Synthesis of triazole dendrimers with a dimethyl isophthalate surface group and their application to dye-sensitized solar cells

Perumal Rajakumar,*[a] Sebastian Raja,[a] Chinnadurai Satheeshkumar,[a] Shanmugam Ganesan,[b] Pichai Maruthamuthu[b] and Samuel Austin Suthanthiraraj[b]

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Dendritic architectures with 1,2,3-triazole as the building unit and dimethyl isophthalate as the surface group are synthesized through a convergent approach employing click chemistry and tested for their application in dye-sensitized solar cells (DSSCs). The studies revealed that the presence of triazole and isophthalate groups in dendritic structures significantly altered the absorption, electrochemical and DSSC behaviors. In DSSCs, the dendritic structures exhibited higher V_{oc} values and higher power conversion efficiency (η) in the I^-/I_3^- redox couple under simulated conditions at 40 mW cm^{-2}.

Introduction

Dye-sensitized solar cells (DSSCs) have received much attention in recent years due to rapidly increasing energy demands worldwide, their low-cost and high conversion performance.[1] DSSCs with 11% power conversion efficiency were well developed by Gratzel *et al.* during 1991.[2]

DSSCs are fabricated from nanocrystalline TiO_2 film absorbed with [*cis*-di-thiocyanato-*N*,*N*-bis(2,2-bipyridyl-4,4-dicarboxylic acid) ruthenium(II)] (N3 dye), a redox electrolyte such as the I^-/I_3^- redox couple and platinum as a counter electrode. Recently, organic materials with excellent optical and electrochemical properties have been developed and used in photovoltaic devices and light harvesting systems.[3]

Among several methodologies for improved functional organic materials, a building block approach based on the dendrimer structure has been suggested to be an efficient design criterion for new artificial light harvesting and solar energy conversion devices.[4] Dendrimers provide perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture for a wide variety of applications in optoelectronic and electronic devices.[5] Recently, Yamamato *et al.*[6] reported novel dendrimers and their application in DSSCs.

Methodology has played a crucial role in the synthesis of dendrimers in recent years. In particular, click chemistry happens to be an important tool for the synthesis of dendrimers in modern chemistry. Click chemistry refers to Cu(I) catalyzed 1,3-dipolar cycloaddition of azide to alkyne to give 1,2,3-triazole. 1,2,3-Triazole is an important heterocycle with a wide range of applications in the field of biology and pharmacology.[7] Moreover, their derivatives find industrial applications as fluorophores, chemosensors and charge transfer agents.[8]

Recently, we have reported novel dendrimers bearing chalcone and carbohydrate moieties at the periphery through the click chemistry approach.[9] Inspired by the wide application of triazoles, we report herein 1,2,3-tirazole and methyl carboxylate based dendrimers **1a–c**, **2a–c**, **3a,b** and **4a,b** (Fig. 1) through a click chemistry approach. In addition the optical and electrochemical properties of the resulting dendrimers and their performance in DSSCs have also been systematically investigated. All the dendrimers reported herein have both triazole and dimethyl isophthalate units and hence might show a conjugative effect of both functionalities with respect to photophysical and electrochemical properties.

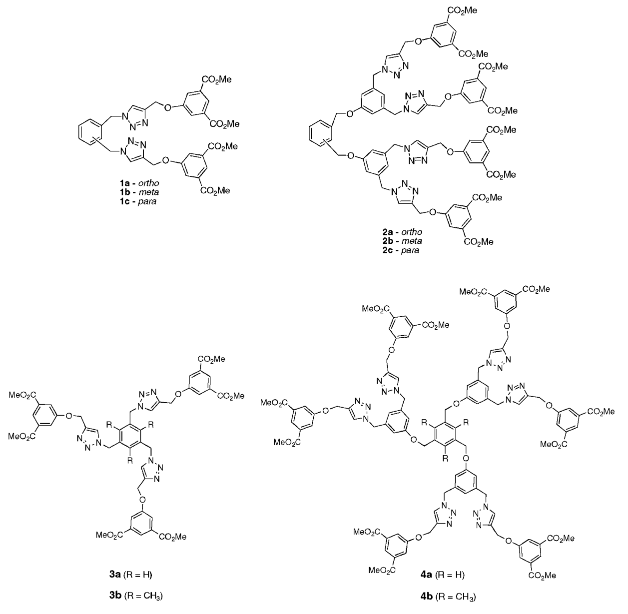

Fig. 1 Molecular structure of dendrimers **1–4**.

