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PAPER
Jason B. Benedict et al.
The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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Synthesis, photophysical, electrochemical properties and DSSC application of triphenylamine chalcone dendrimers via click chemistry

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Abstract

Fluorene-cored dendrimer containing triphenylamine chalcone unit at the periphery has been synthesized by divergent methodology using click chemistry approach and their photophysical and electrochemical properties have been investigated. All the dendrimers exhibited quasireversible oxidation reduction signals in cyclic voltammetry. All the dendrimers are used as additives in dye-sensitized solar cells (DSSCs) and the higher-generation dendrimer exhibit better power conversion efficiency than the lower-generation dendrimers in solar energy harvesting systems.

Keywords: Dendrimers, Fluorene, Triphenylamine, Click chemistry.

Introduction

Emitting organic compounds possessing extended π-conjugated system are of great interest in recent years owing to their variety of applications in OLEDs,[1] solid-state lasers,[2] sensors,[3] fluorescence imaging,[4] nonlinear optical materials,[5] photophysical and in charge transport devices. The energy demand increases worldwide but the fossil fuel reserves wear out rapidly and hence there is an increase in pressure to use renewable energy sources to have sustainable progress and development. Along these lines, Dye-sensitized solar cells (DSSCs)

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have involved significant attention due to their low cost fabrication and high power conversion efficiency (PCE) values. With the aim of increasing and improving renewable energy sources, recently a large number of functional π-conjugated polymers,[6] oligomers[7] and dendrimers[8] have been synthesized and used in DSSC and organic light emitting diodes (OLEDs). DSSC fabricated using ruthenium complex[9] first reported by Grätzel and coworkers in 1991 had 11% power conversion efficiency. Recently,[10] the record of high conversion efficiency (η) of 13.0% has been achieved with Zn-porphyrin complex-based DSSC. Dendrimers[11] are highly branched macromolecules combining the merits of well-defined structure with superior chemical purity and with excellent emissive property that depend on the dendrimer generation. Dendrimers have attracted great attention in the past few decades due to their variety of applications including optical data storage,[12] solar cells[13] and medical applications.[14]

Triphenylamine (TPA) moiety possesses three-dimensional propeller structure and its derivatives have an important place in DSSC due to the electron donating property linked as a sensitized dye with hole transporting ability. Extension of the dye linker stabilizes the charge separation condition but delays electron donation.[15] In photoelectric research TPA has been reported as a good p-doping unit and used as a hole-injection moiety.[16,17] Triphenylamine and its derivatives have interesting properties in the development of photovoltaic devices as donor moieties and hence they can be used as good antenna for the charge transfer and/or energy transfer to the emitting center. TPA-based star-shaped oligomeric and polymeric materials are used as important organic semiconductors and as hole transporting materials in organic light emitting diodes, solar cells, organic field effect transistors and in photorefractive holography.[18]

Fluorene is a major component of fossil fuels and 9,9-dialkyl-substituted fluorene derivatives often exhibit high fluorescence quantum yields, good solubility in organic

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solvents, with excellent thermo- and photostability. Therefore, fluorenyl functionalized materials have been extensively explored as active ingredients for electronic devices, such as light emitting diodes, charge-transfer agents,[19] field effect transistors[20] and sensors.

Click chemistry is the most promising cycloaddition reaction in which copper (I) is used as a catalyst for 1,3-dipolar cycloaddition of terminal alkyne to azide developed by Sharpless[21a] and Meldal.[21b] Click reaction[21c] is characterized by very high yields, mild and simple reaction conditions and easy product isolations, with excellent chemoselective affording reliable 1,4-regiospecific 1,2,3-triazole even in the presence of a large variety of other functional groups, which is a breakthrough in the synthesis of dendrimers[22, 23] and polymeric materials.[24, 25]

Recently, we have used dendrimers with pyrene,[26] dimethyl isophthalate[27] and benzothiazole[28] surface groups as additives to increase the open-circuit voltage (V_{oc}) in DSSC. We report herein the synthesis of triphenylamine chalcone-based triazole dendrimers **1–6** (Fig. 1) with their photophysical property and also their application to increase the efficiency of DSSC when they are used as additives.

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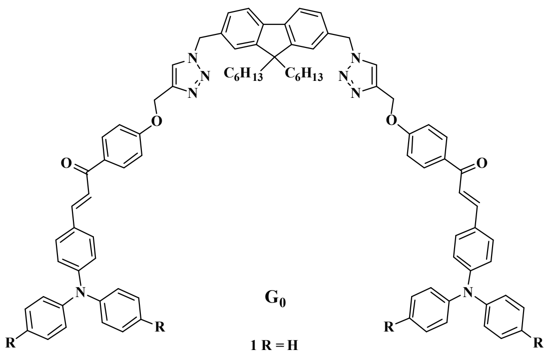
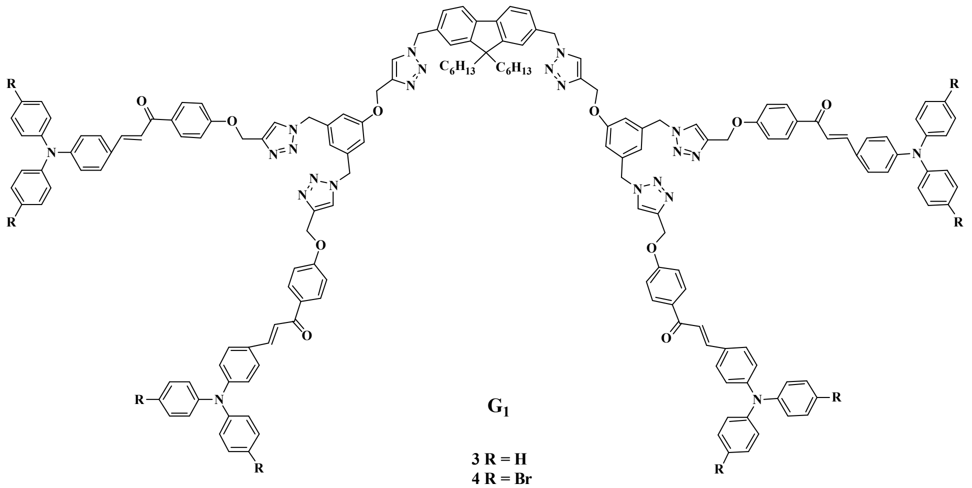


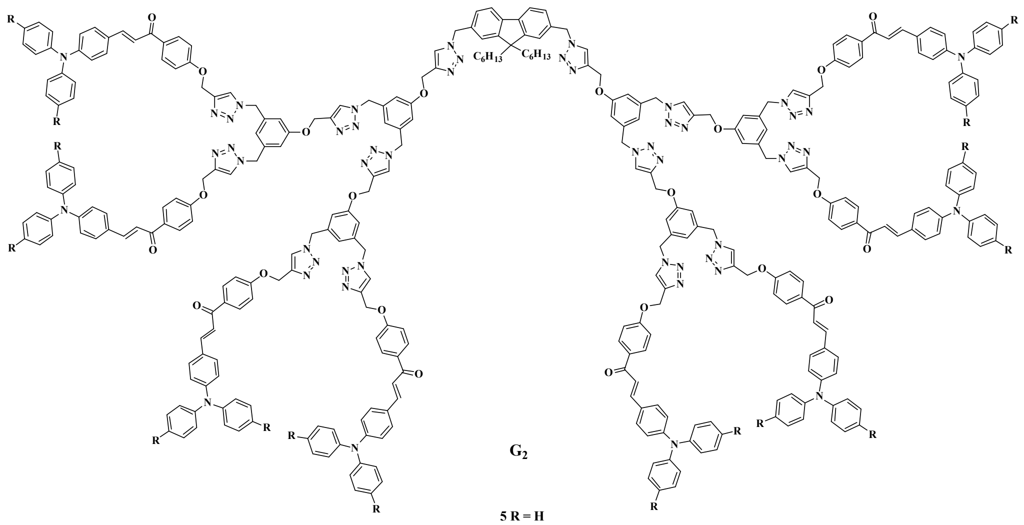
G_0

1 R = H
2 R = Br



G_1

3 R = H
4 R = Br



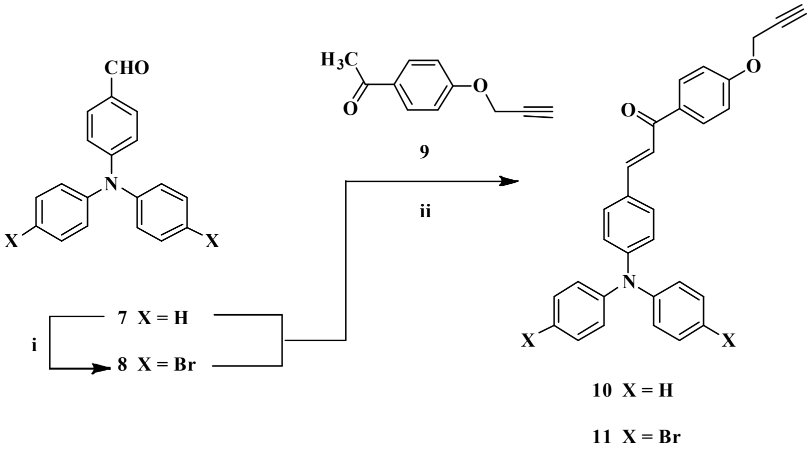
G_2

5 R = H
6 R = Br

Fig. 1 The molecular structure of triphenylchalcone dendrimers 1-6.

