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Synthesis of benzothiazole–benzoxazole dendrimers with triazole as bridging unit and their application in dye-sensitized solar cells[†]

Perumal Rajakumar, *
a Venkatesan Kalpana, a Shanmugam Ganesan $^{\rm b}$ and Pichai Marutha
muthu $^{\rm b}$

Dendrimers with benzothiazole-benzoxazole surface groups and electron transporting triazole as bridging units and diphenyl sulfone as core unit were synthesized successfully by Cu(i)-catalysed Huisgen 'click reaction' using a convergent approach. All the dendrimers exhibit excellent optical and electrochemical properties. Higher-generation dendrimers exhibit better current generating capacity and show better power conversion efficiency than lower-generation dendrimers when used as additives in dye-sensitized solar cells.

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Introduction

The world's energy needs are growing constantly and all the while more and more environmental issues are observed as a consequence of increasing carbon dioxide emission. Hence there is an increase in pressure to use renewable energy sources, such as solar energy, but the production of solar cells is still too costly to compete with available energy sources. Though in 1991, Michael Grätzel and Brian O'Regan¹ invented the Grätzel cell in order to reduce the energy demand, still practical applications require further research to be carried out in this area. Dye-sensitized solar cells (DSSCs) are low cost solar cells characterized by thin films. DSSCs are electrochemical devices comprising a light-absorbing molecule anchored on to semiconducting titanium dioxide (TiO₂) nanoparticles which make use of sunlight to generate electricity.

Frechet² and Vögtle³ made a revolutionary breakthrough in the field of dendrimer chemistry through the synthesis of various types of dendrimers with varied applications. Dendrimers have received much attention in the areas of material science and biological science such as in versatile biomimetic catalysts,⁴ drug delivery systems,⁵ sensors,⁶ solar cell⁷ additives and efficient light harvesting antenna,⁸ multivalent diagnostics for magnetic resonance imaging (MRI),⁹ molecular encapsulation¹⁰ and bioconjugate¹¹ chemistry.

Heterocycles¹² such as thiazole,¹³ oxazole,¹⁴ imidazole¹⁵ systems play a vital role in the conformational landscape because of chargecharge interaction and charge delocalization over two or more sites. Such charges can rapidly and efficiently explore all sites of the molecule with respect to their reactivity so affecting the photophysical properties. In this context benzothiazoles, benzoxazoles and benzimidazoles have the capability of producing a range of colours with good transport properties, so that they can be used as both emissive and electron transport materials in OLEDs.

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Benzoheterazole-based dendrimer systems have been applied as additives in DSSCs¹⁶ and light emitting materials. According to the literature survey, only very few benzothiazole dendrimers have been synthesized through click chemistry in order to study their application in material chemistry. The architypal click reaction that has gained tremendous attention since it was reported by Fokin and Sharpless¹⁷ and which fulfills all the criteria for the construction of dendritic structures is the Cu(1) salt catalyzed reaction of azides with terminal alkynes. This reaction is highly efficient and occurs under benign conditions in the presence of other reactive groups with no byproducts. Due to its orthogonal, robust nature, click chemistry has attracted significant attention of the material science community, especially for the construction of complex polymeric materials and dendrimers. Characteristics of click reactions include high yields, short time duration, stereospecificity, mild reaction conditions, inexpensive, environmentally as well as eco-friendly reagents and with no protection and deprotection protocols, in addition to air- and moisture-tolerant reaction conditions.

Recently, water-soluble glycodendrimers,¹⁸ chalcone dendrimers,¹⁹ quinolone dendrimers,²⁰ benzothiazole dendrimers¹⁶ and diphenylamine dendrimers²¹ have been reported from our laboratory through click chemistry. We report herein the synthesis, photophysical properties as well as DSSC²² application of dendrimers **1–6**

^a Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, Tamilnadu, India. E-mail: perumalrajakumar@gmail.com; Tel: +91 44 2220 2810

^b Department of Energy, University of Madras, Guindy Campus, Chennai 600 025, Tamilnadu, India

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Scheme 1 Molecular structures of dendrimers 1–6.

with benzothiazole–benzoxazole as surface groups and 1,2,3-triazole as bridging units and diphenyl sulfone as core unit through click chemistry using a convergent approach (Scheme 1).

Results and discussion

The synthetic pathway leading to dendritic wedges **12** and **13** from 2-mercaptobenzothiazole/2-mercaptobenzoxazole is outlined

in Scheme 2. 2-(Prop-2-ynylthio)benzo[*d*]thiazole 7^{23} and 2-(prop-2-ynylthio)benzo[*d*]oxazole 8^{23} were obtained in 95 and 94% yield by the reaction of 2-mercaptobenzothiazole/2-mercaptobenzoxazole with 1.1 equiv. of propargyl bromide, TBAB (5 mg) and KOH (1.5 equiv.) in a mixture of toluene and water (1:1) at room temperature for 2 h (Scheme 2). Reaction of 3,5-bis-(azidomethyl)phenol 9^{21} with 2.1 equivalents of *S*-propargyl benzoheterazole 7 and 8 in the presence of CuSO₄·5H₂O



Scheme 2 Reagents and conditions: (i) CuSO₄·5H₂O (5 mol%), NaAsc (10 mol%), THF–H₂O (1:1), rt, 10 h, 10 (82%), 11 (80%), 14 (75%), 15 (74%); (ii) K₂CO₃, DMF, 60 °C, 48 h, 12 (85%), 13 (84%), 16 (79%), 17 (78%).

