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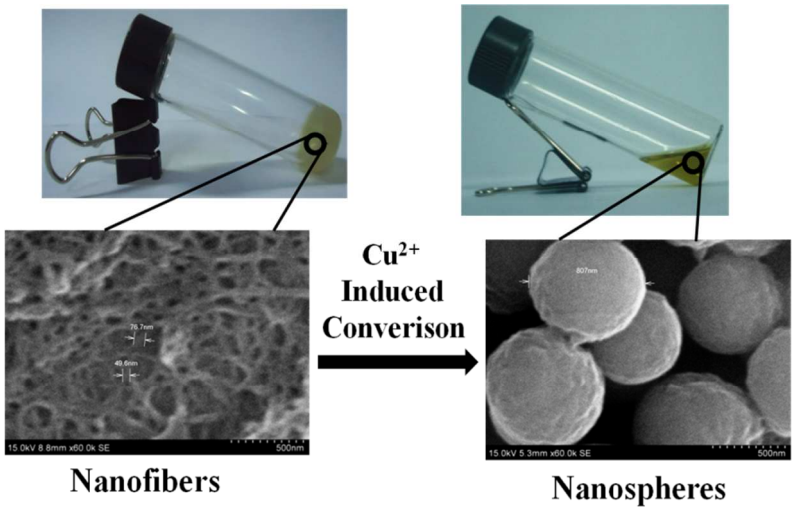
GRAPHICAL ABSTRACT

Self-assembly of novel benzimidazole *N*-glycosylamines into nano-fibers and nano-spheres

Manivannan Kalavathi Dhinakaran,[a] Kamalakannan Soundarajan,[b] Thangamuthu Mohan Das[a,b]*

[a]Department of Organic Chemistry, University of Madras, Gunidy Campus, Chennai 600025, India.

[b] Department of Chemistry, School of Basic and Applied Sciences, Central University of Tamil Nadu, Thiruvarur-610 004, India. E-mail: tmohandas@cutn.ac.in; Tel:+91-9489054278, Fax: 04366-225312.



Cu^{2+} ions induces the change in morphology of self-assembled benzimidazole *N*-glycosylamines from nano-fibers to nano-spheres

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ARTICLE TYPE

Self-assembly of novel benzimidazole *N*-glycosylamines into nanofibers and nanospheres

*Manivannan Kalavathi Dhinakaran,[a] Kamalakannan Soundarajan[b] and Thangamuthu Mohan Das[a,b]**

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Novel class of benzimidazole based partially protected *N*-glycosylamine amphiphiles possessing different alkyl chains were synthesized in good yield. The identities of the synthesized *N*-glycosylamines were confirmed using ^{1}H, ^{13}C NMR and molecular mass of representative samples were confirmed with MALDI-TOF mass analysis. All the benzimidazole based *N*-glycosylamines were found to exist in β-anomeric form, which was confirmed by ^{1}H NMR analysis. Gelation studies showed these compounds gelates both aromatic and aliphatic solvents, even with lower CGC (0.8 %). The representative gel was studied using SEM, TEM and XRD techniques. The conversion of nano fibres in the gel state (CGC : 0.8 %) into nano spheres was observed upon addition of Cu^{2+} ions.

Introduction

Gelators are organic molecules, which can entrap larger volume of solvent in least proportion, resulting in viscoelastic immobilized materials called gels.[1] Based on the solvents used for gelation they are classified as hydro and organogels.[2] Gels were also classified as chemical and physical gels based on the mode of gel formation. Chemical gels were formed through the chemical bonding or polymeric cross linking of the monomers, while physical gels formed through the aggregation of organic molecules by the non-bonding interactions, such as π-π stacking, intermolecular hydrogen bonding, vander Waal interaction, coordination, *etc*.[3,4] The gels formed by low molecular weight gelators through the self-assembly, lead by the above mentioned non-bonding interactions are called as supramolecular gels and these gels also falls under the category of physical gels.[5] These self-assemblies leads to the formation of different morphologies, such as fibers, rods, tubes, ribbons *etc*.[6] Since the morphology at the gel state was controlled by the non covalent interactions, thus self-assemblies can be tuned by the solvents, external stimuli or minor modifications in the gelator molecules to achieve the desired goal.[7] The changes taking place due the external stimuli and self assembly path were very well studied using the recent advancements in the analytical techniques, such as SEM, TEM, XRD *etc*.[8]

Supramolecular gels are more advantageous than chemical gels. Since these gels are responsive towards stimuli, such as heat, light, pH, ultrasound, shearing, ions and oxidation/reduction. The changes caused by the stimuli are reversible, which can be attained by the cancellation using appropriate stimuli. Such reversibility is not possible in case of chemical gels.[9] These changes were well documented and these properties influence the study of gels and their gel-sol and *vice versa* transitions, this enhances their applications in the field of biology and material science.[10,11] Gels have good applications in tissue engineering,[12] as a vehicles for controlled drug and bio molecule deliveries,[13,14] biosensors[15] *etc*., They were also utilized for the construction of photo-harvesting materials,[16] optoelectronic devices,[17] sensors,[18] water purifiers,[19] templates for synthesis of inorganic nanostructures [20] and also an active media for organic reactions.[21]

In view of developing a series of novel low-molecular mass organogelators (LMOG) with multiple functionalities, benzimidazole unit was incorporated into the designed gelator as chromophoric spacer. Benzimidazoles are interesting heterocycles, they gained considerable attention from the later days to till date both as novel materials and active pharmaceuticals.[22] Benzimidazoles have good biological applications, such as anti-inflammatory,[23] antiviral,[24] DNA binding[25] *etc*. They also have considerable contribution towards the development of OLEDs,[26] photoluminescent materials,[27] DSSCs.[28] And also benzimidazole based gelators were reported as gas and dye adsorption materials,[29] phase transfer catalyst,[30] organic nano-materials,[31] and chemosensors.[32] The two nitrogen atoms on the benzimidazoles made them as good ligands to coordinate with metals. Some of the benzimidazole derivatives coordinate with metals to form metallo polymers, which can self-

[a] *Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India.*
[b] *Department of Chemistry, School of Basic and Applied Sciences, Central University of Tamil Nadu, Thiruvarur-610 004, India. E-mail: tmohandas@cutn.ac.in; Tel: +91-9489054278; Fax: 04366-225312.*

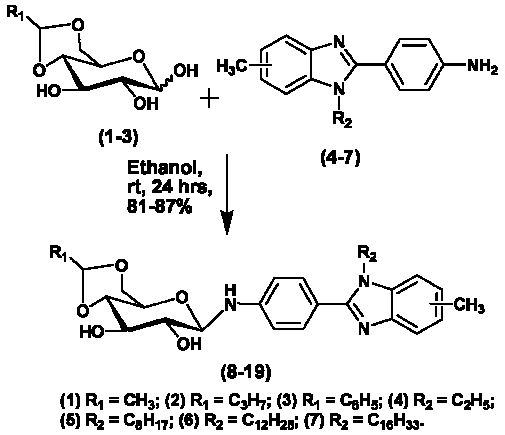
† Electronic supplementary information (ESI) available. ^{1}H, ^{13}C, HH COSY NMR and MALDI-TOF Mass spectra, EDAX spectrum.

assemble to nano-fibrous gels.[33] In order to construct gels with potential application, we have designed a series of amphiphilic gelators with hydrophilic sugar head and hydrophobic alkyl tail, both are connected through chromophoric benzimidazole core, thus the design favours the balance between the solubility and crystallization.

Result and discussion

Recent focus towards the development of organogels with stimuli response induced the synthesis of benzimidazole *N*-glycosylamines **8-19** bearing alkyl group of different chain length and different acetal protecting groups. Benzimidazole *N*-glycosylamines **8-19** were achieved by the *N*-glycosylation protocol of benzimidazole amines **4-7** with 4,6-*O*-protected-D-glucose **1-3**. All the synthesized benzimidazole *N*-glycosylamines were characterized using NMR (^{1}H & ^{13}C) and compound **12** and **18** were analyzed with MALDI-TOF mass analysis for confirming the molecular mass. All the synthesized compounds **8-19** were subjected to gelation with wide range of solvents. Conversion of nano-fibers into nano-spheres was observed upon addition of Cu^{2+} ions. Representative gel was studied using analytical techniques, *viz.,* SEM, TEM, XRD and DSC.