Results and discussion

The synthesis of propargyloxy triphenylamine chalcone dendrons **10** and **11** was achieved by controlled Vilsmeier-Haack formylation of triphenyl amine to give 4-formyl triphenylamine **7,** which was brominated using NBS in DMF at rt to give 4-(bis(4-bromophenyl)amino)benzaldehyde **8** in good yield. Claisen-Schmidt condensation of triphenylamine aldehydes **7** and **8** with 1.0 equiv. of 4-(propargyloxy)acetophenone **9** using ethanol as solvent and 10% sodium hydroxide as the base gave the corresponding propargyloxy triphenylamine chalcones **10** and **11** in 83% and 84% yields respectively (**Scheme 1**).



Scheme 1

Reagents and conditions: (i) NBS, DMF, rt, 5h. (ii) aq.NaOH, EtOH, 80°C, 7 h, **10** (83%) and **11** (84%).

In the ^{1}H NMR spectrum, the alkyne dendron **10** displayed a triplet at δ 2.56 (J = 2.1 Hz) and a doublet at δ 4.76 (J = 1.8 Hz) for the acetylenic and propargyloxy protons and the *trans* olefinic protons appeared at δ 7.40 (J = 15.6 Hz) and δ 7.76 (J = 15.6 Hz) respectively in addition to the signals for the other aliphatic and aromatic protons. The ^{13}C NMR spectrum of **10** showed propargyl and carbonyl carbon at δ 55.9, 76.2, 77.9 and 188.8 respectively in addition to the signals for the other aromatic carbons. In the mass spectrum (ESI) of the

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alkyne dendron **10,** a peak appeared at *m/z* 430 $(M+H)^+$ corresponding to the molecular ion. The structure of the alkyne dendron **10** was further confirmed from elemental analysis. Similarly, the structure of the alkyne dendron **11** was also confirmed from spectral and analytical data.

The synthetic pathway leading to the chloro and the azidodendrimers **14**, **16** and **15**, **17** is shown in **scheme 2**. The divergent synthesis begins with the reaction of 1.0 equiv. of 2,7-bis(azidomethyl)-9,9-dihexyl-9*H*-fluorene **13** with 2.1 equiv. of 1,3-bis(chloromethyl)-5-(propargyloxy)- benzene **12** under Cu(I) catalyzed click reaction conditions to give the chloro dendrimer **14** in 93% yield, which on further treatment with NaN_3 in DMF at 90 ºC afforded the corresponding azido dendrimer **15** in 89% yield **(Scheme 2).** The ^1H NMR spectrum of the compound **15** displayed a singlet at δ 4.31 ppm for the azidomethyl protons and two singlets at δ 5.20, 5.61 ppm for the *O*-methylene and *N*-methylene protons and a sharp singlet at δ 7.53 ppm for the triazolyl proton in addition to the signals for the other aliphatic and aromatic protons. The ^{13}C NMR spectrum of the azido compound **15** displayed the azidomethyl carbon at δ 54.4 ppm and two signals at δ 55.3, 62.2 ppm for the *N*-methylene and *O*-methylene carbons respectively in addition to the signals for the other aliphatic and aromatic carbons. The mass spectrum (ESI-MS) of the azidodendrimer **15** showed the molecular ion peak at *m/z* 930 (M+1). Further the structure of the azidodendrimer **15** was also confirmed from elemental analysis.

After synthesizing the first-generation azido dendrimer, we focused our attention on the synthesis of the second-generation azido dendrimer. The reaction of 4.1 equiv. of 1,3-bis(chloromethyl)-5-(propargyloxy)benzene **12** with 1.0 equiv. of the azidodendrimer **15** under Cu(I) catalyzed click reaction conditions gave the second generation chloro dendrimer **16** in 89% yield, which on further treatment with NaN_3 in DMF at 90 °C afforded the corresponding azido dendrimer **17** in 80% yield **(Scheme 2)**.

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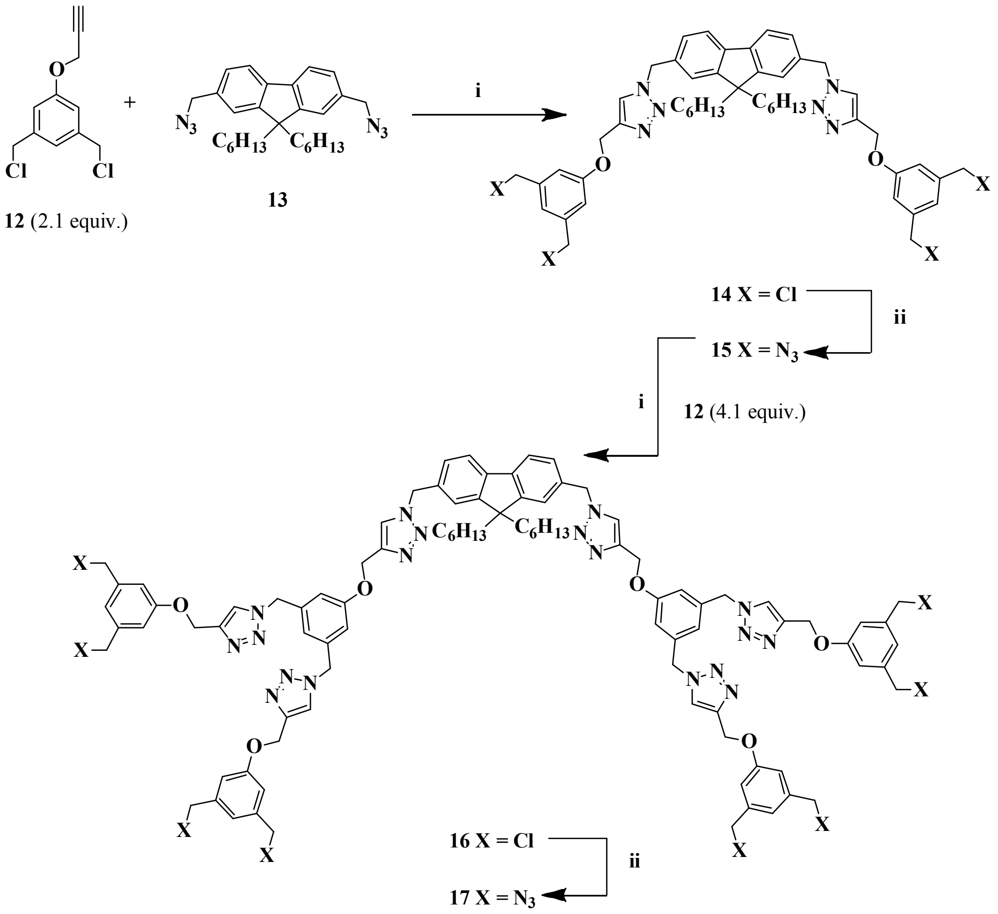

Scheme 2

Reagents and conditions: (i) $CuSO_4.5H_2O$ (5 mol %), sodium ascorbate (10 mol %), H_2O–THF (1:3); rt, 12 h. **14** (93%), **16** (89%). (ii) 9 equiv. NaN_3, DMF, 90 ºC, 3 h. **15** (89%), **17** (80%).

