Substituted Tetraoxa[8]circulenes – New Members of the Liquid Crystal Family

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A general method for the synthesis of substituted tetraoxa-[8]circulenes based on alkylation of 2,3-bis(bromomethyl)-1,4-dimethoxybenzene with acetylides is reported. Four of the compounds shows LC behavior, and the tetraoxa[8]circulenes are thus new candidates for discotic mesogens.

Introduction

The family of circulenes has gained renewed interest in recent years following the discovery of the fullerenes.[1,2] They can be viewed as fragments (or slices) of fullerenes. All circulenes except [6]circulene are nonplanar, and can thus serve as models for the study of aromaticity in nonplanar systems. Graphite slices are also of high current interest as candidates for discotic liquid crystals.[3,4] Discotic liquid crystals are interesting candidates for molecular wires[5] for nanoscale electronics, sensors,[6] components for solar cells[7] or components for LED display applications.[8]

One of the missing links[9] in the circulene family is [8]circulene (Figure 1), which has been predicted to be aromatic[10] but nonplanar possessing a D_{2d} symmetry.[11] However, the corresponding oxygen analogue has been known for a number of years,[12] although an investigation of the properties of the tetraoxa[8]circulenes has so far been hampered by the extremely low solubility of the few derivatives known.[13]

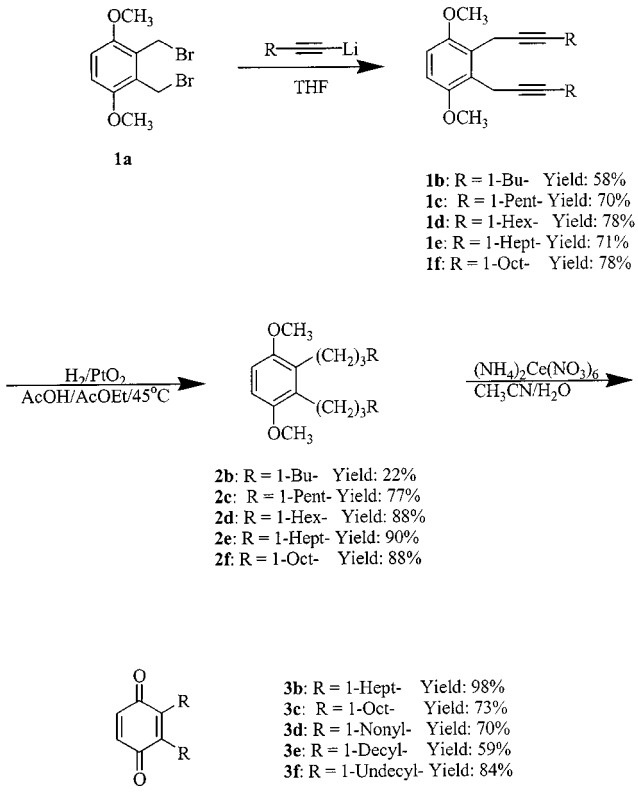
Figure 1. [8]Circulene and Tetraoxa[8]circulene

Results and Discussion

Synthesis

Tetraoxa[8]circulenes were originally isolated from the oligomerization reaction of 1,4-benzo- and naphthoquinones with various Lewis acids.[12,13] Their isolation was facilitated by an extremely low solubility. It was thus an open question as to whether circulenes would be formed or would be the terminal product from oligomerization of 2,3-disubstituted 1,4-benzoquinones substituted with solubilizing long chains. There were no general methods described for the synthesis of 2,3-disubstituted 1,4-benzoquinones, so our initial efforts were concentrated on developing a suitable method.

Our synthetic approach is outlined in Scheme 1, and starts from 2,3-bis(bromomethyl)-1,4-dimethoxybenzene[14,15] (**1a**). In order to attach solubilizing chains, coupling with a number of organometallic reagents was attempted, but the only procedure that worked in a satisfactory yield was reaction with an acetylide followed by reduction of the triple bonds. Conversion of the 1,4-



Scheme 1. Synthesis of 2,3-dialkyl-1,4-benzoquinones from 2,3-bis-(bromomethyl)-1,4-dimethoxybenzene

