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Synthesis of Components for Supramolecules Incorporating Cycloheptatriene Building Blocks

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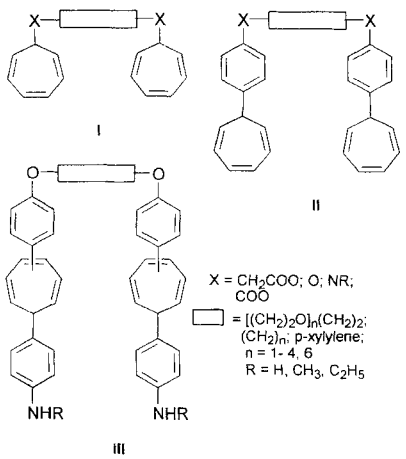
Abstract. Molecular threads **I** – **III** incorporating 1,3,5-cycloheptatriene units have been synthesized by three methods. Bridges were designed as ether (**9**, **14**, **18** and **22**), ester (**4** and **14**) and amino functions (**25**), respectively. The attachment of a second aryl residue at the seven-membered ring by nucleophilic attack of activated aromatic compounds such as anilines on tropylium salts resulted in the formation of two regioisomers (**26** and **27**). The macrocycles **28** were formed under high dilution conditions in good yields.

Switchable supramolecular assemblies such as rotaxanes and host–guest complexes comprise an important field of supramolecular chemistry [1]. Our intention is the design of macrocycles [2] and rotaxanes with arylcycloheptatriene subunits which can easily be transformed to the corresponding tropylium ions by thermal [3], electrochemical [4] and photochemical methods [4, 5]. In contrast to cycloheptatrienes, tropylium salts are strong electron acceptors which can be used to recognize donor partners. On the other side, cycloheptatrienes are electron donors which can be applied to bind electron acceptors.

So far only some cyclophanes [6] containing aliphatic bridges and crown compounds [7] incorporating cycloheptatriene were reported. However, the methods used are not suitable in order to synthesize a wide variety of supramolecular components.



Here we report on the synthesis of molecular threads **I** – **III** with arylcycloheptatriene units and on the synthesis of macrocycles which incorporate these building blocks.

Three methods were used to synthesize compounds with two cycloheptatriene units:

1. Cycloheptatrienes with suitable functionalities attached to aliphatic or aryl substituents, can be used to form the bridge between two cycloheptatrienes (method A).
2. A bridge with a suitable function is used to introduce cycloheptatrienyl substituents (method B).
3. The molecular thread was lengthened by nucleophilic attack of aromatic amines on tropylium salts which were obtained by oxidation of the bridged cycloheptatrienes (method C).

Results and Discussion

Method A

Oligoethylene Glycol Esters of Cycloheptatrienylacetic Acid (type I)

Esterification of cyclohepta-2,4,6-trienyl acetic acid **1** with the oligoethylene glycol **2** results mainly in the monoacylated glycol **3** even by using an excess of **1**

(Scheme 1). The diacylated glycol **4** is the minor product which can be separated from **3** with the aid of flash chromatography.

Compounds **3** and **4** undergo the sigmatropic 1,5-H-shift very slowly by heating at 155 °C (refluxing xylene). The hydrogen shift can easily be followed by NMR spectroscopy. The additionally observed triplet in the region of 3 ppm is attributed to the primarily formed 1,3,6-isomer of the cycloheptatriene derivative. The subsequent 1,5-H-shift leading to the 1,3,5-isomer can be recognized by the doublet of the hydrogen atoms in the 7-position. After 5 hours only 50% of **4** were converted into 42% 1,3,6- and 8% 1,3,5-isomer.

The oxidation of **3** and **4** by hydride transfer to trityl cation is achieved in high yields without prior isomerization as it was necessary with other cycloheptatriene derivatives (see Scheme 1) [8].

Ether Bridged Aryl Substituted Cycloheptatrienes (type II)

4-(Cyclohepta-1,3,6-trienyl)-phenol **7** obtained by distillation of the corresponding 2,4,6-isomer can be bridged by reaction with dihalides such as xylylene dibromide or bis(2-chloro-ethyl)ether (see Scheme 1).

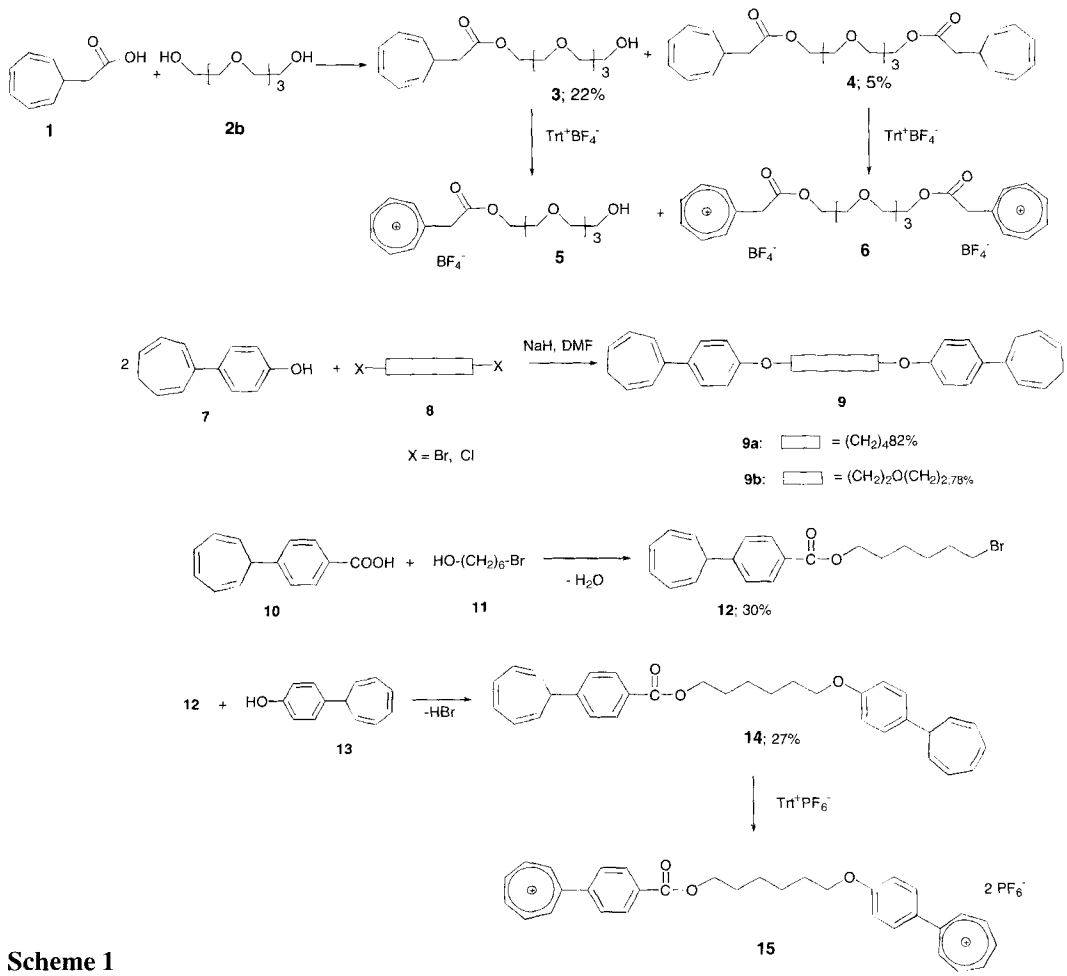
Two aryl cycloheptatriene (compound **14**) and tropylium units (compound **15**), respectively, with different electron donor and electron acceptor strength, respectively, are linked by using an ester and an ether bond as it is shown in Scheme 1.