The ^{1}H NMR spectrum of the compound **17** displayed a singlet at δ 4.31 ppm for the azidomethyl protons and four singlets at δ 5.10, 5.21, 5.45 and 5.59 ppm for the different types of *O*-methylene and *N*-methylene protons and a sharp singlet at δ 7.54 and 7.59 ppm for the two different triazolyl protons in addition to the signals for the other aliphatic and aromatic protons. The ^{13}C NMR spectrum of the compound **17** displayed the azidomethyl carbon at δ 54.4 ppm and four signals at δ 53.7, 55.3, 61.9 and 62.1 ppm for the four types of *N*- methylene and *O*- methylene carbons respectively in addition to the signals for the other

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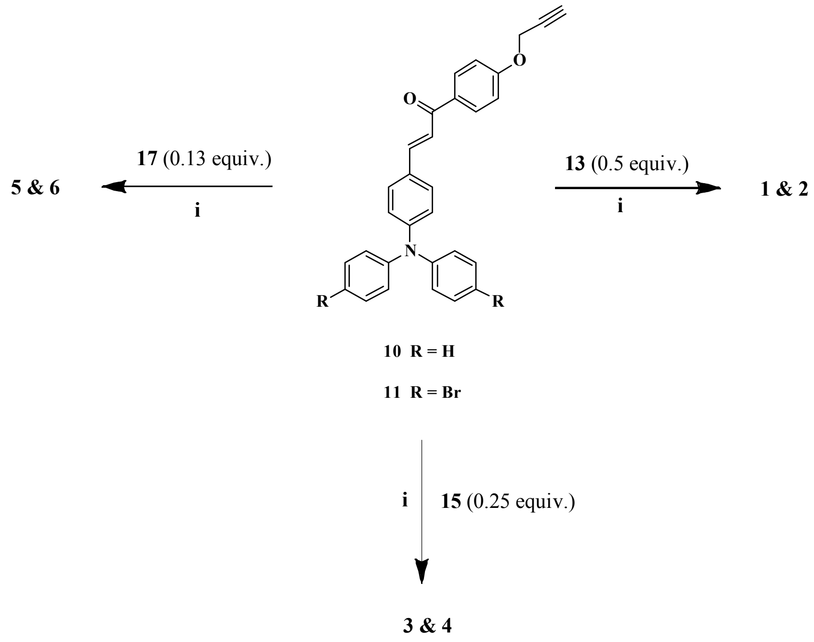
aliphatic and aromatic carbons. The mass spectrum (MALDI-TOF) of the azido dendrimer **17** showed the molecular ion peak at *m/z* 1921 $[M + Na]^+$. Further the structure of azido dendrimer **17** was also confirmed from elemental analysis.

The zeroth, first and second generation dendrimers **1** and **2** (G_0), **3** and **4** (G_1) and **5** and **6** (G_2) could be achieved by 'click' chemistry approach using 2,7-bis(azidomethyl)-9,9-dihexyl-9*H*-fluorene **13** as the core unit. The functionalization reaction of the zeroth, first and second generation azidodendrimers **13, 15** and **17** with 2.1/4.1/8.1 equivalents of propargyloxy triphenylamine chalcones **10** and **11** under Cu (I) catalyzed click reaction conditions afforded the triphenylamine chalcone dendrimers **1, 2, 3, 4, 5** and **6** in 86%, 78%, 76%, 81%, 71% and 74% yields, respectively **(Scheme 3).**

The ^{1}H NMR spectrum of the dendrimer (G_0) **2** showed a set of four proton singlets at δ 5.26 and 5.62 for the *O*-methylene and *N*-methylene protons and a sharp singlet at δ 7.55 ppm for the triazolyl proton in addition to the signals for the other aliphatic and aromatic protons. The ^{13}C NMR spectrum of the dendrimer **2** showed signals at δ 55.4 and 62.1 for the *O*-methylene and *N*-methylene carbons and the carbonyl carbon appeared at δ 188.6 in addition to the signals for the other aliphatic and aromatic carbons. The mass spectrum (MALDI-TOF) of the compound **2** showed the molecular ion peak at *m/z* 1642 $[M + Na]^+$. Further, the structure of the compound **2** was also confirmed from elemental analysis. Similarly, the structure of the zeroth, first and second generation dendrimers **1, 3, 4, 5** and **6** was also confirmed from spectral and analytical data.

The symmetrical structures of **1-6** and their extensive spectral studies viz NMR, MALDI-TOF MS, and size exclusion chromatography (SEC) led to an unambiguous structural determination. The formation of triazole chalcone **2, 3** and **6** was evidenced by the appearance of newly formed triazolyl protons at δ 7.55, 7.60 and 7.60 ppm, respectively, from the corresponding ^{1}H NMR spectrum.



Scheme 3

Reagents and conditions: (i) $CuSO_4.5H_2O$ (5 mol %), sodium ascorbate (10 mol %), THF: H_2O (3:1), rt, 12 h, **1** (86%), **2** (78%), **3** (76%), **4** (81%), **5** (71%), **6** (74%).

UV-vis absorption studies

The UV-Vis absorption spectra of the dendrimers **1-6** recorded in CH_2Cl_2 (1×10^{-6} M) are presented in **Fig. 2** and the λ_{max} values are summarized in **Table 1**. In the absorption spectra, dendrimers **1-6** exhibited two absorption bands at 308 and 408 nm which corresponds to π–π*and n–π* transitions due to the presence of triphenylamine and fluorene units. The dendrimers **1, 3** and **5** shows a small red shift of 14 nm compared to the dendrimers **2, 4** and **6,** due to the presence of electron withdrawing bromine atom. Molar extinction coefficient of the dendrimers **1-6** increases significantly with increase in the dendrimer generation. As the number of triphenylamine units increases from zeroth generation to second generation, the absorption intensity also increases which indicates that the amount of light absorbed by the dendritic antenna increases from lower generation to higher generation which is otherwise known as valence effect in dendrimer chemistry.[29]

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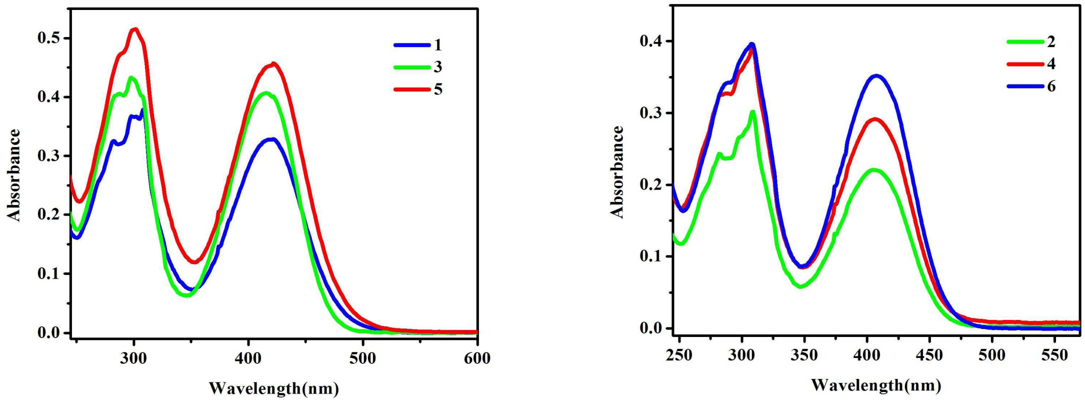

Fig. 2 UV absorption spectra of dendrimers **1-6** in CH_2Cl_2 (1 x 10^{-6} M).

