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Bis-triazologlycolipid mimetics – low molecular weight organogelators†

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A facile regioselective synthesis of bis-triazologlycolipids, a class of organogelators, has been accomplished by "Click reaction". The morphology and self-assembly of the gelators were examined by FESEM and HRTEM analysis.

Introduction

Glycolipids are membrane components composed of lipids that are covalently bonded to monosaccharides or polysaccharides and they serve as markers for cellular recognition. They are universally distributed in nature constituting the cell membranes of almost all living organisms. Owing to their intrinsic amphiphilic feature as well as their low toxicity and high biocompatibility, they have broad applications in numerous biochemical and especially physicochemical studies.[1–11] However, the majority of natural glycolipids have 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] materials science[14] and biology[15] and it is used for preparing a large number of new compounds which include glycodendrimers, glycopolymers and glycopeptides.[16] However, there are few reports[17] on the preparation and potential functions of triazole-linked glycolipids. Loganathan and co-workers first described the synthesis of a series of triazologlycolipid mimetics in which the 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 organogelators (LMOG) are an important class of soft matter and have 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 sites, long alkyl chains and π–π stacking units 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 sodium bicarbonate using THF–H_2O as solvent.[23,24] Aldol condensation of two different β-*C*-glycosidic ketones **1** and **2** with bis-propargylated aromatic aldehydes, **3** and **4**, resulted in the formation of the corresponding α-,β-unsaturated-β-*C*-glycosidic ketones, **5a**, **5b**, **6a** and **6b**, in 70–90% yield. The newly synthesized bis-propargylated compounds, **3**, **4**, **5a**, **5b**, **6a** and **6b**, were well characterized using NMR (^{1}H and ^{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** and **6b**, with two equivalents of dodecyl-azide, **7**, using copper sulphate and sodium ascorbate in catalytic

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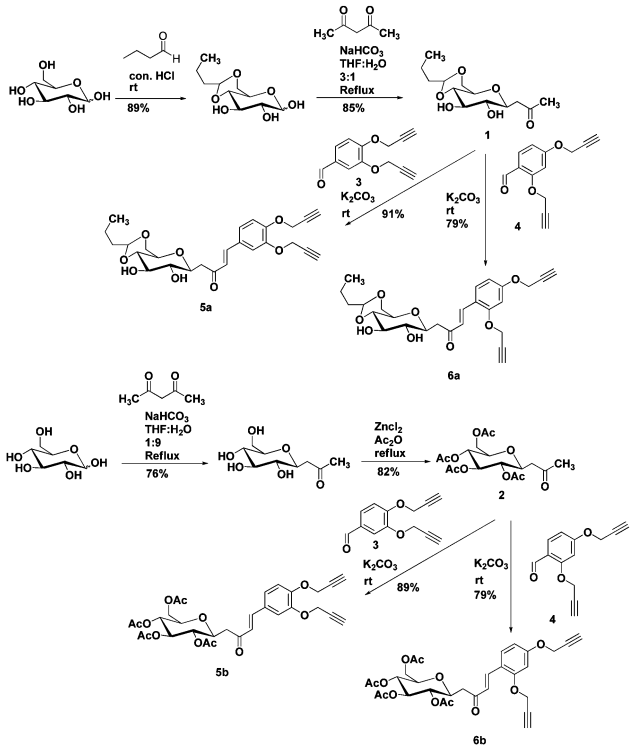
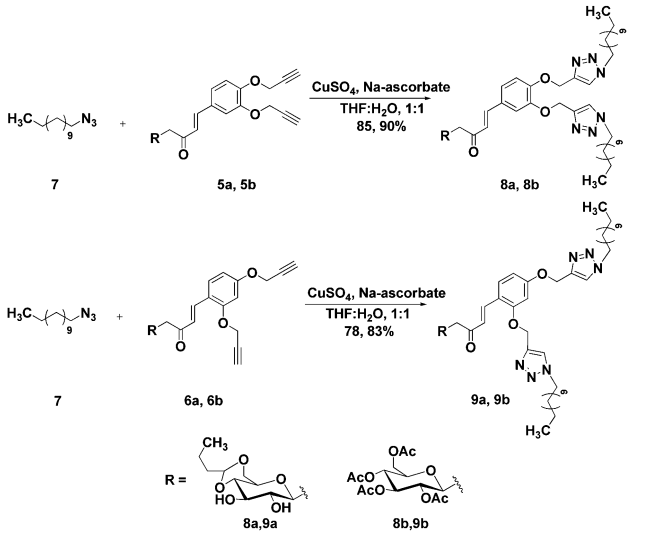


Scheme 1 Structures of sugar–chalcone based bis-propargylated derivatives.



