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Synthesis and catalytic application of glycodendrimers decorated with Gold nanoparticle-Reduction of 4-Nitrophenol

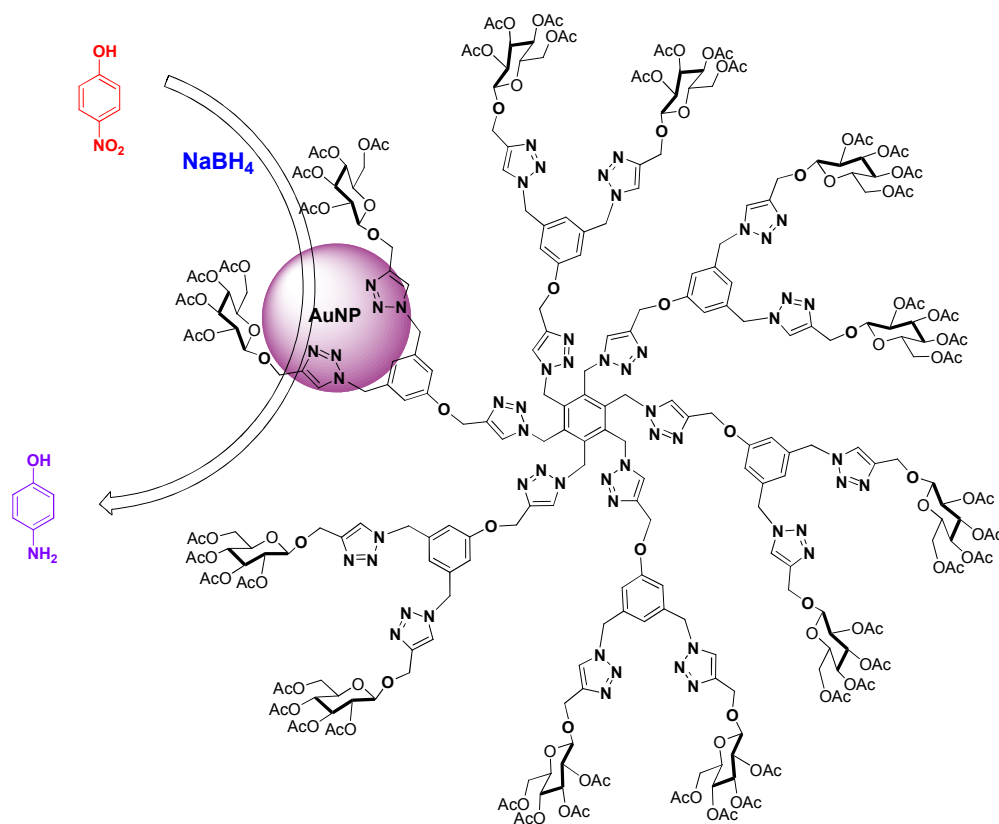
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DSNp AND DENp of Au with average diameter of 2.6 nm has been synthesized and proved to be good catalyst for the reduction of 4-Nitrophenol



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Abstract

Gold nanoparticle decorated glycodendrimers **1**, **2**, **3** and **4** were synthesized by click chemistry approach. Gold nanoparticles (NPs) were synthesized in good yields either by stabilization or encapsulation of the triazolyl glycodendrimers. Gold nanoparticles are stabilised (DSNPs) by the zeroth generation dendrimer and encapsulated (DENPs) by the first generation glycodendrimer. The Au-DSNPs and Au-DENPs were characterized by UV-Vis spectroscopy and high resolution transmission electron microscopy (HRTEM) which shows that Au-DSNPs and Au-DENPs have an average diameter 7.2 nm and 4.0 nm respectively. The catalytic activity of Au-DSNPs for the reduction of 4-nitrophenol (4NP) to 4-aminophenol (4AP) with NaBH₄ under aqueous condition was examined by UV-Vis spectroscopy.

