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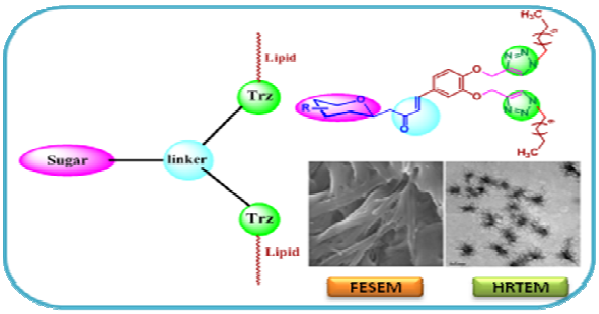
Graphical Abstract



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ARTICLE TYPE

Bis-Triazologlycolipid mimetics - Low molecular weight organogelator

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Introduction

Glycolipids are membrane components composed of lipids that are covalently bonded to monosaccharide or polysaccharide where it serves as a marker for cellular recognition. It is universally distributed in nature constituting cell membranes of almost all living organisms. Owing to their intrinsic amphiphilic feature as well as their low toxicity and high biocompatiblity, they have broad applications in numerous biochemical and especially physicochemical studies.[1–11] However, the majority of natural glycolipids encounter unsatisfactory limitations such as their structural instability towards acidic and enzymatic cleavage due to the presence of an *O*-glycosidic linkage between the lipid aglycons and the glycons.

Copper catalyzed azide-alkyne 1,2,3–triazole forming click reaction is useful for efficient coupling of two entities.[12] "Click reaction" has a wide range of applications including drug discovery,[13] material science[14] and biology[15] and it is used for making a large number of new compounds which include glycodendrimers, glycopolymers and glycopeptides.[16] Moreover, there are few reports[17] on the preparation and its potential functions of triazole-linked glycolipids. Loganathan and co-workers first described the synthesis of series of triazologlycolipid mimetics where in which triazole ring acts as a linker between various carbohydrates and lipid chains.[18] Krausz and co-workers subsequently showed the potential utility of this unique non-ionic lipid class for the development of green surfactants.[19]

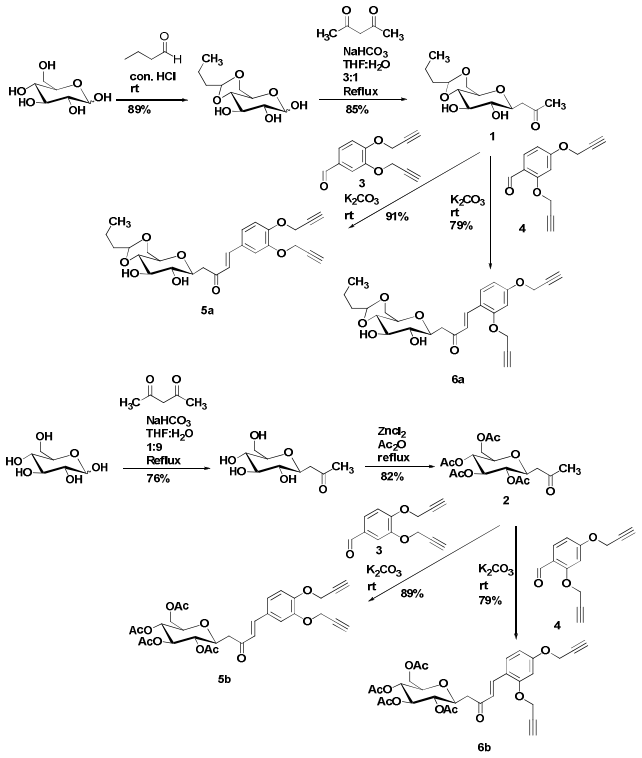
Low-molecular-weight organogels (LMOG) is an important class of soft matters and has received increasing attention in recent years due to their easy fabrication into soft materials and wide applications in the field of sensing, catalysis, oil recovery, template synthesis of nanoporous materials etc.[20] It is very important to design suitable gelator molecules involving H-bond forming site, long alkyl chain and π–π stacking unit which are necessary for the gelation. Baddeley *et al*.[21] emphasized the delicate balance between both the molecular structure and electronic properties of LMWGs as well as the solvent polarity in the medium to achieve gelation and to control the morphology of the assembled fibers. In this paper we report a systematic investigation of gel forming chalcone based glycolipid mimetics.

