# NJC

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## Introduction

As mankind has depleted non-renewable sources of energy, energy crises are faced by domestic and industrial consumers. Many researchers have focused on harvesting solar energy as an alternate route. Mankind started to tap solar energy (a renewable source) through silicon based solar panels. But the cost and manufacturing difficulties associated with silicon based solar panels have provided the big challenge to the scientific community of providing low cost solar cells as a permanent solution to the energy crisis. The introduction of dye-sensitized solar cells (DSSCs)<sup>1</sup> by Grätzel and O'Regan was a remarkable breakthrough in the history of the development of solar cells and they have gained much research interest since 1991 due to their advantages over other available solar cells. A DSSC is a typical photoelectrochemical cell,<sup>2</sup> which works with a similar

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Cyclohexadienone core 3,6-di-*tert*-butylcarbazole decorated triazole bridged dendrimers are synthesised up to the second generation using click chemistry *via* a convergent approach. The molar extinction coefficient and the intensity of the emission band increase with an increase in the dendrimer generation. The HOMO-LUMO energy level and the energy gap  $E_g$  obtained from photophysical and electrochemical parameters coincide with the results obtained from DFT calculations. The higher generation dendrimer **3** (G<sub>2</sub>) shows a higher  $V_{oc}$  value and an increased efficiency of 9.01% when used as additive in DSSCs compared to the lower generation dendrimers **2** (G<sub>1</sub>) and **1** (G<sub>0</sub>) under 100 mW cm<sup>-2</sup> illumination. Further, Nyquist plots obtained from electrochemical impedance measurements also show that the higher generation dendrimer G<sub>2</sub> provides an increased number of charge transport pathways, which enhances interfacial electron transport and reduces the recombination dynamics.

> mechanism to how photosynthesis happens in leaves. Dye molecules are present at the interface between transparent nanocrystalline TiO<sub>2</sub> and an electrolyte, which absorb solar photons and result in the excitation of the molecules. The excited molecules inject electrons into the conduction band of semiconducting TiO<sub>2</sub>. The electrons are conducted quickly and that governs the behavior of external circuits. The conversion of an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox mediator is the main focus for the enhancement of DSSC efficiency; this mainly bridges the photoanode and counter electrode that form the internal circuit in DSSCs. To obtain high performance DSSCs, the counter electrode also plays a key role by regenerating the  $I^{-}/I_{3}^{-}$  redox mediator in the cell, which allows the flow of electrons into the internal circuit of a DSSC. The electrocatalytic reduction and regeneration of the  $I^{-}/I_{3}^{-}$  mediator via the flow of electrons from the external circuit into the internal circuit is done by a platinum (Pt) counter electrode, due to its high conductivity and electrocatalytic activity. For the past two decades, the replacement of expensive Pt counter electrodes happens to be the main focus of research, owing to their stability issues. Recently, carbon-based materials, like graphene and CNTs, are widely used as alternatives to Pt counter electrodes, and the efficiency of carbon-based electrodes can be enhanced through the doping of non-metallic ions such as N, P, B, S and Se.<sup>3</sup>

> Organic molecules are explored either in the form of metalbased<sup>4</sup> or metal-free dye<sup>5</sup> molecules to increase the efficiency of DSSCs. Ru(n) based dye molecules are the most commonly used dyes throughout the world that result in better DSSC performance.

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#### Paper

Other than dye molecules, electrolytes present in cells also play a vital role in determining the solar energy harvesting efficiency.<sup>6</sup> They are responsible for the inner electron flow and rapid regeneration of the dye molecules. The leakage and evaporation of the electrolyte are the major problems faced when liquid electrolytes are used, thus reducing the durability of cells and resulting in very low performance when harvesting solar energy. When  $I^-/I_3^-$  redox mediators are used in the electrolyte, the sublimation of iodine from the cell affects drastically the performance of DSSCs. Nitrogen-based heterocycles, such as pyrazole, imidazole, triazole, pyridine, pyrimidine, and pyrazine, are employed as additives in redox couple electrolyte solutions to improve the efficiency of DSSCs.<sup>7</sup>

Dendrimers8 are a class of macromolecule, with a well-defined tree-like monodisperse structure, that has received much interest in the fields of material and biological science. They are used as scaffolds for delivering drugs to targets,<sup>9</sup> as biomimetic catalysts,10 in organic light emitting diodes11 and in light harvesting devices.<sup>12</sup> Vogtle et al.,<sup>13</sup> Tomalia et al.,<sup>14</sup> Frechet et al.,15 and Newkome et al.16 are pioneers in developing dendrimer chemistry over the last decade. Yamamoto et al. synthesised fifth generation hole transporting dendrimers with phenylazomethine on the surface and triphenylamine at the core position and used these as additives to increase the efficiency of a solar energy harvesting system with N719, a Ru(II)-based dye molecule.<sup>17</sup> Dendrimers with an imine (azomethine) linkage are an excellent electron transporting material and are considered an interesting class of molecules for new material applications.<sup>18</sup> An alternative to the azomethine linkage is 1,2,3-triazole, which is synthesised via Cu(1) catalysed 1,3-dipolar cycloaddition between an alkyne and an azide (click chemistry).<sup>19</sup> Rajakumar et al. have applied click chemistry to the synthesis of 1,2,3-triazole-based dendrimers with various electron transporting and electron accepting molecules, such as phenothiazine,<sup>20</sup> diphenyl amine,<sup>21</sup> pyrene,<sup>22</sup> dimethyl isophthalate,<sup>23</sup> benzoheterazole,<sup>24</sup> and triphenyl amine with chalcone,<sup>25</sup> at the periphery and used these as additives to increase the power conversion efficiency (PCE) of solar cells.

Carbazole has excellent electron transporting properties and great stability, with unique photophysical and luminescence properties; hence it is used in OLEDs<sup>26</sup> and DSSCs.<sup>27</sup> Due to its increased performance in electronic devices, we are prompted to use carbazole dendrimers as additives in DSSCs. Herein, we report the synthesis of the cyclohexadienone core 3,6-di-*tert*-butylcarbazole decorated triazole bridged dendrimers **1**, **2** and **3** (Fig. 1) through a convergent approach and investigate their photophysical and electrochemical properties along with their application as an additive to improve solar energy harvesting efficiency in DSSCs.

## **Results and discussion**

The alkylation of carbazole **4** with *t*-butyl chloride in the presence of  $\text{ZnCl}_2$  gave 3,6-di-*tert*-butylcarbazole **5**, which was reacted with 4-bromobenzaldehyde to give 4-carbazolyl benzaldehyde **6** as a yellow coloured solid. The aldehyde **6** was converted to the corresponding alcohol 7 *via* reduction with NaBH<sub>4</sub>. The reaction of the alcoholic compound 7 with SOCl<sub>2</sub>/pyridine gave the respective chloro-compound 8 and, further, the chloro-compound 8 was converted into the azido compound (G<sub>0</sub>-N<sub>3</sub> dendron) 9 *via* a reaction with 1.2 equiv. of NaN<sub>3</sub> in acetone under refluxing conditions. In the <sup>1</sup>H NMR spectrum, the azido dendron (G<sub>0</sub>-N<sub>3</sub>) 9 displayed a singlet at  $\delta$  4.26 ppm from the benzylic protons attached to the azido group, in addition to signals from the other aliphatic and aromatic protons. In the <sup>13</sup>C NMR spectrum, the azido dendron 9 showed a signal at  $\delta$  54.5 ppm from the benzylic CH<sub>2</sub> carbon attached to the azido group, along with the other aliphatic and aromatic carbon signals.