Keywords: Glycodendrimers, gold, nano particles, reduction and spectroscopy

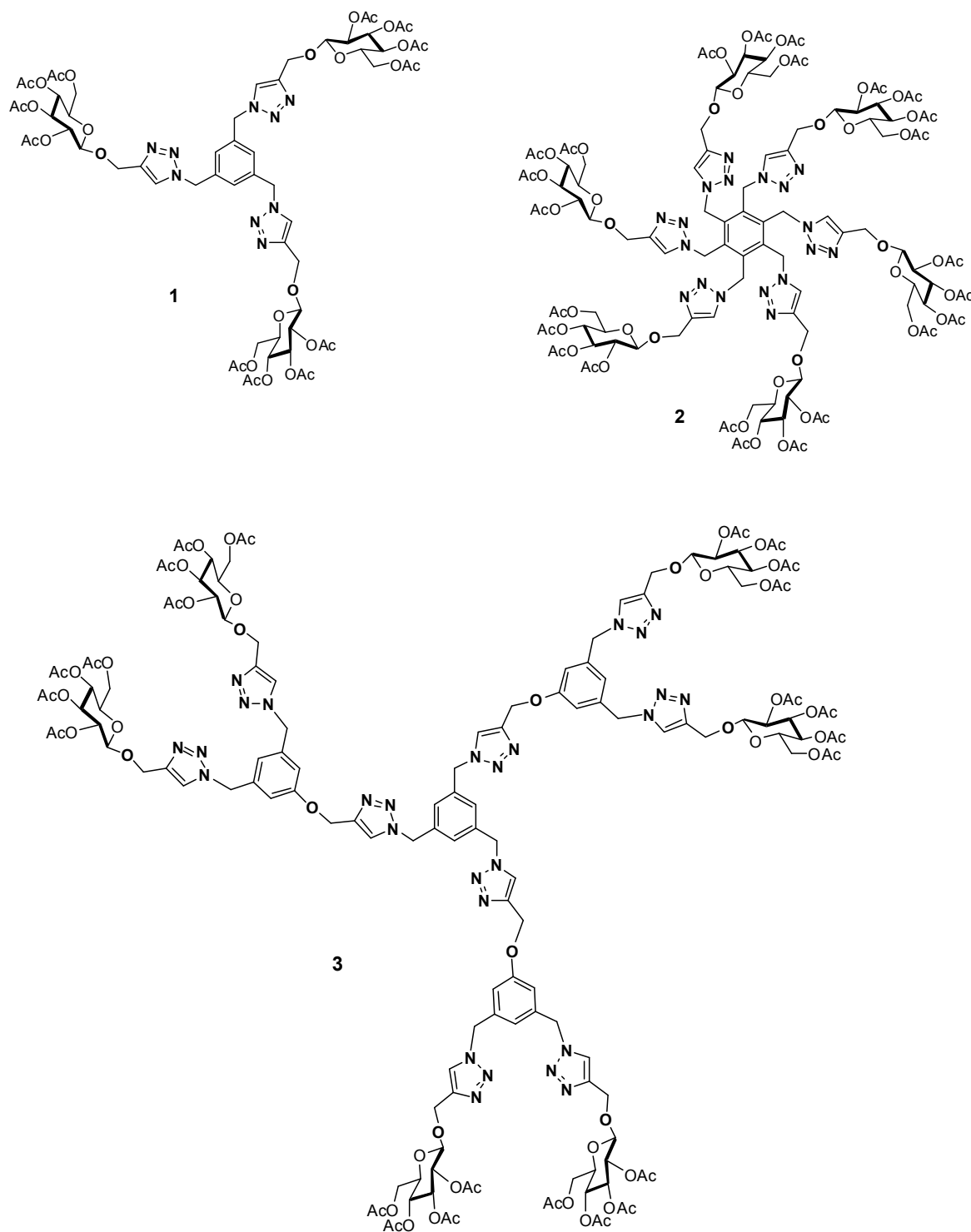
Introduction

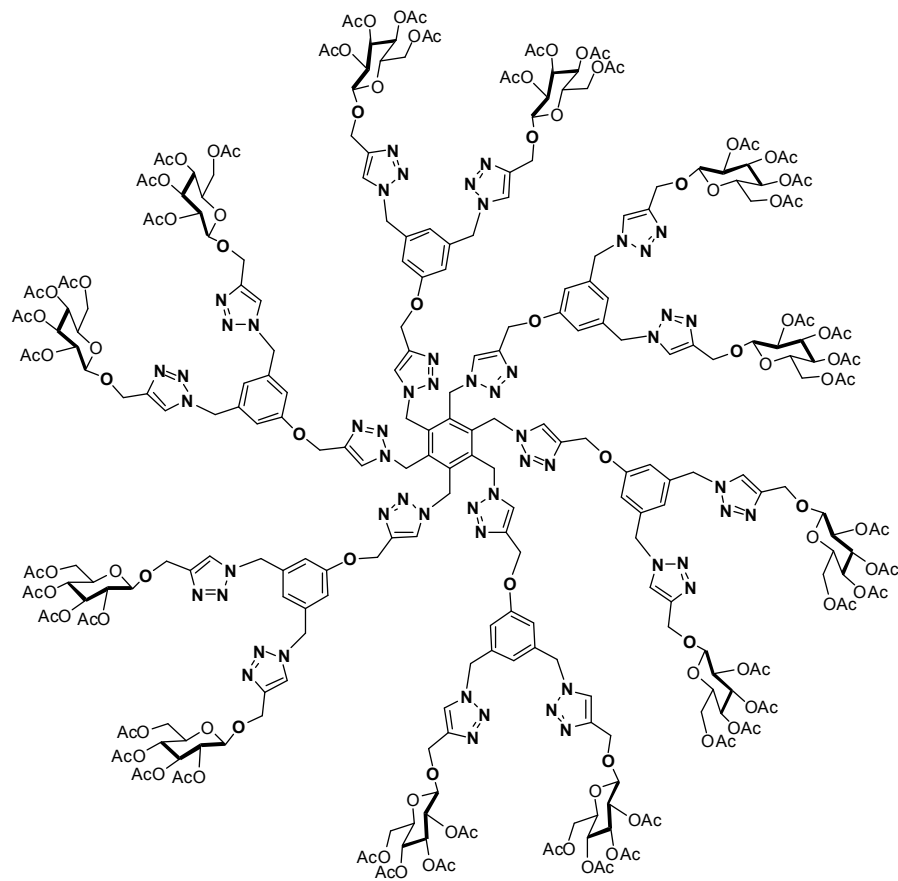
During recent times, the synthesis and the generation of gold nanoparticles stabilised or encapsulated by Dendrimers¹ as capping agent happens to be a challenge and of great interest in the field of biomedical, nanoelectronics, material chemistry and also in nanocatalysis. The AuNp stabilised or encapsulated by glycodendrimer have potential application in many areas such as nanosciences, photophysics, biological sensing, nanomedicine,² nanocatalysis,³ labeling agent,⁴ CT-imaging and therapeutic interventions⁵.