Method B

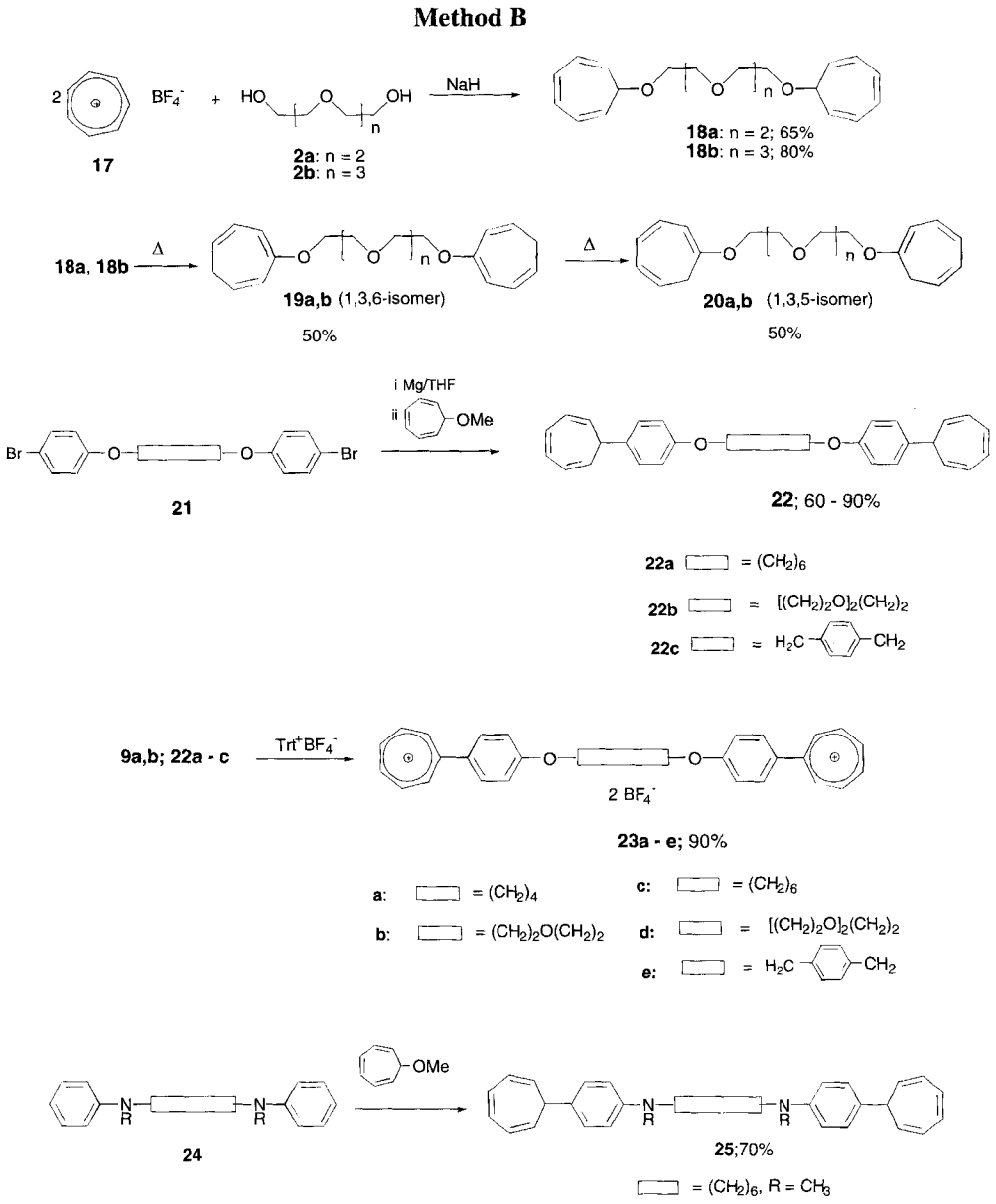
Bridged Cycloheptatrienyl Ethers (type I)

Tropylium cations are known to react with alcohols affording cycloheptatrienyl ethers [3]. We found that tri- and tetraethylene glycol (**2a** and **2b**) react with tropylium tetrafluoroborate **17** yielding the bridged cycloheptatrienyl ethers **18a** and **18b**, respectively, which upon distillation rearrange by successive hydrogen shift to the 1,3,5-isomer **20** *via* the isomer **19** as depicted in Scheme 2. The ratio of the isomers depends on the temperature used. Purification with the aid of column chro-

Method A



Scheme 1



Scheme 2

matography (CC) affords 1-substituted 2,4,6-cycloheptatrienes **18**.

The cycloheptatriene unit can also be attached to the bridge by using the reaction of a Grignard compound with 7-methoxy-cyclohepta-1,3,5-triene (see Scheme 2). The mild conditions of method B are advantageous because 1-substituted 2,4,6-isomers can easily be obtained without isomerization by 1,5-H-shift observed with method A.

The oxidation of the cycloheptatriene derivatives leads to the tropylium salts **23** independently of the used isomers.

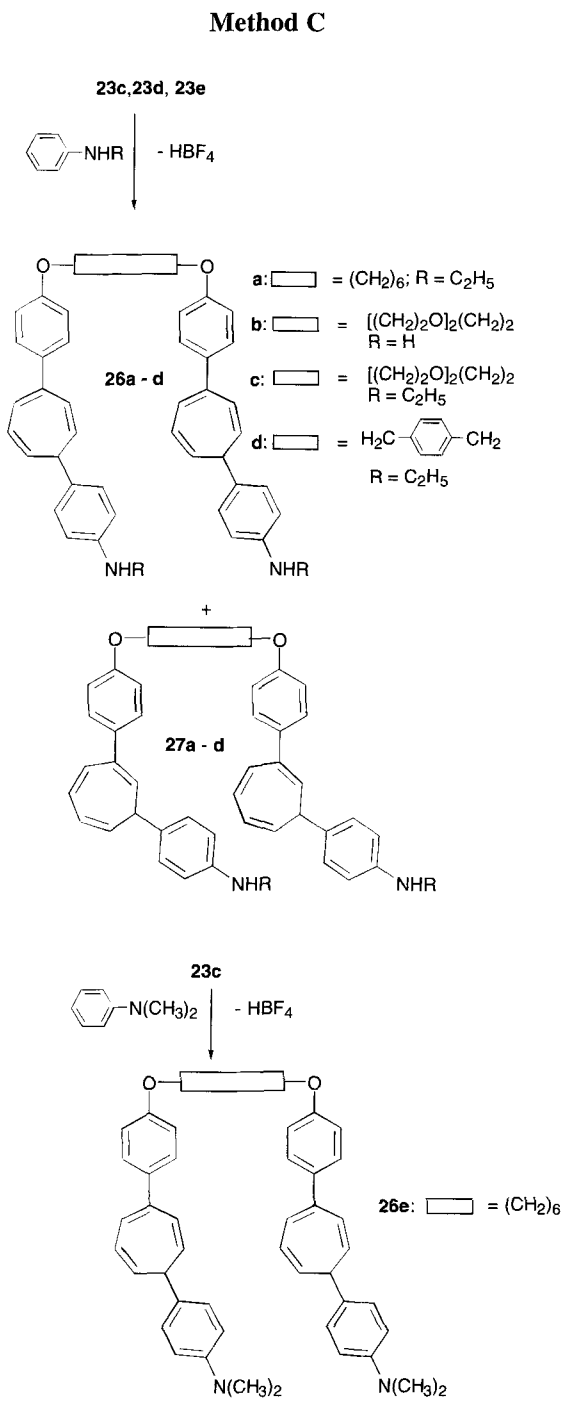
Activated aromatic compounds such as the bridged anilino derivative **24** react directly with 7-methoxy-cyclohepta-1,3,5-triene yielding **25** as is also depicted in scheme 2.

Method C

Bridged Diarylcycloheptatrienes (type III)

Aryltropylium salts react with aromatic amines such as *N,N*-dimethylaniline yielding 1,4-diaryl-cyclohepta-2,4,6-trienes regioselectively [9].

This reaction can be used to attach a second aryl



Scheme 3

group to the bridged cycloheptatrienes described above. In order to obtain binding at the nitrogen atom primary and secondary aniline derivatives were used. In this case a lower regioselectivity is observed. The formation of the 1,4-isomers **26** is only slightly favored to the 1,3-isomer **27** formation (see Scheme 3). Because of the steric repulsion the 1,2-isomer is not formed.

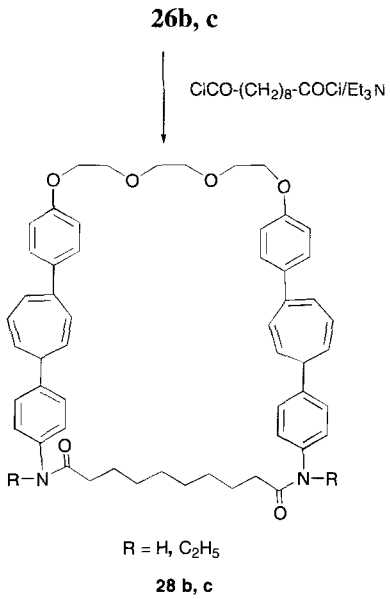
The formation of the mixed isomer which incorporates both the 1,4- and the 1,3-isomer is probable. But, it could not be detected by NMR spectroscopy and could not be isolated from the reaction mixture.

