Accepted Manuscript online: 2023-03-27 Article published online: 2023-05-04

Click Chemistry-Inspired Synthesis and Photophysical Studies of Calix[4]arene-Cored Galactosylated and Mannosylated Glycodendrimers

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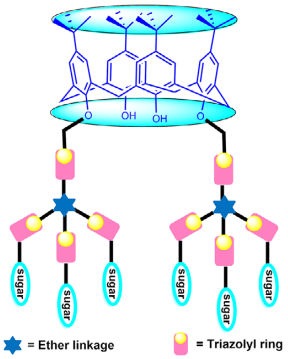


Received: 02.08.2022
Accepted after revision: 10.03.2023
DOI: 10.1055/a-2063-1445; Art ID: OM-2022-12-0053-OA

Abstract A prompt and modular copper(I)-catalyzed azide–alkyne cycloaddition 'click' approach has been exploited for the synthesis of galactose- and mannose-coated calixarene-cored G_1 generation glycodendrimers. The developed calixarene glycodendrimers were characterized by using spectral techniques (^{1}H NMR, ^{13}C NMR and IR). In photophysical evaluation, UV and fluorescence spectra of the developed compounds were recorded in CH_3CN/H_2O.

Key words: calix[4]arenes, click reactions, glycosyl dendrimers

Introduction

Calixarenes are a class of macrocyclic compounds that can serve as building blocks for a wide range of applications in organic synthesis due to their unique three-dimensional architecture and ease of functionalization at the upper and/or lower rim.[1,2] Calixarenes have received great significance as receptors in the synthesis and application of supramolecular scaffolds for molecular recognition, sensing, self-assembling, catalysis, and drug discovery.[3,4] Similar in design to cyclodextrin, these molecules exhibit more diversity and adaptability than cyclodextrin. There are two key factors, i.e., catalysis and reactivity, which have a significant impact on the functional behaviour of host–guest chemistry.[5] These complexes have a great ability to detect and remove heavy metal ions from the environment as well as remediate nuclear waste.[6] Typically, calixarene's host chemistry produces stable compounds with biomolecules that are more relevant for supramolecular chemistry.[7] Furthermore, calixarene-based biomimetic compounds are extremely helpful in biotechnology,[8] biosensing and chemosensing technologies,[9] catalysis,[10] gene transport,[11] platonic micelles,[12] chiral molecular recognition,[13] etc.

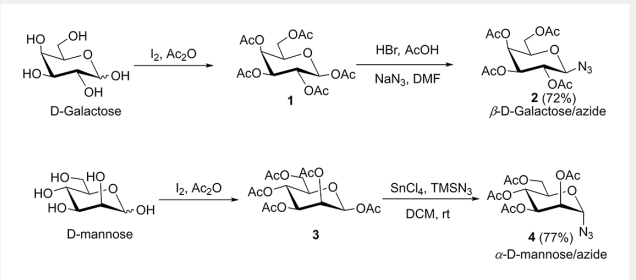
The Cu(I)-catalyzed azide–alkyne coupling reaction (CuAAC), usually known as the click reaction, is the most powerful and popular tool for the regioselective synthesis of 1,4-disubstituted triazoles.[14] Dondoni efficiently demonstrated this ligation tool for the construction of multiple triazolyl glycoconjugates anchoring to calix[4]arene scaffolds.[3] Several reports have been documented for the synthesis of various glycoclusters using this orthogonal azide–alkyne coupling reaction.[15] Regioselective generated triazoles from azide–alkyne coupling are the bioisostere of the amide functional group. The resulting triazole component has been extensively investigated as a useful pharmacophore and also provides an appropriate binding site for various metal ions in molecular sensing.[16] Multivalent glycan–protein interactions play a pivotal role in most of the biological recognition and dissemination transduction processes, including surface sensing and adhesion by bacteria and viruses, drug effector mechanisms, cellular interactions, cell cycle regulation and differentiation, and cancer cell aggregation as well as its metastatic spread.[17,18] Among the multivalent glycocluster architectures, glycodendrimers have received great attention due to their mono-dispersity, ability to organize their size, and various sugar units at the periphery.[19] The versatile nature of these macrocycles (calixarenes) towards their functionalization at the lower rim offers selective coordination for a plethora of metals ions. For instance, G_1 generation glycodendrimers including mannosylated- and galactosylated-dendritic architectures are designed, synthesized, and well elucidated by NMR, IR, and HRMS spectroscopy. Several

designed glycoconjugates and glycodendrimers exhibited a vital role in biological and photophysical processes.[20–22]

