authors warmly thank Professor D. N. Reinhoudt for the details of this reaction procedures in closely related systems.

8. The authors thank to Dr. C. B. Knobler for the X-ray crystal structure resolution.

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Chiral Host. Attempted Synthesis Using McMurry Reaction as a Final Ring Closure Method

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Using the low valent titanium induced carbonyl-carbonyl coupling reaction, it was attempted to synthesize sterically hindered 17-membered cyclic chiral host 2. The semifinal dialdehyde 12 was obtained through 11 step reactions beginning from *p*-tert-butylphenol and dibenzofuran. When dialdehyde 12 was treated with $TiCl_3$-Zn/Cu, only intermolecularly coupled dimer 14 was obtained instead of intramolecularly coupled cyclic alkene 2. The mechanistic consideration leading to 14 was discussed and the cation binding properties of dimer 14 and dicarboxylic intermediate 13 was reported, which implies the significance of the principle of preorganization of host's binding sites prior to complexation.

Introduction

Spherands, of which **1** is the first and the ultimate example, have remarkable binding properties arising from the self-organization of the binding sites prior to complexation (Principle of Preorganization.[1] Even though anisole oxygens are known to be intrinsically weak ligands, their perfect preorganization into an octahedral binding site makes **1** the strongest known host for alkali metal ions ($-\Delta G^\circ_{Li^+} > 23$ kcal/mol and $-\Delta G^\circ_{Na^+} \approx 19.2$ kcal/mol, picrate salts in D_2D-saturated $CDCl_3$ at 25 °C). The crystal structures of spherand **1** and spheraplexes **1·Na⁺** and **1·Li⁺** show almost identical con-

formations for free and complexed host.[1c]

Spherand **1** also shows the greatest selectivity toward alkali metal ions. It only binds Li⁺ or Na⁺. Larger alkali metal ions cannot be incorporated into the binding site (the Principle of Complementarity).[2] This unique selectivity has been applied to a sodium and lithium-selective colorimetric host[3] which changed from yellow to deep blue as it went from its free state to its sodium or lithium complex in 80% dioxane-20% water (v/v). It remains uncomplexed (yellow) in the presence of potassium salts. This chromogenic ion-selective indicating system is capable of detecting Li⁺ and Na⁺ at concentrations as low as 10^{-8} M in the presence of other common ions.

A desirable goal is the design and synthesis of chiral hosts which mimic the exceptional binding properties of spherand **1**. Chiral crown ethers were used as asymmetric catalysts for Michael additions,[4a] addition of alkyllithiums to aldehydes,[4b] and anionic methacrylate polymerizations.[4c] The tetraphenyl hemispherand systems with various bridges were studied extensively.[5] They are chiral, having C_2 symmetry, but their barrier to racemization is less than 27 kcal/mol. This low energy barrier made it impractical to resolve them at room temperature. The inversion of chirality, which occurs by successive passage of the methoxy groups through the center of
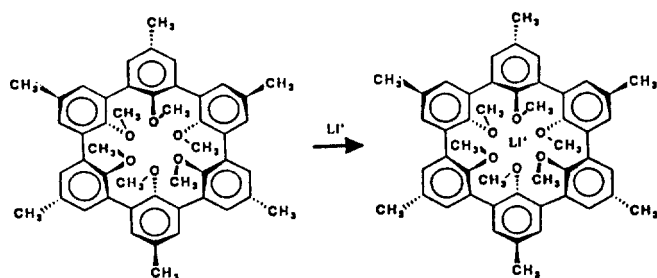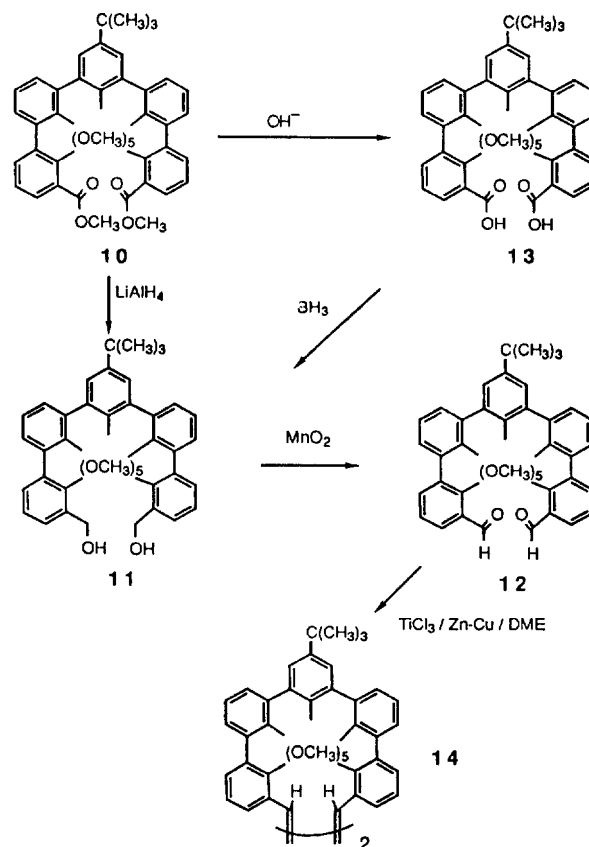

