Synthesis of a new class of difunctional tetraphenylene crown ethers

Harry W. Gibson, Devdatt S. Nagvekar, Yadollah Delaviz, and William S. Bryant

Abstract: Three new substituted tetraphenylene crown ethers have been made. Bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-(3*x* + 6)-crown-*x*, where *x* = 12, 16, and 20 (**11b**–**11d**) were synthesized via [1 + 1] cyclization of methyl 3,5-bis[ω-chloro(oligoethyleneoxy)]benzoates (**13b**–**3d**) with methyl 3,5-bis[ω-(*p*-hydroxyphenoxy)(oligoethyleneoxy)]benzoates (**16b**–**6d**) using K_2CO_3 as base and tetrabutylammonium iodide as a phase transfer agent in dimethylformamide (DMF). The corresponding 30-membered (*x* = 8) macrocycle **11a** could not be made by this approach; only the elimination product, 3,5-bis(vinyloxy)benzoic acid (**19**), was isolated. **16a**–**16d** were made via alkylation of *p*-benzyloxyphenol (**14**) with **13a**–**13d**, respectively, followed by hydrogenolysis with Pd/C as catalyst. No complexation of these macrocycles with dibenzylammonium ions was detected by NMR spectroscopy, but weak complexation of **11d** with a paraquat derivative was observed.

Key words: crown ethers, cyclization, macrocycles.

Résumé : On a préparé trois nouveaux éthers couronnes de type tétraphénylène substitué. On a synthétisé les bis(5-carbométhoxy-1,3-phénylène)-bis(*p*-phénylène)-(3*x* + 6)-couronnes-*x*, dans lesquelles *x* = 12, 16 et 20 (**11b**–**11d**) par le biais d'une cyclisation [1 + 1] des 3,5-bis[ω-chloro(oligoéthylèneoxy)]benzoates de méthyle (**13b**–**13d**) avec les 3,5-bis[ω-(*p*-hydroxyphénoxy)(oligoéthylèneoxy)]benzoates de méthyle (**16b**–**16d**) dans le diméthylformamide (DMF), en présence de K_2CO_3 agissant comme base et d'iodure de tétrabutylammonium agissant comme agent de transfert de phase. Utilisant cette méthode, il n'a pas été possible de préparer le macrocycle correspondant à trente chaînons (*x* = 8) (**11a**); on n'a isolé que le produit d'élimination, l'acide 3,5-bis(vinyloxy)benzoïque (**19**). On a préparé les produits **16a**–**16d** par le biais d'alkylations du *p*-benzylphénol (**14**) avec les esters **13a**–**13d**, suivies d'une hydrogénolyse avec du Pd/C comme catalyseur. Par spectroscopie RMN, on n'a pas pu détecter de complexation de ces macrocycles avec les ions dibenzylammonium; on a toutefois observé une faible complexation du composé **11d** avec un dérivé du paraquat.

Mots clés : éthers couronnes, cyclisation, macrocycles.

[Traduit par la Rédaction]

Introduction

Crown ethers are an interesting class of molecules which are known for their ability to complex with a wide variety of cations, including metal and organic species (1). We are interested in macrocyclic polyethers which are semi-flexible in nature and have the ability to undergo complexation with linear molecules to form pseudorotaxanes, rotaxanes, and polyrotaxanes (see reviews in ref. 2*a*–*f*) of various types. A number of bisphenylene crown ethers with ring sizes from 24–34 atoms have been synthesized previously in our laboratory (3–5) for these purposes (2*a*, *b*, *g*–*o*; for poly(urethane crown ether rotaxane)s see ref. 2*g*; for poly(ester crown ether rotaxane)s see refs. 2*h* and *i*; for poly(methacrylate crown ether side chain rotaxane)s see ref. 2*j*; for self-assembled supramolecular structures see refs. 2*k*–*o*).

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Larger macrocycles are also of interest for these and related applications. Bis(*p*-phenylene)-bis(*m*-phenylene)-66-crown-20 (**1b**) was isolated in 11% yield (6) as a [2 + 2] by-product from the [1 + 1] synthesis of *p*-phenylene-*m*-phenylene-33-crown-10 (**1a**) (7). Cyclization of resorcinol with tetra(ethylene glycol) ditosylate generated [1 + 1], [2 + 2], and [3 + 3] products, *m*-phenylene-16-crown-5 (**2a**), bis-*m*-phenylene-32-crown-10 (**2b**), and tris(*m*-phenylene)-48-crown-15 (**2c**) in 54, 8.4, and 1.7% yields, respectively (8). Tris(*p*-phenylene)-51-crown-15 (**3b)** and tetrakis(*p*-phenylene)-68-crown-20 (**3c**) have been reported (9) and shown to act as templates for paraquat units (**5**) in catenane syntheses and as hosts for dibenzylammonium ion (**6**), forming pseudorotaxanes with varying stoichiometries (10*a*). And recently the corresponding analogous 1,5-dioxynaphthalene family of crown ethers was expanded to include the bis-, tris-, and tetrakis- species **4a**–**4c**; these hosts were used in catenane syntheses using cyclobis(paraquat-arylene)s (10*b*). These reports have prompted us to describe our efforts with bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-(3*x* + 6)-crown-*x* (**11a**–**11d**) systems, which began in 1990.

Our ongoing efforts led us to focus our attention on tetraphenylene macrocycles with ring sizes between 42 and 66 atoms.

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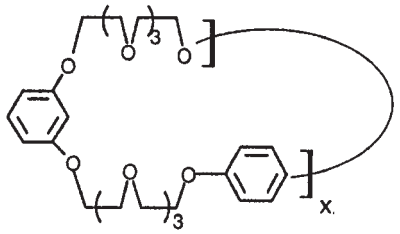

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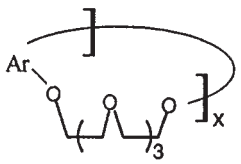
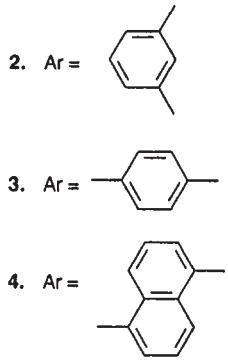
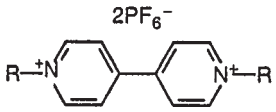
b) x = 2



a) x = 1
b) x = 2
c) x = 3

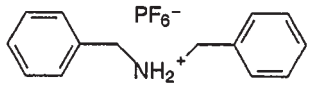


2. Ar =
3. Ar =
4. Ar =



5

a. R = CH_3
b. R = CH_2CH_2OH



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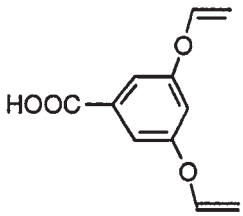

19

Results and discussion

1. The [2 + 2] cyclization approaches

Although it is well known that multistep methods are more efficient for large oligomeric macrocycles than direct [*n* + *n*] approaches (11, 12), the latter have the appeal of using simple starting materials in a one-step procedure reaction sequence. Thus, we initially attempted the synthesis of tetraphenylene crown ethers in this way.