(5 mol%) and sodium ascorbate (10 mol%) in a mixture of water and THF (1:1) at room temperature afforded the phenolic dendron G₁-OH **10** and **11** in 82 and 80% yields, respectively. In the ¹H NMR spectrum, the phenolic dendritic wedge **10** showed a set of four proton singlets at δ 4.59 and 5.29 due to the *S*-methylene and *N*-methylene protons, respectively, and a broad singlet at δ 9.88 for the phenolic proton in addition to the signals for the aromatic protons. In the ¹³C NMR spectrum, the dendron **10** displayed *S*-methylene carbon at δ 27.5 and *N*-methylene carbons. Further, the structure of dendron **10** was confirmed from the ESI-mass spectrum. Similarly the structure of dendron **11** was also confirmed from the spectral and analytical data. The propargyl dendritic wedges **12** and **13** were synthesized from the phenolic dendrons **10** and **11**. Reaction of 1.0 equiv. of each of the phenolic dendrons **10** and **11** with 1.1 equiv. of the propargyl bromide in the presence of K₂CO₃ in DMF at room temperature for 24 h gave dendrons **12** and **13** in 85 and 84% yields, respectively. In the ¹H NMR spectrum, compound **13** showed a triplet at δ 2.49 for the acetylenic proton and a two proton singlet at δ 4.53 for the *O*-methylene proton and a set of four proton singlets at δ 4.60 and 5.37 for *S*-methylene and *N*methylene protons. In the ¹³C NMR spectrum, dendron **13** displayed the *S*-methylene carbon at δ 26.8 and *O*-methylene carbon at δ 53.6 and *N*-methylene carbon at δ 55.9 in addition to the signals for the aliphatic and aromatic carbons. In the mass spectrum (ESI), dendron **13** displayed a peak at m/z 621 corresponding to the molecular ion. The composition of dendron **13** was further confirmed from elemental analysis. Similarly, the structure of the first-generation propargyl dendron **12** was also confirmed from spectral and analytical data.

Dendrons 14 and 15 were synthesized in 75 and 74% yields, respectively, by the reaction of 1 equiv. of 3,5-bis(azidomethyl)phenol 9 with 2.1 equiv. of propargyl dendrons 12 and 13 in the presence of a mixture of CuSO4·5H2O and sodium ascorbate in aqueous THF solution (1:1) (Scheme 2). In the ¹H NMR spectrum, compound 14 showed two set of four and eight proton singlets at δ 4.58, 4.92, 5.23 and 5.30 due to the S-methylene, O-methylene and N-methylene protons, respectively, and one proton broad singlet at δ 9.97 for phenolic proton in addition to the signals for aromatic protons. In the ¹³C NMR spectrum, dendron 14 displayed the S-methylene carbon at δ 27.7, O-methylene carbon at δ 53.5 and *N*-methylene carbons at δ 53.7 and 61.7 in addition to the signals for aromatic carbons. Further the structure and composition of the dendron 14 was confirmed from its ESI-mass spectrum and elemental analysis, respectively. Similarly the structure of dendron 13 was also confirmed based on spectral and analytical data. The second-generation propargyl dendrons 16 and 17 were synthesized in 79 and 78% yields, respectively, by the treatment of 1.0 equiv. of phenolic dendrons 14 and 15 with 1.1 equiv. of the propargyl bromide in the presence of K₂CO₃ in DMF at room temperature for 24 h.

In the ¹H NMR spectrum, compound **16** showed a triplet at δ 2.48 for acetylenic proton, a two proton singlet at δ 4.59 for *O*-methylene proton and a set of eight proton singlets at δ 4.63 and 5.29 for *S*-methylene and *N*-methylene protons, respectively, and a set of four proton singlets at δ 4.98 and 5.44 for *O*-methylene

and *N*-methylene protons, respectively, in addition to the signals for aromatic protons. In the ¹³C NMR spectrum, dendron **16** displayed the *S*-methylene carbon at δ 27.8 and *O*-methylene carbon at δ 53.5, *O*-methylene at δ 53.7 and two *N*-methylene carbons at δ 56.0 and 61.7 in addition to the aliphatic and aromatic carbon signals. In the mass spectrum (ESI), dendron **16** showed a peak at *m*/*z* 1548 corresponding to the molecular ion. The composition of dendron **16** was further confirmed from elemental analysis. Similarly, the structure of the second-generation propargyl dendron **17** was also confirmed from spectral and analytical data.

