# Synthesis and Optical, Electrochemical Properties of Glucose Cored Ferrocenyl Dendrimers

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# Abstract

Triazole based ferrocenyl glycoconjugates **1**, **2** and **3** were synthesized by regiospecific copper (I) catalyzed azide–alkyne cycloaddition (CuAAC) of azidoferrocenyl derivatives with glucose pentaacetylide. Higher generation ferrocenyl glycoconjugates form the stable ferrocenium cation and exhibit increased light harvesting property as revealed from CV studies and UV-Vis spectrum respectively due to the presence of more number of ferrocenyl and triazolyl units, then the lower generation dendrimer.



**KEYWORDS:** Glucose, ferrocene, Click Chemistry, dendrimer and cyclic voltammogram

# **INTRODUCTION**

Ferrocenyl dendrimers<sup>1</sup> play important role in the field of synthetic, material and biological chemistry. Ferrocenyl units mainly play an important role in electron-transfer reaction, which is involved in many living systems as well as in synthetic chemistry as multi-redox nanosystems, especially in polymers,<sup>2</sup> dendrimers,<sup>3</sup> nanoparticles,<sup>4</sup> vectors,<sup>5</sup> biosensors,<sup>6</sup> biological redox processes,<sup>7</sup> molecular conductors and semiconductors,<sup>8</sup> mixed-valence stabilizers,<sup>9</sup> catalysis,<sup>10</sup> redox recognition<sup>11</sup> as redox reagents,<sup>12</sup> redox catalysts,<sup>13</sup> electron transfer catalysts,<sup>14</sup> redox sensors,<sup>15</sup> and as green catalysts.<sup>16</sup> Among all the redox systems, the ferrocenyl dendritic framework becomes important due to  $Fe^{2+}$ and Fe<sup>3+</sup> reversible system. Generally, carbohydrates play an important role in living system because of their interaction with the cell-surface protein which is vital for the explanation of many biological activities, such as viral and bacterial infections, cell-cell adhesion, inflammatory and immune response, fertilisation and cancer metastasis.<sup>17</sup> Generally, carbohydrate-protein interactions are detected based on labelled proteins or carbohydrates with a fluorescent or biotin moiety, so that the recognition event induces a measurable signal.<sup>18</sup> The ferrocenyl glycoconjugates are used as electrochemical biosensor for concanavalin A  $(Con A)^{19}$  through the electro active ferrocenyl ring and multivalent carbohydrate interacts with protein. In few cases, the biosensors are recognized from carbohydrates attached with electroactive moieties such as ferrocene. This triggers electrochemical signals upon binding with the complementary

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supramolecular partner such as lectin.<sup>20</sup> Ferrocenyl-carbohydrate bioconjugates<sup>21</sup> have enormous applications in biology such as anti-tumor,<sup>22</sup> anti-inflammatory,<sup>23</sup> cytotoxic and DNA cleaving-activity towards cancer cells,<sup>24</sup> antimicrobial and anti-malarial activities,<sup>25</sup> and glycoferrocenyl hybrid molecule has been also used as electrochemical probes.<sup>26</sup>

The regiospecific copper (I) catalyzed azide–alkyne cycloaddition (CuAAC), known as click chemistry is mainly used for the synthesis of triazolyl bridged ferrocenyl dendrimers.<sup>27</sup> Triazole nucleus is an ideal choice for its interaction with many anions and transition metals. Thus, the introduction of triazole unit in dendrimers would rather enable the encapsulation of guest molecules. During recent years, we have reported the synthesis and properties of glycodendrimers,<sup>28a,b</sup> carbazole dendrimers,<sup>28c</sup> *m*-terphenyl dendrimers,<sup>28d</sup> phenothiozine thethered dendrimers,<sup>28e</sup> quinoline dendrimers,<sup>28f</sup> benzothiazole dendrimers,<sup>28g</sup> pyrene dendrimers<sup>28h</sup> and chalcone linked dendrimers.<sup>28i</sup> Particularly, synthesis and photophysical, electrochemical properties of 1,2,3-triazolyl bridged ferrocenyl dendrimers reveal that they are used for sensing H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Pd<sup>2+</sup> ion and also exhibit encapsulation of gold nanoparticles.<sup>29</sup> The present investigation mainly deals with synthesis and optical, electrochemical properties of novel ferrocenyl sugar hybrid dendrimers **1**, **2** and **3** (Fig. 1) using click chemistry.