The generic [2 + 2] route to bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-(3*x* + 6)-crown-*x* (**11**) (Schemes 1 and 2) involves preparation of bis[ω-chloro(oligoethyleneoxy)] derivatives (**9**) of hydroquinone and their condensations with methyl 3,5-dihydroxybenzoate (**10**).

This route to bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-30-crown-8 (**11a**) was explored via synthesis of diol **8a** and its conversion to the corresponding dichloride **9a**, both in good yields. However, from the attempted cyclization of **9a** with **10** we were unable to isolate the desired **11a**.

The larger bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-42-crown-12 (**11b**) was approached in an analogous manner. Hydroquinone was alkylated with 2-[2′-(2′′-chloroethoxy)ethoxy]tetrahydropyran (**7b**), and the resultant THP ether was deprotected to afford *p*-bis[2-(2′-hydroxyethoxy)ethoxy]benzene (**8b**). Treatment of **8b** with thionyl chloride produced *p*-bis[2-(2′-chloroethoxy)ethoxy]benzene (**9b**). Attempts to isolate macrocycle **11b** from condensation of bisphenol **10** and **9b** were fruitless.

2. The [1 + 1] cyclization approaches

The more efficient [1 + 1] cyclization approaches to higher cyclic oligomers requires the syntheses of larger building blocks, but allows the more effective use of pseudo-high dilution (syringe pump addition) techniques (11, 12). Tetraphenylene crown ethers **11** were approached by the method depicted in Scheme 3.

*(a) Dihalide intermediates **13***

Methyl 3,5-bis(5-chloro-3-oxapentyloxy)benzoate (**13b**), methyl 3,5-bis(8-chloro-3,6-dioxaoctyloxy)benzoate (**13c**), and methyl 3,5-bis(11-chloro-3,6,9-trioxaundecyloxy)benzoate (**13d**) were each synthesized in one step by reacting large excesses of di-, tri-, and tetra-(ethylene glycol) dichlorides (**12b**–**12d**), respectively, with the disodium salt of methyl 3,5-dihydroxybenzoate (**10**) (Scheme 3), as previously reported (3, 4).

A one-pot synthesis of methyl 3,5-bis(2-chloroethoxy)benzoate (**13a**) was also attempted by reacting a suspension of the disodium salt of methyl 3,5-dihydroxybenzoate (**10**) with a large excess of dichloroethane (**12a**) in DMF. Thin layer chromatography (TLC) indicated a considerable amount of starting benzoate **10** along with the desired product **13a**, which was obtained (10%) upon Soxhlet extraction. Even at longer reaction times considerable amounts of starting material were found.

To synthesize methyl 3,5-bis(2-hydroxyethoxy)benzoate as a precursor to **13a**, the dianion of methyl 3,5-dihydroxybenzoate (**10**), generated in situ with potassium carbonate, was reacted with chloroethanol (**7a**) at 70°C for three days.

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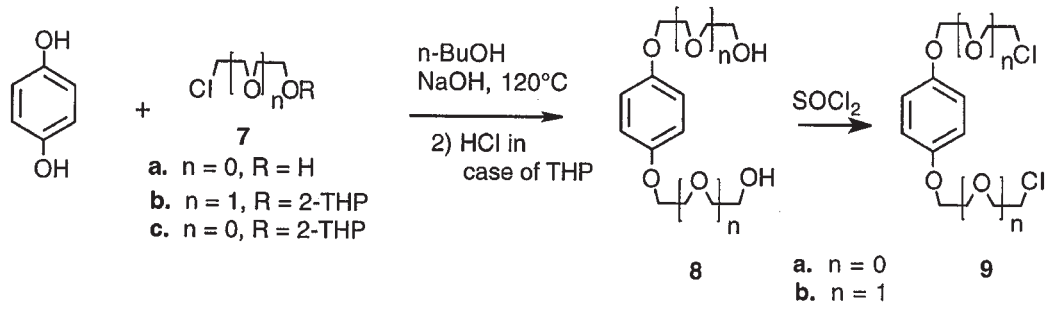
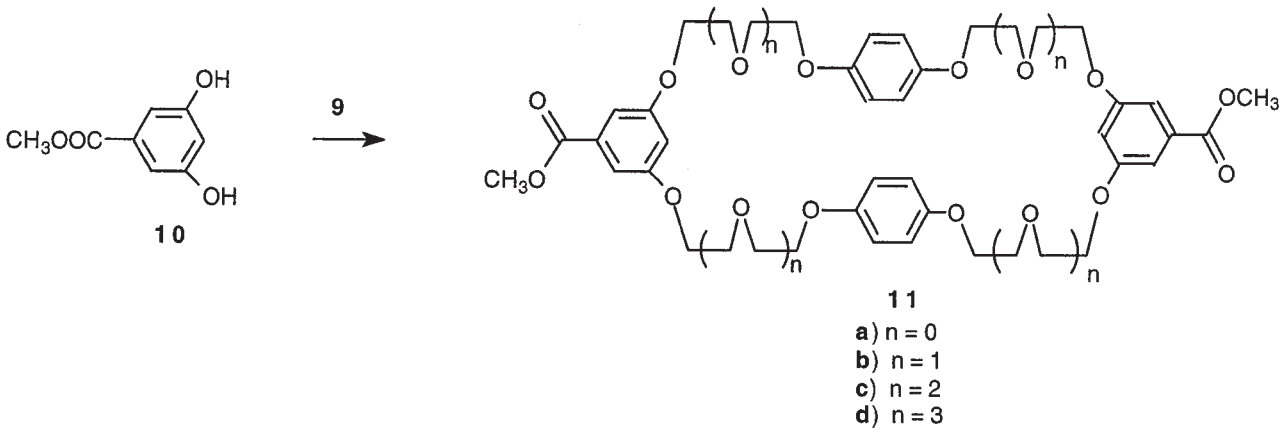
Scheme 1.