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[a] *Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India. E-mail: perumalrajakumar@gmail.com; Fax: +91 044 22300488; Tel: +91 044 22351269 x213*
[b] *Department of Energy, University of Madras, Guindy Campus, Chennai 600 025, India*

Results and discussion

Synthesis

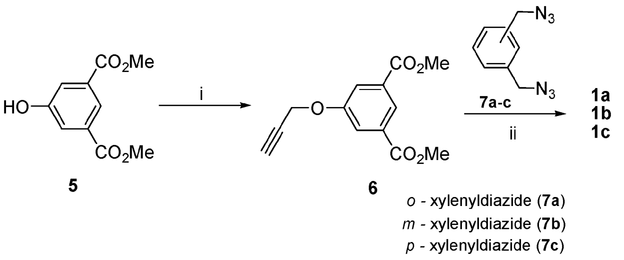
The propargyl dendron **6** was synthesized in 91% yield by treatment of 1.0 equiv. of methyl-5-hydroxyisophthalate (**5**) with 1.25 equiv. of propargyl bromide in the presence of K_2CO_3 in DMF at 60 °C for 24 h (Scheme 1). Zero generation dendrimers **1a–c** could be achieved by click chemistry methodology. Reaction of 1.0 equiv. of the bis-azides **7a–c**[10] with 2.1 equiv. of alkyne **6** in 5 mol% $CuSO_4{\cdot}5H_2O$ and 10 mol% sodium ascorbate in THF–H_2O (1 : 1) for 12 h at room temperature, gave the dendrimers **1a–c** in 83%, 86% and 90% yields, respectively (Scheme 1). The structure of the dendrimers **1a**, **1b** and **1c** was confirmed from spectral and analytical data.

Dibromide **8**[11] was converted into bis-azide **9** in 75% yield using 2.1 equiv. of sodium azide in DMF at room temperature for 48 h, followed by deacylation using ethanolic KOH at reflux for 3 h. The structure of the bis-azide **9** has been confirmed from spectral and analytical data. Treatment of 1.0 equiv. of bis-azide **9** with 2.1 equiv. of alkyne **6** in 5 mol% $CuSO_4{\cdot}5H_2O$ with 10 mol% sodium ascorbate in THF–H_2O (1 : 1) for 12 h at room temperature afforded the hydroxyl dendron **10** in 64% (Scheme 2).

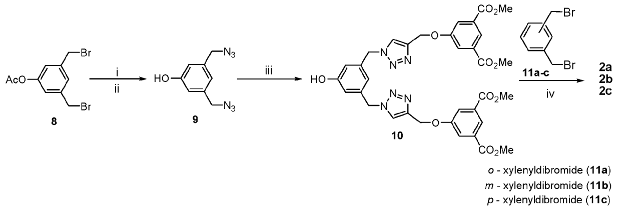
The synthesis of the first generation dendrimers **2a–c** could be achieved by *O*-alkylation methodology using *o*-, *m*- and *p*-xylenyl dibromides **11a–c** as core units and a phenolic dendritic arm **10** as the surface and branching unit. Reaction of 2.1 equiv. of dendron **10** with 1.0 equiv. of corresponding *o*-, *m*- and *p*-xylenyl dibromides **11a–c** in the presence of K_2CO_3 in DMF at 60 °C for 48 h afforded the first generation dendrimers **2a–c** in 67%, 75% and 79% yields, respectively (Scheme 2). The structure of dendrimers **2a**, **2b** and **2c** were confirmed from spectral analytical data.

Zero generation dendrimers **3a** and **3b** with tris branching were obtained in 89% and 87% yields, respectively by the treatment of 1.0 equiv. of triazides **12a** and **12b**[12] with 3.2 equiv. of alkyne **6** under the click reaction conditions as mentioned earlier (Scheme 3). Spectroscopic and analytical methods were used to confirm the structure of the dendrimers **3a** and **3b**.

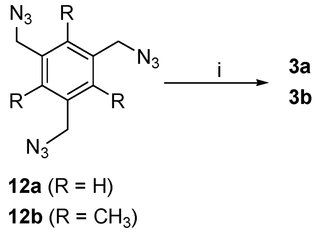
The reaction of 1.0 equiv. of tribromides **13a** and **13b**[13] with 3.2 equiv. of hydroxyl dendron **10** in the presence of K_2CO_3 in DMF at 60 °C for 48 h afforded the first generation dendrimers **4a** and **4b** in 85% and 83% yields, respectively (Scheme 4).



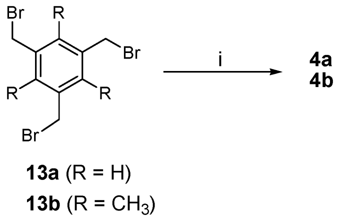
Scheme 1 Reagents and conditions: (i) 1.25 equiv. propargyl bromide, K_2CO_3, DMF, 60 °C, 24 h; (ii) $CuSO_4{\cdot}5H_2O$ (5 mol%), NaAsc, (10 mol%), THF–H_2O (1 : 1), rt, 12 h.