Glycodendrimers have much more applications in the field glyco-nanotechnology, because of their carbohydrate functionality, nanodimensional size, multi-valance, biocompatibility, reduced toxicity, chiral surface for asymmetric induction,⁶ and ability to interact with proteins like lectins via supramolecular interactions, which are useful in nanomedicinal chemistry.⁷ Glycodendrimers can also function as materials with good optical, electronic and magnetic properties. Generally, dendrimers can be utilised for the synthesis of gold nanoparticles under two categories depending on the size of the nanoparticles. In the first type if the size of the gold nanoparticles have an average diameter of 12 nm or more,⁸ they are surrounded by many dendrimer units in which case it is called as dendrimer stabilised nanoparticles (DSNPs). In the second type if the size of the nanoparticles is less than 12 nm, one or more nanoparticle will be trapped or encapsulated by the highly branched three dimensional, monodispersed dendritic architecture, in which case it is called dendrimer encapsulated nanoparticles (DENPs).

In recent years, our research group has reported⁹ the palladium nanoparticles which are either stabilised or encapsulated by the dendrimers of lower generation and higher generation respectively due to the presence of more number of triazole moieties in the higher generation dendrimer. The glycodendrimers can be easily synthesized by click chemistry¹⁰ approach by the ligation of azide to alkyne in the presence of Cu (I) salt to form triazole bridges into the dendrimer. Gold nanoparticles have been used as a catalyst for the oxidation of alcohols,¹¹ and for the reduction of nitrobenzene.¹² Nitrophenols in general are most toxic and hazardous micropollutants. Hence, the degradation of nitrophenols are really challenging from environmental point of view. The present investigation is to synthesis Gold nanoparticle by using glycodendrimer capping agent and to study their catalytic application on the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as a model reaction¹³ and to evaluate the catalytic activity based on stabilisation or encapsulation of the gold nanoparticles

by dendrimers. We report herein the synthesis of dendrimers **1**, **2**, **3** and **4** (Figure 1) which are used for DENp and DSNp of gold and then to study their application as catalyst in the reduction of p-nitrophenol.



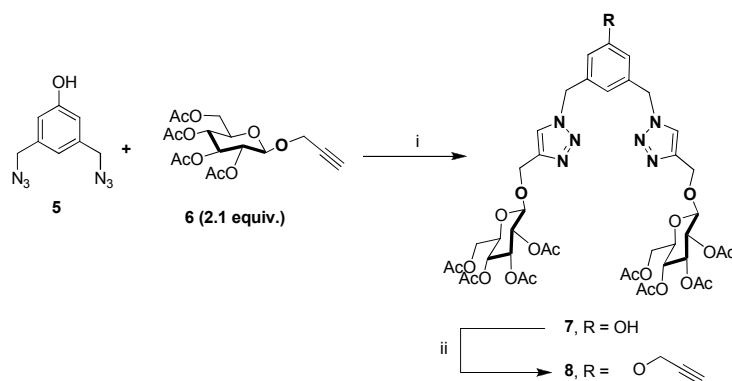


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Fig. 1 The structure of glycodendrimers 1-4.

Results and discussion

Phenolic dendron **7** was synthesized in 86% by the click reaction of 1,3-bis(azidomethyl) phenol **5** with 2.1 equiv. of propargyloxy acetylated glucose **6**. Further, reaction of propargyl bromide with phenolic dendron **7** in the presence of K_2CO_3 in DMF for 8 h gave the alkyne dendron **8** in 72% yield (**Scheme 1**). In 1H -NMR spectrum compound **8** showed a singlet at δ 2.56 ppm for the acetylenic proton, another singlet at δ 5.49 ppm for *N*-methylene protons and the triazole protons also appeared as a singlet at δ 7.52 ppm in addition to the signals of other protons. The ^{13}C NMR spectrum of compound **8** displayed acetylenic carbons at δ 76.6 and δ 77.6 ppm, *N*-methylene carbon at δ 53.6 ppm, *O*-methylene carbon at δ 55.9 ppm and the triazolyl carbon at δ 144.8 ppm. The structure of the alkyne dendron **8** was also confirmed from mass spectrum and elemental analysis.

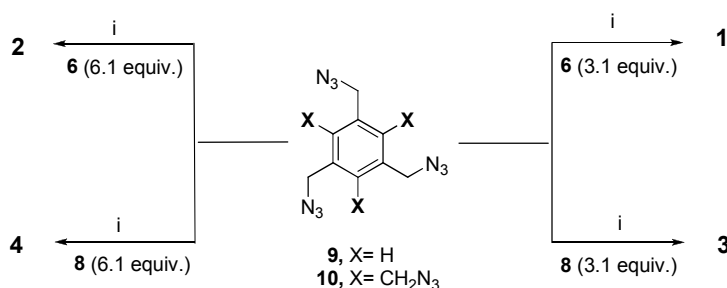


Scheme 1. Reagents and conditions: (i) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5 mol %), sodium ascorbate (10 mol %), H_2O -THF (20 ml, 1:1), rt., 12 h, **7** (86%), (ii) propargyl bromide (1.2 equiv.), K_2CO_3 , DMF, rt, 12 h, **8** (72%).

Zeroth and first generation glycodendrimers **1** and **3** were synthesized in 90 and 92 % yields respectively by the reaction of 1.0 equiv. of 1,3,5-tris(azidomethyl) benzene **9** with 3.1 equiv. of each of the proparglyoxy glucose **6** and the first generation dendron **8** by using Cu (I) catalyzed click chemistry protocol (**Scheme 2**). In ^1H -NMR spectrum the glycodendrimer **1** showed four different singlets at δ 1.93, 1.99, 2.03 and 2.08 ppm for the four different glycoacetoxy protons, sharp singlet at δ 4.36 ppm for the *N*-methylene protons and a sharp singlet at δ 7.52 ppm for triazolyl proton in addition to the signals of other protons. The ^{13}C NMR spectrum of the glycodendrimer **1** displayed the four glycoacetoxy carbons as two signals at δ 20.6, 20.8, *N*-methylene carbon at δ 53.4 ppm and triazolyl carbons at δ 145.0 ppm and four different carbonyl carbons at δ 169.4, 169.5, 170.2 and 170.7 ppm in addition to the signals of other carbons. The structure of the glycodendrimer **1** was further confirmed from analytical data. Similarly, the structure of the glycodendrimer **3** was also confirmed from spectral and analytical data.