Several sensors have recently been constructed using supramolecular architectures. Macrocycle design scaffolds including cyclodextrins, calixarenes, and rotaxanes are typical examples that provide supramolecular platforms for guest molecules or ions.[23] Among all, calixarene-based sensors are employed to determine the presence of cations and anions using diverse techniques, such as electrochemical and photophysical methods.[23,24] Photophysical methods play an important role in examining and identifying particular ions and molecules. Aggregation-induced emission, photoinduced electron transfer (PET), photoinduced charge transfer, and Förster resonance energy transfer are some of the preferred mechanisms used in the photophysical studies. According to the PET mechanism, when an ion binds to the ionophore, the fluorophore emits a signal.[25] Therefore, considering the importance of glycodendrimers, we made a significant effort to amalgamate the synthetic advantages of calixarenes and the multivalency effect of sugar through click coupling of these two moieties to assemble a new class of *p-tert*-butyl-calix[4]arene-tethered glycosyl dendrimers. We, herein wish to report the CuAAC click-inspired synthesis of novel triazole-appended glycosyl dendrimers **14** and **15** with their possible photophysical investigations via UV-Vis and fluorescence spectroscopy.

Results and Discussion

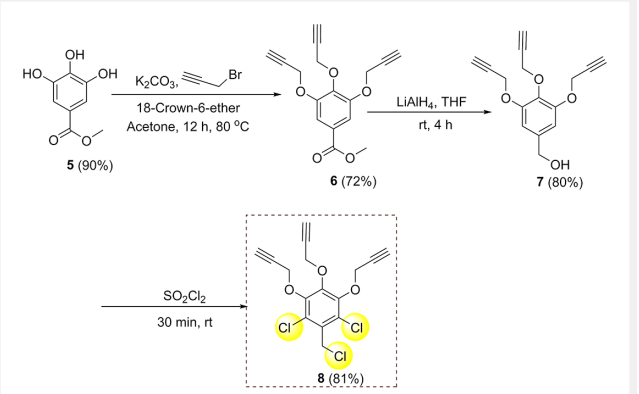
Acetylated D-galactose derivative **1**, obtained from D-galactose, was used to develop 2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl azide **2** by treating it with HBr (33%) in acetic acid followed by azidation in anhydrous DMF while the corresponding acetylated D-mannose derivative **3** was treated with $SnCl_4$ and $TMSN_3$ in anhydrous dichloromethane at room temperature to give 2,3,4,6-tetra-*O*-acetyl-D-mannopyranosyl azide **4** (Scheme 1). The resulting azido derivatives **2** and **4** were characterized by their NMR (^1H and ^{13}C) spectral data which closely matched with the literature.



Scheme 1 Synthesis of *β*-D-galactose and *α*-D-mannose azides (**2** & **4**).

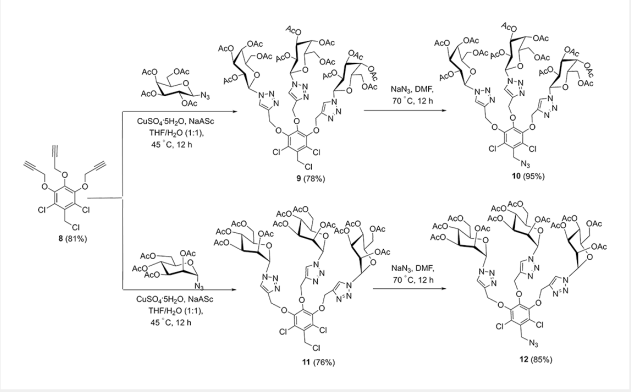
Synthetic Procedure of 1,3-Dichloro-2-(chloromethyl)-4,5,6-tris(prop-2-yn-1-yloxy)benzene (8)[21]