Emission studies

Fluorescence spectra of the dendrimers **1-6** were recorded with fluorescence spectrophotometer using CH_2Cl_2 as solvent and the fluorescence parameters are presented in the **Table 1**. As shown in **Fig. 3**, upon excitation at 420 nm, the dendrimers **1-6** show a strong emission band in the range of 608–665 nm. The emission intensity of the dendrimers **1-6** gradually increases with increase in the dendritic generation due to the higher number of triphenylamine moieties in periphery. The dendrimers **1, 3** and **5** exhibited strong red shift compared to the dendrimers **2, 4** and **6.** Due to the presence of electronegative bromine, the second generation dendrimer **6** shows blue shift of 38 nm compared to the dendrimer **5**

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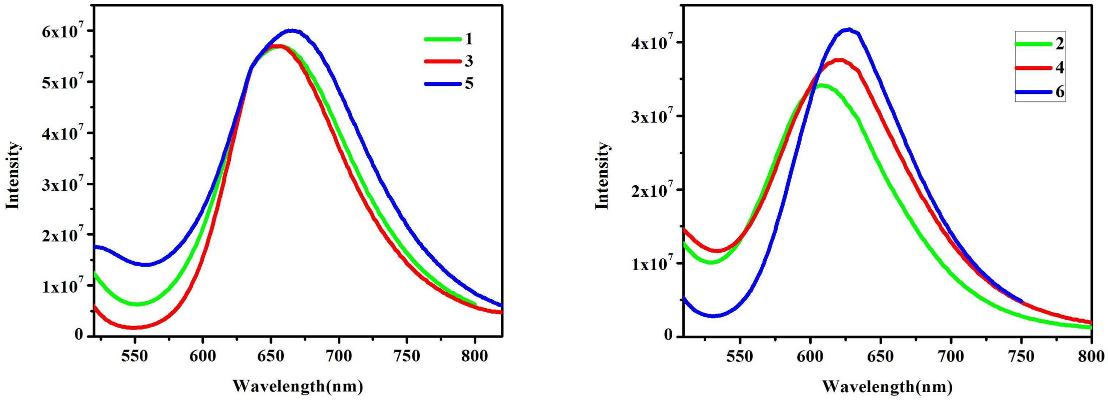

Fig. 3 Fluorescence spectra (λ_{exc} = 420nm) of dendrimers **1-6** in CH_2Cl_2 (1 x 10^{-6} M) at room temperature.

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Table 1 Photophysical studies of dendrimers **1-6** (rt, in CH_2Cl_2).

Dendrimers	λ_{ab}^{max} **(nm)**	ε_{max} **(M^{-1} $cm^{-1} \times 10^6$)**	λ_{em}^{max} **(nm)**	**Stokes shift cm^{-1}**	Φ_f
1	308, 420	3.8, 3.3	657	8589	0.14
2	309, 406	3.0, 2.2	608	8184	0.12
3	299, 416	4.3, 4.1	654	8747	0.11
4	309, 406	3.9, 2.9	621	8528	0.10
5	301, 422	5.2, 4.6	665	8659	0.10
6	308, 408	4.0, 3.5	627	8561	0.08

The fluorescence quantum yields Φ_f of dendrimers **1–6** has been measured in ethanol using coumarin 153 as the standard. The fluorescence quantum yields of **1**, **2**, **3**, **4, 5** and **6** lie in the range of 0.14-0.08 and the compound **6** shows the lowest fluorescence quantum yield of 0.08 (**Table 1**).

The solvatochromism study was carried out for all the dendrimers in different solvents to evaluate the effect of solvent polarity on the optical properties of the molecules. The absorption and emission spectra of **1-6** were recorded in solvents of different polarity such as 1,4-dioxane (Diox), chloroform ($CHCl_3$), tetrahydrofuran (THF), dichloromethane (DCM) and N,N-dimethylformamide (DMF). The absorption and emission data observed in selected solvents are listed in **Table 2**. The dendrimers **1-6** showed small changes in absorption on varying the polarity of the solvent used for the measurement (SI Fig.1 & 2 and table 1). However, the dendrimers **5** and **6** (Figure 5) showed prominent positive solvatochromism in the emission spectra only. The dendrimers **5** and **6** exhibit strong emission band in the range of 621–667 nm in dichloromethane, chloroform, 1,4-dioxane and N,N-dimethylformamide, whereas in tetrahydrofuran the peak were observed at lower emission wavelength of 533 and

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534 nm and the corresponding photographic images of fluorescent solutions are inserted in **Fig. 5**.

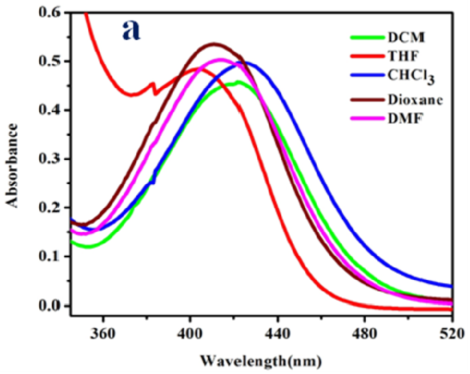

Figure 4 Absorption spectra of **a) 5** and **b) 6** recorded in selected solvents of different polarity.

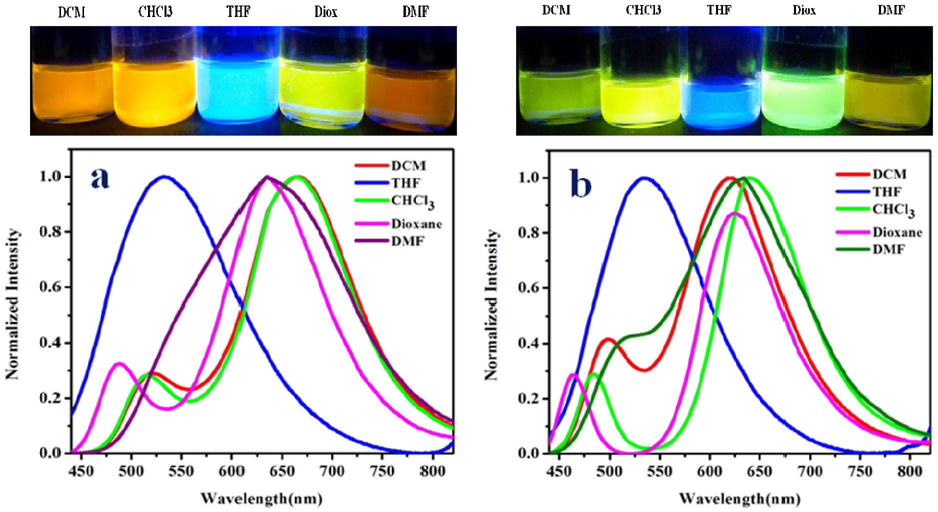

Figure 5 Emission spectra of **a) 5** and **b) 6** recorded in selected solvents of different polarity.

However, in solvents such as dichloromethane, chloroform, 1,4-dioxane and N,N-dimethylformamide the emission peak shifted to the red compared with that of the solvent tetrahydrofuran as shown in **Fig. 5**. Similarly, the Stokes shift is more in polar solvents for the dendrimers **5** and **6** which has more number of triphenylamine moieties at the surface. As they show greater polarization than ground states, excited states will be stabilized in polar solvents. Evidence for this are larger Stokes' sifts and longer emission wavelengths. It is reasonable to assume that the fluorene unit acts as a strong π-acceptor in the excited state.

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Table 2 Absorption and emission data for compounds **5** and **6** recorded in different solvents.

Compound	Solvent	Polarity index	λ_{ab}^{max} (nm)	ε_{max} (L M^{-1} cm^{-1} × 10^{6})	λ_{em}^{max} (nm)	Stokes shift (cm^{-1})
5	DCM	3.1	422	0.4550	667	8704
	THF	4.0	405	0.4827	533	5929
	$CHCl_3$	4.1	425	0.4951	663	8446
	Dioxane	4.8	411	0.5350	635	8608
	DMF	6.4	414	0.5031	635	8407
6	DCM	3.1	409	0.3506	621	8321
	THF	4.0	401	0.5258	534	6211
	$CHCl_3$	4.1	412	0.5404	641	8671
	Dioxane	4.8	402	0.6507	625	8902
	DMF	6.4	405	0.5172	634	8893

Electrochemical properties

The redox behaviour of dendrimers **1-6** was studied by cyclic voltammetry (CV) in CH_2Cl_2 (1 x 10^{-3} M) at room temperature at the scan rate at 50 mV s^{-1} with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and Ag/AgCl electrode as the reference electrode and Pt wire counter electrode. All the compounds exhibit electrochemical response and the cyclic voltammogram of the dendrimers **1-6** are shown in **Fig. 6**, with redox potentials listed in **Table 3**. Oxidation and reduction potential for all the dendrimers appeared in the potential range of -2.0 to +2.0 V. The reversible oxidation potentials for the dendrimers **1, 2, 3, 4, 5** and **6** were obtained at 1.18 V, 1.24 V, 1.20 V, 1.36 V, 1.33 V and 1.49 V, respectively, and the reversible reduction peaks were observed at 0.83 V, 0.87 V, 0.74 V, 0.92 V, 0.80 V and 0.84 V, respectively. All the dendrimers exhibit the quasi-reversible behavior in cyclic voltammogram responsible to the strong electron donating triphenylamine moiety. More importantly, both oxidation and reduction peaks occur at the positive potential regions, revealing that these dendrimers easily lose the electron from the triphenylamine units. Further, the oxidation potential increase with increase in the dendrimer generation in the following order **1** (1.18 V), **3** (1.20 V), **2** (1.24 V), **5** (1.33 V), **4** (1.36 V), and **6** (1.49 V).

