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Oligophenylcalix[4]arenes as Potential Precursors for Funnelenes and Calix[4]triphenylenes: Syntheses and Preliminary Cyclodehydration Studies

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The concept for a new class of nonplanar polyaromatic hydrocarbons – the funnelenes – is presented. Retrosynthetic considerations lead to polyphenyl- and oligophenylcalix[4]arenes as potential precursors. In this paper we describe the synthesis of these calixarenes and the first cyclodehydration studies on a model compound which leads to a hexabenzocoronene derivative.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) can be regarded as partial structures of, and therefore as model compounds for, graphite, fullerenes and carbon nanotubes. Preparative studies in modern hydrocarbon chemistry are frequently aimed at the synthesis of large plane graphite sheets[1] and of geodesic fullerene substructures,[2] such as corannulene[3] or sumanene.[4] Carbon nanotubes are receiving particularly broad interest because of their manifold amazing physical and electronic properties.[5] Small cyclic fragments of carbon nanotubes are objects of theoretical calculations,[6] however, the so called cyclacenes, for example, have not yet been synthesised.[7]

We envisioned a new class of large extended aromatic carbon π-systems with a conical topology (Figures 1 and 2), which we called funnelenes (**1** and **2**) because of their funnel-like shape, and it seemed obvious that calix[4]arenes,[8] which can easily be rigidified in the cone conformation, could be suitable starting materials for funnelenes.

As a result of retrosynthetic analysis the cyclodehydration (dashed lines in Scheme 1) of the oligophenylic calixarenes **3** and **4** would be a straightforward synthetic approach to the funnelenes.

In this paper we describe the synthesis of the oligophenylcalixarenes and preliminary studies on cyclodehydration reactions with an alkoxy-substituted model compound.

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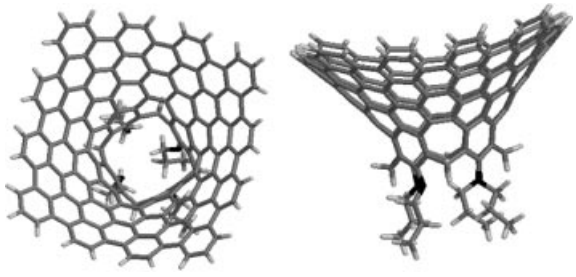


Figure 1. Computer-generated model (MM2-optimised) of the functionalised funnelene **1**.

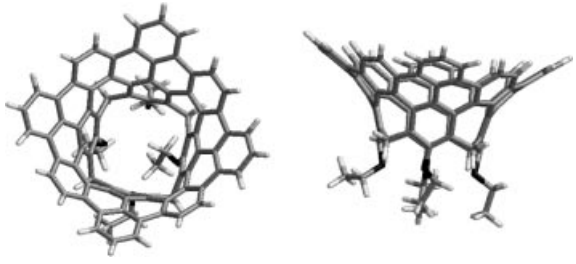
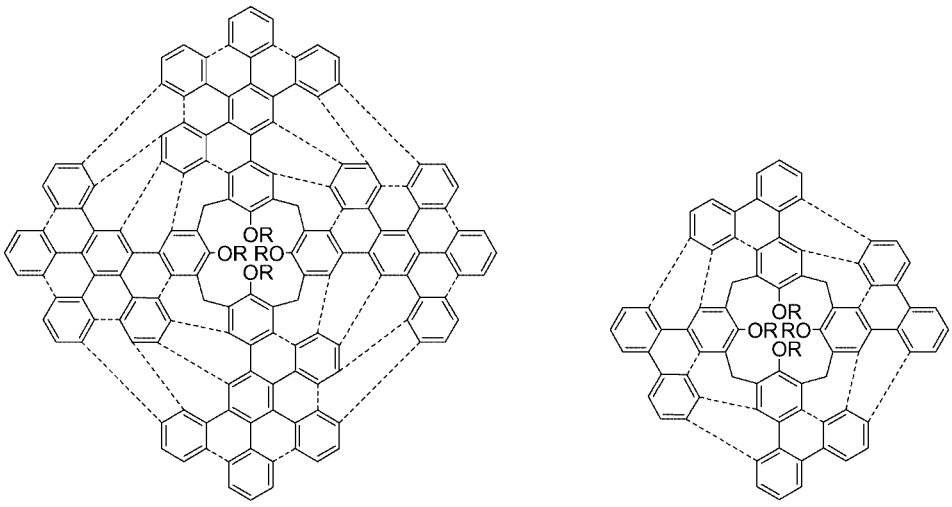


Figure 2. Computer-generated model (MM2-optimised) of the functionalised funnelene **2**.

Results and Discussion

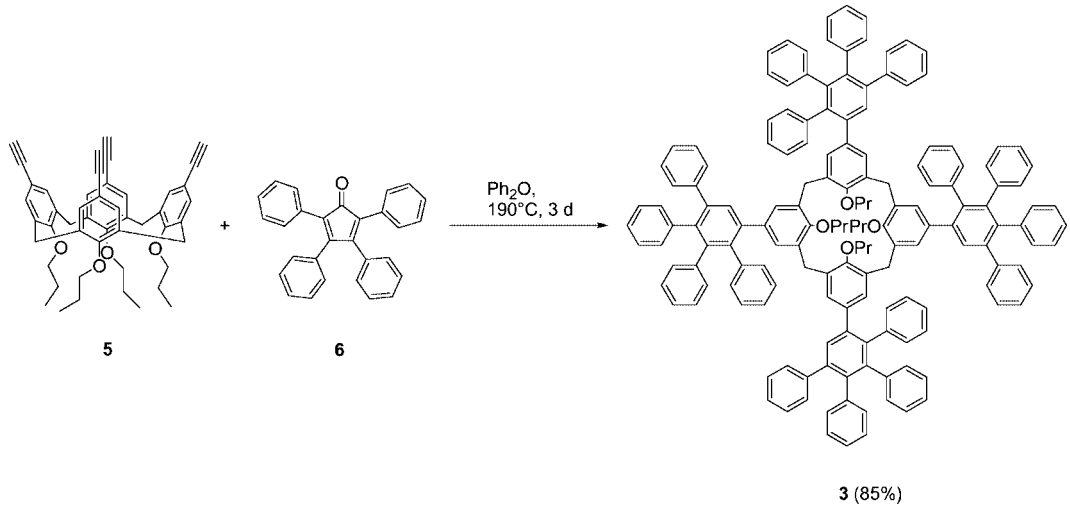
Compound **3** is accessible with excellent yields of up to 85% by a fourfold Diels–Alder reaction of the tetraethynylcalixarene **5**[9] with tetracyclone (**6**), followed by CO extrusion (Scheme 2), and was characterised by NMR spectroscopy and an X-ray crystal structure analysis.

Suitable crystals were obtained by diffusion of methanol into a dichloromethane solution of **3** (Figures 3 and 4);[10] they were found to crystallise in the monoclinic space group



3 **4**

Scheme 1. The polyphenylic calixarenes **3** and **4** as precursors for funnelene syntheses by cyclodehydration. Dashed lines indicate the necessary formation of C–C bonds (R = alkyl).



5 **6** **3** (85%)

Scheme 2. Diels–Alder reaction of the tetraethynylcalixarene **5** with tetracyclone (**6**).

C2/c. Dichloromethane molecules are loosely bound in the lattice voids: when the crystals are removed from the mother liquor they rapidly lose their crystalline brightness due to the decomposition of the clathrate. Statistically, 2.91 dichloromethane molecules are clathrated for each calixarene. The calixarene is fixed in a pinched cone conformation and the peripheral phenyl units are slightly twisted with respect to one another. The *R* value of 7.6% can be explained by disordered propyl moieties and phenyl rings, and the loss of solvent molecules.

In the ^{1}H NMR spectrum the bridging methylene protons appear at δ = 2.60 (equatorial) and 4.15 ppm (axial), whereas the equatorial protons are influenced by the peripheral phenyl units and therefore undergo a relative upfield shift compared to other cone calix[4]arenes. Two singlets are diagnostic in the aromatic region: the signal of the *m*-protons of the calixarene scaffold appear at δ = 6.35 ppm, with an integral of eight protons, and the signal of 6-H of the oligophenyl substituents appears at δ = 7.31 ppm, with an integral of four protons.

Most interestingly, the tetrakis(phenylethynyl)calixarene **7** reacts selectively with two equivalents of tetracyclone (**6**) in diphenyl ether at 190 °C to give **8** in 72% yield (Scheme 3). Neither higher reaction temperatures (269 °C) nor a change of the solvent (benzophenone, 305 °C) gave the fourfold Diels–Alder product **9**, probably for reasons of steric hindrance.