Scheme 2.



Less than a 10% yield of pure product was obtained. The use of THP protected chloroethanol (**7c**) was then examined. Treatment of methyl 3,5dihydroxybenzoate (**10**) with sodium hydride in DMF followed by reaction with **7c** gave (77%) after deprotection the desired intermediate methyl 3,5-bis(2-hydroxyethoxy)benzoate. After work-up this compound was without purification converted (88%) to the corresponding dichloride **13a** with thionyl chloride and pyridine in benzene.

*(b) Bisphenols **16***

The synthesis of the second fragment for cyclization to **11a**, methyl 3,5-bis[2-(*p*-hydroxyphenoxy)ethoxy]benzoate (**16a**), was initiated via reaction of *p*-benzyloxyphenol (**14**) with methyl 3,5-bis(2-chloroethoxy)benzoate (**13a**) using sodium hydride as base (Scheme 3), but this did not result in the formation of product **15a**. A three-step approach to **15a** was then evaluated (Scheme 4). Reaction of THP protected chloroethanol (**7c**) with *p*-benzyloxyphenol (**14**) and subsequent deprotection gave *p*-(2-hydroxyethoxy)benzyloxybenzene (**17**) in quantitative yield. The compound **17** was converted to the chloro derivative **18** with thionyl chloride and pyridine. Reaction of methyl 3,5-dihydroxybenzoate (**10**) with **18** using sodium hydride as base gave (60%) the desired product, methyl 3,5-bis[2(*p*-benzyloxyphenoxy)ethoxy]benzoate (**15a**).

Methyl 3,5-bis{[*p*-(benzyloxy)phenoxy]oligoethyleneoxybenzoates (**15b**–**15d**) were produced via reaction of *p*-benzyloxyphenol (**14**) with dichlorides **13b**–**13d** using sodium hydride as the base (Scheme 3). These intermediates were purified via flash silica gel chromatography and characterized by NMR and FAB MS.

Removal of the benzyl groups from **15a**–**15d** via hydrogenolysis with palladium on carbon as catalyst gave the desired bisphenols **16a**–**16d** in 90–99% yields (Scheme 3).

*(c) Cyclization reactions to form macrocycles **11***

Our previous cyclization studies showed that the yields were either higher (20- and 26-membered) (5) or almost identical (32-membered) (3, 4) with potassium salts, as compared to the more expensive cesium salts. Thus, we used potassium carbonate as the base in the [1 + 1] cyclization of the bisphenols **16b**–**16d** with dichlorides **13b**–**13d** in DMF at 110°C (Scheme 3). This method provided macrocycles **11b**–**11d** in 17–24% yields.

The cyclization of methyl 3,5-bis[2-(*p*-hydroxyphenoxy)ethoxy]benzoate (**16a**) with methyl 3,5-bis(2-chloroethoxy)benzoate (**13a**) under these conditions was not successful. Therefore, cyclization was attempted at 85°C using sodium hydride as base in DMF via the syringe pump technique. Sodium was used as the metal ion to match the small cavity size of 30-membered **11a**. However, we were able to isolate only (19%) 3,5-bis(vinyloxy)benzoic acid (**19**), the product of two elimination reactions.

*(d) Attempted complexation with dibenzylammonium salt **6***

Bis(*o*- and *p*-phenylene) crown ethers are known to complex strongly with secondary ammonium ions, such as dibenzylammonium hexafluorophosphate (**6**), yielding pseudorotaxanes (2*c*, *e*, *f*, 10*a*, 13) In the present work, in the ^{1}H NMR spectra of $CDCl_3$ solutions of **11b**–**11d** (individually) in the presence of solid ammonium salt **6** there were no indi-

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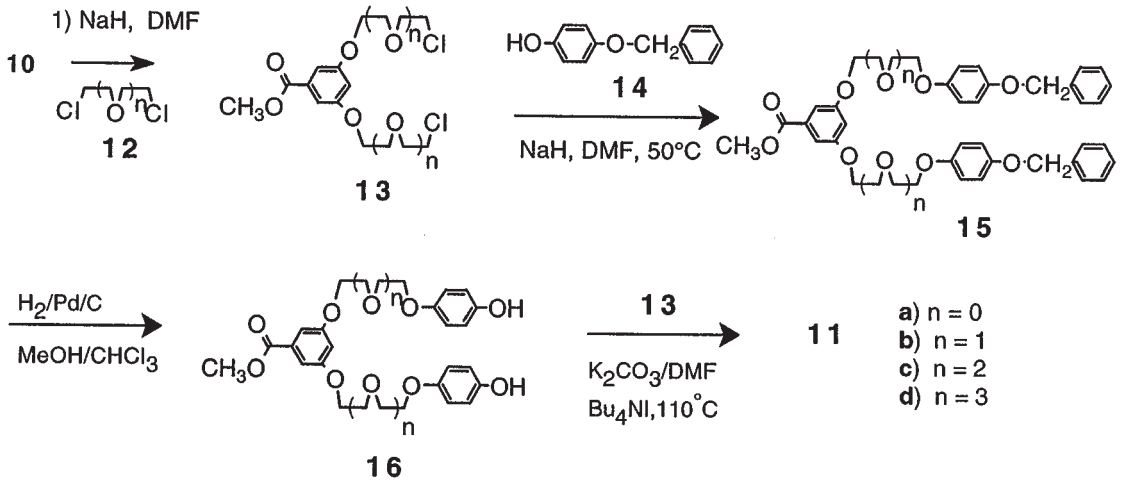
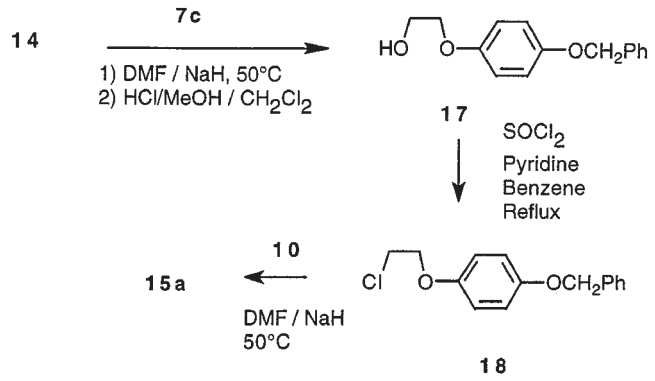
Scheme 3.