Starting with commercially available gallic acid, we first converted it into methyl 3,4,5-trihydroxybenzoate **5** by esterifying it in methanol in an acidic medium. We then converted it into methyl 3,4,5-tris(prop-2-yn-1-yloxy)benzoate **6** by propargylating it with propargyl bromide in the presence of K_2CO_3 and the co-catalyst 18-crown-6. The reduction of the methyl 3,4,5-tris(prop-2-yn-1-yloxy)benzoate with lithium aluminium hydride in dry THF at room temperature furnished the product [3,4,5-tris(prop-2-yn-1-yloxy)-phenyl]methanol **7**. Compound **7** was chlorinated with SO_2Cl_2 to produce 1,3-dichloro-2-(chloromethyl)-4,5,6-tris (prop-2-yn-1-yloxy)benzene **8** (Scheme 2).



Scheme 2 Synthesis of 1,3-dichloro-2-(chloromethyl)-4,5,6-tris(prop-2-yn-1-yloxy)benzene (**8**).

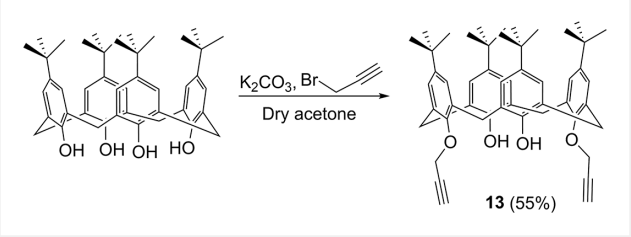
Previously synthesised 1,3-dichloro-2-(chloromethyl)-4,5,6-tris(prop-2-yn-1-yloxy)benzene compound **8** was combined with acetylated galactose sugar azide **2** in the presence of $CuSO_4$/NaAsc in THF/water (1 : 1) to produce the corresponding first-generation dendritic wedge **9**. The appearance of three triazole peaks in the NMR spectra confirmed the presence of compound **9**. Further, the azide-functionalized dendritic molecule **10** was produced by treating the chlorine-containing dendritic architecture **9** with NaN_3 in dry DMF for 12 h. The same technique was used to produce the azide-functionalized compound **12**, which likewise confirmed to IR and NMR spectra (Scheme 3).



Scheme 3 Synthesis of first-generation galactosylated and mannosylated dendritic architectures.

Synthesis of Bis-propargyloxy-*p*-*tert*-butyl-calix[4]arene Hyper Core (13)[4]

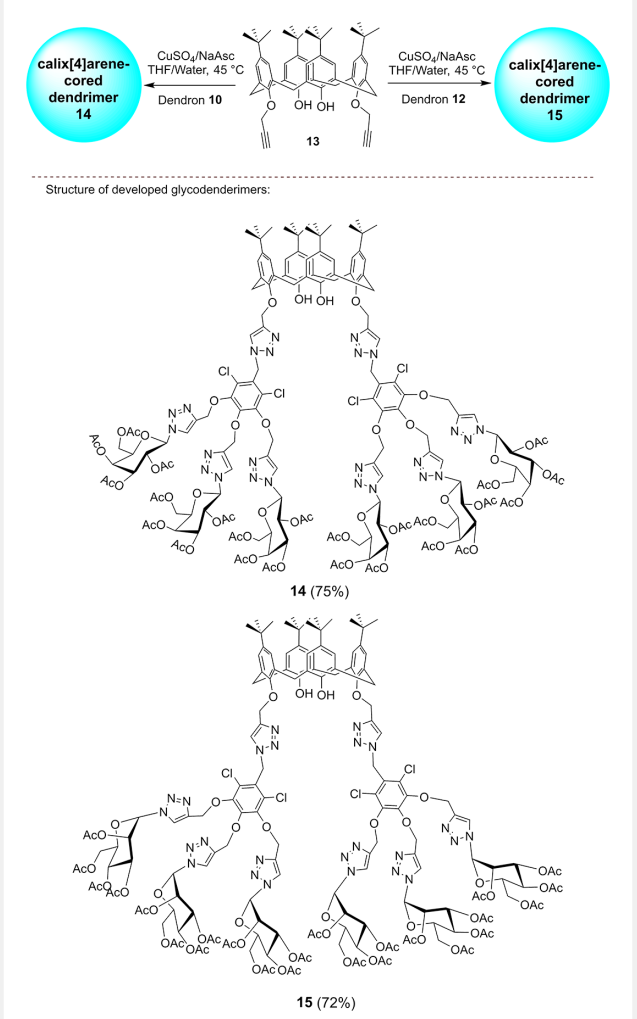
We began by propargylating the commercially available *p*-*tert*-butyl-calix[4]arene with propargyl bromide in the presence of K_2CO_3 as a base in dry acetone for 6 h to generate the bis-propargyloxy-*p*-*tert*-butyl-calix[4]arene **13** (Scheme 4), which was confirmed by its NMR data.