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The second generation dendrimers **5** and **6** exhibited a facile oxidation at the higher positive potential attributed to the removal of electron from the triphenylamine units. The cathodic peak potential is shifted from lower to higher generation dendrimers due to the presence of more number of triphenylamine units at the periphery, which increases the electron density in the dendrimeric system.

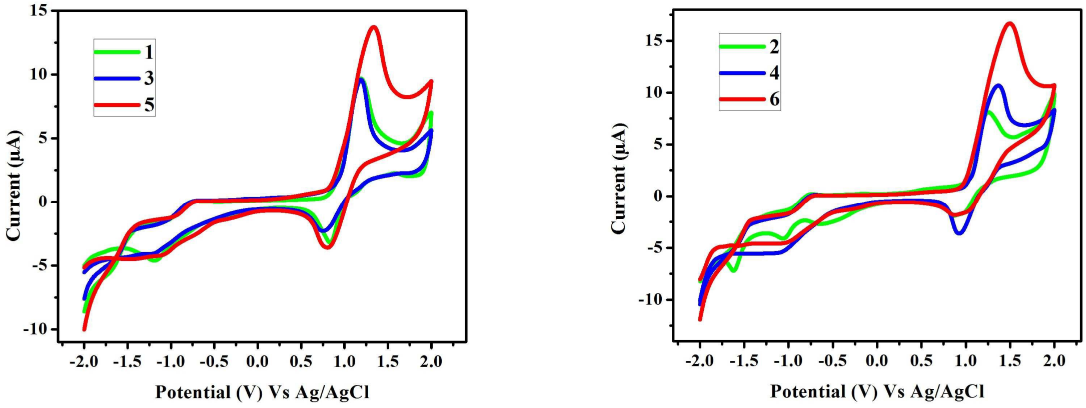

Fig. 6 Cyclic voltammogram of dendrimers **1-6** in CH_2Cl_2 (1 x 10^{-3} mol L^{-1}), scanned at 50 mV s^{-1}

Table 3 Electrochemical parameters of dendrimers **1-6** in CH_2Cl_2 (1 x 10^{-3} mol L^{-1}).

Dendrimers	E_{pc}(V)	E_{pa}(V)	$E_{1/2} = (E_{pc} + E_{pa})/2$	$\Delta E_p = E_{pc} - E_{pa}$
1	1.18	0.83	1.005	0.35
2	1.24	0.87	1.055	0.37
3	1.20	0.74	0.97	0.46
4	1.36	0.92	1.14	0.44
5	1.33	0.80	1.065	0.53
6	1.49	0.84	1.165	0.65

Dye-sensitized solar cell studies

Various nitrogen based organic molecules such as aminopyridine, pyrimidine, pyrrolidinopyridine, pyrrolidinoethylpyridine have been used as additives to increase V_{oc} which ultimately increases the solar energy harvesting efficiency (η) of the DSSCs. In an

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attempt to examine the effect of dendrimers as additive in solar cell performance, studies were carried out to observe the nature of the electrolytic solution in enhancing the performance of DSSC. The efficiency of a dye-sensitized solar cell is related to the various components of DSSC such as TiO_2, dye, iodide/triiodide concentration and Pt surface. Among these, the redox electrolyte system (I^-/I_3^-) occupies an important role in the power conversion efficiency of a DSSC. The redox couples without organic additives show a decreased open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}). After adding the dendrimers as additive the sublimation of iodine is decreased which in turn increases the V_{oc} and J_{sc} and improve the efficiency (η). Hence, nitrogen containing compounds form stable molecular complexes with the (I^-/I_3^-) electrolyte system and drastically alter the V_{oc} due to the electron donating property of the lone pair of electrons on the nitrogen atom. In the present investigation, we have synthesized a new series of 1,2,3-triazole based electron rich triphenylamine chalcone dendrimers **1-6** and employed them as additives for DSSCs. The tested dendrimers significantly affect the performance of the dye-sensitized solar cell as shown in **Fig. 7**.

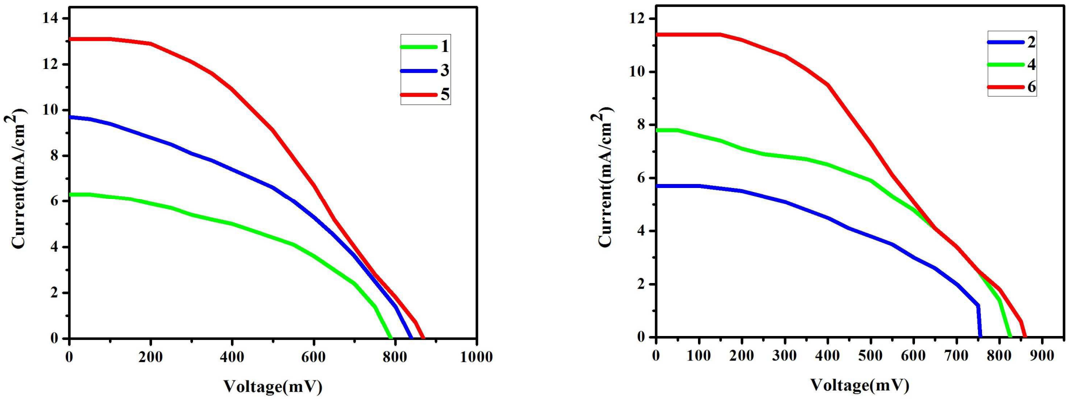

Fig. 7 Current–voltage curves of DSSCs with dendrimer additives **1-6**. The experiments were conducted under simulated solar light at 70 mW cm^{-2}.

On passing from zeroth-generation dendrimers to second-generation dendrimers, V_{oc}, J_{sc} and current also increase due to the presence of increasing number of triazole and

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triphenylamine units. The higher generation dendrimers **5** and **6** shows greater efficiency in harvesting the solar energy than the lower generation dendrimers **1**, **2**, **3** and **4** when used as additive in DSSC. The photovoltaic performance data of the short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor and the electric energy efficiency (η) are summarized in **Table 4**.

Table 4 The photovoltaic properties of the dendrimers **1-6** in the electrolyte system (I^-/I_3^-) under illumination of 70 mW cm^{-2} at AM 1.5.

Electrolyte system	J_{sc}/mA cm^{-2}	V_{oc}/mV	Fill factor	η (%)
N3 dye TiO_2/KI/I_2/**1**/Pt	6.3	790	0.52	3.7
N3 dye TiO_2/KI/I_2/**2**/Pt	5.7	755	0.50	3.0
N3 dye TiO_2/KI/I_2/**3**/Pt	9.7	840	0.51	5.9
N3 dye TiO_2/KI/I_2/**4**/Pt	7.8	825	0.50	4.6
N3 dye TiO_2/KI/I_2/**5**/Pt	13.1	870	0.53	8.6
N3 dye TiO_2/KI/I_2/**6**/Pt	11.4	860	0.51	7.1

In conclusion using click chemistry approach, the dendrimers with triphenylaminochalcone group have been synthesized in good yields. Photophysical studies reveal that the presence of more triazolyl and triphenylamine units increases the light absorbing capacity of the dendritic antenna and hence higher generation dendrimers show greater light absorbing ability than the lower generation dendrimers and in electrochemical studies the cathodic potential also increases as the dendrimer generation increases. Further, from DSSC studies as the dendritic generation increases the power conversion efficiency (η) also increases due to the increased number of triazole and triphenylamine units. Dendrimers **5** and **6** exhibit better power conversion efficiency (η) of 8.6 and 7.1%, respectively, when used as additives in DSSC than the control (N3 dye/KI/I_2) as well as when other triphenylaminochalcone dendrimers are used as additives.