In contrast, using *N,N*-dimethylaniline only the 1,4-isomer **26e** was detected in the reaction mixture.

The separation of the 1,4- and the 1,3-isomer is possible by recrystallization or column chromatography. Mostly, only the 1,4-isomer could be purified. Because of the difficult purification procedure yields of pure isomers are rather low.

Cyclization

The diarylcycloheptatrienes (1,4-isomers) **26b** and **c** were used to form macrocycles incorporating two cycloheptatriene units. Sebacoyl dichloride served as cyclization agent under high dilution conditions, and the cyclophanes **28a** and **b** were obtained in the relatively high yield of 60%.



Scheme 4

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie.

Experimental

Chemicals were purchased from Aldrich and purified by distillation. Column chromatography (CC) was performed with silicagel 60 (Merck). Melting points were determined on a Boëtius heating microscope and are corrected. ^{1}H NMR spectra were performed on a Bruker DPX 300 (300 MHz) and ^{13}C NMR spectra at 75 MHz on a DPX 300 instrument. Mass spectra were performed on a Hewlett-Packard GCMS-5995-A (EI) and on an Autospec Micromass (LSI). Magic

bullet (MB) and 2-nitrobenzylalcohol (NBA) served as matrices.

Method A Esters 3 and 4

Cyclohepta-2,4,6-trienyl-acetic acid-2-[2-(2-hydroxyethoxy)ethoxy]ethyl ester (**3**)

A solution of 2,4,6-cycloheptatriene-1-acetic acid **1** [10] (3 g, 20 mmol), 3 drops conc. H_2SO_4 and dry triethylene glycol 11.5 ml (85 mmol) in benzene (100 ml) was refluxed for 7 h. After washing with water and evaporating of the solvent the remaining brown oil was separated by flash chromatography on silica gel using *t*-butyl-methyl ether as eluent. Colorless oil, yield 1.7 g (22%). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.73 (m, 1H; C-1, seven-membered ring); 2.46 (broad s,1H; OH); 2.72 (d, 2H; CH_2O); 3.67 (m, 10H, CH_2–O–CH_2–CH_2–O–CH_2–CH_2); 4.27 (t, 2H, $COOCH_2$); 5.22 (dd, 2H; H-2,7); 6.2 (m, 2H; H-3,6); 6.66 (m, 2H; H-4,5).

$C_{17}H_{26}O_6$	Calcd.:	C 62.56 H 8.03
(326.4)	Found:	C 62.09 H 7.70.

Cyclohepta-2,4,6-trienyl-acetic acid 2-{2-[2-(cyclohepta-2,4,6-trienyl-acetoxy)ethoxy]-ethoxy}ethyl ester (**4**)

Yield 0.38 g (5%), colorless oil. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.25 (m, 1H; H-1); 2.70 (d, 4H, CH_2O; 3.68 (m, 8H; CH_2–O–CH_2–CH_2–O–CH_2); 4.25 (t, 4H; COO–CH_2); 5.22 (dd, 4H, H-2,7); 6.20 (m, 4H; H-3,6); 6.67 (m, 4H; H-4,5).

$C_{26}H_{34}O_8$	Calcd.:	C 68.10 H 7.74
(458,6)	Found:	C 67.85 H 7.89.

Tropylium Salts 5 and 6

To a solution of **3** or **4** (0.15 mmol) in 1 ml CH_2Cl_2 one and two equivalents, respectively, of trityl fluoroborate were added in portions. After stirring for 3 h the solvent was evaporated. The remained brown tar was twice digested with *t*-butyl-methyl ether yielding the tropylium salts as oily compounds in quantitative yields.

Tropylium-acetic acid-2[2-(2-hydroxyethoxy)ethoxy]ethyl ester perchlorate (**5**)

^{1}H NMR (CD_3CN): δ/ppm = 3.58 (m, 10H; CH_2–O–CH_2–CH_2–O–CH_2–CH_2); 4.40 (s, 2H; CH_2O); 4.47 (m, 2H; $COOCH_2$); 9.12 (s, 6H; tropylium ring).

Tropylium-acetic acid 2-{2-[2-(tropylium-acetoxy)ethoxy]-ethoxy}ethyl ester bis-perchlorate (**6**)

^{1}H NMR (CD_3CN): δ/ppm = 3.54 (s, 4H; CH_2CH_2); 3.66 (m, 4H; $COOCH_2CH_2$); 4.27 (m, 4H; $COOCH_2$); 4.39 (m, 4H; CH_2CO); 9.12 (s, 12H; tropylium ring).

1,4-Bis[4-(cyclohepta-2,4,6-trienyl)phenoxy]butane (**9a**)

4-Cyclohepta-2,4,6-trienyl-phenol **7** [11] (5 g, 27 mmol) dissolved in 20 ml DMF was deprotonated with NaH (1.15 g, 60% in paraffin). At the end of the hydrogen evolution the 1,4-dibromobutane (**8a**) (2.8 g, 14 mmol) was slowly added with stirring. After 2 h water (50 ml) was added. The insoluble product was washed with water and hexane. – Yield 4.7 g (82%) **9a**, white solid (ethyl acetate), *m.p.* 56 °C. – ^{1}H-NMR ($CDCl_3$): δ/ppm = 7.26 (d, 4H; phenyl); 6.89 (d, 4H; phenyl), 6.73 (dd, 4H; H-4,5); 6.24 (dd, 4H, H-3,6), 5.38 (dd, 4H; H-2,7), 4.04 (m, 4H; O–CH_2); 2.66 (t, 5.6 Hz, 2H, H-1); 1.98 (m, 4H; CH_2). – MS: *m/z* (%) = 423 (M^++1; 1), 422 (M^+; 3), 240 (5), 239 (24), 197 (37), 184 (14), 183 (33), 167 (17), 166 (10), 165 (32), 155 (16), 154 (12), 153 (24), 152 (32), 129 (11), 128 (18), 127 (10), 115 (16), 107 (14), 91 (100), 77 (17), 55 (40)

$C_{30}H_{30}O_2$	Calcd.:	C 85.20 H 7.20
(422.6)	Found:	C 85.36 H 7.80.

1,5-Bis[4-(cyclohepta-1,3,6-trienyl)phenoxy]-3-oxa-pentane (**9b**)

From **7** (4 g, 22 mmol), NaH (0.9 g; (60%)) and bis(2-chloroethyl)ether (**8b**) (1.55 g, 11 mmol) according to the procedure described above. **9b** was purified with the help of CC (silica gel/CH_2Cl_2). Yield 3.7 g (78%), viscous, yellowish oil. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.38 (d, 4H; phenyl); 6.86–6.93 (m, 6H; phenyl; H-2); 6.32 (d, 2H; H-7); 6.27 (dd, 2H; H-3), 5.46 (m, 4H, H-4,6); 4.14 (t, 4H; O–CH_2); 3.86 (t, 4H; CH_2–O); 2.66 (t, 2H; H-5). – ^{13}C NMR ($CDCl_3$): δ/ppm = 155.3 (phenyl), 142.5 (C-1), 135.8 (phenyl), 128.2 (phenyl), 127.5 (C-2), 127.1 / 126.8 (C-3,7), 121.5 / 121.3 (C-4,6), 115.3 (phenyl), 71.6 (C–O), 67.5 (O–C), 27.9 (C-5). – MS: *m/z* (%) = 439 (M^++1; 2), 438 (M^+; 5), 211 (15), 184 (66), 183 (100), 182 (22), 167 (46), 166 (40), 165 (86), 155 (47), 154 (33), 153 (53), 152 (86), 129 (23), 128 (42), 127 (23), 115 (40), 91 (47), 77 (19), 55 (18), 45 (35), 43 (34).

$C_{30}H_{30}O_3$	Calcd.:	C 82.16 H 6.90
(438.6)	Found:	C 81.84 H 6.76.

4-Cyclohepta-2,4,6-trienyl-benzoic acid 6-(4-cyclohepta-2,4,6-trienyl-phenoxy)-hexyl ester (**14**)

1-Brom-4-cyclohepta-2,4,6-trienyl-benzene

The compound was obtained according to the literature [11]. In order to avoid isomerization due to sigmatropic H-shift at higher temperature the compound was purified by column chromatography (silicagel, *n*-hexane). A colorless oil was obtained in the yield of 83%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.70 (t, 1H; H-1); 5.33 (m, 2H; H-2,7); 6.23 (m, 2H; H-3,6); 6,72 (m, 2H; H-4,5); 7,17 (d, 2H; phenyl); 7.43 d, 2H; phenyl). – ^{13}C NMR ($CDCl_3$): δ/ppm = 44.58 (C-1); 120.31; 125.46; 131,65; 142.71 (phenyl); 124.70 (C-2,7); 129.25 (C-3,6); 130.96 (C-4,5).