Scheme 4 Synthesis of calix[4]arene hyper core.

Synthesis of Calix[4]arene-Cored Glycodendrimers (14, 15)

Galacto-dendron **10** and manno-dendron **12** of the G_1 generation were subjected to CuAAC click conjugation with bis-propargyloxy-*p*-*tert*-butyl-calix[4]arene **13** using $CuSO_4$•$5H_2O$/NaAsc in THF/water (1 : 1) to provide the glycodendrimers **14** and **15** of the G_1 generation in almost quantitative yield (Scheme 5). The formation of our intended glycodendrimers was ultimately supported by the nonappearance of vibrational peaks of alkyne and azide in the IR spectra of the calix[4]arene glycodendrimer that was created.



Scheme 5 Synthesis of "calix[4]arene-cored" galactosylated G_1 generation glycodendrimer **14** and mannosylated G_1 generation glycodendrimer **15**.

Photophysical Study of Glycodendrimers 14 and 15

The photophysical properties of glycodendrimers **14** and **15** were studied by UV-Vis and fluorescence spectroscopies. Absorption and emission spectra of glycodendrimers **14** and **15** are taken in CH_3CN/H_2O (70/30, v/v, at r.t. 25 °C). In the UV-Vis absorption spectrum, glycodendrimers **14** showed a band at 275 nm and glycodendrimers **15** showed a band at 280 nm due to π–π* transition.[26] The fluorescence properties of glycodendrimers **14** and **15** revealed the most prominent peak at 350 nm (Figure 1).[26] It is anticipated that the new glycodendrimers would show sensitivity towards metal ions and their sensing properties can be studied.

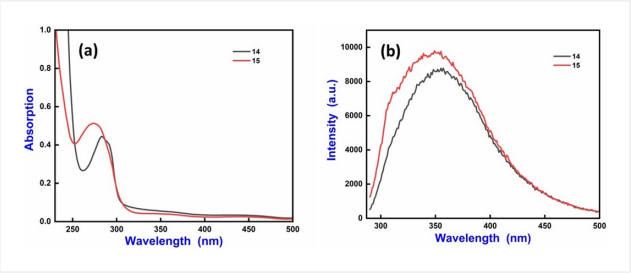


Figure 1 (**a**) UV spectra of compounds **14** and **15** in CH_3CN/H_2O (70/30, v/v). (**b**) Fluorescence spectra of compounds **14** and **15** in CH_3CN/H_2O (70/30, v/v).

Conclusions

Conclusively, herein we wish to report the CuAAC click-inspired synthesis of novel triazole-appended glycosyl dendrimers **14** and **15** with their possible photophysical investigations via UV-Vis and fluorescence spectroscopy, where **14** and **15** are found to be UV and fluorescent active dendrimers.