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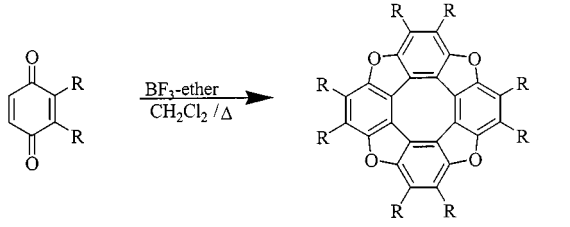
dimethoxybenzenes (**2b**–**f**) to the corresponding quinones was easily performed by oxidation with cerium ammonium nitrate (CAN) in wet acetonitrile.[16] In order to do comparative studies of our compounds with a known tetraoxacirculene, we prepared 2,3-dipropyl-1,4-benzoquinone (**2a**) by the procedure of Fieser, Campbell and Fry.[17]

Tetramerization could either be affected using the reported conditions with $AlCl_3$ in hot nitrobenzene, or by reflux of benzoquinones with BF_3–diethyl ether in CH_2Cl_2 (Scheme 2).



4a: R = 1-Propyl- Yield: 20 %
4b: R = 1-Heptyl- Yield: 44 %
4c: R = 1-Octyl- Yield: 11 %
4d: R = 1-Nonyl- Yield: 26 %
4e: R = 1-Decyl- Yield: 39 %
4f: R = 1-Undecanyl- Yield: 56 %

Scheme 2. Tetramerization of 2,3-dialkyl-1,4-benzoquinones to tetraoxa[8]circulenes

Physical Properties

The synthesized tetraoxacirculenes were investigated by differential scanning calorimetry (DSC). The results are shown in Table 1. Going from the octapropyl compound (**4a**) to the octaheptyl compound (**4b**) caused a significant change in behavior. Compound **4b** undergoes two phase transitions as shown in Table 1 and Figure 2, and shows typical liquid crystalline (LC) behavior such as shearability and birefringence. A further increase in the chain length gave lower transition temperatures from the crystalline to the LC state, but the transition temperature from the LC to the isotropic phase was lowered as well. The magnitude of the measured ΔH values for compounds **4a–d** are of the same order as those reported[18] for columnar mesophases, which are expected to be very crystal-like. However, further investigations are necessary to identify the exact type of mesophase present. Compound **4f**, with 8 undecyl groups, did not show any signs of phase transitions in DSC or any signs of LC behaviour by optical microscopy.

Table 1. Phase transition temperatures of **4a–f** from DSC; heating rate: 20 K/min

Compound	T_1 [°C]	T_2 [°C]	ΔH_1 [kJ/mol]	ΔH_2 [kJ/mol]
4a	333	–	–	–
4b	193	220	28	30
4c	160	183	27	16
4d	148	169	38	14
4e	133	165	53	26
4f	<0	>350	–	–

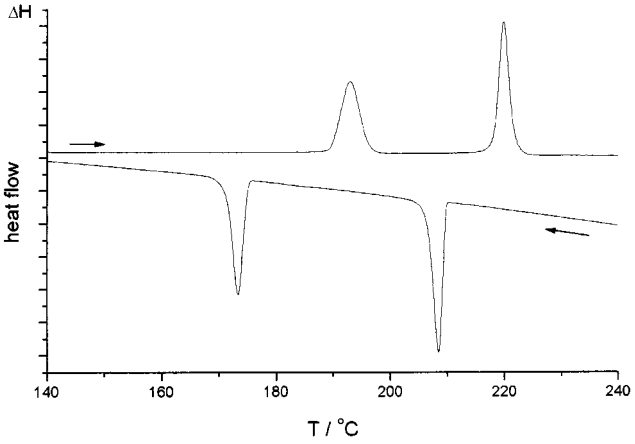


Figure 2. DSC of **4b**; heating/cooling rate: 20 K/min

Conclusion

A method for the synthesis of alkyl-substituted tetraoxa[8]circulenes has been developed, and preliminary results indicate that these compounds can show liquid crystalline behavior. This will be the topic of further investigations.

Experimental Section

General Remarks: THF and diethyl ether were dried by distillation from sodium benzophenone prior to use. – NMR spectra were recorded in $CDCl_3$ with a Bruker AM 250-MHz or a Varian Unity 400-MHz spectrometer, and all chemical shifts are relative to TMS. – GC-MS were recorded with a Hewlett–Packard 5890 Series II instrument with a 5972 series detector, fitted with a 30 m × 0.25 m HP, 5 M.S. (0.25μm, crosslinked 5% Ph Me Silicone) column. – Mass spectra were recorded with a Jeol JMS-HX/HX 110A Tandem Mass Spectrometer.

