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Synthesis, optical, electrochemical, and thermal studies on triazole-based dendrimers with diphenylamine as surface group

Perumal Rajakumar *, Chinnadurai Satheeshkumar, Sebastian Raja

Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India

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ABSTRACT

Fréchet-type dendrimers with hole-transporting diphenylamine as surface group and electron-transporting triazole moiety as building block have been synthesized by convergent synthetic strategy through 'click chemistry' methodology. First generation dendrimer exhibits longer relaxation time, higher quantum yield in the fluorescence spectrum, and better thermal stability than the zero and second generation dendrimers. CV studies showed irreversible reduction potential and the formation of radical cation due to diphenylamine moiety.

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Synthetic aspects of dendrimers with unique physical and chemical properties are receiving high momentum during recent times.[1–3] Dendritic molecules with varied functionalities allow their use in diverse applications including light harvesting,[4] drug delivery,[5] biomedical,[6] catalysis,[7] and material applications.[8] Click chemistry[9,10] refers to the facile, efficient, selective, and versatile chemical transformation to synthesize triazole system through copper(I)-catalyzed addition of azide to alkyne (CuAAC).[11] The synthesis of dendrimers through click chemistry offers three advantages (i) azides and alkynes are clicked together and no protection and deprotection protocols are needed, (ii) 1,2,3-triazole moiety is a good ligand for metal ions and also a proton transport facilitator and, (iii) gives high yield of the dendrimers with stereoselectivity on the triazole branching unit. Recently, click chemistry[12] approach has been used for the synthesis of dendrimers[13] with chalcone and carbohydrate moiety at the periphery.

Diphenyalamine-based dendrimers play an indispensable role in the field of organic light emitting devices (OLEDs),[14] field effect transistors (FET_S)[15], and dye-sensitized solar cells (DSSCs).[16,17] Diphenylamine derivatives have been used for the synthesis of materials for electroluminescence,[18] liquid crystalline,[19] electrolyte additive,[20] and for biological applications.[21] Incorporation of triazole unit into diphenylamine-based dendrimer system would alter the physico-chemical behaviors and also would find applications in the field of material science and biology.[22]

In continuation of our studies on dendrimers, we have investigated the photophysical, electrochemical, and thermal properties of diphenylamine-based triazole dendrimer **1**, **2,** and **3** (Fig. 1). The dendrimers were obtained by a simple convergent route via click chemistry.

Dendrimers **1**, **2,** and **3** have diphenylamine as surface group and hence can loose an electron easily and can generate the hole. By cascade process the triazole branching units can transfer one of their electrons to the hole of the diphenylamine group and hence the whole molecule can function as hole-transporting system. Dendrons **5**, **9,** and **11** were synthesized in good yields as shown in Schemes 1–3. The reaction of 1.0 equiv of diphenylamine **4** with 1.25 equiv of propargyl bromide in the presence of NaH in dry DMF for 4 h afforded the dendron **5**[23] in 68% yield (Scheme 1).

In order to synthesize the first generation alkyne-dendron **9**, 3,5-bis(azidomethyl)phenol **7** was used as a building block, which in turn was obtained in 74% yield by the treatment of 1.0 equiv of 3,5-bis(bromomethyl)phenyl acetate **6**[24] with 2.1 equiv of NaN_3 in DMF at room temperature for 48 h followed by deacylation using ethanolic KOH at reflux for 2 h. The structure of the compound **7** was characterized from spectral and analytical data.

The reaction of the bisazide **7** with acetylenic-dendron **5** under click reaction conditions gave the dendron **8** in 79% yield. The hydroxyl dendron **8** was also characterized from IR, ^1H NMR, ^{13}C NMR, and EI-MS spectra. Further, the hydroxyl dendron **8** undergoes O-alkylation with propargyl bromide in the presence of K_2CO_3 in DMF at 60 °C to afford first generation acetylenic-dendron **9**[25] in 82% yield (Scheme 2). The absorption band at 3259 cm^{-1} in

* Corresponding author. Tel.: +91 44 22202810; fax: +91 44 22300488.
E-mail address: perumalrajakumar@gmail.com (P. Rajakumar).