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Experimental section

General information

All chemicals and solvents were purchased commercially and used as such without further purification. All melting points were determined using a Toshniwal melting point apparatus by open capillary tube method and are uncorrected. Column chromatography was performed on silica gel (ACME, 100-200 mesh). TLC was performed either on glass plates coated with silica gel-G (ACME) of about 0.25 mm thickness and visualized with iodine. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 300 MHz instruments. Chemical shifts are given in parts per million, and *J* values are in hertz. UV-Vis absorption spectra were measured with a Perkin–Elmer Lambda 35 UV-vis spectrometer. Elemental analyses were carried out using a Perkin-Elmer CHNS 2400 instrument. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed with a 2,5-dihydroxy benzoic acid (DHB) matrix.

General procedure for chalcone dendrons (Procedure A):

To a solution of 4-(propargyloxy)acetophenone and 4-formyl triphenylamine/ 4-(bis(4-bromophenyl)amino)benzaldehyde in ethanol (10 mL) added 10% NaOH (5 mL) and the reaction mixture was stirred at 80°C for 8 h after which the reaction mixture was acidified with 1N HCl (1 mL) and evaporated to dryness. The residue obtained was extracted with ethyl acetate (3x 100 mL) washed with water (3x 100 mL), brine (100 mL) and then dried over Na_2SO_4. Evaporation of the organic layer gave the residue, which was purified by column chromatography using hexane:$CHCl_3$ (3:2) as an eluent.

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DOI: 10.1039/C7NJ01059A

General procedure for azidation of dendritic chloride (Procedure B):

To the solution of corresponding dendritic chloride (1 mmol) in dry DMF (20 mL), sodium azide (1.5 mmol) was added and stirred at 75 ºC for 12 h. The reaction mixture was allowed to cool to room temperature. It was then poured into ice-cold water (30 mL) and extracted with $CHCl_3$ (3 × 100 mL). The organic layer was washed with water (100 mL) and saturated NaCl solution (3 × 100 mL), dried over Na_2SO_4. Solvent was evaporated under reduced pressure to afford the crude product, which was purified by column chromatography (SiO_2), using the eluent as mentioned under each compound.

General procedure for Cu (I)-catalyzed azide−alkyne cycloaddition (Procedure C):

A mixture of polypropargylated compound (1.0 equiv per azide functionalization) and azido compound (1.2 equiv), $CuSO_4 \cdot 5H_2O$ (0.3 equiv), and sodium L-ascorbate (0.3 equiv) was stirred at room temperature for 18 h in a 3:1 mixture of THF/water. After confirming the completion of reaction by TLC, chloroform (100 mL) was added to the reaction mixture and the organic layer was washed with water (50 mL), and brine (50 mL), dried over Na_2SO_4 and evaporated to obtain the crude product, which was then purified by column chromatography (SiO_2), using the eluent as mentioned under each compound.

Synthesis of propargyloxy triphenylamine chalcone 10:

Following the general procedure **A**, the alkyne dendron **10** was obtained as yellow colored solid from 4-(propargyloxy)acetophenone **9** (0.35 g, 2.01 mmol) and 4-formyl triphenylamine **7** (0.5 g, 1.83 mmol) and then by eluting from the column with $CHCl_3$:Hexane (3:1). Yield: 0.65g, 83%; M.p.: 108°C; ^1H NMR: (300 MHz, $CDCl_3$): δ_H 2.56 (t, 1H, *J* = 2.1 Hz); 4.76 (d, 2H, *J* = 1.8 Hz); 7.01-7.15 (m, 10H); 7.27-7.32 (m, 4H); 7.40 (d, 1H, *J* = 15.6 Hz); 7.48 (d, 2H, *J* = 8.4 Hz); 7.76 (d, 1H, *J* = 15.6 Hz); 8.03 (d, 2H, *J* = 8.7 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 55.9, 76.2, 77.9, 114.7, 119.2, 121.7, 124.1, 125.4, 128.0, 129.5, 129.7, 130.6, 132.3, 144.1, 146.9, 150.1, 161.0, 188.8. MS (ESI): m/z = 430 [M

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DOI: 10.1039/C7NJ01059A

+ 1]. Anal. Calcd. For $C_{30}H_{23}NO_2$: C, 83.89; H, 5.40; N, 3.26. Found: C, 83.75; H, 5.33; N, 3.37.

Synthesis of propargyloxy triphenylamine chalcone 11:

Following the general procedure **A**, the dendron **11** was obtained as yellow colored solid from the 4-(propargyloxy)acetophenone **9** (0.5 g, 2.76 mmol) and 4-(bis(4-bromophenyl)amino)benzaldehyde **8** (0.5 g, 1.31 mmol) and then by eluting from the column with $CHCl_3$:Hexane (3:1). Yield: 0.65g, 84%; M.p.: 120°C; ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 2.57 (t, 1H, *J* = 2.4 Hz); 4.78 (d, 2H, *J* = 2.4 Hz); 6.98-7.08 (m, 9H); 7.39-7.41 (m, 4H); 7.51 (d, 2H, *J* = 8.7 Hz); 7.75 (d, 1H, *J* = 15.6 Hz); 8.04 (d, 2H, *J* = 8.7 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 55.9, 76.2, 77.8, 114.7, 116.9, 120.0, 122.6, 126.5, 129.8, 130.6, 132.1, 132.7, 133.0, 143.6, 145.7, 149.0, 161.1, 188.7. MS (ESI): m/z = 588 [M + 1]. Anal. Calcd. For $C_{30}H_{21}Br_2NO_2$: C, 61.35; H, 3.60; N, 2.38. Found: C, 61.47; H, 3.43; N, 2.27.

Synthesis of 2,7-bis(azidomethyl)-9,9-dihexyl-9H-fluorene 13:

Following the general procedure **B**, 2,7-bis(azidomethyl)-9,9-dihexyl-9H-fluorene **13** was obtained as colorless oil from 2,7-bis(bromomethyl)-9,9-dihexyl-9H-fluorene (5.3 g, 10.2 mmol) and sodium azide (2.0 g, 25.4 mmol) and then by eluting from the column with hexane. Yield: 4.0g, 89%; ^{1}H NMR(300 MHz, $CDCl_3$): δ_H 0.60 (br s, 4H); 0.76 (t, 6H, *J* = 6.6 Hz); 1.04-1.12 (m, 12H); 1.94 (m, 4H); 4.41 (s, 2H); 7.35-7.37 (m, 6H); 7.63 (d, 2H, *J* = 8.1 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$) δc 14.0, 22.5, 23.6, 23.7, 29.6, 31.4, 40.1, 55.2, 120.1, 128.0, 136.9, 140.8, 151.8. MS (ESI): m/z = 445 [M + 1]. Anal. Calcd. For $C_{27}H_{36}N_6$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.82; H, 8.28; N, 18.75.

First generation chlorodendrimer 14:

Following the general procedure **C**, the chlorodendrimer **14** was obtained as white solid from 2,7-bis(azidomethyl)-9,9-dihexyl-9*H*-fluorene **13** (0.7 g, 1.58 mmol) and 1,3-bis(chloromethyl)-5-(propargyloxy)- benzene **12** (0.79 g, 3.47 mmol) and then by eluting

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from the column with $CHCl_3$: MeOH (19:1). Yield: 1.30g, 93%; M.p.: 118 °C; ^1H NMR: (300 MHz, $CDCl_3$): δ_H 0.54 (br s, 4H); 0.73 (t, 6H, *J* = 6.6 Hz); 1.01-1.08 (m, 12H); 1.88-1.93 (m, 4H); 4.52 (s, 8H); 5.19 (s, 4H); 5.62 (s, 4H); 6.95 (s, 4H); 7.01 (s, 2H); 7.23 (s, 1H); 7.26 (s, 3H); 7.54 (s, 2H); 7.69 (d, 2H, *J* = 7.5 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 14.0, 22.5, 23.8, 29.5, 31.4, 40.0, 45.7, 54.6, 55.4, 62.2, 114.9, 120.6, 121.4, 122.5, 122.8, 127.2, 133.5, 139.5, 140.9, 144.1, 152.0, 158.7. MS (ESI): m/z = 904 [M + 1]. Anal. Calcd. For $C_{49}H_{56}Cl_4N_6O_2$: C, 65.19; H, 6.25; N, 9.31. Found: C, 65.35; H, 6.33; N, 9.17.