2,3-Bis(2′-heptynyl)-1,4-dimethoxybenzene (1b): To a solution of 1-hexyne (8.11 g, 98.7 mmol) in THF (150 mL) at –78 °C was added 2.5 M *n*BuLi in hexane (28 mL, 67.2 mmol) over 10 min. The cooling bath was removed, and the mixture was stirred for a further 1.5 h. Cooling was applied again, and a solution of 2,3-bis(bromomethyl)-1,4-dimethoxybenzene[14,15] (9.00 g, 27.8 mmol) in THF (80 mL) was added over 30 min. The mixture was stirred at room temperature overnight and heated to 50 °C for another 24 hours. Brine (100 mL) was added, and the mixture was extracted with ether (4 × 100 mL). After drying and removal of solvents in vacuo, the residue was purified by column chromatography on silica gel (nC_7H_{16}/EtOAc, 25:1; R_f = 0.52) to give the product as a yellow oil. Yield: 5.28 g (58%). – ^{1}H NMR: δ = 6.74 (s, 2 H), 3.81 (s, 6 H), 3.71 (t, J = 2.5 Hz, 4 H), 2.09–2.14 (m, 4 H), 1.25–1.48 (m, 8 H), 0.88 (t, J = 7.1 Hz, 6 H). – ^{13}C NMR: δ = 151.2, 126.7, 109.7, 79.4, 77.6, 56.2, 31.0, 21.8, 18.5, 15.2, 13.4. – GC MS; *m/z* (%): 326 (43), 311 (61), 283 (100), 269 (66), 227 (82). – $C_{22}H_{30}O_2$ (326.48): C 80.94, H 9.26; found C 80.58, H 9.33.

1,4-Dimethoxy-2,3-bis(2′-octynyl)benzene (1c): This compound was prepared from 1-heptyne by the procedure described for compound **1b**, with the exception that the product was purified by column

chromatography on silica gel with pentane as eluent followed by kugelrohr distillation: 170°C/0.3 Torr. Yield: 4.96 g (70%). Crystalline compound. M.p. 32–33°C. – ^{1}H NMR: δ = 6.70 (s, 2 H), 3.81 (s, 6 H), 3.71 (t, J = 2.5 Hz, 4 H), 2.09 (m, 4 H), 1.46 (m, 4 H), 1.30 (m, 8 H), 0.88 (t, J = 7.5 Hz, 6 H). – ^{13}C NMR: δ = 151.2, 126.7, 109.8, 79.5, 77.6, 56.4, 30.0, 28.6, 22.1, 18.8, 15.3, 13.8. – GC-MS; *m*/*z* (%): 354 (35), 339 (35), 297 (80), 283 (55), 227 (90), 201 (70), 173 (45). – $C_{24}H_{34}O_2$ (354.53): C 81.31, H 9.67; found C 80.92, H 9.84.

1,4-Dimethoxy-2,3-bis(2′-nonynyl)benzene (1d): This compound was prepared from 1-octyne by the procedure described for compound **1b**, with the exception that the product was purified by kugelrohr distillation: 200°C/0.5 Torr followed by crystallization from MeOH. Yield: 12.6 g (78%). Yellow crystals. M.p. 39–41°C. – ^{1}H NMR: δ = 6.73 (s, 2 H), 3.79 (s, 6 H), 3.72 (t, J = 1.4 Hz, 4 H), 2.06 (m, 4 H), 1.43 (m, 4 H), 1.22–1.40 (m, 12 H), 0.87 (t, J = 7.1 Hz, 6 H). – ^{13}C NMR: δ = 151.2, 126.8, 109.8, 79.6, 77.6, 56.3, 31.3, 28.9, 28.5, 22.5, 18.8, 15.3, 13.9. – GC-MS; *m*/*z* (%): 382 (50), 311 (95), 241 (50), 227 (95). – $C_{26}H_{38}O_2$ (382.59): C 81.62, H 10.01; found C 81.20, H 10.54.