The functionalization reaction of 1.0 equiv. of hexakis(azidomethyl)benzene **10** with 6.1 equiv. of each of the proparglyoxy glucose **6** and the first generation alkyne dendron **8** under click chemistry conditions afforded the glycodendrimer **2** and **4** in 81% and 88% yields

respectively. In the $^1\text{H-NMR}$ spectrum the glycodendrimer **4** showed a four different singlets at δ 1.88, 1.96, 2.02 and 2.04 ppm for four different glycoacetoxy protons and two singlets at δ 5.43 and 5.95 ppm for the two different type of *N*-methylene protons and two sharp singlets at δ 7.65 and 7.73 ppm for two different triazolyl protons in addition to the signals for other protons. The ^{13}C NMR spectrum of the glycodendrimer **4** displayed four different glycoacetoxy carbons at δ 22.6, 29.7, 31.9 and 33.8, two different type of *N*-methylene carbons at δ 53.4 and 53.5 ppm, two different triazolyl carbons at δ 143.5 and 144.5 ppm and four different carbonyl carbons at δ 169.5, 170.1 and 170.7 ppm in addition to the signals of other carbons. The structure of the glycodendrimer **4** was also confirmed from mass spectrum and analytical data. Similarly, the structure of the Glycodendrimer **2** was also confirmed from spectral and analytical data.



Scheme 2. Reagents and conditions: (i) CuSO_4 (5 mol %), sodium ascorbate (10 mol %), $\text{H}_2\text{O-THF}$ (20 ml, 1:1), rt., 12 h, **1** (90%), **2** (81%), **3** (92%) and **4** (88%).

Characterization of dendrimer stabilized AuNPs by UV-Vis spectroscopy and HRTEM.

The glycoendrimers **1**, **2**, **3** and **4** are used to stabilize or encapsulate the Au nanoparticles, as confirmed by UV-Vis spectroscopy and High-resolution transmission electron microscopy (HRTEM). The UV-vis spectrum shows that the glycodendrimers **1** and **2** stabilizes the Au nanoparticle as shown by the broad absorption band to confirm the formation of dendrimer stabilised gold nanoparticles with a surface plasmon resonance (SPR)

peak at 528 nm. Dendrimers **3** and **4** shows a sharp absorption peak at 522 nm and the dendrimers **3** and **4** show a blue shift confirming the effective reduction of the size of nanoparticles with a decrease in particle size of less than 4.5 nm. Generally a characteristic hypsochromic shifting of the UV-Vis peak from 544 nm to 515 nm is observed during the decrease in the size of the nanoparticles.¹⁴ The dendrimer generations influences the stabilization or encapsulation of the gold nanoparticles. The DSAuNPs are formed by zeroth generation dendrimers **1** and **2** when the gold nanoparticles are produced in the presence of dendrimer **1** and **2**, the nanoparticles are bigger in size and hence surrounded by one or more number of dendrimer which results in stabilisation and the dendrimers cannot encapsulate the AuNps. Hence in the presence of zeroth generation dendrimer **1** and **2** interdendrimer-stabilized AuNps are surrounded by several number of zeroth generation dendrimers.¹⁵ The mechanism of gold nanoparticle formation was added in the supporting information (ESI). However in the presence of dendrimer **3** and **4** DEAuNPs are produced. The gold nanoparticles produced under such conditions are smaller in size due to encapsulation.

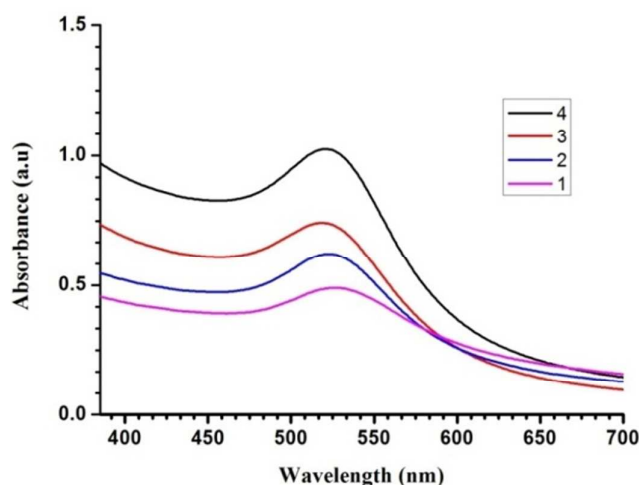


Fig. 2 UV-Vis spectra of dendrimer **1** and **2** (stabilized) and dendrimer **3** and **4** (encapsulated).

Thus the dendrimers **1** and **2** stabilise the gold nanoparticles due to the formation of interdendrimer-stabilized AuNps and the gold nanoparticles are surrounded by the several number of zeroth generation dendrimers and the average size of the nanoparticle size is 8.54 ± 0.14 and 5.83 ± 0.6 nm in the presence of dendrimer **1** and **2** respectively. However, the higher generation dendrimers **3** and **4** encapsulate the Au nanoparticles due to increase in the number of triazole units in the dendrimer system and hence, the nanoparticle size is reduced to a greater extent due to the formation of intradendrimer-encapsulated AuNPs. The average sizes of the AuNps are found to be 4.29 ± 0.7 and 3.7 ± 0.4 nm in the presence of dendrimer **3** and **4** respectively. The particle distribution curve and HRTEM images are shown in Fig. 4. The HRTEM image explains the formation of the gold nanoparticle in smaller size due to the encapsulation of the nanoparticles by the higher generation dendrimer and the nanoparticles in larger size due to the stabilisation of the gold nanoparticles by the dendrimers.