The zeroth, first and second generation dendrimers 1 and 2 (G_0) , 3 and 4 (G_1) and 5 and 6 (G_2) could be achieved by 'click' chemistry approach using 4,4'-sulfonylbis(azidomethyl) benzene 18 as the core unit. Reaction of 1.0 equiv. of the bisazide 18 with 2.1 equiv. of each of the alkyne dendrons 7 and 8 (G_0) in 5 mol% CuSO₄·5H₂O with 10 mol% sodium ascorbate in a 1:1 solvent ratio of THF and H₂O for 12 h at room temperature afforded dendrimers 1 and 2 (G_0) in 85 and 83% yields, respectively (Scheme 3). In the ¹H NMR spectrum, compound 2 showed a set of four proton singlets at δ 4.55 and 5.51 for S-methylene and N-methylene protons, respectively, in addition to the signals for aromatic protons. In the ¹³C NMR spectrum, dendrimer 2 displayed S-methylene carbon at δ 26.7 and *N*-methylene carbon at δ 53.2 in addition to the signals for aromatic carbon. In the mass spectrum (ESI) dendrimer 2 showed a peak at m/z 707 corresponding to the molecular ion. Similarly, the structure of the zeroth generation dendrimer 1 was also confirmed from spectral and analytical data.

Reaction of 1.0 equiv. of the bisazide **18** with 2.1 equiv. of each of the alkyne dendrons **12** and **13** (G_1) in 5 mol% CuSO₄·5H₂O with 10 mol% sodium ascorbate in a 1 : 1 solvent ratio of THF and H₂O for 12 h at room temperature afforded dendrimers **3** and **4**



Scheme 3 Reagents and conditions: (i) CuSO₄:5H₂O (5 mol%), NaAsc (10 mol%), THF-H₂O (1:1), rt, 10 h, 1 (85%), 2 (83%), 3 (80%), 4 (81%), 5 (73%), 6 (72%).

(G₁) in 80 and 81% yields, respectively (Scheme 3). In the ¹H NMR spectrum, compound 3 showed a set of eight proton singlets at δ 4.56 and 5.23 for *S*-methylene and *N*-methylene protons and a set of four proton singlets at δ 4.91 and 5.48 for *O*-methylene and *N*-methylene protons in addition to the signals for aromatic protons. In the ¹³C NMR spectrum, dendrimer 3 displayed the *S*-methylene carbon at δ 27.7 and *O*-methylene at δ 53.5 and two *N*-methylene carbons at δ 53.9 and 61.6 in addition to the aromatic carbon signals. In the mass spectrum (ESI), dendrimer 3 showed a peak at *m*/*z* 1634 corresponding to the molecular ion. The composition of the dendrimer 3 was further confirmed from elemental analysis. Similarly, the structure of the first-generation dendrimer 4 was also confirmed from spectral and analytical data.

Finally, the second generation dendrimers **5** and **6** were synthesized in 73 and 72% yields, respectively, by the reaction of 1.0 equiv. of bisazide **18** with 2.1 equiv. of each of the alkyne dendrons **16** and **17** (G₁) under click chemistry conditions for 12 h at room temperature (Scheme 3). In the ¹H NMR spectrum, compound **5** showed a four proton singlet at δ 4.39 for *O*-methylene proton, a sixteen proton singlet at δ 4.61 for *S*-methylene protons, an eight proton singlet at δ 4.97 for *O*-methylene protons, a sixteen proton singlet at δ 4.99 for *N*-methylene protons, eight proton singlet at δ 5.27 for *N*-methylene protons and a four proton singlet at δ 5.40 for *N*-methylene protons attached to the sulfonyl core, in addition to the signals for the aromatic protons.

In the ¹³C NMR spectrum, dendrimer 5 displayed the *S*-methylene carbon at δ 27.8 and two *O*-methylene carbons at δ 53.2, 53.5 and three *N*-methylene carbons at δ 53.6, 53.8 and 61.7 in addition to the aromatic carbon signals. The mass spectrum (FAB-MS) of the dendrimer 5 showed a peak at *m*/*z* 3424 corresponding to the molecular ion. The composition of the dendrimer 5 was further confirmed from elemental analysis. Similarly, the structure of the second-generation dendrimer 6 was also confirmed from spectral and analytical data.

Absorption studies

The UV absorption emission spectra of compounds 1–6 in CHCl₃ are presented in Fig. 1. The λ_{max} values of UV absorption spectra are shown in Table 1. In their absorption spectra,

 $\mbox{Table 1}$ Optical and electrochemical parameters measured for compounds $\mbox{1-6}$ in \mbox{CHCl}_3

Dendrimer	$\lambda_{\rm max}/{\rm nm}$	$\lambda_{\rm em}{}^a/{\rm nm}$	$E_{\rm pc}{}^a/{\rm V}$	$E_{\rm pa}{}^a/{\rm V}$
1	244, 278, 302	394	-0.52	1.24
2	246, 279, 285	383	-0.43	1.51
3	243, 278, 302	396	-0.55	1.25
4	245, 278, 286	383	-0.44	1.52
5	242, 279, 301	389	-0.60	1.28
6	245, 279, 285	382	-0.46	1.52
^{<i>a</i>} All spectra w	vere recorded in CH	ICl ₃ at room te	mperature at	10^{-4} M.

dendrimers **1**, **3** and **5** are almost identical, exhibiting three absorption bands between 242 and 302 nm.