2,3-Bis(2′-decynyl)-1,4-dimethoxybenzene (1e): This compound was prepared from 1-nonyne[19] by the procedure described for compound **1b**, with the exception that the product was purified by crystallization from MeOH. Yield: 3.4 g (71%). Yellow crystals. M.p. 44–46°C. – ^{1}H NMR: δ = 6.74 (s, 2 H), 3.80 (s, 6 H), 3.69 (t, J = 2.4 Hz, 4 H), 2.09 (m, 4 H), 1.47 (m, 4 H), 1.25–1.42 (m, 20 H), 0.87 (t, J = 7.0 Hz, 6 H). – ^{13}C NMR: δ = 151.2, 126.8, 109.9, 77.2, 76.9, 76.6, 56.4, 31.7, 28.9, 28.8, 28.7, 22.5, 18.9, 15.3, 14.0. – GC MS; *m*/*z* (%): 410 (45), 395 (15), 325 (85), 227 (93). – $C_{28}H_{42}O_2$ (410.64): C 81.90, H 10.31; found C 81.60, H 10.53.

1,4-Dimethoxy-2,3-bis(2′-undecynyl)benzene (1f): This compound was prepared from 1-decyne[19] by the procedure described for compound **1b**, with the exception that the product was purified by crystallization from MeOH. Yield: 2.5 g (78%). White crystalline compound. M.p. 54.3–54.9°C. – ^{1}H NMR: δ = 6.74 (s, 2 H), 3.80 (s, 6 H), 2.09 (t, J = 2.5 Hz, 4 H), 1.43 (m, 4 H), 1.20–1.28 (m, 20 H), 0.88 (t, J = 7.1 Hz, 6 H). – ^{13}C NMR: δ = 151.3, 126.8, 109.9, 79.6, 77.6, 56.4, 31.7, 29.1, 29.0, 28.9, 28.8, 22.6, 18.9, 15.3, 14.0. – GC MS; *m*/*z* (%): 438 (63), 339 (82), 227 (76), 210 (90). – $C_{30}H_{46}O_2$ (438.69): C 82.14, H 10.57; found C 82.12, H 11.10.

2,3-Diheptyl-1,4-dimethoxybenzene (2b): Diyne **1b** (4.13 g, 12.6 mmol) was dissolved in EtOAc/AcOH (1:2, 60 mL). Adams catalyst (250 mg) was then added, and the mixture hydrogenated in a low-pressure hydrogenation apparatus until hydrogen uptake ceased (one week). The mixture was then filtered, concentrated in vacuo and purified by column chromatography on silica gel using nC$_7$H$_{16}$/EtOAc (50:1) as eluent. R_f = 0.70. Yield: 0.94 g (22%) of pure **2b** as a pale yellow oil. – ^{1}H NMR (250 MHz): δ = 6.65 (s, 2 H), 3.77 (s, 6 H), 2.61 (t, J = 7.7 Hz, 4 H), 1.23–1.53 (m, 20 H), 0.90 (t, J = 6.7 Hz, 6 H). – ^{13}C NMR (62 MHz): δ = 151.8, 131.0, 107.7, 55.7, 31.8, 30.2, 29.1, 26.3, 22.6, 14.0. – GC MS; *m*/*z* (%): 334 (100), 165 (76), 151 (18). – $C_{22}H_{38}O_2$ (334.54): C 78.99, H 11.45; found C 78.70, H 11.43.

1,4-Dimethoxy-2,3-dioctylbenzene (2c): Diyne **1c** (5.00 g, 14.1 mmol) was dissolved in EtOAc/AcOH (1:2, 75 mL) and reduced as described for compound **2b**. Purification by kugelrohr distillation: 160–170°C/0.1 Torr. Yield: 3.95 g (77%). Colorless oil. – ^{1}H NMR (400 MHz): δ = 6.66 (s, 2 H), 3.78 (s, 6 H), 2.60 (t, J = 7.5 Hz, 4 H), 1.20–1.50 (m, 24 H), 0.90 (t, J = 6.9 Hz, 6 H). – ^{13}C NMR (100 MHz): δ = 151.7, 131.0, 107.7, 55.7, 31.8, 30.2, 30.0, 29.3, 29.2, 26.3, 22.6, 14.0. – GC MS; *m*/*z* (%): 362 (8), 360 (85), 250 (20), 177 (100), 165 (68). – $C_{24}H_{42}O_2$ (362.60): C 79.50, H 11.67; found C 79.33, H 11.44.

