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An expeditious click approach towards the synthesis of galactose coated novel glyco-dendrimers and dentromers utilizing a double stage convergent method†‡

Anand K. Agrahari, Anoop S. Singh., Rishav Mukherjee and Vinod K. Tiwari *

The primary motive behind this article is to bring to the forefront a unique kind of dendrimer which has remained a dark horse since its discovery, namely dentromer. We herein report the synthesis of glycodendrimers and glycodentromers crowned with galactose units by harnessing an expeditious synthesis of dendrimer core **18** and dentromer core **19**, divergently with branching directionality (1 → 2) and (1 → 3), respectively. A competent, double stage convergent synthetic path was chosen to facilitate ease of refining and spectroscopic elucidations. By exploiting a Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction strategy, we successfully developed a new series of galactosylated dendrimers **20**, **21**, **22**, and **24** containing 6, 12, 18, and 18 peripheral galactose units, respectively. We are first to report the practical synthesis of 9-peripheral galactose coated glycodentromer **23** (0^{th} generation) and 27-peripheral galactose coated glycodentromer **25** (1^{st} generation). These synthesized scaffolds were characterized by spectral studies such as ^{1}H, ^{13}C NMR, FT-IR, MALDI-TOF MS, HRMS and SEC analysis. Additionally, gel permeation chromatography depicted the regular progression in size from 6 to 27-peripheral galactose coated glycodendrimers along with glycodentromers, with their high monodispersity. Also, the glyco-dendrimers and dentromers synthesized from two different hypercore units *i.e.* dendrimers core (**18**) and dentromer core (**19**), have been supported by their UV-visible absorbance and emission spectroscopy.

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1 Introduction

Dendrimers hail from a distinctive family of macromolecules, tailored with a motif to encompass superior branching, three dimensional, high monodispersity and multivalent functional residue, all in one exquisite architecture.[1] The aforementioned attributes of dendrimers have enabled them to have innumerable applications in various fields including drug delivery, gene delivery, photodynamic therapy, biosensors, drugs for cardiovascular diseases, anti-cancer vaccines, anti-microbial vaccines, *etc.*[2–7] However, the field of dendrimers have been widely explored and this provide an origin to a fascinating dendrimer analogue which expands divergently in a 1 → 3 branching fashion, namely dentromer.[8] A significant advantage of dentromers over dendrimers corresponds to its densely distributed peripheral groups for the same generation and when conjoined to carbohydrate units, glycodentromers or sugar-linked dentromers undergo an enhanced hypercluster effect which prompts an enhancement in biological activity in comparison to a conventional glycodendrimer.[9] Carbohydrates are essential scaffolds owing to their diverse role in biological processes, like functioning of the immune system, enhancing inflammatory response, malignancy, metastasis, apoptosis, *etc.*[10–12]

This unique and effective feature of carbohydrates results from carbohydrate–lectin interactions playing a cardinal role in various biological systems such as biological recognition, protein folding, cell growth, cell-agglutination, cell signalling and interaction with bacteria/viruses.[10,13] This mesmerizing unison of carbohydrates and dendrimers have drawn attention owing to its multivalency effect.[14] Incorporating sugar units in a scaffold increases its biological activity as glycan–protein interaction plays a major role in various biological phenomena.[15] Dendrimer chemistry is quiet useful in order to develop monodisperse multivalent glycoconjugates.[16] and it has been excavated from literature that polyester dendrimers are compatible to biological system with an added advantage of easy preparation techniques. In addition, whenever ester linked dendrimers have been tested, they have been found to be non-

Department of Chemistry, Centre of Advanced Study, Institute of Science, Banaras Hindu University, Varanasi-221005, India. E-mail: Tiwari_chem@yahoo.co.in; Vinod.tiwari@bhu.ac.in

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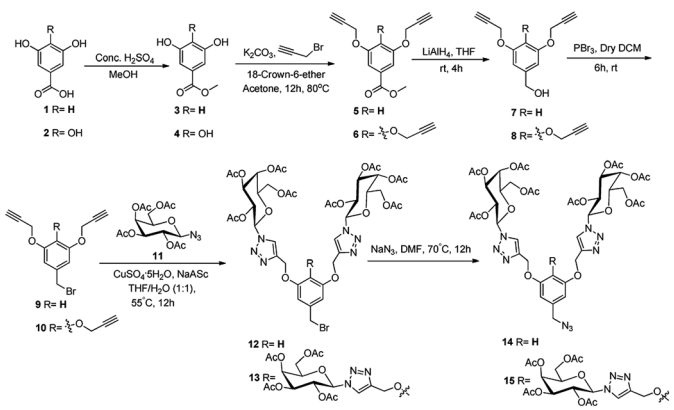
toxic in comparison to other dendrimers.[17] It has been well established, that double stage convergent method is a combination of convergent and divergent methods and in this strategy, the core unit is synthesized divergently followed by a subsequent attachment of a dendritic wedge in a convergent fashion, thereby generating the hypercore (*i.e.* dendrimer or dentromer core in present manuscript) containing dendrimer.[8,18]

The CuAAC 1,3-dipolar cycloaddition reaction has propagated extensively ever since its finding by Sharpless[19a] and Meldal.[19b] The atom economy and versatility of these reactions make them a powerful tool for a diverse spectrum of organic synthesis.[2,20] Particularly, click chemistry involving Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC), has been profusely explored during the last two decades due to an easy synthesis of diverse two or three dimensional motifs, having a plethora of applications ranging from chemical biology to material science.[21] In addition, tailored 1,2,3-triazoles, bioisostere of amides, esters and other heterocycles, are frequently used as pharmacophores in several drugs, exhibiting diverse pharmacological properties. Thus, these moieties play an intriguing role as building blocks of dendrimers and impart to them sufficient biological activity, thereby making them medically important.[22]

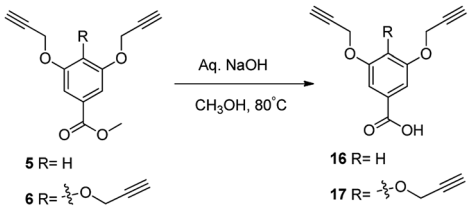
The triply branched glycodendrimer construction is less facile than the doubly branched analogue due to steric reasons.[23] So, in present manuscript, we have successfully synthesized a dendrimer core (hexa-alkynylated) as well as a dentromer core (nona-alkynylated) to develop a series of glycodendrimers along with the first ever 0th '9-peripheral' and 1st generation '27-peripheral' galactose coated glycodentromers.

2 Results and discussion

The first generation azide functionalized dendrons were synthesized from methyl 3,5-dihydroxybenzoic acid (**1**) and methyl 3,4,5-tris-hydroxybenzoic acid (**2**). The crafted first generation dendritic azide was coupled with the alkyne functionalized core unit **18** and **19** to generate a series of six (**20–25**)

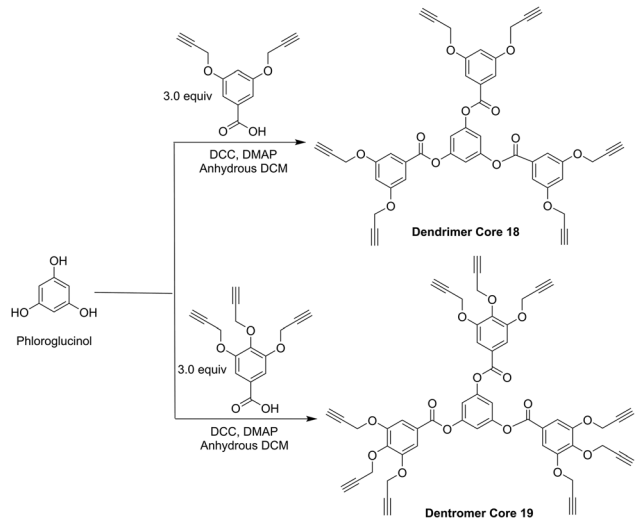


Scheme 1 Synthesis of azide functionalized AB_2 and AB_3 type dendritic structure.