Results and discussion

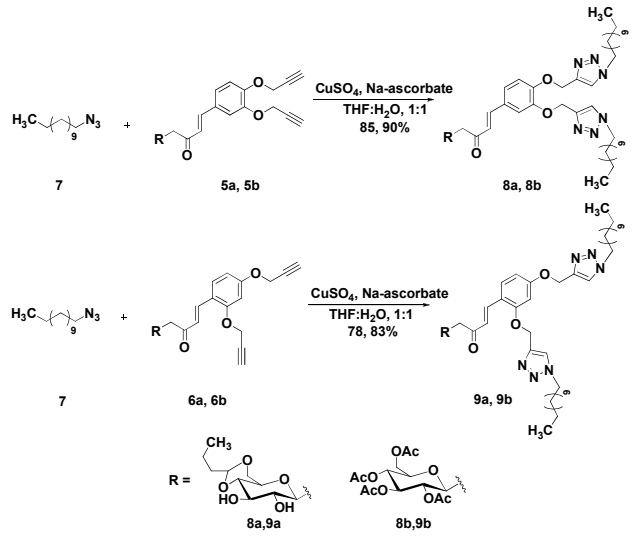
Synthesis and characterization of sugar-based long-chain-bis-triazole derivatives

4,6-*O*-Butylidene-D-glucopyranose was synthesized from D-glucose by adopting the literature procedure.[22] *β*-C-Glycosidic ketone, was synthesized by the Knoevenagel condensation of 2,4-pentanedione with 4,6-*O*-butylidene-D-glucopyranose in the presence of sodiumbicarbonate using THF-H_2O as solvent.[23,24] Aldol condensation of two different *β*-C-glycosidic ketones **1** & **2** with *bis*-propargylated aromatic aldehydes, **3** & **4** resulted in the formation of the corresponding *α*-,*β*-unsaturated-*β*-C-glycosidic ketones, **5a**, **5b**, **6a** & **6b** in 70-90% yield. The newly synthesized *bis*-propargylated compounds, **3**, **4**, **5a**, **5b**, **6a** & **6b** are well characterized using NMR (^{1}H & ^{13}C) and elemental analysis.

Triazole chemistry is implied to link the *bis*-propargylated glycoside to the known azide. The preparation of the azide was accomplished from the corresponding bromide in a single step with an excellent yield. Cycloaddition reaction of *bis*-alkyne compounds, **5a**, **5b**, **6a** & **6b** with two equivalents of dodecyl-azide, **7** using copper sulphate and sodium ascorbate in catalytic amount led to the formation of sugar chalcone-based *bis*-triazole having long alkyl derivatives. However, the compound, **5a** was poorly soluble in tertiary butanol and acetonitrile whereas tetrahydrofuran and water mixture in the ratio 1:1 was used to improve the solubility of the reaction. The cycloadduct obtained in this case was 82%. The reaction condition was optimized using different solvents [**See ESI for more details**]. Thus the reaction of *α*-,*β*-unsaturated-*β*-C-glycosidic ketones, **5a**, **5b**, **6a** & **6b** with dodecyl azide, **7** using THF:water mixture as solvent in the ratio 1:1 resulted in 78-90% yield of the corresponding sugar-based long chain *bis*-triazole derivatives **8a**, **8b**, **9a** & **9b**.



Scheme 1 Structures of sugar-chalcone based *bis*-propargylated derivatives.



Scheme 2 Structures of bis-(triazole-sugar) compounds.

