

# Synthesis of New Photoresponsive Stilbene Dendrons and Dendrimers

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**Abstract:** A new convergent synthetic route for the synthesis of functionalized photoactive dendrimers having bis-stilbenoid skeletons on planar and tetrahedral cores, endowed with methoxy/methyl group has been developed. Optical spectroscopic techniques have been used to study absorption and emission properties and isomerization behavior of the stilbene dendrimers.

**Key words:** convergent, Wittig–Horner, photoluminescence

Dendrimers have become an interesting area of research in recent times due to their unique structures and photonic applications in numerous devices. Photoresponsive dendrimers are attractive candidates for photonic applications such as organic LEDs, optical power limiting devices and nonlinear optics.<sup>1</sup> Various dendritic systems are also known to function as efficient light-harvesting antennae,<sup>2</sup> sensors,<sup>3</sup> unimolecular micelles,<sup>4</sup> catalysts<sup>5</sup> and potential drug-delivery systems.<sup>6</sup>

Meier and Lehman<sup>7</sup> reported the first stilbenoid dendrimer, with the optical response of poly(phenylenevinylene)-<sup>8</sup> and binaphthyl-based chiral phenylenevinylene dendrimers<sup>9</sup> utilizing Heck and Horner–Wordsworth–Emmons reactions subsequently reported. The 5-hydroxyisophthalic acid moiety has been used extensively to construct the dendritic architecture, through the combination of 3,5-aryl branching connectivity.<sup>10</sup>

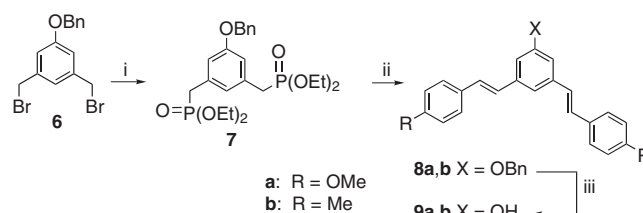
Photochemical and photophysical behavior of stilbenes have become an important field of research due to their potential and practical applications.<sup>11</sup> Arai and co-workers<sup>12</sup> reported the first synthesis of a series of stilbene dendrimers and studied their photoisomerization behavior. The same group also reported the synthesis and photochemical behavior of a series of water-soluble dendrimers with carboxylate-terminated dendron groups.<sup>13</sup>

We recently reported the synthesis of permanent fluorescence-sensing hyperbranched dendritic architectures<sup>14</sup> as well as the bactericidal efficacy of some novel dendrimers<sup>15</sup> and the electrochemical properties of dendrimers with *m*-terphenyl as the peripheral group.<sup>16</sup>

In view of the emerging importance of stilbene dendrimers with their interesting photophysico-chemical properties, we wish to report herein the synthesis and optical properties of new stilbene dendrons **1**, **4**, **5** and dendrimers

**2** and **3** (Figure 1), from relatively simple starting materials.

Our synthesis started with cheap, commercially available 5-hydroxyisophthalic acid, from which the desired dibromide **6** was easily prepared by a four-step literature procedure.<sup>17</sup> This dibromide was then treated with triethyl phosphite at 160 °C for three hours to give the diphosphonate ester **7** in 85% yield. The product was pure enough, as indicated by TLC, for direct use in the subsequent steps. Bis-stilbenes **8a,b** were obtained in good yield, by Wittig–Horner reaction between diphosphonate ester **7** with *p*-anisaldehyde/*p*-tolualdehyde using NaH as base in THF at room temperature. The benzyl group present in stilbenes **8a,b** was successfully cleaved without affecting the methoxy and methyl groups, using TiCl<sub>4</sub>/dioxane<sup>18</sup> to give bis-stilbene phenols **9a,b** in 62% and 65% yields, respectively (Scheme 1). The characteristic <sup>1</sup>H NMR resonance peak of the vinylic proton of dendrons **8a,b**, and **9a,b** displayed a large coupling constant (*J* ~ 16 Hz) indicating the *trans*-configuration in the stilbene units. The phenolic stilbenoid skeletons **9a,b** so-obtained could serve as excellent starting material for the convergent synthesis of stilbene dendrimers.