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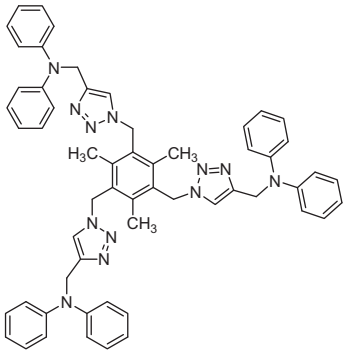

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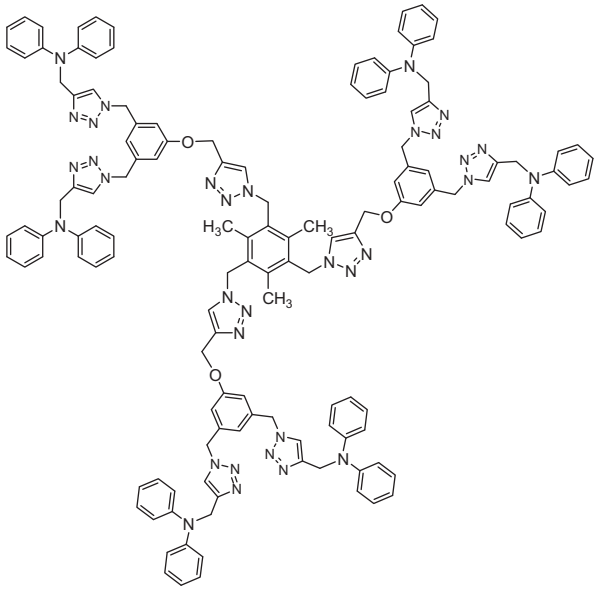

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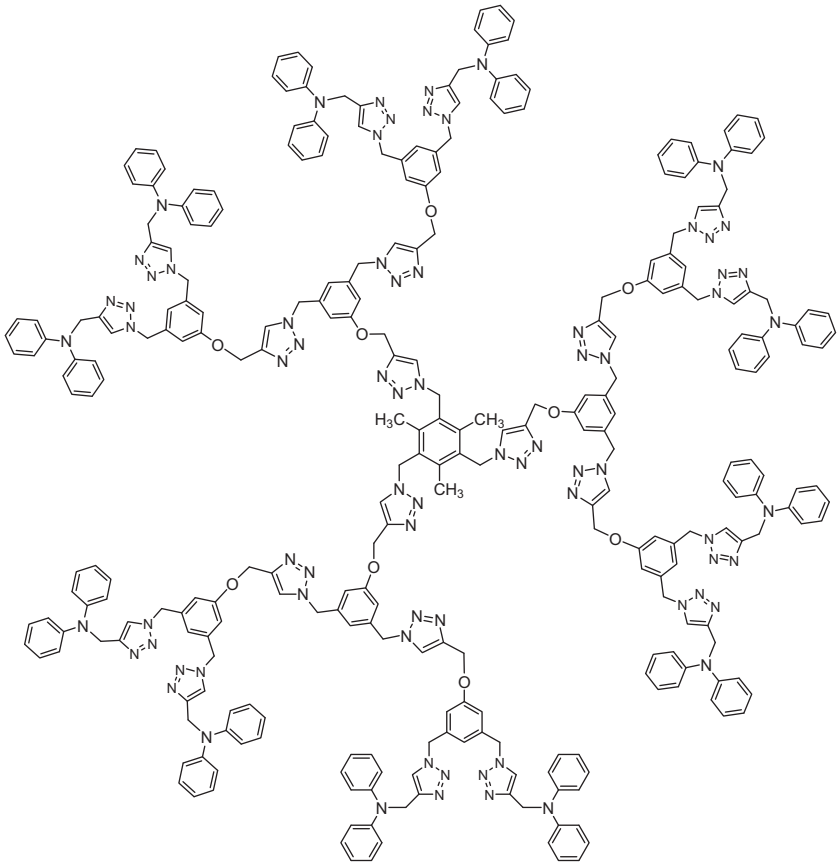

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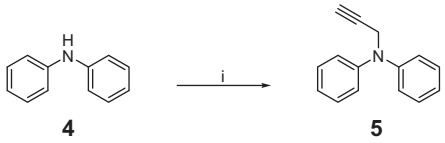
Figure 1. Moelcular structure of dendrimers **1**, **2** and **3**.