In the ^{1}H NMR spectrum of **8** two doublets for the methylene protons, each of which integrates for four protons, appear at δ = 2.67 and 4.05 ppm. Two sets of signals are also observed for the propyloxy substituents, and two singlets for the *m*-aryl protons of the calixarene scaffold resonances at δ = 5.97 and 6.53 ppm (4 H each). The sp-hybridized carbon atoms of the phenylethynyl substituents

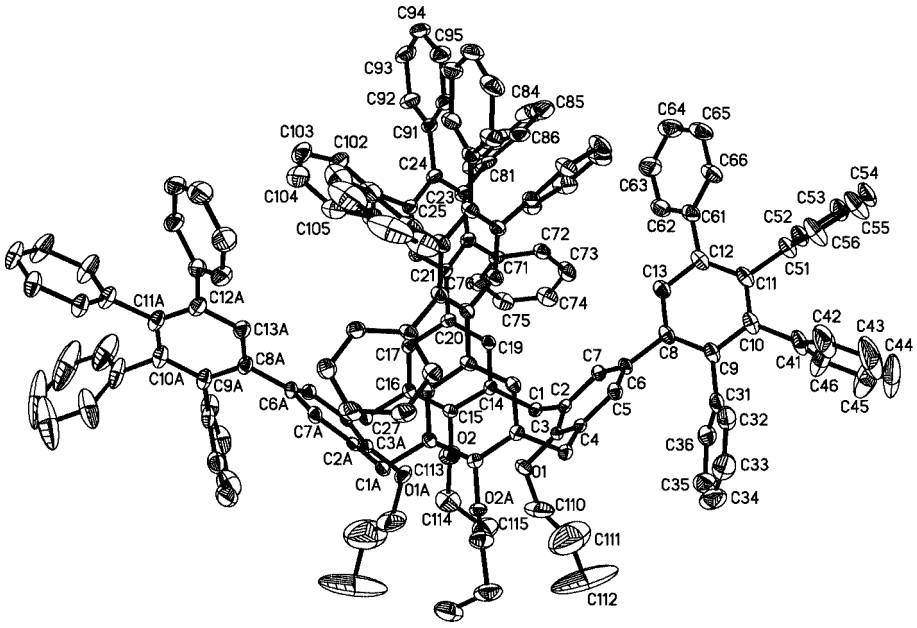


Figure 3. Crystal structure of compound **3** with thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

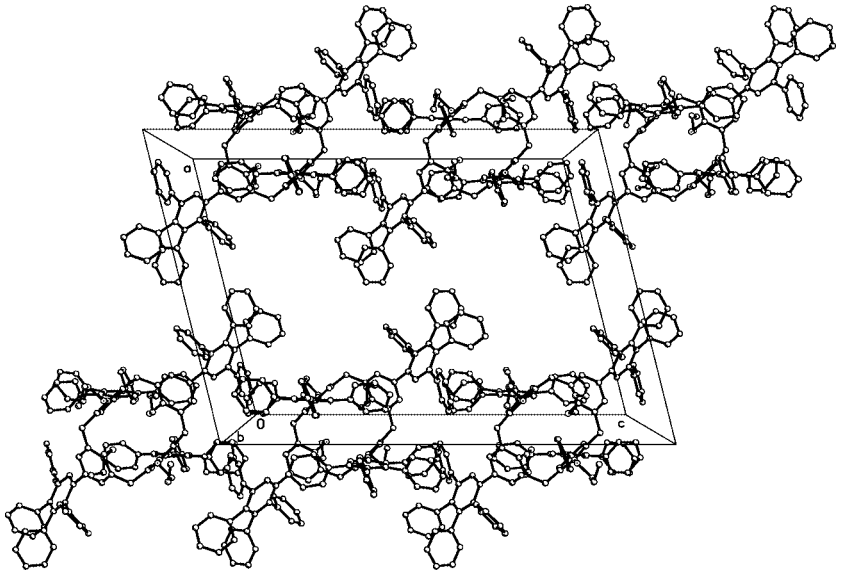


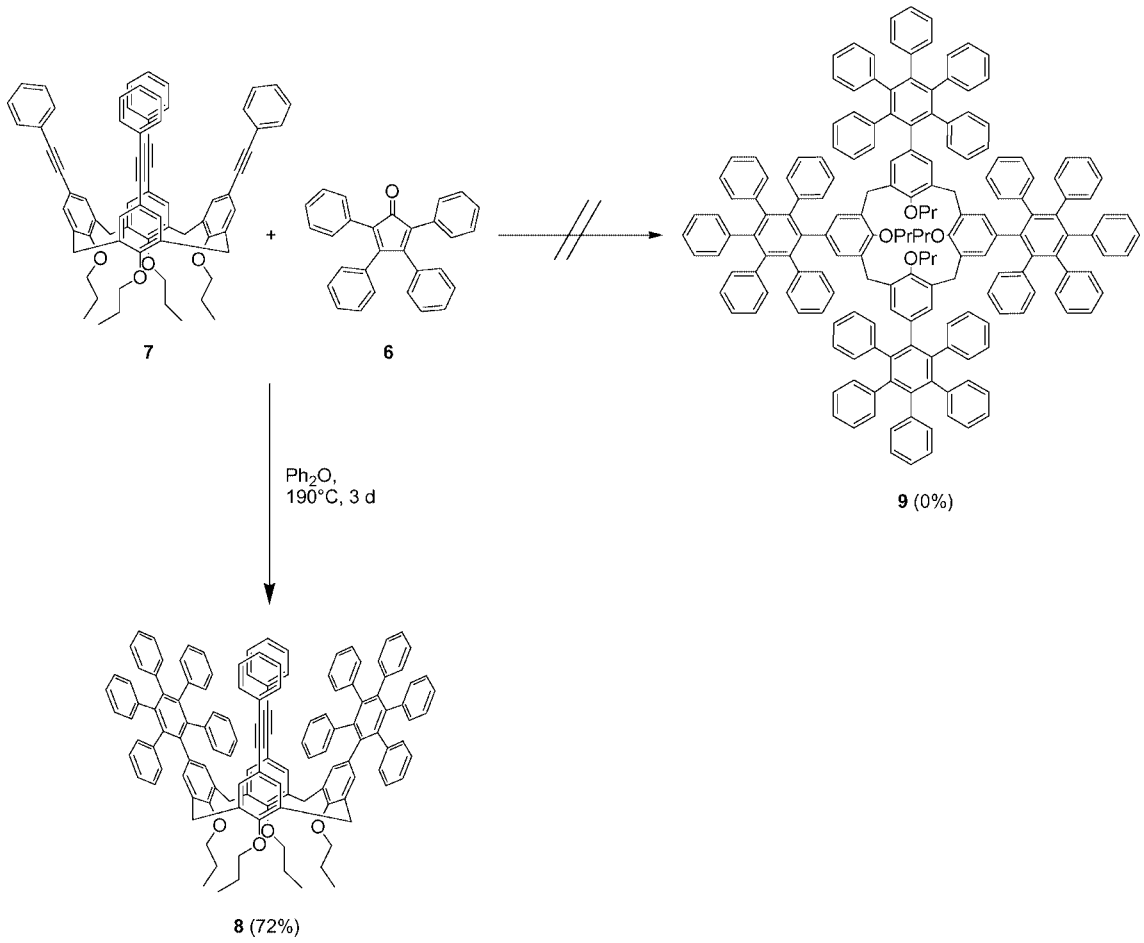
Figure 4. Packing of **3** in the unit cell. View along the crystallographic *b*-axis. Hydrogen atoms and solvent molecules have been omitted for clarity.

can be clearly seen as two signals at δ = 116.7 and 124.35 ppm in the ^{13}C NMR spectrum. Upon attempting to grow crystals from dichloromethane/methanol molecules of the alcohol became clathrated and could not be removed even after heating the substance in a kugelrohr oven for several hours. This was confirmed both by recording a ^{1}H NMR spectrum of the crystalline substance and by elemental analysis.

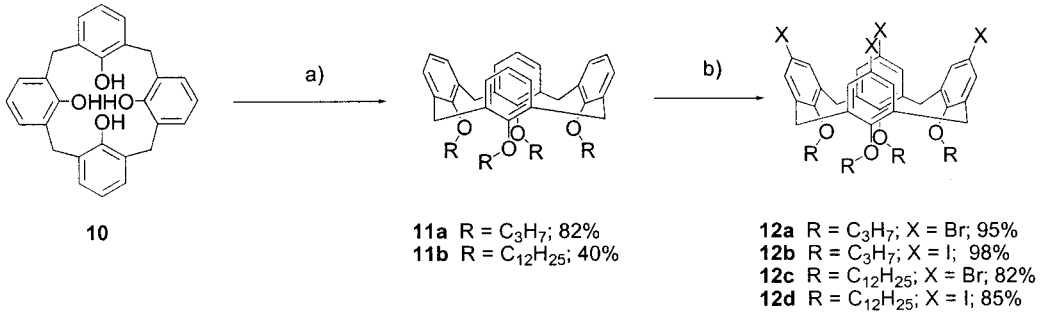
The retrosynthetic analysis of the smaller funnelene **2** suggests the oligophenylcalixarenes **4a** and **4b** as suitable precursors. For their synthesis we started with the fixation of calixarene **10** in a cone conformation and subsequent halogenation in the 4-position, essentially following literature procedures, to give calixarenes **11a** and **11b** in good and moderate yields respectively.[11] The calixarenes **12a**–**12d** were obtained in good yields upon subsequent halogenation (Scheme 4).[12,13]

The halocalixarenes **12a**–**12d** were cross-coupled with 2-biphenylboronic acid (**13**) in a palladium-catalysed Suzuki reaction to give the oligophenylcalixarenes **4a**, **4b**, **14a** and **14b** (Scheme 5 and Table 1).[14]

We obtained a mixture of the twofold (**14a**), threefold (**14b**) and tetra-coupled (**14c**) products in the ratio 15:62:23, as determined from the diagnostic ^{1}H NMR signals, from the coupling reaction of the tetrabromide **12a** with the boronic acid **13**. The product mixture could not be further



Scheme 3. Diels–Alder reaction of tetrakis(phenylethynyl)calixarene **7** with tetracyclone (**6**).



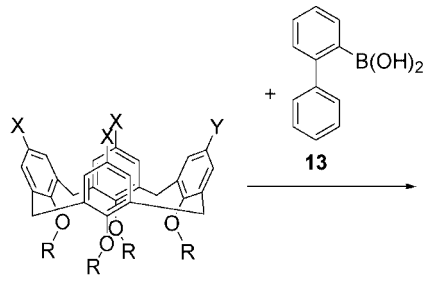
Scheme 4. a) DMF, NaH, RBr, 60–70 °C, 2 h. b) bromination: NBS, 2-butanone, room temperature, 3 d (**12a**), 24 h (**12c**); iodination: 1. $Ag(OOCCF_3)$, $CHCl_3$, 15 min; 2. I_2, 20 min.

separated by flash chromatography; instead, fractional crystallisation from toluene/pentane allowed us to enrich the threefold product **14b** up to a purity of 93%.