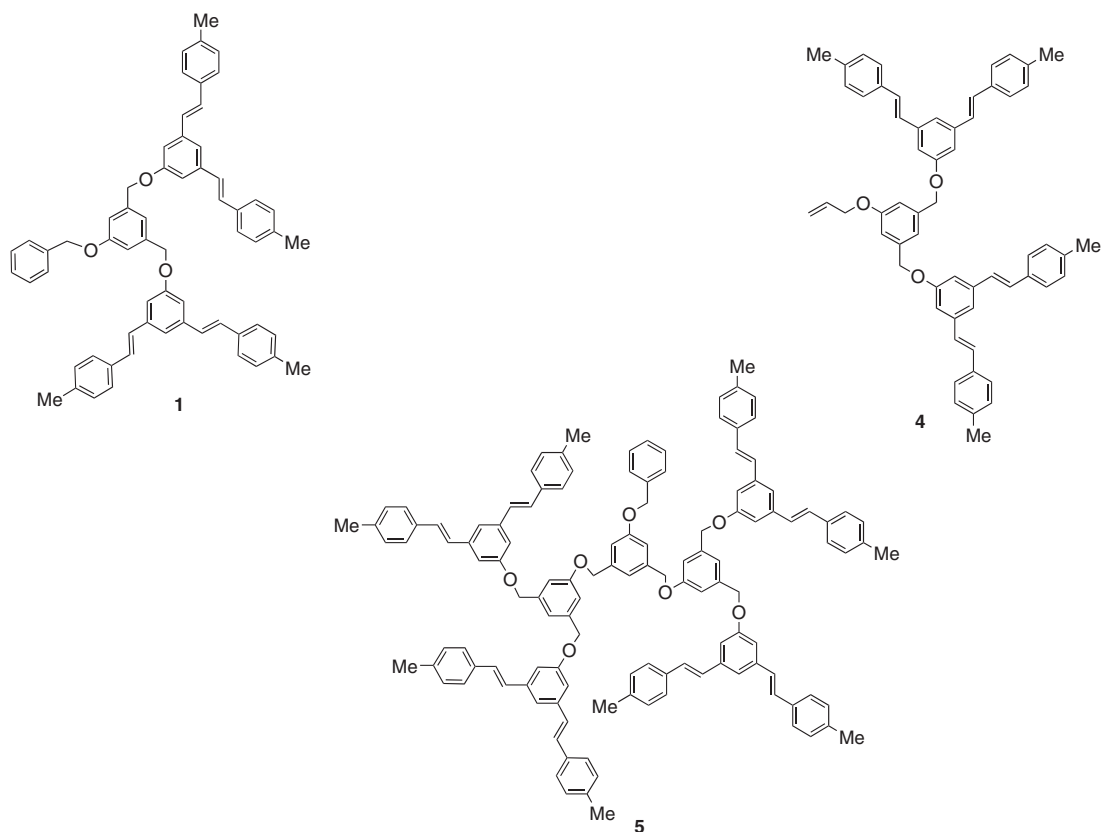


**Scheme 1** Reagents and conditions: (i) Triethyl phosphite, 160 °C, 3 h, 85%; (ii) NaH, THF, *p*-anisaldehyde/*p*-tolualdehyde, 12 h, **8a** (88%), **8b** (92%); (iii) TiCl<sub>4</sub>, dioxane, reflux, 6 h, **9a** (62%), **9b** (65%).

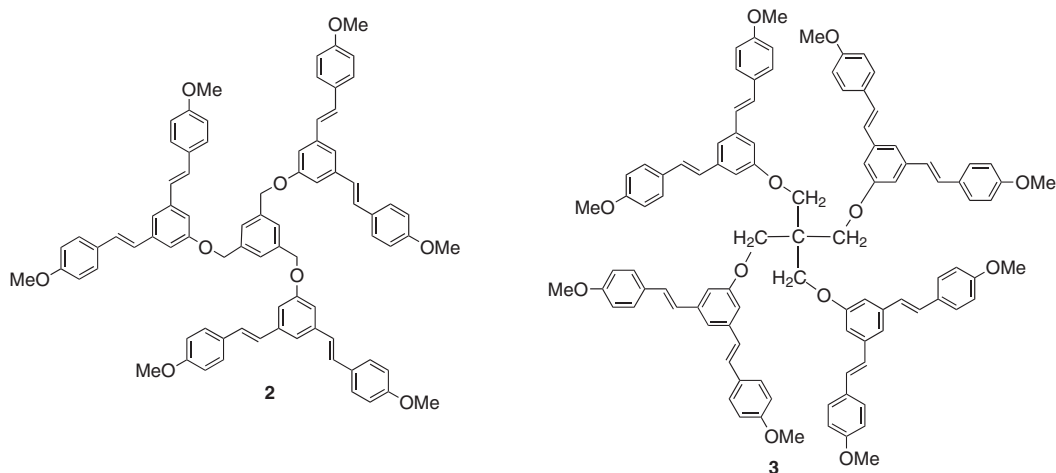
The first-generation dendron **1**, containing two bis-stilbenoid skeletons, was obtained in 76% yield from the coupling reaction of **9a** with dibromide **6** in DMF, in the presence of K<sub>2</sub>CO<sub>3</sub>. In order to make a comparative study of the effect of stilbene units on photochemical behavior, dendrimers **2** and **3** were prepared by similar methodology using 1,3,5-tris(bromomethyl)benzene<sup>19</sup> as the planar core and pentaerythritol tetrabromide<sup>20</sup> as the tetrahedral core (Scheme 2). Dendron **1** and dendrimers **2** and **3** were characterized completely using spectral and analytical techniques.

