



A STUDY OF n-HEXYLOXYBENZENE CORED CHALCONE BASED CARBAZOLE DENDRIMERS WITH TRIAZOLE BRIDGING UNIT

Mrs.Sabina Basheer

Researcher

Nesam College of Health Sciences, Tirunelveli, Tamilnadu, INDIA

Abstract: Dendrimers with their versatile nature in both synthesis and application have gained appreciation and popularity among the other supra molecules. Nowadays, dendrimers find application in the field of medicine for target oriented drug, bioimaging and as diagnostic material tool in MRI88 and X-Ray contrast agent and also used as bactericidal, fungicidal, and anti-viral agents. Recently, dendrimers and dendrimer-based nanoparticles are attractive candidates for improving the solar energy conversion and in OLEDs. The regular and hierarchically branched nature of dendrimers make them very much interesting in the field of photo conversion process. In addition to the biological applications of chalcones, they are also known for their fascinating optical and electronic properties. Chalcones acts as an effective electron accepting unit and by proper usage of the chalcone in the synthesis of dendrimers would results in the enhanced improvement in the power conversion process. Carbazole is known to be as an electron rich fused heterocyclic molecule which bears the nitrogen atom. This simple molecule gets attention in the material field due to its engrossing properties such as low cost, greater stability. This paper is detailed study with results and discussion.

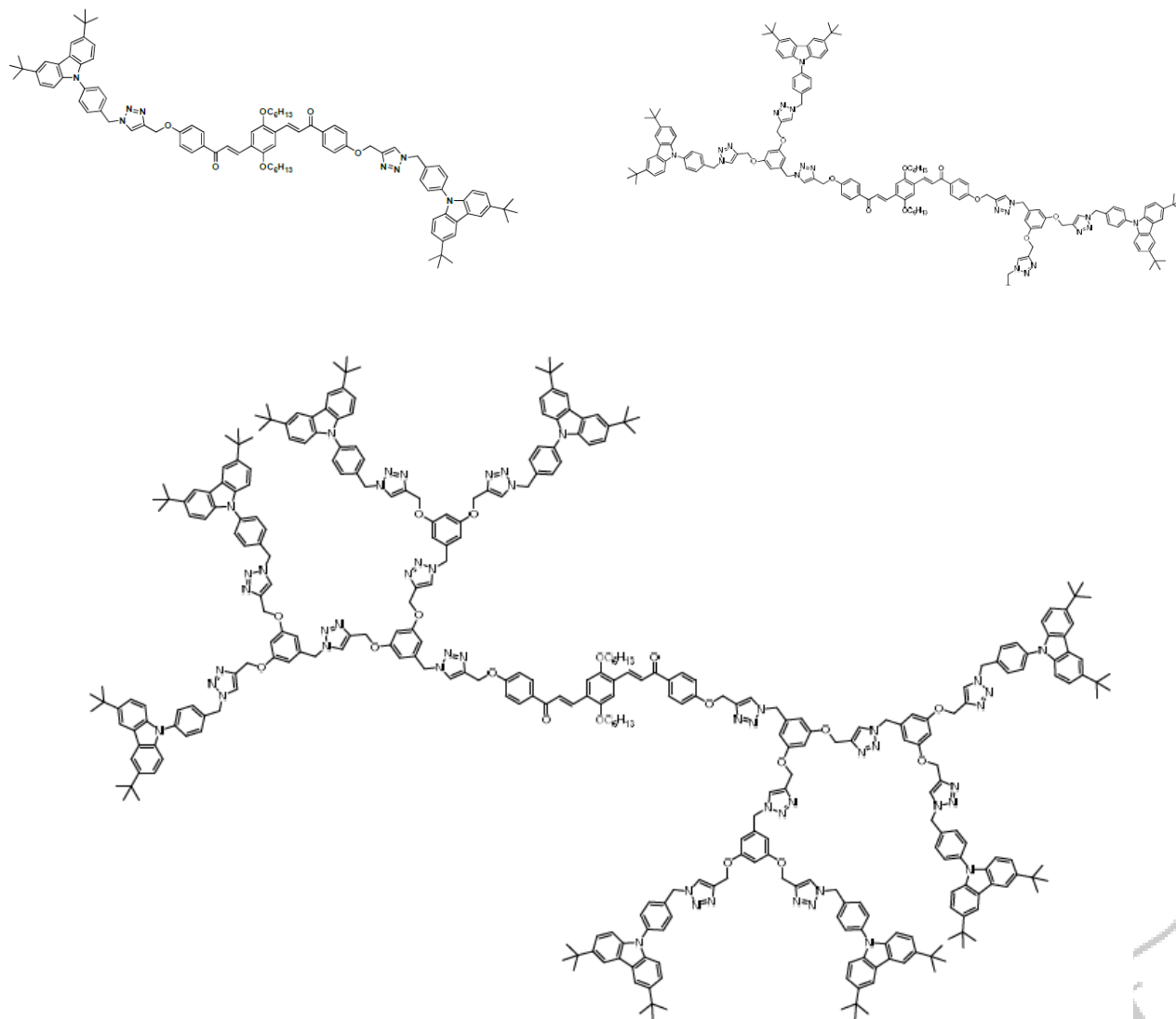
Index Terms – n-Hexyloxybenzene cored chalcone, Carbazole Dendrimers.

I.INTRODUCTION

In the early 2001, Sharpless disclosed a powerful strategy in assembling the simple molecular entities into an amazing molecule through “Click Chemistry” from which the interesting molecules are synthesized to fulfil the demands of the world especially in the field of human therapy and in the material sciences. The reaction between the terminal alkynes and azides in the presence of copper(I) ion to afford stereoselectivity 1,2,3-triazole becomes a remarkable achievement in click chemistry which is useful in the modern synthetic organic chemistry.

Dendrimers are synthesized by the application of “Click Chemistry”⁸⁹ (formation of 1,2,3-triazole ring) and is a very successful route due to the reliability and stereo selectivity of the reaction. Triazole bridged dendrimers have gained interest especially in the field of energy conversion process (DSSC). By careful attachment of chromophores either on the periphery or in the core region of the dendrimers, they are useful as additive to increase the power conversion efficiency in DSSC. Keeping such views, this chapter deals with the synthesis and photophysical properties of carbazole decorated chalconyl n-hexyloxybenzene cored dendrimers through click chemistry and their application as additive in DSSC.

Molecular structure of chalconyl n-hexyloxybenzene cored carbazole decorated dendrimers



II. RESULT AND DISCUSSION

Carbazole based dendrimers have a variety of application in the material field especially in light emitting diode and for solar energy harvesting purpose. By linking the carbazole molecules with triazole and with chalconyl n-hexyloxybenzene as core, in dendrimer interesting results can be obtained. This is deals with the synthesis, photo physical property and application of the synthesized dendrimers as additive in DSSC. This is divided into three sections.