First generation azidodendrimer 15:

Following the general procedure **B**, reaction of the first generation chlorodendrimer **14** (1.2 g, 1.33 mmol, 1.0 equiv.) with NaN_3 (0.52 g, 7.97 mmol, 6.0 equiv.) gave the azidodendrimer **15** as white solid after eluting from the column with $CHCl_3$: MeOH (19:1). Yield: 1.10g, 89%; M. P.: 140 ºC; ^1H NMR: (300 MHz, $CDCl_3$): δ_H 0.55 (br s, 4H); 0.73 (t, 6H, *J* = 6.6 Hz); 1.01-1.08 (m, 12H); 1.88-1.93 (m, 4H); 4.31 (s, 8H); 5.20 (s, 4H); 5.61 (s, 4H); 6.87 (s, 3H); 6.89 (s, 3H); 7.23 (s, 1H); 7.26 (s, 3H); 7.53 (s, 2H); 7.68 (d, 2H, *J* = 7.5 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 13.9, 22.4, 23.8, 29.4, 31.4, 40.0, 54.4, 54.6, 55.3, 62.2, 114.3, 120.5, 120.6, 122.5, 122.8, 127.9, 133.6, 137.7, 140.9, 144.1, 152.0, 158.9. MS (ESI): m/z = 930 [M + 1]. Anal. Calcd. For $C_{49}H_{56}N_{18}O_2$: C, 63.34; H, 6.08; N, 27.14. Found: C, 63.45; H, 6.23; N, 27.27.

Second generation chlorodendrimer 16:

Following the general procedure **C**, reaction of 1,3-bis(chloromethyl)-5-propargyloxybenzene **12** (0.52g, 2.26 mmol, 6.2 equiv.) with the azidodendrimer **15** (0.5g, 0.54 mmol, 1.0 equiv.) gave the chlorodendrimer **16** as white solid after eluting from the column with $CHCl_3$: MeOH (19:1). Yield: 0.88g, 89%; M. P.: 141 ºC; ^1H NMR: (300 MHz, $CDCl_3$): δ_H 0.53 (br s, 4H); 0.70 (t, 6H, *J* = 6.6 Hz); 0.98-1.05 (m, 12H); 1.87-1.92 (m, 4H); 4.50 (s, 16H); 5.08 (s, 4H); 5.18 (s, 8H); 5.44 (s, 8H); 5.58 (s, 4H); 6.77 (s, 2H); 6.84 (s, 4H);

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6.95 (s, 11H); 6.99 (s, 4H); 7.04 (s, 1H); 7.22 (d, 2H, *J* = 7.8 Hz); 7.55 (s, 2H); 7.60 (s, 2H); 7.66 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR: (75 MHz, CDCl$_3$): δ_C 14.0, 22.4, 23.7, 29.4, 31.4, 39.9, 45.7, 53.7, 54.6, 55.3, 56.0, 61.9, 62.1, 76.0, 78.1, 114.7, 115.0, 115.1, 120.1, 120.6, 121.4, 121.7, 122.9, 122.9, 123.0, 127.2, 133.5, 137.1, 139.4, 139.5, 140.9, 143.4, 144.2, 152.0, 158.0, 158.6, 159.2. MS (MALDI-TOF): m/z = 1868 [M + Na]$^+$. Anal. Calcd. For C_{93} H_{96} Cl_8 N_{18} O_6: C, 60.53; H, 5.24; N, 13.66. Found: C, 60.39; H, 5.37; N, 13.57.

Second generation azidodendrimer 17:

Following the general procedure **B**, reaction of the second generation chlorodendrimer **16** (1.0 g, 0.54 mmol, 1.0 equiv.) with NaN_3 (0.35g, 5.42 mmol, 10.0 equiv.) gave the azidodendrimer **17** as colorless gel after eluting from the column with CHCl$_3$: MeOH (19:1). Yield: 0.80g, 80%; M. P.: 135 ºC; ^{1}H NMR: (300 MHz, CDCl$_3$): δ_H 0.53 (br s, 4H); 0.71 (t, 6H, *J* = 6.6 Hz); 0.99-1.08 (m, 12H); 1.87-1.93 (m, 4H); 4.31 (s, 16H); 5.10 (s, 4H); 5.21 (s, 8H); 5.45 (s, 8H); 5.59 (s, 4H); 6.79 (s, 2H); 6.86 (s, 6H); 6.90 (s, 12H); 7.22 (d, 2H, *J* = 7.8 Hz); 7.54 (s, 2H); 7.59 (s, 4H); 7.67 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR: (75 MHz, CDCl$_3$): δ_C 14.0, 22.4, 23.7, 29.4, 29.7, 31.4, 39.9, 53.7, 54.4, 54.6, 55.3, 61.9, 62.1, 77.3, 114.3, 114.7, 120.1, 120.6, 120.6, 122.9, 122.9, 123.0, 127.2, 133.5, 137.1, 137.7, 140.9, 143.4, 144.3, 152.0, 158.8, 159.2. MS (MALDI-TOF): m/z = 1921 [M + Na]$^+$. Anal. Calcd. For C_{93} H_{96} N_{42} O_6: C, 58.85; H, 5.10; N, 30.99. Found: C, 58.97; H, 5.27; N, 30.77.

Synthesis of G_0 dendrimer 1:

Following the general procedure **C**, the dendrimer **1** was obtained as yellow colored solid from 2,7-bis(azidomethyl)-9,9-dihexyl-9*H*-fluorene **13** (0.15 g, 0.34 mmol) and (E)-3-(4-(diphenylamino)phenyl)-1-(4-(prop-2-ynyloxy)phenyl)prop-2-en-1-one **10** (0.33 g, 0.71 mmol) and after eluting from the column with CHCl$_3$-MeOH (19:1). Yield: 0.38g, 86%; M.p.: 96°C; ^{1}H NMR: (300 MHz, CDCl$_3$): δ_H 0.52 (br s, 4H); 0.73 (t, 6H, *J* = 6.6 Hz); 0.98-1.08 (m, 12H); 1.86-1.92 (m, 4H); 5.26 (s, 4H); 5.61 (s, 4H); 7.04-7.15 (m, 18H); 7.22-7.32

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(m, 16H); 7.38 (d, 2H, *J* = 15.6 Hz); 7.48 (d, 2H, *J* = 8.4 Hz); 7.54 (s, 2H); 7.67-7.78 (m, 4H); 8.00 (d, 4H, *J* = 9 Hz). ^{13}C NMR: (75 MHz, CDCl$_3$): δ_C 14.0, 22.4, 23.8, 29.5, 29.7, 31.4, 40.0, 54.6, 55.4, 62.2, 114.5, 119.1, 120.6, 121.7, 122.4, 122.5, 122.8, 124.1, 125.0, 125.1, 125.4, 127.2, 128.0, 129.4, 129.5, 129.6, 130.7, 132.0, 133.5, 140.9, 144.0, 146.9, 147.1, 150.1, 152.0, 161.7, 188.7. MS (MALDI-TOF): m/z = 1326 [M + Na]$^+$. Anal. Calcd. For $C_{87}H_{82}N_8O_4$: C, 80.16; H, 6.34; N, 8.60. Found: C, 80.37; H, 6.27; N, 8.77.

Synthesis of G$_0$ dendrimer 2:

Following the general procedure **C**, the dendrimer **2** was obtained as yellow colored solid from 2,7-bis(azidomethyl)-9,9-dihexyl-9*H*-fluorene **13** (0.1 g, 0.22 mmol) and (E)-3-(4-(bis(4-bromophenyl)amino)phenyl)-1-(4-(prop-2-ynyloxy)phenyl)prop-2-en-1-one **11** (0.29 g, 0.49 mmol) and after eluting from the column with CHCl$_3$-MeOH (19:1). Yield: 0.28g, 78%; M.p.: 108°C; ^{1}H NMR: (300 MHz, CDCl$_3$): δ_H 0.53 (br s, 4H); 0.73 (t, 6H, *J* = 6.6 Hz); 1.00-1.06 (m, 12H); 1.87-1.92 (m, 4H); 5.26 (s, 4H); 5.62 (s, 4H); 7.00-7.06 (m, 18H); 7.23-7.26 (m, 2H); 7.38-7.43 (m, 10H); 7.50 (d, 4H, *J* = 8.4 Hz); 7.55 (s, 2H); 7.67-7.77 (m, 4H); 8.01 (d, 4H, *J* = 8.7 Hz). ^{13}C NMR: (75 MHz, CDCl$_3$): δ_C 14.0, 22.5, 23.8, 29.5, 29.7, 31.4, 40.0, 54.6, 55.4, 62.1, 114.6, 116.9, 119.9, 120.6, 122.6, 122.8, 126.5, 127.2, 129.3, 129.8, 130.7, 131.8, 132.7, 133.5, 141.0, 143.5, 143.9, 145.7, 149.0, 152.0, 161.8, 188.6. MS (MALDI-TOF): m/z = 1642 [M + Na]$^+$. Anal. Calcd. For $C_{87}H_{78}Br_4N_8O_4$: C, 64.53; H, 4.86; N, 6.92. Found: C, 64.35; H, 4.97; N, 6.79.