Spherand **1**   Spheraplex **1·Li⁺**
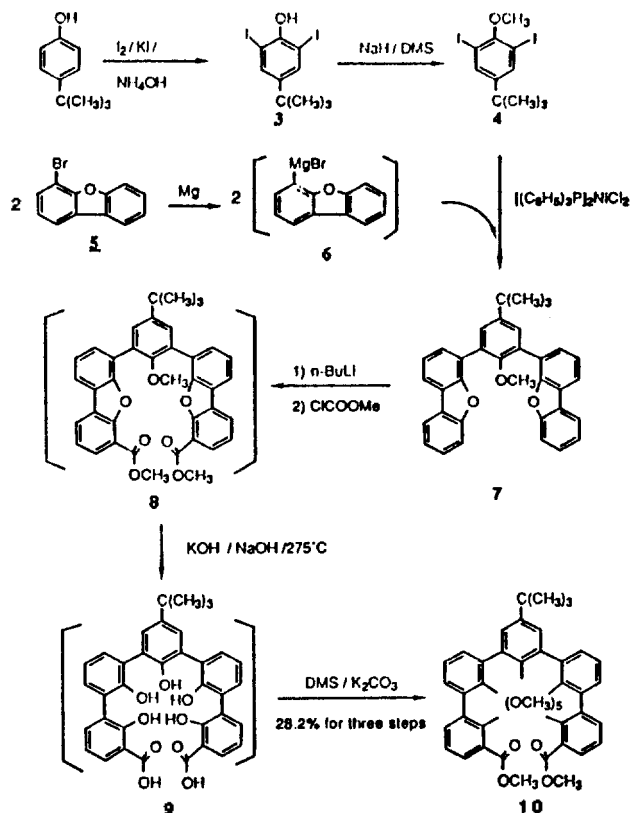
Scheme 1

Scheme 2

the macrocycle, was successfully controlled by making a bridge between the first and third phenoxy oxygens of the quarterphenyl unit.

CPK model examination shows that a 17-membered quin-quephenyl cyclic host could be made by replacing one benzene unit of spherand 1 with an olefinic unit. Both the *cis* (2A) and *trans* (2B) compound appear stable in molecular models. Only the trans isomer 2B is chiral, having asymmetry. This isomer has a more preorganized binding site than the *cis* isomer 2A. The binding site of the *cis* isomer 2A seems to be complementary to sodium or potassium cations. The binding site of the trans isomer 2B seems to be complementary to lithium or sodium cations, but not to potassium or bigger cations. The tertiary butyl group is incorporated as an ^{1}H NMR probe in these systems. The size of the chiral barrier in structure 2B could be controlled by varying the nature of the R group (H, CH_3, C_6H_5, *etc.*).
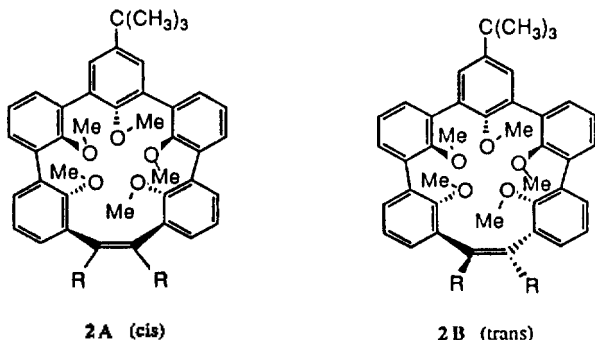
2A (cis)   **2B** (trans)

The low–valent titanium induced carbonyl–carbonyl coupling reaction (McMurry reaction) is known to be the best

method for making sterically hindered alkenes from aliphatic and aromatic aldehydes and ketones.[6] In this paper attempts to synthesize the cyclic hosts 2 using the McMurry reaction as the final ring closure step and the cation binding properties of dicarboxy compound 10 and cyclic alkene 14 were reported.