Under the same reaction conditions (refluxing THF) the tetraiodo compound **12b** gave the desired fourfold product **4a** selectively, but with only a moderate yield of 49%. Carrying out the reaction in a screw-capped vessel at 120 °C allowed the yield of the desired fourfold coupling product to be increased up to 83%. Similar results were obtained for the coupling reactions with tetrahalocalixarenes **12c** and **12d**.

Suitable single crystals of **4a** were grown by slow diffusion of pentane into a saturated solution of **4a** in toluene. This compound crystallises in the monoclinic space group $P2_1$ and contains one clathrated molecule of toluene per calixarene.[10] The calixarene molecules are in a pinched-cone conformation where two of the peripheral phenyl rings are *exo*- and two are *endo*-oriented to the cavity (see Supporting Information).

The synthesis of calixarene **16** was achieved in a very good yield by Suzuki cross-coupling of the monobromide



12a (R = *n*-C_3H_7, X = Y = Br)
12b (R = *n*-C_3H_7, X= Y = I)
12c (R = *n*-$C_{12}H_{25}$, X = Y = Br)
12d (R = *n*-$C_{12}H_{25}$, X = Y = I)
15 (R = *n*-C_3H_7, X= H, Y = Br)

4a (R = *n*-C_3H_7, R^1 = R^2 = 2-biphenyl)
4b (R = *n*-$C_{12}H_{25}$, R^1 = R^2 = 2-biphenyl)
14a (R = *n*-C_3H_7, R^1 = Br, R^2 = 2-biphenyl)
14b (R = *n*-C_3H_7, R^1 = 2-biphenyl, R^2 = Br)
16 (R = *n*-C_3H_7, R^1 = R^2 = H)

Scheme 5. Suzuki cross-coupling reaction of halocalixarenes **12a**–**12d** with 2-biphenylboronic acid (**13**). See Table 1 for conditions and yields.

Table 1. Suzuki cross-coupling reactions of halocalixarenes **12a**–**12d** and **15** with boronic acid **13**.[a]

Entry	Calixarene	Temp. [°C]	Time	Products (yield %)
1[b]	**12a**	67[c]	26 h	**14a** (14) **14b** (59) **4a** (22)
2	**12a**	120[d]	21 h	**4a** (83)
3	**12b**	67[c]	16 h	**4a** (49)
4	**12c**	120[d]	20 h	**4b** (91)
5	**12d**	67[c]	16 h	**4b** (31)
6	**15**	120[d]	24 h	**16** (87)

[a] Reaction conditions: THF as solvent, a 2 N aqueous potassium carbonate solution as base and 6 mol-% [$Pd(PPh_3)_4$] as catalyst were heated under argon. [b] After flash chromatographic purification the yields were determined by the ratio of integrals of diagnostic ^{1}H NMR signals of the calixarene mixture. [c] Reflux temperature. [d] The reaction was carried out in a screw-capped vessel.

15[15] with the boronic acid **13** under the same conditions as for compound **4a** (Scheme 5 and Table 1).

In the ^{1}H NMR spectrum of compound **16** the signals of the aryl protons H^a, H^b and H^c (Figure 5) in the proximity of the triphenylene unit are found in the relatively upfield region at δ = 5.86, 6.25 and 6.31 ppm, probably due to an anisotropic ring-current effect of the peripheral phenyl unit, thus indicating that this substituent is preferably *endo* oriented due to CH–π interactions (see Figure 5).[16] Neither the addition of *N*-methylpyridinium iodide to the NMR solution of **16** nor a solvent change to [D_8]toluene caused a downfield shift of these signals.

The X-ray crystal structure of **16**[10] (see Supporting Information) confirms the hypothesis of intramolecular CH–π interactions. Suitable crystals grown from toluene/pentane showed no clathrated solvent molecules. The peripheral phenyl unit is *endo* oriented, with an average distance to one of the proximal *meta*-protons of about 3.48 Å, in agreement with the typical range of CH–π interactions.[16,17]

The model compound **20** (Scheme 6) was synthesised from commercially available bromophenol **17** as a test substrate for the cyclodehydration under various reaction conditions. *O*-Alkylation was achieved by a procedure described in the literature,[14c] and a Sonogashira cross-coupling reaction with phenylacetylene gave the tolane **19** in good yields. Subsequent Diels–Alder reaction with tetracyclone **6** led to **20**. Different standard procedures for the oxidative cyclodehydration reactions were tested, for example reaction with $AlCl_3/CuCl_2$ in CS_2, $FeCl_3$ in dichloromethane/nitromethane[1,18] and $MoCl_5$ in dichloromethane.[19] The best results were obtained with $FeCl_3$ in dichloromethane/nitromethane. Because of the very low solubility of the hexabenzocoronene (HBC) **21** in usual solvents, the analysis was restricted to IR and UV/Vis spectroscopy and MALDI-TOF mass spectrometry.[20] Chlorinated and partially dehydrogenated products were detected as minor by-products of **21** in the MALDI-TOF mass spectrum of the crude product. Purification by Soxhlet extraction gave pure **21** (no peaks of by-products were observed in the MALDI-TOF mass spectrum) in 41% yield. The UV/Vis spectrum of a benzene solution of **21** reveals three absorptions at λ = 391, 360 and 344 nm, which are typical for the unsubstituted HBC.[21]

First attempts to cyclodehydrate calixarene **16** under the same conditions ($FeCl_3$ in CH_2Cl_2/CH_3NO_2) gave only recovered starting material. In the case of $MoCl_5$ an unselected cleavage of the propyloxy moieties takes place to give the hydroxycalixarenes **23a** and **23b** (Scheme 7) as a 1:1 mixture.[22]

Although the insoluble crude materials we obtained from the reaction of oligophenylcalixarenes **3**, **4a** and **4b** with $FeCl_3$ in nitromethane/dichloromethane exhibit strong fluorescence, we could not detect any signals in the MALDI-TOF mass spectrum that could be evidence for the funnelenes **1** and **2**. In the mass spectrum of the crude product of **3** with $FeCl_3$ signals corresponding to the loss of 20, 48 and 60 hydrogens were observed, besides cleavage of the *O*-alkyl bonds; 64 hydrogen atoms must be eliminated for the formation of the funnelene **1**. In the case of **4a** the mass spectrum of the crude product is best interpreted in terms of partial dehydration in combination with cleavage of *O*-alkyl bonds, which is typical for the formation of spiro-annulated

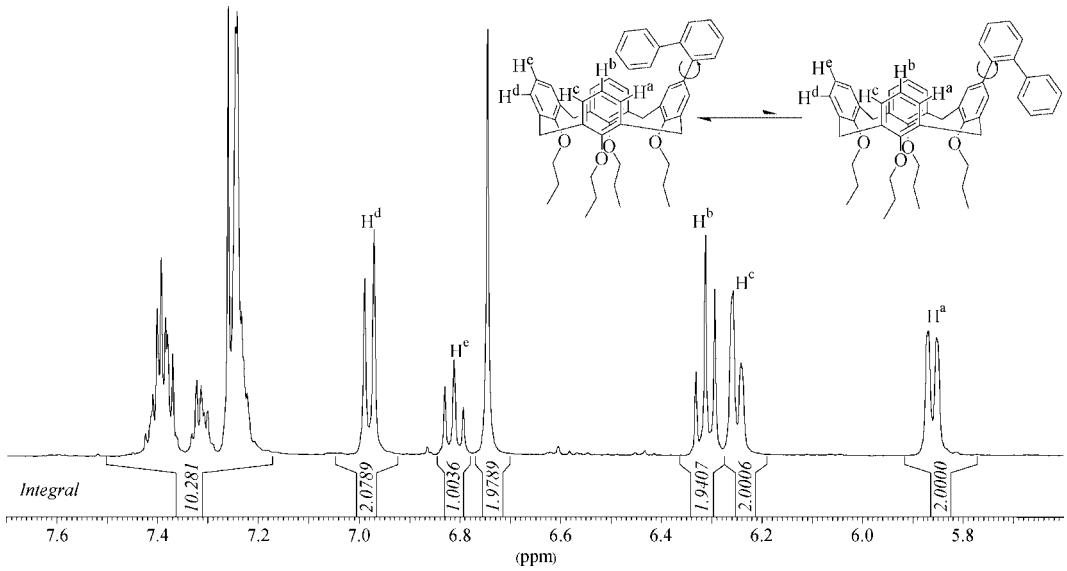
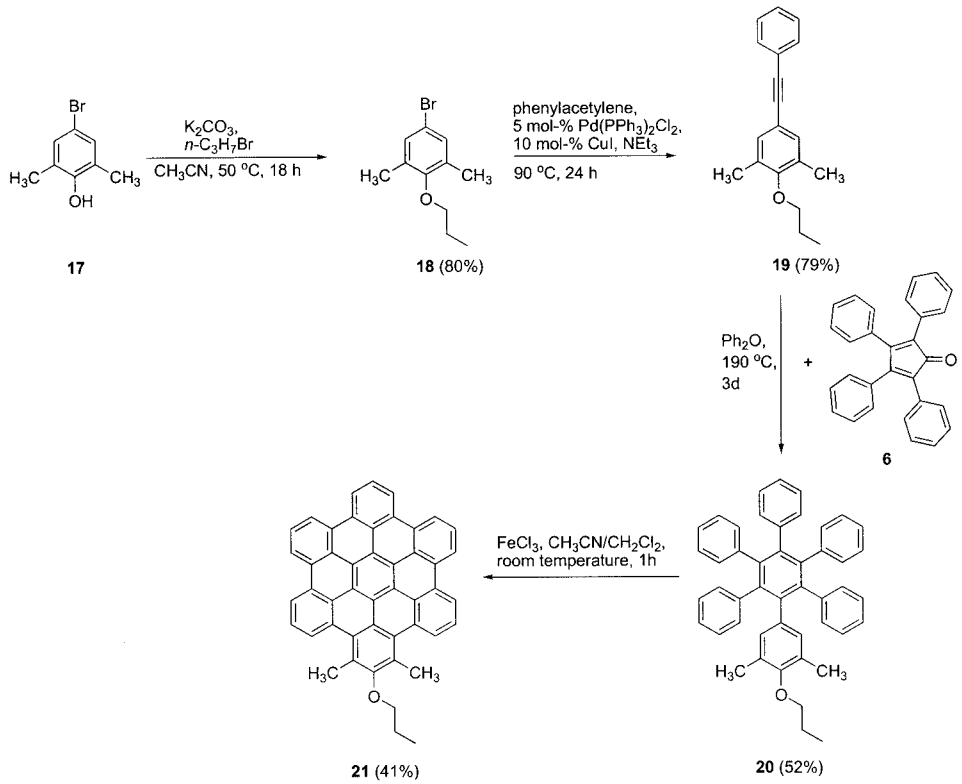


Figure 5. Aromatic region of the ^{1}H NMR spectrum of **16** in $CDCl_3$ (400 MHz).