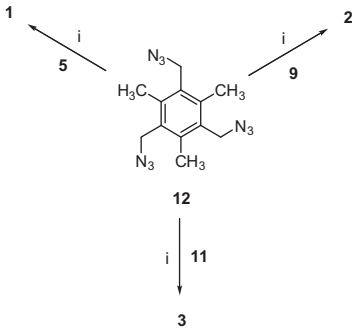
IR spectrum showed the presence of acetylenic unit. In the ^{1}H NMR spectrum of dendron **9**, the acetylenic protons appeared as a triplet at δ 2.33 (J = 2.1 Hz) and *O*-methylene protons appeared as a doublet at δ 4.49 (J = 2.1 Hz). The *N*-methylene and benzylic protons appeared as singlets at δ 5.06 and 5.34, respectively, in addition to the aromatic protons. In ^{13}C NMR spectrum, dendron **9**[26] displayed four sharp peaks at δ 48.6, 53.5, 55.9, and 76.3 for acetylenic, benzylic, *N*-methylene, and *O*-methylene carbons,



Scheme 1. Reagents and conditions: (i) Propargyl bromide, NaH, DMF, room temperature.

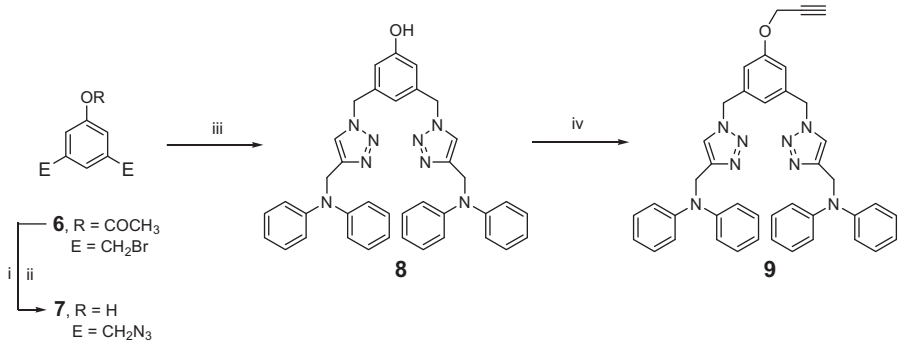
respectively. The triazole carbon appeared at δ 122.2 in addition to 10 aromatic carbons. Further the mass spectrum (EI-MS) of compound **9** showed the molecular ion peak at m/z 656.2.

Similarly, the reaction of 1.0 equiv of phenolic azide **7** with 2.1 equiv of first generation dendron **9** under click reaction condition as mentioned earlier afforded second generation phenolic dendron **10** in 86% yield (Scheme 3). The ^{1}H NMR spectrum of dendron **10** displayed singlets at δ 4.98, δ 5.01, δ 5.23, and δ 5.28 for *N*-methylene and *O*-methylene protons and two sharp singlets appeared at δ 7.40 and 7.51 for –CH– protons of triazole in addition to aromatic protons. The ^{13}C NMR spectrum of dendron **10** displayed four signals at δ 48.2, δ 53.5, δ 53.7, and δ 61.7 for *N*-methylene and *O*-methylene carbons and the –CH– carbon of triazole moiety appeared at δ 120.9 and δ 123.0 in addition to aromatic carbons. The structure of compound **10** was also confirmed by the appearance of molecular ion peak at m/z 1540.7 [M$^+$+Na] in the mass spectrum (MALDI-TOF). Further, 1.0 equiv of second generation phenolic dendron **10** when treated with 1.25 equiv of propargyl bromide in the presence of K_2CO_3 in DMF at 60 °C for 24 h gave the second generation alkyne-dendron **11** in 73% yield (Scheme 3).