Results and Discussion

Synthesis. The synthetic procedure for pentameric intermediate 10 is outlined in Scheme 1. Treatment of *p*–tert–butylphenol with iodine and potassium iodide gave 4–tert–butyl–2,6–diiodophenol 3 in 75% yield.[7] Compound 3 was methylated with dimethy sulfate (DMS) to give compound 4 in 82% yield. The Grignard reagent 6 was made from 5 which was obtained in 83.2% yield (mp. 67–69 °C)[8] from dibenzofuran by treatment with *n*–butyllithium followed by quenching with 1,2–dibromoethane. Compound 4 was coupled with Grignard reagent 6 using a catalytic amount of bis(triphenylphosphine)nickel(II) chloride[9] to give compound 7 in 73.4% yield after recrystallization. Treatment of compound 7 with 2 equivalents of *n*–butyllithium followed by quenching with excess methyl chloroformate at −78 °C gave compound 8. Compound 8 was directly subjected to ring opening reaction in a molten sodium hydroxide–potassium hydroxide mixture at 275 °C. The ring opened compound 9 was permethylated with dimethyl sulfate to provide the pentameric diester 10 in 28.2% overall yield for three steps.

Further functionalization of compound 10 is outlined in Scheme 2. The reduction of the diester 10 with lithium al-

uminium hydride afforded the diol 11 in 90.6% yield after chromatography. The diol 11 was converted to the dialdehyde 12 in 73.8% yield with freshly prepared manganese(IV) oxide.[10] the diester 10 was hydrolyzed to dicarboxylic acid 13 in quantitative yield. Diol 11 was also obtained by reduction of diacid 13 with borane-THF (54.6%).

The dialdehyde 12 was treated with McMurry's reagent in attempts to obtain intramolecularly coupled compound 2, but only intermoleculary coupled dimer 14 was obtained (5.2% yield.). Even though extreme high dilution condition were applied (addition of the dicarbonyl compound to the reagent over 6 days), the desired compound 2A or 2B were not obtained. Different reagents, *i.e* TiCl₃/LiAlH₄ TiCl₄/Zn–Cu, gave the same results. One of the side products was the completely reduced (deoxygenated) pentamer 15. Previous

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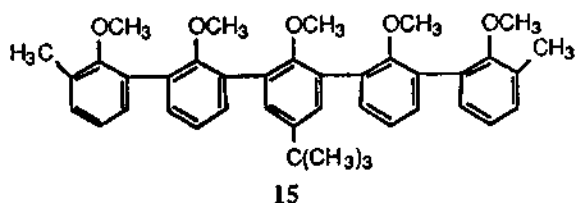
workds[11] have observed reduction of the starting material to the corresponding hydrocarbon in attempts to cyclize sterically hindered diketones. The failure of this reaction to produce detectable amount of 17-member ring product in current work is presumably due to severe steric interactions between the methoxy oxygens in the transition state leading to the cyclic product. Thus two radicals on neighboring titanium centers of the coupling reagent cannot achieve the proper orientation for coupling if they are attached to the termini of the same quinquephenyl unit. The deleterious effect of extreme steric hindrance on this reaction in other systems is illustrated by the observations that attempts to dimerize di-tert-butyl ketone, tert-butyl isopropyl ketone, and tert-butyl neopentyl ketone gave only reduction to the corresponding alcohols.[12]

Cation Binding Properties. Molecular model examination led to the conclusion that 34-member ring cycle 14 is too conformationally mobile to have useful ion-binding properties. This conclusion was confirmed by picrate extraction experiments in which the binding of alkali-metal and ammonium ions was too weak to be measured (-ΔG 6 kcal/mol).
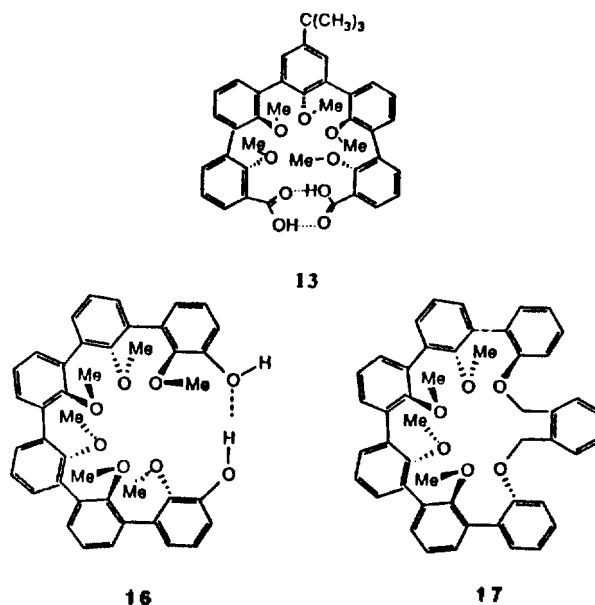
The hydrogen bonding between two carboxyl groups has significant strength. Among the natural compounds, carboxylic ionophores use hydrogen bonding between terminal carboxyl and hydroxyl groups to simulate a macrocycles, particulary when complexing.[13] Molecular model examination reveals that compound 13 can form intramolecular hydrogen bonds between the two terminal carboxyl groups, forming a 20-membered macroring. The molecular model of 13 shows that the 20-membered ring has good ligand organization for binding large cations (*i.e* K⁺, Rb⁺) in a nesting fashion.

