

Yoshitaka Yamakawa,<sup>\*a</sup> Mitsuru Ueda,<sup>b</sup> Ritsuko Nagahata,<sup>c</sup> Kazuhiko Takeuchi<sup>c</sup> and Michihiko Asai<sup>c</sup>

<sup>a</sup> Joint Research Center for Precision Polymerization, Japan Chemical Innovation Institute, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. E-mail: yamy@nimc.go.jp

<sup>b</sup> Department of Human Sensing and Functional Sensor Engineering, Graduate School of Engineering, Yamagata University, 4-3 Jonan, Yonezawa, Yamagata 992-8510, Japan

<sup>c</sup> National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received (in Cambridge) 17th August 1998, Accepted 20th October 1998

Calix[4]resorcinarenes are phenolic macrocyclic compounds, and readily available from resorcinols and aldehydes. We were interested in calix[4]resorcinarenes as highly functionalized core molecules for the rapid synthesis of dendrimers because of their ease of synthesis and because they are less affected by steric constraints. Calix[4]resorcinarenes having 16 **1** and 12 **2** reactive hydroxy groups, respectively, were prepared as polyfunctional core molecules. The second-generation dendrimers were synthesized by the divergent method. The first-generation dendrimer **6** was obtained by etherification of **1** with 3,5-bis(allyloxy)benzyl bromide **5**. After the deallylation of **6**, etherification with **5** afforded the second-generation dendrimer **8**. Dendrimers were characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR, MALDI-TOF mass spectrometry and GPC. The molecular weight of second-generation dendrimers obtained from these calix[4]resorcinarenes and **5** reached 9345 and 7171, respectively.

## Introduction

Dendrimers are well defined, highly branched, three-dimensional compounds with a large number of reactive end groups. Therefore, they are receiving interest as new polymeric materials whose properties should differ significantly from those of linear polymers.<sup>1</sup> A number of synthetic approaches for producing dendrimers have been described in the literature. They can be prepared in two ways, termed the divergent and the convergent methods. The former method starts from a central core molecule and proceeds radially outward.<sup>2</sup> In contrast, the latter approach builds the dendrimer from the periphery towards the central core.<sup>3</sup> Both methods involve stepwise, tedious and time-consuming processes such as several protection-deprotection and extensive purification steps. Recently, several successful attempts to shorten these synthetic approaches were reported, however, these approaches still require multiple steps to obtain high molecular weight dendrimers.

One of the characteristic structures of dendrimers is having a precise central core unit. In many cases, two or three functional molecules are used as a core unit. When more highly functionalized core molecules are used, high molecular weight dendrimers can be prepared rapidly by the divergent method. Fréchet *et al.*<sup>4</sup> reported the double-stage convergent growth approach using hypercores which was effective in the preparation of high molecular weight products in less time and with greater ease than the conventional convergent approach. Furthermore, they pointed out that a hypercore might be constituted of flexible segments, thus providing ample spacing between the reactive groups at each chain end. We were interested in calix[4]resorcinarenes as highly functionalized core molecules because of their ease of synthesis and because they are less affected by steric constraints. In this paper, a successful rapid synthesis of dendrimers using calix[4]resorcinarenes as core molecules is described.

## Results and discussion

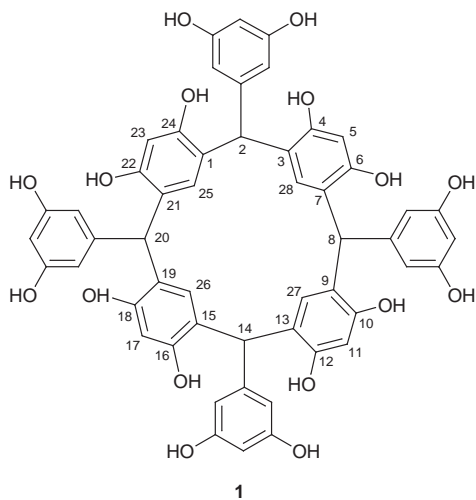
### Synthesis

Calix[4]resorcinarenes are phenolic macrocyclic compounds, and readily available from resorcinols and aldehydes.<sup>5</sup> They

