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Hyperbranched molecules based on calixarenes

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Abstract—Synthesis of the diamide **2** derived from tris(2-aminoethyl)amine and monocarboxymethylcalix[4]arene provides a starting material useful for the preparation of a variety of hyperbranched molecules. Metal ion binding is one of the potentially useful properties of these new materials.

Over the past two decades, dendrimers and hyperbranched molecules have attracted considerable attention because of the special properties determined by their repetitively structured architecture. Intensive studies have been performed of their use as new functional materials in nanotechnology, with both biochemical and medical applications in view.[1] The preparation of such branched structures demands the use of particular building blocks with the appropriate stereochemistry and multiple, equivalent reaction centres. Calixarenes,[2] with their multiple sites for functionalisation on a conformationally restricted, macrocyclic scaffold, are obvious substrates for such synthesis. Their chemistry is well-established and has engendered extensive research not only because of their capacity for forming complexes with a variety of guests, both charged and neutral, but also because of their ease of functionalisation, enabling their use in the construction of sophisticated derivatives such as calixcrowns,[3,4] calixcryptands[4] and calixspherands.[5,6] Particular interest also attends the construction of molecules containing two or more calixarene units and which can be used to form hyperbranched species.[7] Thus, Wang and Gutsche[8] recently reported the synthesis of tricalixarenes from O-alkylcalixarene aldehydes by a two-step conversion to the corresponding ethynyl ketones followed by aryne trimerization. The tricalixarenes are linked together at the upper rim via symmetrical 1,3,5-attachment to a phenyl ring. Importantly, Stany et al.[9] have recently reported the synthesis of hyperbranched polymers derived from tetrathiacalix[4]arene through the linkage of carboxy-substituted thiacalixarene units via amide formation. Given the close analogies in much of the chemistry of thiacalixarenes and 'true' (methylene-bridged) calixarenes, this work should be considered the first step towards the development of calixarene-based dendrimers.

The present note reports the synthesis of hyperbranched molecules constructed by successive amidation reactions via di-calixarene dendron **2**, which is the key-molecule of the construction. In our case, the calixarene is not used as a core to direct the geometry of the growing dendrimer as in Ref. 9 but as an element for further repetitive branching, which may lead to dendrimers of calixarenes.

Dendron **2** was obtained during the preparation of N-tricalix **3** (Scheme 1). *p-tert*-Butyl calix[4]arene[10] was reacted with 1 equiv of $BrCH_2CO_2CH_3$ in refluxing acetone for 24 h using ~1 equiv of K_2CO_3 as base to give the *O*-monomethyl ester **1** in 28% yield.[11] **1** was reacted with 0.3 equiv of tris (2-aminoethyl)amine or 'tren' (amidation reaction) in a 1:1 mixture of CH_3OH/toluene at reflux for six days to afford N-dicalix-$CH_2CH_2NH_2$ **2** in 21% yield. When a similar reaction was carried out in more concentrated conditions (14 times) and with a longer time of reflux (10 days) N-tricalix **3** was obtained in 13% yield. N-tricalix **3** was also obtained in 60% yield by amidation condensation of **1** and **2** in concentrated conditions. **1**–**3** were fully characterized by ^1H NMR, mass spectrometry and elemental analysis. Although