Synthesis and characterization



Scheme 1 Synthesis of alkyl benzimidazole *N*-glycosylamines **8-19.**

The 4,6-*O*-protected-D-glucose derivatives **1-3** were synthesized from D-glucose by following the literature procedures.[34-36] Benzimidazole amines **4-7** were synthesised[37-39] as inseparable regio-isomers and further *N*-glycosylation (Scheme-1) also leads to the formation of inseparable regio-isomers, **8-19** in good yield of 81-87 % (Table 1). All the *N*-glycosylated products were confirmed with ^{1}H & ^{13}C NMR and molecular mass was also confirmed for part of the compounds. From the ^{1}H NMR the presence of the alkyl chains were confirmed by the signal in the range of 0.85-1.90 ppm. The protons from the glucose unit resonate around 3.00-5.57 ppm, the β-anomeric form of the glycosidic unit was confirmed by the triplet in the range of 4.61-4.71 ppm with coupling constant between 6.9-8.4 Hz.[40] From signals in the range of 6.8-7.6 ppm the presence of benzimidazole unit was confirmed. Cross peaks at 3.25, 4.56, 6.68 ppm indicates that the anomeric proton couple with C_2 proton and N*H* proton of glucose unit, this causes the anomeric proton's multiplicity as triplet (See ESI for further details). In the ^{13}C NMR analysis of the compound **8-19**, signal in range of 12.5-35.3 ppm corresponds to the alkyl chain carbons. The carbon atoms of the glucose appears in the range of 66-85 ppm, the peak at 97.8, 100.7 and 101.7 ppm corresponds to acetal carbon of ethylidene, benzylidene and butylidene derivatives, respectively. The presence of the benzimiadzole carbons were identified by the peak in 108-146 ppm. Further molecular mass of compound **12** and **18** were confirmed using MALDI-TOF mass analysis as representative examples.

Table 1 Synthesis of alkyl benzimidazole *N*-glycosylamines **8-19**[a].

Compound	R_1	R_2	Yield %
8	CH_3	C_2H_5	84
9	C_3H_7	C_2H_5	81
10	C_6H_5	C_2H_5	82
11	CH_3	C_8H_{17}	87
12	C_3H_7	C_8H_{17}	85
13	C_6H_5	C_8H_{17}	81
14	CH_3	$C_{12}H_{25}$	83
15	C_3H_7	$C_{12}H_{25}$	83
16	C_6H_5	$C_{12}H_{25}$	86
17	CH_3	$C_{16}H_{33}$	85
18	C_3H_7	$C_{16}H_{33}$	82
19	C_6H_5	$C_{16}H_{33}$	85

[a]Mixture of inseparable regio-isomers

Gelation studies

All the synthesised alkyl benzimidazole *N*-glycosylamines **8-19** were subjected to gelation. The measured quantity of the gelator were added to 1 ml of solvent in a glass vial and warmed gently until a homogenous solution was obtained. The solution was kept at ambient temperature for one hour and gel formation was confirmed by turning vial upside down,[41] solvent was completely trapped to form pale yellow opaque gel (**Figure 1**). The gelation was tested in wide range of solvents. Results of the gelation for benzimidazole *N*-glycosylamines **8-19** were shown in Table 2. These *N*-glycosylamines found to gelate both aliphatic (chloroform, dichloroethane, ethyl acetate, acetone, ethanol, methanol) and aromatic (benzene, toulene, 1,2-dichlorobenzene) solvents. Among the nine solvents used for gelation, ethanol was found to be the best solvent, since it gelates most of the compound at lower concentration than all other solvents tested.

On comparing the gelation behaviour in chlorinated solvents, dichloroethane was found to be the better solvent as it form gels with large number of *N*-glycosylamines than other chlorinated solvents. Among the aliphatic solvents used for gelation, ethanol and dicholoroethane were found to be the better solvents than other aliphatic solvents studied. Toulene was found to be the better aromatic solvent than benzene and *o*-DCB. From the gelation studies it was observed that gelation ability also increases with increment in the alkyl chain length of the *N*-glycosylamines. But there was no ordered increment on the gelation pattern, this was due to influence of the 4,6-*O*-protecting group of the sugar unit. Benzimidazole *N*-glycosylamines with alkyl protecting groups (4,6-*O*-ethylidene & 4,6-*O*-butylidene) preferentially gelate aliphatic solvent, while *N*-glycosylamines

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Figure 1 Photograph of solution to gel transformation of glycosylamine **18** and Cu^{2+} induced conversion of gel to solution (ethanol, 0.8 %).

Table 2 Gelation of alkyl benzimidazole *N*-glycosylamines **8-19**

Compound	Solvent (CGC %)[a]								
	$CHCl_3$	$C_2H_5Cl_2$	E.A	Acetone	EtOH	MeOH	C_6H_6	$C_6H_5CH_3$	*o*-DCB
8	PG	PG	1.5	S	1	1	PG	1.8	1
9	PG	PG	2	S	1.5	1.5	PG	2	1.5
10	S	S	PG	S	1.5	1	1	1	1.5
11	PG	1.3	1.5	2	1.3	P	1.5	2	P
12	2	1.8	2	1.5	1.5	P	1.8	2	PG
13	PG	2	1	2	1	P	1.8	1.5	1.5
14	2	1.2	1.5	1.5	1.2	PG	PG	1.2	PG
15	1.5	1.2	1.8	2	1.8	1.5	PG	2	P
16	1	1	2	1.5	1	PG	1	1.5	1
17	1	1.3	2	2	0.8	PG	PG	1	PG
18	1.5	1	1.5	2	0.8	PG	1.5	1	S
19	1	0.8	1	1	0.8	P	2	2	S

[a] CGC-Critical Gelator Concentration, PG-Partial Gelation, P-Precipitation, S-soluble, E.A-Ethyl Acetate, *o*-DCB-1,2 Dichloro benzene,

with aromatic protecting group (4,6-*O*-benzylidene) preferentially gelates aromatic solvents, due to their π-π interaction with aromatic solvent. In order to assign a molecule as a good gelator, both the number of solvents it gelates and its CGC value are to be considered. In these aspects compound **18** and **19** can be assigned as super gelators among the twelve gelators. Since they gelates seven out of nine solvents used for gelation and even at lower CGC (0.8%).

Recent interest over metallo-gels in particular of benzimidazole based coordination gelators and good coordination ability of *N*-glycosylamines with copper. These properties enhances our interest towards the development of novel class of benzimidazole *N*-glycosylamine-copper based metallo gels.[42,43] However such an attempt failed, even then these results stimulated our interest to study the responsiveness of gels derived from benzimidazole *N*-glycosylamines towards Cu^{2+} ion. Such an investigation was Progressive.

Addition of measured quantity of 0.1 % of $Cu(OAc)_2.H_2O$ in ethanol to 1 ml of gels of *N*-glycosylamines **8-19** in different solvents with respective CGC resulted in conversion of gels to solution. Responsiveness of gels towards Cu^{2+} ions were summarized in Table 3. The complexation of the Cu^{2+} ion with *N*-glycosylamines disrupts the self-assembly which resulted in the conversion of gel to solution.[44] Among the gels of twelve benzimidazole *N*-glycosylamines **8-19** used for the study, gels derived from compound **13** and **19** in ethanol shows response

Table 3 Gel response towards Cu^{2+} ions .