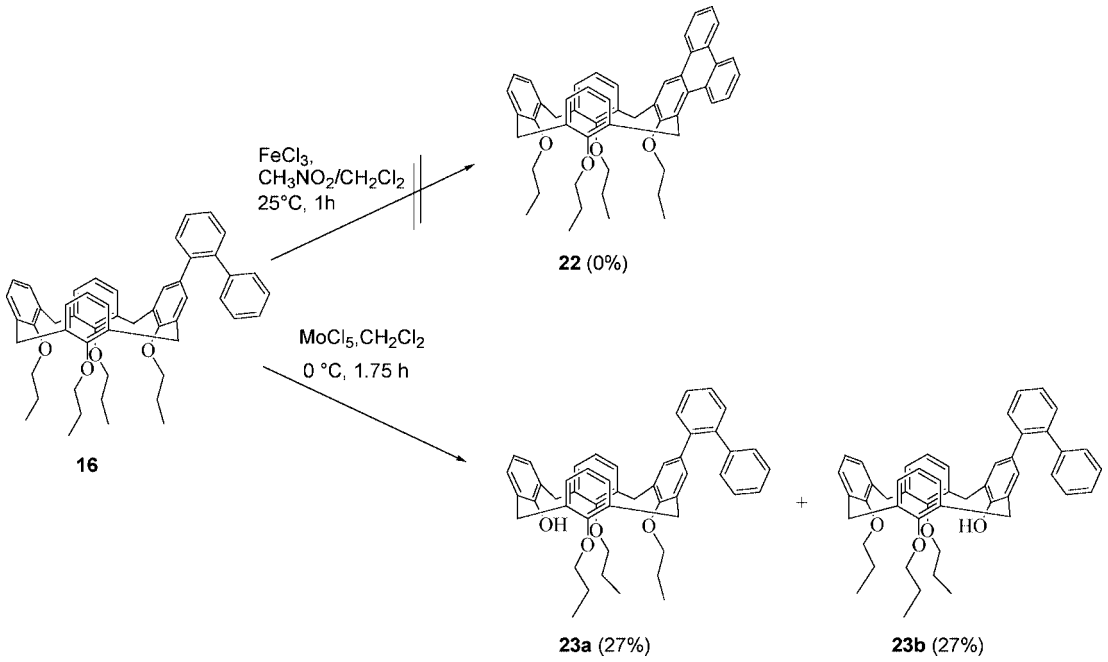


Scheme 6. Synthesis and cyclodehydration of model compound **20**.

products.[14g] Indeed, the strong absorption observed at 1667 cm^{-1} in the IR spectrum of the crude material is typical for the carbonyl bond of a spiro-annulated substructure.[14g,23]

Conclusions

A new class of polyhydrocarbon compounds − the funnelenes − has been conceptually introduced and an access



Scheme 7. Preliminary cyclodehydration experiments of **16** to approach the synthesis of an inherently chiral calix[4]triphenylene.

to these substances from polyphenyl- and oligophenylcalixarenes fixed in the cone conformation as potential precursors evaluated. Although the cyclodehydration of a model compound has been successfully achieved, first attempts to use these conditions for the complete cyclodehydration of the calixarene **16** failed. Future work will focus on derivatives of the oligophenylcalixarenes with increased solubility in order to simplify the purification and analysis of the cyclodehydration products.

Experimental Section

General Remarks: Melting points (uncorrected values) were determined with a Kofler Heizmikroskop, model Reichert Thermovar. Elemental analysis was performed with a Carlo–Erba Elemental Analyser 1106 or a Vario EL. Infrared spectroscopy was performed with a Bruker Vector 22, a Bruker Equinox 55, a Perkin–Elmer 983G or a Perkin–Elmer 841. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 40 apparatus or a Varian Carey 1. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 200, a Bruker WM 300, a Bruker DRX 400 or a Bruker DRX 500 spectrometer. MALDI-TOF spectra were recorded with a Bruker Daltonics flex analysis (α-cyanocinnamic acid as matrix). Mass spectrometry was performed with a Varian MAT 311 A, AMD 604, Varian MAT CH5 or a VG Autospec instrument. SiO_2 plates (Polygram SIL G/UV 254) from Macherey–Nagel were used for TLC. All compounds were purified by flash chromatography on Kieselgel 60 (Merck, 0.030–0.60 mm). All commercially available products were used without further purification. The compounds **5**,[9] **7**,[9] **11**,[11] **12a**,[12] **12b**[13] and **18**[14c] were synthesised as previously described in literature.

***cone*-17,23-Bis[1-(2,3,4,5,6-pentaphenyl)phenyl)-5,11-bis(phenylethynyl)-25,26,27,28-tetrakis(propyloxy)calix[4]arene (8):** Calixarene **7** (49 mg, 0.049 mmol) and tetracyclone **6** (352 mg, 0.92 mmol) were dissolved in diphenyl ether (3 mL) and heated for 4 d at 190 °C. After cooling to room temperature the diphenyl ether was removed by bulb-to-bulb distillation (200 °C, 5.0×10^{-1} mbar) to give 400 mg of a dark-purple solid. TLC (light petroleum ether/ethyl acetate, 5:1): R_f = 0.28, 0.35, 0.44 (**8**), 0.53. Separation by column chromatography (light petroleum ether/ethyl acetate, 10:1; R_f = 0.12) and drying in vacuo gave 65 mg (77%) of calixarene **8** as a pale-yellow solid. Recrystallisation from CH_2Cl_2/MeOH (1:1) gave 61 mg (72%) of pale-yellow crystals (1:1 complex with methanol) with m.p. >320 °C. IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 3055, 3023, 2953, 2921, 2859, 2203, 1594, 1484, 1469, 1453, 1398, 1383, 1297, 1227, 1195, 1180, 1156, 1125, 1102, 1070, 1016, 984, 953, 906, 875, 867, 812, 766, 750, 734, 719, 688, 563, 547. UV/Vis (CH_3CN): $\lambda_{max.}$ (lgε) = 207 nm (6.4, sh), 239 (6.1), 273 (5.8, sh), 306 (5.5, sh). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.74 (t, J = 7.4 Hz, 6 H, $OC_2H_4CH_3$), 0.99 (t, J = 7.4 Hz, 6 H, $OC_2H_4CH_3$), 1.50 (m, J = 7.8 Hz, 4 H, $OCH_2CH_2CH_3$), 1.75 (m, J = 7.3 Hz, 4 H, $OCH_2CH_2CH_3$), 2.67 (d, J = 13.6 Hz, 4 H, Ar-CH_2-Ar), 3.44 (t, J = 6.9 Hz, 4 H, $OCH_2CH_2CH_3$), 3.47 (s, 3 H, CH_3OH) 3.79 (t, J = 8.2 Hz, 4 H, $OCH_2CH_2CH_3$), 4.05 (d, J = 13.5 Hz, 4 H, Ar-CH_2-Ar), 5.97 (s, 4 H, Ar-H), 6.53 (s, 4 H, Ar-H), 6.85 (m, 44 H, Ar-H), 7.04 ("t", "J" = 7.8 Hz, 4 H, Ar-H), 7.10 ("d", "J" = 7.0 Hz, 4 H, Ar-H), 7.16 ("d", "J" = 8.6 Hz, 4 H, Ar-H), 7.22 ("d", "J" = 7.6 Hz, 4 H, Ar-H), 7.35 ("d", "J" = 8.3 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 10.03 (q, $OCH_2CH_2CH_3$), 10.70 (q, $OCH_2CH_2CH_3$), 21.89 (t, $OCH_2CH_2CH_3$), 23.43 (t, $OCH_2CH_2CH_3$), 30.82 (t, Ar-CH_2-Ar), 50.95 (t, $OCH_2CH_2CH_3$), 75.57 (t, $OCH_2CH_2CH_3$), 87.29 (s, Ar-*C*-C-Ar′), 91.07 (s, Ar-C-*C*-Ar′), 116.67 (s, Ar′*C*-CC-Ar), 124.35 (s, Ar*C*-CC-Ar′), 124.68, 125.13, 125.17, 126.29, 126.57, 126.64, 126.96, 127.22, 127.30, 128.25, 130.79, 131.46, 131.50, 131.55, 131.60, 131.65, 132.13 (all d, Ar*C*-H), 133.10, 134.17 (s, Ar*C*-CH_2-Ar), 134.65 (s, Ar*C*-CH_2-Ar), 139.96, 140.06, 140.26, 140.75, 140.85, 140.88, 140.91, 140.93, 141.17 (all s), 154.93 (s, Ar*C*-O-), 155.71 (s, Ar*C*-O-) ppm. MS (EI, 70 eV, 400 °C): *m/z* (%) 1706 (4) [M$^+$ + 2], 1705 (7) [M$^+$ + 1], 1704 (9) [M$^+$], 1703 (7), 592 (5), 564 (5), 91 (9), 78 (8), 69 (7), 44 (100),

43 (11), 42 (48), 41 (71), 40 (16), 39 (46), 38 (10), 37 (8). $C_{128}H_{104}O_4 \cdot CH_3OH$ (1738.2): calcd. C 89.13, H 6.26; found C 89.09, H 6.25.