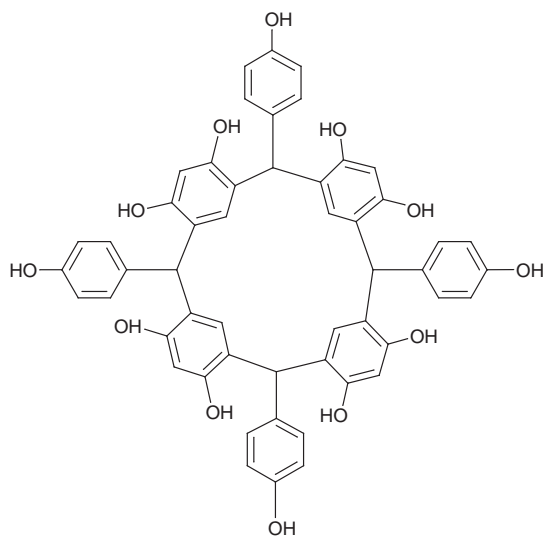
have been used as starting materials for the synthesis of various types of host molecules and their molecular recognition properties have been reported.<sup>6</sup> Several research groups used calixarenes or calixresorcinarenes as core molecules for the dendrimer synthesis. Calix[4]arenes,<sup>7-9</sup> calix[5]arene,<sup>8</sup> calix[8]arene<sup>7</sup> and *C*-benzylcalix[4]resorcinarene<sup>10</sup> have been reported. The functionality of these arenes were 4–8. In the present study, we employed two calix[4]resorcinarenes having 16 and 12 phenolic groups, such as 2,8,14,20-tetrakis(3,5-dihydroxyphenyl)calix[4]resorcinarene **1** and 2,8,14,20-tetrakis(4-hydroxyphenyl)calix[4]resorcinarene **2** (Scheme 1), which were prepared by a one-step reaction of resorcinol with 3,5-dihydroxybenzaldehyde and 4-hydroxybenzaldehyde, respectively. Preparation of **2** in methanol using dried hydrogen chloride was reported.<sup>11</sup> In this study, the reaction was carried out in aqueous solution using hydrochloric acid as catalyst. The products were obtained as precipitates. The structure of these resorcinarenes was confirmed by NMR and MALDI-TOF mass spectrometry. Cyclic tetramers were obtained selectively. Four stereoisomers are possible. These isomers are defined by the orientation of the hydroxyphenyl group with respect to one of the CH(PhOH) bridges and classified as *recc*, *rect*, *rett* and *rtct* (Fig. 1). The two isomers with the *recc* and *rett* configurations are dominant from condensation between resorcinol and benzaldehyde.<sup>11,12</sup> The <sup>1</sup>H-NMR spectra of compounds **1** and **2** showed two characteristic methine signals at 5.4–5.5 ppm. Therefore, there is a mixture of these two stereoisomers. However, there is expected to be very little steric constraint of hydroxy groups of **1** and **2** in these configurations.

The 3,5-dihydroxybenzyl ether unit was selected as the building block to construct dendrimers and its hydroxy groups were protected with allyl groups using allyl bromide and potassium carbonate in acetone. This group was chosen for its selective removal with Pd catalyst.<sup>13</sup> Thus, commercially available methyl 3,5-dihydroxybenzoate was converted into methyl 3,5-bis(allyloxy)benzoate **3** and reduced with lithium aluminium hydride to 3,5-bis(allyloxy)benzyl alcohol **4**. Dendrimer **5** was obtained by bromination of **4** with carbon tetrabromide. The overall yield of **5** was 51%.

Scheme 2 illustrates the synthesis of the second-generation



1



2

Scheme 1 Highly functionalized calix[4]resorcinarenes.

dendrimer **8** by the divergent method using **1** as a core molecule. Etherification of **1** with **5** was carried out by using a 1.5 molar excess amount of the benzyl bromide for every hydroxy group present in **1**. The reaction was performed in acetone in the presence of potassium carbonate and 18-crown-6 at reflux for 48 h to give the completely substituted first-generation dendrimer **6**, which was isolated after vigorous washing of its ether solution with an aqueous solution of 5%  $\text{Na}_2\text{CO}_3$  and reprecipitation with methanol to remove the excess of **5**. Deprotection of dendrimer **6** was achieved by reduction using bis(triphenylphosphine)palladium dichloride and ammonium formate in THF. Reaction was complete in 24 h at reflux and powdery deprotected dendrimer **7** was purified by reprecipitation with water. The etherification of **7** with dendron **5** under the same reaction conditions for the synthesis of dendrimer **6** afforded the second-generation dendrimer **8** in 52% yield after purification by reprecipitation. The second-generation dendrimer **11** (Scheme 3) starting from **2** as a core molecule was also prepared in three steps in an overall yield of 52% just as described above.

#### Characterization

Dendrimers were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, IR, MALDI-TOF mass spectrometry and GPC. Fig. 2 shows  $^1\text{H}$ -NMR spectra of **1**, **6** and **7** measured in  $[\text{D}_6]\text{DMSO}$ .