The allyl-protected dendron **4**, with methyl surface groups, was synthesized similarly in good yield by the re-

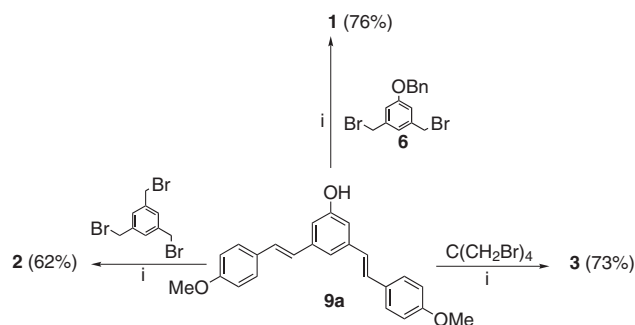
## Dendrons



## Dendrimers



**Figure 1** The structures of stilbene dendrons and dendrimers

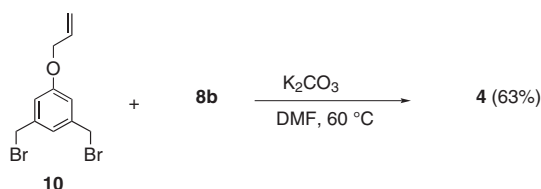


**Scheme 2** Reagents and conditions: i) K<sub>2</sub>CO<sub>3</sub>, DMF, 60 °C, 48 h.

action of one equivalent of allyl-protected dibromide **10** with 2.2 equivalents of phenol **9b** in the presence K<sub>2</sub>CO<sub>3</sub> in DMF under nitrogen (Scheme 3). The desired allyl-protected dibromide **10** was synthesized by a conventional procedure from 5-hydroxyisophthalic acid.<sup>21</sup>

The <sup>1</sup>H NMR spectrum of dendron **4** displayed a twelve-proton singlet at  $\delta = 2.25$  corresponding to the four methyl groups, a two-proton doublet at  $\delta = 4.47$  ( $J = 5.0$  Hz) for the O-methylene protons of the allyl moieties, a four-proton singlet at  $\delta = 5.01$  for benzylic protons, a set of one-proton doublets at  $\delta = 5.19$  with a *cis* coupling constant of

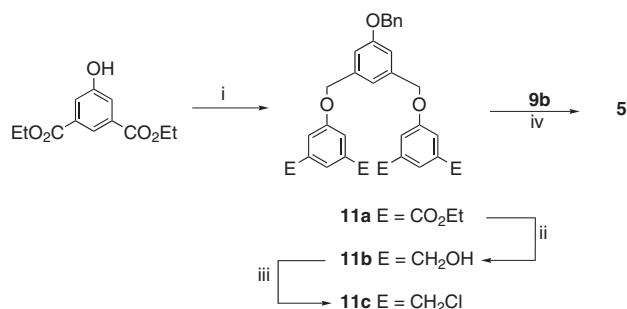
10.2 Hz and  $\delta = 5.33$  with a *trans* coupling constant of 17.2 Hz for terminal methylene (olefin) protons of the allyl moiety, a one-proton multiplet at  $\delta = 5.92$  to 6.02 due to the methine ( $-\text{CH}-$ ) of the allyl moiety and two eight-proton doublets at  $\delta = 7.06$  and  $\delta = 7.31$  ( $J = 7.8$  Hz) for *para*-disubstituted benzene protons, in addition to other aromatic and olefinic protons. The  $^{13}\text{C}$  NMR spectrum of **4** showed methyl carbon at  $\delta = 21.3$  and methylene carbons at  $\delta = 68.9$  and 69.9, in addition to 16 aromatic carbons from  $\delta = 111.7$  to 159.3. The FAB mass spectrum of **4** showed a peak at  $m/z$  811 corresponding to the molecular ion.