Scheme 2 Reagents and conditions: (i) 2.1 equiv. NaN_3, DMF, rt, 48 h; (ii) 2.0 equiv. KOH, ethanol, reflux, 3 h; (iii) 2.1 equiv. **6**, $CuSO_4{\cdot}5H_2O$ (5 mol%), NaAsc, (10 mol%), THF–H_2O (1 : 1), rt, 12 h; (iv) K_2CO_3, DMF, 60 °C, 48 h.



Scheme 3 Reagents and conditions: (i) 3.2 equiv. **6**, $CuSO_4{\cdot}5H_2O$ (5 mol%), NaAsc, (10 mol%), THF–H_2O (1 : 1), rt, 12 h.



Scheme 4 Reagents and conditions: (i) 3.2 equiv. **10**, K_2CO_3, DMF, 60 °C, 48 h.

The ^1H NMR spectrum of **4a** showed a singlet for thirty-six protons at δ 3.82 for the methyl protons of the carboxylate ester, a six-proton singlet at δ 4.92 for *O*-methylene protons attached to the benzene ring, a set of twelve proton-singlets at δ 5.12 and δ 5.41 for *N*-methylene and *O*-methylene protons in addition to thirty-six aromatic protons. In the ^{13}C NMR spectrum, dendrimer **4a** showed four peaks at δ 51.4, δ 52.7, δ 61.3 and δ 68.6 for methyl, *N*-methylene and two sets of *O*-methylene carbons in addition to twelve aromatic carbons and the carbonyl carbon at δ 164.9. The mass spectrum (MALDI-TOF) of **4a** showed a peak at m/z 2216 corresponding to the molecular ion. The structure of **4a** was further confirmed from elemental analysis. Similarly, the structure of dendrimer **4b** was also confirmed from spectral and analytical data.

UV-vis absorption studies

The UV–vis absorption data of compounds **1a–c**, **2a–c**, **3a,b** and **4a,b** in DMSO are presented in Fig. 2. The data of λ_{max} peaks of UV–vis absorption spectra in DMSO are listed in Table 1.

The absorption spectra of all the zero generation dendrimers **1a–c** and **3a,b** are almost identical, and exhibited only one

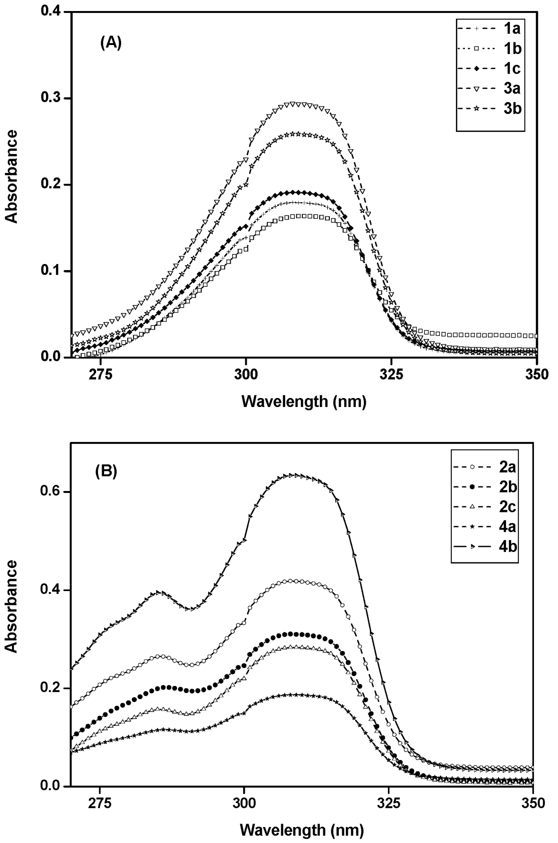


Fig. 2 (a) UV-vis absorption spectra of zero generation dendrimers **1a–c**, **3a** and **3b** in DMSO at room temperature. (b) UV-vis absorption spectra of first generation dendrimers **2a–c**, **4a** and **4b** in DMSO at room temperature.