Compounds	Solvents / µl of $Cu(OAc)_2.H_2O$ (1 % in ethanol)								
	$CHCl_3$	$C_2H_5Cl_2$	E.A	Acetone	EtOH	MeOH	C_6H_6	$C_6H_5CH_3$	*o*-DCB
8	-	-	45	-	28	32	-	122	110
9	-	-	75	-	34	25	-	138	90
10	-	-	-	-	24	30	102	110	98
11	-	69	44	40	36	-	100	95	-
12	70	74	36	58	28	-	108	112	-
13	-	52	55	46	18	-	100	95	110
14	65	68	46	35	30	-	-	98	-
15	40	54	46	20	34	25	-	102	-
16	58	60	38	25	26	-	90	94	90
17	63	78	56	20	32	-	-	90	-
18	75	70	50	30	20	-	98	106	-
19	74	45	30	24	18	-	115	98	-

with the least quantity (18 µl) of Cu^{2+} ions than other gels. Gels in alipahtic solvents responses with lower quantity (18-75 µl) of Cu^{2+} ions, while aromatic gels requires higher concentration (90-138 µl) of Cu^{2+} ions. Figure 1 shows the photograph of Cu^{2+} ion induced conversion of gel to solution.

Morphological studies

In order to investigate the morphology of the gels, compound **18** and **19** were chosen as representatives. The gels of compound **18** and **19** were prepared in ethanol and benzene at their respective CGC. The gels allowed to stand at ambient temperature to obtain their corresponding xerogels and subjected to morphological analysis.[45] The SEM studies of compound **18** in ethanol shows network of nano fibers, while compound **19** self-assemble in the benzene to form entangled fibers (Figure 2). These morphologies of the benzimidazole *N*-glycosylamines shows that they are orderly assembled at the gel state. The influence of Cu^{2+} ions on gel derived from compound **18** in ethanol was alone taken for morphological analysis as a part of study. Since Cu^{2+} ions complexes with *N*-glycosylamine **18**, a drastic morphological change of nanofibers to nanospheres was observed in SEM analysis. Such morphological change leads to the conversion of gel into solution. [46]

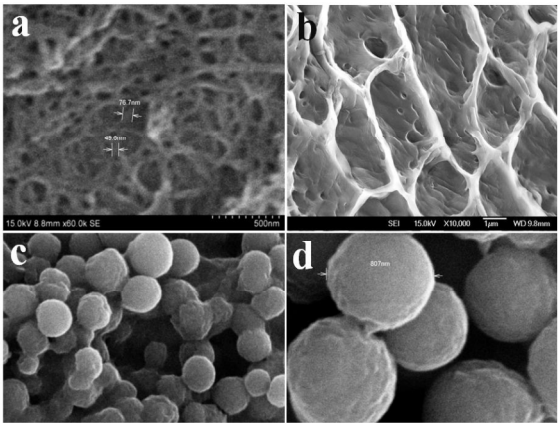

Figure 2 SEM images of a) gel **18** in ethanol (0.8 %), 0.5 µm; b) gel **19** in benzene (2 %) 1 µm; c) 2 µm and d) 0.5 µm of Cu^{2+} (20 µL, 0.1 %) + **18** in ethanol (1 mL, 0.8%).

Transmission Electron Microscopic (TEM) analysis was carried at concentration of 1×10^{-5} M of gelator **18**, such concentration was achieved through the dispersion of gel prepared at 0.8 % in ethanol into the same solvent with utmost care.[47] TEM images of the gelator **18** was shown in Figure 3**.**

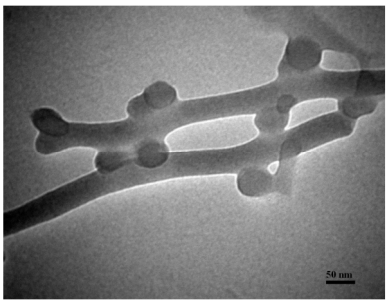

Figure 3 TEM image of gel **18** (50 nm, 1×10^{-5} M).

TEM analysis shows that the gelator **18** can self assemble to form nanofiber. From the SEM and TEM analysis it was inferred that the *N*-glycosylamine gelator **18** can self assemble to form nano structure.[48]

XRD analysis

The assembly of the molecules at the gel state was studied using powder X-ray diffraction studies of Xerogel.[49] Gel of benzimidazole *N*-glycosylamine **18** was prepared at the concentration 1% in ethanol and allowed to stand at ambient temperature to obtain the xerogel. From the XRD (Figure 4) pattern it was confirmed that the self assembly of the gelator **18** was also due to vander Waals force between the alkyl chain and π-π interaction between the benzimidazole core. The strong diffraction at low angle 2θ = 2.85° corresponds to van der Waals force and broad peak at 21.87° arises from π-π interaction of the benzimidazole unit. Peaks at 2θ = 4.91°, 5.85°, 11.33°, 14.14°, 16.38°, 20.72°, 21.87° and 23.39° shows the crystalline nature of the gel fibers.[50]

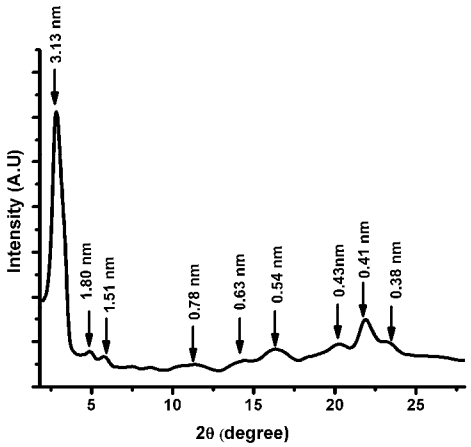

Figure 4 Powder X-ray diffraction of Xerogel **18** (ethanol, 1%).

Thermal Stability

LMOG are thermo-reversible *i.e.* they can easily switch over from gel-sol and *vice versa* transitions upon heating and cooling, which occurs by self-assembly and dis-assembly processes of gelator in the gel state. This thermo reversibility made them as more compactable for wide range of applications. The gel-sol transition temperature (T_{gel}) of the gelators has been determined using dropping ball method.[51] Thermal stability of the gels were measured using the plot of T_{gel} Vs concentration. Gel-sol transitions of benzimidazole *N*-glycosylamine, **18** in various aliphatic ($CHCl_3$, dichloroethane, ethyl acetate, acetone and ethanol) and aromatic (benzene and toluene) solvents were studied. From the concentration dependent T_{gel} plot (Figure 5) it was concluded that gel of compound, **18** is thermally stable in most of the aliphatic solvents. Interestingly ethanolic gel of *N*-glycosylamine **18** shows higher T_{gel} value of 86 °C, which is greater than the boiling point of ethanol (78 °C) this may be due to the strong hydrogen bonding between the gelator and ethanol. Gels prepared in aromatic solvents were not much stable like aliphatic solvents, they melts before the boiling point of the aromatic solvents used for gelation. From the T_{gel} plot it was suggested that the aliphatic solvents were more suitable for the

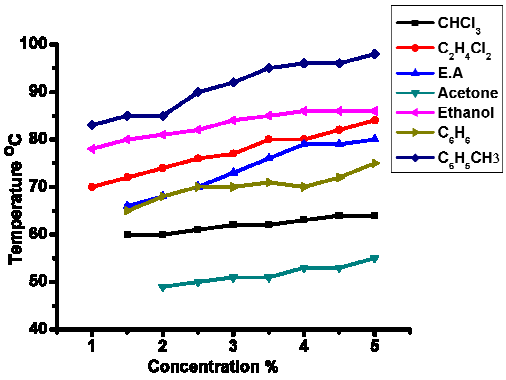

Figure 5 Concentration dependent plot of benzimidazole *N*-glycosylamines **18** in different solvents.

gelation of benzimidazole *N*-glycosylamine **18** than aromatic solvents. This may be due to the strong hydrogen bonding and vander Waals interactions between the solvent molecules and gelators.[52]

Comparative thermal stability of the gelator in the solid and Xerogel state was studied using differential scanning calorimetric analysis (DSC). DSC graph of benzimidazole *N*-glycosylamine **18** and its xerogel were shown in **Figure 6**. Ethanolic gel (1%) was utilized for DSC studies, on heating the gel at the rate of 10°/min the evaporation of solvent will takes place and resulted in formation of xerogel. The solid and the xerogel of *N*-glycosylamine **18** shows the phase transition at 191.79 °C (116 J/g) and 208.34 °C (120 J/g) respectively. From the DSC graph it was evidenced that *N*-glycosylamine **18** is thermally more stable in the xerogel state than in solid state. This due to ordered arrangement of the gelator **18** in self-assembled state which is not available in the solid state.[53]