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

amounts led to the formation of sugar chalcone-based bis-triazole having long alkyl derivatives. However, since compound **5a** was poorly soluble in tertiary butanol and acetonitrile, the tetrahydrofuran and water mixture in 1 : 1 ratio was used to improve the solubility of the reaction. The cycloadduct was obtained in 82% yield in this case (Scheme 1). 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** and **6b**, with dodecyl azide, **7**, using the THF : water mixture in 1 : 1 ratio as solvent resulted in 78–90% yield of the corresponding sugar-based long-chain bis-triazole derivatives **8a**, **8b**, **9a** and **9b** (Scheme 2).

The structures of the resulting chalcone based triazologlycolipid analogues were characterized by FT-IR and (^{1}H, ^{13}C) NMR spectral techniques, mass analysis and elemental analysis. The FT-IR spectrum of compound **8a** shows bands around 1596, 1512, and 1226 cm^{-1} which correspond to the frequency of C=O, C=C (alkene) and C–N respectively. The presence of sugar–chalcone in compound **8a** was further confirmed from ^{1}H NMR spectroscopy by the appearance of doublets at δ 7.51 and 6.69 ppm with a coupling constant of ~16 Hz which correspond to the *trans* alkene double bond whereas the presence of the sugar-triazole core was confirmed from the appearance of two sharp singlets at δ 7.69 ppm and δ 7.68 ppm which correspond to methine protons (trz-H) of the 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 from Rodios calculation where the compound **8a** found to have (δ C4–C5) as 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**, were identified by DEPT-135 experiment. Moreover, the ^{1}H–^{13}C[COSY] spectrum reveals the correlation of characteristic protons with their corresponding carbons. In addition, the mass spectrum of compound **8a** shows the exact mass value of the product, **8a**, which matches with the experimental results ultimately confirming the formation of the bis-triazole derivative.

Absorption and emission spectra were recorded in acetonitrile for all the synthesized sugar derivatives, **8a**, **8b**, **9a** and **9b**. The profile of both the absorption and emission spectra is presented in Fig. 1.

All the four triazole compounds, **8a**, **8b**, **9a** and **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 was found that compounds **8a** and **9a** gave peaks around 650 nm whereas compounds **8b** and **9b** gave bands around 500 nm [Fig. 1]. Thus, it is concluded from the result that irrespective of the position of the triazole moiety, the change in the protecting group of the sugar moiety has led to a shift in the wavelength on emission.

All the four bis-triazole sugar derivatives **8a**, **8b**, **9a** and **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–ethyl acetate mixture was dried under vacuum and then dissolved in a selected solvent or solvent mixture by heating. The homogeneous solution was then cooled to room temperature to obtain the gel [Fig. 2]. The critical gelation concentration (CGC) of compounds **8a**, **8b**, **9a** and **9b** was determined using the hexane–ethyl acetate solvent mixture [Table 2]. The long-chain bis-triazole sugar derivatives, **8a** and **9a**, which have butylidene as the protecting group with two free hydroxyl groups form gel at very low CGC (1%) whereas compounds **8b** and **9b** which have a similar core structure as that of **8a** and **9a** were found to

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

			NMR data		
Compound No.	Time (h)	Yield (%)	δ Ano-H/ppm $^3J_{H1H2}$ Hz	δ Alk-H/ppm $^3J_{H1H2}$ Hz	δ Trz-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[a] 16.2	7.71, 7.67

[a] *Trans* alkene protons are merged with aromatic protons.

have higher CGC (1.5%). This difference in the CGC may presumably be due to hydrogen bond formation of the two hydroxyl groups which lowers the CGC and improves the gelation.