Table 1 Optical and electrochemical parameters were measured for the compounds **1a–c**, **2a–c**, **3a,b** and **4a,b** in DMSO

Compound	UV-Vis ^{a}/nm	$E_{pc1}{}^{a}$ (v)	$E_{pc2}{}^{a}$ (v)	$E_{pc3}{}^{a}$ (v)
1a	308	−0.64	—	—
1b	310	−0.96	—	—
1c	308	−0.99	—	—
2a	287, 308	−1.04	—	—
2b	288, 308	−0.84	−0.91	—
2c	286, 308	−0.64	−0.76	—
3a	310	−0.70	—	−2.50
3b	308	−0.65	−0.75	−2.55
4a	285, 308	−0.64	−0.75	—
4b	285, 308	−0.90	−0.97	−1.06

[a] All spectra were recorded in DMSO at room temperature at $c = 1 \times 10^{-5}$M.

absorption band in between 307–310 nm (Fig. 2A). Similarly, the first generation dendrimers **2a–c** and **4a,b** are also nearly identical, showing two absorption bands – a weak band at 285–287 nm and strong band at 307–308 nm, respectively for all the dendrimers (Fig. 2B).

As the number of triazole and carboxylate units increase from the zero generation to the first generation the absorption also increases which indicates that the amount of light absorbed by the dendritic antenna increases from one generation to the next.[14]

Electrochemical studies

The redox behavior of dendrimers **1a–c**, **2a–c**, **3a,b** and **4a,b** were studied by cyclic voltammetry (CV) in DMSO (1×10^{-5} M) at room temperature. All the compounds have an electrochemical response, and the cyclic voltammogram of all the dendrimers are shown in Fig. 3, with redox potentials listed in Table 1. The redox behaviour of zero generation dendrimers **1a–c**, **3a,b** are almost similar, exhibiting only one irreversible cathodic peak corresponding to a triazole unit. Similarly, the reduction potential of first generation dendrimers **2a–c** and **4a,b** are almost similar however a multi-reduction peak was observed in the cyclic voltammogram (Fig. 3). All the first generation dendrimers showed more than one irreversible reduction peak from cyclic voltammetry measurements. For example, dendrimer **4b** has several triazole units and exhibits three irreversible reduction waves at −0.96 V, −1.07 V and −1.22 V respectively (Fig. 3C).

The CV profile for different dendrimers show that they exhibit generation dependant reduction peaks. Furthermore, as the higher generation dendrimers contain a higher number of triazole units, multi reduction is observed. The presence of the triazole unit is responsible for the CV behaviour of the dendrimers. In conclusion, the electrochemical behavior is altered on increasing the number of triazole-carboxylate moieties in the dendritic architectures.

Dye-sensitized solar cell studies

Organic dye-sensitized solar cells have generated a lot of interest during recent years[15] due to the emerging importance of energy need worldwide. During attempts to improve the performance of solar cells, studies were carried out to examine the role of the electrolytic solution in the cell.[16] In general, the amine derivatives drastically increase the open-circuit voltage (V_{oc}) due to the electron donating properties of the nitrogen lone pair.[17] Various nitrogen based organic molecules like aminopyridine, pyrimidine, pyrrolidinopyridine, pyrrolidinoethylpyridine have been used as additives in DSSC studies.[18] In the present investigation, 1,2,3-triazole based dendrimers with dimethyl isophthalate groups could be tested for better performance in DSSCs studies. Dendrimers **1a–c**, **2a–c**, **3a,b** and **4a,b** form charge transfer complexes with iodine in the redox couple (I^-/I_3^-) in photovoltaic devices. From the present investigation, it is clear that the dendrimer additive in I^-/I_3^- electrolyte solution influences Ru DSSC performance and the V_{oc} values are drastically altered. Typically, cells with dendrimers display higher V_{oc} values when compared to a cell without a dendrimer additive. The chemical reaction of charge-transfer complexation in the electrolyte solution is given below.

$$\text{Dendrimer} + I_3^- \rightarrow \text{Dendrimer } I_2 + I^-$$

Dendrimers bearing triazole and ester groups effectively form charge transfer complexes with I_2 in the redox complexation reaction which results in a decrease in the sublimation of iodine and also reflects the high performance of DSSC.