Scheme 4.



cations of complexation, i.e., no changes of chemical shifts of the proton signals; furthermore, the ammonium salt did not dissolve in $CDCl_3$ solutions of the crown ethers, a good qualitative test for complex formation.

The inclusion complexation of secondary ammonium ions such as **6** by crown ethers appears to be relatively facile based on the isolation of pseudorotaxanes of various stoichiometries for benzo and *p*-phenylene macrocycles ranging from dibenzo-24-crown-8 to tetrakis(*p*-phenylene)-68-crown-20 (**3d**) (10*a*, 13). As deduced from single crystal X-ray structures, the N-H—O bonds in these complexes involve both the phenolic and ethyleneoxy oxygen atoms, as do the benzylic C-H—O bonds, in some cases augmented by π–π interactions. However, we have found that bis(*m*-phenylene) crown ethers complex either very weakly or not at all with secondary ammonium ions (14). Bis(*m*-phenylene)-26-crown-8, in spite of its homology with dibenzo-24-crown-8, which efficiently yields a pseudorotaxane (13), does not give any indication of complexation with **6** by NMR spectroscopy. The larger bis(*m*-phenylene)-32-crown-10 (**2b**), like its 34-membered *p*-analog **3b** (13), gives [3]pseudorotaxanes with two ammmonium ions as guests, but its association constants are quite low (<10 M^{-1}) (14). X-ray analysis of the crystalline [3]pseudorotaxane **2b**:(**6**)$_2$ revealed that the structure and attractive forces are very similar to those reported for **3b**:(**6**)$_2$ (13, 14). The difference in the association constants, therefore, must be a result of poorer preorganization in the case of **2b**. In **11b**–**11d** the electron-withdrawing carbomethoxy groups on the *m*-phenylene units further decrease the tendency for the *m*-phenylene moieties to undergo complexation. However, the hydroquinol ether linkages were expected to provide suitable sites. The only explanation for the lack of complexation of secondary ammonium ions by **11b**–**11d** seems to be that the conformational properties imbued by the *m*-phenylene units are such that complexation is entropically unfavorable.

*(e) Complexation with paraquat diol **5b***

The complexation of paraquat (**5a**) with bis(*m*-phenylene)-32-crown-10 and bis(*p*-phenylene)-34-crown-10 is driven primarily by hydrogen bonding of the α-protons of the bipyridinium units with the ether oxygen atoms, but also involves donor–acceptor, π-stacking, and dipole–dipole attractions (15). It has been deduced that, because four ethyleneoxy units serve to maximize the association constants, hydrogen bonding of the central oxygen atom in the tetra(ethyleneoxy) segment is most important, but that the next nearest oxygen atom plays a role by an allosteric effect (16). X-ray crystallographic results show that both of these interactions are in force in the solid state (6, 9, 15).

Upon mixing solutions of **11d** with **5b** a pale yellow–orange color indicative of charge transfer was observed; in the ^{1}H NMR spectra shifts of the signals for the hydroquinol unit proton, the intra-annular aromatic proton of the *m*-phenylene unit and the CH_2O group adjacent to the hydroquinol unit were observed. Although we have not yet determined the stoichiometry of this complex, it is clear that some relatively weak complexation takes place. Studies with crown ethers containing *m*-phenylene linkages in comparison to their *p*-linked counterparts, e.g., **2b** vs. **3b**, and internally in catenanes derived from **1a**, have demonstrated the preference of paraquat (**5a**) complexation centered on the *p*-phenylene units (6). Thus, we hypothesize that the hydroquinol units of **11d** are the active sites, especially since we have shown that the electron-withdrawing carbomethoxy groups in bis(5-carbomethoxy-1,3-phenylene)-32-crown-10

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are detrimental for complexation of paraquats.[2]

Current work is aimed at determining the stoichiometry of the complex of **11d** with **5b**, so that its association constant can be measured, and, hopefully, obtaining crystals suitable for X-ray analysis.

Experimental

Materials

Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. The compounds **5b** (17), **6** (13), **7b** (18), **7c** (19), **10** (20), **13b** (3), **13c** (3), and **13d** (4) were synthesized according to literature procedures.

Instrumentation and techniques

Melting points were taken in capillary tubes and have been corrected. The ^{1}H and ^{13}C NMR spectra were obtained at room temperature (RT) on a 400 MHz spectrometer using $CDCl_3$ as solvent with $SiMe_4$ (δ = 0) as internal standard, except as noted. The MS was carried out in house, at the Washington University Mass Spectrometry Resource and at the Nebraska Center for Mass Spectrometry using the FAB technique in 3-nitrobenzyl alcohol matrices (HR = high resolution). A syringe infusion pump was used to control the addition rates in the cyclization reactions.

p-Bis(2-hydroxyethoxy)benzene (8a)

A solution of **7c** (52.5 g, 320 mmol) in *n*-BuOH (150 mL) was added dropwise to a refluxing solution of hydroquinone (11.0 g, 101 mmol), NaOH (8.20 g, 200 mmol), sodium dithionite (40 mg), and *n*-BuOH (300 mL). The solution was refluxed for 15 h under N_2, and more NaOH (2.90 g, 72.5 mmol) was added and refluxing was continued for 15 h. The reaction mixture was cooled, filtered, and concentrated in vacuo to remove solvent and excess **7c**. The residue was dissolved in MeOH:CH_2Cl_2 (1:1 v:v, 500 mL), treated with conc. HCl (5 mL) and stirred for 4 h at RT to hydrolyze the THP ether. The solution was neutralized with $NaHCO_3$. The organic layer was dried (Na_2SO_4) and evaporated to give the crude product (17.0 g, 85%), which was recrystallized from EtOAc: mp 105–107°C; this compound is commercially available.

p-Bis[2-(2′-hydroxyethoxy)ethoxy]benzene (8b)

Application of the above procedure using **7b** on twice the scale afforded 43.6 g (76%) of colorless solid after recrystallization from EtOAc: mp 74.5–75.5°C. ^{1}H NMR, δ (ppm): 2.75 (s, 2H), 3.6–4.4 (m, 16H), 6.85 (s, 4H). Anal. calcd. for $C_{14}H_{22}O_6$: C 58.72, H 7.75; found: C 58.64, H 7.78.

p-Bis(2-chloroethoxy)benzene (9a)