Synthesis of G$_1$ dendrimer 3:

Following the general procedure **C**, the dendrimer **3** was obtained as yellow colored solid from the azidodendrimer **15** (0.1 g, 0.11 mmol) and (E)-3-(4-(diphenylamino) phenyl)-1-(4-(prop-2-ynyloxy) phenyl) prop-2-en-1-one **10** (0.19 g, 0.45 mmol) and after eluting from the column with CHCl$_3$-MeOH (19:1). Yield: 0.19g, 76%; M.p.: 138°C; ^{1}H NMR: (300 MHz, CDCl$_3$): δ_H 0.52 (br s, 4H); 0.68 (t, 6H, *J* = 6.3 Hz); 0.97-1.05 (m, 12H); 1.87 (br s, 4H); 5.07

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(s, 4H); 5.24 (s, 8H); 5.44 (s, 8H); 5.44 (s, 8H); 5.58 (s, 4H); 6.75 (s, 2H); 6.84 (s, 4H); 7.00-7.14 (m, 36H); 7.21 (d, 4H, *J* = 7.8 Hz); 7.26-7.40 (m, 16H); 7.47 (d, 8H, *J* = 8.7 Hz); 7.54 (s, 2H); 7.60 (s, 4H); 7.65 (d, 2H, *J* = 7.5 Hz); 7.74 (d, 4H, *J* = 15.6 Hz); 7.98 (d, 8H, *J* = 8.7 Hz). ^{13}C NMR: (75 MHz, CDCl$_3$): δ_C 14.0, 22.4, 23.8, 29.4, 29.7, 31.4, 53.7, 62.1, 114.6, 114.7, 119.1, 119.9, 120.6, 121.6, 122.9, 122.9, 123.0, 124.1, 125.4, 127.2, 128.0, 129.4, 129.5, 129.7, 130.7, 132.0, 133.5, 137.1, 140.9, 143.4, 144.0, 144.1, 146.9, 147.1, 150.1, 152.0, 159.5, 161.7, 188.7. MS (MALDI-TOF): m/z = 2670 [M + Na]$^+$. Anal. Calcd. For $C_{169}H_{148}N_{22}O_{10}$: C, 76.68; H, 5.64; N, 11.64. Found: C, 76.57; H, 5.77; N, 11.57.

Synthesis of G$_1$ dendrimer 4:

Following the general procedure **C**, the dendrimer **4** was obtained as yellow colored solid from the azidodendrimer **15** (0.1 g, 0.11 mmol) and (E)-3-(4-(bis(4-bromophenyl)amino)phenyl)-1-(4-(prop-2-ynyloxy)phenyl)prop-2-en-1-one **11** (0.1 g, 0.45 mmol) and after eluting from the column with CHCl$_3$-MeOH (19:1). Yield: 0.25g, 81%; M.p.: 138°C; ^{1}H NMR: (300 MHz, CDCl$_3$): δ_H 0.54 (br s, 4H); 0.70 (t, 6H, *J* = 6.3 Hz); 0.98-1.05 (m, 12H); 1.88 (br s, 4H); 5.09 (s, 4H); 5.26 (s, 8H); 5.46 (s, 8H); 5.60 (s, 4H); 5.58 (s, 4H); 6.77 (s, 2H); 6.86 (s, 4H); 6.98-7.06 (m, 32H); 7.23 (d, 2H, *J* = 7.8 Hz); 7.39-7.44 (m, 20H); 7.51 (d, 8H, *J* = 8.4 Hz); 7.54 (d, 4H, *J* = 10.2 Hz); 7.62 (s, 2H); 7.74 (d, 4H, *J* = 15.3 Hz); 8.00 (d, 8H, *J* = 8.7 Hz). ^{13}C NMR: (75 MHz, CDCl$_3$): δ_C 14.0, 22.4, 23.8, 31.4, 39.9, 53.7, 69.1, 62.1, 114.6, 114.7, 116.9, 119.9, 120.6, 122.6, 122.9, 123.0, 123.1, 126.5, 127.2, 129.4, 129.8, 130.7, 131.8, 132.7, 133.5, 137.1, 140.9, 143.4, 143.6, 144.0, 145.7, 149.0, 152.0, 159.2, 161.8, 188.5. MS (MALDI-TOF): m/z = 3301 [M + Na]$^+$. Anal. Calcd. For $C_{169}H_{140}Br_8N_{22}O_{10}$: C, 61.92; H, 4.30; N, 9.40. Found: C, 61.79; H, 4.47; N, 9.57.

Synthesis of G$_2$ dendrimer 5:

Following the general procedure **C**, the dendrimer **5** was obtained as yellow colored solid from the azidodendrimer **17** (0.15 g, 0.08 mmol) and (E)-3-(4-(diphenylamino) phenyl)-

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1-(4-(prop-2-ynyloxy) phenyl) prop-2-en-1-one **10** (0.29 g, 0.67 mmol) and after eluting from the column with $CHCl_3$-MeOH (19:1). Yield: 0.30g, 71%; M.p.: 122°C; ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 0.50 (br s, 4H); 0.64 (t, 6H, J = 6 Hz); 0.86-0.92 (m, 12H); 1.85 (br s, 4H); 4.95 (s, 4H); 5.00 (s, 8H); 5.16 (s, 16H); 5.36 (s, 24H); 5.55 (s, 4H); 6.71-6.77 (m, 20H); 6.88-7.73 (m, 166H); 7.98 (d, 12H, J = 8.7 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 14.0, 22.4, 22.7, 29.3, 29.4, 31.3, 31.9, 53.6, 61.9, 114.5, 118.9, 121.5, 122.3, 123.6, 123.7, 124.1, 125.1, 125.4, 127.9, 128.4, 129.2, 129.4, 129.5, 129.7, 130.6, 130.6, 131.9, 137.1, 143.8, 144.0, 146.8, 147.0, 150.1, 158.9, 161.7, 188.6. MS (MALDI-TOF): m/z = 5357 $[M + Na]^+$. Anal. Calcd. For C_{333} H_{280} N_{50} O_{22}: C, 74.98; H, 5.29; N, 13.13. Found: C, 74.87; H, 5.17; N, 13.27.

Synthesis of G_2 dendrimer 6:

Following the general procedure **C**, the dendrimer **6** was obtained as yellow colored solid from the azidodendrimer **17** (0.1 g, 0.05 mmol) and (E)-3-(4-(bis(4-bromophenyl)amino)phenyl)-1-(4-(prop-2-ynyloxy)phenyl)prop-2-en-1-one **11** (0.26 g, 0.45 mmol) and after eluting from the column with $CHCl_3$-MeOH (19:1). Yield: 0.25g, 74%; M.p.: 158°C; ^{1}H NMR: (300 MHz, $CDCl_3$): δ_H 0.51 (br s, 4H); 0.64 (t, 6H, J = 5.7 Hz); 0.93-1.00 (m, 12H); 1.87 (br s, 4H); 4.96 (s, 4H); 5.00 (s, 8H); 5.16 (s, 16H); 5.37 (s, 24H); 5.57 (s, 4H); 6.72-7.79 (m, 166H); 7.93 (d, 16H, J = 8.1 Hz). ^{13}C NMR: (75 MHz, $CDCl_3$): δ_C 14.0, 22.4, 29.4, 29.7, 31.3, 53.5, 61.9, 114.5, 114.6, 116.9, 119.8, 120.0, 122.5, 123.5, 124.1, 124.8, 125.4, 126.5, 129.1, 129.5, 129.7, 129.8, 130.6, 130.7, 131.7, 132.3, 132.4, 132.6, 137.1, 143.4, 143.5, 145.6, 146.7, 148.9, 158.9, 161.7, 188.4. MS (MALDI-TOF): m/z = 6619 $[M + Na]^+$. Anal. Calcd. For C_{333} H_{264} Br_{16} N_{50} O_{22}: C, 60.63; H, 4.03; N, 10.62. Found: C, 60.81; H, 4.17; N, 10.50.

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