We then focused on the synthesis of the first and second generation dendritic wedges. The reaction of 1.1 equiv. of the zeroth generation azido dendron 9 with 0.5 equiv. of 3,5-bis-(propargyloxy)benzyl chloride 10 under click reaction conditions, *i.e.*, CuSO<sub>4</sub>·5H<sub>2</sub>O (5 mol%) and sodium ascorbate (10 mol%) in a mixture of THF and water (1:1) at room temperature, gave the first generation chloro-dendritic wedge (G1-Cl) 11 in good yield. The corresponding first generation azido dendron 12 was synthesised as a colourless solid via the reaction of 1.2 equiv. of NaN<sub>3</sub> with 1.0 equiv. of the chloro-dendritic wedge 11 under refluxing conditions in acetone. The <sup>1</sup>H NMR spectrum of **12** (G<sub>1</sub>-N<sub>3</sub>) displayed three singlets at  $\delta$  4.26, 5.21 and 5.61 ppm from benzylic chloromethane, N-methylene and O-methylene protons, respectively, and the triazole protons appeared as a singlet at  $\delta$  7.66 ppm in addition to signals from the other aliphatic and aromatic protons. The <sup>13</sup>C NMR spectrum of **12** (G<sub>1</sub>-N<sub>3</sub>) showed signals at  $\delta$  53.7, 54.8 and 62.6 ppm, which correspond to benzylic, N-methylene and O-methylene carbon, respectively, along with signals from other aliphatic and aromatic carbons. The conversion of the first generation chloro-dendron 11 to the azido dendron 12 was confirmed via the change in the chemical shift of the benzylic carbon from  $\delta$  46.2 ppm in **11** (G<sub>1</sub>-Cl) to  $\delta$  54.8 ppm for the azido benzylic  $CH_2$  carbon in 12 (G<sub>1</sub>-N<sub>3</sub>).

Similarly, the second generation azido dendron **14** was synthesised from the click reaction of 0.5 equiv. of 3,5-bis(propargyloxy)benzyl chloride **10** with **1.1** equiv. of the first generation azido dendron **12**, in the presence of  $CuSO_4$ · $SH_2O$  (5 mol%) and sodium ascorbate (10 mol%) in a mixture of THF and water (1:1) at room temperature, to give the second generation dendritic wedge **13** (G<sub>2</sub>-Cl) in good yield, which was then converted to the second generation azido dendron **14** *via* a reaction with NaN<sub>3</sub> in refluxing acetone.

In the <sup>1</sup>H NMR spectrum, the dendritic azide **14** displayed benzylic, *O*-methylene, two different *N*-methylene protons (namely methylene protons near benzene ring and another methylene protons near carbazole unit) as four different singlets at  $\delta$  4.16, 5.12, 5.38 and 5.57 ppm, respectively. The outer and inner triazole ring protons appeared as two different singlets at  $\delta$  7.57 ppm for two protons and at  $\delta$  7.66 ppm for four protons, in addition to signals from other aliphatic and aromatic protons. In the <sup>13</sup>C NMR spectrum, the second generation dendritic azide G<sub>2</sub>-N<sub>3</sub> **14** displayed signals at  $\delta$  53.7, 53.9, 54.7 and 62.4 ppm for four different types of methylene carbon, *viz.*, benzylic, *O*-methylene, two different *N*-methylene carbons (namely methylene carbons near







Fig. 1 Molecular structures of the cyclohexadienone core carbazole dendrimers 1, 2 and 3

benzene ring and another methylene carbons near carbazole unit), along with signals from other aliphatic and aromatic carbons. The reaction sequence for the synthesis of the zeroth, first and second generation carbazole dendritic wedges is shown in Scheme 1.

The dienone core unit **16** was synthesised as a yellow coloured solid in 86% yield *via* the aldol condensation of 1.0 equiv. of cyclohexanone **15** with 2.1 equiv. of 4-(prop-2-ynyloxy)benzalde-hyde in ethanol in the presence of NaOH (Scheme 2). The <sup>1</sup>H NMR spectrum of the dienone core compound **16** displayed a triplet at  $\delta$  2.55 ppm (J = 2.1 Hz) and a doublet at  $\delta$  4.72 ppm (J = 2.1 Hz) from the propargylic protons, in addition to other

aliphatic and aromatic proton signals. The <sup>13</sup>C NMR spectrum of **16** also confirmed the presence of a propargylic unit *via* the appearance of signals at  $\delta$  55.8, 75.9, and 78.2 ppm, in addition to other aliphatic and aromatic carbon signals.

The reaction of 1.0 equiv. of the bispropargyloxy compound 16 with 2.2 equiv. of each of the dendritic azides 9, 12 and 14 under click reaction conditions, *viz.*, 5 mol% CuSO<sub>4</sub>·5H<sub>2</sub>O and 10 mol% sodium ascorbate in THF:H<sub>2</sub>O (1:1) for 12 h, afforded the zeroth, first and second generation dendrimers 1, 2 and 3 in 90%, 83% and 77% yields, respectively (Scheme 2).

The <sup>1</sup>H NMR spectrum of the second generation carbazole dendrimer 3 showed signals from the triazolyl protons and  $\beta$ 



Scheme 1 (i) <sup>t</sup>BuCl, ZnCl<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub>, N<sub>2</sub> atm, 5 h, **5** (86%); (ii) Cu<sub>2</sub>O, DMAc, 170 °C, N<sub>2</sub> atm, 24 h, **6** (58%); (iii) NaBH<sub>4</sub>, MeOH/DCM, 6 h, **7** (95%); (iv) SOCl<sub>2</sub>, pyridine, DCM, overnight, **8** (90%); (v) NaN<sub>3</sub>, acetone, reflux, 12 h, **9** (98%), **12** (95%), **14** (94%); (vi) CuSO<sub>4</sub>·5H<sub>2</sub>O (5 mol%), sodium ascorbate (10 mol%), THF : H<sub>2</sub>O (1:1, v/v), rt, 12 h, **11** (85%), **13** (79%).

protons of the enone double bond at  $\delta$  7.50 and 7.61 ppm, respectively, along with other aliphatic and aromatic proton signals. The <sup>13</sup>C NMR spectrum of the G<sub>2</sub> dendrimer 3 showed *N*-methylene and *O*-methylene carbon signals at  $\delta$  53.7, 53.9, 61.8 and 61.9 ppm, in addition to other aliphatic and aromatic carbon signals. The mass spectrum (MALDI-TOF) of the G<sub>2</sub>

dendrimer 3 showed the molecular ion peak ( $M^+$ ) at m/z = 5114.35. The structure of dendrimer 3 was also confirmed from elemental analysis. Similarly, the structures of the zeroth generation carbazole dendrimer 1 ( $G_0$ ) and first generation carbazole dendrimer 2 ( $G_1$ ) were also confirmed from spectral and analytical data.