#### **RESULTS AND DISCUSSION**

Reaction of 3,5-bis(propargyloxy)benzyl chloride **5** with 2.1 equiv. of the ferrocenyl azide **4** under Cu(I)-catalyzed click reaction conditions gave the first generation dendritic chloride **6** in 92% yield, which on further treatment with NaN<sub>3</sub> in a mixture of acetone-

water (4:1) at 60 °C gave the dendritic azide **7** in 96% yield. The second generation dendritic azide **9** was obtained by a similar way by the repeting the above reaction sequence namely Cu(I)-catalyzed click reaction. Reaction of 1.0 equiv. of 3,5-bispropargyloxy benzyl chloride **5** with 2.1 equiv. of the azidodendron **7** under click reaction conditions gave the dendritic chloride **8** in 83% yield, which was further converted into the dendritic azide **9** in 85% yield using NaN<sub>3</sub> in a mixture of acetone-water (4:1) at 60 °C (Scheme 1).

The <sup>1</sup>H NMR spectrum of the dendritic azide **9** displayed three different singlets at  $\delta$  4.16, 4.21 and 4.27 for the ferrocenyl protons, two different singlets at  $\delta$  5.06 and 5.28 for the *O*-methylene and *N*-methylene protons, a singlet at  $\delta$  7.51 for triazolyl proton. The <sup>13</sup>C NMR spectrum of the dendritic azide **9** displayed the ferrocenyl carbon at  $\delta$  68.6, 68.8, 68.9 and 69.1, and two different triazolyl carbons at 143.3 and 144.1 respectively. The appearance of molecular ion peak at *m/z* 723 also confirmed the structure of the dendritic azide **9**. Further the constitution of the dendritic azide **9** was confirmed from elemental analysis.

Propargylated D-glucose tetraacetate **10** on treatment with sodium methoxide in MeOH-THF-CHCl<sub>3</sub> (6:1:1) at pH 9-10 for 1 h (Zemplen condition) gave the deacetylated propargyl glucose **11** in 56 % yield, which on further treatment with 4.1 equiv. of propargyl bromide in presence of NaH in DMF at 0 °C for 10 min gave the penta propargylated glucose core **12** in 68% yield (Scheme 2). The <sup>1</sup>H NMR spectrum of pentaacetylide **12** displayed a multiplet at  $\delta$  2.48 for acetylenic protons in addition to other aliphatic protons. The <sup>13</sup>C NMR spectrum of the penta acetylide derivative **12** displayed five *O*-CH<sub>2</sub> carbons at  $\delta$  55.9, 58.6, 59.2, 60.0 and 60.2 in adition to other aliphatic carbons. The appearance of molecular ion peak at *m/z* 393 (M<sup>+</sup>+Na) also confirmed the structure of the pentaacetylide derivative **12**. The constitution of penta acetylide **12** was further confirmed from elemental analysis.

The synthesis of ferrocenyl dendrimers **1**, **2** and **3** is shown in Scheme 2. Reaction of 1.0 equiv. pentapropargylated glucose core **12** with 5.1 equiv. of azidomethyl ferrocene **4**/ ferrocenyldendritic azide **7**/ ferrocenyl dendritic azide **9** under click reaction conditions for 12 h at room temperature, gave the zeroth, first and second generation ferrocenyl dendrimers **1**, **2** and **3** in 89 %, 86% and 81% yields, respectively (Scheme 2).