***cone*-25,26,27,28-Tetrakis(propyloxy)-5,11,17,23-tetrakis[1-(2,3,4,5-tetraphenyl)phenyl]calix[4]arene (3):** A solution of calixarene **5** (60 mg, 0.087 mmol) and tetracyclone **6** (550 mg, 1.43 mmol) in diphenyl ether (3 mL) was heated for 3 d at 190 °C. After cooling to room temperature the diphenyl ether was removed by bulb-to-bulb distillation (200 °C, 5.0×10^{-1} mbar) to give 620 mg of a dark purple solid. TLC (light petroleum ether/ethyl acetate, 10:1): $R_f = 0.15$, 0.26 (**6**), 0.41, 0.53 (**3**), 0.62. Separation by column chromatography (light petroleum ether/ethyl acetate, 10:1; $R_f = 0.26$) gave calixarene **3** (157 mg, 85%) as a pale-yellow solid after drying in vacuo (200 °C, 5.0×10^{-1} mbar). Recrystallisation from CH_2Cl_2/MeOH (6 mL) and drying in vacuo (200 °C, 5.0×10^{-1} mbar) gave 148 mg (80%) of calixarene **3** as colourless crystals with m.p. > 320 °C. IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 3033, 2961, 2932, 2875, 1600, 1495, 1468, 1441, 1430, 1383, 1220, 1186, 1151, 1072, 1027, 1009, 966, 761, 698. UV/Vis (CH_3CN): $\lambda_{max.}$ (lgε) = 207 nm (5.3, sh), 249 (5.0), 277 (4.9, sh). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.5 Hz, 12 H, $OCH_2CH_2CH_3$), 1.81 (m, J = 7.5 Hz, 8 H, $OCH_2CH_2CH_3$), 2.61 (d, J = 12.3 Hz, 4 H, Ar-CH_2-Ar), 3.72 (t, J = 7.7 Hz, 8 H, $OCH_2C_2H_5$), 4.15 (d, J = 12.3 Hz, 4 H, Ar-CH_2-Ar), 6.35 (s, 8 H, Ar-*H*), 6.63 ("t"), 6.72 (m, together 36 H, Ar′′-H), 6.86 (′t′), 6.90 (m, together 24 H, Ar′′-H), 6.97 (m, 8 H, Ar′′-H), 7.04 (m, 12 H, Ar′′-H), 7.32 (s, 4 H, Ar′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 10.41 (q, $OCH_2CH_2CH_3$), 22.89 (t, $OCH_2CH_2CH_3$), 31.40 (t, Ar-CH_2-Ar), 76.46 (t, $OCH_2CH_2CH_3$), 125.14, 125.21, 125.41, 125.94 126.51, 126.84, 127.58, 129.96, 130.08, 130.73, 131.48, 131.71 (all d, Ar*C*-H), 133.39, 134.79 (s, Ar*C*–CH_2-Ar), 138.46, 139.28, 140.16, 140.22, 140.41, 140.72, 141.16, 141.18, 141.64 (all s), 154.90 (s, Ar*C*–O-) ppm. MS (EI, 70 eV, 380 °C): *m*/*z* (%) 2112 (1) [M^+], 44 (37), 42 (69), 41 (100), 40 (63), 39 (59), 38 (13), 37 (8). $C_{160}H_{128}O_4$ (2114.7): calcd. C 90.87, H 6.10; found C 91.28, H 5.90.

***cone*-25,26,27,28-Tetrakis(dodecyloxy)calix[4]arene (11b):** Sodium hydride (3.65 g, 152 mmol) was suspended in dry DMF (85 mL), calix[4]arene **10** (2.00 g, 4.73 mmol) was added in portions and the reaction mixture was heated for 30 min at 50 °C. After cooling to room temperature 1-bromododecane (10 mL, 41.1 mmol) was added dropwise and the reaction mixture was heated for 2 h at 65 °C. After cooling to room temperature ice/water (100 mL) was added and the mixture extracted with dichloromethane (3 × 50 mL). The organic layer was washed with water (3 × 50 mL), 1 N aqueous ammonia chloride solution (2 × 50 mL) and brine (50 mL), and dried with $MgSO_4$. Dichloromethane was removed by rotary evaporation to give a yellow solution, from which colourless needles precipitated overnight. The needles were collected by filtration, washed with methanol (3 × 4 mL) and dried in vacuo to give 2.05 g (40%) of calixarene **11b** as colourless needles with m.p. 60–62 °C. IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1}, 2919, 2850, 1586, 1466, 1378, 1292, 1245, 1193, 1157, 1127, 1091, 1069, 1043, 1021, 995, 957, 913, 831, 800, 760, 721, 632, 602. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 [t, J = 6.8 Hz, 12 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.29 [m, 72 H, $OCH_2CH_2(CH_2)_9CH_3$] 1.91 ["t", J = 6.5 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 3.15 (d, J = 13.5 Hz, 4 H, Ar-CH_2-Ar), 3.88 [t, J = 7.5 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 4.46 (d, J = 13.0 Hz, 4 H, Ar-CH_2-Ar), 6.56–6.61 (m, 12 H, Ar-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1 (q, $OCH_2(CH_2)_{10}CH_3$], 22.7, 26.4, 29.5, 29.8 (two superimposed signals), 29.9 (two superimposed signals), 30.0, 30.4, 31.1 [all t, $OCH_2(CH_2)_{10}CH_3$], 32.0 (t, Ar-CH_2-Ar), 75.2 [t, $OCH_2(CH_2)_{10}CH_3$], 121.9 (d, Ar*C*-H), 128.1 (d, Ar*C*-H), 135.2 (s, Ar*C*-CH_2-Ar), 156.7 (s, Ar*C*-O-) ppm. MS (FAB): *m*/*z* (%) 1097 (12) [M + H]$^+$, 928 (3) [M – $C_{12}H_{24}$]$^+$, 762 (5) [M – $2C_{12}H_{24}$]$^+$, 591 (4) [M – $3C_{12}H_{24}$]$^+$. $C_{76}H_{120}O_4$ (1097.8): calcd. C 83.15, H 11.02; found C 83.10, H 10.90.

***cone*-5,11,17,23-Tetrabromo-25,26,27,28-tetrakis(dodecyloxy)calix-[4]arene (12c):** NBS (1.61 g, 9.03 mmol) was added to a solution of calixarene **11b** (1.03 g,1.06 mmol) in 2-butanone (20 mL) and the mixture stirred for 24 h at room temperature. 2-Butanone (25 mL) was then added and the mixture washed with aqueous 10% $Na_2S_2O_3$ (10 mL), water (2 × 20 mL) and brine (20 mL), and dried with $MgSO_4$. The solvents were removed by rotary evaporation and methanol (8 mL) was added. The precipitate was collected by filtration, washed with methanol (3 × 2 mL) and dried in vacuo to give 1.234 g (82%) of calixarene **12c** as a colourless solid with m.p. 56 °C. IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1}, 2850, 1570, 1456, 1381, 1296, 1253, 1196, 1159, 994, 921, 855, 721. UV/Vis (*n*-hexane): $\lambda_{max.}$ (lgε) = 286 nm (3.8), 278 (3.8). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.89 [t, J = 6.8 Hz, 12 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.27 [m, 72 H, $OCH_2CH_2(CH_2)_9CH_3$] 1.85 ["t", J = 7.0 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 3.08 (d, J = 13.5 Hz, 4 H, Ar-CH_2-Ar), 3.83 [t, J = 7.5 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 4.34 (d, J = 13.6 Hz, 4 H, Ar-CH_2-Ar), 6.80 (s, 8 H, Ar-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1 [q, $OCH_2(CH_2)_{10}CH_3$], 22.7, 26.3, 29.5, 29.8 (two superimposed signals), 29.9 (three superimposed signals), 30.2, 30.8 [all t, $OCH_2(CH_2)_{10}CH_3$], 32.0 (t, Ar-CH_2-Ar), 75.6 [t, $OCH_2(CH_2)_{10}CH_3$], 115.2 (s, Ar*C*–Br), 131.1 (d, Ar*C*-H), 136.5 (s, Ar*C*–CH_2-Ar), 156.7 (s, Ar*C*–O-) ppm. MS (FAB): *m*/*z* (%) 1412 (2) [M + H]$^+$. $C_{76}H_{116}Br_4O_4$ (1413.4): calcd. C 64.59, H 8.27; found C 64.13, H 8.57.