Experimental Section

General

Pure analytical grade solvents and reagents were used throughout. 60 F-254 silica gel that had been pre-coated on aluminium plates was utilised for thin layer chromatography (TLC) using a UV light and a 5% H_2SO_4/methanol solution (charring solution). Heating the sample in an alkaline potassium permanganate ($KMnO_4$) solution allowed the alkynes to be detected. The developed chemicals were purified using flash column chromatography and silica gel. The spectra for ^1H and ^{13}C were captured at 500 MHz and 125 MHz, respectively. At room temperature, all NMR spectra were captured and given in ppm, about deuterated solvents. The resonance multiplicity in the ^1H NMR spectra is described as: 's' (singlet), 'd' (doublet), 'dd' (double doublet), 't' (triplet), and 'm' (multiplet) and residual protic solvent of $CDCl_3$ (^1H NMR, 7.26 ppm; ^{13}C NMR, 77.0 ppm). IR spectra of the compound were recorded in Nujol mulls in KBr pellet. Absorption spectra were recorded on a 8400S and Systronics double beam UV-Visible spectrometer and emission spectra were recorded on a Fluoromax 4CP plus spectrofluorometer with a 10 mm quartz cell at 25 °C.

Procedures

General Experimental Procedure for the Cu(I)-Catalyzed Azide–Alkyne Cycloaddition Reaction

$CuSO_4 \cdot 5H_2O$ (0.3 equiv per alkyne), sodium ascorbate (0.3 equiv per alkyne), and alkyne-possessing analogues were agitated in a THF/water (1 : 1) solution at 45 °C for 12 h. The reaction was monitored with TLC and after its completion, the reaction mixture was run through celite and extracted with ethyl acetate. Additionally, the organic layers were washed with water (10 mL), saturated aq. NH_4Cl (2 × 10 mL), and then with brine solution (2 × 10 mL). The reaction mixture was concentrated under decreased pressure and the organic layers were recovered. The organic residue was purified by using flash column chromatography (SiO_2) which resulted in a satisfactory yield of the desired dendrons and glycodendrimers.

Experimental Details and Physical Data of the Developed Molecules

Synthesis of First-Generation Azide-Functionalized Galactosylated Dendritic Architecture (10)[15,21]

Galactosylated dendritic architecture **9** (0.35 g, 0.235 mmol) that had been chlorinated was dissolved in dry DMF followed by the addition of NaN_3 (61.3 mg, 0.943 mmol, 4.0 equiv) in an inert atmosphere and the reaction mixture was agitated at 70 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with ethyl acetate in ice cold water. The organic layer was dried under reduced pressure and the obtained crude mass was subjected to column chromatography to get compound **10** in (334 mg) 95% yield. R_f = 0.5 (60% ethyl acetate/*n*-hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1 H), 8.10 (s, 2 H), 5.88 (d, J = 9.5 Hz, 3 H), 5.64 – 5.59 (m, 3 H), 5.54 (d, J = 2.5 Hz, 3 H), 5.35 – 5.23 (m, 9 H), 4.66 – 4.59 (m, 2 H), 4.26 – 4.11 (m, 9 H), 2.22 (d, J = 6.5 Hz, 9 H), 2.02 (d, J = 16.0 Hz, 18 H), 1.88 – 1.82 (m, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 170.09, 170.03, 169.8, 168.88, 168.84, 147.7, 146.8, 143.7, 143.5, 128.0, 126.2, 123.2, 122.7, 86.1, 73.88, 73.84, 70.8, 67.87, 67.83, 66.8, 66.4, 66.3, 61.0, 59.4, 49.5, 20.6, 20.4, 20.18 and 20.12 ppm. IR (KBr): ν_{max} 2925.0, 2857.2, 2105.1 and 1755.1 cm^{-1}.