This may be due to the electronic transition that occurs in the benzothiazole unit. Similarly, dendrimers **2**, **4** and **6** have almost identical surface units, which showed three absorption bands, between 245 and 286 nm (Fig. 1), this may be due to the electronic transition occurring in the benzoxazole unit. As the number of triazole and benzothiazole-benzoxazole units increases from zeroth generation to the second generation, the absorption intensity also increases which indicates that the amount of light absorbed by the dendritic antenna increases from lower generation to higher generation which is otherwise known as valence effect in dendrimer chemistry.²⁴

Emission studies

The fluorescence properties of dendrimers **1–6** parallel the absorption spectra. All the dendrimers showed only one intense band between 382 and 396 nm and $\lambda_{\rm em}$ values of the fluorescence spectra are shown in Table 1.

Unlike in the absorption spectra, the emission spectra showed fluorescence quenching²⁵ with increasing number of triazole and benzothiazole–benzoxazole units (Fig. 2). The fluorescence intensity is found to decrease as the number of triazole and benzoheterazole units increases in the dendritic architectures.

Electrochemical properties

The redox behaviour of dendrimers 1–6 were studied by cyclic voltammetry (CV) in CHCl₃ $(1 \times 10^{-4} \text{ M})$ at room temperature.



Fig. 1 (A) UV absorption spectra of dendrimers 1, 3 and 5 in CHCl₃ (1 × 10⁻⁵ M). (B) UV absorption spectra of dendrimers 2, 4 and 6 in CHCl₃ (1 × 10⁻⁵ M).



Fig. 2 Fluorescence spectra of dendrimers 2, 4 and 6 in CHCl_3 at room temperature.



Fig. 3 Cyclic voltammogram of dendrimers 2, 4 and 6 in CHCl_3 at room temperature.

All the compounds exhibited an electrochemical response, and the cyclic voltammogram of the dendrimers **2**, **4** and **6** are shown in Fig. 3, with redox potentials listed in Table **1**. A glassy carbon working electrode was used with Pt wire counter electrode and Ag/AgCl as reference electrode. CV studies were carried out from solutions of the substrates (1 mM) in CHCl₃ using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. The redox behaviour of zeroth-generation dendrimer **1** and secondgeneration dendrimer **3** are similar, exhibiting one irreversible cathodic peak which is shifted to slightly higher negative potential in **3** and one anodic peak which is shifted towards slightly higher positive potential in **3** due to the presence of additional triazole and benzoheterazole units. The dendrimers **2**, **4** and **6** also show a similar shift in redox potentials (Fig. 3).

Dendrimers 1, 3 and 5 showed a gradual decrease of $E_{\rm pc}$ from -0.52, -0.55 and -0.60 V and $E_{\rm pa}$ increases slightly as 1.24, 1.25 and 1.28 V. Among the dendrimers 2, 4 and 6, $E_{\rm pc}$ varied as -0.43, -0.44 and -0.46 and $E_{\rm pa}$ values as 1.51, 1.52 and 1.52 V. The change in $E_{\rm pc}$ and $E_{\rm pa}$ values for 1, 3 and 5 when compared with 2, 4 and 6 could be due to change in the heterocyclic unit and there is only a gradual change on increasing the dendrimer generation. In conclusion, the electrochemical behaviour is slightly altered on increasing the number

 Table 2
 Performance of cells fabricated with and without additives in the redox couple

Electrolyte system	$J_{\rm sc}/{ m mA~cm}^{-2}$	V _{oc} /mV	Fill factor	η (%)
N3 dye TiO ₂ /KI/I ₂ /Pt	5.6	550	0.50	2.2
N3 dye $TiO_2/KI/I_2/1/Pt$	5.6	714	0.50	2.9
N3 dye TiO ₂ /KI/I ₂ /3/Pt	6.6	725	0.52	3.6
N3 dye TiO ₂ /KI/I ₂ /5/Pt	11.8	883	0.54	8.0
N3 dye TiO ₂ /KI/I ₂ /2/Pt	7.1	730	0.53	4.0
N3 dye TiO ₂ /KI/I ₂ /4/Pt	10.4	865	0.52	6.7
N3 dye TiO ₂ /KI/I ₂ /6/Pt	12.0	885	0.54	8.2

of triazole and benzoheterazole moiety in the dendritic architectures.