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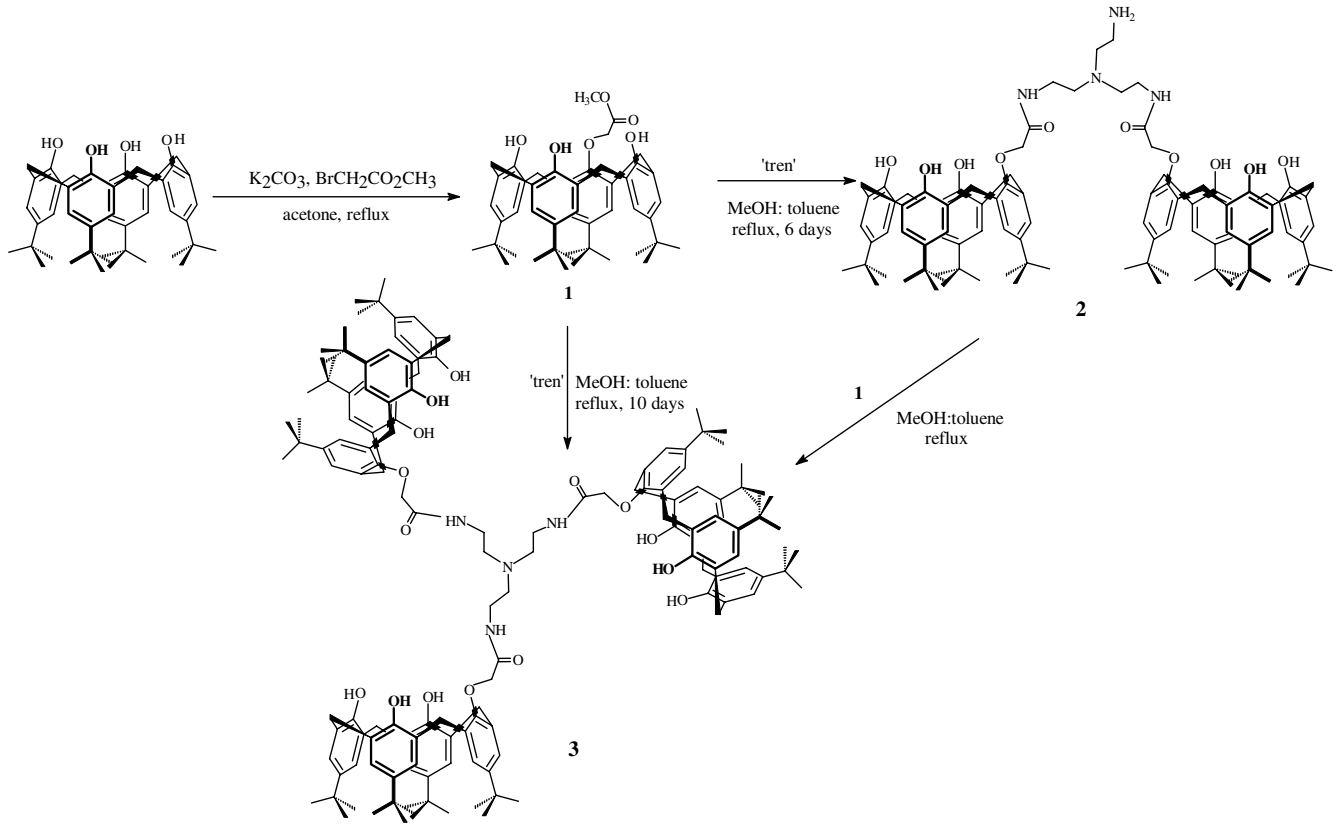
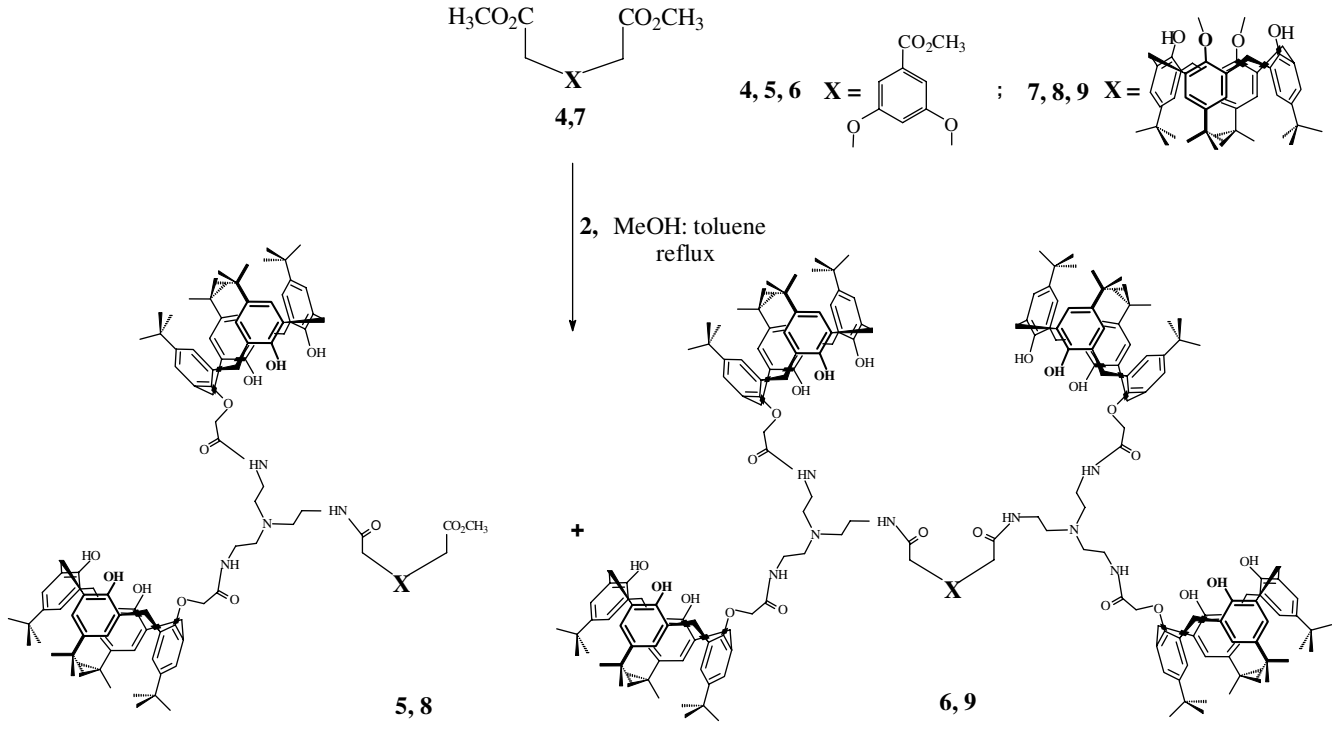