Scheme 2 Synthesis of acid functionalized dentritic scaffolds.

peripheral galactosylated glycodendrimers and glycodentromers. In this regard, methyl 3,5-dihydroxybenzoate was derived from esterification of 3,5-dihydroxybenzoic acid using methanol and sulphuric acid as catalyst. Similarly with the same strategy, methyl 3,4,5-tris-hydroxybenzoate was also prepared. Moreover, esterified dendron initiators **3**, **4** were propargylated by reacting propargyl bromide, K_2CO_3, 18-crown-6 ether (co-catalyst) in dry acetone. Furthermore, the propargylated scaffolds **5** and **6** were reduced with LAH in THF followed by bromination using PBr_3 in DCM, which furnished 3,5-bis(propargyloxy)benzyl bromide **9** and 3,4,5-tris(propargyloxy) benzyl bromide **10**. Owing to their π–π stacking interaction, aromatic 'aglycones' have been of substantial interest for dendron synthesis.[24] To this end, clickable 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl azide **11** was selected as surface group functionality and this was stitched with aromatic scaffolds **9** and **10** to afford the bromine functionalized first generation **12** and **13** dendrons. The single triazolyl peak at 7.91 ppm in ^{1}H NMR, for compound **12**, whereas, for **13**, two distinct signals at δ 8.14 and 8.05 ppm were observed with ratio 2 : 1, which displayed the two chemically non-equivalent triazolyl galactosides. In ^{13}C NMR, the peaks appeared at δ 144.4 and 121.2 ppm for compound **12**, and δ 144.9, 144.2 & 123.0, 122.0 ppm for compound **13**, confirmed the presence of triazolyl carbons. In continuation, the azidation of the compounds **12** and **13** were executed using NaN_3 in DMF, which resulted in azide

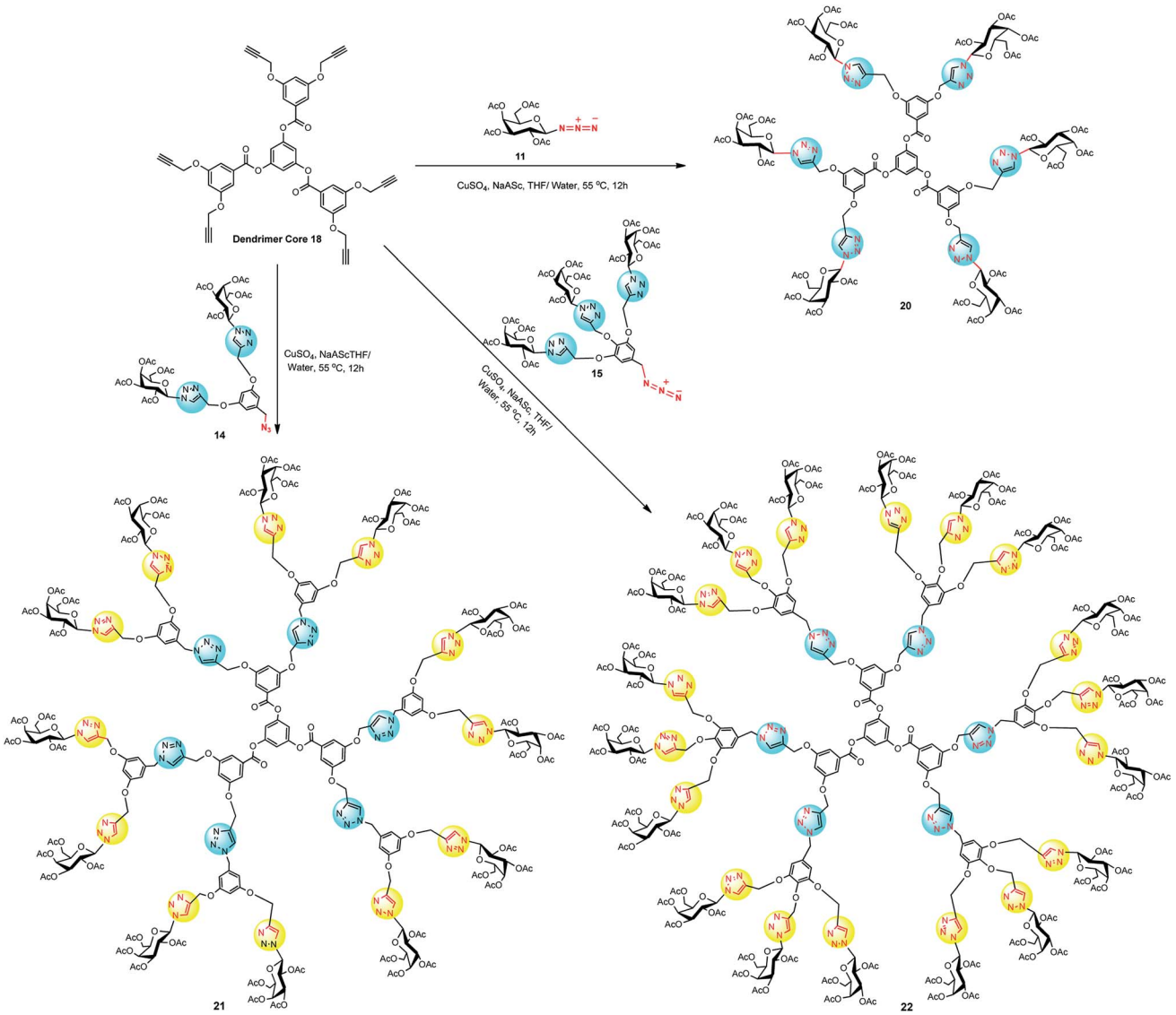


Scheme 3 Synthesis of ester-linked dendrimers core and dentromer core by acid–phenol coupling using DCC/DMAP.