$C_{13}H_{11}Br$	Calcd.:	C 69.18 H 4.49
(247.1)	Found:	C 68.76 H 4.68.

4-(Cyclohepta-2,4,6-trienyl)benzoic acid (**10**)

To 1-bromo-4-(cyclohepta-2,4,6-trienyl)-benzene (28.8 g, 0.117 mol) in THF (250 ml) 73 ml of a 1.6M *n*-butyl lithium solution (*n*-hexane) was added at –75 °C. During 20 h CO_2 was slowly introduced through an gas inlet tube. The mixture was allowed to warm to room temperature during the CO_2-addition. The reaction was stopped by adding of 200 ml water and 100 ml 2M HCl under ice cooling. The aqueous phase was extracted with diethylether. The organic phase was dried and evaporated under reduced pressure. The yellow solid was purified by recrystallization from acetonitrile *m.p.* 157–159 °C (CH_3CN) (lit. 139–142 °C [11]). Yield 13.3 g (54%).

$C_{14}H_{12}O_2$ Calcd.: C 79.23 H 5.70
(212.3) Found: C 79.56 H 5.31.

4-(Cyclohepta-2,4,6-trienyl) benzoic acid-6-bromo-hexyl ester (**12**)

4-(Cyclohepta-2,4,6-trienyl)-benzoic acid **10** (4 g, 18.9 mmol) dissolved in THF (10 ml) was treated with thionyl chloride 2.4 ml, 28 mmol) for 4 hours at 85 °C. After evaporation of the solution under reduced pressure 10 ml dry pyridine were added. 6-Bromo-hexan-1-ol **11** (3.4 g, 18.9 mmol) were dropped to this solution. After stirring for 20 hours at room temperature the solution was acidified with conc. HCl/ice and extracted with dichloromethane. The organic phase was washed with water, dried (Na_2SO_4), filtered, and the solvent removed at reduced pressure. The residue was purified by CC on silica gel (CH_2Cl_2/*n*-hexane) to afford the ester **12** (yellow oil, 2.1 g, 30%). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.48 (m, 4H; CH_2CH_2); 1.76 (m, 4H; CH_2CH_2); 2.80 (t, 1H; C-1); 3.50 (t, 2H, -CH_2–Br); 4.31 (t, 2H; -O–CH_2); 5.37 (m, 2H; H-2,7); 6.24 (m, 2H; H-3,6); 6.72 (m, 2H; H-4,5); 7.43 (d, 2H; H-3,5 phenyl); 8.02 (d, 2H; H-2,6 phenyl). – ^{13}C NMR ($CDCl_3$): δ/ppm = 25.32; 26.47; 28.53; 32.47; 44.82 (hexyl-H); 45.04 (C-1); 64.66 (O–C-); 124.84 (C-2,7); 125.03 (C-2,6; phenyl); 127.55 (C-3,6); 128.09 (C-1, phenyl); 130.01 (C-4,5); 130.98 (C-3,5, phenyl); 148.98 (C-4, phenyl); 166.51 (C=O).

4-(Cyclohepta-2,4,6-trienyl)benzoic acid 6-(4-cyclohepta-1,3,6-trienyl-phenoxy) hexyl ester (**14**)

13 [12] (containing the 1,3,5-isomer) (0.27 g, 1.5 mmol) was dissolved in dried DMF. NaH [0.2 g, 4.9 mmol (60% in paraffin oil)] was added under argon. The mixture was warmed at 50 °C until the evolution of hydrogen stopped. The 4-(cyclohepta-2,4,6-trienyl) benzoic acid 6-bromo-hexyl ester **12** was added at 50 °C, and the solution was stirred for further 4 h at this temperature. After 6 days stirring at room temperature 5 ml of water were added and the mixture was poured into 200 ml of water. The aqueous phase was extracted with diethyl ether. The organic phase was dried (Na_2SO_4), filtered, and the solvent removed at reduced pressure. The residue was purified by CC on silica gel (CH_2Cl_2/*n*-hexane) to afford **14** (yellow oil, 0.19 g, 27%). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.41 (br s, 4H) and 1.67 (br s, 4H, CH_2CH_2-hexyl); 2.23 (m, 3H; C-1, C-5); 3.82 (t, 2 H; CH_2–O); 4.20 (t, 2 H; COO–CH_2); 5.37 (m, 2H, cycloheptatriene); 5.41 (m, 2H, cycloheptatriene); 6.12 (m, 2H; cycloheptatriene); 6.18 (m, 2H, cycloheptatriene); 6.66 (m, 2H; cycloheptatriene); 6.71 (d, 2H; phenyl); 6.75 (m, 1H; cycloheptatriene); 7.25 (d, 2H; phenyl); 7.26 (d, 2H; phenyl); 7.87 (d, 2H; phenyl).
$C_{33}H_{34}O_3$ Calcd.: C 80.81 H 7.16
(478.6) Found: C 80.21 H 7.43.

4-Tropylium-benzoic acid 6-(4-tropylium-phenoxy) hexyl ester bis-hexafluorophosphate (**15**)

To **14** (0.18 g, 0.33 mmol) dissolved in 5 ml CH_2Cl_2 trityl fluoroborate (0.26 g, 0.80 mmol) was added. The reaction mixture was heated to 50 °C for 2 hours and stirred for 12 hours at room temperature. The resulting precipitate was filtered and washed with CH_2Cl_2 and diethyl ether. Recrystallization from CH_3CN/diethyl ether afforded 0.15 g (70%) of a brown solid, *m.p.* 135 °C (dec.). – ^{1}H NMR (CD_3CN): δ/ppm = 1.55 (m. 4H; CH_2CH_2-hexyl); 1.83 (m, 4H; CH_2CH_2-hexyl); 4.12 (t, 2H; CH_2O-); 4.36 (t, 2H; $COOCH_2$); 7.17 (d, 2H; phenyl); 7.93 (d, 2H; phenyl); 8.01 (d, 2H; phenyl); 8.21 (d, 2H; phenyl); 8.88 (m, 4H; tropylium ring); 9.18 (m, 6H; tropylium ring); 9.35 (m, 2H; tropylium ring). – ^{13}C NMR (CD_3CN): δ/ppm = 26.16 (2C; hexyl); 29.14 (2C; hexyl); 29.49 (2C; hexyl); 66.39 (COO–C); 69.55 (C–O-); 117.36; 118.60; 131.35; 131.43; 133.81; 134.29; 143.68; 151.78; 152.40; 152.95; 154.61; 154.77; 154.88; 164.85; 166.26; 167.37; 168.20 (phenyl; tropylium ring).
$C_{33}H_{32}B_2F_8O_3$ Calcd.: C 60.96 H 4.96
(650.2) Found: C 60.47 H 4.89.

Method B Ethers 18a,b

Tri- (5.3 g, 35 mmol) and tetraethylene glycol (6.8 g, 35 mmol), respectively, dissolved in dried dioxane (50 ml) was treated under argon with NaH (60%, paraffin oil, 2.2 g). Tropylium fluoroborate **17** (8.9 g, 50 mmol) was added and the mixture was stirred at room temperature for 48 hours. Water (70 ml) was added and the solution extracted with diethyl ether. The organic phase was washed several times with water, dried (Na_2SO_4) and the solvent was removed at reduced pressure affording **18a** and **18b**, respectively, as viscous oils.

2-{2-[2-(Cyclohepta-2,4,6-trienyl-oxy)ethoxy]ethoxy} ethoxy-cyclohepta-2,4,6-triene (**18a**)

Yield 5.4 g (65%), colorless oil. – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.45 (br s, 2H; H-1); 3.69 (s, 12H; O–CH_2–CH_2–O); 5.52 (m, 4H; H-2,7); 6.15 (m, 4H; H-3,6); 6.65 (br s, 4H; H-4,5).
$C_{20}H_{26}O_4$ Calcd.: C 72.70 H 7.93
(330.4) Found: C 72.86 H 8.07.