Scheme 3

Encouraged by the synthesis of first-generation dendrons **1** and **4** and dendrimers **2** and **3** by a convergent approach, we focused our attention on the synthesis of the second-generation stilbenoid dendron **5**. Reaction of one equivalent of dibromide **6** with 2.1 equivalents of ethyl 5-hydroxyisophthalate in the presence of  $\text{K}_2\text{CO}_3$  in DMF gave the tetraester **11a**, which was then reduced using  $\text{LiAlH}_4$  in THF to give the tetraalcohol **11b**. Treatment of **11b** with  $\text{SOCl}_2$  and pyridine in  $\text{CH}_2\text{Cl}_2$  led to the desired tetrachloride **11c**, which was coupled with 4.4 equivalents of phenol **9b** in the presence of  $\text{K}_2\text{CO}_3$  in DMF to afford the second-generation stilbene dendron **5** in 30% yield (Scheme 4).

The optical properties of the dendron **1** and dendrimers **2** and **3** were investigated by UV-Vis and fluorescence spectral studies. The absorption and photoluminescence (PL) spectra of stilbene dendrimers are shown in Figure 2

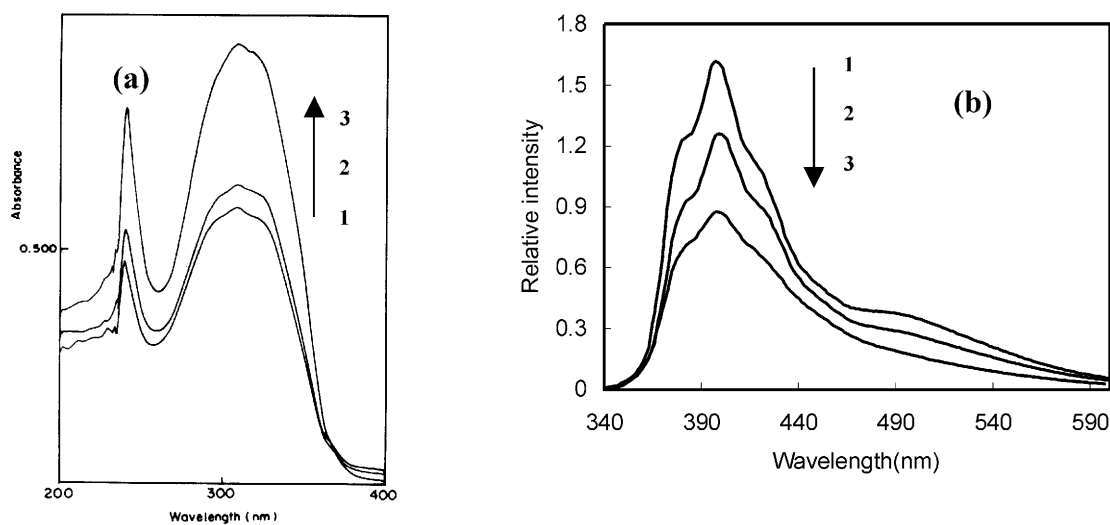


**Scheme 4** Reagents and conditions: (i) **6**, (0.5 equiv),  $\text{K}_2\text{CO}_3$ , DMF, 60 °C, 48 h, 78%; (ii)  $\text{LiAlH}_4$ , THF, 6 h, 80% (iii)  $\text{SOCl}_2$ , Py,  $\text{CH}_2\text{Cl}_2$ , 8 h, 64%; (iv)  $\text{K}_2\text{CO}_3$ , DMF, 60 °C, 48 h, 30%.

and the data obtained are summarized in Table 1. The stilbene dendron **1** and dendrimers **2** and **3** showed similar absorption spectra with maxima at 308 nm in  $\text{CHCl}_3$ . The intensity of absorption becomes much stronger (Figure 2) as the number of light-absorbing stilbene units increases. Hence the dendrimer **3**, with four bis-stilbenoids, showed a relatively high molar extinction co-efficient of  $9.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (Table 1).

Stilbene dendron **1**, and dendrimers **2** and **3** exhibited similar strong fluorescence, with maxima at 398 nm ( $\lambda_{\text{exc}}$  308 nm). However, on increasing the number of stilbenoid units, the emission spectra showed fluorescence quenching (Figure 2). Hence the fluorescence intensity for the dendrimer **3** is substantially lower than that of corresponding dendron **1**. Similar behavior has been previously observed<sup>22</sup> for structurally rigid dendrons and has been accounted for by the number of modes by which the excitation energy is dissipated in larger dendrons, a property that enhances the non-radiative decay. The through-space interactions between the fluorescence units become significant with increasing molecular size, providing additional fluorescence quenching pathways.