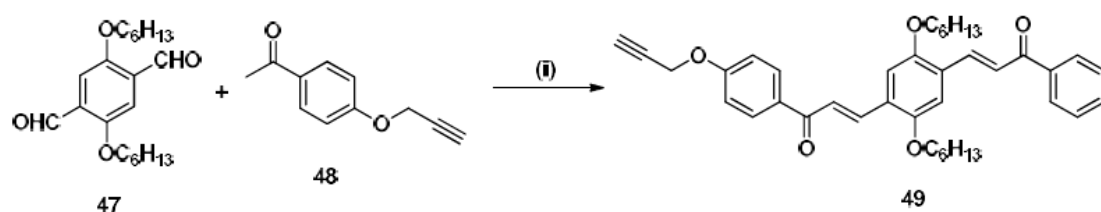
Section 1 : Synthesis of chalconyl n-hexyloxybenzene cored chalcone based carbazole dendrimers

Section 2 : Absorption and emission properties of synthesized dendrimers

Section 3 : Application of the synthesized dendrimers as additive in DSSC

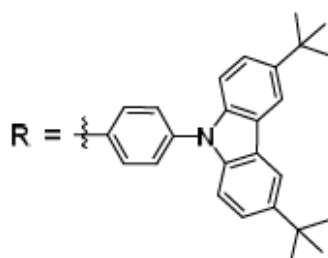
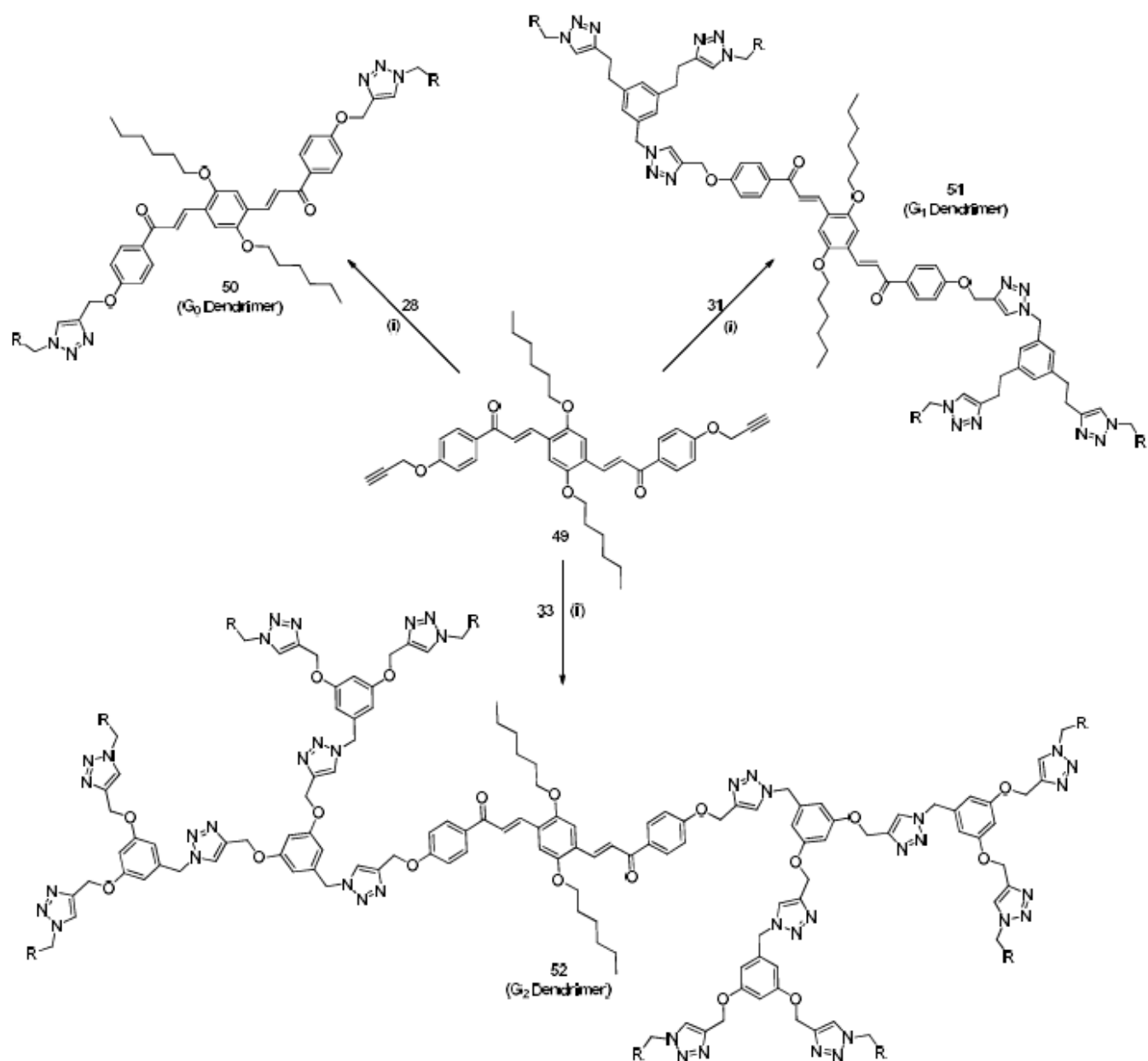
Section 1 : Synthesis of chalconyl n-hexyloxybenzene cored chalcone based carbazole dendrimers

Bis propargyloxy-n-hexyloxy benzene cored chalcone 49 was synthesized as bright orange solid in 83% yield by the aldol condensation between 1.0 equiv. of 2,5-bis(hexyloxy) terephthalaldehyde 47 and 2.0 equiv. of 1-(4-(prop-2-ynyloxy) phenyl) ethanone 48 in the presence of NaOH as base (Scheme 9).