Scheme 1. Preparation of **1**–**3**.

monofunctionalisation of calix[4]arene removes elements of symmetry leading to facile distinction between various conformers of the parent molecule (or its tetra-alkylated derivatives) by ^{1}H NMR, all the present species retain three phenolic hydroxyl groups, which would be expected to be similarly oriented in



Scheme 2. Synthesis of **5**, **6**, **8** and **9**.

order to favour H-bonding, and the coupling constants observed for the diastereotopic methylene protons are very similar to those of genuine *cone* species, so that it is assumed that all do adopt this conformation. For **1**, the ^{1}H NMR spectrum shows two AB systems at 4.47 and 3.49 ppm ($J = 13.2$ Hz) and 4.30 and 3.42 ppm ($J = 13.5$ Hz), and the spectra for **2** and **3** are closely similar. The amide formation was shown by the presence of a broad singlet at 9.75 ppm for N*H* protons of **2** while a triplet was observed for the N*H* protons of **3**. A quartet at 3.65 ppm and a triplet at 3.18 ppm ($J = 5.2$ Hz) were observed for the tren-methylene protons of **3**. The availability of an unreacted primary amino-centre in **2** means it may be considered a dendron suitable for condensation with different cores, adding two calixarene receptor sites in a single step. Thus **2** (see Scheme 2) was reacted (amidation reaction) with trimethyl ester **4** to give hyperbranched molecules **5** and **6** and with 1,3-dimethyl ester *p-tert*-butylcalix[4]arene **7** in its cone conformation to give **8** and **9**. It is worth to notice that the reaction is slow enough to lead to amide formation at only one of the ester centres, giving products with residual ester units suitable for further molecular construction. All the analytical data were in agreement with the proposed structures.[11] As for **2** and **3**, ^{1}H NMR data[11] for **5**, **6**, **8**, and **9** were consistent with their adoption of a *cone* conformation. Preliminary investigations were conducted of the extraction of solid zinc(II) picrate hydrate into $CDCl_3$ solutions (10^{-3} M) of **3** and **6** until the ^{1}H NMR spectra[11] of the resultant solutions remained unchanged. The stoichiometry of the complexes was deduced from the integration ratio between the singlet of the picrate and the aromatic protons of the ligands. Most significant changes to the ligand spectrum involved the protons of the tren residue, possibly consistent with coordination of Zn(II) to the carboxamide-*O* donors. Clearly, metal ion coordination may offer a means of controlling the orientation of pendent groups from a coordinating core as in the present molecules.

In this letter, we have shown the use of the dendron N-dicalix-$CH_2CH_2NH_2$ **2** to prepare hyperbranched molecules. Future work is directed towards (a) the synthesis of various hyperbranched molecules using different cores, (b) growing next generations by taking advantage of the 1,3-selective di-O-functionalisation of calixarenes from **6** and **9**, and (c) the preparation of dendrimers of calixarenes from **3** considered as the first generation.