Table 1 shows the results of picrate extraction experiments of compound 13 along with those of related compounds. The free energies of association for binding alkali and ammonium ions were obtained using the picrate extraction method reported previously.[14] Podand 15 lacks terminal carboxyl groups, and its -ΔG° values for each of the alkali metal ions were<6 kcal/mol. Podan 16 binds, Na⁺, K⁺, Rb⁺, Cs⁺, and NH₄⁺ with -ΔG° values that range from 6.2 to 9.1

Table 1. Comparison of the Average Binding Free Energies (-ΔG°, kal/mol) of 1,[2] 13, 15, 16,[8] and 17[8] Binding Alkali and Ammonium Picrates at 25 °C in Water-saturated CDCl₃

Host	Li⁺	Na⁺	K⁺	Rb⁺	Cs⁺	NH₄⁺	CH₃NH₃⁺	(CH₃)₃CNH₃⁺
1	> 23	19.2	—	—	—	—	—	—
13	—	—	6.64	6.59	6.19	—	—	—
15	—	—	—	—	—	—	—	—
16	—	6.2	7.7	8.6	9.1	7.5	5.9	3.6
17	—	—	—	5.8	5.8	4.4	—	—

-: Below the level of detectability of the extraction experiment (< 6 kal/mol).

13

16   **17**

kcal-mol, showing peak binding with cesium cation. The intramolecular hydrogen bonding between the two terminating hydroxyl groups on this podand substantially enhanced the binding power by organizing the ligands for complexation. Compound 13 binds large ions favorably, showing peak binding with potassium ion (-ΔG° = 6.64 kcal/mol). Clearly the intramolecular hydrogen bonding between two terminating carboxyl groups of this podand also substantially organized the ligands for complexation. Properly designed hydrogen bondings is much better for ligand organization than an improper bridge which can disorganize the binding site. Compound 17 has a xylylene bridging unit between the first and sixth phenoxy oxygens of sexiphenyl units. Both methylene groups of the bridging unit can occupy the bindings site which must therefore be reorganized when complexing. Compound 17 binds cations less strongly than compound 16 or 13. This result implies that the ligand reorganization of host 17 requires a significant amount of energy. Preorganization of the ligands is prerequisite for a strongly complexing host.[14,15] The cycles having intramolecular hydrogen bonding (16 and 13) as an element of the macrocyle show intermediate ligand organization between that of acyclic compound 16 and covalently cyclized spherand 1.

Experimental

General. All chemicals were reagent grade and pur-

chased from common vendors. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl prior to use. Where anhydrous dichloromethane was needed, it was distilled twice from calcium hydride. All anhydrous reactions were conducted under an argon atmosphere. Flash chromatography was carried out silica gel 60 (E. M. Merck, Particle size 0.040-0.063 mm, 230-400 mesh ASTM). Gravity columns were packed with silica gel 60 (E.M. Merck, Particle size 0.063-0.200 mm, 70-230 mesh ASTM). Gel permeation chromatography was performed on 20' by 0.375" (o.d.) column packed with 200 g of styragel (100A, Waters Associates) using methylene chloride as eluent at flow rates of approximately 4.0 ml per minute. Thin layer chromatography was conducted on plastic-backed precoated silica gel plates (E. M. Merck, F254, 0.2 mm thickness) and reverse-phase plates (Whatman, KC 18F, 0.2 mm thickness). Melting points below 240°C were measured on Thomas-Hoover melting point apparatus. Those above 240°C were measured on Mel-Temp apparatus. All melting points are uncorrected. Infra-red spectra were obtained on Perkin-Elmer 297 grating spectrophotometer (KBr pellets). Mass spectra were obtained on an AEI model MS-9 double focusing spectrometer interfaced by Kratos Company to a Data General Nova 3. Regular mass spectra were recorded at 17 or 70 eV at the temperature indicated. Proton NMR spectra were obtained in CDCl$_3$ solution at 200.1 MHz on a Bruker WP-200 spectrometer unless other wise specified. All proton chemical shifts (δ values) are repoted in parts per million using tetramethylsilane at 0.00 ppm. Elemental analyses were performed by Spang Microanalytical laboratory (Eagle Harbor, Michigan).