The spectrum of **1** gave well resolved peaks at 5.4–5.5 ppm,

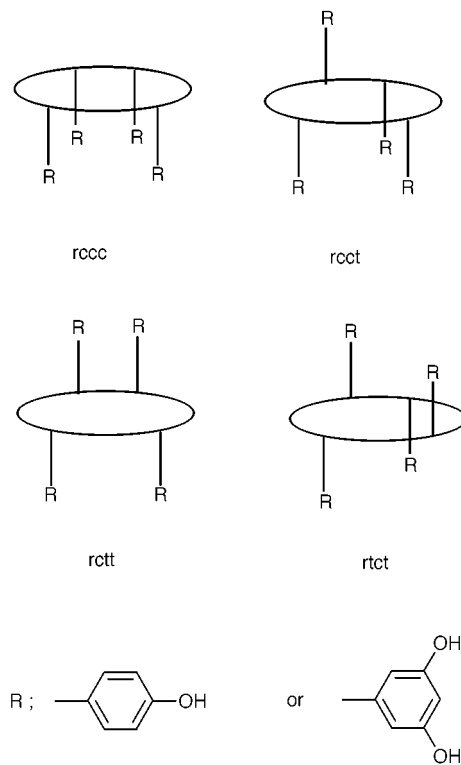


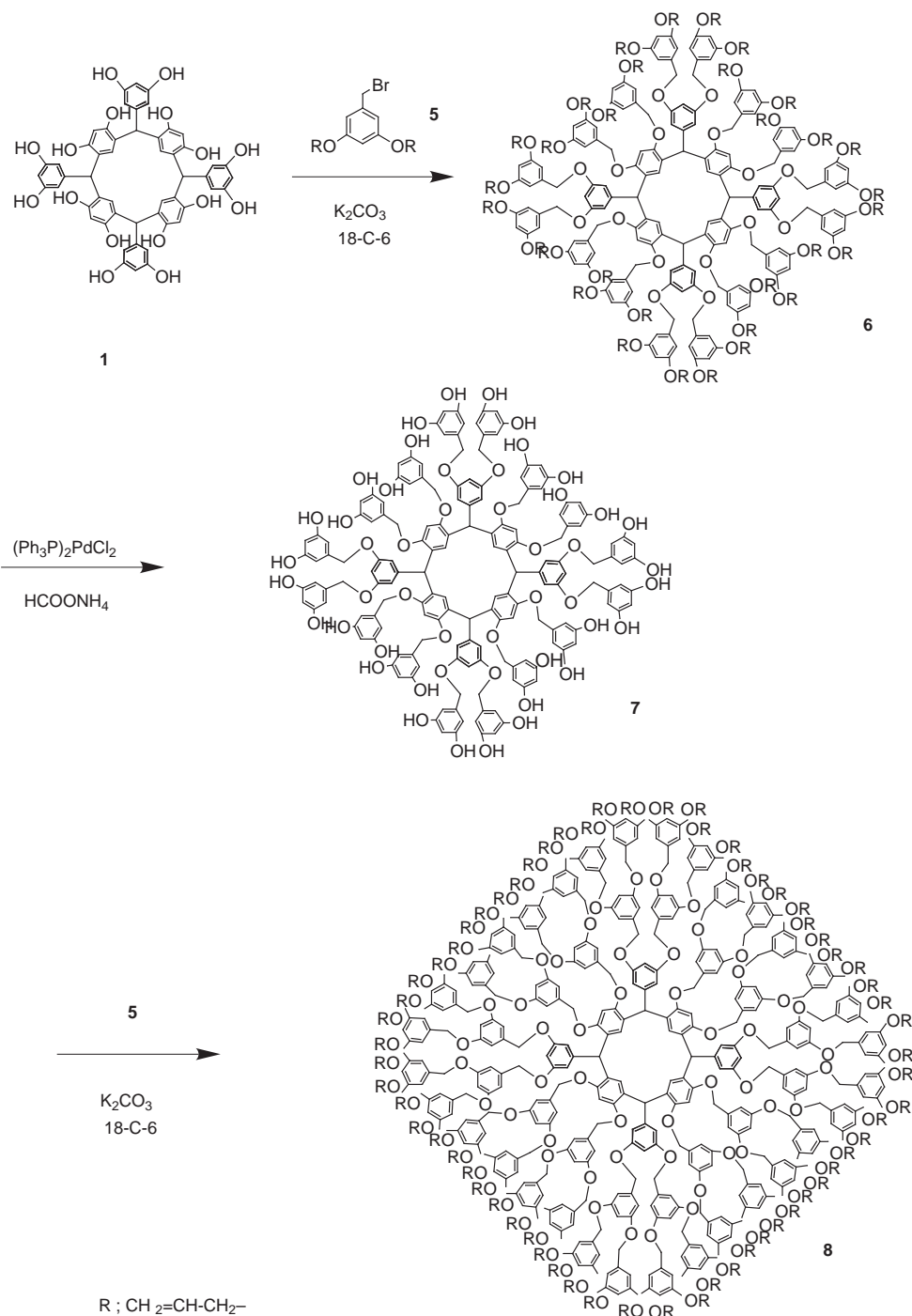
Fig. 1 Stereoisomers of the calix[4]resorcinarenes.