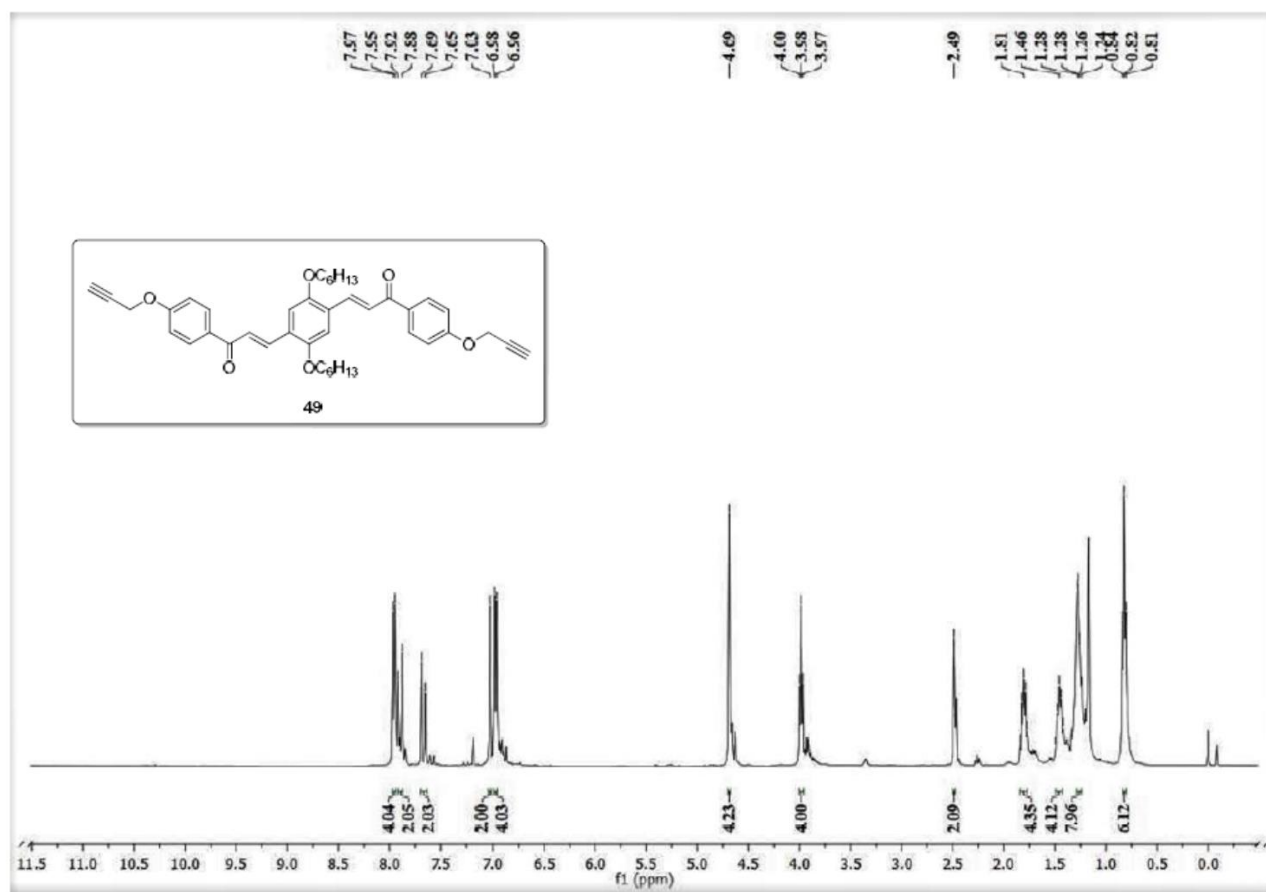
Scheme 9: Reagents and conditions: (i) NaOH, EtOH, rt, 12 h, 49 (83%)

The ^1H NMR spectrum of the bis propargyloxy-n-hexyloxy benzene cored chalcone 49 displayed a triplet at δ 2.49 and a doublet δ 4.69 for the acetylenic protons in addition to the other aromatic, olefinic and alkyl proton signals. The ^{13}C NMR spectrum of the chalconyl core 49 confirmed the presence of acetylenic group by the appearance of signals at δ 55.9, 76.0 and 77.9 and the carbonyl carbon appeared at δ 189.2 in addition to the other aliphatic and aromatic carbon signals.