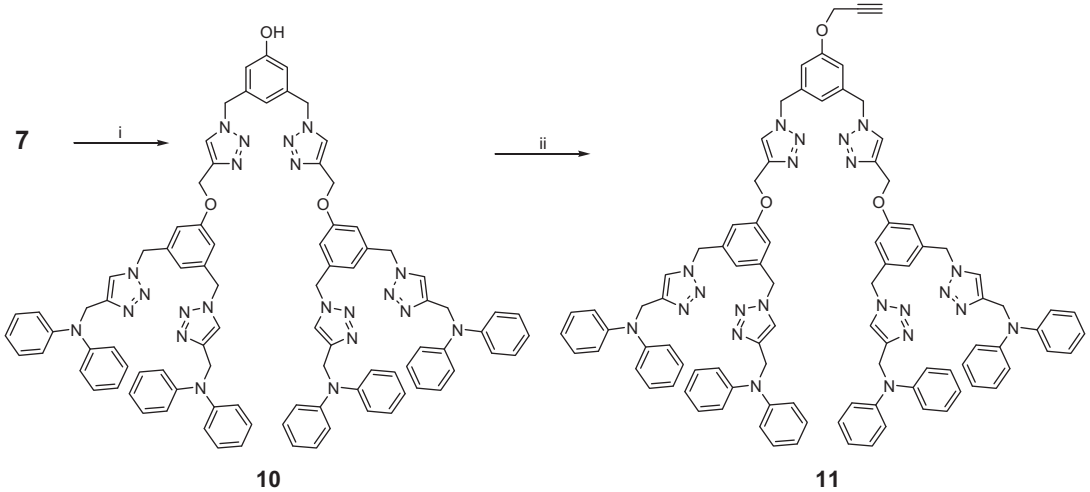


Scheme 4. Reagents and conditions: (i) $CuSO_4{\cdot}5H_2O$ (5 mol %), Na ascorbate (10 mol %), THF/H_2O (1:1), rt, 12 h, **1**, 83%; **2**, 85%; **3**, 71%.

The ^{1}H NMR spectrum of dendron **11** showed a triplet at δ 2.45 (J = 2.1 Hz) for acetylenic proton, a doublet at δ 4.57 (J = 2.1 Hz) for *O*-methylene protons adjacent to the acetylenic unit, and the two different types of triazole –CH– protons appeared as singlets at δ 7.35 and δ 7.56, respectively in addition to the aromatic protons. The ^{13}C NMR spectrum of dendron **11** displayed the acetylenic and *O*-methylene carbons at δ 48.4, 53.3, 53.7, 55.9, 61.7, 76.6,



Scheme 2. Reagents and conditions: (i) NaN_3, DMF, room temperature, 48 h; (ii) EtOH, KOH, reflux, 2 h; (iii) **5** (2.1 equiv), $CuSO_4{\cdot}5H_2O$ (5 mol %), Na ascorbate, (10 mol %), THF/H_2O (1:1), rt, 79%, 12 h, (iv) propargyl bromide, K_2CO_3, DMF, 60 °C, 24 h, 82%.



Scheme 3. Reagents and conditions: (i) **9** (2.1 equiv), $CuSO_4{\cdot}5H_2O$ (5 mol %), Na ascorbate (10 mol %), THF/H_2O (1:1, v/v), rt, 86%, 12 h; (ii) propargyl bromide, K_2CO_3 DMF, 60 °C, 24 h, 73%.

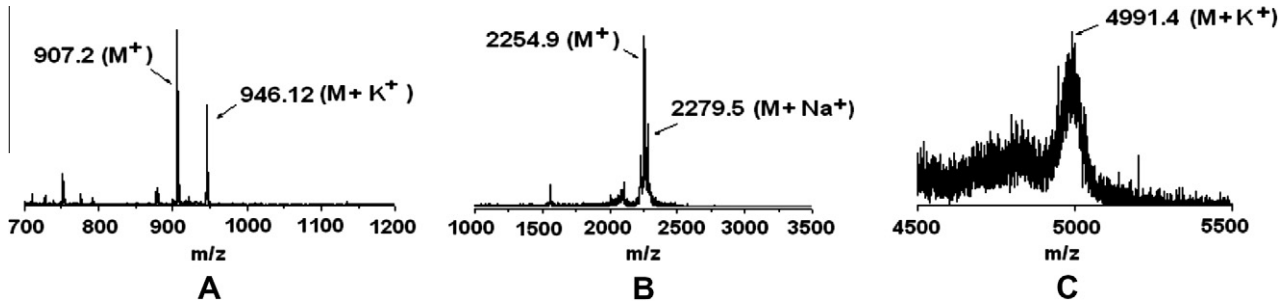


Figure 2. MALDI-TOF-MS spectra of dendrimer **1** (A), **2** (B) and **3** (C).

and 77.5 and the triazole –CH– carbons at δ 120.6 and 123.4. The appearance of molecular ion peak at m/z 1556 in mass spectrum (FAB-MS) further confirmed the structure of the dendrimer **11**.[27]

Synthesis of diphenylamine-based triazole dendrimers **1**, **2,** and **3** through 1,3-dipolar cycloaddition of alkynes **5**, **9,** and **11** with the azide **12**[12] via click chemistry[28] is summarized in Scheme 4. The reaction of 1.0 equiv of triazide **12** with 3.3 equiv dendritic arm **5**, **9,** and **11** in the presence of $CuSO_4{\cdot}5H_2O$ (5 mol %) and sodium ascorbate (10 mol %) in a mixture of THF/water (1:1) afforded the dendrimers **1**, **2,** and **3** in 83%, 85%, and 71% yields, respectively (Scheme 4). The structure of the dendrimers **1**,[29] **2**[30], and **3**[31] was completely characterized from spectral and analytical data. Figure 2 shows the MALDI-TOF MS spectrum of dendrimer **1**, **2,** and **3**.