1,4-Dimethoxy-2,3-dinonylbenzene (2d): Diyne **1d** (2.00 g, 5.23 mmol) was dissolved in EtOAc/AcOH (1:1) (50 mL) and reduced as described for compound **2b**. Purification by kugelrohr distillation: 170°C/0.2 Torr followed by column chromatography on silica gel with pentane/toluene (4:1) as eluent. Yield: 1.80 g (88%). Colorless oil. – ^{1}H NMR (400 MHz): δ = 6.64 (s, 2 H), 3.76 (s, 6 H), 2.60 (t, J = 7.9 Hz, 4 H), 1.28–1.46 (m, 28 H), 0.90 (t, 6 H, J = 6.9 Hz). – ^{13}C NMR (100 MHz): δ = 151.7, 131.0, 107.7, 55.7, 31.9, 30.2, 30.0, 29.5, 29.4, 29.3, 26.3, 22.6, 14.0. – GC MS; *m*/*z* (%): 390 (100), 165 (100). – $C_{26}H_{46}O_2$ (390.65): C 79.94, H 11.87; found C 80.29, H 12.22.

2,3-Didecyl-1,4-dimethoxybenzene (2e): Diyne **1e** (1.18 g, 2.87 mmol) was dissolved in EtOAc/AcOH (1:1) (40 mL) and reduced as described for compound **2b**. Purification by kugelrohr distillation: 180°C/0.2 Torr. Yield: 1.10 g (90%). Colorless oil. – ^{1}H NMR (400 MHz): δ = 6.63 (s, 2 H), 3.75 (s, 6 H), 2.16 (t, J = 7.5 Hz, 4 H), 1.27–1.47 (m, 32 H), 0.90 (t, J = 6.9 Hz, 6 H). – ^{13}C NMR: (100 MHz): δ = 151.8, 131.0, 107.7, 55.7, 31.8, 30.2, 30.0, 29.3, 29.2, 26.3, 22.6, 14.0. – GC MS; *m*/*z* (%): 362 (8), 360 (85), 250 (20), 177 (100), 165 (68). – $C_{26}H_{46}O_2$ (390.65): C 80.32, H 12.04; found C 79.96, H 12.36.

1,4-Dimethoxy-2,3-diundecylbenzene (2f): Diyne **1f** (3.00 g, 6.84 mmol) was dissolved in EtOAc/AcOH (1:1) (100 mL) and reduced as described for compound **2b**. However, in this case, the reduction only took 36 h. Purification by column chromatography on silica gel with pentane/toluene (10:1) as eluent. R_f = 0.40. Yield: 2.70 g (88%). Colorless oil. – ^{1}H NMR (400 MHz): δ = 6.66 (s, 2 H), 3.78 (s, 6 H), 2.62 (t, J = 7.5 Hz, 4 H), 1.20–1.30 (m, 36 H), 0.90 (t, J = 6.9 Hz, 6 H). – ^{13}C NMR: (100 MHz) δ = 151.8, 131.0, 107.7, 55.7, 31.9, 30.2, 30.0, 29.7, 29.6, 29.4, 29.3, 26.3, 22.6, 14.0. – GC MS; *m*/*z* (%): 446 (100), 165 (60). – $C_{28}H_{54}O_2$ (422.74): C 79.56, H 12.88; found C 79.64, H 12.52.

2,3-Diheptyl-1,4-benzoquinone (3b): A solution of $(NH_4)_2Ce(NO_3)_6$ (5.60 g, 6.6 mmol) in water (30 mL) was added over 20 min to a solution of compound **2b** (0.94 g, 2.81 mmol) in CH_3CN (60 mL) with good stirring. After an additional 30 min, the mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined $CHCl_3$ extracts were washed with water (50 mL), dried with $MgSO_4$, concentrated in vacuo and eluted through a small column of silica gel 60 H with $CHCl_3$ as eluent. Yield: 0.84 g (98%) of a yellow oil. – ^{1}H NMR (250 MHz): δ = 6.67 (s, 2 H), 2.43 (t, J = 7.5 Hz, 4 H), 1.40–1.93 (m, 20 H), 0.87 (t, J = 6.7 Hz, 6 H). – ^{13}C NMR (62 MHz): δ = 187.6, 144.7, 136.2, 31.6, 29.9, 29.4, 28.9, 26.3, 22.5, 13.0. – GC MS; *m*/*z* (%): 304 (58), 163 (35), 149 (48), 137 (100). – An analytical sample was purified by preparative HPLC. Column: Nucleosil 50–7. Flow: 3 mL/min with detection at 343 nm and 253 nm. Eluent: heptane/CH_2Cl_2 (5:1). – $C_{20}H_{32}O_2$ (304.47): C 78.90, H 10.59; found C 78.50, H 10.97.