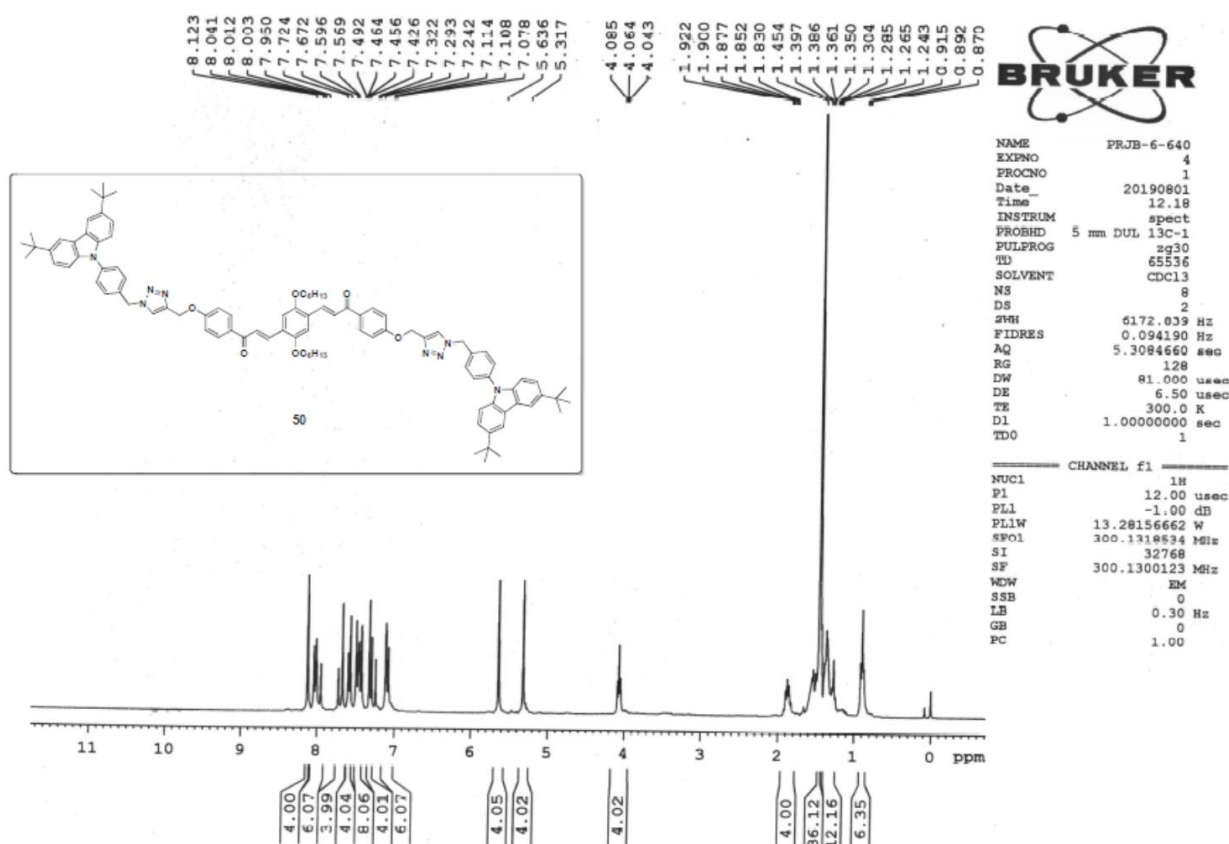
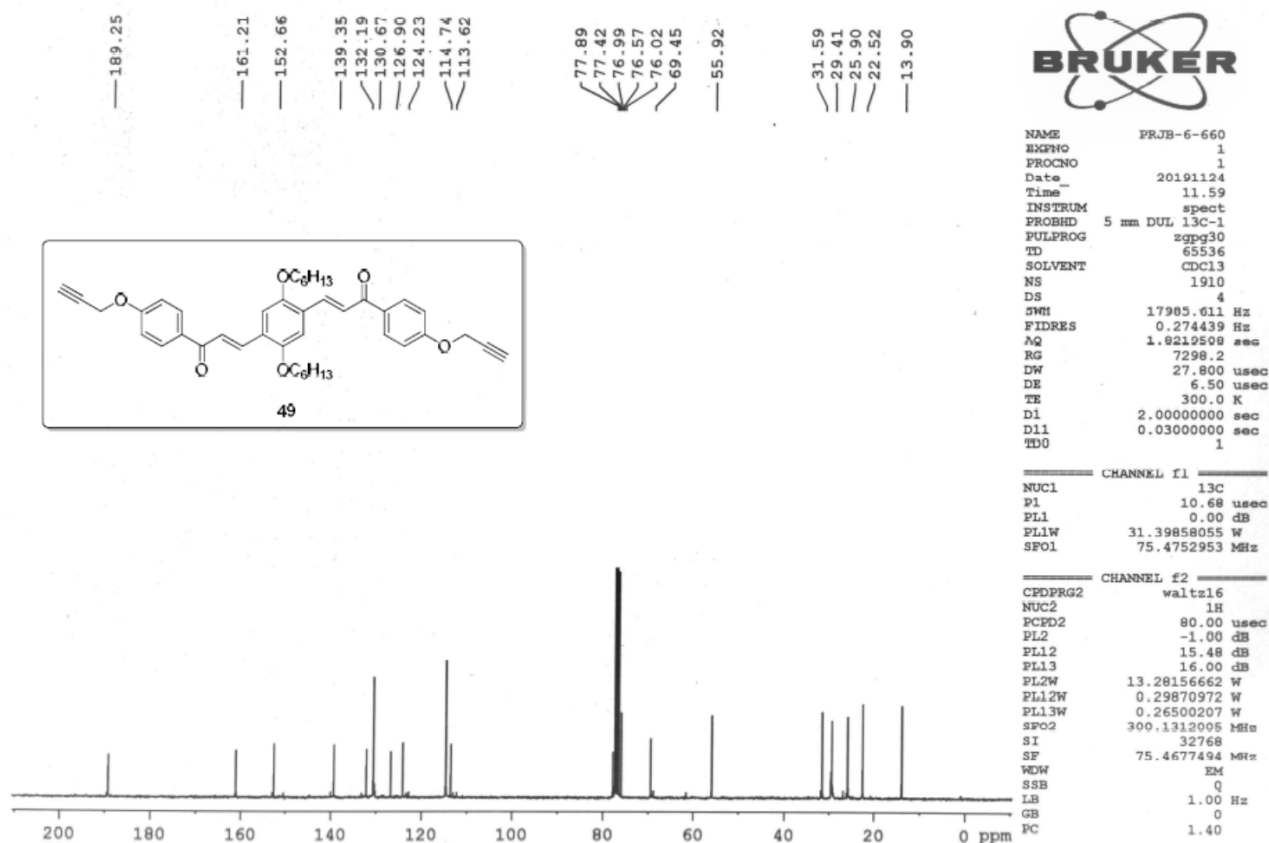


Scheme 10: Reagents and conditions: (i) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5 mol %), sodium ascorbate (10 mol %), THF: H_2O (1:1, v/v), rt, overnight. 50 (89%), 51 (83%) and 52 (73%)