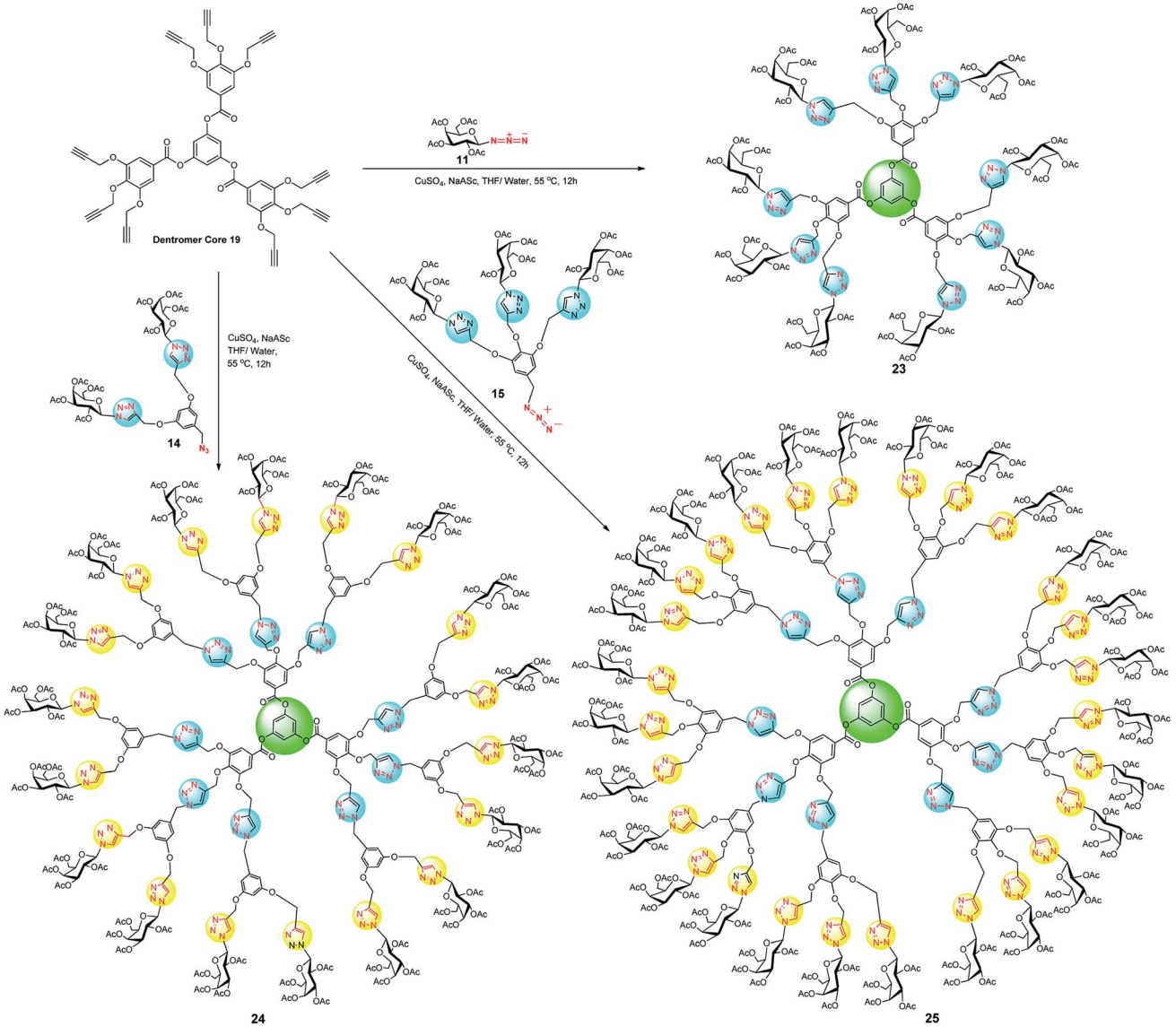
functionalized dendritic architecture **14** and **15** respectively (Scheme 1). This transformation was illustrated by IR spectra, in which, peak at 2104.5 and 2103.8 cm^{-1} confirms the formation of corresponding dendritic azides **14** and **15**. In addition, there was a down field shifting in ^{13}C NMR, during conversion from $-CH_2Br$ (δ 33.2 ppm) to $-CH_2N_3$ (δ 54.6 ppm) for moiety **14** and $-CH_2Br$ (δ 33.7 ppm) to $-CH_2N_3$ (δ 54.6 ppm) for scaffold **15**, which supported the formation of respective azide.

We next, synthesized the other click counterpart of dendritic azides, as depicted in (Scheme 2 and 3). Thus, ester functionalized compound **5** and **6** were separately treated with aqueous NaOH to generate 3,5-bis(propargyloxy)benzoic acid **16** and 3,4,5-tris(propargyloxy)benzoic acid **17**, respectively (Scheme 2). The resulted compounds were further divergently condensed with phloroglucinol using DCC, DMAP to afford the hexavalent dendrimer core **18** and nonavalent alkyne dentromer core **19** (Scheme 3).

At this instant, the synthesized hypercore units were used as starting material for CuAAC coupling with dendritic wedges **14** and **15** to afford a series of glyco-dendrimers and dentromers. In this context, dendrimer core unit **18** was stitched with galactose azide **11**, dendritic wedge **14** and **15** using $CuSO_4 \cdot 5H_2O$ and sodium-L-ascorbate to prepare a series of 6, 12 and 18 peripheral galactose tethered dendrimers **20**, **21** and **22**, respectively (Scheme 4). In the same way, dentromer core unit **19** was clicked with galactose-azide **11**, dendritic architecture **14** and **15**, under similar Cu(I)-catalyzed cycloaddition condition and furnished 9 galactose coated glycodentromer **23**, 18 peripheral glycodendrimer **24**, and 27 galactose coated glycodentromer **25**, respectively with satisfactory to good yield 60–75% (Scheme 5). Interestingly, there was no steric congestion imposed during glycodentromer synthesis. It is to noteworthy to mention that, for the synthesis of higher peripheral galactose tethered dendrimers, elevated equivalents of $CuSO_4 \cdot 5H_2O$ was



Scheme 4 Synthesis of galactosylated dendrimer (**20**, **21** and **22**) derived from hexavalent alkyne core **18**.



Scheme 5 CuAAC mediated synthesis of galactose coated dendrimers (**23**, **24** and **25**) derived from dentromer core **19**.

required for amplified yields, because the size of glycodendrimer had been increased with an increase in void number. These voids enable entrapment of the free metal ions thereby delaying the time for completion of reaction and this could be ameliorated by increasing the catalyst amount.[25] The symmetrical structure of developed glycodendrimers **20**, **21**, **22**, **24** and glycodentromers **23**, **25** was confirmed by their extensive spectral studies (NMR, IR, MALDI-TOF MS, HRMS and size exclusion chromatography) which led to an unequivocal structural illustration. Moreover, the synthesis of glycodendrimer **20**, **21**, **22**, **24** was evidenced by the formation for newly formed triazolyl proton peaks at the desired position (see, ESI‡).

In addition, the formation of 9 and 27 peripheral galactose tethered glycodentromer was established by ^{1}H and ^{13}C NMR, in this regard, two triazolyl proton peaks at 8.22 and 8.11 ppm were obtained, for two different environment of the triazole with ratio 6 : 3 in the dentromer (**23**). In contrast to this, ^{1}H NMR of glycodentromer **25** displayed the six peaks *i.e.* a–f in triazolyl region, each peak for a different environment of the triazole. If, we closely examine only outer triazolyl part of dendritic wedge (Fig. 1), it was noticed that four different triazolyl proton peaks *i.e.* a–d appeared at δ 8.09, 8.04, 8.13 and 8.11 ppm respectively with ratio $a : b : c : d$ (4 : 2 : 2 : 1) on the periphery of glycodentromer. Next, we observed two inner triazolyl proton peak at 8.17 and 8.18 ppm for *e* and *f* with ratio 6 : 3, which established the unequivocal formation of our targeted glycodentromer **25**. Further, the formation of glycodentromers was supported by MALDI-TOF MS.

There is no vibrating band of alkyne and azide in IR spectra of synthesized dendrimers which validates the absence of free alkyne or azide functionality in the developed glycodendrimers and dentromers, thereby supporting the formation of targeted glycoclusters (see, ESI, Fig. S47–S52‡).

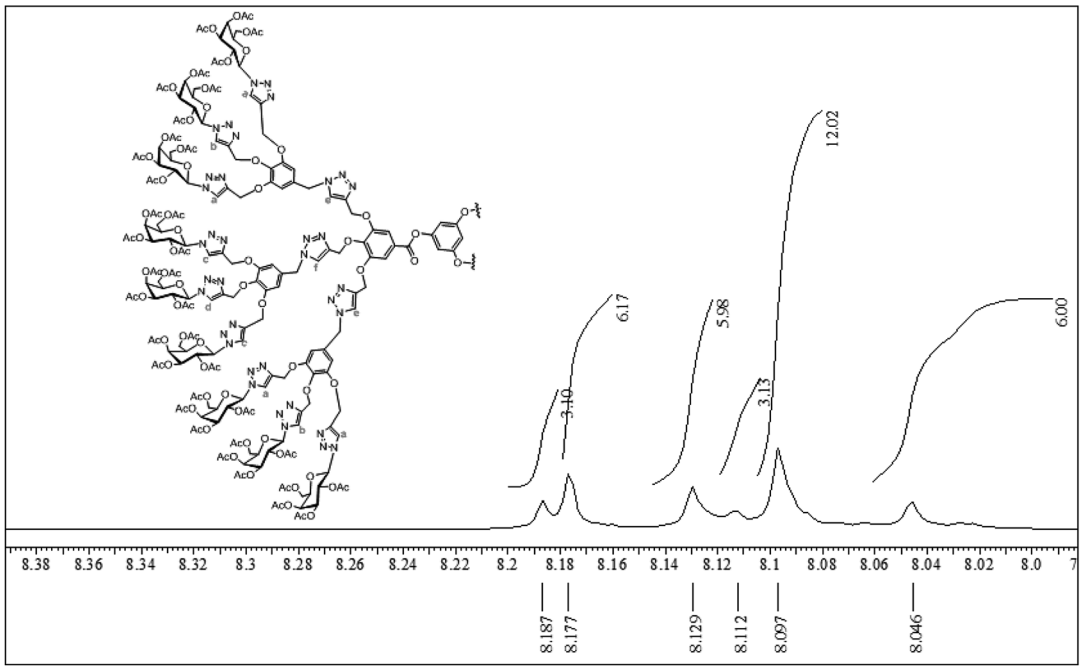


Fig. 1 ^{1}H NMR' spectral elucidation of triazolyl region of first generation glycodentromer.