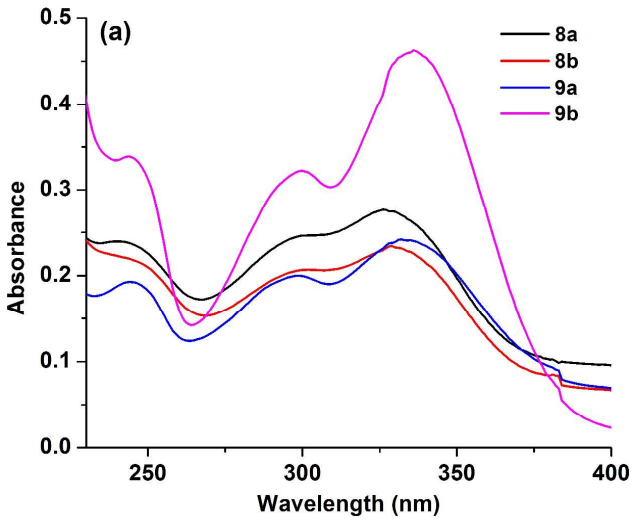
Structures of the resulting chalcone based triazologlycolipid analogues were characterized by FT-IR and (^{1}H, ^{13}C) NMR spectral techniques, mass and elemental analysis. FT-IR spectrum of compound, **8a** shows bands around 1596, 1512, 1226 cm^{-1} which corresponds to the frequency of C=O, C=C (alkene) and C-N respectively. The presence of sugar-chalcone in the compound, **8a** was further confirmed from ^{1}H NMR spectroscopy by the appearance of doublets at δ 7.51 and 6.69 ppm with coupling constant ~16 Hz which corresponds to *trans* alkene double bond whereas the presence of sugar-triazole core is confirmed from the appearance of two sharp singlet at δ 7.69 ppm and δ 7.68 ppm which corresponds to methine protons (trz-*H*) of triazole ring [**Table 1**]. The triazole carbons resonate around δ 151 and 148 ppm. Furthermore, from the ^{13}C NMR spectrum the 1,4 regioisomeric product formation of *bis*-triazole is confirmed where the Rodios calculation (δ C4-C5) for compound, **8a** is found to be 29.1 and 29.2 ppm. The product formation was further confirmed by DEPT-135 and 2D spectrum [**See ESI for more details**]. The methylene carbons in the product, **8a** was identified from DEPT-135 experiment. Moreover, ^{1}H-^{13}C [COSY] spectrum reveals the correlation of characteristic protons with its corresponding carbons. In addition, the mass spectrum of compound, **8a** shows the exact mass value of the product, **8a** that matches with the experimental results ultimately confirms the formation of the *bis*-triazole derivative.

Table 1 Spectral data and optimization of triazole based lipid appended α-,β-unsaturated-β-C-glycosidic ketones, **8a**, **8b**, **9a** & **9b**

Compound No.	Time (h)	Yield (%)	NMR data		
			δAno-H/ppm $^3J_{HH2}$ Hz	δAlk-H/ppm $^3J_{HH2}$ Hz	δTrz-H/ppm
8a	24	85	4.15, 9.9	7.51, 6.69 16.2, 15.9	7.69, 7.68
8b	20	90	5.25, 9.5	7.48, 6.63 15.9, 16.2	7.70, 7.68
9a	24	78	4.12, 9.9	7.88, 6.73 16.2, 16.2	7.67, 7.66
9b	20	83	5.07, 9.6	7.83, 6.72-6.62* 16.2	7.71, 7.67

*trans alkene protons are merged with aromatic protons.

Absorption and emission was recorded in acetonitrile for all the synthesized sugar derivatives, **8a, 8b, 9a & 9b**. Profile of both the absorption and emission spectra are represented in **Figure 2**.



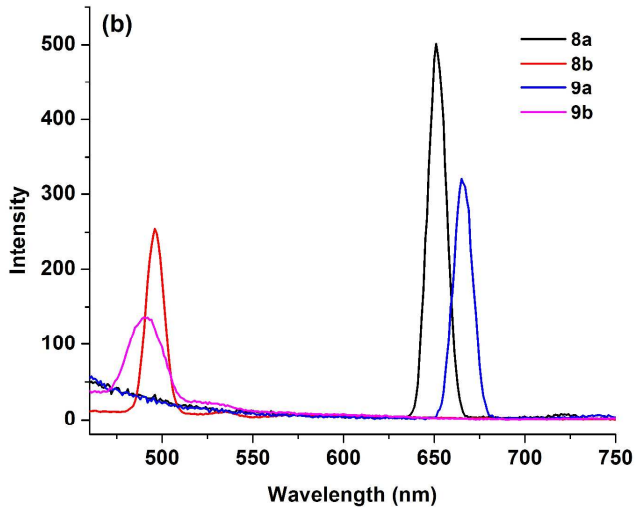


Figure 1 (a), Absorption spectra of compounds, **8a, 8b, 9a, 9b** in acetonitrile (1x10^{-5} M); (b), Emission spectra of compounds, **8a, 8b, 9a,9b** in acetonitrile (1x10^{-5} M).

All the four triazole compounds, **8a**, **8b**, **9a** & **9b** gave three consecutive bands, a weak band around 250 nm and two strong bands around 300 and 350 nm. From the emission spectra, it is found that the compounds, **8a** & **9a** gave peaks around 650 nm whereas the compounds, **8b** & **9b** gave bands around 500 nm [**Figure 1**]. Thus, it is concluded from the result that irrespective of the position of triazole moiety, the change in the protection of the sugar moiety has led to the shift in the wavelength on emission.