Reduction of 4-Nitrophenol (1 equiv.) with NaBH_4 (100 equiv.) to give 4-aminophenol (4AP) in water in the presence of DSNpAu catalysts **1**, **2**, **3** and **4** was monitored by UV-vis spectroscopy. After adding NaBH_4 , the color of the solution changes from light yellow to dark yellow due to the formation of the 4-nitrophenolate anion. Then, the solution loses its dark yellow colour with the time after addition of DSNpAu catalysts **1**, **2**, **3** and **4**. The disappearance of the strong absorption band at λ_{max} 405 nm and the appearance of new band at 300 nm corresponds to the formation of 4-aminophenol (**Scheme 3**). The catalytic reduction was analyzed by a first-order rate law due to the fact that an excess of NaBH_4 was used. The catalytic activities of gold nanoparticles in the reduction of 4-nitrophenol to 4-aminophenol is discussed with the help of the Langmuir - Hinshelwood (LH) model.¹⁶

All the AuNps stabilised and encapsulated glycodendrimers **1-4** showed their catalytic activity as carried out by UV-vis spectra and shown in figure **3a** for dendrimer **1** and for the

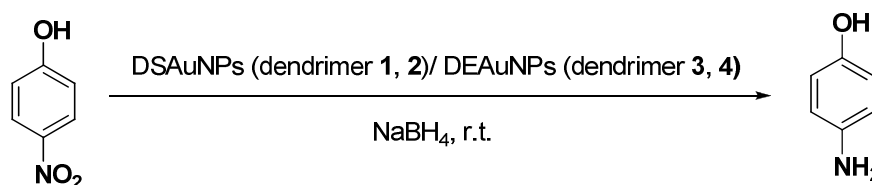
other dendrimers **2**, **3** and **4** catalytic activity was shown in ESI (Electronic supporting informations). The catalytic activity increased on increasing the dendrimer generation. The rate constant k is higher when dendrimer **4** is used as catalyst as shown in Table.1 and the rate constant plot for the catalysis of the glycodendrimer **1** is shown in figure **5a** and the catalytic activity of the other dendrimers are shown in ESI as figure **5b**, **5c** and **5d**.

The reaction of 4NP (4-nitrophenol) to 4AP (4-aminophenol) failed when AuNPs and NaBH₄ are used which shows that for the reduction to proceed successfully dendrimer stabilised nanoparticles (DSNPs) or dendrimer encapsulated nanoparticles (DENPs) are essential. In fact the failure of the reduction is inferred from UV-vis spectroscopy which shows no reduction of the optical density of 4NP at the λ_{max} of 405 nm. However, Schmitzer et al ¹⁷ have shown that the glycodendrimers without AuNPs can catalyze the reduction of cyclohexylphenyl ketone to the corresponding alcohol in poor yield. Hence, AuNPs stabilized or encapsulated by glycodendrimers having one or two or three triazolyl bridge which is essential for the reduction of 4NP to 4AP. During stabilisation due to van der Waals forces and dipole-dipole interactions two or three zeroth generation dendrimers form agglomeration with the help of acetoxy units of glucose and stabilises the gold nanoparticles. The glucose and triazole units in the dendrimer help to form the interdendrimer entities which stabilises the gold nanoparticles. However in the higher generation dendrimers the acetoxy groups of glucose as well as the triazole unit encapsulate the gold nanoparticles and hence the presence of triazole and acetoxy glucose units are essential for this phenomenon to be observed.

It is reported in the literature¹⁸ that glycodendrimer (Table 1, entry 5) with triazolyl bridge unit catalysed the reduction of 4NP to 4AP with a rate constant of 2.4 in the presence of 10 mole% AuNPs. Similarly the reaction rate constants for the reduction of 4NP to 4AP in the presence of G₂ PAMMAM dendrimer¹⁸ (G₂-PAMAM-NH₂) and G₂ Polypropyleneimine dendrimer (G₂-PPI) are also found to be very low¹⁸. G₀ dendrimers **1** and **2** offers

stabilisation of the gold nanoparticles and hence the rate constant for the reduction of 4NP to 4AP is higher when compared to the reduction catalysed by G₀ glycodendrimer (Table 1, entry 5) or G₂ PAMMAM dendrimer (Table 1, entry 6) or G₂-PPI dendrimer (Table 1, entry 7).¹⁸ However the rate constant for the reduction of 4NP to 4AP is higher when G₁ dendrimers **3** and **4** are used as catalyst and the increased catalytic activity is due to the encapsulation of the gold nanoparticles by dendrimer **3** and **4**. Probably the size of the gold nanoparticle is smaller which results in increased surface area when dendrimer **3** and **4** are used for the synthesis of gold nanoparticles and hence the catalytic activity is higher.

Table 1 shows the comparison of rate constants for the reduction of 4NP to 4AP in the presence of dendrimer **1**, **2**, **3** and **4** and the lesser activity as reported¹⁸ with G₀ glycodendrimer, G₂ PAMMAM dendrimer and G₂-PPI dendrimer when used as a catalyst.



Scheme 3. Reduction of 4-NP to 4-AP by NaBH₄ in the presence of glycodendrimer-stabilised/encapsulated AuNPs as catalyst.