4-tert-Butyl-2,6-diiodophenol, 3. The *p*-tert-butylphenol (55 g, 367 mmol) was dissolved in 300 ml of methyl alcohol in a 2-liter three neck round-bottom flask equipped with an overhead stirrer and a dropping funnel. A solution of concentrated ammonium hydroxide (58%, 175 ml) and water (225 ml) was added. The initially-formed turbid mixture turned to clear solution upon stirring. In a 1-liter Erlenmeyer flask 227 g (1.37 mol) of potassium iodide was dissolved in 250 ml of water, and then 186 g (0.73 mol) of iodine was mixed in. About 200 ml of this solution was added through the dropping funnel to the above solution of *p*-tert-butylphenol over the course of one hour with vigorous stitrring. The rest was added over the course of three hours. The whole mixture was stirred overnight. The product was collected by filtration through a coarse fritted glass funnel and washed with water. The powdery product was dried in a vacuum oven at 50°C for three days, then dried at 0.3 torr and 50°C for two days. The product was obtained in 95% yield (140 g). A small portion was recrystallized from methanol; mp: 79-80°C (lit.[7] 82°C); ^{1}H NMR: δ 1.26 (s, 9H, CH$_3$), 7.64 (s, 2H, Ar-H)

4-(1,1-Dimethylethyl)-2,6-diiodoanisole, 4. In a 2-liter round-bottom flask, 101.0 g (252 mmol) of **3** was dissolved in 70 ml of dry THF. To this solution, 14.4 g of sodium hydride (300 mmol, 50% oil dispersion) was added portionwise. There was vigorous evolution of hydrogen gas and the reaction mixture turned to dark green. After stirring for 30 minutes at room temperature, 28.5 ml (301 mmol) of dimethyl sulfate (DMS) was added. The solution was stirred for 3 hours. The excess of dimethyl sulfate and sodium hydride was destroyed with dilute ammonium hydroxide

solution, and then the solution was concentrated under reduced pressure. The residue was partitioned betweeen 200 ml of dichloromethane and 200 ml of water. The organic phase was separated and the aqueous phase was extracted with dichloromethane (2×100 ml). The combined organic extracts were washed with brine, and then dried over anhydrous magnesium sulfate. The solution was concentrated, and the residue was crystallized from a mixture of hexane and pentane at 4°C to give the product in 82% yield (85.7 g, light brown crystals); mp. 46-48°C; ^{1}H NMR;δ 1.27 (s, 9H, C-CH$_3$), 3.8 (s, 3H, OCH$_3$), 7.73 (s, 2H, Ar-H); MS (250°C, 70 eV): 416 (60.8, M$^+$), 401 (94.1%, M$^+$-CH$_3$); IR (KBr): 2995, 2900, 1475, 1274, 1000, 882, 713; Anal. Calcd for C$_{11}$H$_{14}$I$_2$O (MW 416.04): C, 31.76; H, 3.39. Found: C, 31.79; H, 3.36.

4,4'-[5-1,1-dimethylethyl)-2-methoxy-1,3-phenylene]bis-dibenzofuran, 7. Magnesium turnings (6.71 g, 275.6 mmol), dry ether (150 ml), and a speck of iodine were placed in a 1-liter three neck round-bottom flask equipped with a condenser and a 500-ml dropping funnel. The dropping funnel was filled with 48.38 g (195.8 mmol) of 4-bromodibenzofuran **5**[8] dissolved in 200 ml of dry ether. A small portion (2-3 ml) of 4-bromodibenzofuran solution was added and the reaction was cautiously initiated by warming with a heating gum. Once the reaction was initiated, the solution of **5** was added dropwise to maintain a gentle reflux. The whole mixture was refluxed for 5 hours. The resulting greenish-bilayered Grignard reagent **6** was cooled to room temperature. Meanwhile 26.86 g (64.56 mmol) of **4**, 0.85 g (1.3 mmol) of bis (triphenylphosphine) nickel (II) chloride, and 250 ml of dry ether were placed in a 2-liter three neck round-bottom flask equipped with a 500-ml dropping funnel under nitrogen. The Grignard reagent **6** was delivered to the dropping funnel *via* cannula and added dropwise to the nickel catalyst at such a rate as to maintain a gentle reflux. The resulting black mixture was refuxed until **4** was no longer detected by TLC (about two days). The mixture was cooled to room temperature, and then poured into ice-cooled dilute hydrochloric acid. The organic phase was separed and the aqueous phase was extracted with dichloromethane (2×200 ml). The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by gravity column chromatography (silica gel, 6×42 cm, 1/8 dichloromethane/hexane and then dichloromethane). The crude product was recrystallized from a mixture of dichloromethane and hexane to gie 23.5 g (73.4% yeild) of white crystals; mp. 170-173°C; ^{1}H NMR: δ 1.44 (s, 9H, CH$_3$), 3.18 (s, 3H, OCH$_3$), 7.30-8.00 (m, 16H, Ar-H); IR (KBr): 2985, 1460, 1417, 1250, 1195, 755; MS (220°C, 70 eV): 496 (57.6%, M$^+$), 481 (100%, M$^+$-CH$_3$); Anal. Calcd for C$_{35}$H$_{28}$O$_3$ (MW 496.61): C, 84.65; H, 5.68. Found: C, 84.66; H, 5.67.