Dye sensitized solar cell studies

The nature of the electrolytic solution can improve the solar cell performance in dye sensitized solar cells. Against the background provided in the Introduction section, adding various nitrogencontaining heterocycles such as pyrimidine and alkylpyridines to the electrolyte solution increased the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) values and improved the efficiency (η). Hence, nitrogen containing heterocyclic compounds as additives might enhance V_{oc} and J_{sc} due to the electron donating ability of the nitrogen atom. In the current investigation, benzoheterazole dendrimers, whose heterocyclic ring consisted of sulfur, nitrogen, oxygen and carbon were examined as additives in DMF solution of I^-/I_3^- redox electrolyte.

The solar cell performance of dendrimers **1–6** were compared to that without an additive (Table 2). The photophysical and electrochemical properties of the dendrimers were also investigated. It was found that on passing from zeroth to second generation dendrimers, photophysical properties became altered, which helps to elucidate the influence of the dendrimer additives on the dyesensitized solar cell performance.²⁶

In our previous work,¹⁶ V_{oc} , J_{sc} and η values of 780 mV, 6.2 mA cm⁻² and 7.1%, respectively, were reported. In order to achieve higher short circuit current density and efficiency, the benzothiazole–benzoxazole dendrimers were synthesized up to the second generation and used as additive in DSSCs. The tested dendrimers significantly affected the performance of the dye-sensitized solar cell as shown in Fig. 4. On passing from zeroth-generation dendrimers to second-generation dendrimers, V_{oc} , J_{sc} and current also increase due to the presence of increasing number of triazole and benzoheterazole units. All of the V_{oc} values for solar cells containing dendrimers were greater than that for the cell without an additive. Among the tested dendrimers, second-generation dendrimers 5 and 6 displayed the largest V_{oc} (883, 885 mV) and J_{sc} (11.8, 12 mA cm⁻²) values and highest efficiency of 8.0 and 8.2%, respectively.

Conclusions

In conclusion, synthesis of dendritic structures with triazole as bridging unit and benzoheterazole as surface group has been achieved through a 'click' chemistry approach. UV studies indicate that as the number of triazole units increases, absorption

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also increases, and hence the light absorbed by the dendritic antenna increases with increase in the dendrimer generation. The CV study reflects a mild change in the redox behaviour as a function of the dendritic generation. Further as the number of triazole units increase in the dendrimers of higher generation, the DSSC performance also increases. Dendrimers **5** and **6** exhibited better power conversion efficiency (η) values of 8.0 and 8.2%, respectively, when used as additives in DSSC than the control (N3 dye/KI/I₂) as well as other benzothiazole/benzoxazole dendrimers as additives. Synthesis of similar benzoheterazole dendrimers and their DSSC studies with higher efficiency are underway.

Experimental

General

All the reagents and solvents employed were of the best grade available and were used without further purification. Melting points were determined by using a Toshniwal melting point apparatus by the open capillary tube method and are uncorrected. UV/Vis spectra were recorded on a Hitachi U-3210 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-3010 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on Bruker 300 MHz spectrometers. Elemental analyses were performed on a Perkin-Elmer 240B instrument. Electrochemical studies were carried out on a CH Instrument electrochemical analyser.

Syntheses

Phenolic dendrons 10, 11, 14 and 15; general procedure. A mixture of bisazide 9 (1.0 equiv.) and acetylenic derivative (2.0 equiv.) was dissolved in a mixture of THF and H₂O (1:1; 20 mL) and sodium ascorbate (10 mol%) added followed by the addition of $CuSO_4$ ·5H₂O (5 mol%). The reaction mixture was stirred overnight at room temperature. The solvent was evaporated and the crude product was dissolved with CHCl₃ (2 × 100 mL), washed with water (200 mL) and brine (50 mL), dried over Na₂SO₄ and concentrated to give a residue, which was purified by column chromatography (SiO₂). Alkyne dendrons 12, 13, 16 and 17; general procedure. A mixture of the corresponding hydroxyl dendron (1.0 equiv.) and propargyl bromide (1.1 equiv.) in the presence of anhydrous potassium carbonate (5 equiv.) in dry DMF (10 mL) was stirred for 12 h. The reaction mixture was filtered and evaporated to give the crude alkyne product which was purified by column chromatography (SiO₂).

Core 18. To a solution of 4,4'-sulfonyl bis(bromomethyl)benzene (1.0 g, 2.48 mmol) in a mixture of acetone and water (4:1, 30 mL), NaN₃ (0.48 g, 7.43 mmol) was added and the mixture was refluxed for 3 h at 60 °C. When the reaction was complete, the mixture was concentrated and the crude product was dissolved with CHCl₃ (2 × 100 mL), washed with water (200 mL) and brine (50 mL), dried over Na₂SO₄ and concentrated to give a residue, which was purified by column chromatography (SiO₂).