5.6–6.3 ppm and 8.3–8.7 ppm, which are attributed to methine, aromatic and phenolic protons, respectively. The spectrum of **6** gave four regions of 4.0–4.8, 5.0–5.5, 5.6–6.1 and 6.1–7.0 ppm, which are attributed to methine + benzyl methylene + allyl methylene, allylic CH, allylic  $\text{CH}_2$  and aromatic protons, respectively. Signals at 8.2–8.5 ppm attributed to the phenolic protons had completely disappeared which means essentially all the hydroxy groups of **1** had reacted. Comparison of the integral intensity of these signals showed that 16 bis(allyloxy)benzyl ether units had been introduced to the core. In the spectrum of **7**, three regions of 4.3–5.0, 5.7–6.8 and 8.9–9.4 ppm have been assigned to benzyl methylene, aromatic and phenolic hydroxy groups, respectively. Peaks at 5.0–5.5 ppm due to allyl groups seen in the spectrum of **6** had completely disappeared in the spectrum of **7**. Phenolic signals had the same intensity as signals of benzyl groups. Thus the deprotection was essentially completed. The second-generation dendrimer **8** was characterized in a manner similar to **6**. All hydroxy signals of **7** had disappeared. Comparison of the integral intensity of these signals showed that 32 benzyl ether units had been introduced. In the spectra of all dendrimers, each peak was observed to be broad, indicating that the mutual interconversion between several conformers occurs slowly on the NMR timescale.

In order to determine the molecular weight of the dendrimers, the MALDI-TOF mass spectral technique was applied, and the molecular ion peaks for dendrimers were identified successfully, showing essentially the presence of a single molecular compound devoid of statistical defects. Their peaks appeared 23 mass units higher than the corresponding molecular ions, presumably representing sodium adducts. The molecular masses of the higher molecular weight dendrimers **8** and **11** could not be determined by MALDI-TOF mass spectrometry because of their poor volatility properties. However, GPC profiles of these dendrimers showed a sharp unimodal peak suggesting that they essentially consist of a single component.

#### Conclusion

Highly functionalized core molecules are very effective for the rapid synthesis of dendrimers. The second-generation dendrim-



**Scheme 2** Synthetic route to the second-generation dendrimer **8**.

ers **8** and **11** with molecular weights of 9345 and 7171 were synthesized in just three steps from highly functionalized calix[4]resorcinarenes **1** and **2**, respectively, and 64 and 48 end groups were introduced, respectively. Most of the current reports require at least four or five generations to reach a molecular weight of 9345 and 64 end groups in a dendrimer. Macrocyclic compounds like calix[4]resorcinarenes are suitable as core molecules because of easy synthesis and adequate space between functional groups. Also, these dendrimers obtained from calix[4]resorcinarene core units have potential as molecular recognition materials.

## Experimental

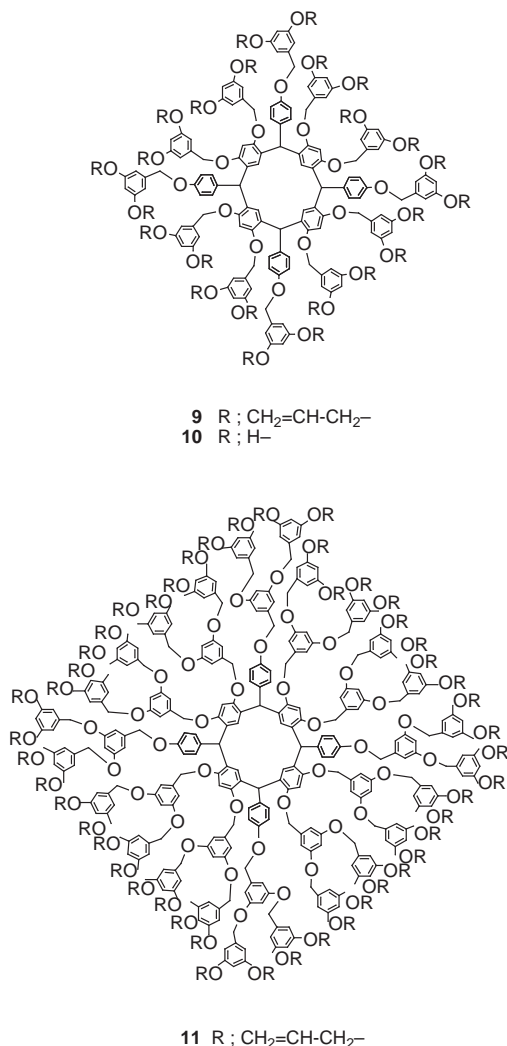
### General

IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer PARAGON1000. <sup>1</sup>H-NMR spectra were recorded in