2-{2-[2-[2-(Cyclohepta-2,4,6-trienyl-oxy)ethoxy]ethoxy} ethoxy]ethoxy-cyclohepta-2,4,6-triene (**18b**)

Yield 7.9 g (84%), colorless oil. Upon distillation the isomerization due to sigmatropic H-shift takes place ($b.p._{0.07}$ 179–200 °C: 50% 1,3,6-isomer **19b** and 50% 1,3,5-isomer **20b**; $b.p._{0.06}$ 200–210 °C: 80% **20b** and 20% **19b**). – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.45 (br s, 2H; H-1); 3.67 (s, 16H; O–CH_2–CH_2–O); 5.51 (m, 4H; H-2,7); 6.15 (m, 4H; H-3,6); 6.66 (br s, 4H; H-4,5).
$C_{22}H_{30}O_5$ Calcd.: C 70.56 H 8.08
(374.5) Found: C 70.47 H 7.89.

2-{2-[2-[2-(Cyclohepta-1,3,5-trienyl-oxy)ethoxy]ethoxy] ethoxy}ethoxy-cyclohepta-2,4,6-triene (**20b**)

^{1}H NMR ($CDCl_3$): δ/ppm = 2.54 (d, 4H; H-1); 3.68 (s, 16H; O–CH_2–CH_2–O); 5.38 (m, 2H; H-6); 6.16 (m, 4H; H-2,5); 6.30, 6.42 m, 4H; H-3,4).

Bridged Dibromo Compounds 21

The dihalide (70 mmol), 4-bromophenol (25 g, 145 mmol) and KOH (8.2 g, 146 mmol) were refluxed in *n*-butanol (70 ml). After cooling the reaction mixture was poured into water (300 ml) and extracted with CH_2Cl_2 (300 ml). The organic phase was washed three times with 1M NaOH (80 ml) and saturated NaCl-solution. The organic phase was dried (Na_2SO_4) and the solvent was removed at reduced pressure.

1,6-Bis(4-bromophenoxy)hexane (**21a**)

4-Bromophenol and 1,6-dibromohexane yielded white crystals after recrystallization of the crude product from acetone (27 g, 90%), *m.p.* 106 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.35 (d, 4H; phenyl), 6.75 (d, 4H; phenyl), 3.91 (t, 4H; O–CH_2), 1.79 (m, 4H, CH_2), 1.51 (m, 4H, CH_2). – ^{13}C NMR ($CDCl_3$): δ/ppm = 158.1 (phenyl), 132.2 (phenyl), 116.2 (phenyl), 112.6 (phenyl), 68.0 (O–C), 29.1 (CH_2), 25.8 (CH_2). – MS: *m/z* (%) = 430 (2), 428 (4), 426 (M^+; 2), 174 (21), 172 (22), 83 (38), 65 (12), 58 (26), 55 (65), 43 (100), 41 (37), 39 (18), 29 (18), 27 (22), 18 (22).

$C_{18}H_{20}Br_2O_2$	Calcd.:	C 50.49	H 4.70
(428.2)	Found:	C 50.51	H 4.48.

1,8-Bis(4-bromophenoxy)-3,6-dioxaoctane (**21b**)

4-Bromophenol and 1,2-bis(2-chloroethoxy)ethane afforded a white solid after recrystallization of the crude product from ethanol (27 g, 85%), *m.p.* 70 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.34 (d, 4H; phenyl); 6.77 (d, 4H; phenyl); 4.07 (t, 4H; OCH_2); 3.83 (t, 4H; CH_2O); 3.72 (s, 4H; OCH_2). – ^{13}C NMR ($CDCl_3$): δ/ppm = 157.8 (phenyl), 132.2 (phenyl), 116.4 (phenyl), 113.0 (phenyl), 70.9 (O–C), 69.7 (O–C), 67.6 (O–C). – MS: *m/z* (%) = 462 (4), 460 (8), 458 (M^+; 4), 289 (7), 287 (7), 201 (30), 199 (31), 157 (25).

$C_{18}H_{20}Br_2O_4$	Calcd.:	C 46.87	H 4.38
(460.2)	Found:	C 46.98	H 4.23.

1,4-Bis[(4-bromophenoxy)methyl]benzene (**21c**)

4-Bromophenol and α,α'-(*p*-xylylene) dibromide afforded after recrystallization of the crude product a white solid (27.2 g, (87%), *m.p.* 183 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.42 (s, 4H; phenyl, bridge); 7.36 (d, 4H; phenyl); 6.84 (d, 4H; phenyl), 5.04 (s, 4H; CH_2, benzyl). – ^{13}C NMR ($CDCl_3$): δ/ppm = 157.7 (phenyl), 136.5 (phenyl, bridge), 132.3 (phenyl), 127.7 (phenyl, bridge), 116.7 (phenyl), 113.2 (phenyl), 68.0 (benzyl). – MS: *m/z* (%) = 450 (1), 448 (2), 446 (M^+; 1), 277 (28), 275 (29), 196 (38), 105 (11), 104 (100), 103 (14), 78 (13), 44 (12).

$C_{20}H_{16}Br_2O_2$	Calcd.:	C 53.60	H 3.60
(448.2)	Found:	C 53.61	H 3.52.

Cycloheptatrienes 22

The bridged dibromo compound **21** (20 mmol) was reacted with Mg (0.27 g, 40 mmol) in THF. 7-Methoxycyclohepta-1,3,5-triene (40 mmol) dissolved in THF (15 ml) was slowly dropped in the Grignard-solution, and refluxed for 4 h. After cooling to room temperature the solution was poured into 1M HCl (50 ml). The aqueous phase was extracted with diethyl ether (50 ml). The organic phase was dried (Na_2SO_4) and the solvent was removed at reduced pressure.

1,6-Bis[4-(cyclohepta-2,4,6-trienyl)phenoxy]hexane (**22a**)

Recrystallization of the residue from acetone afforded **22a** (6.4 g, 70%). White solid, *m.p.* 146 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.26 (d, 4H; phenyl), 6.90 (d, 4H; phenyl), 6.73 (m, 4H; H-4,5); 6.24 (dd, 4H, H-3,6); 5.40 (dd, 4H; H-2,7), 3.98 (t, 4H; O–CH_2), 2.66 (t, 2H; H-1); 1.83 (m, 4H; CH_2); 1.56 (m, 4H; CH_2). – ^{13}C NMR ($CDCl_3$): δ/ppm = 157.8 (phenyl), 135.9 (phenyl), 130.9 (phenyl), 128.5 (C-4,5), 126.7 (C-3,6), 124.2 (C-2,7), 114.6 (phenyl), 67.9 (O–C), 44.5 (C-1), 29.3 (CH_2), 25.9 (CH_2). – MS: *m/z* (%) = 450 (M^+; 1), 360 (1), 184 (30), 183 (33), 165 (16), 153 (11), 152 (11), 107 (15), 106 (10), 91 (74), 83 (39), 55 (100), 41 (25).

$C_{32}H_{34}O_2$	Calcd.:	C 85.29	H 7.60
(450.6)	Found:	C 84.98	H 7.71.

1,8-Bis[4-(cyclohepta-2,4,6-trienyl)phenoxy]-3,6-dioxaoctane (**22b**)

Recrystallization of the residue resulted in pure **22b** (7.5 g, 78%). White solid, *m.p.* 72 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.26 (d, 4H; phenyl); 6.92 (d, 8.7 Hz, 4H; phenyl); 6.3 (m, 4H; H-4,5); 6.24 (dd, 4H; H-3,6); 5.39 (dd, 4H; H-2,7); 4.14 (t, 4H; O–CH_2); 3.88 (t, 4H; CH_2O), 3.77 (s, 4H; O–CH_2); 2.66 (t, 2H, H-1). – ^{13}C NMR ($CDCl_3$): δ/ppm = 157.5 (phenyl), 136.2 (phenyl), 130.9 (phenyl), 128.5 (C-4,5), 126.7 (C-3,6), 124.3 (C-2,7), 114.8 (phenyl), 70.9 (OCH_2), 69.9 (CH_2O), 67.5 (OCH_2), 44.5 (C-1). – MS: *m/z* (%) = 483 (M^++1; 1), 482 (M^+; 3), 211 (17), 184 (33), 183 (47), 182 (16), 167 (19), 166 (20), 165 (38), 155 (22), 153 (24), 152 (38), 128 (17), 115 (21), 91 (100), 77 (17), 55 (12), 45 (43), 43 (25).

$C_{32}H_{34}O_4$	Calcd.:	C 79.64	H 7.10
(482.6)	Found:	C 79.58	H 7.18.