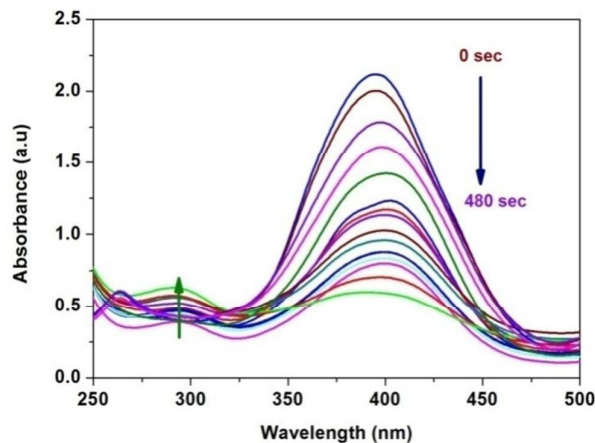


Fig. 3a. Successive spectra monitoring the reduction of 4-NP (0.1mol) in the presence of AuDENs (10 mol-%) stabilized by glycodendrimer **1**.

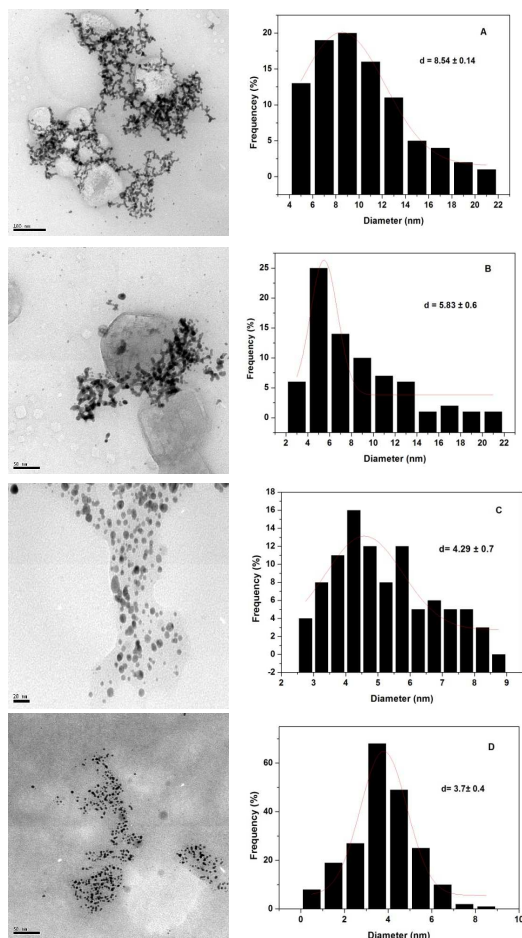


Fig. 4 HRTEM image of (A and B) dendrimer **1** and **2** stabilized, (C and D) dendrimer **3** and **4** encapsulated.

Table 1. Comparison with selected results from the literature obtained with AuNPs stabilized by dendrimer.

Entry No	Dendrimer systems	Mol -% AuNPs	[4-NP] [10 ⁻⁴ m]	NaBH ₄ [equiv.]	<i>K</i> [10 ⁻³ s ⁻¹]
1	DSN-1 (G0)	10	1	100	3.0
2	DSN-2 (G0)	10	1	100	5.9
3	DEN-3 (G1)	10	1	100	9.7
4	DEN-4 (G1)	10	1	100	9.9
5	G0-Glyco	10	1	100	2.4 ¹⁸
6	G2-PAMAM-NH₂	10	1	100	1.74 ¹⁸
7	G2-PPI	10	1	100	1.23 ¹⁸

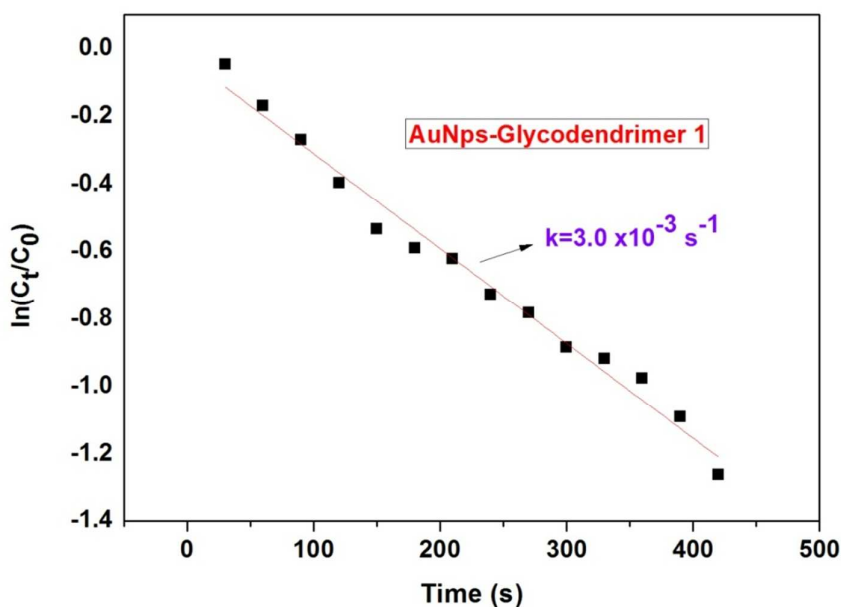


Figure 5a. Plot of $\ln(C_t/C_0)$ as a function of time for the reduction of 4-NP (1×10^{-4} M) in the presence of AuDSNps (10 mol-%) stabilized by glycodendrimer **1**.