## **Photophysical properties**

UV-visible absorption spectra of the dendrimers 1, 2 and 3 were recorded at a concentration of  $1 \times 10^{-5}$  M in DCM (Fig. 2), and the data is summarised in Table 1. The synthesised dendrimers 1, 2 and 3 show almost identical absorption spectra, with two absorption bands at 297 and 346 nm. The absorption band at 297 nm is due to  $\pi$ - $\pi$ \* transitions of localized electrons of carbazole moieties present at the peripheries of the dendrimers. Another absorption band at 346 nm relates to the dienone core unit. It is clear from the absorption spectra that as the generation of the dendrimers increases, the number of carbazole units on the periphery increases; this results in an increase in the molar extinction coefficient. The increase in absorbance from a lower generation to a higher generation amplifies the light absorbing capacity of the dendrimer and is known as the valence effect in dendrimer chemistry;<sup>28</sup> hence dendrimers 1, 2 and 3 can act as good light harvesting materials.

The emission spectra of dendrimers 1, 2 and 3 are recorded at a concentration of 1  $\times$  10  $^{-5}$  M in DCM upon exciting the



Fig. 2  $\,$  UV-vis absorption spectra of the carbazole dendrimers 1, 2 and 3 in DCM (1  $\times$  10 $^{-5}$  M).

Table 1	The photophysica	properties of	dendrimers <b>1</b> , 1	2 and 3
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Dendrimer	$\lambda_{\max}$ (nm)	$\epsilon \ ( imes 10^4 \ \mathrm{L} \ \mathrm{mol}^{-1} \ \mathrm{cm}^{-1})$	$\lambda_{em} (nm)$
Dendrimer 1	297, 346	4.75, 3.31	355, 370
Dendrimer 2	297, 346	7.90, 4.13	355, 371
Dendrimer 3	297, 346	12.60, 4.13	356, 371



Fig. 3 Emission spectra of the carbazole dendrimers 1, 2 and 3 in DCM (1  $\times$  10  $^{-5}$  M).

synthesised dendrimers at 297 nm (Fig. 3), and the data are summarised in Table 1. Dendrimers **1**, **2** and **3** show emission bands at around 355 and 370 nm. These dual emission bands correspond to 9-phenyl carbazole, which gives rise to twisted intramolecular charge transfer  $(\text{TICT})^{29}$  in the polar solvent. Fig. 3 clearly shows that the emission intensities of the dendrimers increase as the generation increases, which is consistent with the fluorophoric dienone and the increased number of carbazole units; this is described as the valence effect in dendrimer chemistry.<sup>28</sup>

#### **Electrochemical properties**

The electrochemical properties of the synthesised carbazole dendrimers 1, 2 and 3 were studied via recording cyclic voltammetry data in dichloromethane at a concentration of 1  $\times$  $10^{-3}$  M, using a 0.1 M solution of *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte; the results are tabulated in Table 2 and the voltammograms are shown in Fig. 4. The experiments were carried out at ambient temperature under a nitrogen atmosphere with a conventional three electrode configuration consisting of a gold disc as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The oxidation and reduction potentials for all the dendrimers appear in the potential range of -2.0 to +2.0 V. In the cyclic voltammetry data, two oxidation peaks appear between -0.66 and 1.58 V and two reduction peaks appear between 1.32 to -0.98 V for all the dendrimers. CV plots of all the dendrimers show the irreversible redox potential. The oxidation and reduction peaks for dendrimers 1, 2 and 3 are attributed to the presence of electron donating carbazole moieties and electron accepting dienone units. It is clear from Fig. 4 that upon increasing the number of carbazoles at the periphery, the anodic peak potential is shifted towards a slightly more negative potential.

The oxidation of carbazole molecules to the respective radical cations is observed as the first oxidation wave for dendrimers **1**, **2** and **3**, which appears at the lower potential of -0.66 to -0.59 V. Electrochemical coupling between carbazole units at the 3 and 6 positions is prevented by the presence of bulky *tert*-butyl units, which was confirmed by multiple CV scans. From the cyclic voltammograms (Fig. 4), it is clear that upon increasing the number of carbazole units, the  $\Delta E_{p2}$  value increases from the G<sub>0</sub>

Table 2	The electrochemical parameters of dendrimers <b>1</b> , <b>2</b> and <b>3</b>	
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Dendrimer (generation)	$E_{\rm pa1}$ (V)	$E_{\mathrm{pa2}}$ (V)	$E_{\rm pc1}$ (V)	$E_{\rm pc2}$ (V)	$\Delta E_{\mathrm{p1}}$ (V)	$\Delta E_{\mathrm{p2}}$ (V)
Dendrimer 1	-0.59	1.51	1.30	-0.89	1.89	2.40
Dendrimer 2	-0.64	1.47	1.27	-0.98	1.91	2.45
Dendrimer 3	-0.66	1.58	1.32	-0.92	1.98	2.50



Fig. 4 Cyclic voltammograms of the carbazole dendrimers 1, 2 and 3 in DCM (1  $\times$  10<sup>-3</sup> M) scanned at 100 mV s<sup>-1</sup>.

to the G<sub>2</sub> dendrimer, *i.e.*, in the order:  $3 (G_2) > 2 (G_1) > 1 (G_0)$ . The  $E_{p2}$  peak shows a gradual increase in value from 2.4 to 2.50 V.

The energy level parameters were obtained from CV and UV data and are summarized in Table 3. The HOMO energy levels of the carbazole dendrimers **1**, **2** and **3** are in the range of -5.49 to -5.61 eV; these values were obtained from the onset oxidation potential, *i.e.*, HOMO =  $-(4.41 + E_{onset}^{ox})$ . Further, the LUMO energy level values of the synthesised carbazole dendrimers were calculated from the HOMO energy level (LUMO = HOMO +  $E_g$ ) and the optical band gap ( $E_g$ ) values were determined from the UV-visible absorption spectra. The higher generation carbazole dendrimer **3** was found to possess a reduced band gap of 2.82 eV when compared to the lower generation dendrimer with a band gap of 2.89 eV.

### **Computational details**

The bulky alkyl chains were replaced with methyl groups to improve the computational efficiency. The ground state geometry of the dendrimer was optimized with the Becke three-parameter and Lee–Yang–Parr correlation hybrid (B3LYP) functional<sup>30</sup> in conjunction with the 6-31G(d,p) basis set.<sup>31</sup> Vibrational frequency analysis was also carried out at the same level of theory to confirm the minimum energy values on the potential energy surface. Time-dependent density functional theory (TD-DFT) calculations were carried out with the B3LYP functional in conjunction with the

6-311+G(d,p) basis set with B3LYP/6-31G(d,p) optimized geometry to calculate the optical and electrochemical properties for the ten lowest spin allowed transitions, employing dichloromethane (DCM,  $\varepsilon$  = 8.93) as the solvent. The polarizable continuum model (PCM) was adopted to include solvation effects.<sup>32</sup> All density functional theory (DFT) calculations were performed using the Gaussian 09 (Revision C.01) suite of programs.<sup>33</sup>

The ground state optimized geometry of dendrimer 1 and the corresponding electron density distributions of the frontier molecular orbitals (FMOs) are depicted in Fig. 5 and 6, respectively. The calculated HOMO-LUMO energy gap  $(E_g)$  is found to be 3.12 eV, with a highest occupied molecular orbital (HOMO) energy value of -5.64 eV and a lowest unoccupied molecular orbital (LUMO) energy value of -2.52 eV. Effective intramolecular charge transfer (ICT) from donor to acceptor during electron excitation is necessary to achieve high photo-to-electric conversion efficiency. It is clear from Fig. 6 that the electron density of the HOMO of dendrimer 1 is primarily located on the carbazole motif (donor) and partially found on the benzene linker. The LUMO of dendrimer 1 is primarily found on the cyclohexanone ring (acceptor) with a minor portion on the benzene linker. These results clearly indicate that there is a high probability for charge separation upon excitation in dendrimer 1.