The <sup>1</sup>H NMR spectrum of the ferrocenyl dendrimer **1** showed three different signals for the ferrocenyl protons at  $\delta$  4.17, 4.28 and 4.31 and five sharp singlets at  $\delta$  7.55, 7.68, 7.75, 7.84 and 7.89 for five different triazolyl protons in addition to the signal for the other aliphatic proton. The <sup>13</sup>C NMR spectrum of **1** showed three different ferrocenyl carbons at  $\delta$  69.1, 69.0, 69.7 and the triazole carbons at  $\delta$  144.3, 144.5, 144.7 and 144.9 in addition to other aliphatic and aromatic carbon signals. The appearance of molecular ion peak at *m*/*z* 1575 [M<sup>+</sup>] also confirmed the structure of the ferrocenyl dendrimer **1**. Further, the constitution of the ferrocenyl dendrimer **1** was confirmed from elemental analysis. In the <sup>1</sup>H NMR spectrum, the ferrocenyl dendrimer **2** should the ferrocenyl protons as a singlet at  $\delta$  4.16 and the triazole protons as another singlet at  $\delta$  7.56 in addition to the signals for the other aliphatic and aromatic protons. In the <sup>13</sup>C NMR spectrum, the ferrocenyl dendrimer **2** displayed the ferrocenyl carbons at  $\delta$  69.0 and 69.2 and the triazole carbon at  $\delta$  143.3 in addition to the signals for the other aliphatic and aromatic carbons. The appearance of molecular ion peak at *m*/*z* 3987[M<sup>+</sup>] also confirmed the structure of the ferrocenyl dendrimer **2**. Further, the structure of the ferrocenyl dendrimer **2** was also confirmed from elemental analysis. The <sup>1</sup>H NMR spectrum of the ferrocenyl dendrimer **3** showed ferrocenyl protons as singlets at  $\delta$  4.13, 4.14, 4.15, 4.20 and 4.28, the triazolyl protons as a singlet at  $\delta$  7.53, 7.58 and 7.71 in addition to the signals for the other aliphatic and aromatic proton. The <sup>13</sup>C NMR spectrum of **3** showed three different ferrocenyl corbons at  $\delta$  68.9, 69.1 and 69.7 and the triazolyl carbons at  $\delta$  143.2 and 143.6 in addition to the signals for other aliphatic and aromatic carbons. The appearance of molecular ion peak at *m*/*z* 8810 [M<sup>+</sup>] also confirmed the structure of the ferrocenyl dendrimer **3**. Further, the constitution of the ferrocenyl dendrimer **3** was confirmed from elemental analysis.

# OPTICAL AND ELECTROCHEMICAL PROPERTIES OF FERROCENYL DENDRIMERS 1, 2 AND 3

# **Optical Studies**

The UV-Vis absorption spectra of all the ferrocenyl dendrimers **1**, **2** and **3** were obtained in DCM (1 X 10<sup>-5</sup> M) and the absorption maxima is listed in Table 1. In the absorption spectra though  $\lambda$ -max remains almost constant between 435 to 438 nm, the absorption intensity of the UV-visible band increases from the dendrimer **1** to **3**. The molar absorptivity coefficient of dendrimer **3** is greater than that of **1** and **2**. When the UV-vis spectrum is recorded for all the dendrimer at the same concentration, dendrimer **3** showed the highest light absorption coefficient value due to the presence of greater number of ferrocenyl and triazolyl units, which is usually called valence effect in dendrimer chemistry.<sup>30</sup> In conclusion, the absorption coefficient increases on increasing of the generation of the dendrimer from **1**, **2** and **3** though  $\lambda$ -max remains almost constant.

# **Electrochemical Studies**

The redox property of the ferrocenyl dendrimers **1**, **2** and **3** was studied using cyclic voltammetry (CV) technique. The cyclic voltammogram for dendrimer **1** to **3** was obtained in the potential range of 0.0 V to 1.0 V at room temperature in  $CH_2Cl_2$  containing 0.1 M TBAP as the supporting electrolyte at the scan rate 50 mV/s (Figure 3). The reversible oxidation potential for the ferrocenyl dendrmer **1**-**3** was observed at 530, 577 and 636 mV and the reversible reduction peak at 425, 356 and 345mV respectively. Thus, in the anodic region single reversible oxidation process corresponding to the generation of ferrocenium cation was observed. Among all the dendrimers, the ferrocenyl dendrimer **3** undergoes electrochemical oxidation much easily than the other dendrimers indicating that the presence of more triazole<sup>31</sup> unit which is responsible for easier oxidation. Similarly on increasing the dendrimer generation from **1** to **3** there is decreases in the redox potential due to the presence of more number of triazolyl units in **3** than in **1** and **2**. The variation of the oxidation and reduction potentials in dendrimers **1**, **2** and **3** could be due to presence of more ferrocenyl units and bridging triazoly units in the higher

generation dendrimer. The Epa and Epc values are shown in Table 1 and the potential difference  $\Delta E$  increases from dendrimer 1 to 3.