2,3-Dioctyl-1,4-benzoquinone (3c): This compound was prepared by the procedure described for compound **3b**. Yellow oil. Yield: 2.0 g (73%). – ^{1}H NMR (400 MHz): δ = 6.67 (s, 2 H), 2.44 (m, 4 H), 1.20–1.41 (m, 24 H), 0.90 (m, 6 H). – ^{13}C NMR (100 MHz): δ = 187.6, 144.7, 136.2, 31.8, 30.1, 29.9, 29.5, 29.1, 26.6, 26.4, 14.0. – FAB MS; *m*/*z*: 332.2 (M^+). – $C_{22}H_{36}O_2$ (332.53): C 79.46, H 10.91; found C 79.05, H 11.19.

2,3-Dinonyl-1,4-benzoquinone (3d): This compound was prepared by the procedure described for compound **3b**. Yellow oil. Yield: 0.90 g (70%). – ^{1}H NMR (400 MHz): δ = 6.67 (s, 2 H), 2.44 (m, 4

H), 1.26–1.40 (m, 32 H), 0.90 (t, J = 8.6 Hz, 6 H). – ^{13}C NMR (100 MHz): δ = 187.3, 144.7, 136.2, 31.8, 30.0, 29.9, 29.5, 26.6, 26.4, 22.6, 14.0. – FAB MS; *m/z*: 360.3 (M^+). – $C_{24}H_{40}O_2$ (360.58): C 79.94, H 11.18; found C 79.58, H 11.60.

2,3-Didecyl-1,4-benzoquinone (3e): This compound was prepared by the procedure described for compound **3b**. Yellow oil. Yield: 0.50 g (59%). – ^{1}H NMR (400 MHz): δ = 6.69 (s, 2 H), 2.42 (m, 4 H), 1.26–1.40 (m, 28 H), 0.89 (t, J = 6.4 Hz, 6 H). – ^{13}C NMR (100 MHz): δ = 187.7, 144.8, 136.3, 32.4, 31.8, 30.1, 29.9, 29.5, 29.1, 26.6, 26.4, 22.6, 14.1. – FAB MS; *m/z*: 388.3 [M^+]. – $C_{26}H_{44}O_2$ (388.63): C 80.35, H 11.41; found C 80.28, H 11.14.

2,3-Diundecyl-1,4-benzoquinone (3f): This compound was prepared by the procedure described for compound **3b**. Yellow oil. Yield: 84%. – ^{1}H NMR (250 MHz): δ = 6.80 (s, 2 H), 2.44 (t, J = 7.4 Hz, 4 H), 1.3–1.5 (m, 8 H), 1.2–1.3 (m, 28 H), 0.90 (t, J = 6.5 Hz, 6 H). – ^{13}C NMR (62 MHz): δ = 187.7, 144.8, 136.3, 31.9, 30.0, 29.7, 29.6, 29.5, 29.4, 26.5, 22.7, 14.1. – FAB-MS; *m/z*: 416.3 [M^+]. – $C_{28}H_{48}O_2$ (416.69): C 80.71, H 11.61; found C 80.30, H 11.91.

2,3,5,6,8,9,11,12-Octaheptyltetraoxa[8]circulene (4b): BF_3–diethyl ether (0.5 mL) was added to a solution of compound **3b** (0.67 g, 2.20 mmol) in CH_2Cl_2 (30 mL). The mixture was refluxed overnight, and stirred vigorously with a mixture of CH_2Cl_2 and 2 M HCl (150 mL). The product was filtered, dried and crystallized from $CHCl_3$. Pale yellow crystals. Yield: 280 mg (44%). M.p. 189.8 °C and 217.2 °C (determined by DSC). – ^{1}H NMR (400 MHz, $CDBr_3$, 70 °C): δ = 3.15 (t, J = 7.7 Hz, 16 H), 1.82–1.89 (m, 16 H), 1.44–1.49 (m, 16 H), 1.40–1.42 (m, 16 H), 1.32–1.37 (m, 32 H), 0.92 (t, J = 7.0 Hz, 24 H). – ^{13}C NMR (100 MHz, $CDBr_3$, 70 °C): δ = 151.2, 122.7, 112.9, 30.6, 29.5, 28.6, 27.9, 26.0, 21.5, 13.4. – FAB MS; *m/z*: 1145 [M^+]. – $C_{80}H_{120}O_4$ (1145.83): C 83.86, H 10.56; found C 83.52, H 10.47.