The calculated vertical excitation energy (*E*), absorption wavelength ( $\lambda_{max}$ ), oscillator strength (*f*) and molar extinction coefficient ( $\varepsilon$ ) from TD-DFT calculations at the B3LYP/6-311+G(d,p) level of theory in dichloromethane solvent are given in Table 4. Dendrimer 1 exhibits an absorption maximum ( $\lambda_{max}$ ) of 407 nm with an oscillator strength of 1.3482 and a molar extinction



Fig. 5 The optimized geometry of dendrimer 1 computed at the B3LYP/ 6-31G(d,p) level of theory. The long alkyl chain is replaced with methyl groups to improve the computational efficiency [color indication: gray – carbon; white – hydrogen; blue – nitrogen; and red – oxygen].

Table 3         The energy level parameters of dendrimers 1, 2 and 3							
Dendrimer (generation)	$\lambda_{\text{onset}}^{a}$ (nm)	$E_{ m g}^{{ m opt}b}$ (eV)	$E_{\text{onset}}^{\text{ox}}(\mathbf{V})$	$HOMO^d$ (eV)	$LUMO^{e}$ (eV)		
Dendrimer 1	428	2.89	1.20	-5.61	-2.72		
Dendrimer 2	434	2.86	1.15	-5.56	-2.70		
Dendrimer 3	439	2.82	1.08	-5.49	-2.67		

<sup>*a*</sup> Onset absorption maximum from UV-vis absorption spectra. <sup>*b*</sup> Optical band gap calculated using the formula  $E_{\rm g} = 1240/\text{UV}_{\rm onset}$ . <sup>*c*</sup> Onset oxidation potential. <sup>*d*</sup> HOMO = -[4.41 +  $E_{\rm onset}^{\rm ox}$ ]. <sup>*e*</sup> LUMO = [HOMO +  $E_{\rm g}^{\rm opt}$ ].

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Fig. 6 Frontier molecular orbital (HOMO and LUMO) contour images of dendrimer **1** with orbital energy values. The isodensity surface value is fixed at 0.03 a.u.

Table 4The calculated vertical excitation energy E (eV), absorption wavelength $(\lambda_{max})$ , oscillator strength (f), and molar extinction coefficient (ɛ) of dendrimer 1 atthe TD-PCM-B3LYP/6-311+G(d,p) level of theory, in dichloromethane

Dendrimer	E(eV)	$\lambda_{\max} (nm)$	f	$\epsilon \left( M^{-1} \ cm^{-1}  ight)$
1	3.05 3.87	406.75 320.47	$1.3482 \\ 0.2363$	103873.30 23902.73
	3.21	386.82	0.1358	67680.16

coefficient of 103873.3  $M^{-1}$  cm<sup>-1</sup>. Similarly, for the dendrimer **1** with different oscillator strength (*f*) values the corresponding excitation energy, absorption wavelength and molar extinction co-efficient are calculated and summarized in Table 4. It can be clearly understood from the above analysis that dendrimer **1** could be a good light harvesting material.

#### DSSC studies

The DSSC performance is mainly dependent on: (i) the minimization of charge recombination losses at the  $TiO_2/N3$  dye/electrolyte

interface; and (ii) the dye regeneration efficiency. Moreover, such charge recombination at the TiO<sub>2</sub>/N3 dye/electrolyte interface leads to losses in the short-circuit current ( $J_{sc}$ ) and the opencircuit voltage ( $V_{oc}$ ), resulting in a decrease in power conversion efficiency. It is well known that the addition of organic nitrogenous compounds to the  $I^-/I_3^-$  electrolyte system would improve the photovoltage significantly; this is commonly attributed to a shift in the conduction band edge of titania towards more negative potentials.<sup>34</sup> This can probably be attributed to higher rates of electron recombination between TiO<sub>2</sub> and the electrolyte in dye-sensitized solar cells.

Fig. 7 shows a typical dye sensitized solar cell with the synthesized dienone core triazole bridged carbazole dendrimer serving as an additive to the redox electrolyte. The nanocrystalline TiO<sub>2</sub> photoelectrode was prepared as described in the literature.<sup>35</sup> Fig. 8 shows current-voltage (J-V) curves from the bare cell and after the addition of carbazole dendrimers 1, 2 and 3 to the redox electrolyte. The photovoltaic performances of the DSSCs (short-circuit current density  $(J_{sc})$ , open-circuit voltage  $(V_{oc})$ , fill factor (ff), and electric energy efficiency  $(\eta)$ ) are summarized in Table 5. For cells constructed with the synthesized carbazole dendrimers, an increase in current is observed, along with an increase in  $V_{\rm oc}$ . The redox electrolyte  $I^-/I_3^-$ , with the newly synthesized dendrimers, shows good stability and improved efficiency owing to its quasi-gel type behaviour. It overcomes the problems of leakage and evaporation shown by standard KI electrolyte. The synthesized organic dendrimers interacted well with iodine in the redox couple and decreased the sublimation of iodine, which enhances the stability and efficiency. The cell involving a carbazole doped redox couple based DSSC is remarkably stable and the photocurrent maintains 92% of the initial value ever after 10 days of storage. On the contrary, cells without carbazole dendrimers in the redox electrolyte are much less stable and show a significant decrease in the open circuit voltage  $(V_{oc})$  and short circuit current  $(J_{sc})$  over a short period of time.



Fig. 7 A schematic representation of the use of carbazole dendrimers as an additive for DSSC performance.



Fig. 8 J-V curves of DSSCs with the dienone core carbazole dendrimers **1**, **2** and **3** under simulated solar light at 1 sun (100 mW cm<sup>-2</sup>).

As the generation increases, the number of carbazole and triazole units increases, which results in an increase in the light-to-electric energy conversion. The carbazole dendrimer 3 shows 9.01% solar power conversion efficiency, with high  $J_{sc}$ and  $V_{\rm oc}$ , due to the presence of a greater number of carbazole units, which in turn increases the chemical capacitance and eventually the photocurrent of the cells with dendrimer additives (Table 5). The presence of a well conjugated triazole group in the second generation dendrimer 3 controls the back reactions of the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox mediator and thus results in high current conversion compared to the other dendrimers. The DSSC without carbazole derivatives shows low efficiency and stability. Further, the COOH moiety in the N3 dye gets deprotonated while anchored on the surface of the TiO<sub>2</sub> photoanode and the conduction band of TiO<sub>2</sub> gets shifted to a more positive potential as a result of possible protonation. The potential difference between the Fermi level of TiO<sub>2</sub> and the HOMO level of the redox electrolyte with a dendrimer additive is responsible for the increased  $V_{oc}$ . It is confirmed that the carbazole dendrimer additives interact well with iodine in the redox couple and decrease the sublimation of iodine, enhancing the lifetime of the redox couple and reducing charge recombination occurring at the  $TiO_2/N3$  dye/redox electrolyte interface.