The compound $SOCl_2$ (223.0 g, 1.874 mol) was added very slowly to a solution of **8a** (148.66 g, 750 mmol), pyridine (150 mL), and toluene (450 mL). The solution was refluxed for 24 h, cooled, and the precipitate was extracted with toluene (2 × 150 mL). The extract was washed with H_2O (200 mL), dried (Na_2SO_4), and evaporated to produce 149.5 g (79%) of crude product, which was recrystallized from EtOAc: mp 102–103°C, lit. (21) oil. ^{1}H NMR, δ (ppm): 3.79 (t, J = 7 Hz, 4H), 4.19 (t, J = 7 Hz, 4H), 6.87 (s, 4H). MS (EI), m/z: 238 [(M $^{37}Cl_2)^+$, 10%], 236 [(M ^{37}Cl $^{35}Cl)^+$, 67%], 234 [(M $^{35}Cl_2)^+$, 100%], 171 [(M $^{35}Cl_2$ – CH_2CH_2Cl), 90%], 109 [(M – 2(CH_2CH_2Cl)), 100%].

p-Bis[2-(2′-chloroethoxy)ethoxy]benzene (9b)

Application of the above procedure to **8b** produced (85%) crude **9b**, which was recrystallized from EtOAc: mp 62.2–64.0°C, lit. (21) oil. ^{1}H NMR, δ (ppm): 3.6–4.2 (m, 16H), 6.85 (s, 4H). MS (EI), m/z: 324 [(M ^{37}Cl $^{35}Cl)^+$, 24%], 322 [(M $^{35}Cl_2)^+$, 35%], 113 (100%). Anal. calcd. for $C_{14}H_{20}Cl_2O_4$: C 52.02, H 6.24; found: C 51.88, H 6.25.

Methyl 3,5-bis(2-hydroxyethoxy)benzoate

NaH (5.14 g, 128 mmol, 60% in mineral oil) was added to a solution of **10** (10.05 g, 59.77 mmol) in 100 mL of DMF, and the mixture was heated at 110°C for 2 h, cooled to 50°C, and **7c** (22.29 g, 135.4 mmol) was added while stirring. After 5 days the mixture was cooled to RT, filtered through Celite, and concentrated in vacuo. The resulting brown oil was extracted with MeOH:CH_2Cl_2 (70:30, 250 mL) containing 20 mL of conc. HCl. After concentration the mixture was diluted with H_2O (250 mL) and treated with satd. aq. $NaHCO_3$. After extraction with EtOAc (3 × 100 mL), the organic layer was washed with H_2O and satd. aq. NaCl. The brown oil (11.85 g, 77%) was used for the next step without further purification. ^{1}H NMR, δ (ppm): 3.89 (s, 3H), 3.96 (t, J = 4.4 Hz, 4H), 4.07 (t, J = 4.4 Hz, 4H), 6.65 (t, J = 2.2 Hz, 1H), and 7.17 (d, J = 2.2 Hz, 2H). ^{13}C NMR, δ (ppm): 52.30, 61.16, 69.48, 106.86, 107.98, 131.90, 159.56, and 166.72 (8 peaks as required).

Methyl 3,5-bis(2-chloroethoxy)benzoate (13a)

A solution of methyl 3,5-bis(2-hydroxyethoxy)benzoate (10.98 g, 42.85 mmol) in C_6H_6 (275 mL) was refluxed for 30 min using a Dean–Stark apparatus. At RT pyridine (7.0 mL, 87 mmol, 2.0 equiv.) was added along with $SOCl_2$ (6.4 mL, 88 mmol) over 1 h. After 48 h at reflux, the mixture was cooled to RT and the salt removed by decantation, washed with C_6H_6, and the organic layers were combined and then washed sequentially with H_2O, dil. HCl, and satd. aq. NaCl. Evaporation resulted in an oil; passage through a short SiO_2 column using $CHCl_3$:EtOAc (20:1) gave **13a** (11.10 g, 88%), an oil, which crystallized: mp 68.2–69.4°C. ^{1}H NMR, δ (ppm): 3.82 (t, J = 5.8 Hz, 4H), 3.90 (s, 3H), 4.25 (t, J = 5.8 Hz, 4H), 6.70 (t, J = 2.4 Hz, 1H), and 7.21 (d, J = 2.4 Hz, 2H). ^{13}C NMR, δ (ppm): 41.70, 52.26, 68.23, 107.06, 108.33, 132.20, 159.18, 166.37 (8 peaks as required). Anal. calc. for $C_{12}H_{14}Cl_2O_4$: C 49.16, H 4.81; found: C 49.48, H 4.77.

p-(2-Hydroxyethoxy)benzyloxybenzene (17)

NaH (1.84 g, 46.0 mmol, 60% in mineral oil) was added to a solution of **14** (8.02 g, 40.1 mmol) in DMF (60 mL). At 50°C, **7c** (7.45 g, 45.3 mmol) was added, and the mixture was stirred for 30 h at 50°C. After filtration, DMF was evaporated, and the oil was diluted with MeOH:CH_2Cl_2 (6:2,

[2] P.B. Balanda and H.W. Gibson. Unpublished results.

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150 mL) containing conc. HCl (5 mL). After 6 h, the solvent was removed, and the mixture was diluted with H_2O. The EtOAc extract was dried (Na_2SO_4) and evaporated to give a white solid, which was recrystallized from EtOH to give **17** (10.02 g, 100%), a white solid: mp 104.2–106.0°C, lit. (22) mp 103.5–104.5. ^{1}H NMR, δ (ppm): 3.90 (m, 2H), 4.00 (t, J = 4.4 Hz, 2H), 5.00 (s, 2H), 6.86 (AB q, J = 9.2 Hz, 4H), and 7.36 (m, 5H). ^{13}C NMR, δ (ppm): 61.45, 69.80, 70.59, 115.49, 115.81, 127.40, 127.83, 128.48, 137.14, 152.88, and 153.20 (11 peaks as required).

p-(2-Chloroethoxy)benzyloxybenzene (18)

Pyridine (7.6 mL, 94 mmol) and then $SOCl_2$ (6.9 mL, 95 mmol) were added to a solution of **17** (9.53 g, 39.0 mmol) in C_6H_6 (150 mL). After 48 h at reflux, the mixture was cooled to RT, and salt was removed by decantation, washed with C_6H_6, and the organic layers were combined, washed with H_2O, dil. HCl, and satd. aq. NaCl. Evaporation gave a light yellow solid, which was recrystallized from EtOH to give **18** (8.38 g, 82%), a white solid: mp 69.7–71.2°C. ^{1}H NMR, δ (ppm): 3.75 (t, J = 5.8 Hz, 2H), 4.14 (t, J = 5.8 Hz, 2H), 4.99 (s, 2H), 6.87 (AB q, J = 9.2 Hz, 4H), and 7.37 (m, 5H). ^{13}C NMR, δ (ppm): 41.97, 68.79, 70.57, 115.83, 115.89, 127.40, 127.86, 128.49, 137.12, 152.44, and 153.46 (11 peaks as required). Anal. calc. for $C_{15}H_{15}ClO_2$: C 68.57, H 5.75; found: C 68.66, H 5.78.