The absorption and emission spectra of dendrimers **1**, **2,** and **3** were recorded in DMSO (1×10^{-5} M) at room temperature and the values are summarized in Table 1. Dendrimers **1**, **2,** and **3** exhibit strong absorption bands in the range of 291–293 nm. The incorporation of more number of triazole moiety with diphenylamine as surface group may cause the resulting molecules to be less coplanar. Furthermore, as the number of diphenylamine chromophores increases from zero to first, then to second generation, the molar extinction coefficient also increases at the constant concentration of dendrimers **1**, **2,** and **3** which indicates that the amount of light absorbed by the dendritic antenna increases with the increase in the generation.[32]

Dendrimers **1**, **2,** and **3** showed strong fluorescence between 350 and 373 nm and the emission maxima at 373 nm was observed for the dendrimer **3** (Fig. 3). A red-shift maxima (λ_{em} = 373 nm) was observed for second generation dendrimer **3** when compared to those of the corresponding zero and first generation dendrimers **1** and **2** due to the increase in the number of donor amine surface group, which is also called the valency effect in dendrimers. The increase in the number of triazole moiety in the dendrimers might perturb the coplanarity altering the fluorescence nature of the dendrimers.

Further, the fluorescence quantum yields (Φ_f) of dendrimers **1**, **2,** and **3** were measured in DMSO using tryptophan[33] as the standard. The quantum yields of dendrimers **1**, **2,** and **3** are found to be 0.16, 0.19, and 0.17, respectively. In general, increase in the number of diphenylamime moiety might lead to increase in the fluorescence quantum efficiency.[34] Hence, dendrimer **3** could be expected to show the higher quantum efficiency among all the

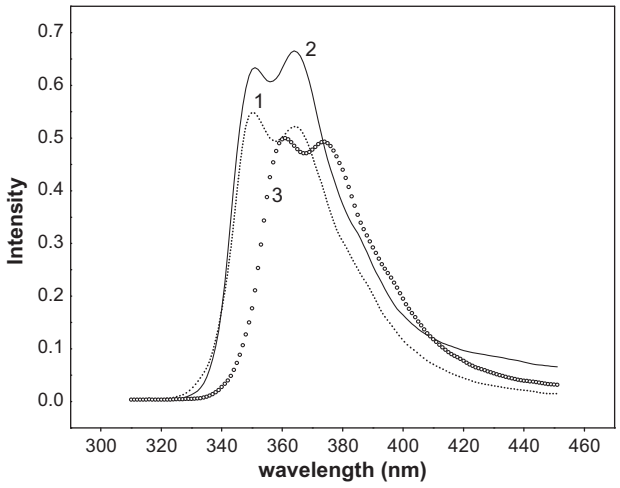


Figure 3. Emission spectrum of dendrimers **1**, **2** and **3**.

dendrimers due to the valency effect. However, in dendrimer **3** extensive steric crowding suppresses the valency effect of the diphenylamine surface group and hence the quantum yield decreases. In dendrimer **3**, steric factor and valency effect[35] act in the opposite direction and the valency effect is suppressed by excess crowding of the surface and branching units. Alternatively, a better solute-solvent interaction for the compound with increasing charge transfer may also decrease the quantum yield.[36]

In order to understand the nature of the excited state, life time measurements of the dendrimers **1**, **2,** and **3** were recorded using IBH, TCSPC technique on excitation at 365 nm in DMSO as solvent. The fluorescence decay fits as bi-exponential with life time τ_1 and τ_2 as 2.97 and 8.72; 2.97 and 10.2; 2.86, and 9.66 ns for dendrimers **1**, **2,** and **3**, respectively (Table 2).