Experimental

All reagents were commercially available and used as such unless otherwise stated. Analytical TLC was performed on commercial Merck plates coated with Silica Gel GF254. Analytical samples were obtained from silica gel chromatography, using silica gel of 100-200 mesh and elution with the solvent system as mentioned under each experiment section. The melting points were determined by using a Metler Toledo melting point apparatus by open capillary tube method and were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz BRUKER AVANCE (75 MHz for ^{13}C NMR,) spectrometer. All chemical shifts values are reported in δ ppm relative to internal standard tetramethylsilane (TMS, δ 0.00). ^{13}C chemical shifts (ppm) are reported in δ relative to CDCl_3 (center of triplet, δ 77.23). The spin multiplicities are indicated by the symbols s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad), dd (doublet of doublets). The coupling constants J , are reported in

Hertz (Hz). UV-Vis absorption spectra were measured with a Perkin–Elmer Lambda 35 UV-vis spectrometer.

Procedure for the Preparation of AuNPs

Au nanoparticles are prepared in situ by the reduction of Au^{3+} using NaBH_4 . In the reaction mixture the Au^{3+} ions are protected well with the triazoles present in the dendrimer with CHCl_3 and MeOH mixture, and by adding NaBH_4 to the reaction mixture, Au^{3+} ions are reduced to Au^0 nanoparticles with a significant color change from yellow to wine red (pink), which was monitored by UV-Vis spectroscopy.

General Procedure for the Reduction of 4-NP:

4-NP (1 equiv.) was mixed with NaBH_4 (100 equiv.) in water under air, then the solution containing the freshly prepared AuNPs was added. After adding NaBH_4 , the solution changed from light yellow to dark yellow owing to the formation of the 4-nitrophenolate ion. Then, this solution loses its dark yellow color with time after addition of AuNPs. The reaction was monitored by UV-Vis spectroscopy.

General procedure for the Cu-Catalyzed Huisgen‘Click reaction’

A mixture of azide (1.0 mmol, 1.0 equiv.), alkyne (3.0 mmol, 3.0 equiv. /6.0 mmol, 6.0 equiv.), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5 mol %) and NaAsc. (10 mol %) in THF- H_2O (1:1, 20 mL) mixture was stirred for 12 h at room temperature. The residue obtained after evaporation of the solvent was dissolved in CHCl_3 (150 mL) and washed with NH_4Cl solution (50 mL) and brine solution (50 mL) and dried over Na_2SO_4 and then concentrated to give a residue, which was purified by column chromatography (SiO_2), using the eluent as mentioned under each compound.

First generation OH Dendron 7

The reaction of 1,3-bis(azidomethyl) phenol **5** (1.0 mmol, 1 equiv.) and propargylated D-glucose **6** (2.0 mmol, 2.1 equiv.) using the general procedure for click chemistry afforded the first generation phenolic dendron **7** as a white solid; yield: 86%; ^1H NMR (300 MHz, CDCl_3) δ_{H} 1.92, 1.99, 2.03, 2.07 (4xs, 24 H), 3.73-3.76 (m, 2H), 4.12-4.26 (m, 4H), 4.67-4.81 (m, 4H), 4.89-4.99 (m, 4H), 5.05-5.11 (m, 2H), 5.27-5.23 (m, 2H), 5.43 (s, 4H), 6.65 (s, 3H), 7.67 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.6, 20.7, 53.8, 61.8, 62.9, 68.3, 71.3, 71.9, 72.7, 100.1, 115.3, 118.3, 123.4, 137.1, 144.6, 158.6, 169.5, 169.6, 170.2, 170.8 ppm. MS(EI): m/z 976 (M^+). Elemental Anal. Calcd for $\text{C}_{42}\text{H}_{52}\text{N}_6\text{O}_{21}$: C, 51.64; H, 5.37; N, 8.60; O, 34.39%. Found: C, 51.34; H, 5.47; N, 8.70; O, 34.19%.

First generation alkyne dendron **8**

The first generation phenolic dendron **7** was reacted with 1.2 equiv. of propargyl bromide in the presence of K_2CO_3 in dry DMF for 12h to afford the alkyne dendron **8** as a white powder in 86% yield. ^1H NMR (300 MHz, CDCl_3) δ_{H} 1.93, 1.99, 2.03, 2.08 (4xs, 24 H), 2.56 (s, 1H), 3.73-3.76 (m, 2H), 4.12-4.28 (m, 4H), 4.66-4.69 (m, 6H), 4.79-5.24 (m, 10H), 5.49 (s, 4H), 6.82 (s, 3H), 7.52 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.6, 20.7, 53.6, 55.9, 61.8, 63.4, 68.4, 71.3, 72.74, 76.6, 77.6, 100.0, 114.8, 120.2, 122.9, 137.2, 144.8, 158.5, 169.3, 169.4, 170.2, 170.6 ppm. MS(EI): m/z 1014 (M^+). Elemental Anal. Calcd for $\text{C}_{45}\text{H}_{54}\text{N}_6\text{O}_{21}$: C, 53.25; H, 5.36; N, 8.28; O, 33.10%. Found: C, 53.45; H, 5.66; N, 8.18; O, 33.30%

Glycodendrimer **1**

Glycodendrimer **1** was synthesized as a colourless solid from 1,3,5-tris(azidomethyl)benzene **9** (1.0 mmol, 1.0 equiv.) with alkynated D-glucose **6** (3.0 mmol, 3.1 equiv.) by using the click chemistry; yield: 90%; mp.: 81-83 °C; R_f = 0.46 (CHCl_3 :Methanol,