Dendrimers 1–6; general procedure. A mixture of acetylenic derivative (2.0 equiv.) and azide (1.0 equiv.) was dissolved in a mixture of THF and H₂O (1:1; 20 mL) and sodium ascorbate (10 mol%) added followed by the addition of CuSO₄·5H₂O (5 mol%). The reaction mixture was stirred overnight at room temperature. The solvent was evaporated and the crude product was dissolved with CHCl₃ (2 × 100 mL), washed with water (200 mL) and brine (50 mL), dried over Na₂SO₄ and concentrated to give a residue, which was purified by column chromatography (SiO₂).

Phenolic dendron 10 (G₁-OH). Yield 82%; mp 112–115 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.59 (s, 4H), 5.29 (s, 4H), 6.55 (s, 1H), 6.76 (s, 2H), 7.27 (t, *J* = 8.1 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.56 (s, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 9.88 (br s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 27.5, 53.8, 115.5, 118.0, 121.1, 121.4, 123.3, 124.5, 126.2, 135.4, 136.7, 144.2, 152.9, 158.6, 165.5 ppm; MS (ESI) *m*/*z* 615 (M⁺). Anal. calc. for C₂₈H₂₂N₈OS₄: C 54.70, H 3.61, N 18.23. Found: C 54.62, H 3.72, N 18.31%.

Phenolic dendron 11 (G₁-OH). Yield 80%; mp 172–175 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.56 (s, 4H), 5.33 (s, 4H), 6.61 (s, 1H), 6.76 (s, 2H), 7.20–7.29 (m, 4H), 7.38–7.41 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.64 (s, 2H), 9.66 (s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 26.5, 53.9, 110.1, 115.5 118.2, 118.4, 123.2, Paper

(ESI) m/z 582 (M⁺). Anal. calc. for C₂₈H₂₂N₈O₃S₂: C 57.72, H 3.81, N 19.23. Found: C 57.62 H 3.72, N 19.31%.

Alkyne dendron 12 (G₁). Yield 85%; mp 91–94 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.49 (t, J = 2.4 Hz, 1H), 4.49 (s, 2H), 4.63 (s, 4H), 5.31 (s, 4H), 6.55 (s, 1H), 6.69 (s, 2H), 7.26 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.56 (s, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 27.7, 53.5, 55.8, 76.4, 76.8, 114.4, 120.0, 121.2, 121.4, 123.2, 124.5, 126.2, 135.4, 137.1, 144.3, 152.9, 158.3, 165.7 ppm; MS (ESI) m/z653 (M⁺). Anal. calc. for C₃₁H₂₄N₈OS₄: C 57.03, H 3.71, N 17.16. Found: C 57.12, H 3.79, N 17.21%.

Alkyne dendron 13 (G₁). Yield 84%; mp 143–145 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.49 (t, J = 2.4 Hz, 1H), 4.53 (s, 2H), 4.60 (s, 4H), 5.37 (s, 4H), 6.71 (s, 1H), 6.73 (s, 2H), 7.21–7.3 (m, 4H), 7.42 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 6.9 Hz, 2H), 7.63 (s, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 26.8, 53.6, 55.9, 76.4, 78.9, 110.0, 114.6, 118.4, 120.1, 123.0, 124.1, 124.4 137.1, 141.7, 144.1, 152.0, 158.4, 164.2 ppm; MS (ESI) *m*/*z* 621 (M⁺). Anal. calc. for C₃₁H₂₄N₈O₃S₂: C 59.99, H 3.90, N 18.05. Found: C 59.89, H 3.87, N 18.15%.

Phenolic dendron 14 (G₂-OH). Yield 75%; mp 98–102 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.58 (s, 8H), 4.92 (s, 4H), 5.23 (s, 8H), 5.30 (s, 4H), 6.58 (s, 2H), 6.64 (s, 5H), 6.68 (s, 2H), 7.19– 7.27 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.47 (s, 2H), 7.59 (s, 4H), 7.66 (d, *J* = 8.1 Hz, 4H), 7.78 (d, *J* = 8.1 Hz, 4H), 9.97 (br s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 27.7, 53.5, 53.7, 61.7, 114.6, 115.5, 118.6, 119.8, 121.1, 121.4, 123.3, 123.5, 124.5, 126.2, 135.3, 136.8, 137.1, 143.4, 144.1, 152.9, 158.6, 158.9, 165.7 ppm. MS (ESI): *m/z* 1510 (M⁺). Anal. calc. for C₇₀H₅₆N₂₂O₃S₈: C 55.68, H 3.74, N 20.41. Found: C 55.59, H 3.79, N 20.31%.