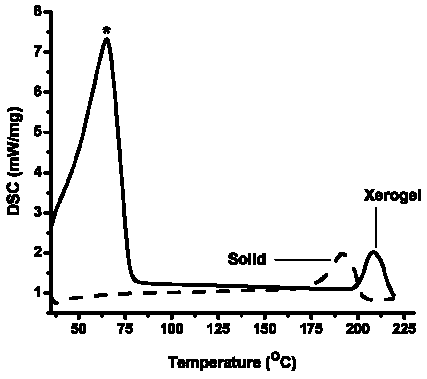

Figure 6 DSC graph of gelator **18** (* peak due to solvent)**.**

Absorption and emission studies

The absorption and emission spectra of the benzimidazole *N*-glycosylamines **8-19** were recorded at the concentration of 5×10^{-5} M in ethanol. *N*-Glycosylamines **8-19** shows characteristic absorption bands around 260 nm and 309 nm (Figure 7). The number of methylene unit in alkyl chain and 4,6-*O*-protecting group in D-glucose unit does not influences the

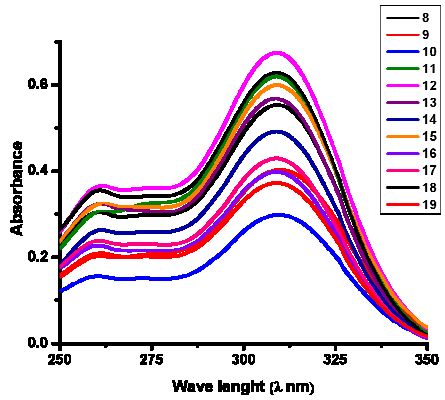

Figure 7 Absorption spectra of benzimidazole *N*-glycosylamines **8-19** (5×10^{-5} M in ethanol).

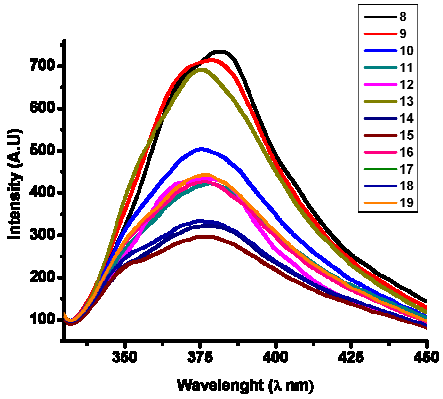

Figure 8 Emission spectra of benzimidazole *N*-glycosylamines **8-19** (5×10^{-5} M in ethanol).

absorption maxima. On exciting the *N*-glycosylamines **8-19** at their absorption maxima of 309 nm they show corresponding emission band around 380 nm (Figure 8).

Conclusion

Alkyl benzimidazole *N*-glycosylamines were synthesized in good yield and the identities of the compounds were confirmed using ^{1}H & ^{13}C NMR and molecular mass of representative samples were confirmed using MALDI-TOF mass analysis. From the ^{1}H NMR it was confirmed that all the synthesized *N*-glycosylamines were found to exist as β-anomers. All the *N*-glycosylamines with different substitution gelates wide range of solvents. As the alkyl chain length increases the gelation ability of the benzimidazole *N*-glycosylamines increases. Representative gel sample was studied using SEM, TEM, XRD and DSC analysis. All the gels were responsive towards Cu^{2+} ions and conversion of nanofibres into nanospheres induced by Cu^{2+} ion was evidenced by SEM analysis.

Experimental section

Materials

5-Methyl-1,2-diaminobenzene, 4-nitrobenzaldehyde, 1-bromoethane, 1-bromooctane, 1-bromododecane, 1-bromohexadecane, palladium carbon 10%, butyraldehyde and paraldehyde were purchased from Sigma Aldrich chemicals Pvt. Ltd. USA. Hydrazine hydrate, glycerol, con. hydrochloric acid,

con. sulphuric acid, D-glucose and ethanol were purchased from SRL India Ltd., were of high purity and used without further purification. Column chromatography was performed on silica gel (100-200 mesh). NMR spectra were recorded on a Bruker DRX 300 MHz instrument in $CDCl_3$ (with a few drops of DMSO-d_6). Chemical shifts are referenced to internal TMS.

General procedure for the synthesis of alkyl benzimidazole *N*-glycosylamines (8-19).

5-Methyl-2-(4-nitrophenyl)-1*H*-benzo[d]imidazole was synthesized from the reaction of 5-methyl 1,2-diamino-benzene with 4-nitrobenzaldehyde in glycerol according to literature.[37] Alkylation of nitrobenzimidazole to alkyl derivatives was carried by following the literature with good yield (83-92 %).[38] Alkyl-nitrobenzimidazole was reduced to alkyl-benzimidazole amines using Pd/C, hydrazine hydrate and ethanol as solvent. To the stirred solution of 6 mmol alkyl-nitro-benzimidazole at room temperature 0.6 g of Pd/C (10 %) was added and the temperature was raised to 50 °C. To this solution 12 ml of hydrazine hydrate (80 %) in 24 ml of ethanol was added slowly, and then the reaction mixture was refluxed for 3 hrs. After cooling to room temperature, the solution was filtered over celite to remove the catalyst. The filtrate was evaporated under reduced pressure to dryness and purified by column chromatography to obtain alkyl-benzimidazole amines (**4**-**7**) in good yield.[39]

To a stirred solution of 1 mmol of 4,6-*O*-protected-D-glucose derivatives (**1**-**3**) in 5 ml of ethanol, 1 mmol of alkyl benzimidazole amine (**4**-**7**) was added. The reaction mixture was stirred at 50 °C for 10 min and at room temperature for 24 hrs. The reaction was monitored through TLC. The solid *N*-glycosylamine (**8**-**19**) which separated was filtered off, washed with ethanol and dried with ether. These *N*-glycosylamines are of satisfactory purity and have been characterized using ^{1}H & ^{13}C NMR and molecular mass of representative samples were further confirmed using MALDI-TOF mass analysis.

Synthesis of 2-(4-(1-amino 4,6-*O*-ethylidene β-D-glucopyranosyl)phenyl)-1-ethyl-5-methyl benzimidazole (8).

Compound, **8** was obtained by the reaction of ethyl benzimidazole amine, **4** (1 mmol, 0.251 g), with 4,6-*O*-ethylidene-D-glucopyranose, **1** (1 mmol, 0.206 g) as orange solid. Yield : 84 % (0.369 g). Melting point : 179-182 °C. **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): 7.52(d, J = 7.5 Hz, 4H, Ar-*H*), 7.46(s, 2H, Gly-N*H*), 7.33(d, J = 8.1 Hz, 2H, Ar-*H*), 7.23(s, 2H, Ar-*H*), 7.06(t, J = 8.4 Hz, 2H, Ar-*H*), 6.87(d, J = 8.1 Hz, 4H, Ar-*H*), 5.30(s, 4H, Sacc-O*H*), 4.74(d, J = 5.1 Hz, 2H, Ace-*H*), 4.64(t, J = 7.8 Hz, 2H, Ano-*H*), 4.26(d, J = 6.3 Hz, 4H, NCH_2), 4.12(d, J = 6 Hz, 2H, Sacc-*H*), 3.65(m, 3.61-3.65, 4H, Sacc-*H*), 3.31(m, 3.21-3.31, 6H, Sacc-*H* & O*H*), 2.50(s, 3H, CH_3), 2.46(s, 3H, CH_3), 1.46(m, 1.44-1.46, 6H, CH_3), 1.35(m, 1.30-1.35, 6H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): 146.6(2C, Ar-C), 130.4(2C, Ar-*C*), 129.8(2C, Ar-*H*), 128.6(4C, Ar-*C*), 122.1(2C, Ar-*C*), 118.2(2C, Ar-*C*), 117.4(2C, Ar-*C*), 117.2(2C, Ar-*C*), 112.1(4C, Ar-*C*), 108.5(2C, Ar-*C*), 108.2(2C, Ar-*C*), 97.8(2C, Ace-*C*), 84.6(2C, Ano-*C*), 79.2(2C, Sacc-*C*), 72.6(2C, Sacc-*C*), 72.5(2C, Sacc-*C*), 66.8(2C, Sacc-*C*), 65.6(2C, Sacc-*C*), 42.6(2C, N*C*H_2), 20.1(2C, *C*H_3), 19.1(2C, *C*H_3), 13.8(2C, *C*H_3).