Dimethyl 5"-(1,1-dimethylethyl)-2,2',2",2"',2""-pentamethoxy [1,1':3',1": 3", 1"':3"', 1""-quinquephenyl]-3,3""-dicarboxylate, 10. This compound was obtained in three steps and 28.2% overall yield from compound **7** without purifying the intermediates **8** and **9**. Compound **7** (23.0 g, 46.4 mmol) was dissolved in 200 ml of dry THF in a 500-ml round-bottom flask under nitrogen and the solution was cooled to −40°C. To this solution was added 46 ml (110.4 mmol) of 2.4 M *n*-butyllithium in hexane for 10

minutes, then the reaction mixture was allowed to warm to room temperature. The reddish black solution was stirred for 5 hours at room temperature, then cooled to -78 °C, and quenched with 21.0 m*l* (270 mmol) of methyl chloroformate. The solution was warmed to room temperature and stirred for 3 hours. The reaction mixture was concentrated under reduced pressure, and the residue was partitioned between 300 m*l* of dichloromethane and 200 m*l* of water. The aqueous phase was extracted with 200 m*l* of dichloromethane and the combined organic extracts were dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the crude product was dried at 300 torr overnight to give about 24 g of solid 8.

Approximately two thirds of a mixture of 160.0 g (2.85 mol) of potassium hydroxide and 114.0 g (2.85 mol) of sodium hydroxide was heated in a steel crucible to 200 °C whereupon fusion occurred. To the molten base was added 20.0 g of the above solid 8 followed by the remaining sodium/potassium hydroxide mixture such that the organic mixture was convered by the base mixture. The mixture was mechanically stirred as the temperature was raised to 275 °C, and the stirring at this temperature was continued for 50 minutes. The creamy mixture was poured into a large porcelain mixer and cooled. The solid was crushed to a powder, and then the powder was dissolved in 3 liters of water. The solution was filtered through a coarse fritted glass funnel to remove insoluble impurities, and the filtrant was washed with water. The filtrate was cooled in an ice bath and the amber aqueous solution was carefully acidified with concentrated hydrochloric acid. The precipitate was collected by filtration throgh a large Buchner funnel. The filtrant was washed with water and dried in a vacuum over at 80 °C for two days to give 13.37 g of crude 9. The crude product 9 was added to a mixture of 1 liter of acetone, 125 g (905 mmol) of potassium carbonate, and 50 m*l* (528 mmol) of dimethyl sulfate. The whole mixture was refluxed for 30 hours with vigorous mechanical stirring. The mixture was cooled and then filtered through a coarse fritted glass funnel. The collected solid was washed with acetone. The filtrate was concentrated under reduced pressure, and the residue was partitioned between 500 m*l* of ether and 100 m*l* of 7 M ammonium hydroxide solution. The aqueous phase was extracted with 100 m*l* of ether, and the combined organic extracts were dried over anhydrous magnesium sulfate. The solution was concentrated and the residue was purified by gravity column chromatography (silica gel, 6 × 50 cm, dichloromethane and then 5% methanol in dichloromethane) to afford the pure diester 10 as a white foam (9.2 g, 28.2% for 3 steps); ^{1}H NMR: δ 1.36 (s, 9H, CH$_3$), 3.30 (s, 6H, Ar-OCH$_3$), 3.33 (s, 3H, Ar-OCH$_3$), 3.62 (s, 6H, Ar-OCH$_3$, 3.92 (s, 6H, COOCH$_3$), 7.17–7.82 (m, 14H, Ar–H); IR (KBr): 2995, 2900, 1748, 1605, 1475, 1420, 1250, 1020, 774; MS (250 °C, 70 eV): 704 (100, M$^+$), 689 (69.6, M$^+$-CH$_3$); Anal. Calcd for C$_{43}$H$_4$O$_9$ (MW 704.82): C, 73.28; H, 6.29. Found: C, 73.46; H, 6.12.