***cone*-25,26,27,28-Tetrakis(dodecyloxy)-5,11,17,23-tetraiodocalix[4]-arene (12d):** A solution of calixarene **11b** (785 mg, 0.72 mmol) in dry chloroform (25 mL) was added dropwise to a boiling suspension of silver trifluoroacetate (642 mg, 2.91 mmol) in dry chloroform (25 mL). The mixture was refluxed for an additional 15 min. Iodine (983 mg, 3.87 mmol) was then added in small portions and refluxed for 20 min. After cooling to room temperature, the mixture was filtered through a pad of Celite 535. The filtrate was washed with 10% aqueous $Na_2S_2O_3$ (60 mL), water (4 × 20 mL) and brine (25 mL), and dried with $MgSO_4$. Solvents were removed by rotary evaporation to give a yellow oil. Purification by flash chromatography (5 g silica gel, light petroleum ether) and subsequent drying in vacuo (60 °C, 0.8 mbar) gave 974 mg (85%) of calixarene **12d** as a colourless solid with m.p. 59 °C. IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1}, 2850, 1563, 1455, 1402, 1380, 1295, 1249, 1195, 1160, 1072, 994, 966, 919, 877, 858, 839, 802, 763, 721, 677, 648, 611, 585, 561, 531. UV/Vis (*n*-hexane): $\lambda_{max.}$ (lgε) = 290 nm (3.5), 280 (3.6). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.89 ppm [t, J = 6.8 Hz, 12 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.27–1.35 [m, 72 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.84 ["t", J = 7.0 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 3.04 (d, J = 13.6 Hz, 4 H, Ar-CH_2-Ar), 3.84 [t, J = 7.6 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 4.28 (d, J = 13.6 Hz, 4 H, Ar-CH_2-Ar), 7.00 (s, 8 H, Ar-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.14 [q, $OCH_2(CH_2)_{10}CH_3$], 22.74, 26.29, 29.45, 29.78, 29.83, 29.92 (three superimposed signals), 30.16, 30.44 [all t, $OCH_2(CH_2)_{10}CH_3$], 31.99 (t, Ar-CH_2-Ar), 75.57 [t, $OCH_2(CH_2)_{10}CH_3$], 86.11 (s, Ar*C*–I), 136.88 (d, Ar*C*-H), 137.19 (s, Ar*C*-CH_2-Ar), 156.45 (s, Ar*C*-O-) ppm. MS (FAB): *m*/*z* (%) 1601 (0.5) [M + H]$^+$. $C_{76}H_{116}I_4O_4 \cdot C_5H_{12}$ (1673.5): calcd. C 58.13, H 7.71; found C 57.73, H 7.71.

***cone*-5-Bromo-11,17,23-tris[(2-phenyl)phenyl]-25,26,27,28-tetrakis-(propyloxy)calix[4]arene (14b):** Calixarene **12b** (602 mg, 0.38 mmol) and 2-diphenylboronic acid (1.112 g, 5.62 mmol) were dissolved in a mixture of THF (18 mL) and an aqueous 2 N potassium carbonate solution (18 mL). Tetrakis(triphenylphosphane)palladium(0)

(194 mg, 160 μmol) was then added and the reaction mixture refluxed for 26 h. After cooling to room temperature the layers were separated and dichloromethane (10 mL) added to the organic layer. The organic layer was washed with water (2 × 10 mL), brine (10 mL) and dried with $MgSO_4$. The solvents were then removed by rotary evaporation to give a brown residue. TLC (light petroleum ether/ethyl acetate, 8:1): R_f = 0.55, 0.45 (**14a**, **14b**, **4a**), 0.30, 0.18, 0.03, 0.55. Separation by column chromatography (light petroleum ether/ethyl acetate, 20:1) gave 712 mg of the ternary calixarene mixture (**14a**, **14b**, **4a**). Further fractional crystallisation allowed calixarene **14b** to be enriched to a grade of purity >93%. Yield: 291 mg (39%) with m.p. 220–225 °C. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1}, 3021, 2960, 2932, 2873, 1948, 1596, 1572, 1484, 1463, 1432, 1384, 1322, 1287, 1225, 1196, 1180, 1164, 1113, 1074, 1045, 1034, 1008, 965, 904, 880, 864, 777, 762, 743, 699, 637, 614, 598, 559. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (lgε) = 273 nm (sh, 4.5), 231 (5.1). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.3 Hz, 6 H, $OCH_2CH_2CH_3$), 1.01 (t, J = 7.3 Hz, 3 H, $OCH_2CH_2CH_3$), 1.06 (t, J = 7.3 Hz, 3 H, $OCH_2CH_2CH_3$), 1.81 (sext, J = 7.4 Hz, 4 H, $OCH_2CH_2CH_3$), 1.91 (m, 4 H, $OCH_2CH_2CH_3$), 2.85 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 2.86 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 3.53 (t, J = 7.0 Hz, 2 H, $OCH_2C_2H_5$), 3.60 (t, J = 7.3 Hz, 2 H, $OCH_2C_2H_5$), 4.00 (m, 4 H, two superimposed signals, $OCH_2C_2H_5$), 4.27 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 4.30 (d, J = 13.0 Hz, 2 H, Ar-CH_2-Ar), 5.92 (s, 2 H, Ar*H*), 6.16 (s, 2 H, BrAr*H*), 6.71 (d, J = 2.0 Hz, 2 H, Ar*H*), 6.80 (d, J = 2.0 Hz, 2 H, Ar*H*), 6.95–7.05 (m, Ar*H*), 7.09 (t, J = 7.5 Hz, Ar*H*), 7.18 (d, J = 7.0 Hz, Ar*H*), 7.28–7.41 (m, Ar*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.59 ($OCH_2CH_2CH_3$), 10.38 ($OCH_2CH_2CH_3$), 10.58 ($OCH_2CH_2CH_3$), 22.45 ($OCH_2CH_2CH_3$), 23.06 ($OCH_2CH_2CH_3$), 23.11 ($OCH_2CH_2CH_3$), 30.77 (t, Ar-CH_2-Ar), 30.88 (t, Ar-CH_2-Ar), 76.02 ($OCH_2CH_2CH_3$), 76.06 ($OCH_2CH_2CH_3$), 76.94 ($OCH_2CH_2CH_3$), 114.56 (s, Ar*C*-Br), 125.56, 126.35, 126.60, 126.66, 126.93, 126.99, 127.06, 127.19, 127.83, 128.87, 129.45, 129.49, 129.89, 129.93, 130.26, 130.44, 130.61 (all d, all Ar*C*-H), 131.50, 134.61, 134.97, 135.05, 135.19, 135.90, 139.98, 140.14, 140.22, 140.93, 141.37, 141.66, 141.97 (all s), 153.92, 154.40 (both s, both Ar*C*-O-), 156.02 (s, BrAr*C*-O-) ppm. MS (FAB): *m*/*z* (%) 1201 (23) (impurity of **4a**), 1129 (22) [M^+]. $C_{76}H_{71}BrO_4$ (1128.3): calcd. C 80.90, H 6.34; found C 80.53, H 6.58.

***cone*-5,11,17,23-Tetrakis[(2-phenyl)phenyl]-25,26,27,28-tetrakis(propyloxy)calix[4]arene (4a). a) From Iodocalixarene 12b:** Calixarene **12b** (415 mg,0.38 mmol) and 2-diphenylboronic acid (600 mg, 3.03 mmol) were dissolved in a mixture of THF (10 mL) and an aqueous 2 N potassium carbonate solution (10 mL). Tetrakis(triphenylphosphane)palladium(0) (105 mg, 90 μmol) was then added and the reaction mixture refluxed for 16 h. After cooling to room temperature the layers were separated and dichloromethane (10 mL) was added to the organic layer. The organic layer was washed with water (2 × 10 mL), brine (10 mL) and dried with $MgSO_4$. Solvents were removed by rotary evaporation to give a brown residue. TLC (light petroleum ether/ethyl acetate, 8:1): R_f = 0.03, 0.18, 0.30, 0.45 (**4a**), 0.55. Separation by column chromatography (PE/EA, 20:1) gave 223 mg (49%) of calixarene **4a**.

b) From Tetrabromocalixarene 12a: Calixarene **12a** (399 mg, 0.44 mmol) and 2-diphenylboronic acid (752 mg, 3.79 mmol) were dissolved in a mixture of THF (10 mL) and an aqueous 2 N potassium carbonate solution (10 mL) in a 50-mL, screw-capped vessel. Tetrakis(triphenylphosphane)palladium(0) (132 mg, 110 μmol) was added and the reaction mixture heated to 120 °C for 21 h. After workup, 440 mg (83%) of calixarene **4a** was isolated as colourless crystals with m.p. 178–186 °C. IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 3021, 2959, 2929, 2873, 1596, 1463, 1432, 1384, 1322, 1285, 1226, 1179, 1161, 1115, 1074, 1043, 1008, 965, 884, 777, 761, 743, 700, 615. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (lgε) = 272 nm (sh, 4.4), 234 (4.9). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.5 Hz, 12 H, $OCH_2CH_2CH_3$), 1.88 (m, J = 7.5 Hz, 8 H, $OCH_2CH_2CH_3$), 2.74 (d, J = 12.5 Hz, 4 H, Ar-CH_2-Ar), 3.77 (t, J = 7.5 Hz, 8 H, $OCH_2C_2H_5$), 4.24 (d, J = 12.5 Hz, 4 H, Ar-CH_2-Ar), 6.31 (s, 8 H, Ar-*H*), 6.92–7.03 (m, 24 H, Ar′-H), 7.19 (dt, J = 1.7, 6.9 Hz, 4 H, Ar′-H), 7.30–7.31 (m, 8 H, Ar′-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.1 ppm ($OCH_2CH_2CH_3$), 22.8 ($OCH_2CH_2CH_3$), 30.7 (t, Ar-CH_2-Ar), 76.7 (t, $OCH_2CH_2CH_3$), 125.8, 126.4, 126.9, 127.2, 129.4, 129.8, 130.2 (all d, Ar*C*-H), 133.5 (s), 134.5 (s, Ar*C*-CH_2-Ar), 140.0, 140.5, 141.6 (all s), 154.9 (s, Ar*C*-O-) ppm. MS (FAB): *m*/*z* (%) 1201 (58) [M + H]$^+$. $C_{88}H_{80}O_4$ (1201.6): calcd. C 87.96, H 6.71; found C 87.66, H 6.38.

