelation whereas 1D hydrogen bonding system was nongelator.