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11. *General*: Melting points (Mp's), Büchi 500. ^{1}H NMR, Bruker SY 200 (δ in ppm from tms, J in Hz). Fast atomic absorption (positive) (FAB(+)) mass spectra, VG-Analytical ZAB HF and Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra, Biflex Bruker. Elemental analysis was done at the Service de Microanalyse of the Institut de Chimie de Strasbourg. All the reactions were run under nitrogen atmosphere. SiO_2 (Geduran 1.11567) was used for column chromatography. TLC plates were from Merck (Silica 60, F_{254}-0.5 mm, Art 5744). All reagents and solvents were commercial and used without further purification. *Preparation of monomethyl ester* **1**: *p-tert*-butyl calix[4]arene (6.481 g, 10.0 mmol), K_2CO_3 (0.719 g, 5.2 mmol) and acetone (250 mL) were stirred at rt for 1 h. $BrCH_2CO_2CH_3$ (1.529 g, 10.0 mmol) was added and the reaction mixture was refluxed for 24 h. The solvents were removed under reduced pressure and the residue was treated with dichloromethane and 1 M HCl–H_2O until pH ~4. The organic layer was dried over Na_2SO_4. After filtration and removal of the solvents, the residue was purified by column chromatography (SiO_2/CH_2Cl_2) to yield **1** (2.002 g, 28%) as a white solid. Mp 148–149 °C. ^{1}H NMR ($CDCl_3$): 10.24 (s, 1H, O*H*), 9.26 (s, 2H, O*H*), 7.12 (s, 2H, Ar*H*), 7.08 (s, 4H, Ar*H*), 7.01 (s, 2H, Ar*H*), 4.93 (s, 2H, $ArOCH_2$), 4.47 (d, $J = 13.2$ Hz, 2H, AB system, $ArCH_2Ar$), 4.30 (d, $J = 13.5$ Hz, 2H, A′B′ system, $ArCH_2Ar$), 3.95 (s, 3H, OCH_3), 3.49 (d, $J = 13.2$ Hz, 2H, AB system, $ArCH_2Ar$), 3.42 (d, $J = 13.5$ Hz, 2H, A′B′ system, $ArCH_2Ar$), 1.26 (s, 9H, *tert*-butyl), 1.06 (s, 18H, *tert*-butyl), 0.93 (s, 9H, *tert*-butyl). Anal. Calcd for $C_{47}H_{60}O_6$, 0.5 CH_2Cl_2: C, 78.31; H, 8.39. Found: C, 78.25; H, 8.56. *Preparation of* N-*dicalix-*$CH_2CH_2NH_2$ **2**: monomethyl ester **1** (1.601 g, 2.2 mmol), tris(2-aminoethyl)amine or 'tren' (0.120 g, 0.8 mmol) and a 1:1 mixture of CH_3OH/toluene (70 mL) were refluxed for six days. The solvents were evaporated under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on a column (SiO_2: 9:1 CH_2Cl_2–acetone)