[<sup>2</sup>H<sub>6</sub>]DMSO on a JEOL GSX270 (270.05 MHz) spectrometer using the tetramethylsilane signal as standard. <sup>13</sup>C-NMR spectra were recorded on a JEOL JNM-LA600 (150.80 MHz) spectrometer. MALDI-TOF mass spectra were obtained on a Kratos MALDI III using 2,5-dihydroxybenzoic acid as the matrix. GPC was performed using TOSOH 8020 HPLC apparatus (column, TSKgel SuperHM-H × 2; standard, polystyrene; solvent, THF; temp., 40 °C).

### 2,8,14,20-Tetrakis(3,5-dihydroxyphenyl)calix[4]resorcinarene **1**

Resorcinol (3.6 g, 32.6 mmol) and 3,5-dihydroxybenzaldehyde (4.5 g, 32.6 mmol) were dissolved in water (90 ml) and heated to 80 °C. Hydrochloric acid (15 ml) was added dropwise and the mixture was stirred for 5.5 h at 80 °C. The precipitated product was isolated by filtration, washed with methanol and dried in vacuum to give **1** (3.6 g, 48%) as powder (Found: C, 67.7; H, 4.4. C<sub>52</sub>H<sub>40</sub>O<sub>16</sub> requires C, 67.8; H, 4.4%); ν<sub>max</sub>(KBr)/cm<sup>-1</sup>



**Scheme 3** The first and second-generation dendrimers using **2** as the core molecule.

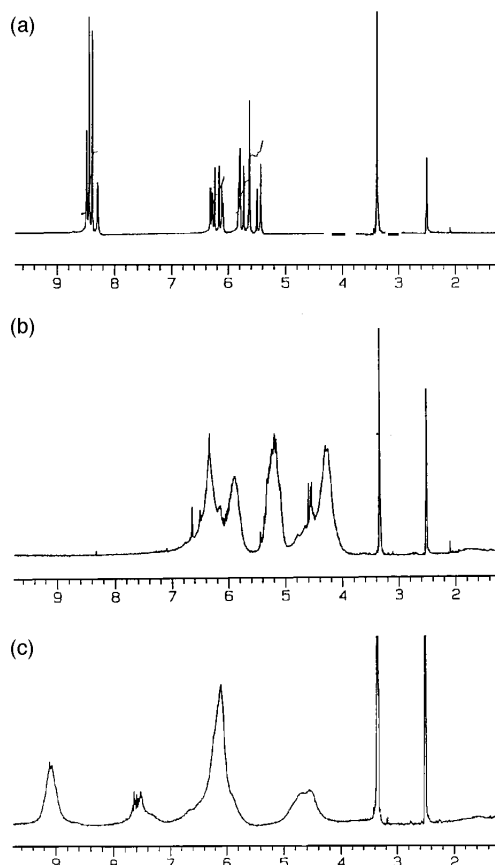
3370, 1622, 1430, 1293 and 1159;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 5.4–5.5 (4H, CH), 5.6–6.3 (20H, ArH), 8.3–8.7 (16H, OH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 48.9 (CH), 99.3, 101.6, 101.9, 102.1 (resorcinol C-2, dihydroxyphenyl C-2), 107.3, 107.6 (dihydroxyphenyl C-4, C-6), 120.5, 120.6 (resorcinol C-4, C-6), 129.7, 131.6 (resorcinol C-5), 147.0, 147.2 (dihydroxyphenyl C-5), 152.5, 152.6, 152.9, 156.8, 156.8 (resorcinol C-1, C-3, dihydroxyphenyl C-1, C-3); *m/z* (MALDI-TOF) 940.8 (100%, M + Na<sup>+</sup>).

### 2,8,14,20-Tetrakis(4-hydroxyphenyl)calix[4]resorcinarene **2**

The synthesis of **2** was carried out analogous to that of **1**: yield 79%. Powder (Found: C, 72.9; H, 4.7. C<sub>52</sub>H<sub>40</sub>O<sub>12</sub> requires C, 72.9; H, 4.7%);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 3370, 1611, 1429, 1238 and 1076;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 5.4–5.5 (4H, CH), 5.9–6.6 (24H, ArH), 8.4–8.8 (12H, OH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 55.9 (CH), 101.5, 101.6, 101.9 (resorcinol C-2), 113.7, 113.9 (hydroxyphenyl C-2, C-6), 120.7, 120.9, 121.8 (resorcinol C-4, C-6), 128.4, 129.4, 129.7, 131.4, 134.3, 135.8 (resorcinol C-5, hydroxyphenyl C-3, C-4, C-5), 152.1, 152.2, 152.4, 154.1, 154.3 (resorcinol C-1, C-3, hydroxyphenyl C-1); *m/z* (MALDI-TOF) 880.7 (100%, M + Na<sup>+</sup>).