1,4-Bis[(4-cyclohepta-2,4,6-trienyl-phenoxy)methyl] benzene (**22c**)

Recrystallization from ethanol afforded pure **22c** (5.5 g, 58%). White crystals, *m.p.* 185 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.45 (s, 4H; phenyl, bridge); 7.27 (d, 4H, phenyl), 6.96 (d, 4H; phenyl); 6.73 (m, 4H; H-4,5); 6.24 (dd, 4H; H-2,5), 5.39 (dd, 4H; H-2,7), 5.08 (s, 4H, CH_2, benzyl), 2.66 (t, 2H, H-1). – MS: *m/z* (%) = 471 (M^++1; 4), 470 (M^+; 10), 286 (6), 184 (13), 183 (60), 182 (33), 165 (16), 155 (72), 154 (20), 153 (32), 129 (18), 128 (23), 127 (15), 115 (24), 105 (29), 104 (100), 103 (18), 91 (20), 77 (33), 55 (20).

$C_{34}H_{30}O_2$	Calcd.:	C 86.77	H 6.43
(470.6)	Found:	C 86.26	H 6.72.

Tropylium Salts 23a–e (General Procedure)

A solution or suspension of **22** (10 mmol) in CH_2Cl_2 was treated with trityl tetrafluoroborate and tritylperchlorate, respectively. The solution was stirred at 30 °C for 5 h. **7** was filtered from the solution or precipitated with *t*-butyl-methyl ether or ethyl acetate.

1,4-Bis(4-tropylium-phenoxy)butane bisperchlorate (**23a**)

Yield 7.4 g (98%), orange crystals, dec. >200 °C. – ^{1}H NMR (CD_3CN): δ/ppm = 9.23 (d, 4H; tropylium); 8.82–8.98 (m, 8H; tropylium); 7.98 (d, 4H; phenyl); 7.23 (d, 4H; phenyl); 4.24 (t, 4H; OCH_2), 2.02 (m, 4H; CH_2).

$C_{30}H_{28}Cl_2O_{10}$	Calcd.:	C 58.17	H 4.56
(619.5)	Found:	C 57.68	H 5.28.

1,5-Bis[4-(tropylium)phenoxy]-3-oxapentane bistetrafluoroborate (**23b**)

Yield 5.6 g (92%), orange solid, dec. > 200 °C. – ^{1}H NMR (CD_3CN): δ/ppm = 9.21 (d, 4H; tropylium); 8.83–8.95 (m, 8H; tropylium), 7.96 (d, 4H; phenyl); 7.21 (d, 4H; phenyl); 4.29 (t, 4H; OCH_2); 3.84 (t, 4H; CH_2O). – ^{13}C NMR (CD_3CN): δ/ppm = 168.6 (phenyl), 162.8 (tropylium), 152.9 (tropylium), 152.5 (tropylium), 151.9 (tropylium), 132.9 (phenyl), 131.5 (phenyl), 117.3 (phenyl), 69.9 (CH_2), 68.8 (CH_2).

$C_{30}H_{28}B_2F_8O_3$	Calcd.:	C 59.06	H 4.63	
(610.2)	Found:	C 58.96	H 4.71.	

1,6-Bis[4-(tropylium)phenoxy]hexane bistetrafluoroborate (**23c**)

Yield 5.8 g (94%), orange-yellow solid, dec. >210 °C. – ^{1}H NMR (CD_3CN): δ/ppm = 9.24 (d, 4H; tropylium); 8.82–8.94 (m, 8H; tropylium); 7.99 (d, 4H; phenyl), 7.23 (d, 4H; phenyl); 4.18 (t, 4H; OCH_2);1.87 (m, 4H, CH_2); 1.58 (m, 4H, CH_2). – ^{13}C NMR (CD_3CN): δ/ppm = 169.3 (phenyl), 165.7 (tropylium), 153.7 (tropylium), 153.2 (tropylium), 152.8 (tropylium), 134.5 (phenyl), 132.1 (phenyl), 118.1 (phenyl), 70.3 (OCH_2), 30.2 (CH_2); 26.9 (CH_2). – MS (LSIMS (MB)): 621 (M^++1).

$C_{32}H_{32}B_2F_8O_2$	Calcd.:	C 61.77	H 5.18	
(622.2)	Found:	C 61.50	H 5.12	

1,8-Bis[4-(tropylium)phenoxy]-3,6-dioxaoctane bistetrafluoroborate (**23d**)

Yield 6.2 g (94%), orange solid, *m.p.* 118 °C. – ^{1}H NMR (CD_3CN): δ/ppm = 9.20 (d, 4H; tropylium), 8.82–8.93 (m, 8H; tropylium); 7.94 (d, 4H; phenyl); 7.19 (d, 4H, H-5); phenyl); 4.26 (t, 4H; OCH_2); 3.86 (t, 4H, CH_2O); 3.70 (s, 4H: OCH_2). – ^{13}C NMR (CD_3CN): δ/ppm = 168.1 (phenyl), 164.3 (tropylium), 152.8 (tropylium), 152.3 (tropylium), 151.9 (tropylium), 133.5 (phenyl), 131.4 (phenyl), 117.1 (phenyl), 71.1 (OCH_2), 69.7 (CH_2O), 68.9 (CH_2O). – MS (LSIMS (NBA)): 566 (M^+-BF_4)

$C_{32}H_{32}B_2F_8O_4$	Calcd.:	C 58.75	H 4.93	
(654.2)	Found:	C 58.61	H 5.25.	

1,4-Bis{(4-(tropylium)phenoxy)methyl}benzene bisperchlorate (**23e**)

Yield 6.0 g (94%), orange-yellow crystals (acetonitrile/ethyl acetate), *m.p.* 203 °C. – ^{1}H NMR (CD_3CN): δ/ppm = 9.22 (d, 4H; tropylium), 8.80–8.90 (m, 8H; tropylium); 7.96 (d, 4H; phenyl), 7.50 (s, 4H, phenyl bridge), 7.21 (d, 4H; phenyl), 5.27 (s, 4H; benzyl). – MS (LSIMS (NBA)): 554 (M^+-BF_4), 468 (M^+-2BF_4).

$C_{34}H_{28}Cl_2O_{10}$	Calcd.:	C 61.18	H 4.23	
(667.5)	Found:	C 60.98	H 4.11.	

N,N'-Hexamethylene-bis(N-methylaniline) (**24**)

N-Methylaniline (11.8 g, 110 mmol), 1,6-dibromohexane (6,1 g (25 mmol) and Na_2CO_3 (2.7 g, 25 mmol) were heated at 160 °C for 5 h. After cooling water (100 ml) was added and the mixture was extracted with diethyl ether (200 ml). The organic phase was dried. The solvent and the excess of the aniline was removed at reduced pressure. The residue was purified by CC (silica gel, CH_2Cl_2/hexane) affording a colorless oil, 5.2 g (71%). – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.32 (dd, 4H; phenyl); 6.80 (d, 4H; phenyl); 6.78 (t, 2H; phenyl); 3.40 (t, 4H; NCH_2); 3.01 (s, 3H; NCH_3); 1.69 (m, 4H; CH_2), 1.44 (m, 4H; CH_2). – ^{13}C NMR ($CDCl_3$): δ/ppm = 149.2 (phenyl), 129.0 (phenyl), 115.8 (phenyl), 112.0 (phenyl), 52.6 (NCH_2), 38.2 (NCH_3), 27.0 (CH_2), 26.5 (CH_2). – MS: *m/z* (%) = 297 (M^++1; 1), 296 (M^+;3), 189 (2), 146 (4), 121 (10), 120 (100), 105 (8), 104 (8), 91 (5), 77 (16), 42 (7).

$C_{20}H_{28}N_2$	Calcd.:	C 81.03	H 9.52	N 9.45
(296.5)	Found:	C 81.01	H 9.73	N 9.22.