The fluorescence decay (Fig. 4) of dendrimer **2** shows a longer relaxation time τ_2 than for the dendrimer **1** and **3** and the amplitude A1 is comparatively greater than A2 for all the dendrimers. However, A1 for dendrimer **3** is greater than for dendrimer **1** and **2**. Excessive crowding in dendrimer **3** dominates and hence the lifetime (τ_2) and relative amplitude (A2) are found to be less. The presence of more number of triazole and diphenylamine surface

Table 1
Absorption, emission and thermal data of dendrimers **1**, **2** and **3**

Dendrimers	λ_{abs} max (nm)	ε (mol/L)	λ_{em} max (nm)	Φ_F	T_{dec}[g] (°C)
1	291	8.44×10^4	350, 364	0.16	390
2	293	1.35×10^5	351, 364	0.19	522
3	293	1.87×10^5	360, 373	0.17	481

[g] Determined by thermal gravimetric analyzer with a heating rate of 10 °C/min under N_2.

Table 2
Lifetime relaxation and amplitude of dendrimers **1**, **2** and **3**

Dendrimers	Analysis	Life time (ns)		Amplitude (%)	
		τ_1	τ_2	A1	A2
1	Bi-exponential	2.97	8.72	92.98	07.02
2	Bi-exponential	2.97	10.2	70.20	29.80
3	Bi-exponential	2.86	9.66	96.93	03.07

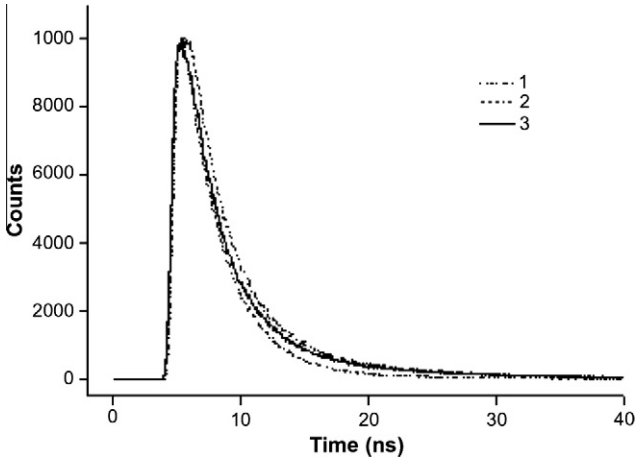


Figure 4. Fluorescence decay of dendrimers **1**, **2** and **3**.

Table 3
The electrochemical parameters obtained for the dendrimers **1**, **2** and **3** in DMF at 26 °C

Dendrimers	Epa (mV)	Epc (mV)
1	1.30	−0.83
2	1.37	−1.11
3	1.13	−0.85

groups with less steric interaction makes dendrimer **2** as a better fluorescence-sensing material than dendrimers **1** and **3**.

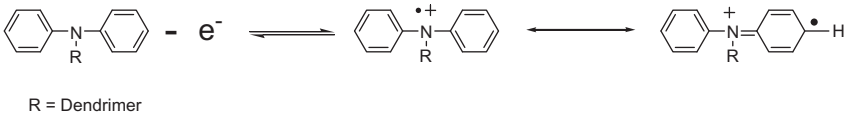
All the dendrimers showed good thermal stability as determined by thermo gravimetric analysis. However, dendrimer **2** exhibited higher thermal stability with decomposition temperature (T_{dec}) 522 °C (Table 1) than dendrimer **1** and **3**. The excess crowding in dendrimer **3** slightly decreased its thermal stability.

The electrochemical behavior of diphenylamine-terminated dendrimers has been investigated using cyclic voltammetry technique. A single compartment cell containing 0.1 mM concentration of the dendrimers in the presence of 0.1 M of Bu_4NPF_6 as a supporting electrolyte was used in all the experiments. All solutions were purged with purified N_2 gas for about 10 min before carrying out the CV studies. The cyclic voltammogram was recorded from 2.0 to −1.6 against Ag/AgCl reference electrode. We have observed an irreversible cyclic voltammetry response in both anodic and cathodic side for all the three dendrimers. The resulting peak potential and peak current values are given in Table 3.

During the anodic scan there is a possibility for the formation of carbocation due to the loss of single electron from the diphenylamine molecules. On the other hand, there is an irreversible reduction peak at about −1.3 V due to the reduction of diphenylamine molecule. A similar oxidation peak potential +1.0 V versus Ag/AgCl for diphenylamine was noted in the literature.[37] This indicates the formation of radical cation and the reaction mechanism for the electron transfer process is shown in Scheme 5.