## Electrochemical impedance spectroscopy and Nyquist plots

The interfacial charge transport kinetics of the fabricated DSSCs based on dendrimer addition along with an  $I^{-}/I_{3}^{-}$  electrolyte were studied via EIS Nyquist plots, as shown in Fig. 9a. For the applied open circuit potential (OCP), measurements were taken using a two electrode solar device configuration over the frequency range of 100 kHz to 0.1 Hz under ambient conditions. This resulted in two examples of semicircle behaviour, respectively in the high and mid-frequency regions of the Nyquist plots, affirming the presence of two interfacial charge transport resistance processes in the fabricated devices. The intersections of these semicircles with the real axis of impedance give the total charge transport resistance at every interface. The semicircular arc in the high frequency region corresponds to the charge transport resistance at the Pt/KI electrolyte interface  $(R_{ct1})$  and the mid-frequency semicircle represents the charge transport resistance (recombination resistance) at the TiO<sub>2</sub>/N3/KI + dendrimer electrolyte interface  $(R_{ct2})$ . The existence of two semicircles was further confirmed from the phase angle shifts in the Bode phase plots (Fig. 9b). Using the equivalent circuit model shown in the inset of Fig. 9a, the obtained semicircles were fitted and the corresponding electrochemical parameters are summarized in Table 6, where  $R_{\rm s}$  represents the series resistance, which seems to be nearly equal for all devices (this is ascribed to the sheet resistance of fluorinated tin oxide (FTO)), and  $C_{\mu}$  represents the total chemical capacitance of the photoanode.

From Table 6, it is noted that pure KI electrolyte has higher  $R_{ct1}$  and  $R_{ct2}$  values compared to all dendrimer based devices. The sublimation of iodine over a short time period in aqueous KI electrolyte is responsible for the high charge transport resistance in the pure KI based device.<sup>36</sup> In the case of the

System	Current $(J_{sc})$ (mA)	Voltage $(V_{\rm oc})$ (mV)	Fill factor (ff) %	Efficiency $(\eta)$ %
TiO <sub>2</sub> /N3dye/KI/I <sub>2</sub> /Pt TiO <sub>2</sub> /N3dye/KI/I <sub>2</sub> /1/Pt TiO <sub>2</sub> /N3dye/KI/I <sub>2</sub> /2/Pt TiO <sub>2</sub> /N3dye/KI/I <sub>2</sub> /3/Pt	$\begin{array}{c} 10.1 \ (\pm 0.2) \\ 12.4 \ (\pm 0.2) \\ 16.4 \ (\pm 0.2) \\ 18.3 \ (\pm 0.3) \end{array}$	$780 (\pm 3) \\825 (\pm 4) \\870 (\pm 4) \\895 (\pm 5)$	$51 (\pm 3) \\ 53 (\pm 1) \\ 54 (\pm 2) \\ 55 (\pm 5)$	$\begin{array}{c} 4.01 \ (\pm 0.02\%) \\ 5.42 \ (\pm 0.01\%) \\ 7.70 \ (\pm 0.03\%) \\ 9.01 \ (\pm 0.04\%) \end{array}$

Table 5The photoelectrochemical properties of carbazole doped redox couple  $(I^-/I_3^-)$  based DSSCs under 1 sun illumination (100 mW cm<sup>-2</sup>)



Fig. 9 (a) EIS Nyquist plots (the inset shows the high frequency region and the equivalent circuit model) and (b) Bode phase plots for the fabricated DSSCs.

Table 6 The electrochemical parameters of the fabricated DSSCs

System	$R_{\rm s}(\Omega)$	$R_{\mathrm{ct1}}\left(\Omega\right)$	$R_{\mathrm{ct2}}\left(\Omega\right)$	$C_{\mu}$ ( $\mu$ F)	$\tau_{e} (ms)$	$\chi^{2}$ (× 10 <sup>-3</sup> )
KI	2.21	61.21	334.5	1.214	0.42	1.01
Dendrimer 1 + KI	1.52	12.23	232.1	1.306	0.31	0.92
Dendrimer 2 + KI	1.2	2.37	36.14	2.038	0.08	1.43
Dendrimer 3 + KI	0.97	2.13	15.12	2.805	0.04	3.70

dendrimer + KI electrolyte based devices, the interfacial charge transport resistances were reduced owing to the usage of a quasi-gel type dendrimer electrolyte. This can reduce the sublimation of iodine in the electrolyte system and increase the charge transportation in a device. It is noteworthy that  $R_{ct1}$  gets reduced for all dendrimer based devices, which reveals that efficient charge transportation occurred at the Pt/electrolyte interface. In particular, dendrimers 2 and 3 being added into the KI electrolyte system resulted in low  $R_{ct1}$  values of 2.37  $\Omega$ and 2.13  $\Omega$ , respectively, due to the presence of an anchoring cyclohexadienone unit with a greater number of carbazole dendron units. This can offer efficient charge transportation at the Pt/electrolyte interface and reduce the recombination dynamics. Further, the obtained  $R_{ct2}$  and  $C_{\mu}$  values of the fabricated DSSCs determine the charge injection efficiency and recombination possibility, which can be estimated using the electron relaxation lifetime ( $\tau_e$ ). This can be calculated from the peak frequency  $(f_{\rm mid})$  in the mid-frequency region of the EIS Bode phase plot (Fig. 9b) using the relationship  $\tau_e = 1/2\pi f_{mid}$ . The standard KI and dendrimer 1 + KI based devices revealed high electron relaxation lifetimes of 0.42 and 0.31 ms, respectively, owing to their high  $R_{ct2}$ values. Even though the chemical capacitances of the dendrimer 2 and 3 + KI based devices were high, their very low  $R_{ct2}$  values can decrease the electron relaxation lifetime ( $\tau_e$ ) values, which results in them having more significant charge injection processes than charge recombination.<sup>37</sup> The increased chemical capacitance could possibly originate from the number of  $\pi$ -conjugation units (carbazole), which increase the current densities of devices fabricated with dendrimer 2 and 3 + KI based electrolyte systems (as evidenced from the obtained high  $J_{sc}$  values). In particular, the device fabricated with dendrimer 3 + KI realized a very low  $\tau_e$  value of 0.04 ms owing to its reduced  $R_{ct2}$ . A larger number of anchoring units in dendrimer 3 can provide an increased number of charge transport pathways, which enhances the charge injection efficiency and reduces the recombination dynamics.

## Conclusions

In summary, we have synthesized a series of cyclohexadienone core, triazole bridged carbazole decorated dendrimers, up to the second generation, using a convergent approach. As the number of carbazole units increases from lower ( $G_0$ ) to higher ( $G_2$ ) generation dendrimers, the molar extinction coefficients and intensities of the emission bands also increase, which is supported by DFT calculations. From the CV studies, all the dendrimers show irreversible redox signals, with the first oxidation peak corresponding to the formation of a radical cation of the carbazole unit. The  $G_2$  dendrimer **3** shows the best power energy conversion of 9.01%, with a short circuit current density  $(J_{sc})$  of 18.3 mA cm<sup>-2</sup>, an open circuit voltage  $(V_{oc})$  of 895 mV and a fill factor (ff) of 55%, when used as an additive with a redox mediator in a DSSC, compared to the other lower generation dendrimers G<sub>0</sub> (1) and G<sub>1</sub> (2). Further, detailed analysis of the interfacial electron transport kinetics, such as the charge transport resistance, chemical capacitance and electron relaxation lifetimes, was conducted *via* electrochemical impedance measurements.