***cone*-25,26,27,28-Tetrakis(dodecyloxy)-5,11,17,23-tetrakis[(2-phenyl)phenyl]calix[4]arene (4b). a) From Tetraiodocalixarene 12d:** Calixarene **12d** (910 mg, 0.57 mmol) and 2-diphenylboronic acid (967 mg, 4.88 mmol) gave 298 mg (31%) of calixarene **4b** under the same conditions described for **4a**.

b) From Tetrabromocalixarene 12c: Calixarene **12c** (334 mg, 0.23 mmol) and 2-diphenylboronic acid (327 mg, 1.65 mmol), under the same conditions as described for **4a**, gave 355 mg (91%) of calixarene **4b** as a colourless solid with m.p. 88–93 °C. IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 3021, 2919, 2849, 1595, 1464, 1433, 1380, 1323, 1285, 1231, 1176, 1116, 1079, 1009, 888, 762, 744, 722, 700, 615, 558. UV/Vis (*n*-hexane): $\lambda_{max.}$ (lgε) = 262 nm (sh, 4.7), 243 (4.7). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.90 [t, J = 6.8 Hz, 12 H, $OCH_2(CH_2)_{10}CH_3$], 1.29, 1.36 [both br. "s", 72 H, $OCH_2CH_2(CH_2)_9CH_3$], 1.86 [br. "t", 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 2.74 (d, J = 13.0 Hz, 4 H, Ar-CH_2-Ar), 3.80 [t, J = 7.2 Hz, 8 H, $OCH_2CH_2(CH_2)_9CH_3$], 4.24 (d, J = 13.0 Hz, 4 H, Ar-CH_2-Ar), 6.31 (s, 8 H, Ar*H*), 6.89–7.04 (m, 24 H, Ar′*H*), 7.20 (dt, J = 1.7, J = 6.9 Hz, 4 H, Ar′*H*), 7.29–7.34 (m, 8 H, Ar′*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.14 [q, $OCH_2CH_2(CH_2)_9CH_3$], 22.75 [t, $OCH_2CH_2(CH_2)_9CH_3$], 26.47, 29.49, 29.82, 29.89, 29.93, 30.05, 30.20 [all t, $OCH_2CH_2(CH_2)_9CH_3$], 31.08 (t, Ar-CH_2-Ar), 32.01 [t, $OCH_2CH_2(CH_2)_9CH_3$], 75.19 [t, $OCH_2CH_2(CH_2)_9CH_3$], 126.17, 126.71, 127.21, 127.48, 129.69, 130.15, 130.50 (all d, Ar*C*-H), 133.82 (s), 134.79 (s, Ar*C*-CH_2-Ar), 140.27, 140.84, 141.86 (all s), 154.22 (s, Ar*C*-O-) ppm. MS (FAB): *m*/*z* (%) 1706 (1.7) [M^+]. $C_{124}H_{152}O_4$ (1706.6): calcd. C 87.27, H 8.98; found C 86.89, H 9.15.

***cone*-5-[(2-Phenyl)phenyl]-25,26,27,28-tetrakis(propyloxy)calix[4]arene (16):** Calixarene **15** (656 mg, 0.98 mmol) and 2-diphenylboronic acid (318 mg, 1.61 mmol) were dissolved in a mixture of THF (20 mL) and an aqueous 2 N potassium carbonate solution (20 mL) in a screw-capped vessel. Tetrakis(triphenylphosphane)palladium(0) (132 mg,110 μmol) was then added and the reaction mixture heated at 120 °C for 21 h. After cooling to room temperature dichloromethane (50 mL) was added and the layers separated. The organic layer was washed with water (2 × 50 mL) and brine (50 mL) and dried with magnesium sulfate. Solvents were removed by rotary evaporation to give 1.020 g of an orange-coloured solid. Dichloromethane (15 mL) was added and the insoluble material filtered off. The dichloromethane was removed by rotary evaporation, methanol (15 mL) was added to the residue and the mixture ultra-sonicated. The resulting solid was collected by filtration, washed with methanol (3 × 2 mL) and dried in vacuo to give 726 mg (99%) of calixarene **16** as a colourless solid with a high grade of purity (>95%). Purification by flash chromatography (light petroleum ether/ethyl acetate, 15:1, R_f = 0.40) and subsequent drying in vacuo (0.6 mbar, 120 °C) gave 635 mg (87%) of calixarene **16** as a colour-

less solid with m.p. 169–171 °C. IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2963, 2920, 2874, 1587, 1456, 1432, 1383, 1288, 1248, 1225, 1211, 1194, 1156, 1088, 1067, 1034, 1008, 967, 884, 844, 798, 756, 743, 701, 668, 627, 498. UV/Vis (*n*-hexane): $\lambda_{max.}$ (lgε) = 265 nm (sh, 4.1), 216 (4.8). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.5 Hz, 3 H, $OCH_2CH_2CH_3$), 0.93 (t, *J* = 7.4 Hz, 3 H, $OCH_2CH_2CH_3$), 1.06 (t, *J* = 7.3 Hz, 6 H, $OCH_2CH_2CH_3$), 1.87 (sext, *J* = 7.2 Hz, 4 H, $OCH_2CH_2CH_3$), 1.95 ("sext", "*J*" = 7.7 Hz, 4 H, $OCH_2CH_2CH_3$), 2.97 (d, *J* = 13.4 Hz, 2 H, Ar′CH_2Ar), 3.14 (d, *J* = 13.4 Hz, 2 H, Ar′CH_2Ar′′), 3.69 (t, *J* = 7.0 Hz, 4 H, $OCH_2CH_2CH_3$), 3.95 (t, *J* = 7.8 Hz, 2 H, $OCH_2CH_2CH_3$), 3.98 (t, *J* = 7.8 Hz, 2 H, $OCH_2CH_2CH_3$), 4.37 (d, *J* = 13.2 Hz, 2 H, Ar′-CH_2Ar), 4.44 (d, *J* = 13.4 Hz, 2 H, Ar′CH_2Ar′′), 5.86 (d, *J* = 6.6 Hz, 2 H, Ar′-3-H), 6.25 (d, *J* = 6.3 Hz, 2 H, Ar′-5-H), 6.31 (t, *J* = 7.5 Hz, 2 H, Ar′-4-H), 6.74 (s, 2 H, Ar-3/5-H), 6.81 (t, *J* = 7.5 Hz, 1 H, Ar′′-4-H), 6.98 (d, *J* = 7.4 Hz, 2 H, Ar′′-3/5-H), 7.22–7.25 (m, 6 H, diphenyl-*H*), 7.30–7.33 (m, 1 H, diphenyl-*H*), 7.36–7.42 (m, 3 H, diphenyl-*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.99, 10.03, 10.71 (all q, all $OCH_2CH_2CH_3$), 23.08, 23.13, 23.47 (all t, all $OCH_2CH_2CH_3$), 30.88 (t, Ar-CH_2Ar′), 31.03 (t, Ar′-CH_2Ar′′), 76.50, 76.56, 76.87 (all t, all $OCH_2CH_2CH_3$), 121.79 (d, Ar′′-C-4), 121.98 (d, Ar′-C-4), 126.12 (d, diphenyl-C), 126.88 (s, Ar-C-4), 127.12 (d, diphenyl-C), 127.49 (d, Ar′-C-5), 127.88 (d, Ar′-C-3), 127.94 (d, diphenyl-C), 128.71 (d, Ar′′-C-3/5), 130.01 (d, diphenyl-C), 130.36 (d, Ar-C-3/5), 130.53 (d, diphenyl-C), 133.54 (s, Ar′*C*-CH_2-Ar), 133.61 (s, Ar′*C*-CH_2-Ar′′), 135.91 (s, Ar*C*-CH_2-Ar′), 136.61 (s, Ar′′*C*-CH_2-Ar′), 140.87 (s, diphenyl-C), 141.23 (s, diphenyl-C), 142.16 (s, diphenyl-C), 155.51 (s, Ar′*C*-O-), 156.42 (s, Ar*C*-O-), 157.66 (s, Ar′′*C*-O) ppm. MS (FAB): *m*/*z* (%) 768 (11) [M + Na^+], 745 (100) [M + H^+]. $C_{52}H_{56}O_4$ (745.01): calcd. C 83.83, H 7.57; found C 83.77, H 7.83.

2,6-Dimethyl-4-(phenylethynyl)propyloxybenzene (19): A solution of bromophenol ether (**18**; 624 mg, 2.57 mmol) and phenylacetylene (680 mg, 6.66 mmol) in trimethylamine (10 mL) was degassed with argon for 10 min then [$PdCl_2(PPh_3)_2$] (92 mg, 0.13 mmol) and CuI (45 mg, 0.24 mmol) were added and the reaction mixture heated for 24 h at 90 °C. After cooling to room temperature dichloromethane (25 mL) was added and the mixture washed with water (4 × 25 mL) and brine (25 mL). Dichloromethane was removed by rotary evaporation to give a brown residue. TLC (light petroleum ether/CH_2Cl_2, 4:1): R_f = 0.03, 0.12 (**19**), 0.33. Purification by flash chromatography (light petroleum ether/CH_2Cl_2, 10:1) gave 533 mg (79%) of **19** as a pale-yellow solid with m.p. 58–61 °C. IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1}, 2957, 2924, 2872, 2328, 2212, 1725, 1594, 1491, 1441, 1383, 1337, 1277, 1238, 1201, 1120, 1068, 1025, 963, 915, 886, 866, 816, 754, 691, 609, 525, 414. UV/Vis (CH_3CN): $\lambda_{max.}$ (lgε) = 207 nm (4.3), 284 (4.3), 301(4.3). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.5 Hz, 3 H, $OCH_2CH_2CH_3$), 1.86 (sext, *J* = 7.1 Hz, 2 H, $OCH_2CH_2CH_3$), 2.30 (s, 6 H, Ar-CH_3), 3.76 (t, *J* = 7.3 Hz, 2 H, $ArOCH_2C_2H_5$), 7.23 (s, 2 H, ArH),7.35 (m, 3 H, Ar′H), 7.52 (m, 2 H, Ar′H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.6 (q, $OCH_2CH_2CH_3$), 16.2 (t, $OCH_2CH_2CH_3$), 23.7 (t, Ar-CH_3), 74.0 (t, $OCH_2CH_2CH_3$), 88.2 (s, Ar*C*CAr′), 89.5 (s, ArC*C*Ar′), 118.2 (s), 123.6 (s), 128.0 (d), 128.3 (d), 131.2 (s), 131.5 (d), 132.1 (d), 156.5 (s, Ar*C*-O-) ppm. MS (EI): *m*/*z* (%) 265 (10) [M + 1]$^+$, 264 (48) [M]$^+$, 223 (18), 222 (100), 221 (17), 189 (5), 115 (5), 59 (7), 43 (9), 41 (9), 27 (7). $C_{19}H_{20}O$ (264.37): calcd. C 86.32, H 7.62; found C 86.24, H 7.76.