The oxidation peak potential values for **1** and **3** are almost similar whereas for dendrimer **2** the peak potential is less positive than the others. From the CV (Fig. 5) it is clear that on increasing the number of diphenylamine group in the periphery, the oxidation potential abruptly decreases which could be due to the intramolecular interactions within diphenylamine moiety. Recent studies have shown that there is no redox reaction for triazole group present in ferrocene monolayer assembly, which was generated by click reaction between azidoundecanethiol and ferrocenepropynone.[38] Hence, the present study confirms that the redox process is purely due to single electron transfer reaction on the diphenylamine moiety.

In conclusion, a highly efficient synthesis of triazole-based dendrimers **1**, **2,** and **3** with diphenylamine as surface group has been achieved in excellent yields. All the dendrimers synthesized were thoroughly characterized from spectral and analytical data and all the dendrimers exhibit UV absorption at 291–293 nm and emission at 350–373 nm. Dendrimer **2** exhibits higher quantum yield, longer relaxation time in the fluorescence spectrum, and better thermal stability than dendrimers **1** and **3**, and in CV studies, dendrimer **2** showed multi-reduction wave potentials with large positive value than the dendrimer **1** and **3**. The antioxidant properties of the other similar dendrimers are underway.



Scheme 5. Formation of radical cation in diphenylamine moiety.

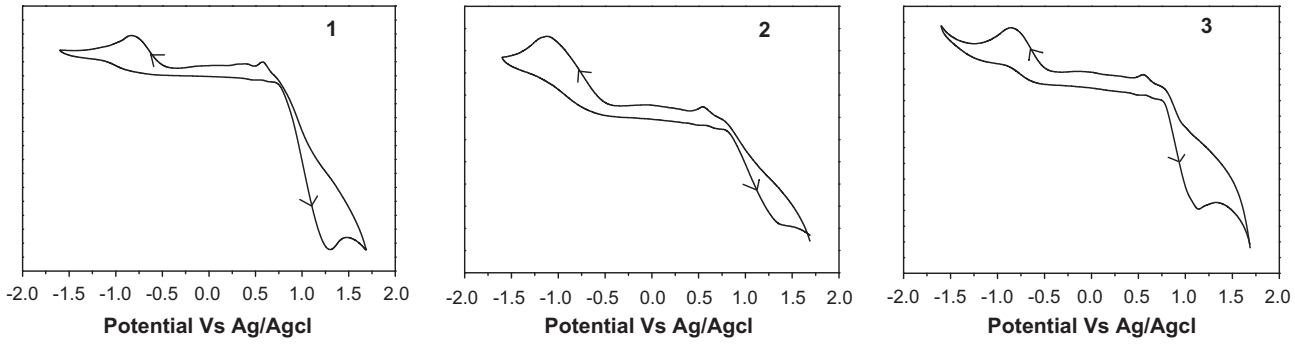


Figure 5. Cyclic voltammograms of dendrimers **1**, **2** and **3** in DMF (1×10^{-5} M) presence of Bu_4NPF6 (0.1 M) at 50 mV/s scan rate.