to give N-dicalix-$CH_2CH_2NH_2$ **2** (0.705 g, 21%) as a yellow solid. Mp 170–172 °C. ^{1}H NMR ($CDCl_3$): 9.75 (br s, 2H, N*H* amide), 7.05 (d, *J* = 2.04 Hz, 4H, Ar*H*), 7.03 (d,*J* = 2.4 Hz, 4H, Ar*H*), 6.97 (s, 4H, ArH), 6.96 (d, *J* = 2.4 Hz, 4H, Ar*H*), 4.58 (s, 4H, ArOCH_2), 4.29 (d, *J* = 12.6 Hz, 4H, AB system, ArCH_2Ar), 4.17 (d, *J* = 13.5 Hz, 4H, A′B′ system, ArCH_2Ar), 3.65 (br s, 4H, CH_2-tren), 3.33 (d, *J* = 13.5 Hz, 4H, A′B′ system, ArCH_2Ar), 3.28–3.30 (br s, 2H, CH_2-tren), 3.19 (d, *J* = 12.6 Hz, 4H, AB system, ArCH_2Ar), 3.13–3.15 (br s, 2H, CH_2-tren), 3.04 (br s, 4H, CH_2-tren), 1.24 (s, 36H, *tert*-butyl), 1.22 (s, 18H, *tert*-butyl), 1.14 (s, 18H, *tert*-butyl). Molecular weight calcd for $C_{98}H_{130}O_{10}N_4$: MW = 1524.13. FAB(+): Found *m*/*z* = 1524.1 *Preparation of* N-*tricalix* **3** *from* **1**: monomethyl ester **1** (0.501 g, 0.69 mmol) and tris(2-aminoethyl)amine or 'tren' (0.025 g, 0.17 mmol) and a 1:1 mixture of methanol/toluene (5 mL) were refluxed for 10 d. The solvents were evaporated under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on a column (SiO_2: 8:2 CH_2Cl_2/acetone) to yield N-tricalix **3** (0.201 g, 13 %) as a white solid. Mp 189–190 °C. ^{1}H NMR ($CDCl_3$): 10.29 (br s, 3H, OH), (br s, 3H, OH), 9.22 (t, *J* = 5.2 Hz, 3H, N*H* amide), 7.06 (d, *J* = 2.3 Hz, 6H, Ar*H*), 7.03 (s, 6H, Ar*H*), 7.01 (s, 6H, Ar*H*), 6.94 (d, *J* = 2.3, 6H, Ar*H*), 4.58 (s, 6H, ArOCH_2), 4.28 (d, *J* = 13.3 Hz, 6H, AB system, ArCH_2Ar), (d, *J* = 14.0 Hz, 6H, A′B′ system, ArCH_2Ar), 3.65 (q, *J* = 5.2 Hz, 6H, CH_2-tren), 3.36 (d, *J* = 13.3 Hz, 6H, AB system, ArCH_2Ar), 3.30 (d, *J* = 14.0 Hz, 6H, A′B′ system, ArCH_2Ar), 3.18 (t, *J* = 5.2 Hz, 6H, CH_2-tren), 1.24 (s, 27H, *tert*-butyl), 1.22 (s, 54H, *tert*-butyl), 1.14 (s, 27H, *tert*-butyl). Molecular weight calcd for $C_{141}H_{186}O_{15}N_4$: MW = 2213.4. FAB(+): Found *m*/*z* = 2213.4. *Preparation of* N-*tricalix* **3** *from* **2**: N-dicalix-$CH_2CH_2NH_2$ **2** (0.250 g, 0.164 mmol), **1** (0.320 g, 0.492 mmol) and a 1:1 mixture of CH_3OH/toluene (5 mL) were refluxed for six days. The solvents were evaporated under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on a column (SiO_2: 8:2CH_2Cl_2/acetone) to yield **3** (0.220 g, 60 %). *Preparation of* **4**: 1-carbomethoxy-3,5-dihydroxy-benzene[12] (1.201 g, 7.13 mmol), K_2CO_3 (1.971 g, 14.27 mmol), $BrCH_2CO_2CH_3$ (4.310 g, 28.54 mmol), acetone (75 mL) were refluxed for 24 h. The solvents were evaporated under reduced pressure. The residue was dissolved in dichloromethane and washed with 1 M HCl–H_2O until pH ~2. The organic layer was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on a column (SiO_2/CH_2Cl_2) to yield **4** (2.070 g, 93%) as a white solid. Mp 124–125 °C. ^{1}H NMR ($CDCl_3$): 7.22 (d, *J* = 2.4 Hz, 2H, Ar*H*-2), 6.73 (t, *J* = 2.4 Hz, 1H, Ar*H*-4), 4.66 (s, 4H, ArOCH_2), 3.90 (s, 3H, OCH_3), 3.82 (s, 6H, OCH_3). *Preparation of* **5** *and* **6**: **4** (0.025 g, 0.08 mmol), N-dicalix-$CH_2CH_2NH_2$ **2** (0.250 g, 0.16 mmol) and a 1:1 mixture of CH_3OH/toluene (5 mL) were refluxed for 10 days. The solvents were evaporated under reduced pressure. The residue was purified by chromatography on a column (SiO_2: 9.5:0.5 CH_2Cl_2–acetone) to yield mono-substituted **5** (R_f = 0.71, TLC with 8:2 CH_2Cl_2–acetone as eluent, 0.025 g, 8%) as a yellow solid (Mp 145–146 °C) and di-substituted **6** (R_f = 0.38, TLC with 8:2 CH_2Cl_2/acetone as eluent, 0.015 g, 3%) as a brownish solid (Mp 159–160 °C). ^{1}H NMR ($CDCl_3$) of **5**: 9.26 (t, *J* = 5,6 Hz, 2H, N*H* amide), 7.41 (t, *J* = 4.9 Hz, 1H, N*H*), 7.23–7.20 (m, 2H, Ar*H*-2), 7.05 (d, *J* = 2.3 Hz, 4H, Ar*H*), 7.04 (d, *J* = 2.3 Hz, 8H, Ar*H*), 6.99 (d, *J* = 2.3 Hz, 4H, Ar*H*), 7.83 (t, 1H, *J* = 2.2 Hz, Ar*H*-4), 4.64 (s, 2H, ArOCH_2), 4.58 (s, 4H, ArOCH_2), 4.41 (s, 2H, ArOCH_2), 4.23 (d, *J* = 13.6 Hz, 4H, AB system, ArCH_2Ar), 3.41 (d, *J* = 13.0 Hz, 4H, AB system, ArCH_2Ar), 4.18 (d, *J* = 13.9 Hz, 4H, A′B′ System, ArCH_2Ar), 3.37 (d, *J* = 13.0 Hz, 4H, A′B′ system, ArCH_2Ar), 3.84 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.66–3.70 (m, 4H, CH_2-tren), 3.57–3.60 (m, 2H, CH_2-tren), (t, 4H, *J* = 5.5 Hz CH_2-tren), 3.80 (t, *J* = 5.5 Hz, 2H, CH_2-tren), 1.22 (s, 18H, *tert*-butyl), 1.21(s, 36H, *tert*-butyl), 1.16 (s, 18H, *tert*-butyl). Molecular weight of **5** calcd for $C_{111}H_{142}O_{17}N_4$: MW = 1804.37. MALDI-TOF: found *m*/*z* = 1803.4. ^{1}H NMR ($CDCl_3$) of **6**: 9.23 (t, *J* = 5.5 Hz, 4H, N*H*), 7.42 (br s, 2H, N*H* amide), 7.23 (d, *J* = 2.3 Hz, 2H, Ar*H*-2), 7.06 (s, 4H, Ar*H*), 7.05 (s, 4H, Ar*H*), 7.03 (d, *J* = 13.4 Hz, 16H, Ar*H*), 6.97 (s, 4H, Ar*H*), 6.96 (s, 4H, Ar*H*), 6.89 (br t, 1H, Ar*H*-4), 4.57 (s, 8H, ArOCH_2), 4.43 (s, 4H, ArOCH_2), 4.22 (d, *J* = 13.4 Hz, 16H, ArCH_2Ar), 3.80 (s, 3H, OCH_3), 3.69–3.65 (m, 8H, CH_2-tren), 3.57–3.55 (m, 4H, CH_2-tren), 3.38 (d, *J* = 13.4 Hz, 16H, ArCH_2Ar), 3.01 (br t, 8H, CH_2-tren), 2.90 (br t, 4H, CH_2-tren), 1.22 (s, 36H, *tert*-butyl), 1.20 (s, 72H, *tert*-butyl), 1.16 (s, 36H, *tert*-butyl). Molecular weight of **6** calcd for $C_{208}H_{268}O_{26}N_8$: MW = 3296.45. MALDI-TOF. Found *m*/*z* = 3297.6. *Preparation of* **8** *and* **9**: cone-1,3-dimethyl ester *p*-*tert*-butylcalix[4]arene **7**[13] (0.045 g, 0.055 mmol) and N-dicalix-$CH_2CH_2NH_2$ **2** (0.25 g, 0.16 mmol), a 1:1 mixture of methanol: toluene (5 mL) were refluxed for eight days. The solvents were evaporated under reduced pressure. The residue was purified by chromatography on a column (SiO_2: 9.5:0.5 CH_2Cl_2–acetone) to yield mono-substituted **8** (R_f = 0.52, TLC with 9:1 CH_2Cl_2–acetone as eluent, 0.102 g, 27%) as a white solid (Mp = 174–175 °C) and di-substituted **9** (R_f = 0.36, TLC with 9:1 CH_2Cl_2–acetone as eluent, (0.072 g, 12%) as a pale yellow solid (Mp = 166–168 °C). ^{1}H NMR ($CDCl_3$) of **8**: 9.00 (t, *J* = 5.2 Hz, 2H, N*H*), 8.74 (t, *J* = 5.8 Hz, 1H, N*H* amide), 7.30 (s, 2H, Ar*H*), 7.27 (s, 2H, Ar*H*), 7.10–6.90 (m, 16H, Ar*H*), 6.81 (s, 4H, Ar*H*), 4.63 (s, 2H, ArOCH_2CONH), 4.60 (s, 4H, ArOCH_2), 4.46 (s, 2H, ArOCH_2), 4.30 (d, *J* = 13.0 Hz, 4H, AB system, ArCH_2Ar), 3.49 (d, *J* = 13.0 Hz, 4H, AB system, ArCH_2-Ar), 4.25 (d, *J* = 13.7 Hz, 4H, A′B′ system, ArCH_2Ar), 3.38 (d, *J* = 13.7 Hz, 4H, A′B′ system, ArCH_2Ar), 4.13 (d, *J* = 13.0 Hz, 4H, A″B′ system, ArCH_2Ar), 3.28 (d, *J* = 13.0 Hz, 4H, A′B′ system,ArCH_2Ar), 3.84 (s, 3H, OCH_3), 3.80–3.78 (m, 2H, CH_2-tren), 3.77 (s, 2H, ArOCH_2CO$_2$CH$_3$), 3.67–3.63 (m, 4H, CH_2-tren), 3.80–3.03 (m, 6H, CH_2-tren), 1.28 (s, 18H, *tert*-butyl), 1.27 (s, 9H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl), 1.21 (s, 45H, *tert*-butyl), 1.17 (s, 18H, *tert*-butyl). Molecular weight calcd for $C_{147}H_{190}O_{17}N_4$: MW = 2285.12. MALDI-TOF. Found *m*/*z* = 2285.10. ^{1}H NMR ($CDCl_3$) of **9**: ^{1}H NMR ($CDCl_3$): 8.89 (br t, 4H, N*H*), 8.13 (br t, 2H, N*H*), 6.93–7.06 (m, 40H, Ar*H*), 4.57 (s, 8H, ArOCH_2), 4.30 (s, 4H, ArOCH_2), 4.28–4.10 (m, 20H, ArCH_2Ar), 3.76–3.72 (m, 4H, CH_2-tren), 3.70–3.63 (m, 4H, CH_2-tren), 3.53–3.45 (m, 8H, CH_2-tren), 4.34 (d, *J* = 13.4 Hz, 20H, ArCH_2Ar), 2.96–2.83 (m, 8H, CH_2-tren), 1.28 (s, 18H, *tert*-butyl), 1.25 (s, 18H, *tert*-butyl), 1.22 (s, 36H, *tert*-butyl), 1.20 (s, 72H, *tert*-butyl), 1.16 (s, 36H, *tert*-butyl). Molecular weight of **9** calcd for $C_{244}H_{316}O_{26}N_8$: MW = 3777.24. MALDI-TOF: Found: *m*/*z* = 3777.16. ^{1}H NMR ($CDCl_3$) of **3**·Zn(Pic)$_2$: 10.15 (br s, 6H, OH), 9.34 (br s, 6H, OH + N*H*), 8.52 (br s, 4H, Ar*H*pic), 7.00 (s, 12H, Ar*H*), 6.91 (s, 12H, Ar*H*), 4.72 (s, 6H, ArOCH_2), 4.29–4.15 (m, 12H, CH_2-tren), 4.06 (d, *J* = 12.4 Hz, 6H, AB system, ArCH_2Ar), 4.06 (d, *J* = 12.4 Hz, 6H, A′B′ system, ArCH_2Ar), 3.32 (d, *J* = 13.9 Hz, 6H, AB system, ArCH_2Ar), 3.32 (d, *J* = 13.9 Hz,

6H, A′B′ system, ArCH_2Ar), 1.19 (s, 27H, *tert*-butyl), 1.18 (s, 54H, *tert*-butyl), 1.14 (s, 27H, *tert*-butyl). ^{1}H NMR ($CDCl_3$) of 6·2Zn(Pic)$_2$: 10.14 (br s, 4H, N*H*), 9.40 (br s, 2H, N*H*), 8.57 (s, 8H, Ar*H*pic), 7.27 (s, 2H, *H*-2), 6.96 (s, 24H, Ar*H*), 6.89 (s, 13H, Ar*H* and *H*-4), 4.66–4.62 (m, 12H, ArOCH_2), 4.14–4.05 (m, 28H, CH_2-tren and ArCH_2Ar), 3.77 (s, 3H, OCH_3), 3.40–3.34 (m, 28H, CH_2-tren and ArCH_2Ar), 1.22 (s, 36H, *tert*-butyl), 1.19 (s, 72H, *tert*-butyl), 1.17 (s, 36H, *tert*-butyl).

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