Methyl 3,5-bis[2-(*p*-benzyloxyphenoxyethoxy]benzoate (15a)

Method A: NaH (316 mg, 13.2 mmol,) was added to a solution of **10** (1.02 g, 6.07 mmol) in DMF (60 mL), and the solution was stirred for 1 h at 110°C. At 65°C, **18** (3.30 g, 12.6 mmol) was added as a solid, and the mixture was stirred for 48 h. After filtration, DMF was evaporated, and the oil was subjected to column chromatography (SiO_2) with $CHCl_3$:EtOAc (20:1). The resultant oil upon trituration with hexane gave **15a**, a white solid (2.27 g, 60%): mp 79.4–81.7°C. ^{1}H NMR, δ (ppm): 3.90 (s, 3H), 4.28 (m, 8H), 5.02 (s, 4H), 6.76 (brs, 1H), 6.90 (AB q, 8H, J = 9.2 Hz, 8H), 7.25 (d, J = 2.0 Hz, 2H), and 7.37 (m, 1 OH). ^{13}C NMR, δ (ppm): 52.25, 66.95, 67.11, 70.66, 107.15, 108.22, 115.78, 115.86, 127.44, 127.87, 128.52, 132.02, 137.19, 152.878, 153.33, 159.66, and 166.69 (17 peaks as required). Anal. calc. for $C_{38}H_{36}O_8$: C 73.53, H 5.85; found: C 73.14, H 6.13.

Method B: The same except using 1.82 g (13.2 mmol) of K_2CO_3 instead of NaH at 80°C; 3.03 g (80%) of **15a**.

Methyl 3,5-bis[5-(*p*-benzyloxyphenoxy)-3-oxapentyloxy]benzoate (15b)

NaH (680 mg, 17 mmol, 60% in mineral oil) was added to a stirred solution of **14** (3.24 g, 16.2 mmol) in DMF (50 mL). After 30 min a solution of **13b** (2.95 g, 7.74 mmol) in DMF (20 mL) was added, and the mixture was stirred for 2 days at RT, filtered, and concentrated to give an oil, which was purified via flash SiO_2 chromatography using Et_2O to give 3.38 g (62%) of **15b**, a white solid, which was recrystallized from EtOAc:pet. ether (bp 39–59°C): mp 60.9–62.4°C. ^{1}H NMR, δ (ppm): 3.88 (s, 3H), 3.90 (m, 8H), 4.10 (t, J = 4.8 Hz, 4H), 4.16 (t, J = 4.8 Hz, 4H), 5.00 (s, 4H), 6.71 (t, J = 2.4 Hz, 1H), 6.87 (AB q, J = 9.2 Hz, 8H), 7.20 (d, J = 2.4 Hz, 2H), and 7.37 (m, 10H). ^{13}C NMR, δ (ppm): 52.22, 67.79, 68.13, 69.76, 70.06, 70.64, 106.93, 108.12, 115.65, 115.77, 127.46, 127.86, 128.52, 131.90, 137.25, 153.06, 153.15, 159.72, and 166.74 (19 peaks as required). MS (FAB), m/z (rel. int.): 708 [M^+, 100%], 677 [$(M - OCH_3)^+$, 76%], and 586 [$(M - OCH_3 - CH_2C_6H_5)^+$, 12%]. HRFAB, m/z, calcd. for $C_{42}H_{44}O_{10}$ [$M]^+$: 708.2934; found: 708.2955 (error 2.8 ppm).

Methyl 3,5-bis[8-(*p*-benzyloxyphenoxy)-3,6-dioxaoctyloxy]benzoate (15c)

A procedure similar to that used for **15b** was utilized to prepare **15c** (63%), which crystallized slowly to give a light yellow solid: mp 61–63°C. ^{1}H NMR, δ (ppm): 3.74 (m, 8H), 3.84 (m, 8H), 3.87 (s, 3H), 4.07 (t, J = 4.8 Hz, 4H), 4.13 (t, J = 4.8 Hz, 4H), 6.69 (s, 4H), 6.70 (t, J = 2.2 Hz, 1H), 6.86 (AB q, J = 9.2 Hz, 8H), 7.19 (d, J = 2.2 Hz, 2H), and 7.35 (m, 10H). ^{13}C NMR, δ (ppm): 52.16, 67.68, 68.00, 69.58, 69.86, 70.58, 70.79, 70.84, 106.86, 107.99, 115.71, 115.56, 127.42, 127.81, 128.48, 131.84, 137.22, 153.05, 153.08, 159.71, and 166.70 (21 peaks as required). MS (FAB), m/z (rel. int.): 819.4 [$(M + Na)^+$, 5%], 796.4 (M^+, 85%), 765.4 [$(M - OCH_3)^+$, 42%], 706.4 [$(M - COOCH_3)^+$, 8%], and 674 [$(M - OCH_3 - CH_2C_6H_5)^+$, 5%], 76 [100%]. HRFAB, m/z, calcd. for $C_{46}H_{52}O_{12}$ [$M]^+$: 796.3459; found: 796.3476 (error 2.2 ppm). Anal. calc. for $C_{46}H_{52}O_{12}$: C 69.33, H 6.58; found: C 69.48, H 6.63.