Gelation ability refers to the ability of the compound (glycosidic ketone) to gelate the solvent used for gelation.[24]

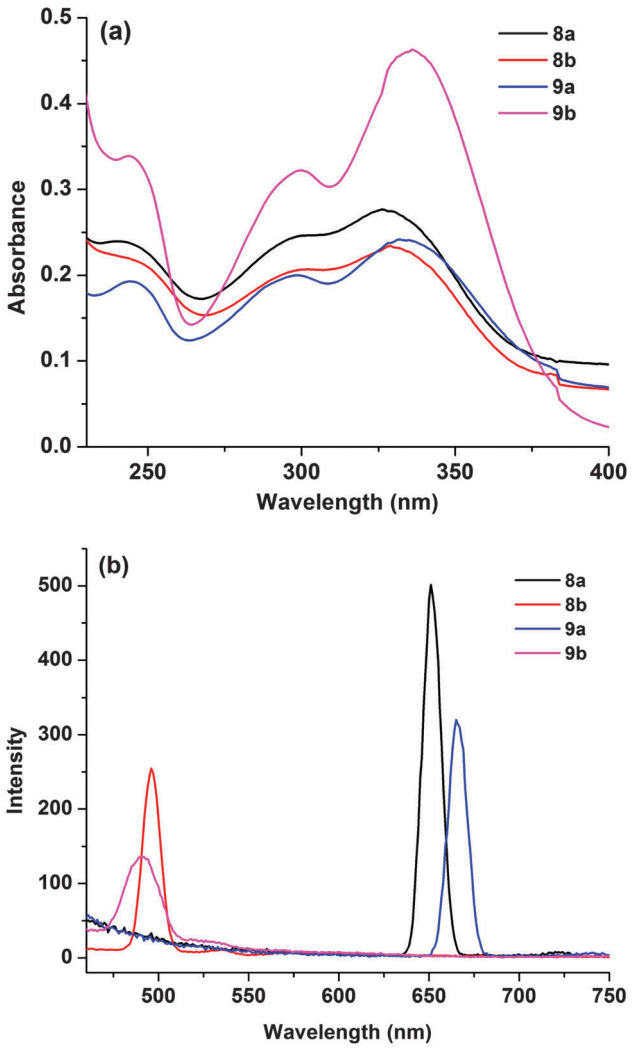


Fig. 1 (a) Absorption spectra of compounds **8a**, **8b**, **9a**, and **9b** in acetonitrile (1×10^{-5} M) and (b) emission spectra of compounds **8a**, **8b**, **9a**, and **9b** in acetonitrile (1×10^{-5} M).

It is well known that for gelation the participation of both hydrophilic and hydrophobic groups is necessary. Here in this paper, the precursors, **5a** and **6a**, utilized for the synthesis of bis-triazolyl derivatives, **8a** and **9a**, formed a partial gel with hexane–ethyl acetate whereas gel formation was not observed with the precursors **5b** and **6b**. This is because in the former, the presence of two hydroxyl groups which are responsible for the hydrogen bonding may result in partial gelation whereas in the latter since there is no site of hydrophilic groups in the molecules **5b** and **6b**, self-assembly was not observed and hence they acted as non-gelators.

The xerogel of the organogelator was subjected to morphological studies using FESEM and HRTEM analysis. SEM images of the organogelators **8a** and **8b** are shown in Fig. 3. From FESEM, the morphology of compound **8a** is observed to be a fibrous network. The size of the fibril is found to be around 58 nm. A crystal clear picture of the interior morphology of the gelator which exhibits a fibrous network was obtained 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 with nanopores [Fig. 3a], whereas the corresponding completely protected sugar, **8b**, exhibits a lamellar structure with less voids [Fig. 3b]. In addition, compound **8b** does not show any branched structure; instead it has an aggregated mode of each individual layer. Generally, fibrous structures can incorporate more solvent than lamellar structures because of their greater void volume as documented from FESEM and HRTEM analysis. In the SEM image of gelator **8a**, the larger flat tubules are composed of a fibrous network as shown in Fig. 3a. The bulk structure of the organogelator **8b** is lamellar. Except the difference in the protecting group of the sugar moiety, the core architecture of molecules **8a** and **8b** was found to be similar and hence it was assumed that for compound **8b**, the fibrils aggregate together to form a lamellar-like structure [Fig. 3b]. The interior morphology of compound **8a** was determined using HRTEM and the representative HRTEM image of compound **8a** is shown in Fig. 4. The aggregation mode is identified based on fibrils joined together to form an interlinked network structure. The repeated interlinks which gave an aggregated form confirmed the formation of an organogelator.