All the four *bis*-triazole sugar derivatives **8a**, **8b**, **9a** & **9b** form gel in organic solvents [**Table 2**]. The gelation property of the dendritic *bis*-triazole sugar derivatives in other dielectric media was examined in a wide range of solvents and mixture of solvents. The instant gel formed from the hexane-ethylacetate mixture was dried under vaccum and then dissolved in a selected solvent or solvent mixture by heating. The homogeneous solution is then cooled to room temperature to obtain the gel [**Figure 2**]. Critical gelation concentration (CGC) of the compounds, **8a**, **8b**, **9a** & **9b** were determined using hexane-ethylacetate solvent mixture [**Table 2**]. The long-chain *bis*-triazole sugar derivatives, **8a** & **9a** which has butylidene as the protecting group with two free hydroxyl group forms gel at very low CGC (1%) whereas the compounds, **8b** & **9b** which has the similar core structure as that of **8a** & **9a** found to have CGC (1.5%). This difference in the CGC may be presumably due to the hydrogen bonding formation of the two hydroxyl group which lowers the CGC and improves the gelation.

The gelation ability of α,β-unsaturated β-*C*-glycosidic ketone where the presence of partial protection of the saccharide was employed for gelation.[24] It is well known that for gelation both the participation of hydrophilic and hydrophobic groups are necessary. Here in this paper, the precursors, **5a** & **6a** utilized for the synthesis of *bis*-triazolyl derivatives, **8a** & **9a** formed a partial gel with hexane-ethylacetate whereas gel formation was not observed with the precursors, **5b** & **6b**. This is because in the former, the presence of two hydroxyl groups which are responsible for the hydrogen bonding may result in the partial gelation whereas in the latter since there is no site of hydrophilic group in the molecules, **5b** and **6b**, self-assembly was not observed and hence acts as non-gelators.

Figure 2 Gel picture of compound **8a**; (a) Heating followed by cooling, (b) upon inversion.

Table 2 Gelation studies of compound, **8a**,**8b**,**9a**&**9b**

Solvent	8a	8b	9a	9b
Water	I	I	I	I
Methanol	S	S	S	S
Ethanol	S	S	S	S
DMSO+water (3:1)	P	P	P	P
DMF+water (3:1)	P	P	P	P
Acetonitrile	S	S	S	S
Dichloroethane	S	S	S	S
Hex+EtOAc (1:10)	G (CGC = 1)	G (CGC = 1.5)	G (CGC = 1)	G (CGC = 1.5)
Hex+$CHCl_3$ (1:10)	G (CGC = 1.2)	PG	G (CGC = 1.2)	PG
Ethylacetate	G (CGC = 1.8)	PG	G (CGC = 1.6)	PG
Chloroform	G (CGC = 1.5)	PG	G (CGC = 1.4)	PG

Note: G-Gelator, PG-Partial gelator, S-Solution, I-Insoluble, P-Precipitation; CGC represented in % (gmL^{-1})

The xerogel of the organogelator was subjected to morphological studies using FESEM and HRTEM analysis. SEM images of the organogelator **8a** & **8b** are shown in **Figure 3**. From FESEM, the morphology of the compound, **8a** is observed to be fibrous network. The size of fibril is found to be around 58 nm. The crystal clear picture of interior morphology of the gelator which exhibits a fibrous network is observed from HRTEM.

Two types of aggregation modes, fibrous and lamellar are proposed for the observed morphology. Compound **8a**, the long chain *bis*-triazole derivative bearing partially protected sugar exhibits fibrous aggregated morphology which has nanopores [**Figure 3a**], whereas the corresponding completely protected sugar, **8b** exhibits lamellar structure with less voids [**Figure 3b**]. In addition, the compound **8b** does not show any branched structure, instead has aggregated mode of each individual layer. Generally, fibrous structures can incorporate more solvent than the lamellar structures because of their greater void volumes as it is documented from FESEM and HRTEM analysis. In the SEM image of gelator, **8a**, the larger flat tubules are composed of fibrous network as shown in **Figure 3a**. The bulk structure of the organogelator, **8b** is lamellar. Except for the difference in protection of sugar moiety, the core architecture of molecules, **8a** & **8b** found to

be similar and hence it is assumed that for compound **8b**, the fibrils aggregate together to form lamellar-like structure [**Figure 3b**]. The interior morphology of compound, **8a** was determined using HRTEM and its representative images of the compound, **8a** is shown in **Figure 4**. The aggregation mode is identified as fibrils which join together to form interlinked network structure. The repeated interlinks which gave an aggregated form confirmed the formation of organogelator.