Synthesis of 2-(4-(1-amino 4,6-*O*-butylidene β-D-glycopyranosyl)phenyl) 1-ethyl-5-methyl benzimidazole (9).

Compound, **9** was obtained by the reaction of ethyl benzimidazole amine, **4** (1 mmol, 0.251 g), with 4,6-*O*-butylidene-D-glucopyranose, 2 (1 mmol, 0.234 g) as yellow solid. Yield : 81 % (0.393 g). Melting point : 162-165 °C. **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): 7.59(d, J = 8.4 Hz, 6H, Ar-*H* & Gly-N*H*), 7.37(d, J = 8.1 Hz, 2H, Ar-*H*), 7.28(s, 2H, Ar-*H*), 7.15(t, J = 8.4 Hz, 2H, Ar-*H*), 6.93(d, J = 8.4 Hz, 4H, Ar-*H*), 4.71(d, J = 8.1 Hz, 2H, Ano-*H*), 4.65(t, J = 5.1 Hz, 2H, Ace-*H*), 4.33(m, 4.31-4.33, 4H, NCH_2), 4.28(m, 4.28-4.23, 2H, Sacc-*H*), 3.79(t, J = 8.4 Hz, 4H, Sacc-*H*), 3.59(m, 3.39-3.59, 10H, Sacc-*H* & O*H*), 2.58(s, 3H, CH_3), 2.54(s, 3H, CH_3), 1.74(m, 1.74-1.68, 4H, CH_2), 1.55(m, 1.52-1.55, 10H, CH_2 & CH_3), 0.96(t, J = 6.6 Hz, 6H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): 146.9(2C, Ar-C), 131.2(2C, Ar-*C*), 130.8(2C, Ar-*H*), 129.2(4C, Ar-*C*), 122.8(2C, Ar-*C*), 119.2(2C, Ar-*C*), 118.0(2C, Ar-*C*), 117.7(2C, Ar-*C*), 112.8(4C, Ar-*C*), 108.9(2C, Ar-*C*), 108.6(2C, Ar-*C*), 101.8(2C, Ace-*C*), 85.3(2C, Ano-*C*), 79.6(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 73.0(2C, Sacc-*C*), 67.5(2C, Sacc-*C*), 66.4(2C, Sacc-*C*), 42.6(2C, N*C*H_2), 35.4(2C, *C*H_2), 21.0(2C, *C*H_3), 16.5(1C, *C*H_3), 14.3(2C, *C*H_3), 13.1(2C, *C*H_3).

Synthesis of 2-(4-(1-Amino 4,6-*O*-benzylidene β-D-glycopyranosyl)phenyl)-1-ethyl-5-methyl benzimidazole (10).

Compound, **10** was obtained by the reaction of ethyl benzimidazole amine, **4** (1 mmol, 0.251 g), with 4,6-*O*-benzylidene-D-glucopyranose, **3** (1 mmol, 0.268 g) as yellow solid. Yield : 82 % (0.410 g). Melting point : 173-178 °C. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): 7.61(m, 7.61-7.52, 10H, Ar-*H* & Gly-N*H*), 7.37(m, 7.31-7.37, 6H, Ar-*H*), 7.23(s, 2H, Ar-*H*), 7.09(t, J = 8.1 Hz, 2H, Ar-*H*), 6.91(d, J = 8.4 Hz, 4H, Ar-*H*), 5.57(s, 2H, Sacc-O*H*), 5.37(s, 2H, Sacc-O*H*), 4.73(t, J = 7.5 Hz, 2H, Ano-*H*), 4.37(m, 4.37-4.26, 6H, NCH_2 & Ace-*H*), 3.83(m, 3.73-3.83, 4H, Sacc-*H*), 3.64(m, 3.54-3.64, 10H, Sacc-*H* & O*H*), 2.52(s, 3H, CH_3), 2.49(s, 3H, CH_3), 1.46(t, J = 6 Hz, 6H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ ppm): 146.9(2C, Ar-C), 136.8(4C, Ar-*C*), 131.0(2C, Ar-*C*), 130.5(2C, Ar-*H*), 129.2(4C, Ar-*C*), 128.2(4C, Ar-*C*), 127.2(4C, Ar-*C*), 125.7(4C, Ar-*C*), 122.7(2C, Ar-*C*), 119.0(2C, Ar-*C*), 118.0(2C, Ar-*C*), 117.8(2C, Ar-*C*), 112.7(4C, Ar-*C*), 108.9(2C, Ar-*C*), 108.6(2C, Ar-*C*), 100.7(2C, Ace-*C*), 85.4(2C, Ano-*C*), 80.3(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 73.0(2C, Sacc-*C*), 67.9(2C, Sacc-*C*), 66.2(2C, Sacc-*C*), 43.3(2C, N*C*H_2), 21.0(2C, *C*H_3), 14.4(2C, *C*H_3).

Synthesis of 2-(4-(1-amino 4,6-*O*-ethylidene β-D-glycopyranosyl)phenyl)-1-octyl-5-methyl benzimidazole (11).

Compound, **11** was obtained by the reaction of octyl benzimidazole amine, **5** (1 mmol, 0.336 g), with 4,6-*O*-ethylidene-D-glucopyranose, **1** (1 mmol, 0.206 g) as yellow solid. Yield : 87 % (0.456 g). Melting point : 182-184 °C. **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): 7.52(d, J = 6.9 Hz, 6H, Ar-*H* & GlyN*H*), 7.29(d, J = 7.8 Hz, 2H, Ar-*H*), 7.18(s, 2H, Ar-*H*), 7.08(t, J = 7.5 Hz, 2H, Ar-*H*), 6.86(d, J = 8.1 Hz, 4H, Ar-*H*), 5.19(s, 2H, Sacc-O*H*), 4.85(s, 2H, Sacc-O*H*), 4.77(d, J = 4.8 Hz, 2H, Ace-*H*), 4.66(t, J = 7.2 Hz, 2H, Ano-*H*), 4.18(m, 4.18-4.16, 6H, NCH_2 & Sacc-*H*), 3.75(t, J = 8.1 Hz, 2H, Sacc-*H*), 3.58(m, 3.49-3.58, 6H, Sacc-*H* & O*H*), 3.39(m, 3.33-3.39, 2H, Sacc-*H*), 2.52(s, 3H, CH_3), 2.48(s, 3H, CH_3),1.85(m, 1.79-1.85, 4H, CH_2), 1.40(m, 1.40-1.38, 8H, CH_2), 1.30(m, 1.30-1.24, 18H, CH_2 & CH_3), 0.87(t, J = 6 Hz, 6H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ +

DMSO-d_6, ppm): 146.0(2C, Ar-C), 134.2(4C, Ar-*C*), 128.5(4C, Ar-*C*), 121.9(2C, Ar-*C*), 118.7(2C, Ar-*C*), 117.3(2C, Ar-*C*), 117.0(2C, Ar-*C*), 112.8(2C, Ar-*C*), 112.0(2C, Ar-*C*), 108.4(2C, Ar-*C*), 108.0(2C, Ar-*C*), 97.8(2C, Ace-*C*), 84.7(2C, Ano-*C*), 78.9(2C, Sacc-*C*), 72.5(2C, Sacc-*C*), 72.3(2C, Sacc-*C*), 66.7(2C, Sacc-*C*), 65.5(2C, Sacc-*C*), 43.1(2C, N*C*H$_2$), 30.0(2C, *C*H$_2$), 27.9(2C, *C*H$_2$), 27.3(2C, *C*H$_2$), 25.0(2C, *C*H$_2$), 21.0(2C, *C*H$_2$), 20.2(2C, *C*H$_3$), 19.9(2C, *C*H$_2$), 18.8(2C, *C*H$_3$), 12.5(2C, *C*H$_3$).