Table 2 Gelation studies of compounds **8a**, **8b**, **9a** and **9b**[a]

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
Ethyl acetate	G (CGC = 1.8)	PG	G (CGC = 1.6)	PG
Chloroform	G (CGC = 1.5)	PG	G (CGC = 1.4)	PG

[a] Note: G – gelator, PG – partial gelator, S – solution, I – insoluble, P – precipitation; CGC represented in % (g mL^{-1}).

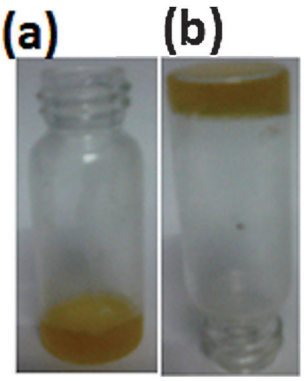


Fig. 2 Gel picture of compound **8a**: (a) heating followed by cooling and (b) upon inversion.

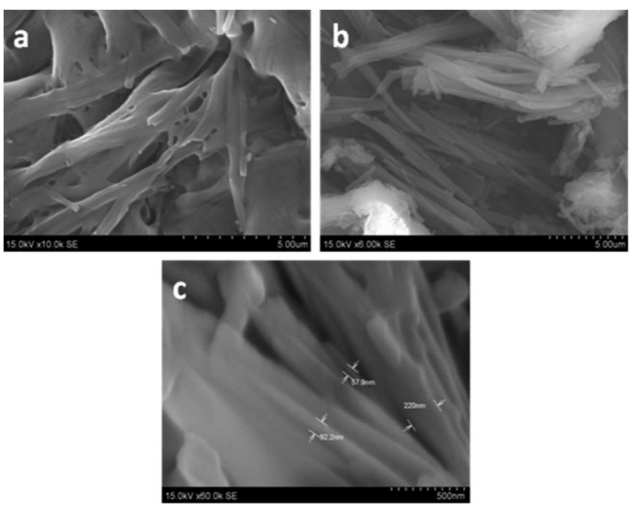


Fig. 3 FESEM images of organogels formed from $CHCl_3$: (a) **8a** [5 μm], (b) **8b** [5 μm] and (c) **8b** [500 nm].

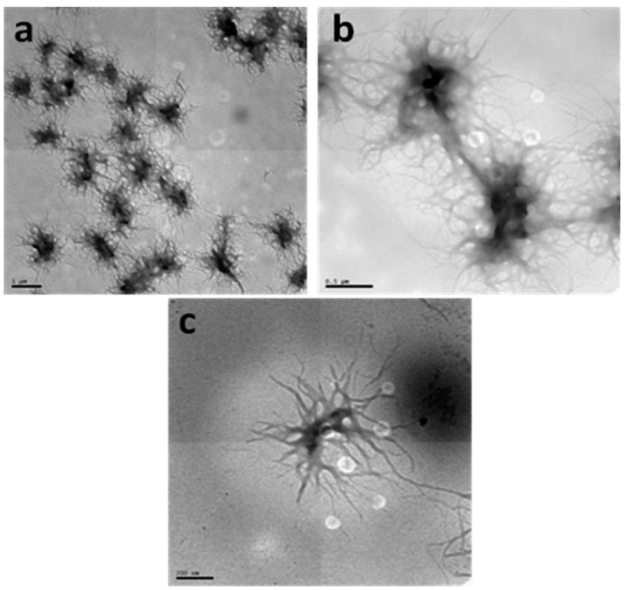


Fig. 4 HR-TEM images of compound **8a** in $CHCl_3$ under different magnifications: (a) 1 μm, (b) 0.5 μm and (c) 200 nm.