2,9-Bis[4-(cyclohepta-2,4,6-trienyl)phenyl]-2,9-diazadecane (**25**)

24 (4 g, 13.5 mmol) and 7-methoxy-1,3,5-cycloheptatriene (3.3 g, 27 mmol) dissolved in 50 ml CH_3CN were warmed up to 50 °C for 2 h. The white precipitate was filtered and recrystallized from methanol. White crystals 4.5 g (70%), *m.p.* 75 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.06 (d, 4H; phenyl); 6.56 (m, 8H; phenyl; H-4,5); 6.07 (m, 4H; H-3,6); 5.27 (dd, 4H; H-2,7), 3.15 (t, 4H; NCH_2); 2.76 (s, 6H; NCH_3), 2.46 (t, 2H; H-1); 1.43 (m, 4H; CH_2); 1.22 (m, 4H; CH_2). – ^{13}C NMR ($CDCl_3$): δ/ppm = 148.1 (phenyl), 131.0 (phenyl), 130.8 (phenyl), 128.2 (C-4,5), 127.1 (C-3,6), 123.9 (C-2,7), 52.8 (CH_2–N), 44.3 (C-1), 38.4 (CH_3–N), 27.1 (CH_2), 26.7 (CH_2). –MS: *m/z* (%) = 477 (M^++1, 2), 476 (M^+, 5), 211 (18), 210 (100), 196 (23), 167 (15), 165 (15), 152 (8), 118 (8), 91 (37), 89 (8), 42 (11).

$C_{34}H_{40}N_2$	Calcd.:	C 85.56	H 8.46	N 5.88
(476.7)	Found:	C 85.09	H 8.65	N 5.83.

Method C

Synthesis of Bridged Diarylcycloheptatrienes 26 and 27 (General Procedure)

The freshly distilled aniline compound (60 mmol) was dissolved in 10 ml dried acetonitrile. The tropylium salts **23** (7.5 mmol) dissolved in 30 ml acetonitrile were slowly added under an argon atmosphere. After 4h stirring the reaction mixture was removed from the solvent. The residue was treated with 1M NaOH (100 ml) and extracted with CH_2Cl_2 (80 ml). The organic phase was washed with saturated aqueous NaCl-solution, dried and evaporated at reduced pressure.

1,6,-Bis{4-[4-(4-ethylaminophenyl)-cyclohepta-1,3,6-trienyl]phenoxy}hexane (**26a**)

According to the general procedure from **23c** (4.7 g) and *N*-ethylaniline (7.5 ml). The crude isomer mixture was roughly purified by CC (silica gel, CH_2Cl_2) affording 2.7 g (52%) of a mixture of two isomers which contains besides **26a** the isomer 1,6-bis{4-[3-(4-ethylaminophenyl)-cyclohepta-1,4,6-trienyl] phenoxy}-hexane (**27a**). The mixture was separated by repeated recrystallizations from methanol affording pure **26a**, 0.75 g (14%). Yellow solid, *m.p.* 156–59 °C. – ^{1}H NMR (CD_3CN): δ/ppm = 7.42 (d, 4H; phenyl); 7.16 (d, 4H; phenyl); 7.00 (d, 2H; H-2); 6.90 (d, 4H; phenyl), 6.60 (d, 4H; phenyl), 6.34 (d, 2H, H-7), 6.30 (dd, 2H; H-3), 5.54 (dd, 2H; H-6), 5.44 (dd, 2H; H-4), 3.97 (m, 4H, OCH_2), 3.13 (q, 4H; NCH_2), 2.74 (t, 2H; H-5); 1.80 (m, 4H; CH_2); 1.53 (m, 4H; CH_2), 1.23 (t, 6H, CH_3). – ^{13}C NMR (CD_3CN): δ/ppm = 159.2 (phenyl), 147.8 (phenyl), 142.9 (C-1), 134.8 (phenyl), 132.6 (phenyl), 128.6/128.4 (phenyl), 127.9/127.8 /127.1 (C-1,2,3), 125.1/124.9 (C-5,6), 114.8 (phenyl), 113.3 (phenyl), 68.4 (OCH_2), 44.9 (C-5), 39.0 (NCH_2), 29.6 (CH_2), 26.2 (CH_2), 15.1 (CH_3). –MS (LSIMS (MB)): 689 (M^++1).

$C_{48}H_{52}N_2O_2$	Calcd.:	C 83.68	H 7.90	N 4.06
(689.0)	Found:	C 83.75	H 8.25	N 4.03.

1,8-Bis{4-[5-(4-aminophenyl)-cyclohepta-1,3,6-trienyl] phenoxy}-3,6-dioxaoctane (**26b**)

According to the procedure described above from **23d** (5 g) and aniline (6 ml). The oily residue was dissolved in boiling

methanol. At –20 °C a yellow solid (2.5 g, 49%) resulted which contained **26b** and *1,8-bis{4-[3-(4-aminophenyl)-cyclohepta-1,4,6-trienyl]phenoxy}-3,6-dioxaoctane* **27b** in the ratio 1.5:1. CC (silicagel, hexane/ethylacetate 2:1) afforded pure **26b**, 1.10 g (22%), *m.p.* 88 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43 (d, 4H; phenyl); 7.17 (d, 4H; phenyl); 7.00 (d, 2H; H-2); 6.92 (d, 4H; phenyl), 6.70 (d, 4H; phenyl); 6.35 (d, 2H; H-7), 6.30 (dd, 2H; H-3); 5.55 (dd, 2H, H-6), 5.47 (dd, 2H; H-4); 4.15 (t, 4H, OCH_2), 3.87 (t, 4H; CH_2O), 3.77 (s, 4H; OCH_2); 3.64 (br, 4H, NH_2), 2.77 (t, 2H, H-5). – ^{13}C NMR (acetone-d_6): δ/ppm) = 159.5 (phenyl), 147.8 (phenyl), 143.1 (C-1), 135.2 (phenyl), 132.6 (phenyl), 128.8 (phenyl), 128.2/128.1/127.4 (C-2,3,7), 125.4/125.3 (C-4,6), 115.5 (phenyl), 115.4 (phenyl), 71.4 (O–C), 70.3 (C-O), 68.3 (O–C), 45.4 (C-5). – MS (LSIMS (NBA)): 664 (M^++1).

$C_{44}H_{44}N_2O_4$	Calcd.:	C 79.49	H 6.67	N 4.21
(664.9)	Found:	C 79.58	H 6.87	N 4.16.

1,8-Bis{4-[5-(4-ethylaminophenyl)-cyclohepta-1,3,6-trienyl]phenoxy}-3,6-dioxaoctane (**26c**)

From **23d** (5g) and *N*-ethylaniline (7.5 ml). The residue was treated with boiling methanol. Cooling at –20 °C afforded the mixture of **26c** and *1,8-bis{4-[3-(4-ethylaminophenyl)-cyclohepta-1,4,6-trienyl]phenoxy}-3,6-dioxaoctane* **27c** in the ratio of 1.3:1 (according to ^{1}H NMR) (3.1 g, 56%). Repeated recrystallizations from methanol yielded **26c** (0.8 g, 15%), *m.p.* 91 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43 (d, 4H; phenyl), 7.19 (d, 4H; phenyl), 7.00 (d, 2H; H-2); 6.92 (d, 4H; phenyl); 6.63 (d, 4H; phenyl), 6.34 (d, 2H; H-7); 6.30 (dd, 2H; H-3); 5.56 (dd, 2H; H-6); 5.49 (dd, 2H; H-4); 4.66 (br, 2H; NH); 4.14 (m, 4H; OCH_2); 3.87 (m, 4H; CH_2O); 3.76 (s, 4H; OCH_2); 3.16 (q, 4H; NCH_2); 2.76 (t, 2H; H-5); 1.25 (t, 6H; CH_3). – ^{13}C NMR (acetone-d_6): δ/ppm = 159.2 (phenyl), 148.7 (phenyl), 143.0 (C-1), 135.2 (phenyl), 132.1 (phenyl), 128.7 (phenyl), 128.2/128.1/127.4 (C-2,3,7), 125.4 / 125.3 (C-4,6), 115.3 (phenyl), 113.5 (phenyl), 71.4 (O–C), 70.3 (C–O), 68.3 (O–C), 45.4 (C-5), 38.8 (N–C), 15.0 (CH_3). – MS: *m/z*(%) = 721 (14), 720 (M^+; 27), 602 (16), 601 (37), 588 (42), 587 (100), 512 (13), 511 (38), 479 (19), 478 (13), 303 (17), 302 (24), 288 (16), 286 (18), 210 (19), 209 (12), 197 (32), 183 (21), 170 (27), 165 (47), 152 (46), 134 (42), 121 (39), 115 (34), 106 (34), 91 (50), 77 (55), 45 (82).

$C_{48}H_{52}N_2O_4$	Calcd.:	C 79.97	H 7.27	N 3.89
(721.0)	Found:	C 79.98	H 7.12	N 3.98.