Therefore, as far as the peak positions are concerned, the absorption and emission spectra of dendrimers **2** and **3**



**Figure 2** a) Absorption spectra and b) fluorescence spectra of dendron **1**, dendrimers **2** and **3** in  $1 \times 10^{-5}$  M  $\text{CHCl}_3$  solution at room temperature.

**Table 1** Absorption Maxima, Extinction Coefficients and Fluorescence Maxima of Stilbene Dendrimers

Compound	$\lambda_{\text{max}}(\text{abs})^{\text{a}}$ (nm)	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{max}}(\text{fl})^{\text{a}}$ (nm)
1	308.4	58600	398
2	308.4	63900	399
3	308.4	93700	398

<sup>a</sup> All spectra were recorded in  $\text{CHCl}_3$  at room temperature at  $c = 1 \times 10^{-5}$  M.

virtually mimic those of the dendron **1**. Thus, all stilbene units present in these dendrimers behave as isolated chromophores.

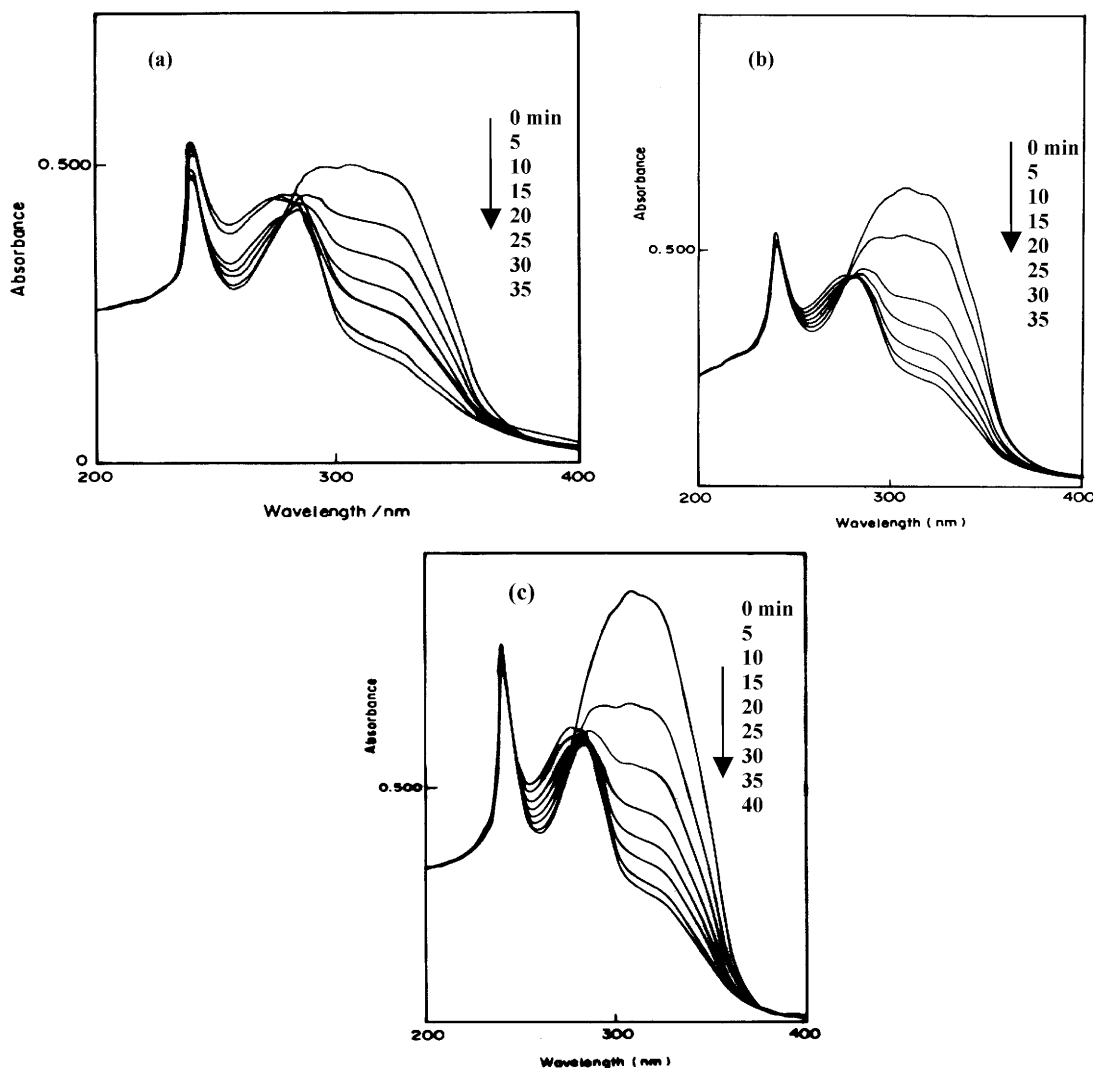
The photoisomerization behavior of the stilbene core in a dendritic molecule is well known and has been thoroughly studied.<sup>13</sup> However, the photoisomerization behavior of peripheral stilbenoid skeletons in dendritic molecules remains to be explored. Hence, it is of interest to study the