## **Experimental section**

### Materials and methods

All reagents and solvents were obtained from the chemical companies Sigma-Aldrich, LOBA, SRL and Avra. The known products were identified via a comparison of their melting points and from spectral data already reported in the literature. All melting points reported are uncorrected and were determined using Toshniwal melting point apparatus via the open capillary tube method. The UV-vis spectra were recorded using an Agilent 8453 spectrophotometer. The emission spectra were recorded using a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker 300 MHz and 75 MHz spectrometers. The chemical shifts are reported in ppm ( $\delta$ ) with TMS as an internal standard, and the coupling constants (J) are expressed in Hz. MALDI-TOF mass spectra were recorded using a Voyager-DE PRO mass spectrometer using an a cyano-4-hydroxy cinnamic acid (CHCA) matrix. Elemental analyses were performed with a PerkinElmer 240B elemental analyzer. Electrochemical studies were carried out using a CH Instruments electrochemical analyzer. Current-voltage (J-V) curves and electrochemical impedance measurements were performed using an Autolab PGSTAT 302N potentiostat/galvanostat with an FRA32M module controlled by NOVA 1.10 software. TLC was performed on glass plates coated with silica gel-G (ACME) of about 0.25 mm thickness and visualized with iodine. Column chromatography was carried out with silica gel (ACME, 100-200 mesh).

# General procedure for the formation of the 1,2,3-triazole ring (procedure A)

A mixture of  $CuSO_4 \cdot 5H_2O$  (5 mol%) and sodium ascorbate (10 mol%) was added to a stirred solution of acetylenic compound (0.5 equiv.) and azide compound (1.1 equiv.) in THF:H<sub>2</sub>O (1:1) solvent mixture, and this was further stirred at room temperature for 12 h. THF was removed from the reaction mixture under reduced pressure and the residue obtained was diluted with CHCl<sub>3</sub>. The organic layer was washed with water (2 × 50 mL) and brine solution (1 × 50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated under vacuum. The crude product obtained was purified *via* column chromatography using SiO<sub>2</sub>. The corresponding triazole compounds were eluted from the column using a CHCl<sub>3</sub>:MeOH solvent mixture.

#### General procedure for the synthesis of azido dendrons (procedure B)

To a stirred solution of the chloro-dendritic wedge (1.0 equiv.) in acetone,  $NaN_3$  (1.2 equiv.) was added and then this was

refluxed for 12 h. The solvent was evaporated under vacuum and the residue obtained was dissolved in  $CHCl_3$  (100 mL). The organic layer was washed with water (2 × 50 mL) and brine solution (1 × 50 mL) and dried over anhydrous sodium sulphate, and the solvent was distilled out under vacuum to afford the corresponding dendritic azide as a colourless solid.

Dendrimer 1. Following general procedure A, dendrimer 1 was synthesised from the acetylenic dienone core 16 (0.3 g)0.78 mmol) and the azido dendron  $9(G_0-N_3)(0.71 \text{ g}, 1.73 \text{ mmol})$ . The crude product obtained was purified via column chromatography using silica gel with  $CHCl_3:MeOH$  (9:1) as eluent to afford dendrimer 1 as a yellow coloured solid. Yield: 90% (0.85 mg); melting point: 158-160 °C; <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ):  $\delta_H$  1.46 (s, 36H), 1.72–1.79 (m, 2H), 2.88 (t, 4H, J = 6 Hz), 5.26 (s, 4H), 5.63 (s, 4H), 7.03 (d, 4H, J = 8.4 Hz), 7.33 (d, 4H, J = 8.4 Hz), 7.46–7.49 (m, 12H), 7.57 (d, 4H, J = 8.1 Hz), 7.68 (s, 2H), 7.75 (s, 2H), 8.14 (s, 4H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  22.9, 28.5, 31.9, 34.7, 53.8, 62.1, 109.1, 114.7, 116.3, 122.8, 123.5, 123.7, 127.1, 129.3, 129.5, 132.3, 132.9, 134.6, 136.3, 138.8, 138.9, 143.2, 144.4, 158.5, 190.1 ppm; MALDI-TOF m/z: 1203.56 (M)<sup>+</sup>; anal. calc. for C<sub>80</sub>H<sub>82</sub>N<sub>8</sub>O<sub>3</sub>: C, 79.83; H, 6.87; N, 9.31%; found: C, 78.86; H, 6.96; N, 9.49%.

Dendrimer 2. Following general procedure A, dendrimer 2 was synthesised from the acetylenic dienone core 16 (0.3 g, 0.78 mmol) and the azido dendron 12 (G<sub>1</sub>-N<sub>3</sub>) (1.83 g, 1.73 mmol). The crude product obtained was purified via column chromatography using silica gel with  $CHCl_3$ : MeOH (4:1) as eluent to afford dendrimer 2 as a yellow coloured solid. Yield: 83% (1.64 g); melting point: 170–172 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.45 (s, 72H), 1.69–1.77 (m, 2H), 2.84 (t, 4H, J = 5.1 Hz), 5.14 (s, 8H), 5.19 (s, 4H), 5.43 (s, 4H), 5.59 (s, 8H), 6.52 (s, 4H), 6.65 (s, 2H), 6.98 (d, 4H, J = 8.4 Hz), 7.32 (d, 8H, J = 8.7 Hz), 7.38–7.47 (m, 20H), 7.55 (d, 8H, J = 7.8 Hz), 7.60 (s, 2H), 7.68 (s, 4H), 7.71 (s, 2H), 8.13 (s, 8H) ppm;  $^{13}{\rm C}$  NMR (75 MHz, CDCl\_3):  $\delta_{\rm C}$  22.9, 28.5, 32.0, 34.8, 53.8, 54.1, 62.0, 62.1, 102.1, 107.5, 109.1, 114.8, 116.3, 123.1, 123.2, 123.6, 123.7, 127.1, 129.3, 129.6, 132.3, 132.9, 134.6, 136.4, 136.9, 138.8, 138.9, 143.3, 144.0, 144.3, 158.5, 159.9, 190.1 ppm; MALDI-TOF m/z: 2507.16  $(M)^+$ ; anal. calc. for  $C_{160}H_{164}N_{22}O_7$ : C, 76.65; H, 6.59; N, 12.29%; found: C, 75.86; H, 6.15; N, 12.09%.

Dendrimer 3. Following general procedure A, dendrimer 3 was synthesised from the acetylenic dienone core 16 (0.2 g, 0.52 mmol) and the azido dendron 14  $(G_2-N_3)$  (2.72 g, 1.15 mmol). The crude product obtained was purified via column chromatography using silica gel with  $CHCl_3$ : MeOH (7:3) as eluent to afford dendrimer 3 as a yellow coloured solid. Yield: 77% (2.06 g); melting point: 204–206 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.35 (s, 144H), 1.56-1.58 (m, 2H), 2.75 (t, 4H), 5.00 (s, 28H), 5.23 (s, 4H), 5.29 (s, 8H), 5.49 (s, 16H), 6.33 (s, 4H), 6.38 (s, 8H), 6.48 (s, 2H), 6.52 (s, 4H), 6.85 (d, 4H, J = 8.4 Hz), 7.22 (d, 16H, J = 8.7 Hz), 7.30-7.38 (m, 36H), 7.45 (d, 16H, J = 8.1 Hz), 7.50 (s, 6H), 7.58 (s, 8H), 7.61 (s, 2H), 8.04 (s, 16H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  22.7, 29.7, 32.0, 34.7, 53.7, 53.9, 61.8, 61.9, 101.9, 102.0, 107.4, 107.6, 109.1, 114.1, 114.8, 116.3, 123.3, 123.5, 123.8, 127.0, 129.2, 129.6, 132.3, 133.0, 134.6, 136.4, 136.9, 137.1, 138.7, 138.9, 139.3, 143.3, 143.8, 143.9, 144.1, 158.5, 159.7, 159.9, 190.1 ppm; MALDI-TOF m/z: 5114.35 (M)<sup>+</sup>; anal. calc.

for  $C_{320}H_{328}N_{50}O_{15}$ : C, 75.15; H, 6.46; N, 13.69%; found: C, 74.86; H, 6.15; N, 13.49%.