2,6-Dimethyl-4-[(2,3,4,5,6-pentaphenyl)phenyl]propyloxybenzene (20): A solution of tolane (**19**; 783 mg, 2.97 mmol) and tetracyclone (**6**; 1.229 g, 3.20 mmol) in diphenyl ether (4 mL) was heated for 3 d at 190 °C. After cooling to room temperature, methanol (5 mL) was added to precipitate about 1.1 g of an off-white solid. TLC (light petroleum ether/ethyl acetate, 10:1): R_f = 0.09, 0.18, 0.27, 0.36 (**20**). Separation by column chromatography (light petroleum ether/ethyl acetate, 20:1) and washing of the resulting solid with light petroleum ether gave 960 mg (52%) of **20** as a colourless solid with m.p. 243–245 °C. IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 3024, 2961, 2927, 2329, 1941, 1600, 1495, 1441, 1403, 1384, 1278, 1221, 1186, 1134, 1070, 1028, 1011, 966, 906, 878, 814, 779, 755, 736, 698, 611. UV/Vis (CH_3CN): $\lambda_{max.}$ (lgε) = 216 nm (4.6), 243 (4.6), 271 (4.0, sh). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.3 Hz, 3 H, $OCH_2CH_2CH_3$), 1.66 (sext, *J* = 7.3 Hz, 2 H, $OCH_2CH_2CH_3$), 1.87 (s, 6 H, Ar-CH_3), 3.47 (t, *J* = 7.3 Hz, 2 H, $ArOCH_2C_2H_5$), 6.38 (s, 2 H, ArH), 6.81 (m, 25 H, Ar′H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.6 (q, $OCH_2CH_2CH_3$), 15.8 (t, $OCH_2CH_2CH_3$), 23.5 (t, Ar-CH_3), 73.6 (t, $OCH_2CH_2CH_3$), 125.0, 125.1, 126.4, 126.5 (all s), 128.5 (s), 131.4, 131.5, 132.1 (all d), 135.6 (s), 140.0, 140.1, 140.2 (all d), 140.4 (s), 140.7 (s), 140.8 (s, five superimposed signals), 153.3 (s, Ar*C*-O-) ppm. MS (FAB): *m*/*z* (%) 622 (11) [M + 2]$^+$, 621 (36) [M + 1]$^+$, 620 (33) [M]$^+$, 578 (6). $C_{47}H_{40}O{\cdot}1/4CH_2Cl_2$ (642.06): calcd. C 88.39, H 6.36; found C 88.60, H 6.36.

1,3-Dimethyl-2-(propyloxy)hexa-*peri*-hexabenzocoronene (21): Polyphenyl **20** (130 mg, 0.21 mmol) was dissolved in dry dichloromethane (100 mL) and degassed with argon (15 min). A solution of iron(III) chloride (1.36 g, 8.40 mmol) in dry nitromethane (20 mL) was added dropwise with a syringe and the mixture stirred for an additional 50 min at room temperature. During the whole reaction time a moderate stream of argon was bubbled through the reaction mixture. Methanol (100 mL) was added, the volume reduced to about 20 mL by rotary evaporation and water (50 mL) added. The resulting precipitate was filtered off and washed with water (6 × 5 mL) and methanol (6 × 3 mL) to give, after drying, about 80 mg of a green-yellow solid. Impurities were removed by column chromatography (10 g silica gel and 500 mL petroleum ether/CH_2Cl_2, 5:2). The dried silica gel was extracted with a Soxhlet apparatus and dichloromethane (20 h). The dichloromethane was then removed by rotary evaporation to give, after drying in vacuo, 52 mg (41%) of **21** as a yellow solid with m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2962, 2923, 2848, 1456, 1371, 1313, 1261, 1180, 1155, 1075, 882, 801, 759, 739. UV/Vis (benzene): $\lambda_{max.}$ (lgε) = 328 nm (sh, 4.0), 344 (4.4), 360 (4.8), 391 (4.3), 403 (sh, 3.8) ppm. MS (MALDI-TOF): *m*/*z* (calcd.) 608.21 (100), 609.21 (53), 610.22 (14); *m*/*z* (found) 608.81 (100), 609.68 (55), 610.84 (13).

***syn,syn*-28-Hydroxy-5-[(2-phenyl)phenyl]-25,26,27-tris(propyloxy)calix[4]arene (23b) and *syn,syn*-26-Hydroxy-5-[(2-phenyl)phenyl]-25,27,28-tris(propyloxy)calix[4]arene (23a):** $MoCl_5$ (153 mg, 0.56 mmol) was added to a cooled (0 °C) solution of calixarene **16** (100 mg, 0.13 mmol) in dry dichloromethane (10 mL) under argon and the mixture stirred at 0 °C for 1.75 h. Saturated aqueous $NaHCO_3$ solution (25 mL) was added, the layers separated and the aqueous layer extracted with dichloromethane (25 mL). The combined organic layers were washed with water (25 mL) and brine (25 mL) and dried with magnesium sulfate. Dichloromethane was removed by rotary evaporation to give 83 mg of a brown solid. Separation by flash chromatography (light petroleum ether/ethyl acetate, 50:1) and subsequent recrystallization from 2-propanol gave, from the mother liquor, 53 mg (58%) of a 1:1 mixture[22] of **23a** and **23b** as a colourless solid with m.p. 94–98 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.93 (t, 6 H, $OCH_2CH_2CH_3$), 1.10 ("t", 12 H, $OCH_2CH_2CH_3$), 1.88 ("sept", 8 H, $OCH_2CH_2CH_3$), 2.27 (sext, 4 H, $OCH_2CH_2CH_3$), 3.05 (d, *J* = 12.8 Hz, 2 H, ArCH_2Ar), 3.11 (d, *J* = 13.4 Hz, 2 H, ArCH_2Ar), 3.21 (d, *J* = 13.2 Hz, 2 H, ArCH_2Ar), 3.29 (d, *J* = 13.9 Hz, 2 H, ArCH_2Ar), 3.67–3.75 (m, 8 H, $OCH_2CH_2CH_3$), 3.82–3.87 (m, 4 H, $OCH_2CH_2CH_3$), 4.31 (d, *J* = 14.1 Hz, 2 H, ArCH_2Ar), 4.34 (d, *J* = 12.9 Hz, 2 H, ArCH_2Ar),

4.38 (d, J = 13.2 Hz, 2 H, ArCH_2Ar), 4.41 (d, J = 13.2 Hz, 2 H, ArCH_2Ar), 4.58 (s, 1 H, -O*H*), 4.61 (s, 1 H, -O*H*), 5.89 (dd, ^3J = 7.1, ^4J = 2.0 Hz, 2 H, Ar′-3-H), 6.02 (dd, ^3J = 6.7, ^4J = 2.4 Hz, 2 H, Ar′′-3-H), 6.35–6.41 (m, 8 H, Ar′-4/5-H und Ar′′-4/5-H), 6.79 (s, 1 H, Ar-*m*H), 6.87 (s, 1 H, Ar-*m*H), 7.11 (d, 2 = H, J = 7.3 Hz, Ar′′′-4-H), 7.17–7.26 (m, 12 H, Ar′′′-H and biphenyl-H), 7.39–7.50 (m, 8 H, biphenyl-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.63, 10.83 (both q, both -OCH$_2$CH$_2$*C*H$_3$), 22.38, 23.46, 25.41 (all t, all -OCH$_2$*C*H$_2$CH$_3$), 30.52, 30.62, 30.77, 30.81 (all t, all Ar-*C*H$_2$-Ar), 76.57, 76.61, 77.51 (all t, all -O*C*H$_2$CH$_2$CH$_3$), 119.30, 122.88, 122.93, 122.97, 125.98, 126.09, 126.90, 127.22, 127.28, 127.47, 127.68, 127.80, 127.94, 128.05, 128.14, 128.42, 129.21, 129.76, 129.99, 130.05, 130.42, 130.50, 130.84, 130.89, 131.37 (d), 132.49, 132.53, 132.80, 133.24, 133.31, 136.46, 136.73, 137.28, 140.81, 140.89, 140.97, 141.20, 141.97, 142.20 (all s), 152.07, 153.36, 154.33, 154.42, 155.63, 156.97 (all s, all Ar*C*O) ppm. MS (FAB): *m/z* (%) 703 (79) [M + H$^+$], 661 (10) [M – C_3H_6]$^+$.

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR spectrum of calixarene **3**. ^{1}H NMR spectrum of calixarene **8**. Crystal structures of **4a** and **16**. MALDI-TOF mass spectra of benzocoronene **21**, the solid (crude material) resulting from the cyclodehydration of calixarene **3** and the solid (crude material) resulting from the cyclodehydration of calixarene **4a**.

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