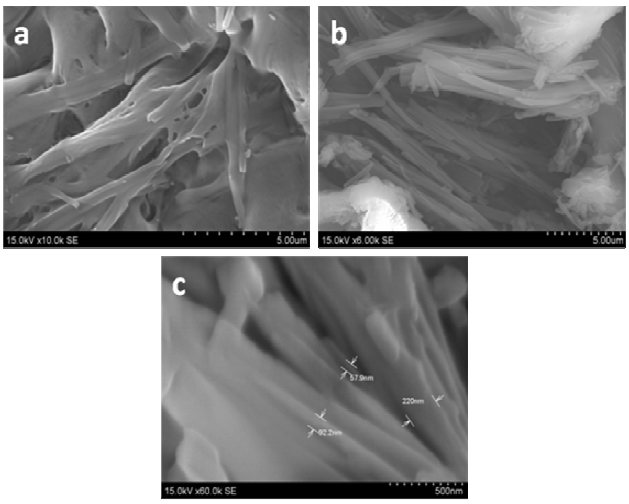


Figure 3 FESEM images of organogel formed from $CHCl_3$ (a) **8a** [5 μm], (b) **8b** [5μm] and (c) **8b** [500 nm].

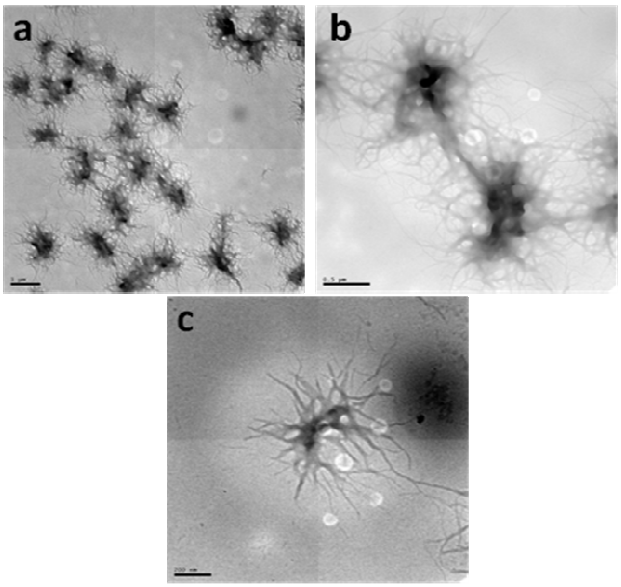


Figure 4 HR-TEM images of compound **8a** in $CHCl_3$ under different magnifications, (a) 1μm; (b) 0.5 μm and (c) 200 nm.

X-ray powder Diffraction Analysis was carried out for the organogelators, **8a** & **8b**. The xerogel of compound, **8a** & **8b** was subjected to X-ray for diffraction pattern. In general, the X-ray diffraction pattern gives an idea about the molecular packing in the gel. The X-ray diffractogram of compounds, **8a** & **8b** are shown in **Figure 5**. In **Figure 5a** one can recognize a sharp peak at $2\theta = 2.28°$ with an interlayer distance of 38.6 nm arises from the packing of long alkyl chain due to van der Waals interaction. The diffraction pattern in the wide angle gave two broad peaks at $2\theta = 11.96°$ and 20.39° with an interlayer distance of 7.3 nm and 4.3 nm respectively. This may be due to the π–π interaction of aromatic as well as with the two triazole rings. **Figure 5b** shows the same pattern as that of **8a**, where the observation of peak at low angle 2.87° with an interlayer distance of 30.6 nm followed by a broad peak in the higher angle around 11.17° and 19.86° with an interlayer distance of 7.1 and 4.4 nm respectively. The only difference observed is the variation in the intensity of the peaks at the low angle. The intensity of the peak was found to be around 255 for compound, **8a** whereas it is only 70 in the case of compound, **8b**. This shows that the compound, **8a** is much more crystalline compared to that of the compound, **8b**.

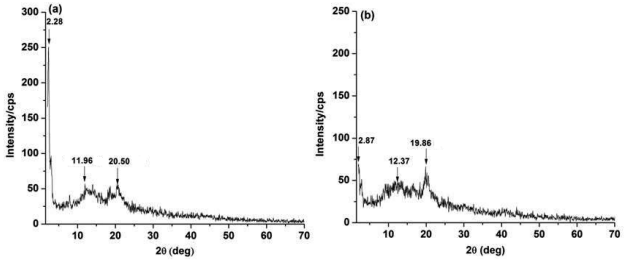


Figure 5 Powder XRD of organogelators, (a), **8a** and (b), **8b**.

Thus the XRD studies confirm the formation of both the gels obtained from the organogelators, **8a** & **8b** are one dimensional aggregate. Thus, XRD analysis gives an additional information for the morphology that has been determined using FESEM.