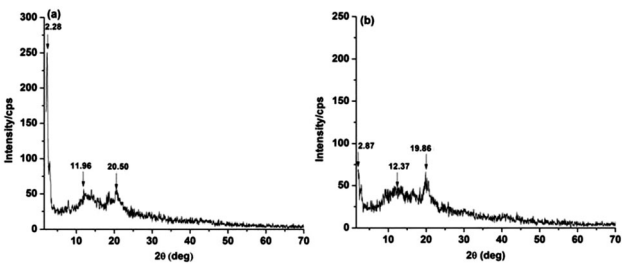


Fig. 5 Powder XRD of organogelators: (a) **8a** and (b) **8b**.

X-ray powder diffraction analysis was carried out for the organogelators **8a** and **8b**. The xerogel of compounds **8a** and **8b** was subjected to X-ray diffraction pattern. In general, the X-ray diffraction pattern gives an idea about the molecular packing in the gel. The X-ray diffractograms of compounds **8a** and **8b** are shown in Fig. 5. In Fig. 5a one can recognize a sharp peak at $2\theta = 2.28^\circ$ with an interlayer distance of 38.6 nm which arises from the packing of long alkyl chains due to van der Waals interaction. The diffraction pattern in the wide angle gave two broad peaks at $2\theta = 11.96^\circ$ 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 rings as well as two triazole rings. As shown in Fig. 5b, compound **8b** has the same pattern as that of **8a**, where one can observe a peak at a low angle of

2.87° with an interlayer distance of 30.6 nm followed by a broad peak at a 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 was only 70 in the case of compound **8b**. This shows that compound **8a** is more crystalline than compound **8b**.

Thus the XRD studies confirm that both the gels obtained from the organogelators **8a** and **8b** are one-dimensional aggregates. Thus, XRD analysis gives additional information about the morphology that has been determined using FESEM.

Conclusion

We have designed and synthesized several chalcone based glycolipid derivatives, which are prone to form organogels, and characterized them using different spectral techniques. The existence of the 1,4-regioisomer of triazole and the β-anomeric form of the sugar derivatives was identified using NMR studies. A CGC value of 1.5 was observed for almost all sugar triazole derivatives. The morphology of the gel forming compounds was studied using FESEM and HRTEM. Both fibrous and lamellar structures were 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 is 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 hydrochloric acid, sodium hydrogen carbonate, and solvents (AR Grade), were obtained from Sd-fine, India, in high purity and were used without any further purification. Acetylacetone, copper sulphate and sodium ascorbate were purchased from Loba-chemie, India. Acetic anhydride 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 a 1800 Shimadzu UV spectrophotometer in the range of 190–800 nm. Emission studies were recorded using a Perkin Elmer LS 45 fluorescence spectrometer. The electro-spray ionization mass spectrum was recorded using a WATERS-Q-TOF Premier-HAB213 spectrometer. Elemental analysis was performed using a Perkin-Elmer 2400 series CHNS/O analyzer.

Spectral characterization of organogelators

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

General procedure for the synthesis of sugar-bis-triazole derivatives (8a, 8b, 9a and 9b). To a solution of sugar–chalcone (1 equiv.) the tetrahydrofuran and water mixture in 1 : 1 ratio was added. To the reaction mixture, 2.2 equiv. of dodecylazide, **7**, was added. $CuSO_4{\cdot}5H_2O$ (0.2 equiv.) and sodium ascorbate (0.4 equiv.) were added in catalytic amounts. The reaction mixture was then stirred at room temperature for 24 h. After completion of the reaction, the solvent was evaporated and the product was extracted with $CHCl_3$ (200 ml) and water (200 ml). The organic layer was then evaporated, slurried and purified by column chromatography.

Synthesis, physicochemical properties 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 °C; yield 0.76 g (85%); ^{1}H NMR (300 MHz, $CDCl_3$): 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 properties 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 °C; yield: 0.91 g (90%); ^{1}H 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 properties 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 °C; yield: 0.69 g (78%); ^{1}H 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 properties 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 °C; yield: 0.84 g (83%); ^{1}H 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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