5″-(1,1-Dimethylethyl)-2,2′,2″,2″′,2″″-pentame-thoxy-[1,1′:3′,1″:3″,1″′:3″′,1″″-quinquephenyl]-3,3″″-dimethanol, 11. From diester 10. To a -78 °C solution of 7.04 g (10 mmol) of diester 10 in 250 m*l* of ether was added 0.84 g (21 mmol, 95% purity) of lithium aluminium hydride. After being stirred for 30 minutes at -78 °C, the reaction mixture was slowly allowed to warm to room

temperature. After an additional 5 hours stirring, the reaction mixture was cooled to 0 °C and cautiously quenched with about 1 m*l* of 15% sodium hydroxide solution. The mixture was filtered and the filtrant was washed with ether. The organic phase was washed with 150 m*l* of water and the aqueous phase was neutralized to pH 7 with 3 N hydrochloric acid followed by extraction with 300 m*l* of ether. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was flash chromatographed (silica gel, 4 × 40cm, 1/1 ethyl acetate/hexane and then 1/1 ethyl acetate/dichloromethane) to afford the pure diol as a light yellow foam after drying in vacuo (5.87 g, 90.6% yield).

From dicarboxylic acid 13. To a solution of 2.87 g (4.2 mmol) of dicarboxylic acid 13 in 200 m*l* of THF was added 19.9 m*l* (19.9 mmol) of 1 M borane–THF complex solution for 5 minutes with stirring. Stingy white precipitates were formed after 1 hour at room temperature. The reaction mixture was refluxed overnight. It was cooled to room temperature, cautiously quenched with water (3 m*l*), and then stirred for 12 hours with 40 m*l* of saturated potassium carbonate solution. The clear solution was concentrated under reduced pressure, and the residue was partitioned between 100 m*l* of 2 N hydrochloric acid and 150 m*l* of ethyl acetate. The aqueous layer was extracted with ethyl acetate (2 × 50 m*l*). The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated at reduced pressure, and the residue was purified by gravity chromatography (silica gel, 3 × 40 cm, dichloromethane followed by 5 to 20% of ethyl acetate in dichloromethane and finally by 3% methanol in dichloromethane) to afford 1.5 g (54.6% yield) of product after drying in vacuo; ^{1}H NMR: δ 1.34 (s, 9H, C-CH$_3$), 2.36 (s, 2H, OH), 3.30 (s, 9H, OCH$_3$), 3.51 (s, 6H, OCH$_3$), 4.77 (s, 4H, CH$_2$O), 7.12–7.45 (m, 14H, Ar–H); IR (KBr): 3427, 2951, 1454, 1398, 1228, 1009, 764; MS (300 °C, 70 eV): 648 (100, M$^+$), 633 (82.5, M$^+$-CH$_3$); Anal. Calcd for C$_{41}$H$_{44}$O$_7$ (MW 648.79): C, 75.90: H, 6.84. Found: C, 75.94; H, 6.71.

5″-(1,1-Dimethylethyl)-2,2′,2″,2″′,2″″-pentame-thoxy-[1,1′:3′,1″:3″,1″′:3″′, 1″″-quinquephenyl]-3,3″″-dicarboxyaldehyde, 12. Diol 11 (3.0 g, 4.6 mmol), freshly prepared manganese (IV) oxide[10] (9.0 g, 104 mmol), and ether (200 m*l*) were mixed in a 500-m*l* round-bottom flask, and the mixture was stirred at room temperature for several days unitl TLC revealed that all of 11 had been consumed. If necessary, several more grams of manganese (IV) oxide were added. The reaction mixture was filtered through celite. The filtrate was concentrated and the residue was crystallized from a mixture of chloroform and ethanol. The product was obtained as white fine crystals (2.2 g, 73.8% yield); mp. 191-193 °C; ^{1}H NMR: δ 1.38 (s, 9H, t-Bu), 3.33 (s, 6H, OCH$_3$), 3.38 (s, 3H, OCH$_3$), 3.66 (s, 6H, OCH$_3$), 7.24–7.89 (m, 14H, Ar–H), 10.48 (s, 2H, CHO); IR (KBr): 2970, 2900, 2680, 1595, 1470, 1395, 1240, 1010, 770; MS (250 °C, 16 eV): 644 (100, M$^+$), 629 (26.8, M$^+$-CH$_3$); Anal. Calcd for C$_{41}$H$_{40}$O$_7$ (MW 644.77): C, 76.38; H, 6.25. Found: C, 76.11; H, 6.25.