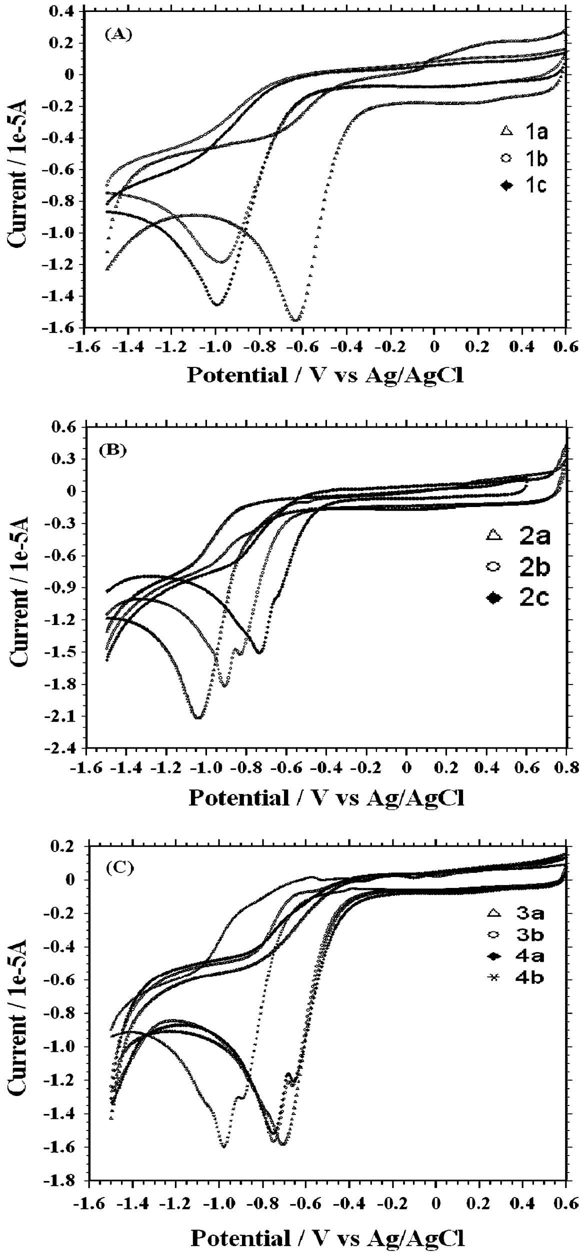


Fig. 3 (a) Cyclic voltammogram of dendrimers **1a–c** in DMSO at room temperature. (b) Cyclic voltammogram of dendrimers **2a–c** in DMSO at room temperature. (c) Cyclic voltammogram of dendrimers **3a,b** and **4a,b** in DMSO at room temperature.

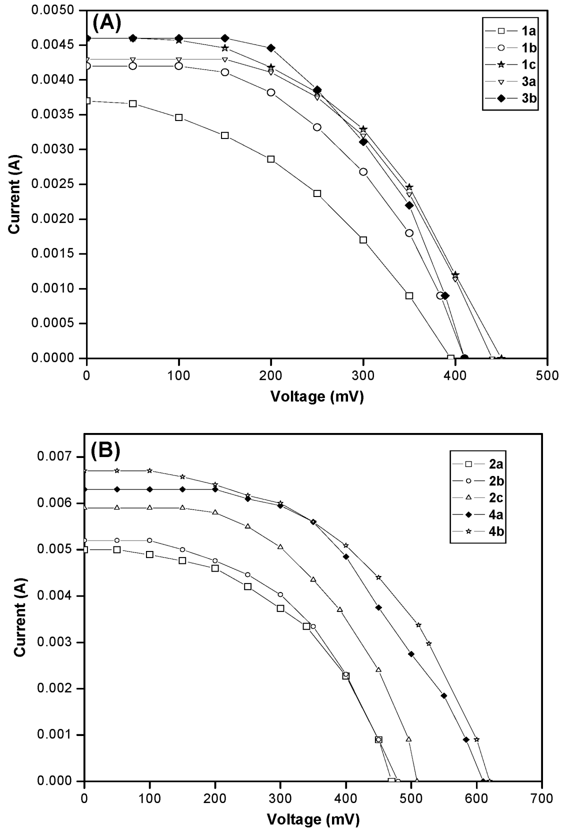


Fig. 4 (a) Current–voltage response of zero generation dendrimer **1a–c**, **3a** and **3b** at 40 mW cm^{-2}. (b) Current–voltage response of first generation dendrimer **2a–c**, **4a** and **4b** at 40 mW cm^{-2}.

The photovoltaic performance of the dendrimers at 40 mW cm^{-2} are shown in Fig. 4. Fig. 4A shows the current–voltage response of the zero generation dendrimers **1a–c**, **3a** and **3b**. The performance of zero generation dendrimers are almost similar and the presence of two or three triazole moieties do not affect the current–voltage curve to a greater extent. Fig. 4B displays the photovoltaic response of first generation dendrimers at 40 mW cm^{-2}. It is found that the photoelectrochemical properties increase with increasing core length of the dendrimers leading to better performance. Moreover, the efficiency of the DSSCs increase with the increase in the number of triazole units in the first generation dendritic structures, which is usually referred to as the multivalent effect[19] in dendrimer chemistry.

The additives **4a** and **4b** drastically enhance the open-circuit voltage (V_{oc}) and the solar energy conversion efficiency (η) and hence show a better performance in DSSC studies due to the higher number of electron donating triazole units. The photovoltaic performance data for the dendrimers **1a–c**, **2a–c**, **3a,b** and **4a,b** are summarized in Table 2.