photoisomerization behavior of stilbene units in dendron **1** and dendrimers **2** and **3**.

On UV irradiation at 254 nm at room temperature, the *trans*-dendron **1**, *trans*-dendrimers **2** and **3** underwent isomerization at the carbon–carbon double bond to give the *cis* isomers as revealed by the decrease of the absorbance<sup>23</sup> (Figure 3).

In summary, we have developed a new convergent synthetic route to dendrimeric compounds that combines bis-stilbenoid skeletons obtained from relatively simple starting materials. The synthesis of stilbenoid building blocks **9a,b** makes use of the Wittig–Horner reaction, and paves the way for the convergent synthesis of higher-generation dendrimeric systems. The synthesis and photophysical properties of such systems, with bis-stilbenoid skeletons, are in progress.

All melting points were uncorrected. Reagents were purchased from commercial sources and used as received without purification. Solvents were dried by standard procedures. Column chromatography was carried out on silica gel (grade 60, mesh size 230–400, Merck).



**Figure 3** Change of absorption spectrum of (a) *trans*-**1**, (b) *trans*-**2** and (c) *trans*-**3** upon UV-irradiation with 254 nm light in  $1 \times 10^{-5}$  M  $\text{CHCl}_3$  solution at room temperature.

IR spectra were recorded on a Shimadzu 8300 instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Jeol 400 MHz spectrometer with solvent signals as internal standard. Mass spectra were obtained on a Jeol DX-303 (electron impact, 70 eV) and a Jeol SX 102/DA (FAB, NBA matrix) spectrometer, respectively. Elemental analyses were carried out on a Perkin-Elmer 240B analyzer. UV-Vis spectra were recorded on a Shimadzu UV 260 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS 5B luminescence spectrophotometer.

#### Tetraethyl [[5-(Benzyloxy)-1,3-phenylene]di(methyl-ene)]bis(phosphonate) (7)

The dibromide **6** (1.9 g, 5.14 mmol) was stirred with triethylphosphite (2.6 mL, 15.4 mmol) for 3 h under nitrogen atmosphere at 160 °C. The reaction mixture was then cooled to room temperature, poured into ice-water (100 mL) and then extracted with EtOAc (2 × 150 mL). The combined extracts were washed with  $\text{H}_2\text{O}$  (2 × 50 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated under reduced pressure to give **7**, as a pale-yellow liquid in 85% yield. The product was pure enough as indicated by TLC and used as such for the subsequent step.

#### Synthesis of Bis-stilbenes; General Procedure

To a stirred suspension of NaH (0.68 g, 28.5 mmol) in dry THF (100 mL), a solution of the diphosphonate ester **7** (2.3 g, 4.75 mmol) in dry THF (50 mL) was added dropwise, under nitrogen atmosphere. The mixture was stirred for 30 min and then added over 1 h to a solution of *p*-substituted benzaldehyde (10.4 mmol) in dry THF (20 mL). The reaction was stirred for 12 h at r.t., then the excess NaH was quenched with ice-cold  $\text{H}_2\text{O}$  (5 mL) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography ( $\text{SiO}_2$ , hexane- $\text{CHCl}_3$ , 9:1) and afforded the bis-stilbene as a colorless solid.

#### Bis-stilbene 8a

Yield: 88%; colorless solid; mp 138–140 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.76 (s, 6 H), 5.06 (s, 2 H), 6.83 (d,  $J$  = 8.8 Hz, 4 H), 6.87 (d,  $J$  = 16.1 Hz, 2 H), 6.93 (br s, 2 H), 7.00 (d,  $J$  = 16.1 Hz, 2 H), 7.15 (s, 1 H), 7.27–7.35 (m, 5 H), 7.38 (d,  $J$  = 8.8 Hz, 4 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 70.1, 111.4, 114.2, 117.8, 126.4, 127.6, 127.8, 128.0, 128.6, 128.7, 130.0, 137.0, 139.3, 159.4.