5″-(1,1-dimethylethyl)-2,2′,2″2″′,2″″-pentame-thoxy-[1,1′:3′,1″:3″,1″′:3″′, 1″″-quinquephenyl]-3,3″″-dicarboxylic acid, 13. In a 500 m*l* round-bottom flask, diester 10 (7.02 g, 9.97 mmol), ethyl alcohol (100 m*l*,

and 1.73 g (43.3 mmol) of sodium hydroxide dissolved in a minimum amount of water were mixed. The mixture was refluxed for 5 hours, and then two thirds of the solvent was evaporated. The solution was diluted five-fold with water and cooled in bath. The mixture was acidified with 3 N hydrochloric acid to pH 4. The precipitate was filtered through a medium fritted glass funnel and the filtrant was washed with water. The product was dried over phosphorous pentoxide in vacuo (6.71 g, white powder, 99.6% yield); mp. 140-144 °C; ^{1}H NMR: δ 1.36 (s, 9H, t-Bu), 3.28 (s, 6H, OCH$_3$), 3.31 (s, 3H, OCH$_3$), 3.64 (s, 6H, OCH$_3$), 7.30-8.20 (m, 14H, Ar-H); IR (KBr): 3200, 2953, 1731, 1585, 1462, 1396, 1233, 1009, 766; MS (280 °C, 16 eV): 676 (100, M$^+$), 661, (67.4, M$^+$-CH$_3$), 632 (38.8, M$^+$-CO$_2$); Anal. Calcd for C$_{41}$H$_{40}$O$_9$ (MW 676.77): C, 72.77; H, 5.96. Found: C, 72.69; H, 5.89.

9,36-Bis(1,1-dimethylethyl)-55,56,57,58,59,60-61, 62,63,64-decamethoxy-undecacyclo[49.3.1.1$_2$, 6.1$_7$,11.1$_{12}$,16.1$_{17}$,21.1$_{24}$,28.1$_{29}$,33.1$_{34}$,38.1$_{39}$,-43. 1$_{44}$. 48] tetrahexaconta-1(55),2, 7,9,11(63),12,1-4,16(62),17,19,21(61),22,24,26,28(60),29,31,33(5-9),34,36,38(58),39,41,43(57),44,46,48(56),49,51,53-dotriacontaene, 14. In a 1-liter three neck round-bottom flask flushed with argon were placed zinc-copper couple (4.5 g, 69 mmol) and 4.0 g (26 mmol) of titanium trichloride under nitrogen. Dimethoxyethane (400 m*l*, freshly distilled from lithium and dibenzophenone) was then added. A condenser and reflux-dilution thimble (30 m*l* capacity) was attached to the round-bottom flask. The black mixture was refluxed for 1 hour to form the active titanium coupling agent. A solution of dialdehyde 12 (0.68 g, 1.06 mmol) dissolved in 185 m*l* of dimethoxyethane was added over the course of 6 days *via* a constant additional funnel. The reaction mixture was further refluxed for 2 days, then cooled to room temperature. Saturated potassium carbonate solution (15 m*l*) was added. After an additional 12 hours stirring at room temperature, the black suspension turned off-white. The mixture was filtered through celite, and the fitrate was concentrated under reduced pressure. The residue was partitioned between 200 m*l* of dichloromethane and 100 m*l* of water. The organic phase was separated. The aqueous phase was extrated with 100 m*l* of dichloromethane, and the combined organic extracts were concentrated to about 5 m*l*. The solution was washed with 10 m*l* of deionized water three times by vortexing and centrifuging. About 2.0 m*l* of this mixture was subjected to gel permeation chromatography (3 runs). The fractions with retention volume of 130-160 m*l* were combined and concentrated to about 30 m*l*. As the dichloromethane was slowly further a fine fritted glass funnel (34 mg, 5.2% yield); mp. >340 °C (decompose); ^{1}H NMR: δ1.37 (s, 18H, C-CH$_3$), 3.11 (s, 6H, OCH$_3$), 3.26 (s, 12H, OCH$_3$), 3.46 (s, 12H, OCH$_3$), 7.13-7.43 (m, 32H, Ar-H and olefinic H); MS (350 °C 16 eV): 1224 (100, M$^+$), no other peaks below 1178; Anal. Calcd for C$_{81}$H$_{80}$O$_{10}$ + 1/2 NaCl (MW 1242.76): C, 78.49; H, 6.43. Found: C, 78.46; H, 6.40.

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