Synthesis of 2-(4-(1-amino 4,6-*O*-butylidene β-D-glycopyranosyl)phenyl)-1-octyl-5-methyl benzimidazole (12).

Compound, **12** was obtained by the reaction of octyl benzimidazole amine, **5** (1 mmol, 0.336 g), with 4,6-*O*-butylidene-D-glucopyranose, **2** (1 mmol, 0.234 g) as yellow solid. Yield : 85 % (0.469 g). Melting point : 170-175 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): 7.52(m, 7.49-7.52, 6H, Ar-*H* & Gly-N*H*), 7.28(d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.17(s, 2H, Ar-*H*), 7.08(t, *J* = 7.2 Hz, 2H, Ar-*H*), 6.84(d, *J* = 8.4 Hz, 4H, Ar-*H*), 4.65(t, *J* = 6.9 Hz, 2H, Ano-*H*), 4.59(t, *J* = 4.8 Hz, 2H, Ace-*H*), 4.21(m, 4.18-4.21, 6H, Sacc-*H* & N*C*H$_2$), 3.77(t, *J* = 6 Hz, 2H, Sacc-*H*), 3.56(m, 3.48-3.56, 6H, Sacc-*H*), 3.35(t, *J* = 4.5 Hz, 2H, Sacc-H), 2.51(s, 3H, C*H*$_3$), 2.48(s, 3H, C*H*$_3$), 1.78(m, 1.70-1.78, 4H, C*H*$_2$), 1.67(m, 1.63-1.67, 4H, C*H*$_2$), 1.49(m, 1.41-1.49, 2H, C*H*$_2$), 1.30(m, 1.23-1.30, 20H, C*H*$_2$), 0.95(m, 0.85-0.95, 12H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): 146.6(2C, Ar-C), 134.8(2C, Ar-*C*), 132.6(2C, Ar-*C*), 130.6(2C, Ar-*C*), 129.2(4C, Ar-*C*), 122.6(2C, Ar-*C*), 117.9(2C, Ar-*C*), 117.7(2C, Ar-*C*), 112.7(4C, Ar-*C*), 108.9(2C, Ar-*C*), 108.6(2C, Ar-*C*), 101.3(2C, Ace-*C*), 85.3(2C, Ano-*C*), 79.5(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.4(2C, Sacc-*C*), 66.3(2C, Sacc-*C*), 43.8(2C, N*C*H$_2$), 35.3(2C, *C*H$_2$), 30.6(2C, *C*H$_2$), 28.7(2C, *C*H$_2$), 27.9(2C, *C*H$_2$), 25.6(2C, *C*H$_2$), 21.5(2C, *C*H$_2$), 20.8(2C, *C*H$_3$), 20.5(2C, *C*H$_2$), 16.3(2C, *C*H$_2$), 13.0(2C, *C*H$_3$), 12.9(2C, *C*H$_3$). **MALDI-TOF**: m/z calcd for $C_{32}H_{45}N_3O_5$ **551.34**, found **552.63** (M+H).

Synthesis of 2-(4-(1-amino 4,6-*O*-benzylidene β-D-glycopyranosyl)phenyl)-1-octyl-5-methyl benzimidazole (13).

Compound, **13** was obtained by the reaction of octyl benzimidazole amine, **5** (1 mmol, 0.336 g), with 4,6-*O*-benzylidene-D-glucopyranose, **3** (1 mmol, 0.268 g) as yellow solid. Yield : 81 % (0.475 g). Melting point : 166-170 ^{o}C. ^{1}H **NMR** (300 MHz, $CDCl_3$+ DMSO-d_6, ppm): 7.56(s, 4H, Ar-*H*), 7.51(d, *J* = 7.5Hz, 8H, Ar-*H* & Gly-N*H*), 7.33(s, 4H, Ar-*H*), 7.26(d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.16(s, 2H, Ar-*H*), 7.05(t, *J* = 7.2 Hz, 2H, Ar-*H*), 6.86(d, *J* = 8.1 Hz, 4H, Ar-*H*), 5.13(s, 2H, Sacc-O*H*), 5.02(s, 2H, Sacc-O*H*), 4.69(t, *J* = 7.5 Hz, 2H, Ano-*H*), 4.36(m, 4.32-4.36, 2H, Ace-*H*), 4.16(s, 4H, N*C*H$_2$), 3.80(m, 3.80-3.71, 4H, Sacc-*H*), 3.63(m, 3.54-3.63, 6H, Sacc-*H*), 3.00(m, 2.80-3.00, 2H Sacc-*H*), 2.49(s, 3H, C*H*$_3$), 2.45(s, 3H, C*H*$_3$),1.77(m, 1.70-1.77, 4H, C*H*$_2$), 1.30(m, 1.21-1.30, 20H, C*H*$_2$), 0.85(m, 0.83-0.85, 6H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$+ DMSO-d_6, ppm): 146.7(2C, Ar-C), 136.6(2C, Ar-*C*), 130.9(2C, Ar-*C*), 130.4(2C, Ar-*C*), 129.2(4C, Ar-*C*), 128.1(2C, Ar-*C*), 127.1(2C, Ar-*C*), 125.6(2C, Ar-*C*), 122.5(2C, Ar-*C*), 119.4(2C, Ar-*C*), 118.0(2C, Ar-*C*), 117.7(2C, Ar-*C*), 112.6(4C, Ar-*C*), 109.0(2C, Ar-*C*), 108.7(2C, Ar-*C*), 100.7(2C, Ace-*C*), 85.4(2C, Ano-*C*), 80.2(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.9(2C, Sacc-*C*), 66.2(2C, Sacc-*C*), 44.2(2C, N*C*H$_2$), 30.6(2C, *C*H$_2$), 28.7(2C, *C*H$_2$), 28.0(2C, *C*H$_2$), 25.6(2C, *C*H$_2$), 21.5(2C, *C*H$_2$), 20.9(2C, *C*H$_2$), 20.6(2C, *C*H$_3$), 13.1(2C, *C*H$_3$).

Synthesis of 2-(4-(1-amino 4,6-*O*-ethylidene β-D-glycopyranosyl)phenyl)-1-dodecyl-5-methyl benzimidazole (14).

Compound, **14** was obtained by the reaction of dodecyl benzimidazole amine, **6** (1 mmol, 0.392 g), with 4,6-*O*-ethylidene-D-glucopyranose, **1** (1 mmol, 0.206 g) as yellow solid. Yield : 83 % (0.481 g). Melting point : 181-184 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm): 7.53(d, *J* = 8.7 Hz, 4H, Ar-*H*), 7.46(s, 2H, GlyN*H*), 7.29(d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.18(s, 2H, Ar-*H*), 7.10(t, *J* = 8.7 Hz, 2H, Ar-*H*), 6.86(d, *J* = 9 Hz, 4H, Ar-*H*), 4.79(d, *J* = 4.5 Hz, 2H, Ace-*H*), 4.68(t, *J* = 8.4 Hz, 2H, Ano-*H*), 4.50(s, 2H, Sacc-O*H*), 4.22(m, 4.19-4.22, 4H, N*C*H$_2$), 3.80(t, *J* = 5.4 Hz, 2H, Sacc-*H*), 3.61(m, 3.51-3.61, 6H, Sacc-*H*), 3.42(m, 3.37-3.42, 2H, Sacc-*H*), 2.53(s, 3H, C*H*$_3$), 2.50(s, 3H, C*H*$_3$), 1.80(m, 1.70-1.80, 4H, C*H*$_2$), 1.41(m, 1.40-1.41, 4H, C*H*$_2$), 1.30(m, 1.20-1.30, 38H, C*H*$_2$ & C*H*$_3$), 0.89(t, *J* = 5.4 Hz, 6H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$ ppm): 146.9(2C, Ar-C), 134.9(2C, Ar-*C*), 130.6(2C, Ar-*C*), 129.0(4C, Ar-*C*), 122.4(2C, Ar-*C*), 119.0(2C, Ar-*C*), 117.8(2C, Ar-*C*), 117.6(2C, Ar-*C*), 112.4(4C, Ar-*C*), 109.0(2C, Ar-*C*), 108.7(2C, Ar-*C*), 98.2(2C, Ace-*C*), 85.0(2C, Ano-*C*), 79.7(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.2(2C, Sacc-*C*), 66.0(2C, Sacc-*C*), 43.2(2C, N*C*H$_2$), 30.7(2C, *C*H$_2$), 28.6(2C, *C*H$_2$), 28.4(2C, *C*H$_2$), 28.3(2C, *C*H$_2$), 28.1(2C, *C*H$_2$), 27.9(2C, *C*H$_2$), 25.5(2C, *C*H$_2$), 21.5(2C, *C*H$_2$), 20.8(2C, *C*H$_2$), 20.4(2C, *C*H$_3$), 19.5(2C, *C*H$_2$ & C*H*$_3$), 13.1(2C, *C*H$_3$).