Phenolic dendron 15 (G₂-OH). Yield 74%; mp 120–123 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.59 (s, 8H), 5.02 (s, 4H), 5.32 (s, 8H), 5.56 (s, 4H), 6.67 (s, 2H), 6.72 (s, 5H), 7.21–7.24 (m, 6H), 7.35–7.41 (m, 4H), 7.54 (s, 2H), 7.57 (s, 4H), 7.64 (s, 4H), 7.91 (d, J = 8.1 Hz, 4H), 9.97 (br s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 26.8, 53.3, 53.5, 61.7, 110.0, 114.5, 118.4, 119.8, 123.2, 123.5, 124.1, 124.4, 128.6, 128.8, 137.1, 141.6, 141.7, 143.7, 144.0, 152.0, 158.9, 164.1 ppm; MS (ESI) m/z 1445 (M⁺). Anal. calc. for C₇₀H₅₆N₂₂O₇S₄: C 58.16, H 3.90, N 21.32. Found: C 58.24, H 3.85, N 21.21%.

Alkyne dendron 16 (G₂). Yield 79%; mp 85–88 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.48 (t, J = 2.4 Hz, 1H), 4.59 (s, 2H), 4.63 (s, 8H), 4.98 (s, 4H), 5.29 (s, 8H), 5.44 (s, 4H), 6.61 (s, 2H), 6.70 (s, 4H), 6.81 (s, 3H), 7.22 (s, 1H), 7.23–7.28 (m, 3H), 7.34–7.40 (m, 4H), 7.53 (s, 2H), 7.57 (s, 4H), 7.69 (d, J = 7.8 Hz, 4H), 7.80 (d, J = 8.1 Hz, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 27.8, 53.5, 53.7, 56.0, 61.7, 76.5, 77.7, 114.4, 114.9, 119.6, 120.5, 121.1, 121.5, 123.2, 123.3, 124.5, 126.2, 135.4, 137.1, 137.2, 143.5, 144.3, 152.9, 158.4, 159.0, 165.7 ppm; MS (ESI) m/z 1548 (M⁺). Anal. calc. for C₇₃H₅₈N₂₂O₃S₈: C 58.64, H 3.78, N 19.91. Found: C 58.22, H 3.85, N 19.81%.

Alkyne dendron (G₂) 17. Yield 78%; mp 125–126 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.49 (t, *J* = 2.4 Hz, 1H), 4.56 (s, 2H), 4.63 (s, 8H), 4.98 (s, 4H), 5.29 (s, 8H), 5.46 (s, 4H), 6.61 (s, 2H), 6.70 (s, 4H), 6.82 (s, 3H), 7.21 (s, 1H), 7.23–7.28 (m, 3H), 7.34–7.43

(m, 4H), 7.53 (s, 2H), 7.57 (s, 4H), 7.69 (d, J = 7.8 Hz, 4H), 7.83 (d, J = 8.1 Hz, 4H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 27.9, 53.6, 53.7, 56.9, 61.4, 76.2, 78.4, 114.4, 114.9, 119.6, 120.5, 121.1, 121.5, 123.2, 123.3, 124.5, 126.2, 135.4, 137.1, 137.2, 143.5, 144.3, 152.9, 158.4, 158.0, 165.9 ppm; MS (ESI) m/z 1483 (M⁺). Anal. calc. for C₇₃H₅₈N₂₂O₇S₄: C 59.10, H 3.94, N 20.77. Found: C 59.20, H 3.99, N 20.65%.

4,4'-**Sulfonylbis(azidomethyl)benzene 18.** Yield 95%; mp 134–138 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.43 (s, 4H), 7.46 (d, *J* = 9.6 Hz, 4H), 7.95 (d, *J* = 9.0 Hz, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 53.9, 128.3, 128.7, 141.2, 141.4 ppm; MS (ESI) *m*/*z* 328 (M⁺). Anal. calc. for C₁₄H₁₂N₆O₂S: C 51.21, H 3.68, N 25.59. Found: C 51.29, H 3.74, N 25.65%.

Dendrimer (G₀) 1. Yield 85%; mp 78–80 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.66 (s, 4H), 5.50 (s, 4H), 7.01 (d, J = 8.4 Hz, 1H), 7.24–7.34 (m, 5H), 7.42 (d, J = 8.1 Hz, 2H), 7.59 (s, 2H), 7.66–7.81 (m, 6H); 7.81 (s, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 27.7, 53.2, 110.3, 121.2, 121.5, 123.2, 124.5, 124.7, 126.2, 128.5, 135.5, 140.3, 144.9, 152.9, 165.5 ppm; MS (EI) m/z 739 (M⁺). Anal. calc. for C₃₄H₂₆N₈O₂S₅: C 55.26, H 3.55, N 15.16. Found: C 55.16, H 3.42, N 15.20%.

Dendrimer (G₀) 2. Yield 83%; mp 135–136 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.55 (s, 4H), 5.51 (s, 4H), 7.07 (d, J = 8.1 Hz, 2H), 7.29 (s, 2H), 7.42 (d, J = 6.9 Hz, 2H), 7.53–7.55 (m, 2H), 7.66 (s, 2H), 7.77–7.84 (m, 4H), 8.03 (s, 2H), 8.21 (s, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 26.7, 53.2, 110.1, 118.5, 123.3, 123.8, 124.3, 124.4, 124.5, 127.8, 128.6, 141.6, 148.8, 152.0, 163.6 ppm; MS (EI) *m*/*z* 707 (M⁺). Anal. calc. for C₃₄H₂₆N₈O₄S₃: C 57.78, H 3.71, N 15.85. Found: C 57.86, H 3.62, N, 15.90%.