The variation of  $\Delta E = Epa-Epc$  values reveals that the dendrimer **3** undergoes anodic oxidation in the usual potential range as similar to that of the other dendrimers, but the ferrocenium cation is relatively stable and hence the cathodic reduction value is less and probably  $\Delta E$  for dendrimer **3** is slightly higher (0.29) than the value of  $\Delta E$  for the dendrimer **1** and **2** ( $\approx$ 0.11 and 0.22). Further the current intensity values obtained for dendrimer **3** (Figure 3) is much greater than that of dendrimer **1** and **2** which shows that the ferrocenyl moieties are placed more closely and hence high current intensity is observed. Further, the increases in the value of  $\Delta E$  on going from dendrimer **1** to **3** indicates that the electrochemical reversibility decreases from **1** to **3**, which further supports the formation of stable ferrocenyl cation for dendrimer **3**. In conclusion, the electrochemical behavior is altered on increasing the number of ferrocenyl and triazole moieties in the dendritic architectures.

#### **EXPERIMENTAL**

# **Materials And Methods**

All reagents were commercially available and used as such unless otherwise stated. Analytical TLC was performed on commercial Merk 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.<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 300 MHz BRUKER AVANCE (75 MHz for <sup>13</sup>C NMR,) spectrometer and Mass spectra (MS) were recorded using Voyager-DE PRO mass spectrometer by either Fast Atom Bombardment or MALDI-TOF technique. UV-Vis absorption spectra were measured with a Perkin–Elmer Lambda 35 UV-vis spectrometer Cyclic voltammetry measurements were performed in a conventional three electrode system on a CHI model 1100A series electrochemical analyzer (CH Instrument, Austin, TX). The measurements were based on a three electrode system, with a glassy carbon (GC) electrode (of geometric area 0.07 cm<sup>2</sup>) being used as the working electrode, a Pt wire in the form of a spiral (with a high geometrical surface area B20 cm<sup>2</sup>) being used as the auxiliary electrode and Ag/AgCl as the reference electrode with a scan rate of 100 mV s<sup>-1</sup>. The supporting electrolyte of 0.1 M TBAP.

# General Procedure For The Cu (I) Catalyzed Click Reaction (Procedure A)

A mixture of acetylenic derivative (1.0 mmol, 1equiv.) and azido derivative (5.1 mmol, 5.1equiv.) was dissolved in THF/H<sub>2</sub>O (1:1; 8 mL) and added sodium ascorbate (0.4 mmol, 0.4 equiv.) followed by the addition of CuSO<sub>4</sub> (0.2 mmol, 0.2 equiv.). The reaction mixture was stirred overnight at room temperature. The solvent was evaporated and the crude product was dissolved with EtOAc (2 X 100 mL), washed with NH<sub>4</sub>Cl solution (50 mL) and brine solution (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give a residue, which was purified by column chromatography (SiO<sub>2</sub>), using the eluent as mentioned under each compound