Synthesis of 2-(4-(1-amino 4,6-*O*-butylidene β-D-glycopyranosyl)phenyl)-1-dodecyl-5-methyl benzimidazole (15).

Compound, **15** was obtained by the reaction of dodecyl benzimidazole amine, **6** (1 mmol, 0.392 g), with 4,6-*O*-butylidene-D-glucopyranose, **2** (1 mmol, 0.234 g) as yellow solid. Yield : 83 % (0.504 g). Melting point : 175-178 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$+ DMSO-d_6, ppm): 7.53(m, 7.47-7.53, 6H, Ar-*H* & GlyN*H*), 7.32(d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.22(s, 2H, Ar-*H*), 7.10(t, *J* = 8.4 Hz, 2H, Ar-*H*), 6.88(d, *J* = 8.4 Hz, 4H, Ar-*H*), 5.13(s, 2H, Sacc-O*H*), 4.66(t, *J* = 7.8 Hz, 2H, Ano-*H*), 4.60(t, *J* = 4.8 Hz, 2H, Ace-*H*), 4.21(m, 4.16-4.21, 6H, N*C*H$_2$ & Sacc-*H*), 3.68(t, *J* = 6.3 Hz, 2H, Sacc-*H*), 3.50(m, 3.44-3.50, 6H, Sacc-*H* & Sacc-O*H*), 3.33(m, 3.25-3.33, 4H, Sacc-*H*), 2.52(s, 3H, C*H*$_3$), 2.48(s, 3H, C*H*$_3$), 1.90(m, 1.80-1.90, 4H, C*H*$_2$), 1.66(m, 1.61-1.66, 4H, C*H*$_2$), 1.50(m, 1.42-1.50, 4H, C*H*$_2$), 1.30(m, 1.20-1.30, 36H, C*H*$_2$), 0.97(m, 0.87-0.97, 12H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$ ppm): 146.8(2C, Ar-C), 132.8(2C, Ar-*C*), 130.6(2C, Ar-*C*), 129.0(4C, Ar-*C*), 122.4(2C, Ar-*C*), 119.0(2C, Ar-*C*), 117.8(2C, Ar-*C*), 117.5(2C, Ar-*C*), 112.4(4C, Ar-*C*), 109.0(2C, Ar-*C*), 108.6(2C, Ar-*C*), 101.0(2C, Ace-*C*), 85.1(2C, Ano-*C*), 79.7(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.3(2C, Sacc-*C*), 66.2(2C, Sacc-*C*), 43.3(2C, N*C*H$_2$), 35.2(2C, *C*H$_2$), 30.7(2C, *C*H$_2$), 28.6(2C, *C*H$_2$), 28.4(2C, *C*H$_2$), 28.2(2C, *C*H$_2$), 28.1(2C, *C*H$_2$), 28.0(2C, *C*H$_2$), 25.5(2C, *C*H$_2$), 21.4(2C, *C*H$_2$), 20.8(2C, *C*H$_2$), 20.5(2C, *C*H$_3$), 16.3(2C, *C*H$_2$), 13.1(2C, *C*H$_3$), 13.0(2C, *C*H$_3$).

Synthesis of 2-(4-(1-amino 4,6-*O*-benzylidene β-D-glycopyranosyl)phenyl)-1-dodecyl-5-methyl benzimidazole (16).

Compound, **16** was obtained by the reaction of dodecyl

benzimidazole amine, **6** (1 mmol, 0.392 g), with 4,6-*O*-benzylidene-D-glucopyranose, **3** (1 mmol, 0.268 g) as yellow solid. Yield : 86 % (0.552 g). Melting point : 160-164 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6, ppm) : 7.54(m, 7.51-7.53, 8H, Ar-*H*), 7.37(m, 7.31-7.37, 6H, Ar-*H*), 7.23(s, 2H, Ar-*H*), 7.07(t, *J* = 8.1 Hz, 2H, Ar-*H*), 6.90(d, *J* = 7.8 Hz, 4H, Ar-*H*), 5.57(s, 2H, GlyN*H*), 5.41(s, 2H, Sacc-O*H*), 5.22(s, 2H, Sacc-O*H*), 4.72(t, *J* = 7.5 Hz, 2H, Ano-*H*), 4.35(m, 4.30-4.35, 2H, Sacc-*H*), 4.28(m, 4.22-4.28, 4H, NCH_2), 3.74(m, 3.71-3.74 Hz, 4H, Sacc-*H*), 3.63(m, 3.52-3.63, 6H, Sacc-*H*), 3.30(m, 3.20-3.30, 2H, Sacc-*H*), 2.52(s, 3H, CH_3), 2.48(s, 3H, CH_3), 1.90(m, 1.80-1.90, 4H, CH_2), 1.40(m, 1.30-1.40, 36H, CH_2), 0.89(t, *J* = 6.6 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$ ppm): 146.4(2C, Ar-C), 136.4(2C, Ar-*C*), 130.9(2C, Ar-*C*), 130.5(2C, Ar-*C*), 129.2(4C, Ar-*C*), 128.0(2C, Ar-*C*), 127.1(4C, Ar-*C*), 125.4(4C, Ar-*C*), 122.4(2C, Ar-*C*), 119.6(2C, Ar-*C*), 118.0(2C, Ar-*C*), 117.7(2C, Ar-*C*), 108.9(2C, Ar-*C*), 108.5(2C, Ace-*C*), 100.7(2C, Ace-*C*), 85.4(2C, Ano-*C*), 80.1(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.8(2C, Sacc-*C*), 67.9(2C, Sacc-*C*), 66.1(2C, Sacc-*C*), 43.8(2C, N*C*H_2), 30.8(2C, *C*H_2), 28.7(2C, *C*H_2), 28.4(2C, *C*H_2), 28.3(4C, *C*H_2), 28.0(2C, *C*H_2), 25.6(2C, *C*H_2), 21.5(2C, *C*H_2), 20.8(2C, *C*H_2), 20.4(2C, *C*H_3), 13.1(2C, *C*H_3).

Synthesis of 2-(4-(1-amino 4,6-*O*-ethylidene β-D-glycopyranosyl)phenyl)-1-hexadecyl-5-methyl benzimidazole (17).