### Methyl 3,5-bis(allyloxy)benzoate **3**

A mixture of methyl 3,5-dihydroxybenzoate (30 g, 178 mmol), sodium carbonate (73.8 g, 534 mmol) and sodium iodide (0.8 g, 5.34 mmol) in dry acetone (600 ml) was heated to reflux and



**Fig. 2** <sup>1</sup>H-NMR spectra (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO): (a) 16 functionalized calix[4]resorcinarene **1**, (b) first-generation dendrimer **6**, (c) deprotected dendrimer **7**.

stirred vigorously under nitrogen. Allyl bromide (64.6 ml, 634 mmol) was added dropwise to the mixture and the reaction was continued for 30 h. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue dissolved in diethyl ether was washed with an aqueous solution of 5% Na<sub>2</sub>CO<sub>3</sub> (3 times). The organic layer was dried using MgSO<sub>4</sub> and evaporated to dryness. Recrystallization of the crude product afforded **3** (32 g, 73%). Mp 39–40 °C (Found: C, 67.7; H, 6.6. C<sub>14</sub>H<sub>16</sub>O<sub>4</sub> requires C, 67.7; H, 6.5%);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1721, 1599, 1350, 1302, 1177, 1061 and 1036;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 3.9 (3H, CH<sub>3</sub>), 4.6 (4H, CHCH<sub>2</sub>O-), 5.4 (4H, CH<sub>2</sub>=), 6.1 (2H, =CH-), 6.7 (1H, C-4-H), 7.2 (2H, C-2-H, C-6-H);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 52.2 (CH<sub>3</sub>), 68.4 (CHCH<sub>2</sub>O-), 106.5, 107.6, 117.5 (CH<sub>2</sub>=), 131.5, 133.3 (=CH-), 159.3, 165.8 (C=O).

### 3,5-Bis(allyloxy)benzyl alcohol **4**

A suspension of LiAlH<sub>4</sub> (4.0 g, 105 mmol) in THF (200 ml) was heated to reflux and stirred under nitrogen. A THF (50 ml) solution of **3** (11.7 g, 47.2 mmol) was added dropwise and the reaction was continued for 6 h. The reaction mixture was allowed to cool and water (15 ml) was added dropwise. The precipitate was filtered and the filtrate was evaporated to dryness. The residue was dissolved in diethyl ether and washed with an aqueous solution of 5% Na<sub>2</sub>CO<sub>3</sub>. The organic layer was dried using MgSO<sub>4</sub> and evaporated to yield **4** (8.5 g, 82%) (Found: C, 70.6; H, 7.5. C<sub>13</sub>H<sub>16</sub>O<sub>3</sub> requires C, 70.9; H, 7.3%);  $\nu_{\text{max}}$ (liquid film)/cm<sup>-1</sup> 3348, 1596, 1450, 1422, 1359, 1293, 1166, 1049 and 925;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 2.1 (1H, OH), 4.5 (4H, CHCH<sub>2</sub>O-), 4.6 (2H, PhCH<sub>2</sub>OH), 5.4 (4H, CH<sub>2</sub>=), 6.1 (2H, =CH-), 6.5 (1H, C-4-H), 6.6 (2H, C-2-H, C-6-H);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 62.9 (PhCH<sub>2</sub>OH), 68.2 (CHCH<sub>2</sub>O-), 99.9 (C-4), 104.9 (C-2, C-6), 117.1 (CH<sub>2</sub>=), 133.5 (=CH-), 145.2 (C-1), 159.3 (C-3, C-5).

### 3,5-Bis(allyloxy)benzyl bromide **5**

Compound **4** (11.4 g, 51.8 mmol), carbon tetrabromide (24.2 g, 73 mmol) and triphenylphosphine (19.1 g, 73 mmol) were dissolved in THF (100 ml) and stirred for 3 h at room temperature. The precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane, 2:3) afforded **5** as an oil (8.12 g, 55%) (Found: C, 54.8; H, 5.3. C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>Br requires C, 55.1; H, 5.3%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1595, 1451, 1423, 1322, 1296, 1171, 1053 and 928;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.3 (2H, PhCH<sub>2</sub>Br), 4.5 (4H, CHCH<sub>2</sub>O-), 5.2–5.4 (4H, CH<sub>2</sub>=), 6.0 (2H, =CH-), 6.3 (1H, ArH), 6.5 (2H, ArH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 33.9 (PhCH<sub>2</sub>Br), 68.3 (CHCH<sub>2</sub>O-), 101.4 (C-4), 108.0 (C-2, C-6), 117.4 (CH<sub>2</sub>=), 133.2 (=CH-), 139.9 (C-1), 159.3 (C-3, C-5).