Moreover, size exclusion chromatogram (SEC) depicts the size progression from 6 peripheral glycodendrimer to 27 peripheral glycodentromer, with polydispersity index (PDI) ranging from 1.0–1.03 showing the monodispersity of the synthesized glycoclusters (Fig. 2).

Absorption and emission studies of developed glycodendrimer and dentromers were also investigated, glycodendrimer **20**, **21**, **22** have shown UV-visible absorbance at 309.90, 310.14, 311.38 nm, respectively, whereas for compound **23**, **24**, **25**, peaks were appeared at 274.25, 275.78, 274.61 nm. Thus, compound **20**, **21**, **22** were excited at the wavelength of ~309 nm where as scaffold **23**, **24**, **25**, at ~274 nm, and their emission spectra were also recorded (Fig. 3).

By observing the absorbance and emission pattern of developed glycodendrimer and dentromer, it can be inferred that, two different series of glycoclusters were formed, one with compounds **20**, **21** and **22** derived from dendrimers core unit (**18**) whereas, the second series comprising of compounds **23**, **24** and **25** were derived from dentromer core (**19**). Thus, we reach to a successful end where two different type of cores are involved to construct these glyco-motifs, which was also supported by UV-Vis spectroscopy.

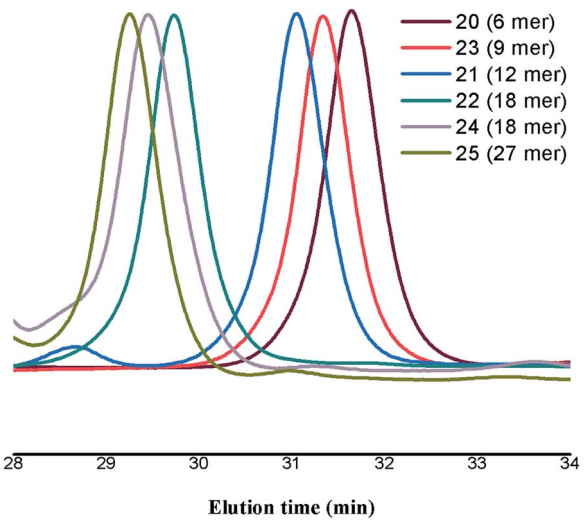


Fig. 2 SEC chromatogram of the developed glycodendrimers (**20**, **21**, **22**, **24**) and glycodentromers (**23**, **25**).

3 Conclusions

In summary, we have fulfilled our objective to synthesize a novel class of dendrimer which was coined as dentromer by Astruc and co-workers. This has highly branched tethers and possesses an unique triple branched architecture which is quite prominent from the scaffolds that we have developed. On this aspect of hyper-branching, dentromers hold superiority over dendrimers and we have portrayed both the development of novel dentromer as well as dendrimer core scaffolds, together with the novel galactose tethered glycodentromer and dendrimers respectively by amalgamation with surface carbohydrate ligands. These hybrid architectures may serve as potential therapeutics owing to the highly biologically active carbohydrate clusters present over the periphery. It has already been disseminated that, glycodendrimers have been employed as anti-adhesives for viral and bacterial adhesion along with anti-biofilms activity but the biological activity of dentromers awaits exploring.

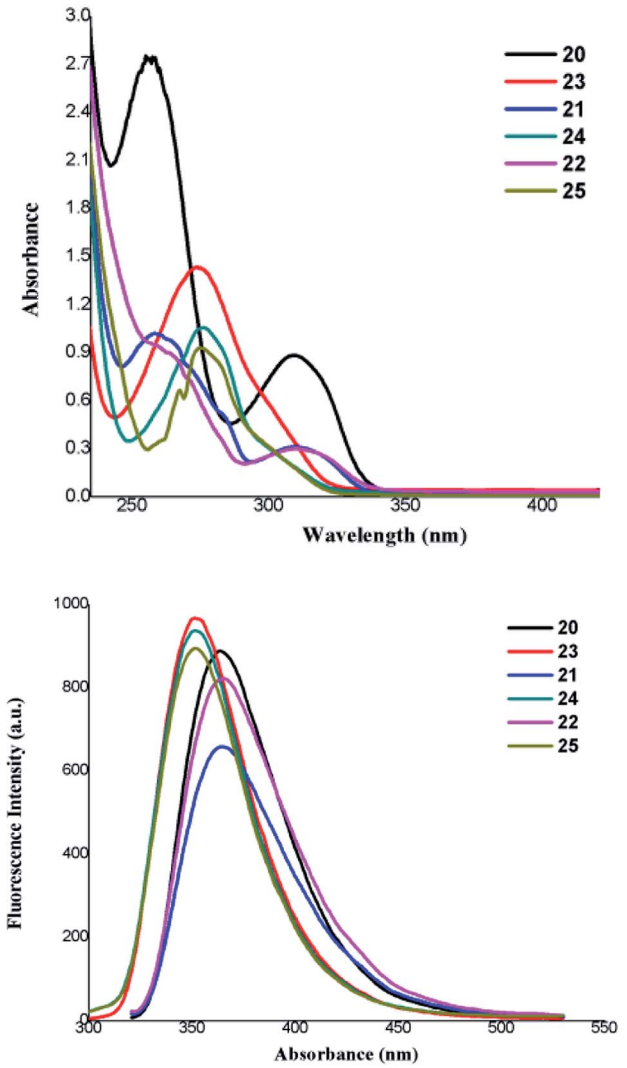


Fig. 3 Absorbance and emission spectra of the developed glyco-dendrimers (**20**, **21**, **22**, **24**) and glycodentromers (**23**, **25**).

4 Experimental

4.1 General methods

All chemicals and solvent were of pure analytical grade. Thin layer chromatography (TLC) was executed on 60 F-254 silica gel, coated on aluminium plates and visualized by UV lamp, 5% H_2SO_4 methanol solution with subsequent charring by heating. In addition, alkaline $KMnO_4$ solution was used to locate the alkynes with subsequent heating. Flash column chromatography was performed using silica gel (230–400) mesh size. ^1H and ^{13}C spectra were recorded in 500 and 125 MHz respectively. Mass spectra were recorded on Sciex-X500R QTOF, MALDI-TOF MS (with 2,5-dihydroxy benzoic acid matrix). IR was recorded in Nujol mulls in KBr pellets. The polydispersity index (M_n/M_w) of the samples was investigated in DMF at 40 °C with a flow rate of 0.5 mL min^{-1}. The calibration of columns was done against polystyrene standard samples. The absorbance and emission spectra were also recorded by using UV-visible spectroscopy.

4.1.1 Experimental procedure (1) for Cu(I) azide–alkyne cycloaddition reaction. The synthesized polypropargylated alkynes and azido functionalized scaffolds were taken in round bottom flask, already having THF/water (1 : 1), using $CuSO_4 \cdot 5H_2O$ (0.3 equiv. per propargyl group) and sodium ascorbate (0.3 equiv. per propargyl), stirred for 12 h at 55 °C, while for glyco-dentromer and dendrimer synthesis (0.8 equiv. of $CuSO_4 \cdot 5H_2O$, NaASc for per propargyl) were used. After completion of reaction (monitored by TLC), it was passed through cellite followed by extraction with ethyl acetate. The organic layer was washed with saturated aq. NH_4Cl (2 × 10 mL), water (10 mL) and finally, aq. Brine solution (10 mL). The ethyl acetate layer was collected and dried over anhydrous sodium sulphate followed by evaporation to obtain the crude mass. Moreover, the crude mass was subjected to flash column chromatography (SiO_2) to afford the targeted glyco-conjugate with good yield.