Conclusion

Thus, we have designed and synthesized several chalcone based glycolipid derivatives, which prone to form organogel and characterized using different spectral techniques. The existence of 1,4-regioisomer of triazole and *β*-anomeric form of the sugar derivatives were identified using NMR studies. CGC value of 1.5 has been observed for almost all sugar triazole derivatives. The morphology of the gel forming compounds was studied using FESEM and HRTEM. Both fibrous and lamellar structure has been obtained for the *bis*-triazole derivatives. In addition to the morphological structure, the molecular packing in the gel was identified from powder XRD studies. Further manipulation of *α*-, *β*-unsaturated-*β*-*C*-glycosidic ketones for the synthesis of several gelator molecules are under progress in our laboratory.

Experimental

Materials and methods

D-Glucose, dodecylbromide, propargyl bromide, 3,4-dihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., USA and were of high purity. Butyraldehyde and organic catalyst (pyrrolidine) were obtained from SRL, India. Other reagents, such as, hydrochloricacid, sodiumhydrogencarbonate, and solvents (AR Grade) were obtained from Sd-fine, India, in

high purity and were used without any further purification. Acetylacetone, coppersulphate and sodiumascorbate were purchased from Loba-chemie, India. Aceticanhydride was obtained from Fischer chemicals Pvt. Ltd., India. The solvents were purified according to the standard methods. Column chromatography was performed on silica gel (100 – 200 mesh). NMR spectra were recorded on a Bruker DRX 300 MHz instrument in either $CDCl_3$ or DMSO-d_6. Chemical shifts were referenced to internal TMS. SEM images were recorded using Hitachi-S-3400W and HRTEM was recorded using a JEOL, JEM 3010 model (LaB6 filament). Absorption studies were carried out on 1800 Shimadzu UV spectrophotometer in the range 190-800 nm. Emission studies were recorded using a Perkin Elmer LS 45 fluorescence spectrometer. Electro-spray ionization mass spectrum was recorded using WATERS-Q-TOF Premier-HAB213 spectrometer. Elemental analysis was performed using Perkin-Elmer 2400 series CHNS/O analyzer.

Spectral characterization of organogelator

Abbreviation such as Trz, Sac, Alk and Ar correspond to triazole, saccharide alkene and aromatic respectively.

General procedure for synthesis of sugar-*bis*-triazole derivatives (8a, 8b, 9a & 9b):

To a solution of sugar-chalcone (1 equiv.) in tetrahydrofuran and water mixture in 1:1 ratio were added. To the reaction mixture dodecylazide, **7** (2.2 equiv.) was added. $CuSO_4.5H_2O$ (0.2 equiv.) and sodiumascorbate (0.4 equiv.) was added in catalytic amount. It was then stirred at room temperature for 24 hrs. After completion of the reaction, the solvent was evaporated and it was then extracted with $CHCl_3$ (200 ml) and water (200 ml). The organic layer was then evaporated, slurried and purified by column chromatography.

Synthesis, physicochemical and spectral data of (*E*)-1-(4,6-O-butylidene-*β*-D-glucopyranosyl)-4-{3,4-*bis*[1'-(dodecyl)-4'-hydroxy-methylene-triazolo]phenyl}but-3-ene-2-one (8a):

Compound, **8a** was obtained by the "Click reaction" of propargylated-sugar derivative, **5a** (0.47 g, 1 mmol) and dodecylazide, **7** (0.46 g, 2.2 mmol) as a dark yellow solid.
Mp 172-174 ^oC; Yield 0.76 g (85%); ^1H NMR (300 MHz, CDCl3): δ 7.69 (s, 1H, Trz-H), 7.68 (s, 1H, Trz-H), 7.51 (d, J = 16.2 Hz, 1H, Alk-H), 7.34 (s, 1H, Ar-H), 7.17-7.05 (m, 2H, Ar-H), 6.69 (d, J = 15.9 Hz, 1H, Alk-H), 5.32 (s, 2H, -OCH_2), 5.31 (s, 2H, -OCH_2), 4.55 (t, J = 5.1 Hz, 1H, Sac-H), 4.35 (t, J = 7.2 Hz, 4H, -CH_2), 4.15 (dd, J = 4.2 Hz, J = 9.9 Hz, 1H, Sac-H), 3.97-3.91 (m, 1H, Sac-H), 3.75 (t, J = 8.7 Hz, 1H, Sac-H), 3.45 (t, J = 9.3 Hz, 1H, Sac-H), 3.26 (t, J = 9.0 Hz, 1H, Sac-H), 3.10 (dd, J = 4.2 Hz, J = 15.9 Hz, 1H, -CH_2), 2.98 (dd, J = 6.9 Hz, J = 15.9 Hz, 1H, -CH_2), 1.33-1.27 (m, 43H, -CH_2, -CH_3), 0.96-0.87 (m, 7H, -CH_2, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.9, 150.8, 148.4, 143.7, 143.5, 143.1, 128.3, 124.9, 123.9, 123.0 (2C), 114.6, 114.3, 102.4, 80.5, 77.2, 76.3, 75.4, 74.6, 70.6, 68.3, 63.4, 63.2, 50.5, 43.7, 36.3, 31.9, 30.2, 29.6, 29.5, 29.4, 29.3, 29.0, 26.5, 22.7, 17.5, 14.1, 13.9; ESI-MS:Calc. for $C_{50}H_{80}N_6O_8$, 892.60; m/z found, 893.61 $[M+H]^+$; Elemental analysis: Anal. Calc. for $C_{50}H_{80}N_6O_8$: C, 67.23; H, 9.03; N, 9.41%. Found: C, 67.28; H, 9.07; N, 9.46.