Acknowledgments

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25. *General procedure for the synthesis of alkyne dendrons*: A mixture of phenolic dendron (1.1 mmol), propargyl bromide (1.2 mmol) and K_2CO_3 (0.3 g, 2.1 mmol) in dry DMF (10 mL) was stirred at 60 °C for 10 h. The reaction mixture was then extracted with $CHCl_3$ (2 × 100 mL) washed with water (100 mL), dried (Na_2SO_4) and concentrated in vacuo and the resulting crude product was purified by column chromatography (SiO_2) using $CHCl_3$/MeOH (99:1) as the eluent.
26. *Dendron* **9**: Yield 0.67 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (t, J = 2.1 Hz, 1H); 4.49 (d, J = 2.1 Hz, 2H); 5.06 (s, 4H), 5.34 (s, 4H); 6.54 (s, 1H); 6.62 (s, 2H); 6.93 (t, J = 7.5 Hz, 4H); 7.05 (d, J = 8.1 Hz, 8 H); 7.22 (t, J = 7.5 Hz, 8H); 7.26 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.6, 53.5, 55.9, 76.3, 77.6, 114.1, 119.6, 120.9, 121.9, 122.2, 129.4, 137.2, 146.3, 147.4, 158.4. MS (EI) m/z = 656.2 [M$^+$]. Elemental Anal. Calcd for $C_{41}H_{36}N_8O$: C, 74.98; H, 5.52; N, 17.06. Found: C, 74.87; H, 5.43; N, 17.13.
27. *Dendron* **11**: Yield 0.85 g (73%); mp 95–98 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (t, J = 2.1 Hz, 1H); 4.57 (d, J = 2.1 Hz, 2H); 4.97 (s, 4H); 5.04 (s, 8H); 5.29 (s, 8H); 5.43 (s, 4H); 6.49 (s, 2H); 6.63 (s, 4H); 6.82 (s, 3H); 6.89 (t, J = 7.2 Hz, 8H); 7.04 (d, J = 8.4 Hz, 16H); 7.19 (t, J = 7.8 Hz, 16H); 7.35 (s, 4H); 7.56 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.4, 53.3, 53.7, 55.9, 61.7, 76.4, 77.5, 114.1, 114.8, 119.3, 120.6, 120.9, 121.9, 122.7, 123.4, 129.9, 137.1, 137.2, 143.5, 146.0, 147.3, 158.5, 158.9. MS (FAB): m/z = 1556 [M$^+$]. Elemental Anal. Calcd for $C_{93}H_{82}N_{22}O_3$: C, 71.80; H, 5.31; N, 19.81. Found: C, 71.93; H, 5.45; N, 19.73.
28. *General procedure for Cu-catalyzed Huisgen click reaction*: A mixture of azide (0.32 mmol), alkyne (1.04 mmol), $CuSO_4.5H_2O$ (5 mol %), and sodium ascorbate (10 mol %) in a mixture of THF/H_2O (1:1, v/v, 20 mL) was stirred for 12 h at room temperature. The residue obtained after evaporation of the solvent was washed thoroughly with water and dissolved in $CHCl_3$ (150 mL). The organic layer was separated, washed with brine (1 × 150 mL), dried (anhydrous Na_2SO_4), and evaporated to give the crude triazole, which was purified by column chromatography (SiO_2) using the eluent as mentioned under each compound.
29. *Dendrimer* **1**: Yield 0.75 g (83%); mp 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 9H); 5.02 (s, 6H); 5.43 (s, 6H); 6.92 (t, J = 7.2 Hz, 6H); 7.02 (d, J = 8.1 Hz, 12H); 7.20 (t, J = 7.5 Hz, 12H); 7.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.5, 48.3, 48.9, 121.0, 121.6, 121.7, 129.3, 130.4, 139.5, 145.6, 147.5. MS (MALDI-TOF): m/z = 907.2 [M$^+$], 946.12 [M+K$^+$]. Elemental Anal. Calcd for $C_{57}H_{54}N_{12}$: C, 75.47; H, 6.00; N, 18.53. Found: C, 75.56; H, 6.14; N, 18.64.
30. *Dendrimer* **2**: Yield 0.5 g (85%); mp 103–106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 9H); 4.92 (s, 6H); 5.02 (s, 12H); 5.25 (s, 12H); 5.61 (s, 6H); 6.47 (s, 3H); 6.61 (s, 6H); 6.88 (t, J = 7.2 Hz, 12H); 7.02 (d, J = 7.8 Hz, 24H); 7.18 (t, J = 7.8 Hz, 24H); 7.33 (s, 6H); 7.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8, 48.4, 49.1, 53.5, 61.8, 114.1, 119.2, 120.9, 121.9, 122.7, 122.8, 129.4, 130.6, 137.2, 139.9, 143.1, 146.1, 147.3, 158.9. MS (MALDI-TOF): m/z = 2254.9 [M$^+$], 2279.5 [M+Na$^+$]. Elemental Anal. Calcd for $C_{135}H_{123}N_{33}O_3$: C, 71.88; H, 5.50; N, 20.49. Found: C, 71.95; H, 5.59; N, 20.57.
31. *Dendrimer* **3**: Yield 0.19 g (71%); mp 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 9H); 4.84 (s, 12H); 4.91 (s, 24H); 5.15 (s, 24H); 5.26 (s, 18H); 5.46 (s, 6H); 6.36 (s, 9H); 6.51 (s, 18H); 6.69–7.20 (m, 120H); 7.35 (s, 12H); 7.48 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8, 28.7, 47.3, 52.3, 52.5, 60.6, 112.9, 113.6, 116.8, 119.1, 119.9, 120.7, 121.5, 122.0, 122.6, 128.3, 129.6, 136.2, 136.3, 138.8, 142.4, 145.3, 146.4, 157.9. MS (MALDI-TOF): m/z = 4991.4 [M+K$^+$]. Elemental Anal. Calcd for $C_{291}H_{261}N_{75}O_9$: C, 70.57; H, 5.31; N, 21.21. Found: C, 70.69; H, 5.28; N, 21.16.
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