4.1.2 Synthesis of methyl 3,5-bis(hydroxyl) benzoate (3). The compound **1** (5.0 g, 32.4 mmol) was dissolved in dry methanol (80 mL), then after catalytic amount of conc. H_2SO_4 (1.0 mL) was added drop wise in cold condition. Further, the reaction was refluxed for 4 hour with constant stirring, after completion of reaction (monitored by TLC), and evaporated to obtain the crude mass. Further, solid was extracted with ethyl acetate (2 × 200 mL) and washed with saturated $NaHCO_3$ solution (2 × 50 mL), after then, organic layer was dried over anhydrous Na_2SO_4 followed by evaporation to afford targeted benzoate **3**. Yield (5.06 g, 95%); R_f = 0.4 (40% ethyl acetate/hexane); ^1H NMR (500 MHz, DMSO-D_6): δ 6.80 (d, J = 2 Hz, 2H), 6.43 (d, J = 1.5 Hz, 1H), 3.79–3.70 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 158.9, 131.9, 107.8, 107.7, and 52.5 ppm.[25]

4.1.3 Synthesis of methyl 3,4, 5-tris(hydroxyl) benzoate (4). Compound **2** (5.0 g, 29.39 mmol) was reacted with methanol (80 mL), and catalytic amount of conc. H_2SO_4 (1 mL) according to the procedure involved in the formation of compound **3**. Yield (5.08 g, 94%); R_f = 0.4 (40% EtOAc/*n*-hexane); ^1H NMR (500 MHz, DMSO-D_6): δ 9.27 (s, 2H), 8.93 (s, 1H), 6.93 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 145.4, 138.3, 119.2, 108.4, and 51.4 ppm.[27]

4.1.4 Synthetic procedure for methyl 3,5-bis(propargyloxy) benzoate (5). The compound **3** (4.0 g, 23.7 mmol) was dissolved in dry acetone followed by addition of K_2CO_3 (26.3 g, 190 mmol, 8 equiv.) as a base, 18-crown-6-ether (200 μL) as co-catalyst and at the end propargyl bromide (14.32 mL, 190 mmol, 8 equiv.). The said set up was refluxed for overnight, and after that the solvent was evaporated to obtain the crude mass. Moreover, the crude mass was subjected to chromatography to afford the desired compound **5** as white powder. Yield (4.23 g, 73%); R_f = 0.5 (15% EtOAc/*n*-hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, J = 2.0 Hz, 2H), 6.81 (s, 1H), 4.71 (d, J = 2.0 Hz, 4H), 3.90 (s, 3H), 2.54 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 158.4, 132.1, 108.8, 107.5, 77.9, 75.9, 56.1, and 52.3 ppm.[26]

4.1.5 Synthesis of methyl 3,4,5-tris (propargyloxy)benzoate (6). The compound **4** (4.0 g, 21.7 mmol, 1.0 equiv.) was reacted with propargyl bromide (13.1 mL, 173.7 mmol, 8.0 equiv.), potassium carbonate (24.03 g, 173.7 mmol, 8.0 equiv.) and 18-

crown-6-ether (200 μL) in the presence of dry acetone (50.0 mL) according to the procedure of compound **5**. Yield (4.40 g, 68%); $R_f = 0.4$ (15% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 2H), 4.81–4.79 (m, 6H), 3.90 (s, 3H), 2.53 (t, $J = 2.4$ Hz, 2H), 2.45 (t, $J = 2.4$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 151.2, 141.0, 125.7, 109.8, 78.6, 77.9, 76.1, 75.5, 60.2, 57.0, and 52.3 ppm.[27]

4.1.6 3,5-Bis (propargyloxy)phenyl methanol (7). To a stirred solution of methyl 3,5-bis(propargyloxy)benzoate (3.0 g, 12.28 mmol) in anhydrous THF (30.0 mL), $LiAlH_4$ (0.56 g, 14.7 mmol, 1.2 equiv.) was added portion wise in cold condition then after it was stirred for 4 h at room temperature till completion of reaction. The reaction was quenched by 5% aq. NaOH solution with continuous stirring which resulted in the fine precipitate. Further, the precipitate was filtered using sintered funnel; the obtained filtrate was extracted with ethyl-acetate and washed with water (2 × 20.0 mL) followed by brine solution. The extracted part was evaporated to get the crude mass which was subjected to column chromatography to obtain the targeted compound **7** with excellent yield. Yield (2.36 g, 89%); $R_f = 0.4$ (25% EtOAc/*n*-hexane). NMR data was in close agreement with the available literature data.[26]

4.1.7 Synthesis of 3,4,5-tris (propargyloxy)phenyl methanol (8). Methyl 3,4,5-tris (propargyloxy)benzoate (3.0 g, 10.1 mmol, 1.0 equiv.) was reacted with $LiAlH_4$ (0.46 g, 12.1 mmol, 1.2 equiv.) in the presence of dry THF (30.0 mL) according to the procedure of compound **7**. Yield (2.28 g, 84%); $R_f = 0.5$ (25% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.77 (s, 2H), 4.758–4.753 (m, 4H), 4.72 (d, $J = 2.0$ Hz, 2H), 4.64 (s, 2H), 2.51–2.50 (m, 2H), 2.45 (t, $J = 2.4$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6, 137.2, 136.3, 106.9, 79.1, 78.4, 75.8, 75.1, 65.1, 60.2 and 56.9 ppm.[27]

4.1.8 3,5-Bis (propargyloxy)phenyl bromide (9). To a stirred solution of compound **7** (2.2 g, 10.1 mmol) in anhydrous dichloromethane PBr_3 (1.06 mL, 11.1 mmol, 1.1 equiv.) was added drop-wise in cold condition, after this, it was stirred for overnight. The reaction progress was (monitored by TLC) after completion of reaction, it was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate (2 × 100 mL) to produce the crude mass. The obtained residue was subjected to column chromatography (SiO_2) to afford compound **9**. Yield (2.49 g, 88%); $R_f = 0.6$ (10% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (d, $J = 2.0$ Hz, 2H), 6.55–6.54 (m, 1H), 4.67 (d, $J = 2.0$ Hz, 4H), 4.41 (s, 2H), 2.55 (t, $J = 2.4$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 158.6, 139.8, 108.5, 102.2, 78.1, 75.8, 55.8, and 33.2 ppm.

4.1.9 Synthesis of 3,4,5-tris (propargyloxy)phenyl bromide (10). Compound **8** (2.0 g, 6.0 mmol) was reacted with PBr_3 (0.63 mL, 6.60 mmol, 1.1 equiv.) in the presence of dichloromethane according to the procedure of compound **9**. Yield (1.84 g, 75%); $R_f = 0.5$ (15% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.79 (s, 2H), 4.76 (d, $J = 2.5$ Hz, 4H), 4.72 (d, $J = 3.0$ Hz, 2H), 4.45 (s, 2H), 2.53 (t, $J = 2.4$ Hz, 2H), 2.47 (t, $J = 2.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.5, 137.1, 133.6, 109.4, 78.9, 78.1, 76.0, 75.3, 60.3, 57.0, and 33.6 ppm. Mass data HRMS: *m*/*z* $C_{16}H_{14}BrO_3^+$; calculated = 333.0121; found = 333.0115 $(M + H)^+$.