Conclusions

In conclusion, the synthesis of dendritic structures with triazole as the building block and dimethyl isophthalate as the surface group has been achieved through a click chemistry approach. The optical properties indicate that as the number of triazole units increases absorption also increases and hence the light absorbed by the dendritic antenna increases as the generation increases. The CV studies clearly reflect multireduction peaks as the dendritic generation increases from lower to higher. Further as the number of triazole units increases in the dendrimers of higher generation, DSSC performance also increases. Among all the dendritic structures, dendrimers **4a** and **4b** exhibited higher V_{oc} of 0.610V and 0.620V and higher η values of 5.5% and 5.4% respectively than the other dendrimers synthesized in the present investigation.

Table 2 The photovoltaic properties of the dendrimers with KI and I_2 redox couple under illumination of 40 mW cm^{-2}

S. No	Electrolyte system	J_{sc}/mAcm^{-2}	V_{oc}/mV	fill factor	efficiency% (η)
1	KI/I_2	1.8	420	0.44	0.8
2	KI/I_2/**1a**	3.7	395	0.43	1.5
3	KI/I_2/**1b**	4.2	410	0.45	1.9
4	KI/I_2/**1c**	4.6	450	0.48	2.5
5	KI/I_2/**2a**	5.0	470	0.50	2.9
6	KI/I_2/**2b**	5.2	480	0.55	3.4
7	KI/I_2/**2c**	5.9	509	0.56	4.2
8	KI/I_2/**3a**	4.3	440	0.42	2.0
9	KI/I_2/**3b**	4.6	410	0.50	2.4
10	KI/I_2/**4a**	6.3	610	0.58	5.5
11	KI/I_2/**4b**	6.7	620	0.60	5.4

Experimental

Materials and methods

Chemicals and solvents (AR quality) were used as received without any further purification. All melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER 300 MHz instruments. ^{1}H NMR spectra were recorded using deuterated chloroform ($CDCl_3$) as solvent. Tetramethylsilane (TMS) was used as the internal standard. Mass spectra were recorded by JEOL-DX303 HF mass spectrometer. Elemental analyses were carried out by Perkin-Elmer CHNS 2400 instrument. Column chromatography was performed on silica gel (ACME, 100–200 mesh). Routine monitoring of the reaction was made using thin layer chromatography developed on glass plates coated with silica gel-G (ACME) of 25 mm thickness and visualized with iodine. The UV-vis spectra were recorded on a Shimadzu 260 spectrophotometer.

General procedure (A) for dye-sensitized solar cell studies

The TiO_2 photoelectrode was prepared as described earlier.[20] The N3 dye was adsorbed on to the TiO_2 surface by soaking the TiO_2 photoelectrode in an ethanol solution of the N3 dye (5×10^{-5} M concentration) for 24 h at room temperature. The photoelectrode was washed, dried and immediately used for the measurement of solar cell performance. A sandwich-type photoelectrochemical cell was composed of a dye-coated TiO_2 photoanode, and a platinum coated Fluorinated Tin Oxide (FTO) conducting glass to act as the counter electrode. The electrolyte solution was injected into the space between two electrodes. The electrolyte solution was composed of 3.2×10^{-5} M of KI, 4.1×10^{-6} M of I_2, and 6.4×10^{-6} M of the dendrimer additives in 10 ml DMF solvent. The solar to electric energy conversion efficiency was measured under simulated solar light at 40 mWcm^{-2}. The photocurrent-photovoltage was measured using a BAS 100A Electrochemical analyzer. The apparent cell area of TiO_2 photoelectrode was 1 cm^2 (1 cm × 1 cm).

General procedure (B) for electrochemical studies

Cyclic voltammetric measurements were performed in a conventional three electrode system on CHI model 1100A series electrochemical analyzer (CH Instrument, USA). Glassy carbon electrode (GCE) was used as working electrode with Pt foil (large surface area) and a silver-silver chloride (Ag/AgCl) as counter and reference electrodes, respectively. Prior to each electrochemical experiment, this GCE was mechanically polished with 0.05 micron alumina powder and cleaned in a 1 : 1 acetone/ethanol mixture in an ultrasonic bath to remove impurities, rinsed with water and then dried in air. Then the electrode was cleaned by cycling between the potentials of −1.6 to +0.6 V *versus* AgCl in 1×10^{-5} M of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in DMSO at a scan rate of 50 mV s^{-1} for approximately 30 min until reproducible scans were recorded. All the electrochemical experiments were performed in a quiescent solution at room temperature (25 ± 1 °C).