Methyl 3,5-bis[11-(*p*-benzyloxyphenoxy)-3,6,9-oxaundecyloxy]benzoate (15d)

A procedure similar to that used for **15b** was utilized to prepare **15d** (64%), an oil. ^{1}H NMR, δ (ppm): 3.70 (m, 16H), 3.82 (m, 8H), 3.87 (s, 3H), 4.06 (t, J = 4.8 Hz, 4H), 4.12 (t, J = 4.8 Hz, 4H), 4.99 (s, 4H), 6.68 (t, J = 2.4 Hz, 1H), 6.86 (AB q, J = 9.2 Hz, 8H), 7.19 (d, J = 2.4 Hz, 2H), and 7.36 (m, 10H). ^{13}C NMR (ppm): 52.19, 67.68, 67.98, 69.54, 69.80, 70.59, 70.63, 70.74, 70.79, 106.84, 107.97, 115.54, 115.71, 127.43, 127.82, 128.48, 131.82, 137.22, 153.03, 153.08, 159.70, and 166.72 (22 peaks; theory 23). MS (FAB), m/z (rel. int.): 907 [$(M + Na)^+$, 2%], 884 [M^+, 41%], 853 [$(M - OCH_3)^+$ 32%], and 762 [$(M - C_8H_{10}O)^+$, 3%], 225 (56%), 200 (100%); HRFAB, m/z, calcd. for $C_{50}H_{60}O_{14}$ [$M]^+$: 884.3983, found: 884.3982 (error 0.1 ppm).

Methyl 3,5-bis[2-(*p*-hydroxyphenoxy)ethoxy]benzoate (16a)

A solution of **15a** (1.08 g, 1.74 mmol) in $CHCl_3$:MeOH (1:1, 40 mL) containing Pd/C (100 mg) was subjected to hydrogenolysis at 60 psi for 48 h, filtered, and concentrated to give an oil, which was purified by SiO_2 column chromatography. Addition of $CHCl_3$ to the resulting oil gave **16a** (0.96 g, 90%), a white solid: mp 130.3–131.9°C. ^{1}H NMR, δ (ppm): 3.84 (s, 3H), 4.20 (m, 4H), 4.32 (m, 4H), 6.76 (AB q, J = 9.2 Hz, 8H), 6.90 (t, J = 2.2 Hz, 1H), 7.12 (d, J = 2.2 Hz, 2H), and 8.95 (s, 2H). ^{13}C NMR, δ (ppm): 52.32, 66.67, 66.98, 106.30, 107.58, 115.50, 115.74, 131.65, 151.04, 151.38, 159.61, and 165.83 (12 peaks, as required). Anal. calc. for $C_{24}H_{24}O_8 \cdot H_2O$: C 62.87, H 5.72; found: C 62.72, H 5.36.

Methyl 3,5-bis[5-(*p*-hydroxyphenoxy)-3-oxapentyloxy]benzoate (16b)

A solution of **15b** (2.58 g, 3.64 mmol) in $CHCl_3$:EtOAc (1:1, 30 mL) was subjected to hydrogenolysis (60 psi) at RT

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in the presence of 10% Pd/C (150 mg) for 10 h, filtered, and concentrated in vacuo to give **16b** (1.9 g, 98%), an oil. ^{1}H NMR, δ (ppm): 3.87 (m, 11 H), 4.07 (m, 8H), 6.55 (t, *J* = 2.2 Hz, 1 H), 6.72 (s, 8H), and 7.15 (d, *J* = 2.2 Hz, 2H). ^{13}C NMR, δ (ppm): 52.33, 67.59, 68.09, 69.63, 69.98, 107.06, 108.02, 115.85, 116.07, 131.60, 150.05, 152.36, 159.53, and 167.04 (14 peaks as required). MS (FAB), *m*/*z* (rel. int.): 528 [M^+, 100%], 497 [$(M - OCH_3)^+$, 49%], and 420 ($M^+ - CH_3 - C_6H_4OH$, 16%); HRFAB, *m*/*z*, calcd. for $C_{28}H_{32}O_{10}$ $[M]^+$: 528.1995, found: 528.1981 (error 2.7 ppm).

Methyl 3,5-bis[8-(*p*-hydroxyphenoxy)-3-,6-dioxaoctyloxy]benzoate (16c)

A procedure similar to that used for **16b** was utilized to prepare **16c**, an oil (99%). ^{1}H NMR (DMSO), δ (ppm): 3.58 (m, 8H), 3.68 (t, *J* = 4.6 Hz, 4H), 3.73 (t, *J* = 4.6 Hz, 4H), 3.81 (s, 3H), 3.94 (t, *J* = 4.6 Hz, 4H), 4.12 (t, *J* = 4.6 Hz, 4H), 6.68 (AB q, *J* = 9.2 Hz, 8H), 6.80 (t, *J* = 2.2 Hz, 1 H), 7.05 (d, *J* = 2.2 Hz, 2H), and 8.89 (s, 2H). ^{13}C NMR (DMSO), δ (ppm): 52.28, 67.51, 67.60, 68.82, 69.12, 69.90, 69.95, 106.15, 107.45, 115.36, 115.69, 131.57, 151.20, 151.24, 159.69, and 165.87 (16 peaks as required). MS (FAB), *m*/*z* (rel. int.): 639 [$(M + Na)^+$, 5%], 616 [M^+, 34%], and 585 [$(M - OCH_3)^+$, 20%), 163 (100%); HRFAB, *m*/*z*, calcd. for $C_{32}H_{40}O_{12}$ $[M]^+$: 616.2520, found: 616.2511 (error 1.4 ppm).

Methyl 3,5-bis[11-(*p*-hydroxyphenoxy)-3,6,9-oxaundecyloxy]benzoate (16d)

A procedure similar to that used for **16b** was utilized to prepare **16d**, an oil (98%). ^{1}H NMR, δ (ppm): 3.69 (m, 16H), 3.79 (m, 8H), 3.87 (s, 3H), 3.96 (t, *J* = 4.8 Hz, 4H), 4.00 (t, *J* = 4.8 Hz, 4H), 6.56 (t, *J* = 2.4 Hz, 1 H), 6.65 (s, 2H), 6.69 (AB q, *J* = 9.2 Hz, 8H), 7.13 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR, δ (ppm): 52.29, 67.50, 67.99, 69.57, 69.78, 70.52, 70.56, 106.644, 108.06, 115.67, 116.06, 131.62, 150.36, 152.28, 159.61, and 167.04 (16 peaks; theory 18). MS (FAB), *m*/*z* (rel. int.): 704 [$(M + Na)^+$, 8%], 391 [$(M - COOCH_3 - 2HOC_6H_4 - OCH_2CH_2)^+$, 80%], 167 (100%); HRFAB, *m*/*z*, calcd. for $C_{34}H_{48}O_{14}$ $[M + Na]^+$: 703.2941, found: 703.2952 (error 1.4 ppm).