4.1.10 Synthesis of compound (11). This compound was synthesized by the previous available standard reaction protocol and well elucidated by our previous synthetic work.[20]

4.1.11 Glycoconjugate dendron (12). 3,5-Bis (propargyloxy) phenyl bromide **9** (2.0 g, 7.16 mmol, 1.0 equiv.) was clicked with galactose azide **11** (6.4 g, 17.1 mmol, 2.4 equiv.) using $CuSO_4 \cdot 5H_2O$ (1.1 g, 4.29 mmol, 0.6 equiv.) and NaASc (0.86 g, 0.29 mmol, 0.6 equiv.) in the presence of THF/H_2O (1 : 1) according to the procedure **1**. Yield (6.02 g, 82%); $R_f = 0.4$ (60% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 2H), 6.63 (s, 2H), 6.55 (1H), 5.84 (d, $J = 9.0$ Hz, 2H), 5.54–5.51 (m, 4H), 5.23 (dd, $J = 7.0$, 3.0 Hz, 2H), 5.18–5.15 (m, 4H), 4.39 (s, 2H), 4.22 (t, $J = 6.0$ Hz, 2H), 4.17–4.06 (m, 5H), 2.18 (s, 6H), 2.00 (s, 6H), 1.97 (s, 6H), 1.84 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.8, 169.7, 168.9, 153.3, 144.4, 139.9, 121.2, 108.4, 101.9, 86.1, 73.9, 70.6, 67.8, 66.7, 61.9, 61.1, 60.2, 33.2, 20.57, 20.56, 20.4, and 20.1 ppm.

4.1.12 Synthesis of glycoconjugate dendron (13). 3,4,5-Tris (propargyloxy)phenyl bromide **10** (1 g, 3.0 mmol, 1.0 equiv.) was clicked with galactose azide **11** (4.03 g, 10.8 mmol, 3.6 equiv.) using $CuSO_4 \cdot 5H_2O$ (0.67 g, 2.70 mmol, 0.9 equiv.) and NaASc (0.54 g, 2.70 mmol, 0.9 equiv.) in the presence of THF/H_2O (1 : 1) according to the procedure **1**. Yield (0.3.44 g, 79%); $R_f = 0.4$ (80% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.06 (s, 2H), 6.74 (s, 2H), 5.94–5.88 (m, 3H), 5.69 (t, $J = 10.0$ Hz, 1H), 5.59–5.42 (m, 5H), 5.31–5.20 (m, 8H), 4.43 (d, $J = 4.5$ Hz, 2H), 4.30–4.10 (m, 10H), 2.21 (s, 9H), 2.02–1.99 (m, 18H), 1.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 170.0, 169.9, 169.8, 168.9, 168.7, 151.9, 144.9, 144.2, 137.7, 133.6, 123.0, 122.0, 108.8, 86.2, 85.7, 73.9, 73.5, 71.0, 70.7, 67.9, 66.7, 66.88, 66.80, 66.4, 62.8, 61.1, 60.9, 60.3, 33.7, 20.6, 20.5, 20.4, and 20.1 ppm.

4.1.13 Glycoconjugate dendron (14). To a stirred solution of glycoconjugate dendron **12** (1.5 g, 1.46 mmol) in DMF (5.0 mL), sodium azide (0.38 g, 5.84 mmol, 4.0 equiv.) was added. Further, the reaction was stirred for 12 h at 80 °C, the reaction mixture was diluted with ethyl acetate and washed with chilled saturated brine solution (3 × 10 mL). The organic layer was collected and dried over anhydrous sodium sulphate followed by evaporation to produce the crude mass, further which was subjected to column chromatography to afford dendritic azide **13** as white solid. Yield (1.35 g, 94%); $R_f = 0.4$ (60% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 2H), 6.62 (s, 1H), 6.59 (s, 2H), 5.85 (d, $J = 9.5$ Hz, 2H), 5.55–5.54 (m, 4H), 5.25 (dd, $J = 7.5$, 3.0 Hz, 2H), 5.20 (s, 4H), 4.28 (s, 2H), 4.23–4.14 (m, 6H), 2.21 (s, 6H), 2.04 (s, 6H), 2.00 (s, 6H), 1.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 169.9, 169.7, 169.0, 159.6, 144.5, 137.8, 121.2, 107.5, 101.6, 86.2, 74.0, 70.7, 67.8, 66.7, 62.0, 61.1, 54.6, 20.6, 20.4, and 20.1 ppm. IR (KBr): ν_{max} 3471.75, 2936.37, 2104.55, 1755.31, 1671.90, 1598.72 and 1372.00 cm^{-1}. HRMS: *m*/*z* $C_{41}H_{50}N_9O_{20}^+$; calculated = 988.3167; found = 988.3083 $(M + H)^+$.

4.1.14 Synthesis of glycoconjugate dendron (15). Glycoconjugate **13** (1.5 g, 1.03 mmol) was reacted with sodium azide (0.27 g, 4.12 mmol, 4.0 equiv.) in anhydrous DMF (10.0 mL) according to the procedure of compound **14** as white solid.

Yield (1.36 g, 93%); R_f = 0.4 (80% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 8.04 (s, 2H), 6.65 (s, 2H), 5.59–5.87 (m, 3H), 5.69–5.65 (m, 1H), 5.61–5.59–5.52 (m, 5H), 5.29–5.18 (m, 8H), 4.30–4.08 (m, 12H), 2.20 (s, 9H), 2.028–2.024 (m, 18H), 1.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 170.0, 169.9, 169.8, 168.9, 168.7, 152.2, 144.9, 144.3, 137.4, 131.5, 122.9, 121.9, 107.9, 86.2, 85.8, 77.2, 77.0, 76.7, 73.9, 73.5, 71.0, 70.7, 67.9, 66.7, 66.8, 66.7, 66.3, 62.9, 61.9, 60.9, 54.6, 20.5, 20.48, 20.45, and 20.1 ppm. IR (KBr): ν_{max} 3453.88, 2932.34, 2103.88, 1755.03, 1669.15, 1371.83 and 1223.35 cm^{-1}. HRMS: *m*/*z* $C_{58}H_{71}N_{15}O_{30}^+$; calculated = 1415.4393; found = 1415.4313 $(M + H)^+$.

4.1.15 Synthesis of 3,5-bis (propargyloxy)benzoic acid (16). To a stirred solution of 3,5-bis (propargyloxy)methyl benzoate (1.0 g, 4.1 mmol) in methanol (10 mL), NaOH (1.63 g, 40.9 mmol, 10 equiv.) in water (2.0 mL) was added drop-wise at room temperature. The reaction mixture was stirred for 12 h at 80 °C, then, the hydrochloric acid (4 M, 4 mL) was poured in reaction mixture with continuous stirring below 5 °C. Further, the reaction mixture was extracted with dichloromethane (3 × 20 mL), followed by evaporation to obtain the crude mass, which was purified by column chromatography (SiO_2) to afford white floppy solid with yield (0.895 g, 95%); R_f = 0.5 (40% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, DMSO-D_6) δ 13.14 (s, 1H), 7.16 (d, J = 2.5 Hz, 2H), 6.84–6.83 (1H), 4.84 (d, J = 2.0 Hz, 4H), 3.59–3.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 158.1, 132.9, 108.3, 106.9, 78.8, 78.5, and 55.7 ppm.[28]

4.1.16 Synthesis of 3,4,5-tris (propargyloxy)benzoic acid (17). 3,4,5-Tris (propargyloxy)methyl benzoate (1.0 g, 3.35 mmol) was reacted with aqueous sodium hydroxide (1.34 g, 33.5 mmol, 10.0 equiv.) in methanol according to the procedure of compound **16**, as white solid. Yield (0.886 g, 93%); R_f = 0.4 (40% EtOAc/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 2H), 4.85 (d, J = 1.5 Hz, 2H), 4.83 (d, J = 2.0 Hz, 4H), 2.55 (s, 2H), 2.47–2.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 146.6, 137.1, 119.9, 105.8, 73.9, 73.1, 71.6, 70.9, 55.6, and 52.4 ppm.[29]