3,6-Di-tert-butyl-9H-carbazole 5. Anhydrous ZnCl<sub>2</sub> (12.23 g, 89.70 mmol) was added to carbazole (5.0 g, 29.90 mmol) in dissolved nitromethane (100 mL) under a N2 atmosphere and this was stirred for 10 min followed by the dropwise addition of t-butyl chloride (9.88 mL, 89.70 mmol). The reaction mixture was allowed to stir at room temperature for 5 h. The reaction mixture was then slowly added to water (200 mL) and then extracted with  $CHCl_3$  (3  $\times$  100 mL). The combined organic layer  $(CHCl_3)$  was washed with water  $(3 \times 100 \text{ mL})$  and brine solution (100 mL) and dried over anhydrous sodium sulphate. The organic layer was evaporated, and the crude product was recrystallised using hexane to afford 3,6-di-tert-butyl-9H-carbazole 5 as a colourless solid. Yield: 85% (7.09 g); melting point: 217–219 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.44 (s, 18 H), 7.24 (d, 2 H, J = 8.4 Hz), 7.44 (dd, 2H, J = 8.4 Hz, 1.5 Hz), 7.69 (s, 1 H), 8.07 (d, 2H, J = 1.2 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  32.0, 34.7, 110.0, 116.1, 123.2, 123.5, 138.0, 142.2 ppm.

4-(3,6-Di-tert-butyl-9H-carbazol-9-yl)benzaldehyde 6. A mixture of 3,6-di-tert-butyl-9H-carbazole 5 (3.0 g, 10.73 mmol), 4-bromo benzaldehyde (1.98 g, 10.73 mmol) and Cu<sub>2</sub>O (3.07 g, 21.47 mmol) in DMAc (20 mL) was heated at 170 °C under a N2 atmosphere for 24 h. The reaction mixture was filtered through Celite to remove the inorganic residue, and it was then washed with ethyl acetate  $(2 \times 150 \text{ mL})$ . The combined organic layer was washed with water (3  $\times$  50 mL) and brine solution (50 mL) and dried over anhydrous sodium sulphate; it was then evaporated under reduced pressure to give the crude product. The crude product thus obtained was purified through column chromatography using SiO<sub>2</sub>, elution with hexane: CHCl<sub>3</sub> (7:3) gave 4-(3,6-di-tertbutyl-9H-carbazol-9-yl)benzaldehyde 6 as a yellow coloured solid. Yield: 58% (2.38 g); melting point: 134-136 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 1.47(s, 18 H), 7.44-7.50 (m, 4H), 7.78 (d, 2H, J = 8.4 Hz), 8.10 (d, 2H, J = 8.1 Hz), 8.14 (s, 2H), 10.09 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  31.9, 34.8, 109.3, 116.5, 124.0, 124.1, 126.2, 131.4, 134.2, 138.4, 143.9, 144.0, 191.0 ppm.

(4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)methanol 7. NaBH<sub>4</sub> (0.36 g, 9.38 mmol) was added in portions to a solution of the aldehyde 6 (3.0 g, 7.822 mmol) in methanol/DCM (50 mL, 1 : 1) and this was stirred at room temperature for 6 h. The reaction mixture was then poured into water and extracted with CHCl<sub>3</sub> (2 × 100 mL). The combined organic layer was washed with water (3 × 50 mL) and brine solution (50 mL) and dried over anhydrous sodium sulphate. The organic layer was evaporated to give (4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)methanol 7 as a colourless solid. Yield: 95% (2.86 g); melting point: 188– 190 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.47 (s, 18 H), 4.61 (s, 2H) 7.44–7.50 (m, 4H), 7.78 (d, 2H, *J* = 8.4 Hz), 8.10 (d, 2H, *J* = 8.1 Hz), 8.14 (s, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$ 31.9, 34.8, 64.5,109.3,116.5, 124.0, 124.1, 126.2, 131.4, 134.2, 138.4, 143.9, 144.0 ppm.

9-(4-(Chloromethyl)phenyl)-3,6-di-*tert*-butyl-9*H*-carbazole 8. The alcoholic compound 7 (3.0 g, 7.78 mmol) was dissolved in DCM (100 mL) and stirred at 0  $^{\circ}$ C, thionyl chloride (0.67 mL, 9.34 mmol) was added, followed by the addition of pyridine

(0.75 mL, 9.34 mmol), and then the reaction mixture was stirred overnight. It was then poured over crushed ice and extracted with DCM (2 × 100 mL). The combined organic layer was washed with water (3 × 100 mL) and brine (100 mL). The organic layer was dried over anhydrous sodium sulphate and evaporated under vacuum to afford the desired chloro-compound **8** as a colourless gel. Yield: 90% (2.83 g); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.46 (s, 18H), 4.60 (s, 2H), 7.36 (d, 2H, *J* = 8.7 Hz), 7.46 (d, 2H, *J* = 8.7 Hz), 7.54 (d, 2H, *J* = 8.1 Hz), 7.59 (d, 2H, *J* = 8.1 Hz), 8.14 (s, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  32.0, 32.9, 34.7, 109.2, 116.3, 123.5, 123.7, 126.8, 130.5, 136.2, 138.3, 138.9, 143.1 ppm.

**9-(4-(Azidomethyl)phenyl)-3,6-di-***tert***-butyl-9***H***-carbazole 9.** Following general procedure B, the dendritic azide **9** (G<sub>0</sub>-N<sub>3</sub>) was obtained as a colourless gel by reacting 9-(4-(chloromethyl)-phenyl)-3,6-di-*tert*-butyl-9*H*-carbazole **8** (2.5 g, 6.19 mmol) with NaN<sub>3</sub> (1.2 equiv.). Yield: 98% (2.48 g); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.46 (s, 18H), 4.26 (s, 2H), 7.34 (d, 2H, *J* = 9 Hz), 7.47 (d, 2H, *J* = 8.7 Hz), 7.50 (d, 2H, *J* = 8.4 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 8.14 (d, 2H, *J* = 1.8 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  32.1, 34.8, 54.5, 109.3, 116.4, 123.6, 123.8, 127.0, 129.6, 134.2, 138.3, 139.2, 143.1 ppm.