49:1); ^1H NMR (300 MHz, CDCl_3) δ_{H} 1.93, 1.99, 2.03, 2.08 (4xs, 36H), 3.73-3.76(m, 3H), 4.13-4.29 (m, 6H), 4.36 (s, 6H), 4.66-4.69 (m, 3H), 4.79-4.84(m, 3H), 4.92-5.24 (m, 12H), 5.53 (s, 6H), 7.19 (s, 3H), 7.52 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 20.6, 20.8, 53.5, 61.8, 63.1, 68.3, 71.3, 71.9, 72.7, 100.1, 122.9, 127.6, 138.1, 144.9, 169.5, 170.2 ppm. MS(EI): m/z 1402 (M^+). Elemental Anal. Calcd for $\text{C}_{60}\text{H}_{75}\text{Fe}_3\text{N}_9\text{O}_{30}$: C, 51.39; H, 5.39; N, 8.99; O, 34.23%. Found: C, 51.69; H, 5.29; N, 8.89; O, 34.63

Glycodendrimer 2

Glycodendrimer **2** was synthesized as a pale pink colour solid from hexakis(bromomethyl) benzene **10** (1.0 mmol, 1.0 equiv.), alkynated D-glucose **6** (6.0 mmol, 6.0 equiv.) by using click chemistry; yield: 81%; mp.: 98-100 °C; R_f = 0.54 (CHCl_3 :Methanol, 19:1); ^1H NMR (300 MHz, CDCl_3): δ_{H} 2.01, 2.03, 2.05 (3xs, 72 H), 3.74 (m, 6H), 4.19 (m, 12H), 4.65-5.25 (m, 36H), 5.84 (s, 12H), 7.55 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 20.6, 20.7, 20.8, 29.6, 48.0, 61.7, 63.1, 68.3, 71.2, 71.9, 72.7, 100.4, 123.6, 137.5, 144.8, 169.4, 169.5, 170.2, 170.8 ppm. MS(EI): m/z 2726 (M^+). Elemental Anal. Calcd for $\text{C}_{114}\text{H}_{114}\text{N}_{18}\text{O}_{60}$: C, 50.22; H, 5.32; N, 9.25; O, 35.21%. Found: C, 50.12; H, 5.52; N, 9.15; O, 35.51%.

Glycode ndrimer 3

Glycodendrimer **3** was synthesized from 1,3,5-tris(azidomethyl)benzene **9** (1.0 mmol, 1.0 equiv.) with first generation alkyne dendron **8** (3.0 mmol, 3.0 equiv.) using click chemistry to obtained a dust white solid; yield: 92%; R_f = 0.51 (CHCl_3 : Methanol, 95.5:4.5); mp. 112-114 °C; ^1H NMR (300 MHz, CDCl_3) δ 4.11-4.21 (m, 54H), 4.36 (s, 12H), 4.58 (s, 12H), 5.10 (s, 6H), 5.36 (s, 18H), 6.72 (s, 3H), 6.76 (s, 6H) 7.11 (s, 3H) 7.43 (s, 6H), 7.54 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ_{C} 20.5, 20.7, 29.6, 53.3, 53.5, 61.8, 63.0, 68.4, 71.3,

71.9, 72.7, 100.1, 114.6, 119.9, 123.3, 123.5, 127.8, 136.9, 137.4, 143.6, 144.6, 159.1, 169.4, 169.1, 170.1, 170.6 ppm. MS(EI): m/z 3286 (M^+). Elemental Anal. Calcd for $C_{144}H_{171}N_{27}O_{63}$: C, 52.60; H, 5.24; N, 11.50; O, 30.66%. Found: C, 52.50; H, 5.14; N, 11.70; O, 30.36 %.

Glycodendrimer 4

Glycodendrimer **4** was synthesized from hexakis(bromomethyl) benzene **10** (1.0 mmol, 1.0 equiv.) with first generation alkyne dendron **8** (3.0 mmol, 3.0 equiv.) using click chemistry to give pale pink solid; yield: 91%; R_f = 0.42 ($CHCl_3$: Methanol, 49:1); mp. 120-122 °C; 1H NMR (300 MHz, $CDCl_3$) δ_H 1.88, 1.96, 2.02, 2.04 (4xs, 144H), 3.78 (d, 12H, J = 2.6 Hz), 4.07-4.26 (m, 24H), 4.69-5.23 (m, 72H), 5.43 (s, 36H), 5.95 (s, 12H), 6.73 (s, 6H), 6.78 (s, 12H), 7.65 (s, 12H), 7.73 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 22.6, 29.7, 31.9, 33.8, 53.5, 61.8, 62.9, 68.4, 71.2, 71.9, 72.7, 100.0, 114.0, 114.7, 123.6, 137.4, 139.3, 143.5, 144.5, 158.9, 169.5, 170.1, 170.7 ppm. MS(EI): m/z 6494 (M^+). Elemental Anal. Calcd for $C_{282}H_{336}N_{54}O_{126}$: C, 52.12; H, 5.21; N, 11.64; O, 31.02%. Found: C, 52.32; H, 5.41; N, 11.34; O, 31.22%.

Conclusion

In conclusion, the glycodendrimers **1**, **2** **3** and **4** were successfully synthesized in excellent yield by Cu(I) catalysed click reaction and the glycodendrimers are used to synthesize the gold nanoparticles, the dendrimers **1** and **2** stabilizes the gold nanoparticles and higher generation glycodendrimers **3** and **4** encapsulates the gold nanoparticles into the interior side of the dendrimer. Glycodendrimers stabilised or encapsulated gold nanoparticles are used to reduce the 4-nitrophenol into 4-amino phenol successfully, which is important in controlling the environmental pollutant. Dendrimer stabilised and encapsulated gold nanoparticles have excellent catalytic activity and the bioactivity of such glyco-gold nanoparticles are underway.

Supporting Information

see footnote on the first page of this article): UV/Vis spectra of the reduction of 4-nitrophenol by AuNPs stabilized and encapsulated by glycodendrimers and the corresponding plots of $\ln(C_t/C_0)$ as a function of the time can be found in the Supporting Information.

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