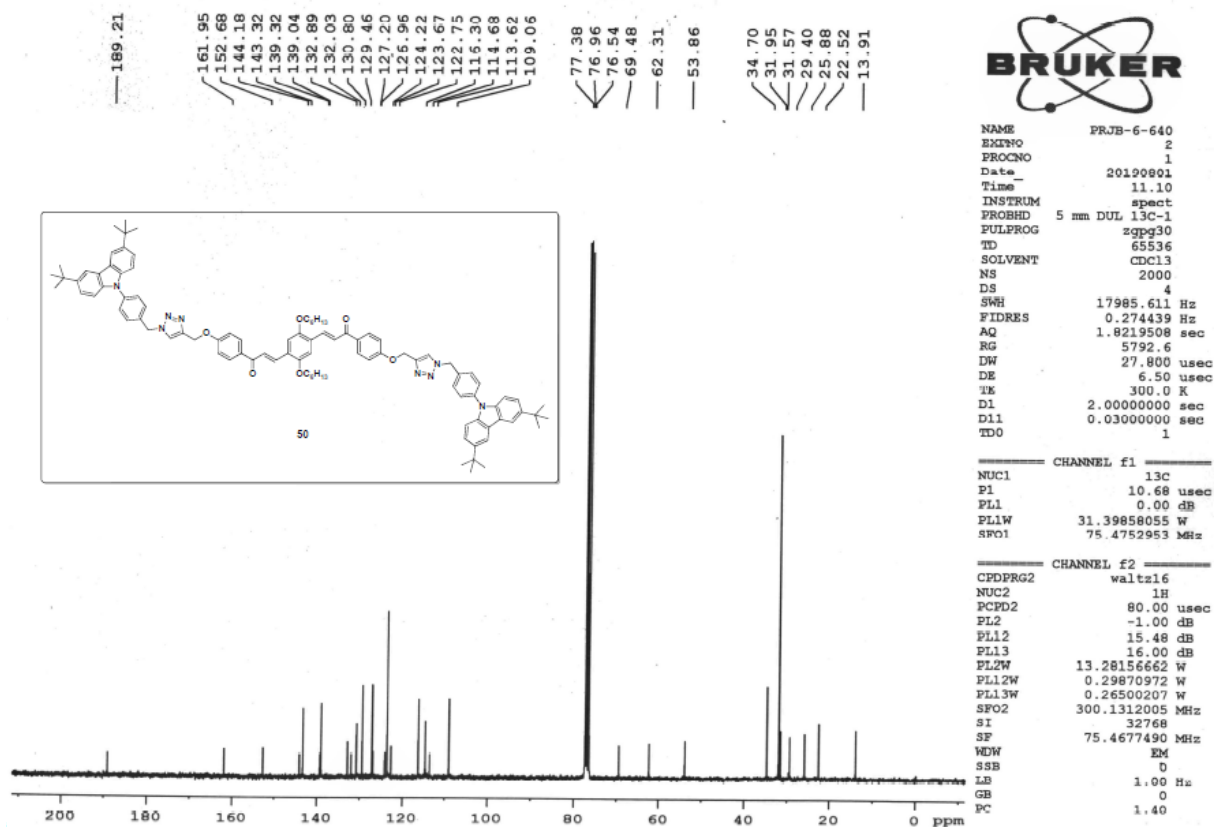
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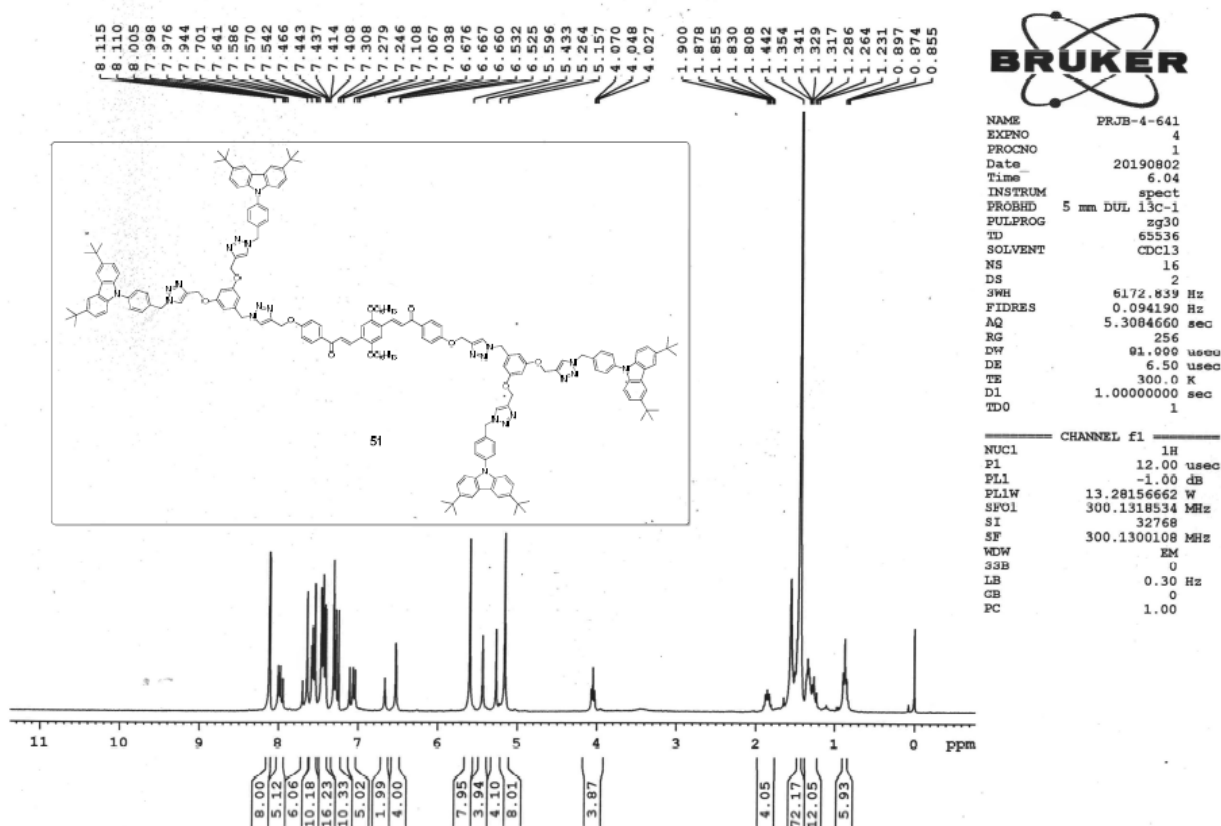
^1H NMR Spectrum (400 MHz, CDCl_3) of Bis propargyloxy-*n*-hexyloxy benzene cored chalcone 49



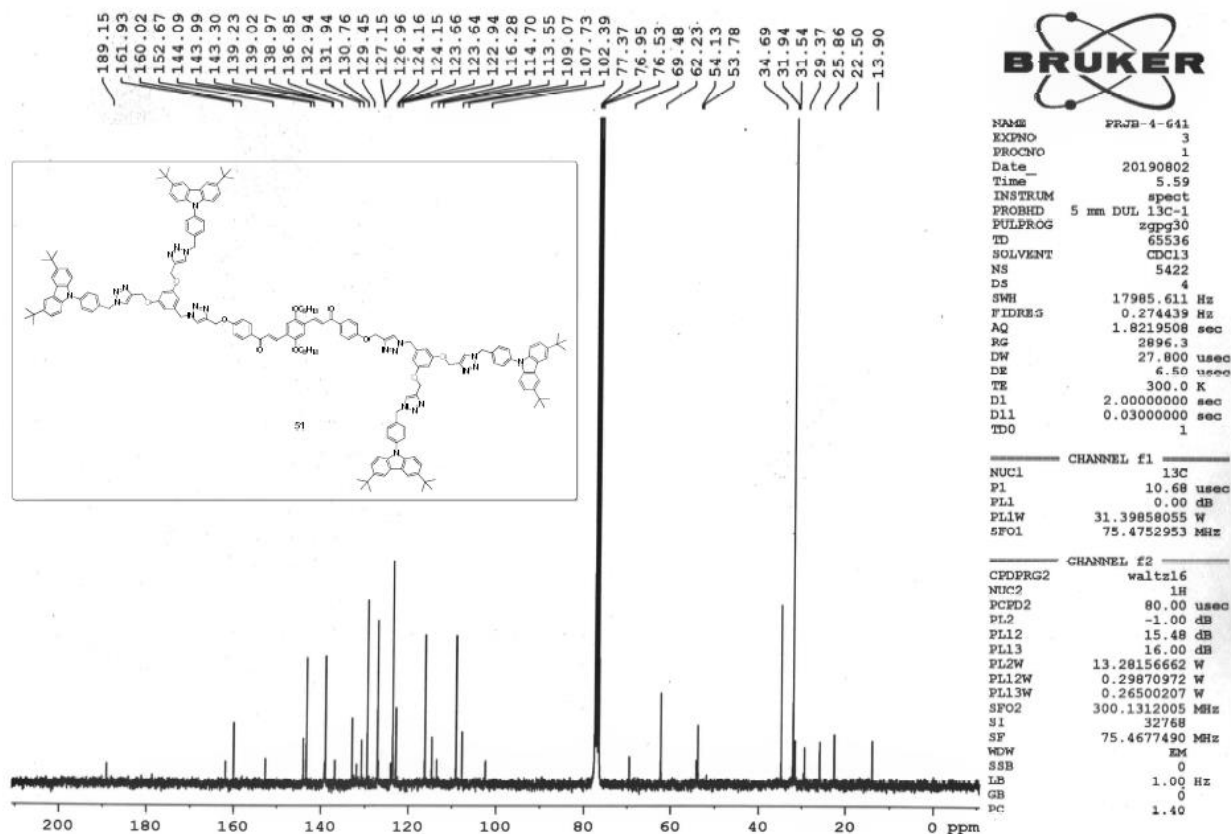
¹H NMR Spectrum (300 MHz, CDCl₃) of Zeroth generation dendrimer (G₀) 50