3,5-Bis(vinyloxy)benzoic acid (19) from attempted synthesis of 11a

A solution of **13a** (814.1 mg, 2.780 mmol) and **16a** (1.16 g, 2.63 mmol) in DMF (total volume = 12 mL) was added via a syringe pump at 2.0 mL/h to a suspension of NaH (1.2 g, 30 mmol, 60% in mineral oil) in DMF (175 mL) at 110°C. After addition, the mixture was stirred at 85°C for 4 days, cooled, evaporated, treated with $CHCl_3$, and filtered. Removal of $CHCl_3$ followed by flash SiO_2 column chromatography eluting with $CHCl_3$:EtOAc (20:1) gave pure **19** (110 mg, 19%): mp 115.7–117.5°C. ^{1}H NMR, δ (ppm): 4.57 (dd, *J* = 6.0 and 2.4 Hz, 1H), 4.87 (dd, *J* = 13.6 and 2.0 Hz, 1H), 6.66 (dd, *J* = 13.6 and 2.0 Hz, 1H), 6.91 (t, *J* = 2.2 Hz, 1H), and 7.46 (d, *J* = 2.2 Hz, 2H). ^{13}C NMR, δ (ppm): 97.04, 111.42, 112.75, 131.66, 147.09, 157.86, and 170.71 (7 peaks as required). Anal. calc. for $C_{11}H_{10}O_4 \cdot 1/4\ H_2O$: C 62.70, H 5.02; found: C 62.80, H 4.93.

Bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-42-crown-12 (11b)

A solution of **16b** (1.91 g, 3.61 mmol) and **13b** (1.38 g, 3.62 mmol) in DMF (total volume 20 mL) was added via a syringe pump at 1.5 mL/h to a suspension of K_2CO_3 (5.20 g, 37.6 mmol) and tetra(*n*-butyl)ammonium iodide (20 mg) in DMF (175 mL) at 110°C. After complete addition, the mixture was stirred vigorously at 110°C for 5 days, cooled, and evaporated. The residue was dissolved in CH_2Cl_2 and filtered. Removal of CH_2Cl_2 followed by flash column (SiO_2) chromatography eluting with Et_2O gave pure **11b** (700 mg, 23%): mp 140–142°C. ^{1}H NMR, δ (ppm): 3.89 (m, 22H), 4.08 (t, *J* = 4.6 Hz, 8H), 4.14 (t, *J* = 4.6 Hz, 8H), 6.71 (t, *J* = 2.2 Hz, 2H), 6.82 (s, 8H), and 7.19 (d, *J* = 2.2 Hz, 4H). ^{13}C NMR, δ (ppm): 52.19, 67.84, 68.16, 69.65, 69.97, 107.18, 108.09, 115.64, 131.81, 153.05, 159.70, and 166.72 (12 peaks as required). MS (FAB), *m*/*z* (rel. int.): 859.1 [$(M + Na)^+$, 14%], 836.1 (M^+, 100%), and 805.1 [$(M - OCH_3)^+$, 16%]; HRFAB, *m*/*z*, calcd. for $C_{44}H_{52}O_{16}$ [M^+]: 836.3255, found 836.3286 (error 3.6 ppm).

Bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-54-crown-16 (11c)

A procedure similar to that used for **11b** was utilized to prepare **11c** (18%), a white solid: mp 102.9–104.3°C. ^{1}H NMR, δ (ppm): 3.73 (m, 16H), 3.83 (m, 8H), 3.89 (s, 6H), 4.05 (t, *J* = 4.8 Hz, 8H), 4.12 (t, *J* = 4.8 Hz, 8H), 6.70 (t, *J* = 2.2 Hz, 2H), 6.81 (s, 8H), and 7.18 (d, *J* = 2.2 Hz, 4H). ^{13}C NMR, δ (ppm): 52.19, 67.76, 68.07, 69.60, 69.87, 70.83, 70.91, 106.92, 108.06, 115.58, 131.84, 153.05, 159.74, and 166.72 (14 peaks as required). MS (FAB), *m*/*z* (rel. int.): 1012.9 (M^+, 100%), 981.9 [$(M - OCH_3)^+$, 15%], and 950.9 [$(M - 2OCH_3)^+$, 12%]; HRFAB, *m*/*z*, calcd. for $C_{52}H_{69}O_{20}$ $[M + H]^+$ 1013.4382; found 1013.4399 (error 1.6 ppm).

Bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-66-crown-20 (11d)

A procedure similar to that used for **11b** was utilized to prepare **11d** (19%), a white solid: mp 77.5–79.5°C. ^{1}H NMR, δ (ppm): 3.69 (m, 32H), 3.82 (m, 16H), 3.88 (s, 6H), 4.04 (t, *J* = 4.8 Hz, 8H), 4.12 (t, *J* = 4.8 Hz, 8H), 6.69 (t, *J* = 2.2 Hz, 2H), 6.81 (s, 8H), and 7.18 (d, *J* = 2.2 Hz, 4H). ^{13}C NMR, δ (ppm): 52.17, 69.72, 68.00, 69.51, 69.77, 70.64, 70.74, 70.80, 106.86, 107.98, 115.51, 131.81, 153.01, 159.71, and 166.70 (15 peaks; theory 16). MS (FAB), *m*/*z* (rel. int.): 1211 [$(M + Na)^+$, 1%], 1188.4 (M^+, 100%), 1173.3 [$(M - CH_3)^+$, 5%], and 1157.4 [$(M - OCH_3)^+$, 16%], 1125 [$(M - 2OCH_3)^+$, 8%]; HRFAB, *m*/*z*, calcd. for $C_{60}H_{85}O_{24}$ $[M + H]^+$: 1189.5431; found 1189.5440 (error 0.8 ppm).

Conclusions

We have synthesized three new functionalized cyclic tetraphenylene polyethers, namely bis(5-carbomethoxy-1,3-phenylene)-bis(*p*-phenylene)-(3*x* + 6)crown-*x*, where *x* = 12, 16, and 20 (**11b**–**11d**) with ring sizes of 42, 54, and 66 atoms in 17–24% yields by [1 + 1] condensations of dichlorides **13b**–**13d** with the corresponding bisphenols **16b**–**16d**. These macrocycles do not complex with second-

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ary ammonium ions, but in at least in one case, **11d**, do complex with paraquats such as **5b**.

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