Dendrimer (**G**₁) **3.** Yield 80%; mp 74–76 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.56 (s, 8H), 4.91 (s, 4H), 5.23 (s, 8H), 5.48 (s, 4H), 6.55 (s, 2H), 6.62 (s, 4H), 7.17–7.21 (m, 2H), 7.27– 7.37 (m, 8H), 7.47 (s, 2H), 7.49 (s, 4H), 7.63 (d, *J* = 7.8 Hz, 4H), 7.74 (d, *J* = 8.1 Hz, 4H), 7.91 (d, *J* = 8.7 Hz, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 27.7, 53.5, 53.9, 61.6, 114.4, 119.7, 121.2, 121.5, 123.3, 124.5, 126.2, 128.3, 128.5, 128.7, 128.8, 135.4, 137.1, 140.1, 143.7, 144.4, 152.9, 158.9, 165.7 ppm; MS (ESI) *m*/*z* 1634 (M⁺). Anal. calc. for C₇₆H₆₀N₂₂O₄S₉: C 55.86, H 3.70, N 18.86. Found: C 55.75 H 3.62, N 18.90%.

Dendrimer (**G**₁) 4. Yield 81%; mp 102–105 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.59 (s, 8H), 5.02 (s, 4H), 5.32 (s, 8H), 5.56 (s, 4H), 6.67–6.73 (m, 6H), 7.19–7.29 (m, 10H), 7.38 (t, *J* = 9.0 Hz, 6H), 7.54–7.57 (m, 4H), 7.65 (s, 4H), 7.91 (d, *J* = 7.8 Hz, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 26.8, 53.3, 53.5, 61.7, 110.0, 114.5, 118.4, 119.8, 123.2, 123.5, 124.1, 124.4, 128.6, 128.8, 137.1, 141.6, 141.7, 143.7, 144.0, 152.0, 158.9, 164.1 ppm; MS (ESI) *m/z* 1569 (M⁺). Anal. calc. for C₇₆H₆₀N₂₂O₈S₅: C 58.15, H 3.85, N 19.63. Found: C 58.25, H 3.79, N 19.70%.

Dendrimer (G₂) 5. Yield 73%; mp 136–140 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.39 (s, 4H), 4.61 (s, 16H), 4.97 (s, 8H), 4.99 (s, 16H), 5.27 (s, 8H), 5.40 (s, 4H), 6.59 (s, 4H), 6.67–6.79 (m, 14H), 7.22–7.27 (m, 4H), 7.31–7.44 (m, 12H), 7.54 (s, 4H), 7.58 (s, 8H), 7.60 (s, 2H), 7.69 (d, J = 7.8 Hz, 8H), 7.80 (d, J = 8.1 Hz, 8H), 7.83–7.91 (m, 8H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 27.8, 53.2, 53.5, 53.6, 53.8, 61.7, 114.4, 114.6, 119.6, 120.2, 121.2, 121.5, 123.3, 123.5, 123.7, 124.5, 126.2, 128.3, 128.4, 128.7, 128.8, 135.4,

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137.2, 141.6, 143.5, 143.7, 144.3, 152.9, 158.9, 159.0, 165.7 ppm; MS (FAB) m/z 3424 (M⁺). Anal. calc. for $C_{160}H_{128}N_{50}O_8S_{17}$: C 56.12, H 3.77, N 20.45. Found: C 56.20, H 3.79, N 20.50%.

Dendrimer (**G**₂) **6.** Yield 72%; mp 82–86 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.40 (s, 4H), 4.71 (s, 16H), 4.97 (s, 8H), 4.99 (s, 16H), 5.37 (s, 8H), 5.40 (s, 4H), 6.59 (s, 4H), 6.67–6.80 (m, 14H), 7.22–7.28 (m, 4H), 7.31–7.44 (m, 12H), 7.54 (s, 4H), 7.58 (s, 8H), 7.60 (s, 2H), 7.69 (d, *J* = 7.8 Hz, 8H), 7.81 (d, *J* = 8.1 Hz, 8H), 7.83–7.95 (m, 8H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 26.7, 53.2, 53.5, 53.8, 56.0, 61.6, 110.0, 114.5, 115.1, 118.4, 119.7, 120.7, 121.4, 122.9, 123.3, 124.1, 124.4, 125.2, 127.7, 128.1, 128.4, 128.8, 137.2, 141.7, 143.9, 145.2, 151.9, 158.9, 159.3, 164.0 ppm; MS (FAB) *m*/*z* 3295 (M⁺). Anal. calc. for C₁₆₀H₁₂₈N₅₀O₁₆S₉: C 58.31, H 3.91, N 21.25. Found: C 58.26, H 3.89, N 21.30%.

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