4.1.17 Synthesis of dendrimers core unit 1 (18). Phloroglucinol (0.1 g, 0.793 mmol, 1.0 equiv.), 3,5-bis (propargyloxy) benzoic acid (0.730 g, 3.17 mmol, 4.0 equiv.), *N*,*N*′-dicyclohexylcarbodiimide 'DCC' (0.817 g, 3.96 mmol, 5.0 equiv.), 4-dimethylaminopyridine 'DMAP' (0.213 g, 1.74 mmol, 2.2 equiv.) in anhydrous dichloromethane were stirred at room temperature for 95 h. After completion of reaction (monitored by TLC), the reaction mixture was concentrated and subjected to column chromatography using DCM as the eluent to afford the desired dendrimers core unit with good yield. Yield (0.429 g, 71%); R_f = 0.6 (DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 2.4 Hz, 6H), 7.15 (s, 3H), 6.90 (t, J = 2.4 Hz, 3H), 4.75 (d, J = 2.4 Hz, 12H), 2.569–2.560 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 158.6, 151.4, 130.8, 113.3, 109.4, 108.4, 77.7, 76.1, and 56.2 ppm. IR (KBr): ν_{max} 3280.88, 2924.37, 2853.95, 2119.54, 1738.95, 1608.82, 1447.51 and 1295.84 cm^{-1}. HRMS: *m*/*z* $C_{45}H_{31}O_{12}^+$; calculated = 763.1811; found = 763.1794 $(M + H)^+$.

4.1.18 Synthesis of dentromer core unit 2 (19). Pholroglucinol (0.1 g, 0.892 mmol, 1.0 equiv.) was reacted with 3,4,5-tris (propargyloxy)methyl benzoic (0.901 g, 3.17 mmol, 4.0 equiv.), DCC (0.817 g, 3.96 mmol, 5.0 equiv.), and DMAP (0.213 g, 1.74 mmol, 2.2 equiv.) in anhydrous CH_2Cl_2 according to the procedure of compound **18** as white solid yield (0.44 g, 60%); R_f = 0.4 (DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (s, 6H), 7.14 (s, 3H), 4.87 (d, J = 2.0 Hz, 6H), 4.84 (d, J = 2.0 Hz, 12H), 2.55 (s, 6H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 163.7, 151.5, 142.0, 124.3, 113.4, 110.5, 78.5, 77.7, 76.4, 75.7, 60.4, and 57.1 ppm. IR (KBr): ν_{max} 3285.31, 2923.70, 2853.39, 2119.13, 1738.21, 1733.17, 1591.29, 1500.55, 1434.53 and 1317.32 cm^{-1}. HRMS: *m*/*z* = $C_{54}H_{36}O_{15}^+$; calculated = 947.1946; found = 947.1947 $(M + H)^+$.

4.1.19 Synthetic procedure for 6 peripheral galactosylated glycodendrimer (20). The compound **11** (0.391 g, 1.04 mmol, 8.0 equiv.) was reacted with dendrimer core **18** (0.10 g, 0.131 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (0.156 g, 0.628 mmol, 4.8 equiv.), and sodium-L-ascorbate (0.124 g, 6.29 mmol, 4.8 equiv.) according to procedure **1** to afford the glycodendrimer **20**. Yield (0.291 g, 74%); R_f = 0.5 (5% methanol/DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (s, 6H, triazolyl-*H*), 7.45 (d, J = 2.0 Hz, 6H, aromatic-C*H*), 7.16 (s, 3H, aromatic-C*H*), 6.93 (s, 3H), 5.86 (d, J = 9.5 Hz, 6H, H_4), 5.57–5.54 (m, 12H, H_2, H_3), 5.26–5.23 (m, 18H, H_1, H_{6a}, H_{6b}), 4.24–4.14 (m, 18H, H_5, CH_2OAr), 2.21 (s, 18H, 6 × $COCH_3$), 2.03 (s, 18H, 6 × $COCH_3$), 1.99 (s, 18H, 6 × $COCH_3$), 1.87 (s, 18H, 6 × $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 169.9, 169.7, 169.0, 163.8, 159.3, 151.4, 144.0, 130.9, 121.4, 113.3, 109.3, 107.7, 86.2, 74.0, 73.8, 77.7, 67.8, 66.8, 62.1, 61.1, 20.6, 20.5, 20.4, and 20.1 ppm. IR (KBr): ν_{max} 2958.6, 2925.14, 2854.48, 1749.11, 1597.85, 1455.19, 1372.46, 1220.10 and 923.60 cm^{-1}. HRMS: *m*/*z* $C_{129}H_{146}N_{18}O_{66}^{2+}$ calculated = 1501.9322; found = 1501.9310 $(M + H)^{2+}$.

4.1.20 Synthetic procedure for 12 peripheral galactosylated glycodendrimer (21). The glycoconjugate dendron **14** (0.21 g, 0.21 mmol, 8.0 equiv.) was reacted with dendrimers core **18** (20 mg, 0.026 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (31 mg, 0.126 mmol, 4.8 equiv.), and sodium-L-ascorbate (25 mg, 0.126 mmol, 4.8 equiv.) according to procedure **1** to afford the glycodendrimer **21**. Yield (0.149 g, 85%); R_f = 0.4 (5% methanol/DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 12H), 7.69 (s, 6H), 7.39 (s, 6H), 7.11 (s, 3H), 6.90 (s, 3H), 6.60 (s, 6H), 6.53 (s, 12H), 5.87 (d, J = 9.0 Hz, 12H), 5.55–5.51 (m, 24H), 5.46 (s, 12H), 5.26–5.13 (m, 48H), 4.26–4.24 (m, 12H), 4.17–4.09 (m, 24H), 2.17 (s, 36H), 1.98–1.96 (m, 72H), 1.80 (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.9, 169.7, 169.0, 163.8, 159.7, 159.3, 151.3, 144.1, 143.6, 136.8, 130.8, 123.1, 121.5, 113.3, 109.2, 107.5, 101.9, 86.1, 73.9, 70.6, 67.8, 66.8, 62.2, 61.8, 61.1, 53.9, 20.56, 20.54, 20.4, and 20.1 ppm. IR (KBr): ν_{max} 3473.00, 2925.79, 2853.53, 1754.48, 1598.94, 1460.89, 1372.11, 1223.38 and 1050.88 cm^{-1}. MALDI-TOF MS: exact mass; $C_{291}H_{324}N_{54}O_{132}Na^+$; calculated = 6709.0193; found = 6704.0401 $(M + Na)^+$.

4.1.21 Synthetic procedure for 18 peripheral galactosylated glycodendrimer (22). The glycoconjugate dendron **15** (0.148 g, 0.104 mmol, 8.0 equiv.) was reacted with dendrimer core **18** (10 mg, 0.013 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (16 mg, 0.062 mmol, 4.8 equiv.), and sodium-L-ascorbate (14 mg, 0.062 mmol, 4.8 equiv.) according to procedure **1** to afford the glycodendrimer **22**. Yield (79 mg, 65%); R_f = 0.35 (5% methanol/DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 6H, middle

triazolyl-*H*), 8.05 (s, 12H, outer triazolyl-*H*), 7.76 (s, 6H, inner triazole-*H*), 7.44 (d, J = 1.5 Hz, 6H, –ArH), 7.14 (s, 3H, phloroglucinol H), 6.97 (s, 3H, Core ArH), 6.69 (s, 12H, dendron Ar–*H*), 5.93–5.90 (18H, H4), 5.69–5.65 (m, 6H, H_2), 5.56–5.52 (m, 36H, H_2, H_3, H_1), 5.45 (s, 12H, –CH_2Ar), 5.29–5.14 (m, 60H, H_1, H_{6a}, H_{6b}), 4.30–4.27 (18H, H_5), 4.21–4.17 (12H, –OCH_2 para triazole), 4.14–4.11 (m, 24H, –OCH_2 meta triazole), 2.18–2.17 (m, 54H, 18 × $COCH_3$), 1.99–1.95 (m, 108H, 36 × $COCH_3$), 1.75 (s, 54H, 18 × $COCH_3$) ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 170.08, 170.06, 169.8, 169.7, 168.9, 168.7, 163.9, 159.4, 152.3, 151.3, 144.4, 143.9, 143.6, 139.1, 137.8, 130.9, 130.5, 123.3, 123.0, 122.2, 113.9, 109.2, 108.0, 86.0, 85.7, 73.8, 73.5, 70.9, 70.6, 67.9, 67.7, 66.8, 66.2, 62.6, 62.2, 61.1, 60.9, 54.0, 20.5, 20.4, 20.1, and 20.0 ppm. IR (KBr): ν_{max} 3470.41, 2925.65, 2853.11, 1753.98, 1596.63, 1445.34, 1372.45, 1223.83 and 1050.76 cm^{-1}. MALDI-TOF MS: exact mass: $C_{393}H_{450}N_{72}O_{192}H^+$ calculated = 9249.7735; found = 9242.5430 $(M + H)^+$.