MS (EI, 70 eV):  $m/z$  = 57, 91 (100%), 129, 173, 256, 448 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{O}_3$ : C, 83.01; H, 6.29. Found: C, 82.87; H, 6.18.

#### Bis-stilbene 8b

Yield 92%; colorless solid; mp 150–152 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.26 (s, 6 H), 5.01 (s, 2 H), 6.90 (s, 1 H), 6.92 (d,  $J$  = 16.3 Hz, 2 H), 7.00 (d,  $J$  = 16.3 Hz, 2 H), 7.07 (d,  $J$  = 8.3 Hz, 4 H), 7.11–7.38 (m, 7 H), 7.32 (d,  $J$  = 8.3 Hz, 4 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 70.1, 111.4, 114.2, 117.8, 126.4, 127.6, 127.8, 128.0, 128.6, 128.7, 130.0, 137.0, 139.3, 159.4.

MS (EI, 70 eV):  $m/z$  = 57, 91 (100%), 105, 155, 179, 265, 297, 325, 416 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{O}$ : C, 89.38; H, 6.78. Found: C, 89.55; H, 6.52.

#### Synthesis of Bis-stilbenephénols

A solution of benzylic ether **8a** or **8b** (2.4 mmol) in dry dioxane (100 mL) was treated with  $\text{TiCl}_4$  (1.4 g, 7.2 mmol) under nitrogen atmosphere. The reaction mixture was refluxed for 6 h, then the mixture was poured over ice (150 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with  $\text{H}_2\text{O}$

(2 × 100 mL), and brine solution (1 × 100 mL). The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give the crude product that was purified by column chromatography (silica gel, hexane-EtOAc, 2:3) to yield the phenol.

#### Phenol 9a

Yield 62%; pale-brown solid; mp 185–188 °C.

IR (KBr): 3485  $\text{cm}^{-1}$  (O–H).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.76 (s, 6 H), 6.78 (s, 2 H), 6.84 (d,  $J$  = 8.8 Hz, 4 H), 6.85 (d,  $J$  = 16.6 Hz, 2 H), 7.00 (d,  $J$  = 16.6 Hz, 2 H), 7.10 (s, 1 H), 7.39 (d,  $J$  = 8.8 Hz, 4 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 111.7, 114.2, 117.8, 126.1, 127.8, 128.9, 129.9, 139.5, 156.0, 159.4.

MS (EI, 70 eV):  $m/z$  = 57, 121, 179, 218, 248, 358 (100%) [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{O}_3$ : C, 80.42; H, 6.19. Found: C, 80.21; H, 6.12.

#### Phenol 9b

Yield 65%; pale-brown solid; mp 172–175 °C.

IR (KBr) 3455  $\text{cm}^{-1}$  (O–H).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.11 (s, 6 H), 6.82 (s, 1 H), 6.94 (d,  $J$  = 16.2 Hz, 2 H), 7.02 (d,  $J$  = 16.2 Hz, 2 H), 7.10 (d,  $J$  = 8.0 Hz, 4 H), 7.18 (s, 2 H), 7.30 (d,  $J$  = 8.0 Hz, 4 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.2, 112.1, 117.5, 126.4, 127.3, 129.0, 134.3, 137.5, 139.2, 156.6.

MS (EI, 70 eV):  $m/z$  = 55, 115, 165, 219, 278, 326 (100%) [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{O}$ : C, 88.16; H, 6.79. Found: C, 88.23; H, 6.60.

#### Construction of Dendrons and Dendrimers; General Procedure

A mixture of the di/tri/tetrabromide (1 equiv), bis-stilbene phenol (1.1 equiv for each bromide unit) and potassium carbonate (3 equiv with respect to phenol) in dry DMF (25 mL) was vigorously stirred at 80 °C under nitrogen atmosphere for 60 h. The reaction mixture was allowed to cool to r.t. and poured into ice-water (100 mL). The resulting precipitate was dissolved in  $\text{CHCl}_3$  (100 mL). The organic layer was separated, washed with  $\text{H}_2\text{O}$  (3 × 100 mL), brine (2 × 100 mL) and dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give the crude product, which was purified by column chromatography ( $\text{SiO}_2$ , hexane- $\text{CHCl}_3$ , 3:2).