#### **FERROCENYL DENDRIMER 1**

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Ferrocenyl dendrimer **1** (0.38 g) was obtained as brownish solid from propargyl 2,3,4,6tetra-*O*-propargyl-β-D-glucopyranoside **12** (0.1 g, 0.27 mmol) and azidomethyl ferrocene **4** (0.33 g, 1.4 mmol) under click reaction conditions following the general procedure A. Yield: 89%, MP: 144-146 °C <sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  3.25-3.27 (m, 1H), 3.29-3.31(m, 1H), 4.17, 4.28 (s, 45H, cp), 4.31 (s, 10H) 4.62 (s, 1H), 4.74-4.78 (m, 2H), 4.80-4.87 (m, 2H), 5.25 (s, 10H), 7.55 (s, 1H), 7.68 (s, 1H), 7.75 (s, 1H), 7.84 (s, 1H), 7.89 (s, 1H). <sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  50.0, 68.9, 69.0, 69.7, 81.4, 84.0, 122.5, 123.0, 123.1, 123.2, 123.4, 141.0, 144.3, 144.5, 144.7, 144.9, 145.4, 147.9. MS (ES): *m/z* = 1575 [M<sup>+</sup>]. Elemental Anal. Calcd for C<sub>76</sub>H<sub>77</sub>Fe<sub>5</sub>N<sub>15</sub>O<sub>6</sub>: C, 57.93, H, 4.93, N, 13.33%. Found: C, 57.86, H, 4.88, N, 13.26%.

# CONCLUSION

In conclusion, glycoferrocenyl conjugated dendrimers **1**, **2** and **3** with triazole as the bridging unit has been obtained through click chemistry in excellent yield. The presence of more triazolyl and ferrocenyl units increases the light absorbing capacity of the dendrimer. The electrochemical behaviour of the ferrocenyl-sugar conjugated dendrimers also indicate that the presence of a greater number of ferrocenyl and triazolyl units increases the current potential in the cyclic voltammogram curve and all the ferrocenyl dendrimers shows oxidation–reduction curve. Applications of such dendrimer for the synthesis of nanoparticles of transition metals such as Au, Pd and Ag are underway.

#### SUPPORTING INFORMATION

The full experimental part, <sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass spectra details are present in the electronic supporting information (ESI).

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Table 1. Optical and electrochemical parameters of ferrocenyl dendrimers 1, 2 and 3 in DCM (1 X  $10^{-5}$  M). Ferrocenyl dendrimers 1, 2 and 3 are almost identical and exhibit an intense absorption band at 435-438 nm (Figure 2).

Dendrimers	$\lambda_{abs}$	Optical	Molar absorptivity	Epc	E <sub>pa</sub>	E <sub>1/2</sub>	$\Delta E =$
	max	density	coefficient ( $\epsilon$ ) L mol <sup>-1</sup>				Epa-
	(nm)		cm <sup>-1</sup> )				Ерс
1	438	0.06	6000	0.42	0.53	0.47	0.11
2	437	0.13	13000	0.36	0.58	0.47	0.22
3	435	0.25	25000	0.35	0.64	0.49	0.29

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Scheme 1. Reagents and conditions: (i) CuSO<sub>4</sub> (5 mol%), sodium ascorbate (10 mol%), H<sub>2</sub>O/THF (1:1), rt, 12 h, **6** (92%), **8** (83%) (ii) 1.5 equiv. NaN<sub>3</sub>, CH<sub>3</sub>COCH<sub>3</sub>/H<sub>2</sub>O, 60 °C, 1-3 h, **7** (96%), **9** (85%).



Scheme 2. Reagents and conditions: (i) NaOMe (0.1N), MeOH/CH<sub>2</sub>Cl<sub>2</sub>/THF (6:1:1), **11** (56%). (ii) 4.1 equiv of Propargyl bromide, NaH, anhydrous THF, N<sub>2</sub> for 24 h. **12** (68 %). (iii) 5.1 equiv. of **4**/**7**/**9**, CuSO<sub>4</sub> (5 mol%), sodium ascorbate (10 mol%), H<sub>2</sub>O/THF (1:1), rt, 12 h, **1** (89%), **2** (86%) and **3** (81%).



Figure 1. Structure of the ferrocenyl dendrimers 1, 2 and 3



Figure 2. UV-Vis absorption spectra of ferrocenyl dendrimers 1, 2 and 3 in DCM (1 X  $10^{-5}$  M) at room temperature.



Figure 3. Cyclic votammogram of ferrocenyldendrimers **1**, **2** and **3** in DCM at room temperature. (scan rate at 50 mV s-1) and 0.1 m tetrabutylammonium perchlorate as a supporting electrolyte in dry DCM.