Compound, **17** was obtained by the reaction of hexadecyl benzimidazole amine, **7** (1 mmol, 0.448 g), with 4,6-*O*-ethylidene-D-glucopyranose, 2 (1 mmol, 0.206 g) as yellow solid. Yield : 85 % (0.540 g). Melting point : 190-193 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): 7.56(m, 7.51-7.56, 6H, Ar-*H* & GlyN*H*), 7.30(d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.20(s, 2H, Ar-*H*), 7.12(t, *J* = 8.1 Hz, 2H, Ar-*H*), 6.85(d, *J* = 8.4 Hz, 4H, Ar-*H*), 4.79(d, *J* = 4.2 Hz, 2H, Ace-*H*), 4.68(t, *J* = 7.2 Hz, 2H, Ano-*H*), 4.30(m, 4.10-4.30, 8H, NCH_2 & Sacc-O*H*), 3.83(t, *J* = 6.6 Hz, 2H, Sacc-*H*), 3.60(m, 3.56-3.60, 8H, Sacc-*H*), 3.44(m, 3.37-3.44, 2H, Sacc-*H*), 2.54(s, 3H, CH_3), 2.51(s, 3H, CH_3),1.90(m, 1.82-1.90, 4H, CH_2), 1.42(d, *J* = 4.2 Hz, 8H, CH_2), 1.40(m, 1.20-1.40, 50H, CH_2 & CH_3), 0.90(t, *J* = 6 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$+ DMSO-d_6, ppm): 146.5(2C, Ar-C), 134.7(2C, Ar-*C*), 130.9(2C, Ar-*C*), 129.1(4C, Ar-*C*), 122.5(2C, Ar-*C*), 119.3(2C, Ar-*C*), 117.9(2C, Ar-*C*), 117.6(2C, Ar-*C*), 112.6(4C, Ar-*C*), 108.9(2C, Ar-*C*), 108.3(2C, Ar-*C*), 98.4(2C, Ace-*C*), 85.2(2C, Ano-*C*), 79.4(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.3(2C, Sacc-*C*), 66.1(2C, Sacc-*C*), 43.8(2C, N*C*H_2), 30.7(2C, *C*H_2), 28.5(2C, *C*H_2), 28.3(2C, *C*H_2), 28.2(4C, *C*H_2), 28.0(4C, *C*H_2), 25.6(4C, *C*H_2), 21.5(4C, *C*H_2), 20.8(4C, *C*H_2), 20.5(2C, *C*H_3), 19.5(2C, CH_3), 13.1(2C, *C*H_3).

Synthesis of 2-(4-(1-amino 4,6-*O*-butylidene β-D-glycopyranosyl)phenyl)-1-hexadecyl-5-methyl benzimidazole (18).

Compound, **18** was obtained by the reaction of hexadecyl benzimidazole amine, **7** (1 mmol, 0.448 g), with 4,6-*O*-butylidene-D-glucopyranose, **2** (1 mmol, 0.234 g) as yellow solid. Yield : 82 % (0.544 g). Melting point : 181-183 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.51(m, 7.44-7.51, 6H, Ar-*H* & GlyN*H*), 7.31(d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.21(s, 2H, Ar-*H*), 7.05(t, *J* = 8.4 Hz, 2H, Ar-*H*), 6.86(d, *J* = 8.7 Hz, 4H, Ar-*H*), 5.18(m, 5.15-5.18, 4H, Sacc-O*H*), 4.64(t, *J* = 7.2 Hz, 2H, Ano-*H*), 4.57(t, *J* = 4.8 Hz, 2H, Ace-*H*), 4.19(m, 4.13-4.19, 6H, NCH_2 & Sacc-*H*), 3.70(m, 3.63-3.70, 2H, Sacc-*H*), 3.47(m, 3.39-3.47, 8H, Sacc-*H*), 2.50(s, 3H, CH_3), 2.46(s, 3H, CH_3), 1.90(m, 1.80-1.90, 4H, CH_2), 1.63(m, 1.59-1.63, 4H, CH_2), 1.48(m, 1.40-1.48, 4H, CH_2), 1.30(m, 1.25-1.30, 52H, CH_2 & CH_3), 0.95(m, 0.85-0.95, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$ ppm): 146.9(2C, Ar-C), 134.9(2C, Ar-*C*), 130.1(2C, Ar-*C*), 129.0(4C, Ar-*C*), 122.4(2C, Ar-*C*), 118.9(2C, Ar-*C*), 117.8(2C, Ar-*C*), 117.6(2C, Ar-*C*), 112.4(4C, Ar-*C*), 109.0(2C, Ar-*C*), 108.6(2C, Ar-*C*), 101.0(2C, Ace-*C*), 85.0(2C, Ano-*C*), 79.7(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.3(2C, Sacc-*C*), 66.2(2C, Sacc-*C*), 44.0(2C, N*C*H_2), 35.3(2C, *C*H_2), 30.7(2C, *C*H_2), 28.5(4C, *C*H_2), 28.4(2C, *C*H_2), 28.3(4C, *C*H_2), 28.1(6C, *C*H_2), 27.9(2C, *C*H_2), 25.5(2C, *C*H_2), 21.5(4C, *C*H_2), 20.8(2C, *C*H_2), 20.5(2C, *C*H_3), 16.3(2C, *C*H_2), 13.1(2C, *C*H_3), 13.0(2C, *C*H_3). **MALDI-TOF:** m/z calcd for C40H61N3O5 663.46, found 664.13 (M+H).

Synthesis of 2-(4-(1-amino 4,6-*O*-benzylidene β-D-glycopyranosyl)phenyl)-1-hexadecyl-5-methyl benzimidazole (19).

Compound, **19** was obtained by the reaction of hexadecyl benzimidazole amine, **7** (1 mmol, 0.448 g), with 4,6-*O*-benzylidene-D-glucopyranose, **3** (1 mmol, 0.268 g) as yellow solid. Yield : 85% (0.586g). Melting point : 152-154°C. **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): 7.58(m, 7.50-7.58, 10H, Ar-*H* & GlyN*H*), 7.36(m, 7.34-7.36, 6H, Ar-*H*), 7.27(d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.17(s, 2H, Ar-*H*), 7.07(t, *J* = 7.2 Hz, 2H, Ar-*H*), 6.87(d, *J* = 8.4 Hz, 4H, Ar-*H*), 5.10(s, 2H, Sacc-O*H*), 4.84(s, 2H, Sacc-O*H*), 4.71(t, *J* = 8.4 Hz, 2H, Ano-*H*), 4.39(m, 4.34-4.39, 2H, Sacc-*H*), 4.20(m, 4.16-4.20, 4H, NCH_2), 3.85(t, *J* = 8.4 Hz, 2H, Sacc-*H*), 3.80(m, 3.74-3.80, 2H, Sacc-*H*), 3.69(m, 3.57-3.69, 6H, Sacc-*H*), 2.51(s, 3H, CH_3), 2.47(s, 3H, CH_3), 1.90(m, 1.70-1.90, 4H, CH_2), 1.30(m, 1.20-1.30, 52H, CH_2), 0.87(t, *J* = 6.9 Hz, 6H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$+ DMSO-d_6, ppm): 146.4(2C, Ar-C), 136.5(2C, Ar-*C*), 131.1(2C, Ar-*C*), 130.6(2C, Ar-*C*), 129.2(4C, Ar-*C*), 128.1(2C, Ar-*C*), 127.2(4C, Ar-*C*), 125.2(4C, Ar-*C*), 122.6(2C, Ar-*C*), 119.4(2C, Ar-*C*), 118.0(2C, Ar-*C*), 117.8(2C, Ar-*C*), 112.7(4C, Ar-*C*), 109.0(2C, Ar-*C*), 108.6(2C, Ace-*C*), 100.8(2C, Ace-*C*), 85.4(2C, Ano-*C*), 80.2(2C, Sacc-*C*), 73.1(2C, Sacc-*C*), 72.9(2C, Sacc-*C*), 67.9(2C, Sacc-*C*), 66.2(2C, Sacc-*C*), 43.8(2C, N*C*H_2), 30.9(2C, *C*H_2), 28.8(2C, *C*H_2), 28.6(4C, *C*H_2), 28.5(4C, *C*H_2), 28.3(4C, *C*H_2), 28.1(2C, *C*H_2), 25.7(2C, *C*H_2), 21.6(4C, *C*H_2), 20.9(2C, *C*H_2), 20.6(2C, *C*H_3), 13.1(2C, *C*H_3).

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