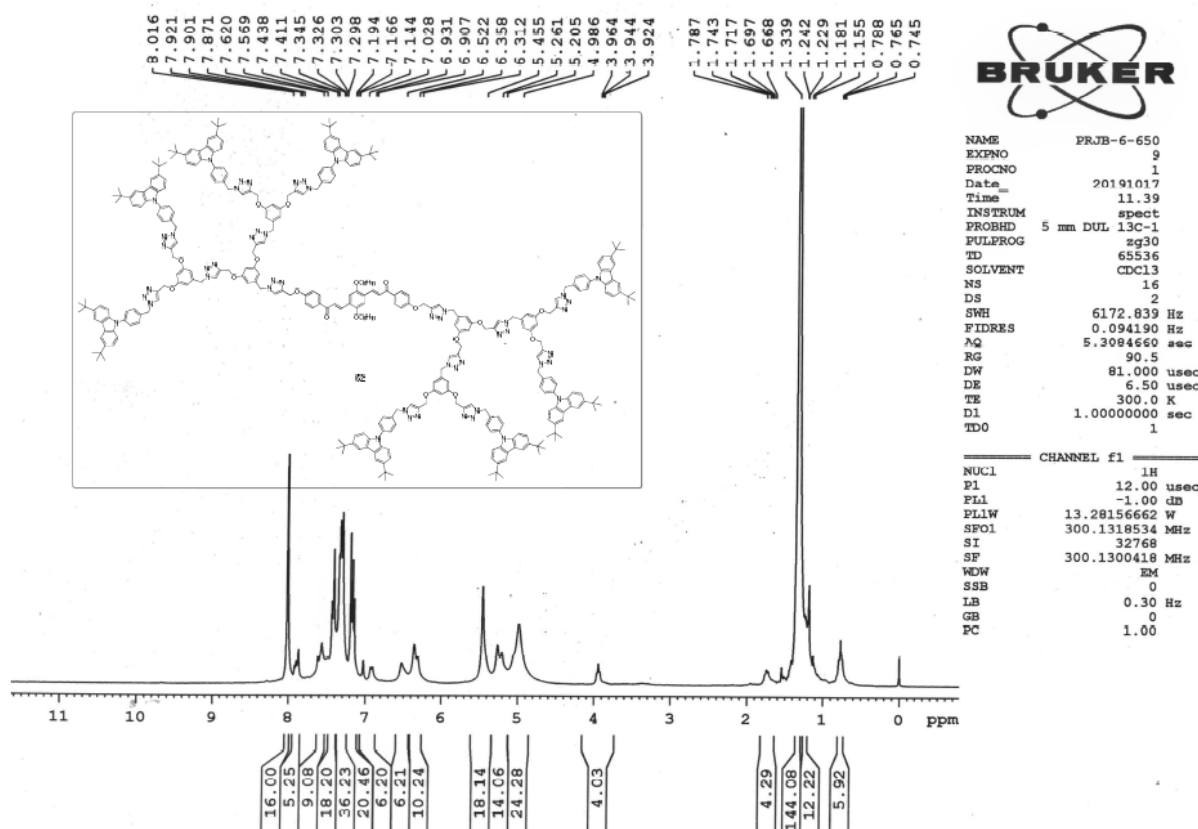
¹³C NMR Spectrum (75 MHz, CDCl₃) of Zeroth generation dendrimer (G₀) 50



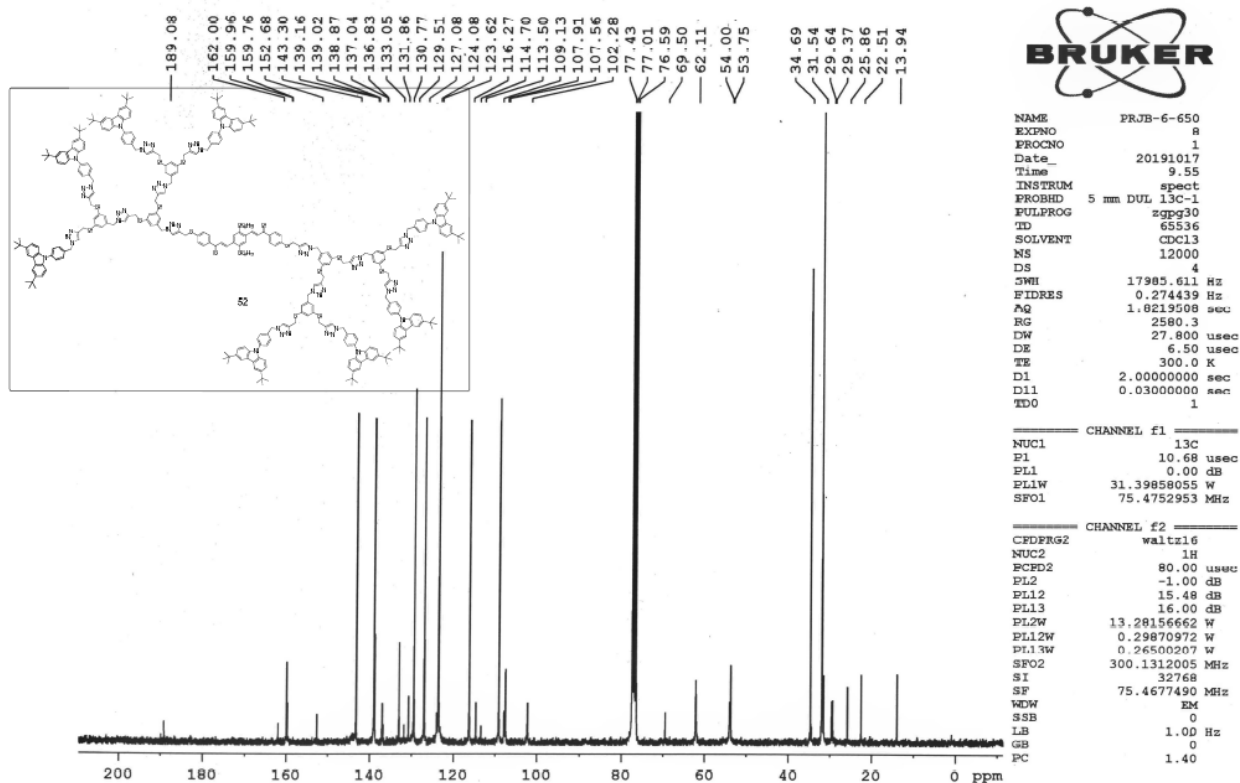
¹H NMR Spectrum (300 MHz, CDCl₃) of First generation dendrimer (G₁) 51



¹³C NMR Spectrum (75 MHz, CDCl₃) of First generation dendrimer (G₁) 51



¹H NMR Spectrum (300 MHz, CDCl₃) of Second generation Dendrimer (G₂) 52



¹³C NMR Spectrum (75 MHz, CDCl₃) of Second generation Dendrimer (G₂) 52

Reaction of 1.0 equiv. of bis propargyloxy-n-hexyloxy benzene cored chalcone 49 with 2.2 equiv. of each of the dendritic azides 28, 31 and 33 under click reaction conditions. viz., 5 mol% CuSO₄·5H₂O and 10 mol % sodium ascorbate in THF:H₂O (1:1) for 12 h afforded zeroth, first and second generation carbazole dendrimers 50, 51 and 52 in 89%, 83% and 73% yields respectively (Scheme 10).