4.1.22 Synthetic procedure for 9 peripheral galactosylated glycodendrimer (23). The compound **11** (0.444 g, 1.189 mmol, 11 equiv.) was reacted with dentromer core unit **19** (0.1 g, 0.108 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (194 mg, 0.778 mmol, 7.2 equiv.), and sodium-L-ascorbate (154 mg, 0.778 mmol, 7.2 equiv.) according to procedure **1** to afford the glycodentromer **23**. Yield (0.277 g, 60%); R_f = 0.5 (5% methanol/DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 3H, triazolyl H), 8.11 (s, 6H, triazolyl-*H*), 7.57 (s, 6H, Ar–C*H*), 7.14 (s, 3H, core-Ar–CH), 5.95–5.92 (m, 9H, H_4), 5.72 (t, J = 9.5 Hz, 3H, H_2), 5.61–5.55 (m, 18H, H_2, H_3, (6H) H_1), 5.39–5.27 (m, 24H, H_1, H_{6a}, H_{6b}), 4.37–4.16 (m, 27H, H_5, –OCH_2Ar), 2.21 (s, 27H, 9 × $COCH_3$), 2.03 (s, 27H, 9 × $COCH_3$), 1.99 (s, 27H, 9 × $COCH_3$), 1.83 (s, 27H, 9 × $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 170.3, 170.1, 170.0, 169.9, 169.8, 168.9, 168.6, 163.6, 151.9, 144.6, 143.8, 142.4, 124.3, 123.4, 122.2, 114.0, 109.8, 86.1, 85.7, 73.9, 73.5, 71.0, 70.7, 67.9, 67.8, 66.8, 66.4, 62.8, 61.1, 60.9, 20.6, 20.5, 20.4, and 20.1 ppm. IR (KBr): ν_{max} 3454.86, 2925.58, 2854.19, 1754.96, 1433.58, 1373.10, 1224.37 and 1050.62 cm^{-1}. MALDI-TOF MS: exact mass: $C_{180}H_{207}N_{27}O_{96}Na^+$ calculated = 4305.2038; found = 4303.9077 $(M + Na)^+$.

4.1.23 Synthetic procedure for 18 peripheral galactosylated glycodendrimer (24). The glycoconjugate dendron **14** (0.293 g, 0.297 mmol, 11.0 equiv.) was reacted with **19** (25 mg, 0.027 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (48 mg, 0.194 mmol, 7.2 equiv.), and sodium-L-ascorbate (38 mg, 0.194 mmol, 7.2 equiv.) according to procedure **1** to afford the glycodendrimer **24**. Yield (0.165 g, 63%); R_f = 0.6 (10% methanol/DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (s, 6H, peripheral inner triazolyl-*H*), 7.94 (s, 18H, outer triazolyl-*H*), 7.89 (s, 3H, inner middle triazolyl-*H*), 7.56 (s, 6H, aromatic-C*H*), 7.12 (s, 3H, phloroglucinol core-C*H*), 6.58–6.56 (m, 27H, periphery-C*H*, AB_2), 5.99 (d, J = 19.5 Hz, 18H, H_4), 5.57–5.41 (m, 54H, H_2, H_3, –CH_2Ar), 5.28–5.23 (m, 36H, H_1, H_{6a}), 5.11 (s, 36H, H_{6b}, –OCH_2 triazole inner-*H*), 4.27–4.11 (m, 54H, H_5, –OCH_2 triazole outer-*H*), 2.18 (s, 54H, 18 × $COCH_3$), 1.99–1.97 (m, 108H, 36 × $COCH_3$), 1.795–1.790 (m, 54H, 18 × $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 170.0, 169.8, 169.0, 163.4, 159.7, 159.6, 144.1, 143.5, 139.2, 137.1, 123.79, 123.74, 121.8, 121.7, 113.9, 107.5, 101.9, 86.0, 73.9, 70.7, 67.8, 66.8, 61.8, 61.1, 53.9, 20.6, 20.5, 20.4, and 20.1 ppm. IR (KBr): ν_{max} 3449.82, 2924.54, 2852.77, 1754.32, 1599.95, 1462.09, 1372.17, 1223.79 and 1053.35 cm^{-1}. MALDI-TOF MS: exact mass: $C_{423}H_{477}N_{81}O_{195}H^+$, calculated = 9815.0106; found = 9817.8810 $(M + H)^+$.

4.1.24 Synthetic procedure for 27 peripheral galactosylated glycodentromer (25). The glycoconjugate dendron **15** (0.252 g, 0.178 mmol, 11.0 equiv.) was reacted with dentromer core unit **19** (15 mg, 0.016 mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (29.1 mg, 0.117 mmol, 7.2 equiv.), and sodium-L-ascorbate (23 mg, 0.117 mmol, 7.2 equiv.) according to procedure **1** to afford the glycodentromer **25**. Yield (0.128 g, 58%); R_f = 0.55 (10% methanol/DCM); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 3H, triazolyl H), 8.18 (s, 6H, triazolyl-*H*), 8.12 (s, 6H), 8.11 (s, 3H), 8.09 (s, 12H, triazolyl-*H*), 8.04 (s, 6H, triazolyl-*H*), 7.64 (s, 6H, core Ar–*H*), 7.17 (s, 3H, core Ar–*H*), 6.85 (s, 6H, AB_3 dendron Ar–*H*), 6.79 (s, 12H, AB_3 dendron Ar–*H*), 5.95–5.92 (m, 27H, H_4), 5.72–5.67 (m, 9H, H_2), 5.61–5.46 (m, 63H, H_2, H_3, –CH_2Ar), 5.30–5.12 (m, 99H, H_1, H_{6a}, H_{6b}, –OCH_2 *para* triazole-*H*), 4.34–4.30 (m, 27H, H_5), 4.22–4.10 (m, 54H, –OCH_2, triazole outer-*H*), 2.18–2.17 (m, 81H, 27 × $COCH_3$), 1.99–1.95 (m, 162H, 56 × $COCH_3$), 1.75–1.71 (m, 81H, 27 × $COCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 169.9, 169.7, 168.9, 168.7, 163.8, 152.28, 152.24, 151.3, 144.8, 144.4, 144.06, 144.02, 143.5, 142.4, 139.2, 137.7, 137.5, 131.2, 130.7, 124.5, 124.0, 123.9, 123.4, 123.2, 122.5, 122.4, 113.9, 109.9, 108.1, 85.9, 85.6, 73.7, 73.4, 71.0, 70.7, 67.9, 67.7, 66.8, 66.2, 63.2, 63.1, 62.6, 61.1, 60.9, 54.0, 20.5, 20.4, 20.1, and 20.0 ppm. IR (KBr): ν_{max} 3485.35, 3147.14, 2922.89, 2851.93, 1755.09, 1595.23, 1441.07, 1372.82, 1223.87, 1103.89 and 1051.39 cm^{-1}. MALDI-TOF MS: exact mass: $C_{576}H_{666}N_{108}O_{285}H^+$ calculated = 13 660.1182; found = 13 627.0547 $(M + H)^+$.

Conflicts of interest

There are no conflicts to declare.

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