### 16CA-G1-(OAlI)<sub>32</sub> **6**

A mixture of **1** (0.81 g, 0.883 mmol), potassium carbonate (2.93 g, 21.2 mmol) and 18-crown-6 (0.56 g, 2.12 mmol) in dry acetone (80 ml) was heated to reflux and stirred vigorously under nitrogen. Compound **5** (6.0 g, 21.2 mmol) dissolved in dry acetone (40 ml) was added dropwise and the reaction was continued for 48 h. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue dissolved in diethyl ether was washed with an aqueous solution of 5% Na<sub>2</sub>CO<sub>3</sub> (3 times). The organic layer was dried and evaporated to dryness. Re-precipitation with chloroform-methanol afforded **6** as a viscous oil (2.91 g, 79%) (Found: C, 75.2; H, 5.9. C<sub>260</sub>H<sub>264</sub>O<sub>48</sub> requires C, 75.1; H, 6.4%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1597, 1454, 1296, 1168 and 1054;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.0–4.8 (96H, CHCH<sub>2</sub>O-, PhCH<sub>2</sub>O-), 5.0–5.5 (68H, CH<sub>2</sub>=, CH), 5.6–6.1 (32H, =CH-), 6.1–7.0 (68H, ArH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 68.1 (PhCH<sub>2</sub>O-, CHCH<sub>2</sub>O-), 99.7, 105.0 (ArC), 117.1 (CH<sub>2</sub>=), 133.5 (=CH-), 139.6, 159.1 (ArC);  $m/z$  (MALDI-TOF) 4240 (100%, M + Na<sup>+</sup>);  $M_n$ (GPC) 2997 ( $M_w/M_n = 1.05$ ).

### 16CA-G1-(OH)<sub>32</sub> **7**

A mixture of **6** (0.96 g, 0.231 mmol), bis(triphenylphosphine)-palladium dichloride (144 mg, 0.205 mmol) and ammonium formate (2.6 g, 41.1 mmol) in THF (80 ml) was heated to reflux and stirred for 24 h. The mixture was evaporated to dryness. The residue was dissolved in aqueous solution of 10% sodium hydroxide and washed with diethyl ether. The water layer was acidified by hydrochloric acid. The precipitated product was extracted by ethyl acetate (3 times). Combined organic layers were dried and evaporated to dryness. Re-precipitation with methanol-water afforded **7** (0.27 g, 41%) as powder (Found: C, 68.5; H, 5.1. C<sub>164</sub>H<sub>136</sub>O<sub>48</sub> requires C, 68.5; H, 4.8%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3370, 1606, 1457, 1330 and 1159;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.3–5.1 (32H, PhCH<sub>2</sub>O-), 5.6–6.9 (72H, ArH, CH), 8.9–9.3 (32H, OH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 69.3 (PhCH<sub>2</sub>O-), 101.8, 105.4, 128.9, 131.6, 139.5, 158.4 (ArC);  $m/z$  (MALDI-TOF) 2898 (100%, M + Na<sup>+</sup>).

### 16CA-G2-(OAlI)<sub>64</sub> **8**

The synthesis was carried out as described for **6** with **7** and **5**: yield 58%. Viscous oil (Found: C, 74.4; H, 6.0. C<sub>580</sub>H<sub>584</sub>O<sub>112</sub> requires C, 74.5; H, 6.3%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1596, 1451, 1296, 1166 and 1053;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.0–4.8 (224H, CHCH<sub>2</sub>O-, PhCH<sub>2</sub>O-), 4.8–5.5 (132H, CH<sub>2</sub>=, CH), 5.6–6.1 (64H, =CH-), 6.1–7.0 (164H, ArH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 68.1 (PhCH<sub>2</sub>O-, CHCH<sub>2</sub>O-), 100.7, 105.7 (ArC), 117.1 (CH<sub>2</sub>=), 133.4 (=CH-), 139.0, 159.2 (ArC);  $M_n$  (GPC) 5774 ( $M_w/M_n = 1.04$ ).

### 12CA-G1-(OAlI)<sub>24</sub> **9**

The synthesis was carried out as described for **6** with **2** and **5**:

yield 91%. Viscous oil (Found: C, 76.2; H, 5.6. C<sub>208</sub>H<sub>208</sub>O<sub>36</sub> requires C, 76.1; H, 6.4%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1597, 1454, 1296, 1169 and 1051;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.0–4.8 (72H, CHCH<sub>2</sub>O-, PhCH<sub>2</sub>O-), 5.0–5.5 (52H, CH<sub>2</sub>=, CH), 5.6–6.1 (24H, =CH-), 6.1–7.0 (60H, ArH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 68.2 (PhCH<sub>2</sub>O-, CHCH<sub>2</sub>O-), 100.4, 104.9, 105.1, 113.8 (ArC), 117.1 (CH<sub>2</sub>=), 129.9 (ArC), 133.4 (=CH-), 138.9, 139.4, 154.7, 156.2, 159.2 (ArC);  $m/z$  (MALDI-TOF) 3304 (100%, M + Na<sup>+</sup>);  $M_n$ (GPC) 2476 ( $M_w/M_n = 1.05$ ).