General procedure (C): Synthesis of compounds 1a–c and 3a,b

A mixture of azide, alkyne and $CuSO_4$/sodium ascorbate mixture in an aqueous THF solution (1 : 1) was stirred for 12 h at room temperature. The residue obtained after evaporation of the solvent was washed thoroughly with water and dissolved in $CHCl_3$ (150 mL). The organic layer was separated, washed with brine (1 × 150 mL), dried (anhydrous Na_2SO_4) and evaporated to give the crude triazole, which was purified by column chromatography (SiO_2) using the mixture of $CHCl_3$ with MeOH (99 : 1) as the eluent.

General procedure (D): Synthesis of compounds 2a–c and 4a,b

A mixture of bromide (1.0 equiv.) and phenol (2.1 equiv./3.2 equiv.) in dry DMF was stirred at 60 °C for 48 h. The reaction mixture was then allowed to cool to room temperature and poured into ice water. The resulting precipitate was filtered, washed thoroughly with water and dissolved in $CHCl_3$ (150 mL). The organic layer was separated, washed with brine (1 × 150 mL), dried (anhydrous Na_2SO_4) and evaporated to give the crude dendrimer, which was purified by column chromatography (SiO_2) using $CHCl_3$–MeOH (99 : 1) as the eluent.

Compound 1a. Following the general procedure C, compound **1a** was obtained as a colorless solid in 83% yield. Mp = 136–139 °C; EI-MS (70 eV): *m/z* 684 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.92 (s, 12H); 5.24 (s, 4H); 5.67 (s, 4H) 7.27–7.31 (m, 2H); 7.40–7.43 (m, 2H); 7.57 (s, 2H); 7.79 (m, 4H); 8.28 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 51.3, 52.4, 62.4, 120.1, 123.1, 123.6, 129.9, 130.6, 131.9, 133.1, 143.9, 158.2, 165.9. Anal. calc. for $C_{34}H_{32}N_6O_{10}$: C, 59.65; H, 4.71; N, 12.27. Found: C, 59.73; H, 4.84; N, 12.36.

Compound 1b. Following the general procedure C, compound **1b** was obtained as a colorless solid in 86% yield. Mp = 67–70 °C; EI-MS (70 eV): *m*/*z* 684 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.83 (s, 12H); 5.15 (s, 4H); 5.46 (s, 4H); 7.15–7.21 (m, 3H); 7.27–7.32 (m, 1H); 7.57 (s, 2H); 7.69 (s, 4H); 8.17 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 51.5, 52.8, 61.4, 118.9, 122.0, 122.5, 126.5, 127.3, 129.0, 130.8, 134.6, 142.8, 157.2, 164.9. Anal. calc. for $C_{34}H_{32}N_6O_{10}$: C, 59.65; H, 4.71; N, 12.27. Found: C, 59.53; H, 4.81; N, 12.36.

Compound 1c. Following the general procedure C, compound **1c** was obtained as a colorless solid in 90% yield. Mp = 137–140 °C; EI-MS (70 eV): *m*/*z* 684 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.93 (s, 12H); 5.26 (s, 4H); 5.56 (s, 4H); 7.29 (s, 4H); 7.59 (s, 2H); 7.81 (s, 4H); 8.29 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.5, 53.7, 62.5, 120.1, 122.8, 123.6, 128.8, 131.9, 135.2, 143.9, 158.2, 165.9. Anal. calc. for $C_{34}H_{32}N_6O_{10}$: C, 59.65; H, 4.71; N, 12.27. Found: C, 59.55; H, 4.83; N, 12.18.

Compound 2a. Following the general procedure D, compound **2a** was obtained as a colorless solid in 67% yield. Mp = 96–100 °C; QTOF-MS: *m*/*z* 1503 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.82 (s, 24H); 4.96 (s, 4H); 5.13 (s, 8H); 5.42 (s, 8H); 6.73 (s, 6H); 7.30 (m, 4H); 7.64 (s, 4H); 7.68 (s, 8H); 8.15 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.4, 53.7, 62.3, 68.2, 114.6, 119.8, 120.0, 123.3, 123.5, 128.8, 129.2, 131.9, 134.3, 137.2, 143.7, 158.2, 159.5, 165.9. Anal. calc. for $C_{76}H_{70}N_{12}O_{22}$: C, 60.72; H, 4.69; N, 11.18. Found: C, 60.83; H, 4.59; N, 11.29.