The ¹H NMR spectrum of the zeroth generation carbazole dendrimer (G₀) 50 showed the signals for N - methylene and O - methylene protons at δ 5.32 and 5.63 along with the other the aliphatic and aromatic proton signals. The ¹³C NMR spectrum of the G₀ dendrimer 50 showed N - methylene and O - methylene carbons at δ 53.8, 62.3, 69.4 and the carbonyl carbon appeared at δ 189.2 in addition to the other aliphatic and aromatic carbon signals.

The ¹H NMR spectrum of the first generation carbazole dendrimer (G₁) 51 showed the signals for N - methylene and O - methylene protons at δ 5.15, 5.26, 5.43, 5.59 along with the other the aliphatic and aromatic proton signals. The ¹³C NMR spectrum of the G₁ dendrimer 51 showed N - methylene and O - methylene carbons at δ 53.7, 54.1, 62.2, 69.4, and the carbonyl carbon appeared at δ 189.1 in addition to other aliphatic and aromatic carbon signals.

The ¹H NMR spectrum of the second generation carbazole dendrimer (G₂) 52 showed the signals for N - methylene and O - methylene protons between δ 4.98 and 5.45 along with the other the aliphatic and aromatic proton signals. The ¹³C NMR spectrum of the G₂ dendrimer 52 showed N - methylene and O - methylene carbons at δ 53.7, 54.0, 62.1 and 69.5 respectively and the carbonyl carbon appeared at δ 189.1 in addition to other aliphatic and aromatic carbon signals. Further, the structure of dendrimers 50-52 was also confirmed from elemental analysis.

Section 2 : Absorption and emission properties of synthesized dendrimers

Figure 1 and 2 shows the UV absorption and emission spectra of dendrimers 50, 51 and 52 recorded at a concentration of 1 × 10⁻⁵ M in DCM and the data are summarized in Table 1. All the synthesized dendrimers 50, 51 and 52 showed almost identical absorption spectrum with absorption bands at 297, 331 and 344 nm. The absorption band at 297 nm is due to π-π* transition of localized electron on carbazole moieties present in the periphery of the dendrimers. Another absorption band at 331 and 344 nm may be due to the chalcone core unit.

It is clear from the absorption spectrum, as the generation of the dendrimer increases the number of carbazole units at the periphery also increases which in turn increases the molar extinction coefficients, when record at the same concentration of the dendrimers 50, 51 and 52. The increase in absorbance from lower generation to higher generation amplifies the light absorbing capacity of the dendrimer and is known as valence effect in dendrimer chemistry^{73a}. The increase in the light absorbing ability of the synthesized carbazole dendrimers 50, 51 and 52 makes them as a good light harvesting material.

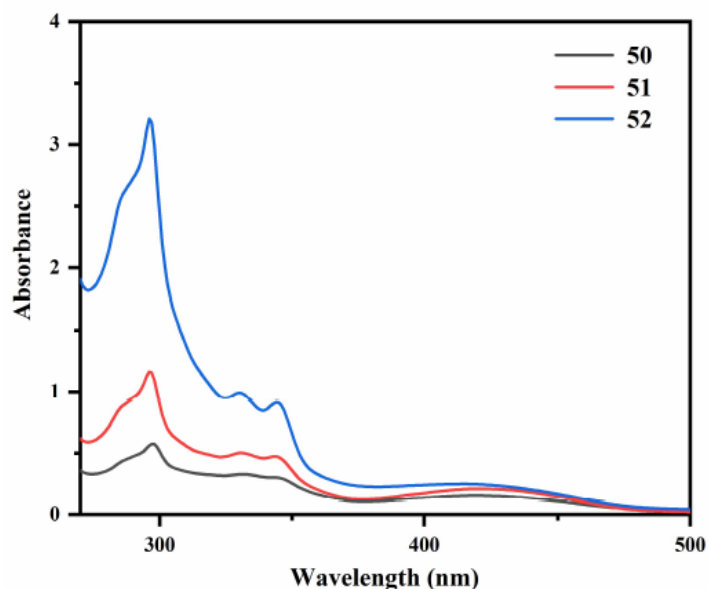


Figure 1: UV-Vis absorption spectra of the carbazole dendrimers 50, 51 and 52 in DCM (1×10^{-5} M)

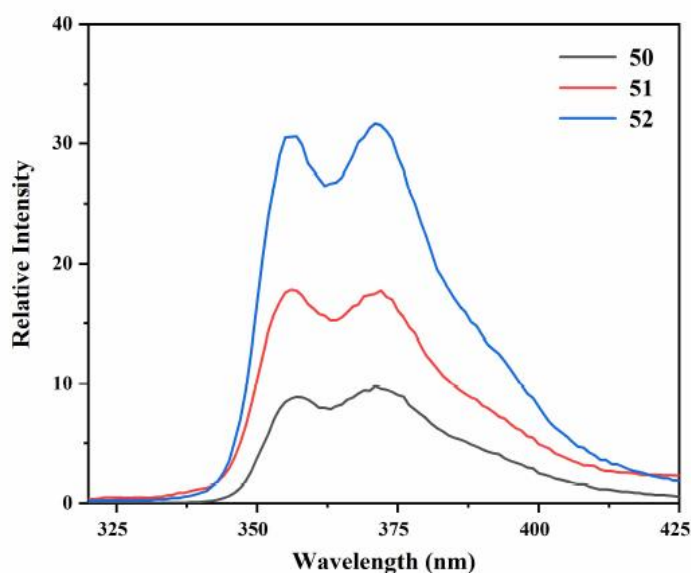


Figure 2: Emission spectra of the carbazole dendrimers 50, 51 and 52 in DCM (1×10^{-5} M) when excited at 297 nm.