Synthesis of First-Generation Azide-Functionalized Mannosylated Dendritic Architecture (12)

Mannosylated dendritic architecture **11** (500 mg, 0.338 mmol) that had been chlorinated was dissolved in dry DMF followed by the addition of NaN_3 (88 mg, 1.35 mmol, 4.0 equiv), in an inert atmosphere and reaction mixture agitated for 12 h. After the completion of the reaction as monitored by the TLC, the reaction mixture was extracted with ethyl acetate in ice cold water. The organic layer was extracted and dried under reduced pressure and the obtained crude mass was subjected to column chromatogra-

phy and the desired compound **12** was produced in (425 mg, 85%) excellent yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1 H), 8.01 (s, 2 H), 6.12 – 5.99 (m, 5 H), 5.96 – 5.83 (m, 4 H), 5.41 – 5.35 (m, 3 H), 5.30 – 5.19 (m, 6 H), 4.65 – 4.61 (m, 2 H), 4.38 – 4.33 (m, 3 H), 4.08 – 4.04 (m, 3 H), 3.90 – 3.88 (m, 3 H), 2.17 – 2.12 (m, 9 H), 2.07 – 1.99 (m, 27 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.6, 169.56, 169.52, 169.4, 147.3, 147.2, 143.5, 143.4, 128.1, 126.4, 124.7, 83.9, 83.8, 72.0, 71.9, 68.9, 68.8, 68.1, 66.3, 65.9, 65.8, 61.5, 49.5, 20.63, 20.60 and 20.4 ppm. IR (KBr): ν_{max} 3424.0, 3147.6, 2924.9, 2853.9, 2105.3 and 1753.8 cm^{-1}.

Synthesis of Bis-propargyloxy-*p*-*tert*-butyl-calix[4]arene (13)[4]

Tert-butyl calix[4]arene (1.0 g 1.5 mmol) was dissolved in dry acetone followed by the addition of base (K_2CO_3, 0.19 g, 1.38 mmol, 0.9 equiv) and propargyl bromide (0.29 mL, 3.85 mmol, 2.5 equiv) was added to the reaction mixture and stirred overnight. After the starting material had completely been consumed as monitored by TLC, the reaction mixture was evaporated under reduced pressure, and the obtained crude mass was subjected to column chromatography to get the desired product (**13**). White solid, yield: (0.61 g, 55%); R_f = 0.4 (10% ethyl acetate/*n*-hexane); m.p. = 210 – 212 °C; IR: 3433.5, 3290.2, 3276.4, 2960.0, 2866.6, 2118.8, 1597.3, 1392.3, 1362.9, 1485.7, 1302.8; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (s, 4 H), 6.72 (s, 4 H), 6.46 (s, 2 H), 4.74 (s, 4 H), 4.38 (d, *J* = 13.5 Hz, 4 H), 3.33 (d, *J* = 13.5 Hz, 4 H), 2.54 (s, 2 H), 1.31 (s, 18 H), 0.90 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 149.5, 147.3, 141.7, 132.6, 128.1, 125.6, 125.1, 78.8, 76.3, 63.3, 33.94, 33.92, 32.1, 31.7 and 31.0 ppm. IR (KBr): ν_{max} 3434.7, 3290.4, 3276.4, 2961.7, 2866.8, 2118.7, 1603.1 and 1486.7 cm^{-1}.

Synthesis of Galactose-Coated Calix[4]arene-Cored G_1 Generation Glycodendrimer (14)