Compound 2b. Following the general procedure D, compound **2b** was obtained as a colorless solid in 75% yield. Mp = 98–102 °C; QTOF-MS: *m*/*z* 1503 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.89 (s, 24H); 4.98 (s, 4H); 5.22 (s, 8H); 5.47 (s, 8H); 6.79 (s, 2H); 6.79 (s, 4H); 7.35 (s, 4H); 7.61 (s, 4H); 7.75 (s, 8H); 8.25 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.6, 53.8, 62.4, 69.9, 114.8, 119.9, 120.1, 120.3, 123.1, 123.6, 127.3, 131.9, 136.7, 137.2, 143.9, 158.3, 159.7, 166.0. Anal. calc. for $C_{76}H_{70}N_{12}O_{22}$: C, 60.72; H, 4.69; N, 11.18. Found: C, 60.63; H, 4. 80; N, 11.31.

Compound 2c. Following the general procedure D, compound **2c** was obtained as a colorless solid in 79% yield. Mp = 92 °C; QTOF-MS: *m*/*z* 1503 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.83 (s, 24H); 4.89 (s, 4H); 5.17 (s, 8H); 5.41 (s, 8H); 6.72–6.74 (m, 6H, J = 6.6 Hz); 7.25-7.29 (s, 4H); 7.55 (s, 4H); 7.72 (s, 8H); 8.18 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.7, 53.7, 62.4, 68.2, 107.4, 114.7, 120.0, 122.9, 123.5, 127.8, 128.3, 129.6, 131.9, 137.1, 143.9, 158.2, 165.8. Anal. calc. for $C_{76}H_{70}N_{12}O_{22}$: C, 60.72; H, 4.69; N, 11.18. Found: C, 60.81; H, 4. 79; N, 11.26.

Compound 3a. Following the general procedure C, compound **3a** was obtained as a colorless solid in 89% yield. Mp = 82 °C; QTOF-MS: *m*/*z* 987 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.92 (s, 18H); 5.25 (s, 6H); 5.52 (s, 6H); 7.18 (s, 3H); 7.66 (s, 3H); 7.78 (s, 6H); 8.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 52.5, 53.4, 62.4, 120.0, 123.1, 123.6, 127.6, 131.9, 136.9, 144.0, 158.2, 165.9. Anal. calc. for $C_{48}H_{45}N_9O_{15}$: C, 58.36; H, 4.59; N, 12.76. Found: C, 58.29; H, 4.67; N, 12.89.

Compound 3b. Following the general procedure C, compound **3b** was obtained as a colorless solid in 87% yield. Mp = 106 °C; QTOF-MS: *m*/*z* 1030 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 2.37 (s, 9H); 3.83 (s, 18H); 5.12 (s, 6H); 5.62 (s, 6H); 7.41 (s, 3H); 7.66 (s, 6H); 8.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 16.7, 49.1, 52.5, 62.3, 119.9, 122.4, 123.5, 130.6, 131.8, 139.9, 143.4, 158.1, 165.9. Anal. calc. for $C_{51}H_{51}N_9O_{15}$: C, 59.47; H, 4.99; N, 12.24. Found: C, 59.39; H, 4.90; N, 12.17.

Compound 4a. Following the general procedure D, compound **4a** was obtained as a colorless solid in 85% yield. Mp = 103−108 °C; MALDI-TOF MS: *m*/*z* 2216 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 3.82 (s, 36H); 4.92 (s, 6H); 5.12 (s, 12H); 5.41 (s, 12H); 6.75 (s, 9H); 7.20 (s, 3H); 7.59 (s, 6H); 7.67 (s, 12H); 8.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 51.4, 52.7, 61.3, 68.6, 113.7, 118.8, 118.9, 122.1, 122.4, 124.9, 130.8, 136.2, 136.3, 142.8, 157.2, 158.5, 164.9. Anal. calc. for $C_{111}H_{102}N_{18}O_{33}$: C, 60.16; H, 4.64; N, 11.38. Found: C, 60.05; H, 4.56; N, 11.45.

Compound 4b. Following the general procedure D, compound **4b** was obtained as a colorless solid in 83% yield. Mp = 116–120 °C; MALDI-TOF MS: *m*/*z* 2258 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$): 2.25 (s, 9H); 3.82 (s, 36H); 4.94 (s, 6H); 5.16 (s, 12H); 5.44 (s, 12H); 6.74 (s, 3H); 6.74 (s, 6H); 7.61 (s, 6H); 7.69 (s, 12H); 8.16 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.1, 51.5, 52.8, 61.4, 64.3, 113.5, 119.0, 122.1, 122.2, 122.5, 130.3, 130.9, 136.3, 138.5, 142.9, 157.2, 159.1, 164.9. Anal. calc. for $C_{114}H_{108}N_{18}O_{33}$: C, 60.63; H, 4.82; N, 11.16. Found: C, 60.75; H, 4.93; N, 11.27

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