Synthesis, physicochemical and spectral data of (*E*)-1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-{3,4-*bis*[1'-(dodecyl)-4'-hydroxy-methylene-triazolo]phenyl}but-3-ene-2-one (8b):

Compound, **8b** was obtained by the "Click reaction" of sugar-propargylated derivative, **5b** (0.58 g, 1 mmol) and dodecylazide, **7** (0.46 g, 2.2 mmol) as a pale yellow solid.
Mp: 128-131 ^oC; Yield: 0.91 g (90%); ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 1H, Trz-H), 7.68 (s, 1H, Trz-H), 7.48 (d, J = 15.9 Hz, 1H, Alk-H), 7.32 (s, 1H, Ar-H), 7.18-7.08 (m, 2H, Ar-H), 6.63 (d, J = 16.2 Hz, 1H, Alk-H), 5.32 (s, 2H, -OCH_2), 5.30 (s, 2H, -OCH_2), 5.25 (t, J = 9.5 Hz, 1H, Sac-H), 5.10 (t, J = 9.6 Hz, 1H, Sac-H), 5.00 (t, J = 9.6 Hz, 1H, Sac-H), 4.36 (t, J = 7.2 Hz, 4H, -CH_2), 4.28 (dd, J = 5.1 Hz, J = 12.5 Hz, 1H, Sac-H), 4.15 (t, J = 7.7 Hz, 1H, Sac-H), 4.06-4.02 (m, 1H, Sac-H), 3.76-3.72 (m, 1H, Sac-H), 3.02 (dd, J = 8.4 Hz, J = 16.1 Hz, 1H, -CH_2), 2.68 (dd, J = 2.7 Hz, J = 16.2 Hz, 1H, -CH_2), 2.04-2.03 (m, 12H, -$COCH_3$), 1.33-1.27 (m, 43H, -CH_2, -CH_3), 0.91-0.87 (m, 7H, -CH_2, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.9, 170.6, 170.2, 170.0, 169.5, 151.0, 148.5, 143.6, 143.5, 143.2, 128.2, 124.8, 123.9, 122.9, 114.6, 114.5, 75.7, 74.3, 74.2, 71.7, 68.6, 63.6, 63.3, 62.1, 50.5, 42.7, 31.9, 30.3, 29.6, 29.5, 29.4, 29.3, 29.0, 26.5, 22.7, 20.7 (2C), 20.6, 14.1; Elemental analysis: Anal. Calc. for $C_{54}H_{82}N_6O_{12}$: C, 64.39; H, 8.21; N, 8.34%. Found: C, 64.43; H, 8.25; N, 8.36.

Synthesis, physicochemical and spectral data of (*E*)-1-(4,6-*O*-butylidene-*β*-D-glucopyranosyl)-4-{2,4-*bis*[1'-(dodecyl)-4'-hydroxy-methylene-triazolo]phenyl}but-3-ene-2-one (9a):