**Dendritic chloride 11 (G<sub>1</sub>-Cl).** From a stirred solution of 1-(chloromethyl)-3,5-bis(prop-2-ynyloxy)benzene **10** (0.5 g, 2.13 mmol) and the zeroth generation dendritic azide **9** (G<sub>0</sub>-N<sub>3</sub>) (1.92 g, 4.68 mmol), and by following general procedure A, the first generation dendritic chloride **11** (G<sub>0</sub>-Cl) was obtained as a colourless solid after elution from a column using CHCl<sub>3</sub>: MeOH (9:1). Yield: 85% (1.86 g); melting point: 124–126 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.45 (s, 36H), 4.48 (s, 2H), 5.19 (s, 4H), 5.59 (s, 4H), 6.63 (s, 1H), 6.65 (s, 2H), 7.32 (d, 4H, J = 8.7 Hz), 7.43–7.46 (m, 8H), 7.55 (d, 4H, J = 8.4 Hz), 7.66 (s, 2H), 8.13 (d, 4H, J = 1.2 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  32.0, 34.8, 46.2, 53.8, 62.2, 101.9, 108.1, 109.1, 116.3, 123.0, 123.6, 126.8, 127.1, 129.5, 132.9, 138.8, 138.9, 139.9, 143.2, 144.4, 159.6 ppm.

**Dendritic azide 12 (G**<sub>1</sub>-**N**<sub>3</sub>). Following general procedure B, the first generation G<sub>1</sub> dendritic azide **16** (G<sub>1</sub>-**N**<sub>3</sub>) was obtained as a colourless solid by reacting the first generation dendritic chloride **11** (G<sub>1</sub>-Cl) (1 g, 0.94 mmol) with NaN<sub>3</sub> (1.2 equiv.). Yield: 98% (976 mg); melting point: 142–144 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.45 (s, 36H), 4.26 (s, 2H), 5.21 (s, 4H), 5.61 (s, 4H), 6.58 (d, 2H, *J* = 1.5 Hz), 6.64 (t, 1H), 7.33 (d, 4H, *J* = 8.7 Hz), 7.43–7.48 (m, 8H), 7.57 (d, 4H, *J* = 8.4 Hz), 7.67 (s, 2H), 8.13 (d, 4H, *J* = 1.2 Hz) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  31.9, 34.7, 53.7, 54.8, 62.6, 102.5, 108.1, 109.1, 116.2, 122.7, 123.6, 123.8, 127.2, 129.3, 133.2, 138.0, 139.1, 139.3, 143.4, 144.5, 160.0 ppm.

**Dendritic chloride 13** (G<sub>2</sub>-Cl). From 1-(chloromethyl)-3,5bis(prop-2-ynyloxy)benzene **10** (0.5 g, 2.13 mmol) and the first generation dendritic azide **12** (4.91 g, 4.68 mmol), and by following general procedure A, the second generation dendritic chloride **13** (G<sub>2</sub>-Cl) was obtained as colourless solid after elution from a column using CHCl<sub>3</sub>: MeOH (4:1). Yield: 79% (2.39 g); melting point: 198–200 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta_{\rm H}$  1.44 (s, 72H), 4.38 (s, 2H), 5.09 (s, 12H), 5.37 (s, 4H), 5.56 (s, 8H), 6.49 (s, 4H), 6.55 (s, 3H), 6.61 (s, 2H), 7.29 (d, 8H, *J* = 8.7 Hz), 7.41–7.44 (m, 16H), 7.53 (d, 8H, *J* = 8.1 Hz), 7.59 (s, 2H), 7.66 (s, 4H), 8.13 (s, 8H) ppm;  $^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  31.9, 34.7, 46.2, 53.7, 54.0, 61.9, 101.8, 102.0, 107.5, 108.1, 109.1, 116.3, 123.2, 123.5, 123.7, 127.0, 129.5, 132.9, 136.9, 138.7, 138.8, 139.7, 143.2, 143.9, 159.4, 159.8 ppm.

**Dendritic azide 14 (G**<sub>2</sub>-**N**<sub>3</sub>). Following general procedure B, the second generation dendritic azide 14 (G<sub>2</sub>-N<sub>3</sub>) was obtained as a colourless solid by reacting the second generation dendritic chloride 13 (G<sub>2</sub>-Cl) (1 g, 0.42 mmol) with NaN<sub>3</sub> (1.2 equiv.). Yield: 94% (940 mg); melting point: 180–182 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta_{\rm H}$  1.44 (s, 72H), 4.16 (s, 2H), 5.12 (s, 12H), 5.38 (s, 4H), 5.57 (s, 8H), 6.49 (s, 6H), 6.57 (s, 1H), 6.62 (s, 2H), 7.30 (d, 8H, *J* = 8.4 Hz), 7.42–7.46 (m, 16H), 7.54 (d, 8H, *J* = 7.8 Hz), 7.57 (s, 2H), 7.66 (s, 4H), 8.12 (s, 8H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  31.9, 34.7, 53.7, 53.9, 54.7, 62.4, 102.3, 102.7, 107.9, 108.1, 109.1, 116.2, 122.9, 123.7, 123.8, 127.2, 129.4, 133.2, 137.1, 137.9, 139.0, 139.2, 143.4, 144.1, 144.3, 159.8, 160.1 ppm.

Cyclohexadienone core 16. To a stirred solution of cyclohexanone 15 (2.0 mL, 19.31 mmol) in ethanol, NaOH (1.55 g, 38.71 mmol) was added, and this was stirred for 15 minutes. 4-(Prop-2-ynyloxy)benzaldehyde (6.82 g, 42.58 mmol) was added dropwise to the reaction mixture and it was stirred for 6 h. It was then poured over water and extracted using  $CHCl_3$  (2  $\times$ 100 mL), and the combined organic layer was washed with water  $(2 \times 50 \text{ mL})$  and brine  $(1 \times 50 \text{ mL})$  and dried over sodium sulphate. The solvent was distilled and the crude product was purified using column chromatography using hexane: CHCl<sub>3</sub> (1:4) as eluent to give the pure dienone 16, which was eluted from the column as a yellow colored solid. Yield: 86% (6.35 g); melting point: 124–126 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  1.75– 1.84 (m, 2H), 2.55 (t, 2H, J = 2.1 Hz), 2.91 (t, 4H, J = 5.4 Hz), 4.72 (d, 4H, J = 1.8 Hz), 7.01 (d, 4H, J = 8.7 Hz), 7.45 (d, 4H, J =8.4 Hz), 7.54 (d, 2H, J = 8.1 Hz), 7.59 (d, 2H, J = 8.1 Hz), 7.75 (s, 2H) ppm;  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  23.0, 28.5, 55.8, 75.9, 78.2, 114.8, 129.6, 132.1, 134.7, 136.4, 157.8, 190.2 ppm.

#### Fabrication of dye-sensitized solar cells

Prepared TiO<sub>2</sub> electrodes on a fluorinated tin oxide (FTO) substrate were immersed in a  $5 \times 10^{-5}$  M solution of photosensitized dye [*cis*-dithiocynato-*N*,*N*-bis(2,2-bipyridyl-4,4-dicarboxylic acid)ruthenium(II)] (N3 dye) in ethanol for 24 h. The dye coated photoelectrode was dried and used for the measurement of the solar energy-to-electric energy conversion efficiency. Initially 30 mg of synthesized dendrimer was made into a paste with DMF solvent, and this was added to 0.3 g of potassium iodide (KI) and 0.03 g of iodine (I<sub>2</sub>) in 25 mL of an acetonitrile + *tert*-butyl alcohol mixture in a 1:1 volume ratio and stirred for 2 h at 50 °C to obtain a homogeneous quasi-gel type dendrimer electrolyte. Finally, the prepared quasi-electrolyte was spread over a dye-sensitized TiO<sub>2</sub> photoanode (active area of  $1 \times 1$  cm<sup>2</sup>) and this was sandwiched with a platinum counter electrode for the fabrication of a DSSC.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

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