1,4-Bis{[4-[5-(4-ethylaminophenyl)-cyclohepta-1,3,6-trienyl]phenoxy]-methyl}benzene (**26d**)

From **23e** (1.3 g) and *N*-ethylaniline (4.4 g). The crude product was washed with cold ethanol and than dissolved in CH_2Cl_2. By addition of *n*-hexane the mixture of isomers **26d** and *1,4-bis{[4-[3-(4-ethylaminophenyl)-cyclohepta-1,4,6-trienyl]phenoxy]-methyl}benzene* **27d** (1.3:1) was obtained. **26d** was purified by repeated recrystallizations from CH_2Cl_2/*n*-hexane. Yellowish solid, 0.13 g (9%), *m.p.* 183 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.45 (m, 8H; phenyl); 7.20 (d, 4H: phenyl); 7.01 (d, 2H; H-2); 6.99 (d, 4H; phenyl); 6.64 (d, 4H; phenyl); 6.35 (d, 2H; H-7), 6.32 (dd, 2H: H-3); 5.57 (dd, 2H; H-6), 5.47 (dd, 2H; H-4); 5.11 (m, 4H; benzyl); 3.53 (br, 2H; NH); 3.17 (q, 4H; NCH_2): 2.76 (t, 2H; H-5); 1.27 (t, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ/ppm = 158.3 (phenyl), 147.2 (phenyl), 142.4 (C-1), 136.8 (phenyl bridge), 135.0 (phenyl), 132.4 (phenyl), 128.3 (phenyl bridge), 127.8/128.2 (phenyl), 127.7 (C-2), 127.6/127.0 (C-3,7), 124.7/124.5 (C-4,6), 114.8 (phenyl), 113.0 (phenyl), 69.8 (benzyl), 44.5 (C-5), 38.7 (N–C), 15.0 (CH_3). – MS: *m/z* (%) = 708 (M^+; 1), 589 (3), 407 (15), 302 (100), 289 (14), 288 (55), 273 (13), 210 (12), 202 (10), 184 (12), 183 (24), 181 (19), 165 (24), 146 (26), 134 (17), 105 (74), 91 (16), 77 (20), 44 (65).

$C_{50}H_{48}N_2O_2$	Calcd.:	C 82.71	H 6.82	N 3.45
(709.0)	Found:	C 82.10	H 6.57	N 3.30.

1,6-Bis{4-[5-(4-N,N'-dimethylaminophenyl]cyclohepta-1,3,6-trienyl]phenoxy}hexane (**26e**)

From 3.4 g **23c** and 4g (33 mmol) *N,N*-dimethylaniline. The residue was recrystallized from diethyl ether, 1.7 g yellowish solid, *m.p.* 162–165 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43 (d, 4H; phenyl); 7.25 (d, 4H; phenyl); 7.00 (d, 2H; H-2); 6.90 (d, 4H; phenyl); 6.76 (d, 4H; phenyl); 6.35 (d, 2H; H-7); 6.30 (dd, 2H, H-3); 5.56 (dd, 2H; H-6), 5.48 (dd, 2H; H-4); 3.99 (t, 4H; OCH_2); 2.94 (s, 12H; NCH_3); 2.77 (t, 2H; H-5); 1.83 (m, 4H; CH_2); 1.23 (m, 4H; CH_2). – MS: *m/z* (%) = 688 (M^+; 10), 570 (14), 556 (26), 555 (62), 303 (48), 302 (71), 301 (27), 259 (13), 258 (16), 210 (35), 184 (21), 183 (24), 170 (44), 146 (32), 134 (56), 84 (24), 55 (100), 44 (50), 42 (44).

$C_{48}H_{52}N_2O_2$	Calcd.:	C 83.68	H 7.90	N 4.06
(689.0)	Found:	C 83.06	H 7.60	N 3.96.

1,12-Diaza-2,11-dioxo-20,22,46,48,57,59-hexadehydro-30,33,36,39-tetraoxa[$2^{19,23}$.$2^{46,50}$][12.5.10.5]paracyclophane (**28a**)

A solution of 0.5 ml triethylamine in 600 ml dried toluene was heated at 50–55 °C. Under argon atmosphere two solutions of **26b** (0.42 g, 0.63 mmol) in 25 ml toluene and sebacoyl dichloride (0.152 g, 0.63 mmol), respectively, in 25 ml toluene were synchronously added during 3 h with the aid of motor syringes. After cooling to room temperature the solution was filtered and the solvents removed at reduced pressure. The remaining residue was washed successively with cyclohexane (50 ml), *t*-butyl methyl ether and methanol. The crude product was purified by CC (silica gel, $CHCl_3$). A yellow solid resulted (0.3 g, 57%), *m.p.* 118–20 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43–7.48 (m, 4H; H-15/17/52/56); 7.36 (d, 4H; H-25/29/42/44); 7.17–7.22 (m, 4H; H-14/18/53/55); 6.96 (d, 2H; H-22/47); 6.92 (d, 4H; H-26/28/41/45); 6.27 (m, 4H; H-21/48/58/60); 5.41 (m, 4H; H-20/49/57/59); 4.07 (t, 4H; H-31/38); 3.88 (t, 4H; H-32/37); 3.76 (s, 4H; H-34/35); 2.75 (t, 2H; H-19/50); 2.39 (m, 4H; H-3/10); 1.4 (m, 12H; H-4/5/6/7/8/9). – ^{13}C NMR ($CDCl_3$): δ/ppm = 172.1 (C-2/11), 158.1 (C-27/40), 142.4 (C-13/54), 139.7/136.4 (C-23/24/43/46), 134.5 (C-16/51), 128.9/128.3/127.9 (C-14/15/17/18/25/29/42/44/52/53/55/56), 126.9 (C-22/47) 126.7/126.5 (C-21/48/58/60), 125.1/124.9 (C-20/49/57/59), 114.7 (C-26/28/41/45), 71.0 (C-34/35), 69.8 (C-32/37), 67.6 (C-31/38), 44.8 (C-19/50), 37.1 (C-3/10), 29.0 (C-4/9), 27.5 (C-5/8), 24.5 (C-6/7). – MS (LSIMS (NBA)): 831 (M^++1).

$C_{54}H_{58}N_2O_6$	Calcd.:	C 78.04	H 7.04	N 3.37
(831.1)	Found:	C 77.88	H 7.36	N 3.10.

1,12-Diaza-1,12-diethyl-2,11-dioxo-20,22,46,48,57,59-hexadehydro-30,33,36,39-tetraoxa[2^{19,23}.2^{46,50}][12.5.10.5]paracyclophane (**28b**)

According to the procedure described above from **26c** (0.37 g, 0.51 mmol) and sebacoyl dichloride (0.12 g, 0.51 mmol). Purification by CC (silica gel/$CHCl_3$) afforded **28b** (0.29 g, 64%), *m.p.* 120–23 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.32 (m, 8H; H-15/17/25/29/42/44/52/56); 7.05 (d, 4H; H-14/18/53/55); 6.86 (d, 2H; H-22/47); 6.81 (d, 4H; H-26/28/41/45); 6.30 (d, 2H; H-58/60); 6.19 (m, 2H; H-21/48); 5.55 (dd, 2H; H-57/59); 5.39 (m, 2H; H-20/49); 4.01 (m, 4H; H-31/38); 3.78 (m, 4H; H-32/37); 3.67 (s, 4H; H-34/35); 3.66 (m, 4H; H-61); 2.81 (m, 2H; H-19/50); 1.92 (t, 4H; H-3/10); 1.1–1.5 (m, 12H; H-4/5/6/7/8/9); 1.01 (t, 6H; H-62). – ^{13}C NMR (acetone-d_6): δ/ppm = 172.0 (C-2/11), 159.6 (C-27/40), 142.3 (C-13/54), 137.4/134.8 (C-23/24/43/46), 133.8 (16/51), 129.7/129.3 (C-15/17/25/29/42/44/52/56), 129.3 (C-22/47), 128.7 (C-14/18/53/55), 127.5/127.4 (C-21/48/58/60), 126.4/126.2 (C-20/49/57/59), 115.6 (C-26/28/41/45), 71.6 (C-34/35), 70.3 (C-32/37), 68.4 (C-31/38), 45.6 (C-19/50), 44.2 (C-61), 34.5 (C-3/10), 29.5/29.4 (C-4/5/8/9), 26.0 (C-6/7), 13.5 (C-62). – MS (LSIMS (MB)): 887 (M^++1).

$C_{58}H_{66}N_2O_6$	Calcd.:	C 78.52	H 7.50	N 3.15
(887.2)	Found:	C 78.08	H 7.16	N 3.00.

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