Compound, **9a** was obtained by the "Click reaction" of sugar-propargylated derivative, **6a** (0.47 g, 1 mmol) and dodecylazide, **7** (0.46 g, 2.2 mmol) as a dark yellow solid.
Mp: 132-134 ^oC; Yield: 0.69 g (78%); ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 16.2 Hz, 1H, Alk-H), 7.67 (s, 1H, Trz-H), 7.66 (s, 1H, Trz-H), 7.48 (d, J = 8.7 Hz, 1H, Ar-H), 6.80 (s, 1H, Ar-H), 6.73 (d, J = 16.2 Hz, 1H, Alk-H), 6.64 (d, J = 8.4 Hz,1H, Ar-H), 5.26 (s, 2H, -OCH_2), 5.24 (s, 2H, -OCH_2), 4.53 (t, J = 5.0 Hz, 1H, Sac-H), 4.39-4.34 (m, 4H, -CH_2), 4.12 (dd, J = 3.9 Hz, J = 9.9 Hz, 1H, Sac-H), 3.93-3.88 (m, 1H, Sac-H), 3.75 (q, J = 7.5 Hz, 1H, Sac-H), 3.43-3.40 (m, 1H, Sac-H), 3.28-3.22 (m, 1H, Sac-H), 3.17 (dd, J = 4.2 Hz, J = 15.5 Hz, 1H, -CH_2), 2.86 (dd, J = 7.2 Hz, J = 15.6 Hz, 1H, -CH_2), 1.32-1.25 (m, 43H, -CH_2, -CH_3), 0.94-0.86 (m, 7H, -CH_2, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 159.9, 156.8, 141.6, 141.4, 137.1, 128.4, 123.1, 121.2, 121.1, 115.7, 106.2, 100.7, 99.1, 78.8, 73.6, 73.2, 68.9, 66.7, 60.8, 60.4, 48.9, 48.8, 41.8, 34.6, 30.2, 28.6, 28.0, 27.9, 27.8, 27.7, 27.6, 27.3, 24.8, 21.0, 15.8, 12.4, 12.2; Elemental analysis: Anal. Calc. for $C_{50}H_{80}N_6O_8$: C, 67.23; H, 9.03; N, 9.41%. Found: C, 67.28; H, 9.07; N, 9.46.

Synthesis, physicochemical and spectral data of (*E*)-1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-{2,4-*bis*[1'-(dodecyl)-4'-hydroxy-methylene-triazolo]phenyl}but-3-ene-2-one (9b):

Compound, **9b** was obtained by the "Click reaction" of sugar-propargylated derivative, **6b** (0.58 g, 1 mmol) and dodecylazide, **7** (0.46 g, 2.2 mmol) as a pale yellow solid.
Mp: 81-84 ^oC; Yield: 0.84 g (83%); ^1H NMR (300 MHz,

$CDCl_3$): δ 7.83 (d, *J* = 16.2 Hz, 1H, Alk-H), 7.71 (s, 1H, Trz-H), 7.67 (s, 1H, Trz-H), 7.49 (d, *J* = 8.7 Hz, 1H, Ar-H), 6.81 (s, 1H, Ar-H), 6.72-6.62 (m, 2H, Ar-H, Alk-H), 5.29 (s, 2H, -OCH_2), 5.24 (s, 2H, -OCH_2), 5.07 (t, *J* = 9.6 Hz, 1H, Sac-H), 4.97 (t, *J* = 9.8 Hz, 1H, Sac-H), 4.38 (q, *J* = 7.5 Hz, 4H, -CH_2), 4.27 (dd, *J* = 4.5 Hz, *J* = 12.5 Hz, 1H, Sac-H), 4.17-4.10 (m, 1H, Sac-H), 4.03-3.99 (m, 1H, Sac-H), 3.75-3.70 (m, 1H, Sac-H), 2.97 (dd, *J* = 8.1 Hz, *J* = 16.5 Hz, 1H, -CH_2), 2.65 (dd, *J* = 3.6 Hz, *J* = 16.4 Hz, 1H, -CH_2), 2.04-2.01 (m, 12H, -$COCH_3$), 1.94-1.93 (m, 4H, -CH_2), 1.25 (m, 36H, -CH_2), 0.90-0.85 (m, 6H, -CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 170.6, 170.2, 170.0, 169.6, 161.8, 158.7, 143.4, 138.7, 130.0, 124.5, 122.7, 116.9, 107.6, 100.5, 75.7, 74.3, 71.8, 68.6, 62.7, 62.2, 62.1, 50.6, 42.5, 31.9, 30.3, 29.6, 29.5, 29.4 (2C), 29.3, 29.0, 26.5, 22.7, 20.7 (2C), 20.6, 14.1; ESI-MS: Calc. for $C_{54}H_{82}N_6O_{12}$, 1006.60; m/z found, 1007.61 $[M+H]^+$; Elemental analysis: Anal. Calc. for $C_{54}H_{82}N_6O_{12}$: C, 64.39; H, 8.21; N, 8.34%. Found: C, 64.43; H, 8.25; N, 8.36.

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