Synthesis of galactose-coated G1 generation glycodendrimer was performed by using the click reaction technique. The synthesised galactoconjugate dendron **10** (246 mg, 0.165 mmol, 3.0 equiv) was reacted with core unit **13** (40 mg, 55.1 µmol, 1.0 equiv) in the presence of $CuSO_4$•$5H_2O$ (11 mg, 44.1 µmol, 0.8 equiv) and sodium ascorbate (9 mg, 44.1 µmol, 0.8 equiv) in THF/H_2O (1 : 1) as the solvent. The reaction mixture was stirred for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered with a sintered funnel and extracted with ethyl acetate and water. The organic layer was dried over reduced pressure and the obtained crude mass was subjected to column chromatography to get the desired product **14**. The synthesized galactose-coated glycodendrimer was characterised by ^{1}H, ^{13}C, and mass spectrometry techniques. Yield (153 mg, 75%); R_f = 0.50 (5% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 2 H), 8.17 (s, 4 H), 8.02 (s, 2 H), 6.98 – 6.96 (m, 6 H), 6.72 (s, 4 H), 5.92 – 5.83 (m, 10 H), 5.66 (q, *J* = 9.5 Hz, 6 H), 5.56 – 5.52 (m, 6 H), 5.30 – 5.10 (m, 22 H), 4.31 – 4.10 (m, 22 H), 3.21 – 3.18 (m, 4 H), 2.23 – 2.19 (m, 18 H), 2.03 – 2.00 (m, 36 H), 1.81 – 1.79 (m, 18 H), 1.20 (s, 18 H), 0.90 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 170.0, 169.8, 168.8, 150.3, 149.6, 147.9, 147.5, 147.1, 144.1, 143.6, 143.5, 141.6, 132.47, 132.42, 127.8, 127.7, 126.8, 126.7, 125.6, 125.5, 125.1, 125.0, 123.7, 123.6, 123.2, 86.0, 73.7, 70.9, 69.8, 67.9, 67.8, 66.87, 66.83, 66.4, 66.3, 61.1, 60.9, 49.4, 33.8, 33.7, 31.8, 31.5, 30.9, 30.1, 20.6, 20.4 and 20.1 ppm.

Synthesis of Mannose-Coated Calix[4]arene-Cored G_1 Generation Glycodendrimer (15)

Synthesis of mannose-coated G1 generation glycodendrimer was performed by using the click reaction technique. The synthesised manno-conjugate dendron **12** (246 mg, 0.165 mmol, 3.0 equiv) was reacted with core unit **13** (40 mg, 55.1 µmol, 1.0 equiv) in the presence of $CuSO_4$•$5H_2O$ (11 mg, 44.1 µmol, 0.8 equiv) and sodium ascorbate (9 mg, 44.1 µmol, 0.8 equiv) in THF/H_2O (1 : 1) as the solvent. The reaction mixture was stirred for 12 h. After the completion of the reaction (monitored by the TLC), the reaction mixture was filtered with a sintered funnel and extracted with ethyl acetate and water. The organic layer was dried over reduced pressure and the obtained crude mass was subjected to column chromatography to get the desired product **15**. Yield (146 mg, 72%); R_f = 0.50 (5% MeOH/CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 2 H), 8.11 (s, 4 H), 8.08 (s, 2 H), 6.95 – 6.94 (m, 6 H), 6.70 (s, 4 H), 6.13 (s, 5 H), 5.99 (s, 2 H), 5.93 – 5.82 (m, 15 H), 5.40 – 5.36 (m, 6 H), 5.15 – 5.06 (m, 16 H), 4.38 – 4.32 (m, 6 H), 4.16 – 3.94 (m, 16 H), 3.20 – 3.14 (m, 4 H), 2.16 – 2.11 (m, 18 H), 2.04 – 1.99 (m, 54 H), 1.16 (s, 18 H), 0.88 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.6, 169.5, 169.3, 150.1, 149.6, 147.78, 147.70, 147.2, 143.49, 143.45, 141.7, 132.3, 127.7, 126.9, 125.5, 125.0, 124.9, 123.6, 83.9, 83.8, 72.0, 71.9, 68.9, 68.8, 68.1, 66.2, 66.1, 65.8, 61.5, 49.3, 33.8, 33.6, 31.8, 31.5, 31.3, 30.8, 20.6 and 20.4 ppm.

Funding Information

V.K.T. gratefully acknowledges Science and Engineering Research Board (Grant No.: CRG/2021/002 776).

Acknowledgment

M.D.P. and V.K.T. acknowledge the Institute of Eminence (IoE)-Banaras Hindu University for the funding and CISC-BHU for providing spectroscopic studies. S.K., M.S.Y., T.M., S.A. and M.K.J. sincerely acknowledge CSIR-UGC New Delhi for the Research Fellowship.

Supporting Information

Supporting Information for this article is available online at https://doi.org/10.1055/a-2063-1445.

Conflict of Interest

The authors declare no conflict of interest.

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