Fluorescence spectra of dendrimers 50, 51 and 52 are recorded at a concentration of 1×10^{-5} M in DCM by exciting the synthesized dendrimers at 297 nm. Dendrimers 50, 51 and 52 show emission band around 355 and 370 nm. This dual emission band corresponds to 9-phenyl carbazole which gives due to the twisted intramolecular charge transfer (TICT)⁷⁹ in the polar solvent. Figure 2 clearly shows that the emission intensity of the dendrimers increases as the generation increases, due to the increased number of carbazole units, which is described as the valence effect in dendrimer chemistry^{73a}.

Table 1 Absorption and emission properties of synthesized dendrimers 50, 51 and 52

Dendrimers (Generation)	$\lambda_{\max}$ (nm)	ϵ ($\times 10^4$ L mol ⁻¹ cm ⁻¹)	λ_{em} (nm)
50, (G ₀)	297, 331, 343	5.7, 3.3, 3.1	355, 371
51, (G ₁)	296, 330, 343	11.7, 5.1, 4.8	356, 371
52, (G ₂)	296, 330, 344	32.0, 9.9, 9.2	356, 371

Section 3 : Application of the synthesized dendrimers as additive in DSSC

The DSSC is typical electrochemical cell, which is considered to have the sandwich structure and consists of photoanode, electrolyte and the counter electrode. The electrolyte is considered to be one of the components of the cell, where the electron transfer occurs effectively. The electrolyte plays an important role in enhancing the performance of the cell. Some factors such as steady sublimation of iodine in the electrolyte medium and the back-ward flow of electron into the electrolyte media are the major reasons for the poor performance of the cell.

The use of nitrogenous compounds such as pyrazole, imidazole, triazole, pyridine, pyrimidine and pyrazine in the electrolyte medium reduces the sublimation of iodine in the electrolyte system and increases the performance of the DSSC. The addition of these compound as the supporting electrolyte or additives increase the short-circuit current (J_{sc}) and the open circuit voltage (V_{oc}) considerably. The nitrogen atom containing molecules attributes to the considerable shift in the conduction band of the TiO_2 more towards the negative potential due to the higher electron recombination at the layer between the TiO_2 and the electrolyte.

Dendrimers which are constructed with many triazole bridging units serves has an excellent additive in the redox medium I^-/I_3^- . Triazole based carbazole decorated dendrimers reduce the charge recombination process and also reduce the sublimation of iodine through effective interaction with the electrolyte medium. Figure 3 shows the current-voltage (I-V) curve for the bare cell and with the addition of carbazole dendrimers 50, 51 and 52 as an additive to the redox electrolyte. The photovoltaic performance of the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (ff), and the electric energy efficiency (η) are summarized in Table 2.

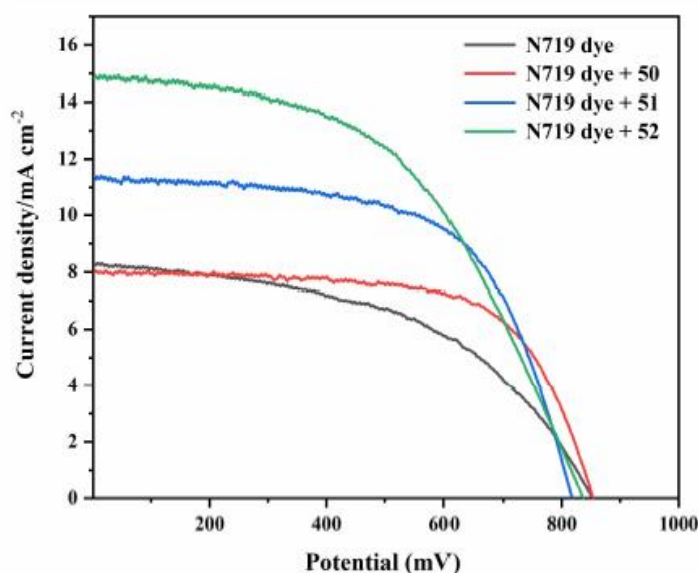


Figure 3: Current voltage (I-V) curve for the bare cell and with addition of dendrimers 50, 51 and 52 as additive simulated solar light at 100 mW cm^{-2}

The cell without the additive shows an efficiency of 3.51% whereas upon addition of carbazole dendrimers 50, 51 and 52 to the electrolyte gives the enhanced efficiency. The efficiency of the cell increases with the increase in the generation of the carbazole dendrimers which accounts to the increase of the carbazole units on the surface and also the triazole ring units. The triazole units binds or coordinates well with the iodine in the electrolyte system, thereby decreases the sublimation of iodine efficiently. This increase in the number of triazole and carbazole units from G_0 to G_2 results in the increase in the electron recombination at the photoanode and electrolyte medium. The cells with carbazole based triazole dendrimers doped in redox couple based DSSC found remarkably stable and the photocurrent maintains above 85% of the initial value after one week of storage.

The higher generation carbazole based triazole dendrimers shows the effective power conversion efficiency of 6.34% because of the effective conjugation of triazole units and carbazole moiety present in the dendrimers which in turn reduces the sublimation rate of I_2 in the redox system. The G_2 dendrimers gives short-circuit current density (J_{sc}) of 14.58 mA cm^{-2} , the open-circuit voltage (V_{oc}) of 830 mV and the fill factor (ff) of 0.51. Thus, the carbazole based triazole linked dendrimers when used as an additive shows the better performance in DSSC than the bare cell without additives and the efficiency increases steadily with increase in the generation of the dendrimers. In addition, these additives provide additional stability to the cell performance.

Table 2 The photo electrochemical properties of n-hexyloxybenzene cored chalcone based carbazole dendrimer doped redox couple (I^-/I_3^-) as additive based DSSC under illumination of 100 mWcm^{-2}

System	Current (J_{sc}) (mA)	Voltage (V_{oc}) (mV)	Fill factor (ff)	Efficiency (η) %
TiO ₂ /N719dye/KI/I ₂ /Pt	8.33	850	0.49	3.51
TiO ₂ /N719dye/KI/I ₂ /50/Pt	7.99	850	0.66	4.48
TiO ₂ /N719dye/KI/I ₂ /51/Pt	11.3	820	0.62	5.74
TiO ₂ /N719dye/KI/I ₂ /52/Pt	14.85	830	0.51	6.34

III.CONCLUSION

In conclusion, the carbazole decorated dendrimers up to second generation with triazole bridging unit and with chalconyl n-hexyloxybenzene core has been synthesized using convergent approach. As the number of carbazole units increases from lower (G_0) to higher (G_2) generation dendrimer the molar extinction coefficient increases in the absorption spectrum and the intensity of the emission band also increases. The G_2 dendrimer 52 shows the better light energy conversion of 6.43% than the other lower generation dendrimers, when used as additive with redox couple (I^-/I_3^-) in DSSC.

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