### 12CA-G1-(OH)<sub>24</sub> **10**

The synthesis was carried out as described for **7** from **9**: yield 73%. Powder (Found: C, 70.2; H, 4.7. C<sub>136</sub>H<sub>112</sub>O<sub>36</sub> requires C, 70.3; H, 4.9%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3306, 1606, 1457, 1337 and 1157;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.5–5.1 (24H, PhCH<sub>2</sub>O-), 5.6–7.0 (64H, ArH, CH), 9.0–9.3 (24H, OH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 69.0, 69.5, 70.0 (PhCH<sub>2</sub>O-), 101.6, 104.8, 104.9, 113.5, 128.7, 129.8, 131.4, 139.3, 154.1, 156.2, 158.0, 158.2 (ArC);  $m/z$  (MALDI-TOF) 2342 (100%, M + Na<sup>+</sup>).

### 12CA-G2-(OAlI)<sub>48</sub> **11**

The synthesis was carried out as described for **6** with **10** and **5**: yield 78%. Viscous oil (Found: C, 75.0; H, 6.0. C<sub>448</sub>H<sub>448</sub>O<sub>84</sub> requires C, 75.0; H, 6.3%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1597, 1452, 1296, 1168 and 1053;  $\delta_{\text{H}}$  (270 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 4.0–5.0 (168H, CHCH<sub>2</sub>O-, PhCH<sub>2</sub>O-), 5.0–5.5 (100H, CH<sub>2</sub>=, CH), 5.6–6.1 (48H, =CH-), 6.1–7.0 (132H, ArH);  $\delta_{\text{C}}$  (150 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 68.1 (PhCH<sub>2</sub>O-, CHCH<sub>2</sub>O-), 100.7, 106.0, 114.0 (ArC), 117.2 (CH<sub>2</sub>=), 129.6 (ArC), 133.4 (=CH-), 139.1, 156.7, 159.3 (ArC);  $M_n$  (GPC) 4802 ( $M_w/M_n = 1.05$ ).

### Acknowledgements

This work was supported by NEDO for the project on Technology for Novel High Functional Materials (AIST).

### References

- 1 G. R. Newkome, C. N. Moorefield and F. Vogtle, *Dendritic Molecules: Concepts, Synthesis and Perspectives*, VCH, Weinheim, 1996.
- 2 D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.*, 1985, **17**, 117; G. R. Newkome, Z.-Q. Yao, G. R. Baker and V. K. Gupta, *J. Org. Chem.*, 1985, **50**, 2003; D. A. Tomalia, A. M. Naylor and W. A. Goddard III, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138; G. R. Newkome, C. N. Moorefield and G. R. Baker, *Aldrichim. Acta*, 1992, **25**, 31; D. A. Tomalia, *Aldrichim. Acta*, 1993, **26**, 91.
- 3 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; C. J. Hawker and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1990, 1010.
- 4 K. W. Wooley, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4252.
- 5 C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, Cambridge, England, 1989; V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
- 6 Y. Tanaka, Y. Kato and Y. Aoyama, *J. Am. Chem. Soc.*, 1990, **112**, 2807; T. Fujimoto, C. Shimizu, O. Hayashida and Y. Aoyama, *J. Am. Chem. Soc.*, 1998, **120**, 601.
- 7 G. R. Newkome, Y. Hu and M. J. Saunders, *Tetrahedron Lett.*, 1991, **32**, 1133.
- 8 G. Ferguson, J. F. Gallagher, M. A. McKervey and E. Madigan, *J. Chem. Soc., Perkin Trans. I*, 1996, 599.
- 9 T. Nagasaki, S. Tamagaki and K. Ogino, *Chem. Lett.*, 1997, 717.
- 10 R. Kleppinger, H. Reynares, K. Desmedt, B. Forier, W. Dehaen, M. Koch and P. Verhaert, *Macromol. Chem., Rapid Commun.*, 1998, **19**, 111.
- 11 F. Weinel and H.-J. Schneider, *J. Org. Chem.*, 1991, **56**, 5527.
- 12 A. G. S. Högberg, *J. Am. Chem. Soc.*, 1980, **102**, 6046.
- 13 J. Tsuji and T. Yamakawa, *Tetrahedron Lett.*, 1979, **7**, 613.