#### Dendron 1

Yield 76%; colorless solid; mp 182–185 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.75 (s, 12 H), 5.05 (s, 2 H), 5.07 (s, 4 H), 6.82 (d,  $J$  = 8.8 Hz, 8 H), 6.87 (d,  $J$  = 16.1 Hz, 4 H), 6.93 (s, 4 H), 7.02 (s, 2 H), 7.12 (s, 1 H), 7.14 (s, 2 H), 7.25–7.33 (m, 5 H), 7.00 (d,  $J$  = 16.1 Hz, 4 H), 7.38 (d,  $J$  = 8.8 Hz, 8 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 69.9, 111.4, 113.4, 114.2, 117.9, 126.4, 127.6, 127.8, 128.0, 128.6, 128.8, 130.0, 132.5, 139.3, 159.4.

MS (FAB):  $m/z$  = 925 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{63}\text{H}_{56}\text{O}_7$ : C, 81.79; H, 6.10. Found: C, 81.51; H, 5.88.

#### Dendrimer 2

Yield 62%; colorless solid; mp 202–208 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.80 (s, 18 H), 5.20 (s, 6 H), 6.88 (d,  $J$  = 8.6 Hz, 12 H), 6.92 (d,  $J$  = 16.3 Hz, 6 H), 7.01 (s, 6 H), 7.06 (d,  $J$  = 16.3 Hz, 6 H), 7.20 (s, 3 H), 7.43 (d,  $J$  = 8.6 Hz, 12 H) 7.58 (s, 3 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 69.9, 111.5, 114.2, 118.0, 126.0, 126.4, 127.8, 128.8, 130.0, 138.1, 139.3, 159.3, 159.4.

MS (FAB):  $m/z$  = 1189 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{81}\text{H}_{72}\text{O}_9$ : C, 81.79; H, 6.10. Found: C, 81.94; H, 6.33.

### Dendrimer 3

Yield 73%; pale-yellow solid; mp 146–152 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.78 (s, 24 H), 4.55 (s, 8 H), 6.84 (d,  $J$  = 8.6 Hz, 16 H), 6.90 (d,  $J$  = 16.3 Hz, 8 H), 7.03 (s, 8 H), 7.06 (d,  $J$  = 16.3 Hz, 8 H), 7.16 (s, 4 H), 7.40 (d,  $J$  = 8.6 Hz, 16 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.3, 67.1, 111.6, 114.2, 118.2, 126.4, 128.8, 128.8, 130.1, 139.3, 159.4, 159.6.

MS (FAB):  $m/z$  = 1497 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{101}\text{H}_{92}\text{O}_{12}$ : C, 80.99; H, 6.19. Found: C, 80.71; H, 6.43.

### Dendron 4

Yield 63%; colorless solid; mp 172–176 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.25 (s, 12 H), 4.47 (d,  $J$  = 5.0 Hz, 2 H), 5.01 (s, 4 H), 5.19 (d,  $J$  = 10.2 Hz, 1 H), 5.33 (d,  $J$  = 17.2 Hz, 1 H), 5.92–6.02 (m, 1 H), 6.87–7.13 (m, 13 H), 6.95 (d,  $J$  = 14.8 Hz, 4 H), 7.06 (d,  $J$  = 7.8 Hz, 8 H), 7.31 (d,  $J$  = 7.8 Hz, 8 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.3, 69.0, 69.9, 111.7, 113.3, 117.9, 118.2, 118.8, 126.6, 127.5, 129.2, 129.5, 133.1, 134.4, 137.7, 139.0, 139.2, 159.2, 159.3.

MS (FAB):  $m/z$  = 811 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{59}\text{H}_{54}\text{O}_3$ : C, 87.37; H, 6.71. Found: C, 87.18; H, 6.88.

### Dendron 5

Yield 30%; pale-brown solid; mp 142–146 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.25 (s, 24 H), 4.96 (s, 2 H), 5.00 (s, 4 H), 5.02 (s, 8 H), 6.92 (s, 4 H), 6.96 (d,  $J$  = 15.6 Hz, 8 H), 7.01–7.17 (m, 30 H), 7.06 (d,  $J$  = 7.8 Hz, 16 H), 7.31 (d,  $J$  = 7.8 Hz, 16 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.2, 69.8, 69.9, 111.7, 113.3, 126.5, 127.4, 127.5, 128.0, 128.5, 129.1, 129.4, 132.7, 134.3, 137.6, 138.8, 139.1, 159.2.

MS (FAB):  $m/z$  = 1750 [ $\text{M}^+$ ].

Anal. Calcd for  $\text{C}_{127}\text{H}_{112}\text{O}_7$ : C, 87.15; H, 6.45. Found: C, 86.99; H, 6.28.

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