2,3,5,6,8,9,11,12-Octaoctyltetraoxa[8]circulene (4c): This compound was prepared by the procedure described for compound **4b**, except that the product did not precipitate. The product was purified by crystallizing three times from $CHCl_3$. Yield: 200 mg (11%). Pale yellow crystals. M.p. 160 °C and 183 °C (determined by DSC). – ^{1}H NMR (400 MHz, $CDCl_3$, 55°C): δ = 3.17 (t, J = 6.5 Hz, 16 H), 1.86 (m, 16 H), 1.51–1.58 (m, 16 H), 1.43 (m, 28 H), 1.23–1.39 (m, 36 H), 0.90 (t, 24 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 152.7, 124.0, 114.2, 31.9, 30.7, 29.8, 29.5, 29.3, 27.1, 22.6, 14.0. – EI MS; *m/z*: 1256.9 [M^+]. – $C_{88}H_{136}O_4$ (1258.05): C 84.02, H 10.90; found C 84.06, H 11.12.

2,3,5,6,8,9,11,12-Octanonyltetraoxa[8]circulene (4d): This compound was prepared by the procedure described for compound **4c**. The product was purified by crystallizing three times from $CHCl_3$. Yield: 200 mg (26%). Pale yellow crystals. M.p. 148 °C and 169 °C (determined by DSC). – ^{1}H NMR (400 MHz, $CDCl_3$, 55°C): δ = 3.14 (t, J = 7.5 Hz, 16 H), 1.84 (m, 16 H), 1.53 (m, 16 H), 1.46 (m, 28 H), 1.35 (m, 52 H), 0.88 (t, J = 6.8 Hz, 24 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 152.8, 124.0, 114.3, 31.9, 30.8, 29.9, 29.6, 29.3, 27.1, 22.6, 13.9. – FAB MS; *m/z*: 1370.3 [M^+]. – $C_{96}H_{152}O_4$ (1370.3): C 84.15, H 11.18; found C 84.35, H 11.58.

2,3,5,6,8,9,11,12-Octadecyltetraoxa[8]circulene (4e): This compound was prepared by the procedure described for compound **4c**. The product was purified by crystallising three times from $CHCl_3$. Yield: 150 mg (39%). Pale yellow crystals. M.p. 133 °C and 165 °C (determined by DSC). – ^{1}H NMR (400 MHz, $CDCl_3$, 55°C): δ = 3.16 (t, J = 7.5 Hz, 16 H), 1.84 (m, 16 H), 1.45–1.52 (m, 16 H), 1.42 (m, 28 H), 1.27 (m, 52 H), 0.87 (t, J = 6.8 Hz, 24 H). – ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 152.8, 124.0, 114.2, 31.9, 30.7, 29.8, 29.6, 29.6, 29.3, 27.1, 22.6, 14.0. – FAB MS; *m/z*: 1482.2 [M^+]. – $C_{104}H_{168}O_4$ (1482.48): C 84.26, H 11.42; found C 84.01, H 11.79.

2,3,5,6,8,9,11,12-Octaundecyltetraoxa[8]circulene (4f): This compound was prepared by the procedure described for compound **4c**. The product was purified by repeated column chromatography on silica gel with *n*-hexane as eluent. Yield: 56%. Pale orange waxy material. – ^{1}H NMR (400 MHz): δ = 3.17 (m, 16 H), 1.86 (m, 16 H), 1.27–1.54 (m, 128 H). – ^{13}C NMR (100 MHz): δ = 152.6, 124.0, 114.1, 31.9, 29.6, 29.3, 22.6, 14.0. – $C_{112}H_{184}O_4$ (1594.69): C 84.36, H 11.63; found C 84.35, H 12.01.

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